

SYNTHESIS AND CHARACTERIZATION OF NOVEL TELECHELIC HIGH PERFORMANCE POLYESTER IONOMERS

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ABSTRACT

Novel poly(ethylene isophthalate) (PEI) and poly(ethylene terephthalate) (PET) polymers containing terminal units derived from sodio 3-sulfobenzoic acid (SSBA) were synthesized using catalyzed melt polymerization techniques. Various concentrations of the ionic end group, SSBA, were successfully incorporated in a telechelic fashion. For comparison, polyesters containing telechelic alkyl groups with controllable molecular weights were also synthesized. Furthermore, ionic copolymers of dimethyl isophthalate and *trans*-cyclohexane dicarboxylate, dimethyl isophthalate and dimethyl terephthalate were synthesized to study the influences of polarity and rigidity of the polymer chain backbone on material properties. Novel branched polyester ionomers using trimellitic anhydride were also prepared. In addition to modifying the polymer compositions, PET ionomers were blended with zinc stearate to investigate the effect of plasticizer on the melt processibility of the ionomers.

FTIR spectroscopy, which was used to quantify the sulfonate end groups for all of the ionomers, indicated an absorbance peak for the S-O stretching mode between 600-700 cm^{-1} . ^1H NMR spectroscopy was used to confirm the structure of the ionic and non-ionic polyesters, as well as to verify the presence of the terminal groups. By systematically varying the chemical structure of these ionomer model systems (i.e., altering the contents of ionic functional groups), detailed characterizations were carried out, wherein the ionic interactions/aggregations in the ionomers were found to play an important role in the resulting material properties. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were performed to study the

effects of ionic groups and oligomer composition on the thermal properties of the polyesters. The glass transition temperatures of the ionomers revealed that the ionic interaction helped to maintain the structural integrity of the polymer chains, thus limiting their mobility. The dilute solution viscosity behavior of the ionomers exhibited upward curvature, which is a key characteristic of an ionomer. In PEI ionomers, the ionic aggregates formed at lower temperatures ($<150\text{ }^{\circ}\text{C}$), while at higher temperatures ($>150\text{ }^{\circ}\text{C}$), the ionic aggregations dissociated and behaved similarly to oligomers with lower molecular weights. Dodecanol was used as an effective end-capper to control the molecular weight of the non-ionic polyesters. In addition to telechelic ionic PEI and PET homopolymers, copolymers of poly(ethylene isophthalate-co-*trans*-1,4-cyclohexane dicarboxylate) (PEI-co-*trans*-CHDC) and poly(ethylene isophthalate-co-terephthalate) (PEIT) telechelic ionomers were also synthesized and characterized. Introducing *trans*-1,4-cyclohexane dicarboxylate into PEI ionomers decreased the polarity and packing regularity of the polymer chains. Also, the kinked-structure of dimethyl isophthalate reduced the regularity of the polymer chains in PET ionomers, thus reducing their propensity for rapid crystallization. Crystallization kinetics were studied for both ionic and alkyl telechelic polyesters, and resulting data revealed that the nature of the endgroup had a dramatic effect on crystallization from the melt state. The catalyst residue in the polymers also affected the crystallization rate for both ionic and non-ionic polyesters. With regard to the ionomers, antimony catalyst interacted with ionic aggregates, further increasing the crystallization rate. Branched PEI and PET ionomers showed an increase in melt strength. After blending with zinc stearate, the melt viscosity of the PET ionomers dropped dramatically.

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LIST OF ABBREVIATIONS

Cumyl Chloride	2-chloro-2-propylbenzene (cumyl chloride)
<i>trans</i> -CHDC	<i>Trans</i> -1,4-cyclohexane dicarboxylate
DEG	Diethylene glycol
DMI	Dimethyl isophthalate
DMT	Dimethyl terephthalate
DVB	Divinyl benzene
EPDM	Ethylene-propylene-diene monomers
EPK	Ethylphenylketene
MHDPE	Maleated-high density polyethylene
LC	Liquid crystal
LCP	Liquid crystalline polymer
MEPDM	Maleated-ethylene-propylene-diene monomers
bis-MPA	2,2'-bis(hydroxymethyl)propionic acid
NTP	Naphthalene thermotropic copolyesters
PFPE	Perfluoropolyethers
PCL	Poly(ϵ -caprolactone)
PDMS	Poly(dimethylsiloxane)
PetOz	Poly(2-ethyl-2-oxazoline)
PEI	Poly(ethylene isophthalate)
PEI- <i>trans</i> -CHDC-SSBA	Sulfonate terminated poly(ethylene isophthalate –co- <i>trans</i> -1,4-cyclohexane dicarboxylate)
PEI-Dode-OH	Dodecanol terminated poly(ethylene isophthalate)

PEI-yDode-OH	Dodecanol terminated poly(ethylene isophthalate), y is the amount of dodecanol used
PEI-SSBA	Sulfonate terminated poly(ethylene isophthalate)
PEI-xSSBA	Sulfonate terminated poly(ethylene isophthalate), x is the amount of SSBA used
PEIT	Poly(ethylene isophthalate-co-terephthalate)
PEIT-SSBA	Sulfonate terminated telechelic ionic poly(ethylene isophthalate-co-terephthalate)
bPEI-SSBA/TMA	Sulfonate terminated amorphous branched PEI ionomers
PE/MAA	Poly(ethylene-co-methacrylic acid)
PET	Poly(ethylene terephthalate)
PET-Dode-OH	Dodecanol terminated poly(ethylene isophthalate-co-terephthalate)
PET-yDode-OH	Dodecanol terminated poly(ethylene isophthalate-co-terephthalate), y is the amount of dodecanol used
PET-SSBA	Sulfonate terminated poly(ethylene isophthalate-co-terephthalate)
PET-xSSBA	Sulfonate terminated poly(ethylene isophthalate-co-terephthalate), x is the amount of SSBA used
PET-SSBA-Zn	Blends of sulfonate terminated PET ionomers with zinc stearate
PIB	Polyisobutylene
PLA	Poly(L-lactide)
PLLA	Poly(L,L-Lactide)
PPO	Poly(phenylene oxide)

PP	Polypropylene
PVC	Poly(vinyl chloride)
SEPDM	Sulfonated ethylene-propylene-diene monomers
SSBA	Sodio 3-sulfobenzoic acid, Sodium salt
TBMA	<i>tert</i> -Butyl methacrylate
TMA	Trimellitic anhydride
ASAXS	Anomalous small-angle x-ray scattering
EXAFS	Extended x-ray absorption fine structure spectroscopy
DMTA	Dynamic mechanical thermal analyzer
DSC	Differential scanning calorimeter
GPC	Gel permeation chromatography
TGA	Thermal gravimetric analyzer
SANS	Small-angle neutron scattering
SAXS	Small-angle X-ray scattering

CHAPTER 1. INTRODUCTION

Traditional high molecular weight, high performance polymers, which are obtained by step-growth and chain polymerization strategies, contain repeat units that are irreversibly connected by covalent bonds. Although physical and mechanical properties improve dramatically with increasing number average molecular weights and the corresponding number of intermolecular chain entanglements, these advantages can be undermined by other disadvantages. For example, poor melt processability, low thermal stability and difficult recyclability of the final product are common disadvantages for high molecular weight polymers.¹

Molecular recognition provides a means for directing the spontaneous formation of supra-species from complementary components. This phenomenon may permit the design and engineering of supramolecular materials by introducing different organic monomer units with varying properties. Since self-assembled units typically contain chemical covalent bonds, ionic interactions, and hydrogen bonds, the potential exists for designing many innovative high performance polymeric materials.

This research describes the synthesis of low molecular weight polymers, which form higher molecular weight aggregates or linear macromolecules via reversible covalent or non-covalent bonding. Some important considerations with regard to these polymer systems are (a) the stability of the intermolecular interaction or covalent bond at typical use temperatures, and (b) the relative instability of the interaction or covalent bond during melt processing. The reversible and reproducible mechanism between the two physical states is depicted schematically below for poly(ethylene terephthalate) (PET) (Figure 1.1).

¹ Nielsen, L. E. in “*Polymer Rheology*”, Marcel Dekker, Inc., 1977, p. 69

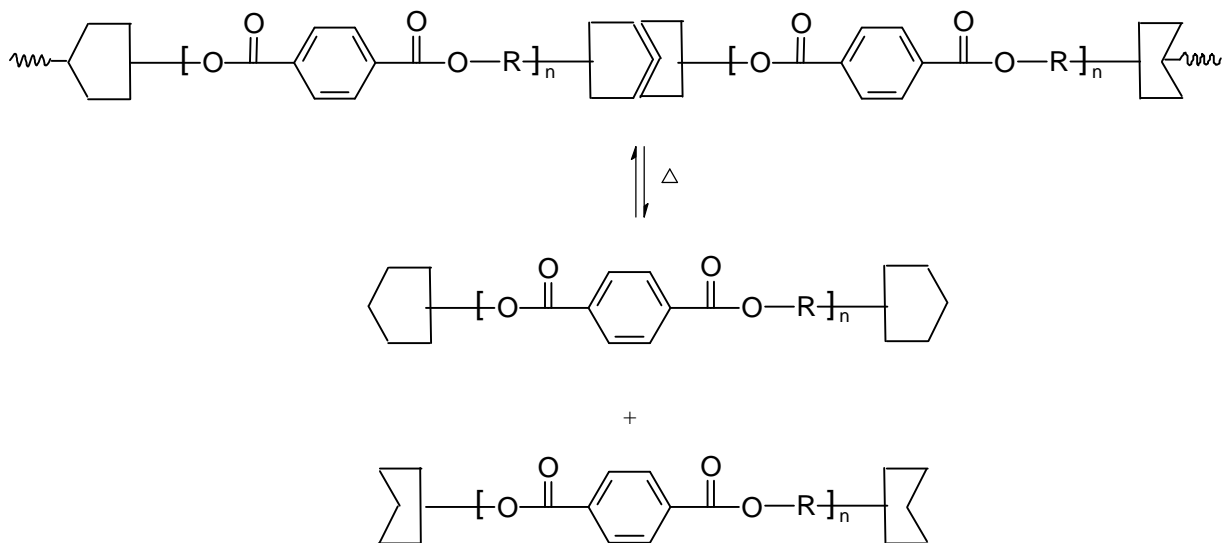


Figure 1.1. Proposed thermally reversible process of PET ($R = (\text{CH}_2)_n$)

Although there are several candidates for either non-covalent or covalent thermo-reversible bonds (e.g., ionic clustering, hydrogen bonding, transition metal coordination, some reversible covalent bonds, and biomolecule-endgroup conjugates²), the bulk of this research focuses on ionic clustering.

Telechelic ionic bonding using metal sulfonates and carboxylates offers a potentially straightforward synthetic method for the formation of reversible polymer structures. Ionic bonds are very effective in improving mechanical properties.^{3,4,5} It is well known that polymers with ionic cross-links are reformed upon heating, while most covalent cross-links are not. This is because ionic bonds are nondirectional and thus easier to reform upon cooling after the melt,⁶ as opposed to covalent bonds, which are highly directional and thus are more difficult to reform, as well as being more susceptible

² Markle, R. A.; Brusky, P. L.; Cremeans, G. E.; US patent 5097010, 1991

³ Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, UK, 1992

⁴ *Liquid Crystalline Polymers*; NMAB-453, National Academy Press: Washington, DC, 1990

⁵ Dang, T. D.; Wang, C. S.; Click, W. E.; Chuah, H. H.; Tsai, T. T.; Husband, D. M.; Arnold, F. E. *Polymer* **1997**, 38, 621

⁶ Holiday, L. In *Ionic Polymers*; Holiday, L., Ed.; Applied Science: London, 1975; Chapter 1.

to degradation.⁷ The widespread use of ionic end cappers is due to the fact that they are easily introduced to the polymer chain ends, and are known to improve the thermal stability and mechanical properties of polymers. Although ionic polymers have been widely studied in academia, they are also of interest in industry because of the ability to control the physical properties of polymers through ionic interactions-- even at low ion concentrations.⁸ Because ions tend to aggregate in media with low dielectric constants, many important characteristics, such as modulus, glass transition temperature, viscosity, melt strength, fatigue, transport, and several other desirable properties, can be dramatically influenced via ion incorporation.

Although telechelic ionic bonding has many advantages, its synthesis is generally more complex because the number of ionic groups that participate in the cluster is difficult to control. Hydrogen bonding, however, is potentially a good model for more complex ionic systems because of well-defined hydrogen bonding scaffolds. In addition, hydrogen bonding can be observed using conventional infrared spectroscopy either in solution or in the melt phase as a function of temperature.⁹ Furthermore, hydrogen bonding is also quite strong (about 2-24 kcal/mole or even higher), thermo-reversible, relatively easy to design, and extremely important in biosystems. Despite the perceived complexity of reversible ionic bonding, the thermal stability (> 200 °C) of ionic groups relative to hydrogen-bonding donors and acceptors is very appealing. Furthermore, it has been shown that introducing ionic groups at the elastomeric chain ends is relatively straightforward.⁸

Thus, the goal of my research was to develop novel thermo-reversible telechelic ionic polyesters that exhibited exceptionally low melt viscosity at high temperatures (processing temperatures), but also possessed the high mechanical and melt strengths of

⁷ Xue Y.; Hara M. *Macromolecules* **1998**, 31, 7806

⁸ Eisenberg A.; Kim J.-S. *Introduction to ionomers*; John Wiley & Sons, Inc: New York, 1998; Chapter 1.

⁹ Painter, P.; Park, Y.; Coleman, M. J. *J. Appl. Polym. Sci.* **1998**, 70(7), 1273

much higher molecular weight polymers at lower temperatures (application temperatures).

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

In this research project, we attempted to develop new polymer structures using polyester as the backbone, combined with functional groups such as ionic terminal groups. Our goal was to maintain the high performance properties of the polymers at higher temperatures (>100 °C), even though the melt viscosity of these materials was much lower (caused by the dissociation of the ionic clusters or hydrogen bonding) than that of normal high molecular weight polymers under reasonable process temperatures (e.g., 200-300 °C). This concept becomes even more critical when we consider the possible thermal and shear degradation in the melt phase or at higher temperatures. In addition, melt phase chemical reactions that lend themselves to environmentally friendly engineering applications will be ubiquitous in the future in order to minimize the generation of chemical waste, reduce energy consumption, avoid deleterious organic side reactions, etc. In short, the thermo-reversible polymer concept will result in reducing high polymer melt viscosities, minimizing polymer degradation during processing, and facilitating the production of miniaturized polymer products.

This literature review focuses on two topics: (1) polyesters, which serve as the polymer backbones in our newly developed thermo-reversible polymer systems, and (2) ionic functional materials (ionomers), which are used as thermo-reversible polymers.

2.2 Synthesis and Applications of Polyesters

2.2.1 Introduction

The first fiber-forming polyesters were prepared by Carothers and Hill in the late 1920s using the melt condensation of dicarboxylic acids and aliphatic diols.¹ In the early 1940s, Whinfield and Dickson discovered the fiber- and film-forming poly(ethylene

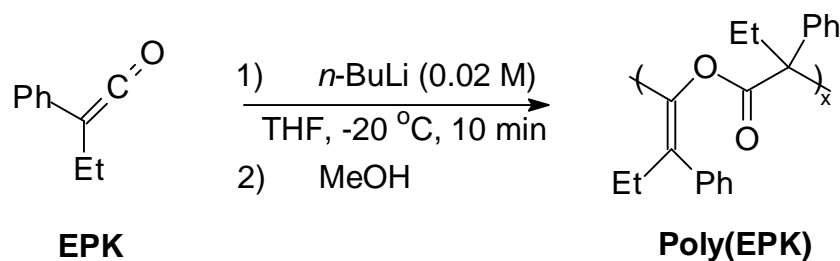
¹ Herman F. M.; Norman G.; Norbert, M. B. Encyclopedia of Polymer Science and Technology, 1964, p 2

terephthalate) (PET), which possessed a higher melting point and displayed better chemical resistance due to the presence of more rigid groups (e.g., phenylene) in the backbone, is now the most important member of polyester group by production volume and sales value.² PET was first commercialized by ICI (Imperial Chemical Industries, Ltd.) as “Terylene”.

Today, polyesters are widely used as both important thermoplastic and thermosetting materials. Due to the limited scope of this thesis, however, only some important later developments in this broad field will be discussed.

2.2.2 Several New Approaches to Polyester Synthesis

Anionic polymerization of ketenes is known to be a useful method for synthesizing polyesters having C=C on their side chains.³ Recently, exciting developments have been achieved by Sudo *et al.*⁴ involving the synthesis of a well-defined polyester by the living anionic polymerization of ethylphenylketene (EPK) using *n*-BuLi as an initiator in THF at -20°C under nitrogen (Scheme 2.1).



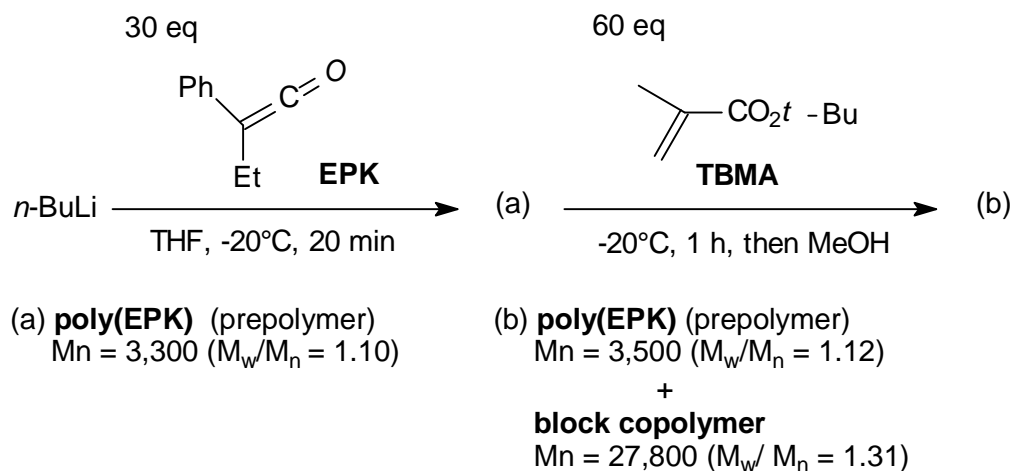
Scheme 2.1. Polymerization of EPK by living anionic polymerization

Based on the GPC data provided by the authors, typical M_n values were 10 ~ 20 k and $M_w/M_n = 1.10 - 1.11$. They also studied the block copolymerization of EPK with *tert*-butyl methacrylate (TBMA) (Scheme 2.2), which revealed a new peak at a higher MW

² Long, T. E.; Turner, S. R., in *Applied Polymer Science 21st Century*, Craver, C. D.; Carraher, C. E., Ed. Elsevier, 2001, p979

³ Sugimoto, H.; Kato, M.; Inoue, S., *Macromol. Chem. Phys.* **1997**, 198, 1605

position (Figure 2. 1), indicating the formation of a block copolymer. Sudo and coworkers concluded that this approach provides a novel strategy for synthesizing polyesters with a predictable molecular weight and a narrow molecular weight distribution.



Scheme 2.2. Copolymerization of EPK and TBMA

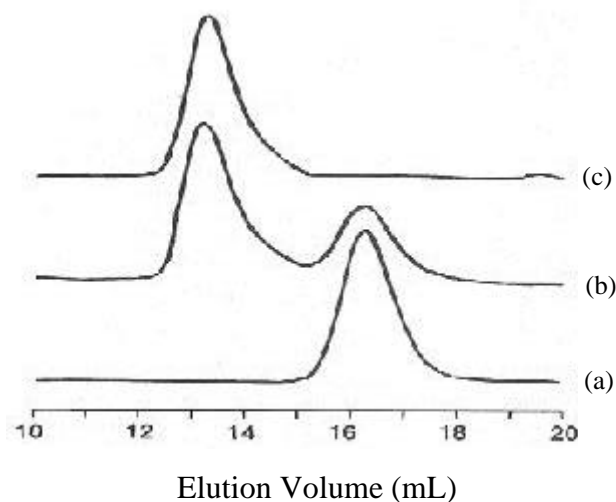


Figure 2.1. GPC profiles in block copolymerization: (a) after prepolymerization of EPK; (b) after block copolymerization; (c) fractionated poly (EPK-*b*-TBMA)

⁴ Sudo, A.; Uchino, S.; Endo, T., *Macromolecules* **1999**, 32, 1711

Many organometallic compounds have been discovered to be effective initiators/catalysts for controlled ring-opening polymerization (ROP), thus allowing the preparation of functional oligomers, random and block copolymers, and polymers with unique topology or architectural control.⁵ A recent paper describes the synthesis and copolymerization of a new cyclic ester, (2-bromo-2-methyl propionyl)-caprolactone, containing a pendent-activated alkyl bromide functional group.⁶ This new compound serves as both a monomer for "living" ring-opening polymerization (ROP), as well as an initiator for controlled atom transfer radical polymerization (ATRP). The new monomer facilitated the synthesis of new graft copolymers having an aliphatic polyester backbone with poly(methyl methacrylate) grafts of controlled molecular weight and narrow polydispersities (~1.3). Other developments utilizing ROP have also been reported in literature, including a new route to aliphatic polyesters bearing functional pendent groups via ROP of 1,4,8-trioxaspiro[4,6]-9-undecanone,⁷ as well as the preparation and polymerization of alkylene phthalate cyclic oligomers.⁸

Solid-state polymerization (SSP), which has been utilized as a method for synthesizing high molecular weight polyesters, has also been comprehensively investigated.⁹ In addition, recent efforts have elucidated the likely mechanism for facilitating the required migration of functional groups for SSP of polyesters (also polyamides) is an interchange reaction.¹⁰ The kinetic analysis showed that migration of functionality via interchange, chemical diffusion, and polymerization has exactly the same mathematical form as that of classical statistical mechanics of (physical) diffusion-controlled reactions of small molecules. The potential implications of this mechanism vis-à-vis the formation of high-performance morphologies in fibers and films of semi-rigid polymers were also studied by these authors.

⁵ Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1997**, 198, 1753

⁶ Atthoff, D. M.; Boduch, K. A.; Trollsas, M.; Hedrich, J. L., *Macromolecules* **1999**, 32, 5175

⁷ Tian, D.; Dubois, P.; Grandfils, C.; Jerome, R., *Macromolecules* **1997**, 30(3), 406

⁸ Brunelle, D. J.; et al, *Macromolecules* **1998**, 31, 4782

⁹ *Polymeric Materials Encyclopedia*, Vol 8, 1996, 6078

¹⁰ Srinivasan, R.; Almonacil, C.; Narayan, S.; Desai, P.; Abhiraman, A. S., *Macromolecules* **1998**, 31, 6813

2.2.3 Polyesters as Nonlinear Optical (NLO) and Liquid Crystal (LC) Materials

The field of nonlinear optical (NLO) materials based on polymers has been a target of intensive research activity during the past several decades.¹¹ Although several rigid chain polymer systems have been reported, there have also been a number of systematic examinations of rigid chain polymers with flexibly attached NLO chromophores. Lee *et al.* recently reported the synthesis of a series of wholly aromatic polyesters containing NLO chromophores in the side group through varying alkyl tether length.¹² As to the principle chain type of NLO materials, a new approach that provides photorefractive polymers with high glass transition temperatures was reported by Dobler *et al.*¹³ based on a blend of polyamides and polyesters.

Liquid crystalline polyesters have also been widely studied.¹⁴ Many research groups, for example, have focused on new methods for synthesizing and characterizing novel combined type (main chain/side chain) LC polyester materials. For example, combined type LCPs, in which the mesogenic side groups with flexible spacers are attached to the mesogenic main chains, are a new design for these LCPs. The recent work of Cooray *et al.*¹⁵ provided a new synthetic route for preparing combined LC polymers with aromatic polyester main chains, utilizing an aromatic diacid chloride/diol solution polycondensation reaction. One of the advantages of their method is that it is free of side reactions, which normally occur in standard transesterification polymerization methods used for the synthesis of combined type polyester LCPs. S. Cheng and coworkers thoroughly characterized a series of combined polyester LCPs,¹⁶ which were comprised of rigid aromatic main chain backbones and flexible aliphatic side chains with 4-cyanobiphenyl end groups. Their experimental results revealed that four phases with different ordered structures were involved in the polymer synthesis. Jin, *et al.* reported the synthesis of a series of combined main chain-side group thermotropic

¹¹ Shi, Y. Q.; Steier, W. H.; Yu, L. P., *Appl. Phys. Lett.* **1991**, 59 (23), 2935

¹² Lee, S.; Kim, Y.; Won, Y., *Macromolecules* **1999**, 32, 342

¹³ Dobler, M.; Weder, C.; Neuenschwander, P.; Suter, U. W., *Macromolecules* **1998**, 31, 6184

¹⁴ (a) Acierno, D.; Concilio, S.; Iannelli, P.; *et al. Macromolecules* **2000**, 33, 9688; (b) Huang, H. W.; Horie, K.; Yamashita, T.; *et al. Macromolecules* **2000**, 29, 3485

¹⁵ Cooray, N. F.; Fujumoto, H.; Kakimoto, M.; Imai, Y., *Macromolecules* **1997**, 30, 3169

polyesters having varying lengths of oxypolymethyleneoxy spacers between the aromatic polyester main chain and the side azobenzene mesogenic unit.¹⁷

2.2.4 Dendritic and Hyperbranched Polyesters

Dendritic and hyperbranched polymers are interesting new classes of materials, not only because of their unique molecular shape, but also for their possible utilization in a variety of ways, such as chemical reagents or catalysts, in biological and pharmaceutical uses, and other functions.¹⁸ Noteworthy examples of both dendritic and hyperbranched polyesters have been reported by Hult and co-workers,¹⁹ involving the self-polymerization of 2,2'-bis(hydroxymethyl)propionic acid (bis-MPA). Dendritic polyesters were prepared by coupling dendrons of certain generations to a polyfunctional core, while hyperbranched polyesters were prepared in the melt via an acid-catalyzed polyesterification reaction. Other examples involve the preparation of 3,5-dihydroxybenzoic acid derivatives and their self-polymerization.²⁰

Bo and coworkers²¹ reported the “rapid synthesis of polyester dendrimers,” in which aryl polyester dendrimers and dendrons were prepared using “branched monomer strategies.”

Novel hyperbranched poly(ϵ -caprolactone)s have been synthesized by Hedrick, *et al.*²² Their versatile synthetic method utilized AB₂ macromonomers, which allowed the thermo-physical properties of the polymers to be tailored. The caprolactone-based AB₂ macromonomers were synthesized through living ring opening polymerization, using

¹⁶ Ge, J. J.; Cheng, S. Z. D., *et al.*, *Macromolecules* **1997**, 30, 6498; Ge, J. J.; Cheng, S. Z. D., *et al.*, *Macromolecules* **1998**, 31, 4093

¹⁷ Piao, X. L.; Kim, J.; Yun, Y.; Jin, J., *Macromolecules* **1997**, 30, 2294

¹⁸ (a) Liu, H. W.; Wilen, C. E., *J. Polym. Sci. Part A: Poly. Chem.* **2001**, 39, 964; (b) Nunez, C. M.; Chiou, B. S.; Andradý, A. L., *et al. Macromolecules* **2000**, 33, 1720

¹⁹ (a) Johansson, M.; Malmström, E.; Hult, A. *J. Polym. Sci., Part A: Chem. Ed.* **1993**, 31, 619. (b) Malmström, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, 28, 1698. (c) Ihre, H.; Hult, A.; Söderlind, E. *J. Am. Chem. Soc.* **1996**, 118, 6388.

²⁰ (a) Hawker, C.; Turner, S. R.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, 113, 1583. (b) Voit, B. I.; Mourey, J. *Macromolecules* **1993**, 26, 8607

²¹ Bo, Z. S.; Zhang, X.; Zhang, C. M.; Wang Z. Q.; Yang, M. L.; She J. C.; Ji, Y. P. *J. Chem. Soc. Perkin Trans.* **1997**, 1, 2931

²² Trollsas, M.; Atthoff, B.; Claesson, H.; Hedrick, J. L. *Macromolecules* **1998**, 31, 3439

aluminum benzyloxide as the initiator. The same research group also described several new approaches for producing biodegradable dendritic aliphatic block copolymers, including hyperbranched and dendrimer-like star structures.²³

2.2.5 Copolymers of Polyesters and Other Functional Polymers

One method of modifying the chemical structure of polyesters for improved physical properties involves the introduction of an additional functional group, which combines and enhances the advantages of both components (the polyester and the particular functional group). For example, high molecular weight poly(dimethylsiloxane) (PDMS) / semicrystalline cycloaliphatic polyester segmented block copolymers based on dimethyl-1,4-cyclohexane dicarboxylate were prepared and characterized by McGrath *et al.*²⁴ The polysiloxane segment was efficiently incorporated into the copolymers via an amide link. Taking advantage of the low T_g of the PDMS segment, the copolymers demonstrated good mechanical properties, and were easily compression molded into films.

As another example, fluoropolymers have low surface energy and thus their presence in a polymer blend, such as through the introduction of a fluorinated segment into a block copolymer, will influence surface composition. Fluoropolymers also exhibit high thermal oxidative stability, chemical resistance, and low coefficient of friction. One of the goals of introducing telechelic perfluoropolyethers (PFPE) into polyester chains (PET or PBT)²⁵ was to take advantage of the spontaneous PFPE surface segregation for the enhancement of PET or PBT performances in all the applications where low coefficient of friction, low wettability, and superior chemical resistance are required.

A significant body of research has been directed at improving the fire retardance of polyesters. For example, several different phosphorus containing polyesters (PET,

²³ Trollsas, M.; Kelly, M. A.; Claesson, H.; Hedrick, J. L. *Macromolecules* **1999**, 32, 4917

²⁴ Kiefer, L. A.; Yoon, T. H.; Glass, T. E.; Jayaraman, S. K.; McGrath, J. E., *J. Polym. Sci. Part A Polym. Chem.* **1997**, 35, 3495

²⁵ (a) Pilati, F.; Toselli, M.; Vallieri, A.; Tonelli, C. *Polym. Bull.* **1992**, 28, 151. (b) Toselli, M.; Pilati, F.; Fusari, M.; Tonelli, C.; Castiglioni, C. *J. Appl. Polym. Sci.* **1994**, 54, 2101. (c) Bottino, F. A.; Pasquale, G. D.; Pollicino, A.; Pilati, F.; Toselli, M.; Tonelli, C., *Macromolecules* **1998**, 31, 7814

PEN, PBT, etc.) have been synthesized by different research groups.^{26, 27, 28} One example of a thermally stable polyester is the poly(phenylene oxide) (PPO) – aromatic polyester multiblock copolymer.²⁹ This material has been synthesized via the polycondensation of bisphenol-A / isophthalic acid or m- and p-hydroxybenzoic acids in the presence of PPO having a carboxylic acid at one end and a phenolic hydroxyl group at the other, using triphenylphosphine / hexachloroethane as coupling agent.

Wu and coworkers copolymerized block diisocyanate polyester with novolak-type phenolic resin.³⁰ The interface between the modified phenolic resin and the glass fiber was improved and the tensile strength of the resulting pultruded composite increased as a result of the modifier content.

More recently, polymeric micelles derived from amphiphilic block copolymers in an aqueous phase have attracted much attention, not only because of their unique morphological behavior, but also because of their potential applications in separation technologies and in the area of drug delivery.^{31, 32, 33, 34, 35}

Several amphiphilic diblock polyester copolymers were synthesized based on poly(2-ethyl-2-oxazoline) (PEtOz) as a hydrophilic block, and aliphatic polyesters such as poly(L-lactide) (PLA) or poly(ϵ -caprolactone) (PCL) as a hydrophobic block.³⁶ Monitored by dynamic light scattering and fluorescence techniques, the micelles

²⁶ Asrar, J.; Berger, P. A.; Hurlbut, J., *J. Polym. Sci. Part A Polym. Chem.* **1999**, 37, 3119

²⁷ Wang, C. S.; Shieh, J. Y.; Sun, Y. M., *European Polym. J.* **1999**, 35, 1465

²⁸ Wang, C. S.; Lin, C. H., *J. Polym. Sci. Part A Polym. Chem.* **1999**, 37, 891

²⁹ Ikeda, R.; Sugihara, J.; Uyama, H.; Kobayashi, S., *Polymer Bull.* **1998**, 40, 367

³⁰ Ma, C. C. M.; Tseng, H. T.; Wu, H. D., *J. Applied Polym. Sci.* **1998**, 69, 1119

³¹ Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskoy, V.; Torchilin, V.; Langer, R. *Science* **1994**, 263, 1600 Xu, R.;

³² Caldérara, F.; Hruska, Z.; Hurtrez, G.; Lerch, J.; Nugay, T.; Riess, G. *Macromolecules* **1994**, 27, 1210.

³³ Hurter, P. N.; Hatton, T. A. *Langmuir* **1992**, 8, 1291.

³⁴ Yokoyama, M.; Kwon, G. S.; Okano, T.; Sakurai, Y.; Seto, T.; Kataoka, K. *Bioconjugate Chem.* **1992**, 3, 295.

³⁵ Kwon, G. S.; Suwa, S.; Yokoyama, M.; Okano, T.; Sakurai, Y.; Kataoka, K. *J. Controlled Release* **1994**, 29, 17.

³⁶ Leadley, S. R.; Davies, M. C.; Vert, M.; Braud, C.; Paul, A. J.; Shard, A. G.; Watts, J. F., *Macromolecules* **1997**, 30, 6920

underwent hydrogen bonding at pH <3.5 with poly(acrylic acid), which produced polymer complex precipitates that could be reversibly dispersed as micelles at pH >3.8.

A series of novel ABA-triblock copolymers with polystyrene and main-chain liquid crystalline polyester, poly(2,2'-dimethyl-4,4'-biphenylene phenylterephthalate) segments were synthesized by Reichelt et al.^{37, 38, 39, 40} The liquid crystalline behavior and the transition temperatures are discussed with respect to the molecular weight of the polystyrene segments and the block copolymer composition.

2.2.6 Polyesters as Biomaterials

In recent years, a great deal of attention has focused on biodegradable materials for use in biomedical applications and as environmentally friendly materials. Among these, synthetic aliphatic polyesters are an important class of biodegradable and hydrolyzable polymers.³³ The biodegradable polyesters developed up until now, however, are almost all linear polyesters. The incorporation of network structures into the backbone is of particular interest for new biodegradable materials, since they are expected to afford better physical and chemical properties, such as resistance to heat and the presence of other chemicals.^{41, 42}

In a recent work by Nagata and coworkers⁴³, network polyesters were prepared from 1,1,1-trimethylolethane (Ye), 1,1,1-trimethylolpropane (Yp), 1,2,3,4-butanetetrol (Xe), and D-glucitol (Zs) with aliphatic dicarboxylic acids containing different numbers of methylene groups ($\text{HOOC}(\text{CH}_2)_{n-2}\text{COOH}$, $n = 4, 6-14, 16, \text{ and } 20$). Their results revealed that the networks were enzymatically degradable. J. F. Watts *et al.* also

³⁷ Lee, S. H.; Chang, Y.; Yoon, J. S.; Kim, C.; Kwon, I. C.; Kim, Y.; Jeong, S. Y., *Macromolecules* **1999**, 32, 1847

³⁸ Reichelt, N.; Schulze, U.; Schmidt, H. W., *Macromolecular Chem. and Phys.*, **1997**, 198, 3907

³⁹ Tokiwa, Y. Sen-i Gakkaishi, *Jpn.* **1991**, 47, P-522.

⁴⁰ Lenz, R. W. *Adv. Polym. Sci.* **1993**, 107, 22.

⁴¹ Albertson, A. C. J. *Macromol. Sci.-Pure Appl. Chem.* **1993**, A30, 757

⁴² Tsutsumi, N.; Kiyotsukuri, T.; Chen, Y. *J. Polym., Sci., Part A: Polym. Chem.* **1991**, 29, 1991.

⁴³ Kiyotsukuri, T.; Takemoto, H.; Tsutsumi, N.; Sakai, W.; Nagata, M. *Polymer* **1996**, 36, 5045

demonstrated that poly(β -malic acid) and their ester derivatives were biodegradable polyesters, which are candidates for innovative drug delivery systems.⁴⁴

In summary, polyesters can be easily modified to meet different application requirements, either by altering the monomer structure or by introducing additional functional groups. Because chemical structures are being better defined by new synthetic approaches (e.g., living anionic and living ROP / ATRP polymerization), as well as a better understanding of polymerization mechanisms, an ever expanding array of applications are being explored in important areas such as optical electronics, adhesion and coatings, high performance materials, and biotechnology.

My M.S. research focuses on new strategies for introducing ionic groups into aromatic polyester backbones in order to fabricate high performance thermo-reversible networks. It is proposed that this work will expand the practical applications of current polyesters and polyester blends.

2.3 Ionomers

2.3.1 Introduction

During the last 30 years, scientists have been fascinated by the class of polymers known as ionomers. Ionomers are normally defined as ion-containing polymers with a maximum ionic group content of about 15 mol % or less.⁴⁵ The literature in this field has grown exponentially and a large number of conferences on the topics have been held.^{46, 47, 48, 49, 50, 51, 52} Many reviews articles^{53, 54, 55, 56, 57} and edited volumes have also been

⁴⁴ Nagata, M.; Machida, T.; Sakai, W.; Tsutsumi, N., *Macromolecules* **1998**, 31, 6450

⁴⁵ Eisenberg, A. *Adv. Polym. Sci.* **1967**, 5, 59

⁴⁶ Leadley, S. R.; Davies, M. C.; Vert, M.; Braud, C.; Paul, A. J.; Shard, A. G.; Watts, J. F., *Macromolecules* **1997**, 30, 6920

⁴⁷ *Ion-Containing Polymers*; Eisenberg, A., Ed.; Journal of Polymer Science, Polymer Symposium 45.

⁴⁸ *Ion-Containing Polymers*; Eisenberg, A., Ed.; Wiley, New York, 974. *Advances in Chemistry* 187; American Chemical Society: Washington DC, 1982

⁴⁹ *Perfluorinated Ionomer Membranes*; Eisenberg, A.; Yeager, H.L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington DC, 1982

published on the subject of ionomers.^{58, 59, 60, 61, 62, 63, 64} The wide range of compositions, molecular architectures, and morphologies present in ionomeric systems are of great interest to experimentalists as well as theoreticians. As expected, polymer scientists are particularly interested in the potential application of these materials, based on an understanding of their fundamental principles. The common thread in most of the research efforts to date was the knowledge that the presence of ionic groups, even in small amounts, dominates the viscoelastic behavior of ionomers, their thermal stability and mechanical properties, their transport properties, and their ability to sorb a variety of solvents.

As reported in many papers, review articles,^{65, 66} and books,^{67, 68} ionomers are extremely complex systems, sensitive to changes in structure and composition, and therefore not easily amenable to modeling and to the derivation of general patterns of behavior.

⁵⁰ *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A.; Bailey, F. E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington DC, 1986

⁵¹ *Structure and Properties of Ionomers*; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C 198; Reidel: Dordrecht, The Netherlands, 1987

⁵² *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A.; Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington DC, 1989

⁵³ *Properties of Ionic Polymers, Natural & Synthetic*; Salmen, L.; Htun, M., Eds.; STFI Meddelande: Stockholm, 1991.

⁵⁴ Otocka, E. P. J. *Macromol. Sci. Rev. Macromol. Chem.* **1971**, C5, 275-294

⁵⁵ Longworth, R. *Plast. Rubber Mater. Appl.* **1978**, 75-86.

⁵⁶ Bazuin, C. G.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, 20, 271-286

⁵⁷ MacKnight, W. J.; Earnest, T. R. Jr. *J. Polym. Sci. Macromol. Rev.* **1981**, 16, 41-122

⁵⁸ Bazuin, C. G. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; 3454-3460

⁵⁹ *Ionic Polymers*, Holliday, L., Ed.; Applied Science: London, 1975

⁶⁰ *Developments in Ionic Polymers* – Wilson, A. D.; Prosser, H. J., Eds; Elsevier: London, 1986

⁶¹ *Advances in Urethane Ionomers*; Xiao, H. X.; Frisch, K. C., Eds.; Technomic: Lancaster, PA, 1995

⁶² *Ionomers: Characterizations, Theory, and Applications*; Schlick, S., Ed.; CRC: Boca Raton, FL 1996

⁶³ *Ionomers: Synthesis, Structure, Properties, and Applications*; Tant, M. R.; Mauritz, K. A.; Wilkes, G. L., Eds.; Chapman & Hall: New York, 1997

⁶⁴ Eisenberg, A.; King, M. *Ion-Containing polymers, Physical Properties and Structure*; Academic: New York, 1977.

⁶⁵ Schlick, S. *Ionomers : Characterization, Theory, and Applications*; CRC Press, Inc., Florida, 1996

⁶⁶ MacKnight, W.J.; McKenna, L.W.; Read, B.E. *J. Appl. Phys.* **1967**, 38, 4208

⁶⁷ Ward, T. C., Tobolsky, A. V. *J. Appl. Polym. Sci.* **1967**, 11, 2403

⁶⁸ Tobolsky, A. V.; Lyons, P.F.; Hata, N. *Macromolecules* **1968**, 1, 515

2.3.2 Ionomer Structures

Ionomers can be interpreted in the context of the restricted mobility (RM) model of Eisenberg and co-workers.⁶⁹ The basic assumption of the RM model is that at low ionic concentrations, ionic moieties aggregate into loosely defined multiplets consisting typically of 2-8 ion pairs (Figure 2.2, left). The formation of these aggregates is induced by electrostatic forces associated with the ionic moieties, which must overcome the entropic and elastic forces exerted by the hydrocarbon chains to which they are attached. This restricted mobility “corona” surrounding the multiplet core is distinct from the bulk polymer matrix, and its size is dependent on the aggregation number of the multiplet and the stiffness of the polymer backbone. Typically, the size of this corona/core entity is too small (<50 Å) to form a distinct phase and, thus, its effect is limited to that of a physical cross-link. As the ion content is increased, the number of multiplets grows and the restricted mobility “corona” of neighboring multiplets start to overlap and coalesce until a point is formed whose size is sufficiently large to be considered a distinct phase (Figure 2.2, right). This aggregate of several multiplets is known as a *cluster*. In a cluster structure, two glass transition temperatures can often be observed due to phase separation.⁷⁰

⁶⁹ Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, 23, 4098

⁷⁰ Eisenberg, A.; King, M. *Ion-Containing polymers, Physical Properties and Structure*; Academic: New York, 1977

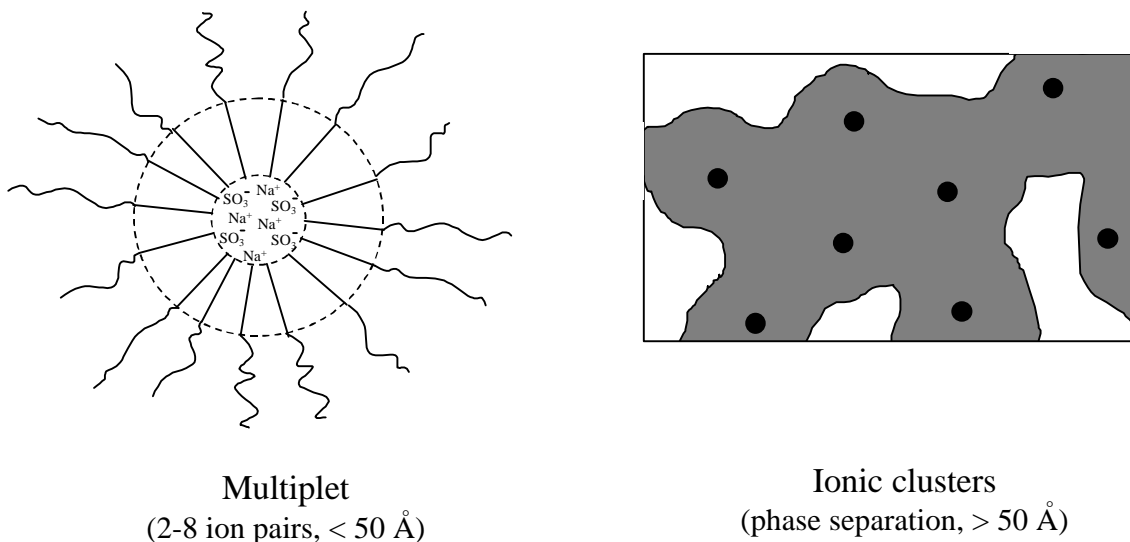


Figure 2.2. Restricted mobility model of Eisenberg et al.: left, a schematic of a multiplet and its restricted mobility shell; right, a schematic two-dimensional representation of a cluster. Solid spheres are the ionic multiplets, the hatched area is the restricted mobility domain, and the unmarked area is the unclustered hydrocarbon matrix.⁷¹

2.3.3 Types of Ionomers

Monochelics - ion at a single chain end

A monochelic is the simplest type of ionomer consisting of a single ion placed at the end of a polymer chain (Figure 2.3). As exemplified by a polystyrene containing a terminal carboxylate anion, a monochelic can be prepared by anionic polymerization.^{71,72}

⁷¹ Eisenberg, A. *Adv. Poly. Sci.* **1967**, 5, 59-112

⁷² McGrath, J. E. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*, ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981

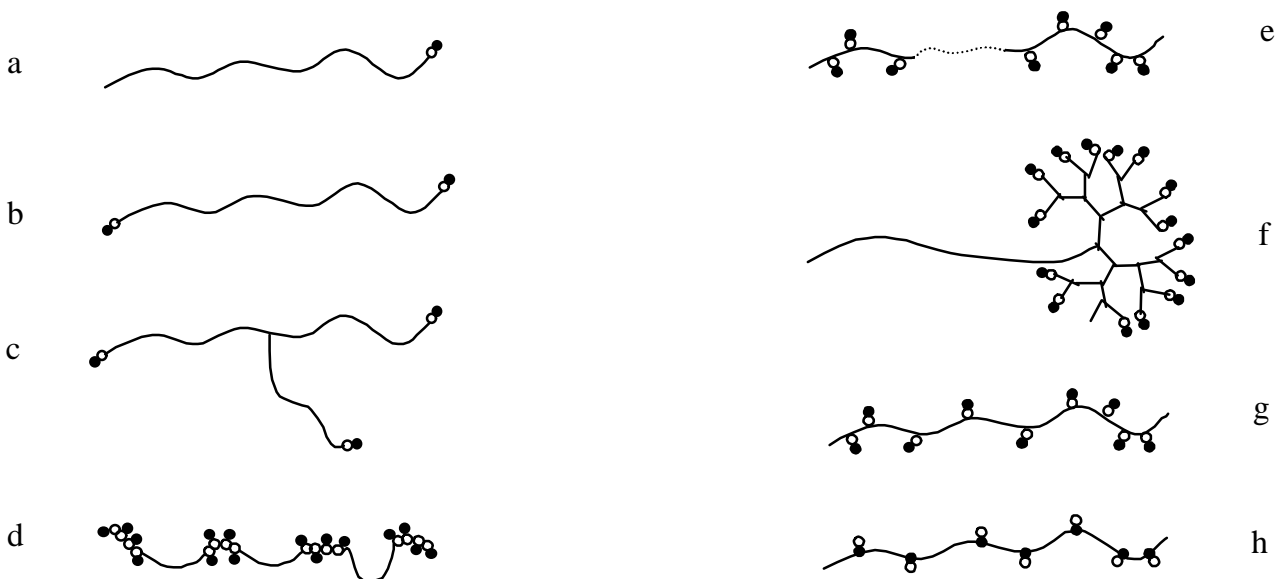


Figure 2.3. (a). Monochelics; (b) Telechelics; (c) Telechelic Stars; (d) AB Block
(e) ABA-Tri Block; (f) Dendrimers; (g) Random; (h) Ionenics.⁷¹

Telechelics

A telechelic, on the other hand, is typified by one ion at each end of a polymer chain (Figure 2.3b). Materials of this type can also be synthesized by anionic polymerization or melt polymerization. Telechelics have been widely investigated since the mid-1940's,^{73, 74, 75} with the most extensive studies of carboxylate ionomers originating from Jerome and Teyssie.⁷⁶ Besides carboxylate end groups, the ionic ends can also consist of a sulfonate, a sulfate, and a borate. It was quickly recognized that substitution of a sulfonate for a carboxylate group drastically changed the properties of the ionomers.⁷⁷ When a three or multiple-arm star is tipped at each arm's end by an ionic group (Figure 2.3c), the result is a telechelic star polymer system. The best known members of this family of materials is the polyisobutylene (PIB) star with sulfonic acids

⁷³ Szwarc, M.; Van Beylen, M. *Ionic Polymerization & Living Polymers*; Chapman & Hall: New York, 1993

⁷⁴ Cowan, J. C.; Teeter, H. M. *Ind. Eng. Chem.* **1994**, 36, 148-152

⁷⁵ Hegedus, R. D.; Lenz, R. W. *J. Polym. Sci. A Polym. Chem.* **1988**, 26, 367-380

⁷⁶ Broze, G.; Jerome, R.; Teyssie, P. *Macromolecules* **1982**, 15, 920-927

⁷⁷ Morrell, R. K.; Service, D. M.; Stewart, M. J.; Viguier, M.; Richards, D. H. *Br. Polym. J.* **1987**, 19, 241-246

in the terminal position, which have been studied intensively by Kennedy and Storey.⁷⁸ This area has also been of keen interest to this researcher and will be discussed in greater detail in the remainder of this thesis.

Block Copolymers

Block copolymers are known in several forms. The AB type, in which one of the segments is nonionic and the other consists of ionic repeat units (Figure 2.3d),⁷⁹ is exemplified by a styrene midblock capped at each end by an N-methyl-4-vinylpyridinium iodide segment. An ABA-type triblock (Figure 2.3e)⁸⁰ consists of one completely nonionic segment and another partly ionic segment. One such example is a block copolymer made of p-tert-butylstyrene or hydrogenated butadiene as one block and styrene as the second block, in which the styrene block is partly sulfonated. Recently, another new type of block ionomer was synthesized by van Hest *et al.*⁸² The acid form of the block copolymer consisted of a block of polystyrene with an acid functionalized poly(propylene imide) dendrimer at one end (Figure 2.3f).

Some Other Ionic Copolymers

In addition to the ionomers discussed above, there are other types of ionomers, such as simple random copolymers (Figure 2.3g), ionenes (in which the ionic groups distribute regularly along the backbone) (Figure 2.3h); grafts; and polymer-salt mixtures.

Among all of the ionomers now discussed, the telechelic ionomers are perhaps the simplest to synthesize and characterize. Lundberg *et al.*⁸¹ compared the rheological behavior of carboxylated polystyrene and sulfonated polystyrene having the same molecular weight, ion level, and the same cation. It was concluded that sulfonated ionomers are more strongly associated, and thus possess more attractive properties than

⁷⁸ Storey, R. F.; Maggio, T. L.; Brister, L. B., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 964, 40(2)

⁷⁹ Bagrodia, S.; Mohajer, Y.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Bull.* **1983**, 9, 174-180

⁸⁰ Selb, J.; Gallot, Y. *J. Polym. Sci. Polym. Lett. Ed.* **1975**, 13, 615-619

⁸¹ Lundberg, R. D.; Makowski, H. S. In *Ions in Polymers*; Eisenberg, k A., Ed.; Advances in Chemistry 187; Am. Chem. Soc.: Washington, DC, 1980; Chapt. 2

the corresponding carboxylate ionomers. As a consequence, this research will particularly focus on aromatic telechelic sulfonated polyester materials.

2.3.4 Ionomers with different types of pendent ions and chemical structures

The most common pendent anions used in the synthesis of ionomers are the carboxylates; the sulfonates; and to a much lesser extent, the phosphite and phosphonates. Carboxylate anions can be incorporated into ionomers by copolymerization with acrylic acid, methacrylic acid, maleic anhydride, and a number of other unsaturated carboxylic acids that tend to polymerize or copolymerize. An alternative method of preparing carboxylated ionomers is via a postpolymerization reaction. This type of reaction is particularly suitable for aromatic substitutions, and a number of reactions have been developed for the carboxylation of, e.g., polystyrene.^{82, 83, 84, 85, 86}

The incorporation of sulfonic acids into polymers is also possible via copolymerization. In this case, the sulfonated group should be relatively distant from the site of the double bond, as its proximity affects the reactivity ratios considerably and might even make copolymerization impossible in some cases.^{87, 88} Furthermore, the strength of the sulfonic acid group reduces the solubility of the monomer, so that identifying a common solvent becomes problematic. Despite these drawbacks, copolymerization of sulfonated monomers with nonionic organic monomers has been successfully achieved.^{89, 90}

The other common route to sulfonation is via a postpolymerization reaction of aromatic or unsaturated sites (Scheme 2.3).

⁸² van Hest, J. C. M.; Baars, M. W. P. L.; elissen-Roman, C., van Genderen, M. H. P.; Meijer, E. W. *Macromolecules* **1995**, 28, 6689-6691

⁸³ Kenyon, W. O.; Waugh, G. P. *J. Polym. Sci.* **1958**, 32, 83-88

⁸⁴ Blanchette, J. A.; Cotman, J. D. *J. Org. Chem.* **1958**, 23, 1117-1122

⁸⁵ Braun, D. *Makromol. Chem.* **1961**, 46, 269-280

⁸⁶ Letsinger, R. L.; Kornet, M. J.; Mahadevan, V.; Jerina, D. M. *J. A. C. S.* **1964**, 86, 5163-5165

⁸⁷ Tomita, H.; Register, R. A. *Macromolecules* **1993**, 26, 2791-2795

⁸⁸ Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience: New York, 1967

⁸⁹ *Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989

⁹⁰ Weiss, R. A.; Lundberg, R. D.; Werner, A. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, 18, 3427-3439

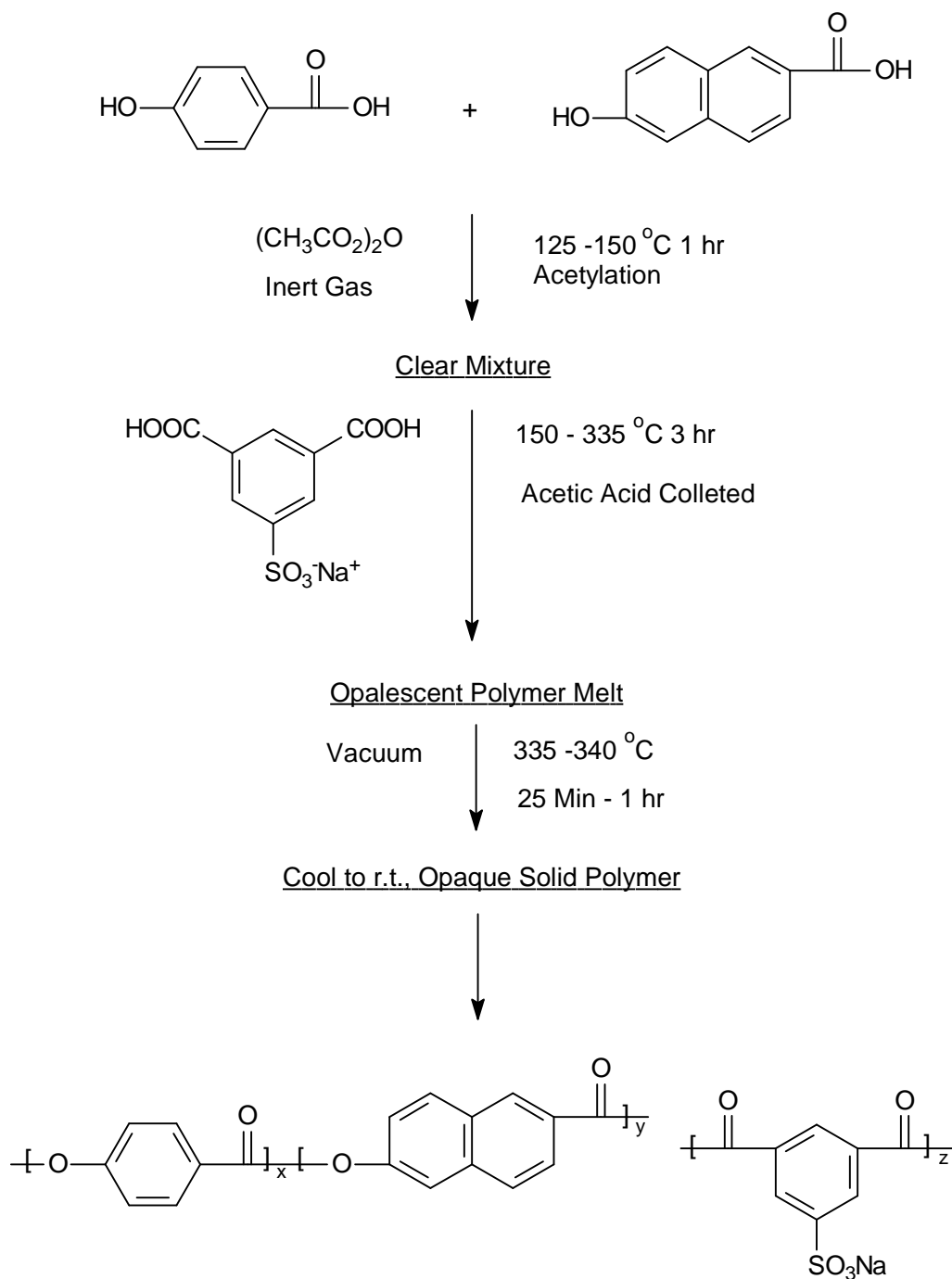


Figure 2.4. Synthesis of ionic NTP

Specifically, their efforts involved incorporating ionic groups into liquid crystalline polymers(LCP) in order to overcome some fundamental problems, such as poor transverse and compressive properties, which contrast to very high axial properties, poor

miscibility and poor adhesion observed in other polymer systems. Thus, LCPs and conventional polymers are frequently mixed to produce polymer blends, which are widely used to enhance polymer properties.⁹⁵ In their work with liquid crystalline polymers, Hara *et al.* demonstrated that ionic groups could be introduced into the polymer chain and confirmed that the very strong ion interaction among ionic clusters affected the properties of the LCP. The ionic clusters not only improved the compatibility between different polymers in polymer blends, but also improved thermal stability.

Storey R. F. *et al.*^{96, 97, 98, 99, 100, 101, 102, 103, 104, 105} examined telechelic multi-arm star-branched polyisobutylene ionomers, which they synthesized via living carbocationic polymerization. Specifically, their method involved the initiation of living isobutylene (IB) polymerization using the 2-chloro-2-propylbenzene (cumyl chloride) (CumCl)/TiCl₄/pyridine initiation system in 60/40 (v/v) hexane/methylene chloride at –80 °C. The monofunctional PIB chains were linked *in situ* via the addition of DVB in 10-fold excess relative to PIB chain ends. The star polymer was then sulfonated on the aromatic rings at the end of each branch, followed by neutralization with a base, to form sulfonate terminated star-telechelic ionomers. This modification affected the bulk physical properties of the star polymers by creating a thermally reversible network through intermolecular aggregation of the ionic chains ends. Although the ionic

⁹⁵ Hara, M.; Sauer, J. A., *J. Macro. Sci. Rev. in Macro. Chem. and Phys. C34*: **1994**, 3, 325-373

⁹⁶ Reuschle, D. A.; Mountz, D. A.; Mauritz, K. A.; Storey, R. F., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 713, 40(2)

⁹⁷ Reuschle, D. A.; Ali, N.; Mauritz, K. A.; Storey, R. F., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 715, 40(2)

⁹⁸ Barber, G. D.; Storey, R. F.; Moor, R. B.; *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 768, 40(2)

⁹⁹ Mountz, D. A.; Reuschle, D. A.; Storey, R. F.; Mauritz, K. A., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 892, 40(2)

¹⁰⁰ Sherman, J. W.; Storey, R. F., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 952, 40(2)

¹⁰¹ Storey, R. F.; Curry, C. L., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 954, 40(2)

¹⁰² Storey, R. F.; Donnalley, A. B., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 956, 40(2)

¹⁰³ Maggio, T. L.; Storey, R. F., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 958, 40(2)

¹⁰⁴ Storey, R. F.; Maggio, T. L.; Brister, L. B., *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 964, 40(2)

¹⁰⁵ Storey R. F.; Shoemaker K. A. *Polymer Bulletin*, **1997**, 393

modification didn't alter the glass transition temperature, the thermal decomposition temperature in N₂ was increased from 375 to 400 °C. It should also be noted that the sulfonation occurred exclusively at the terminal aromatic group, which was confirmed by titration.

Multivalent cations are more difficult to incorporate than are monovalent cations, but techniques do exist for the preparation of such materials.^{106, 107} Pan *et al.*, for example, examined ionic crosslinked poly(vinyl chloride)s containing varying contents of a carboxylic group. These were synthesized by suspension copolymerization of VC/AA; and the ionic crosslinked PVCs were prepared by solution and melt processing in the presence of a metal salt. They demonstrated that the carboxylic groups in copolymers exist in dimer form, and are partially coordinated with metal cation after neutralization. VC/AA copolymers with higher AA content and neutralized with Ca²⁺, Mg²⁺ cations tended to form a thermo-reversible ionic pair aggregation structure. It should be noted that the content and stability of the ionic pair aggregation phase could be affected by ionic pair content and type of metal cation.¹⁰⁸

The thermal properties, stiffness, melt viscosity, and mechanical properties of Na⁺, K⁺, Mg²⁺, Zn²⁺, Mn²⁺, and Co²⁺ sulfonate salts of poly(ethylene-co-methacrylic acid) (E/MAA) were studied by Yano *et al.*¹⁰⁹ Their results showed that the changes in structure and properties with increasing neutralization were greater in the alkaline and alkaline earth metal salts than in the transition metal salts. These differences were attributed to (1) the stronger ionic interactions, and (2) the larger number of carboxyl groups associated with the alkaline and alkaline earth metal salts in the ordered structure of ionic salt groups. The high-strain properties, such as tensile strength and elongation at break, were highly dependent on the strength of the ionic interactions and the valence of the cation.

¹⁰⁶ Broze, G.; Jerome, R.; Teyssie, P., *J. Polym. Sci. Polym. Lett. Ed.* **1983**, 21, 237-241

¹⁰⁷ Eisenberg, A.; King, M. *Ion-Containing polymers, Physical Properties and Structure*; Academic: New York, 1977

¹⁰⁸ Bao, Y. Z.; Huang, Z. M.; Weng, Z. X.; Pan Z. R., *Chemical J. of Chinese Univ.*, **1999**, 20(2) 299-303

¹⁰⁹ Hirasawa, E.; Yamamoto, Y.; Tadano, K.; Yano, S., *J. Appl. Polym. Sci.* **1991**, 42 (2), 351-362

Storey and Shoemake recently described the synthesis of calcium-ion containing telechelic poly(L,L-Lactide) ionomers.¹¹⁰ Calcium-carboxylate telechelic PLLA was synthesized by ion exchange with (carboxylic acid)-telechelic PLLA. (Carboxylic acid)-telechelic PLLA was obtained from ω -hydroxyl- ω -(carboxylic acid) PLLA precursor. The terminal ionic moieties of this calcium-carboxylate telechelic PLLA form reversible, electrostatic crosslinks that affect both the polymer's physical and thermal properties, including the nature and extent of crystallization. With the higher calcium ion content, the T_g increased while the crystallization of the polymers was destroyed.

Although not reviewed here, other research involving mono and multivalent metal ended ionomers, such as the sodium and zinc ionomer poly(ethylene-co-methacrylic acid) (E/MAA), has been done by Koyama and coworkers.¹¹¹

2.4 Some Other Thermo-reversible Bonds

The theory of using self-assembly and thermo-reversibility of hydrogen bonding as the connecting force in the formation of supramolecules has been very popular since it was first discovered.¹¹² In fact, a significant body of research exists in the area of liquid crystalline polymers,^{113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125} telechelic linear polymers

¹¹⁰ Storey R. F.; Shoemake K. A. *Polymer Bulletin* **1997**, 393

¹¹¹ Takahashi, T.; Watanabe, J.; Minagawa, K.; Takimoto J. I.; Iwakura, K.; Koyama, K., *Rheologica Acta* **1995**, 34(2), 163-171

¹¹² Joesten, Melvin D. Hydrogen bonding, p1, New York : M. Dekker, **1974**

¹¹³ Joesten, Melvin D. Hydrogen bonding, p2, New York : M. Dekker, **1974**

¹¹⁴ Kumar, U.; Kata, T.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1992**, 114(17), 6630

¹¹⁵ Kato, T.; Frechet, J. M. J. *Macromolecules* **1989**, 22, 3818

¹¹⁶ Kato, T.; Frechet, J. M. J. *Macromolecules* **1990**, 23, 360

¹¹⁷ Kato, T.; Frechet, J. M. J., *J. A. C. S.* **1989**, 111, 8533

¹¹⁸ Kato, T.; Fujishima, A.; Frechet, J. M. J., *Chem. Lett.* **1990**, 919

¹¹⁹ Kato, T.; Wilson, P. G.; Fujishima, A.; Frechet, J. M. J., *Chem. Lett.* **1990**, 2003

¹²⁰ Kato, T.; Adachi, H.; Fujishima, A.; Frechet, J. M. J., *Chem. Lett.* **1992**, 265

¹²¹ Havard, J. M.; Vladimirov, N.; Frechet, J. M. J.; Yamada, S.; Wilson, C. G.; Byers, J. D., *Macromolecules* **1999**, 32, 86-94

¹²² Chien, M. L.; Griffin, A. C. *Macromol. Symp.* **1997**, 117, 281-290

¹²³ Pourcain, C. B. S.; Griffin, A. C. *Macromolecules* **1995**, 28, 4116-4121

¹²⁴ *Properties of Ionic Polymers, Natural & Synthetic*; Salmen, L.; Htun, M., Eds.; STFI Meddelande: Stockholm, 1991.

¹²⁵ Xue Y.; Hara M.; Yoon, H. N.; *Macromolecules* **1998**, 31, 7806-7813

or polymer networks,^{126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141} and bio-systems.^{142, 143}

Another well-known thermo-reversible bonding process involves the synthesis of thermo-reversible covalent urethane bonds, which was patented in 1991.¹⁴⁴ These urethane bonds afford a good balance of melt processability -- especially at higher temperature where aromatic urethane reversibility occurs -- and excellent physical properties at temperatures up to 150 °C. Wagener and Muria also disclosed monomeric thermoreversible urethanes, whose molecular weight is a function of temperature.¹⁴⁵

Thermo-reversible bonds can also occur in some bio-systems with transition metal coordination.^{146, 147} To date, both covalent and noncovalent interconnect strategies have been used to assemble nanoscale inorganic building blocks into two- and three-dimensional macroscopic structures. Synthetic metalloporphyrins have been extensively studied as a model system for biomimetic catalysts and oxygen carriers in a blood.

¹²⁶ Lee, C. M.; Jariwala, C. P.; Griffin, A. C. *Polymer* **1994**, 35, 4550-4554

¹²⁷ Bladon, P.; Griffin, A. C. *Macromolecules* **1993**, 26, 6604-6610

¹²⁸ Eisenberg, C. D.; Goldel, A.; Terskan-Reinold, M.; Schubert, U. S.; *Macromol. Chem. Phys.* **1995**, 196, 1077

¹²⁹ Alexander, C.; Jariwala, C. P.; Lee, C. M.; Griffin, A. C., *Macromol. Symp.* **1994**, 77, 283

¹³⁰ Ducharme, Y.; Wuest, J. D., *J. Org. Chem.* **1988**, 53, 5787

¹³¹ Fouquey, C.; Lehn, J. M.; Levelut, A. M., *Adv. Mater.* **1990**, 2, 254

¹³² Kotera, M.; Lehn, J. M.; Vigneron, J. P., *J. Chem. Soc. Chem. Commun.* **1994**, 1994, 197

¹³³ Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F.M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, 278, 1601

¹³⁴ Beijer, F. H.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *Angew Chem Int Ed* **1998**, 37, 75-78

¹³⁵ Beijer, F. H.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W., *J. Org. Chem.* **1996**, 61, 6371-6380

¹³⁶ Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W., *J. A. C. S.*, **1998**, 120, 6761

¹³⁷ Sijbesma, R. P.; KyHirschberg, J. H. K.; Sontjens, S. H. M.; Meijer, E. W., *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.*, **1999**, 40(2) 1103

¹³⁸ Lillya, C. P.; et al., *ibid.* **1992**, 25, 2076

¹³⁹ Stadler, R. *Macromolecules* **1988**, 21, 121

¹⁴⁰ Hilger, C.; Stadler, R. *Polymer* **1991**, 32, 3244

¹⁴¹ de Lucca Freitas, L.; Auschra, C.; Abetz, V.; Stadler, R. *Colloid Polym. Sci.* **1991**, 269, 566

¹⁴² Hilger, C.; Drager, M.; Stadler, R. *Macromolecules* **1992**, 25, 2498

¹⁴³ Stadler, R. *Macromolecules* **1996**, 29, 2577-2583

¹⁴⁴ Kato, T.; Frechet, J. M.J, US Patent 5037574, **1991**

¹⁴⁵ Wagener and Muria, *Polym. Prepr. Am. Chem. Soc. Polym. Chem. Div.* **1989**, 30(1)

¹⁴⁶ Mucic, R. C.; Storhoff, J. J.; Mirkin, C. A.; Letsinger, R. L., *J.A.C.S.* **1998**, 120, 12674-12675

¹⁴⁷ Gonzalez, L.; Mo, O.; Yanez, M.; Elguero, J. *J Chem. Phy.* **1998** 109: (7) 2685-2693

Yamagishi *et al.* showed that cobalt and silver porphyrin moieties as biomimetic catalysts and oxygen carriers can bond to a polymer and interact with each other through reversible magnetic and electronic interactions.¹⁴⁸

2.5 Characterization Techniques

Special characterization techniques exist for both ionomeric and hydrogen bonding self-assembly systems. Since these polymeric systems possess unique ionic clusters, the size, strength and spatial arrangement of the ions in the ionomers are very important. In this respect, small-angle X-ray scattering (SAXS)^{149, 150, 151, 152} and small-angle neutron scattering (SANS)^{153, 154} were the primary physical techniques for determining ionic and polymer structures. In some instances, extended X-ray absorption fine structure (EXAFS) spectroscopy were used to directly observe the ionic aggregations,^{155, 156, 157} as well as to determine information on the local coordination structures of the metal cations in the ionomers. In combination, SAXS and anomalous SAXS (ASAXS) were used to study ionic pairing, multiplets, and clusters, which are responsible for the thermoreversible crosslinking and reinforcement of the polymer backbones of ionomers.

Gel permeation chromatography (GPC) was needed to determine molecular weight, while information about the structure of the oligomers and reaction parameters was obtained from NMR results. In addition, the existence of the terminal sulfonate ends in the oligomers was confirmed by FTIR, which was also used in connection with the ionomeric systems to observe the interaction of ionic clusters. Thermostability, melt rheology, and mechanical properties of the materials were investigated by thermo-

¹⁴⁸ Aramata, K.; Kajiwara, A.; Kamachi, M.; Umemura, Y.; Yamagishi, A. *Macromolecules* **1998**, 31, 3398

¹⁴⁹ Sazov, D.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M.; Kadish, K. M. *JACS* **1990**, 112, 7879

¹⁵⁰ Aramata, K.; Kajiwara, A.; Kamachi, M.; Umemura, Y.; Yamagishi, A. *Macromolecules* **1998**, 31, 3398

¹⁵¹ Kajiwara, A.; Aramata, K.; Kamachi, M.; Sumi, K. *Polym. J.* **1994**, 43, 2129

¹⁵² Chu, B.; Wu, D. Q.; Lundberg, R. D.; MacKnight, W. J. *Macromolecules* **1993**, 26, 994

¹⁵³ Wang, J.; Li, Y. J.; Peiffer, D. G.; Chu, B. *Macromolecules* **1993**, 26, 2663

¹⁵⁴ Tomita, H.; Register, R. A. *Macromolecules* **1993**, 26, 2791

¹⁵⁵ Grad, B. P.; Matsuoka, H.; Nakatani, Y.; Cooper, S. L.; Ise, N. *Macromolecules* **1993**, 26, 4064

¹⁵⁶ Roche, E. J.; Pineri, M.; Duplessix, R.; Levelut, A. M. *J. Polym. Sci. Polym. Phys. Ed.* **1981**, 19, 1

¹⁵⁷ Earnest, T. R.; Higgins, J. S.; MacKnight, W. J. *Macromolecules* **1982**, 15, 1390

gravimetric analysis (TGA), differential scanning calorimetry (DSC), melt rheometry, and dynamic mechanical thermal analysis (DMTA).

CHAPTER 3. SYNTHESIS AND CHARACTERIZATION OF IONIC AND NON-IONIC TELECHELIC AMORPHOUS POLY(ETHYLENE ISOPHTHALATE) (PEI)

3.1 Introduction

The presence of even a small amount of covalently bonded ionic moieties in organic polymers is known to exert a profound effect on their physical and rheological properties.^{1, 2, 3, 4} In fact, ionomers (polymers containing less than 20 mol % of ionic groups) have been shown to exhibit considerably higher moduli, and higher glass transition temperatures compared to their non-ionic analogues. Improvements in mechanical and thermal performance are generally attributed to the formation of ionic aggregates within the organic matrix, which act as thermo-reversible cross-links¹ and effectively retard the translational mobility of the chains. The precise form and size of these aggregates continues to receive significant attention, but their existence, as evidenced by small angle X-ray scattering (SAXS), neutron scattering, and other techniques, is firmly established for many compositions.⁴ Significant attention has been devoted to ionomers derived from chain-growth polymers, such as polyethylene, polystyrene and polyisobutylene, and only limited attention has been directed towards step-growth polymers containing ionic functionalities.⁵ Most investigations dealing with polyester ionomers have focused on random polyester ionomers, in which ionic groups were randomly distributed on the polymer main chains as pendent groups. However, there are significantly fewer studies concerning telechelic polyester ionomers, where the

¹ Eisenberg, A.; King, M. *Ion-containing Polymers*; Academic Press: New York, 1977; pp 15

² MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, 16, 41

³ Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Macromol. Chem Phys.* **1988**, C28, 99

⁴ Tant, M. R.; Wilkes, G. L. *J. Mater. Sci. Macromol. Chem Phys.* **1988**, C28, 1

ionic groups are located at the polymer chain ends.^{6, 7, 8, 9} Telechelic ionomers are generally recognized as model systems for random ionomers since the molecular weight between ionic endgroups is controlled and the ionic groups are located exclusively at the polymer chain ends.¹⁰ Telechelic association, coupled with adjacent ordered sequences, serves to strengthen subsequent non-covalent association.^{11, 12, 13, 14, 15} Metal sulfonates are known to strongly associate in the solid state as ionic aggregates and subsequently disassociate at elevated temperatures. Sulfonated isophthalates have received significant attention in the past as modifiers for polyester fibers to improve organic dye adhesion.^{16, 17} Amorphous polyester ionomers were initially investigated due to their improved solubility compared to semicrystalline polyesters such as poly(ethylene terephthalate). Improved solubility will facilitate subsequent molecular weight and solution viscosity characterization. These features will facilitate the initial establishment of structure-property relationships for telechelic polyester ionomers, and subsequent efforts will involve the investigation of semicrystalline telechelic polyester ionomers. In our current research, a series of novel amorphous poly(ethylene isophthalate) (PEI) ionomers were synthesized using sodio 3-sulfobenzoic acid (SSBA) as a monofunctional, ionic, endcapping reagent. In addition, this chapter will describe the preparation of dodecanol

⁵ Greener, J.; Gillmor, J. R.; Daly, R. C. *Macromolecules* **1993**, 26, 6420

⁶ Chassenieux, C.; Tassin, J.; Gohy, J.; Jerome, R. *Macromolecules* **2000**, 33, 1796

⁷ Sobry, R.; Fontain, F.; Ledent, J.; Foucart, M.; Jerome, R. *Macromolecules* **1998**, 31, 4240

⁸ Broze, G.; Jerome, K.; Teyssie, P.; Macro, G. *Polym. Bull.* **1981**, 4, 241

⁹ Broze, G.; Jerome, K.; Teyssie, P.; *J. Polym. Sci., Polym. Lett. Ed.* **1981**, 28, 8504

¹⁰ Broze, G.; Jerome, K.; Teyssie, P.; *J. Polym. Sci., Polym. Lett. Ed.* 1981, 28, 8504

¹¹ Kumar, U.; Kato, T.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1992**, 114(17), 6630.

¹² Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, 278, 1601.

¹³ Chien, M. L.; Griffin, A. C., *Macromol. Symp.* **1997**, 117, 281-290.

¹⁴ Hilger, C.; Drager, M.; Stadler, R., *Macromolecules* **1992**, 25, 2498.

¹⁵ Stadler, R., *Macromolecules* **1988**, 21, 121.

¹⁶ Rao, B. R.; Datye, K. V. *Textile Chemist and colorist*, 1996, October, 17

¹⁷ Toray Industries Inc., Japanese Patent No. 8006514, January 1980

terminated poly(ethylene isophthalate) as non-ionic telechelic oligomers for comparison to the ionic telechelic oligomers.

3.2 Experimental

3.2.1 Materials

All reagents were used without further purification. Ethylene glycol and 3-sulfobenzoic acid, sodium salt (SSBA, 97 %) were generously donated by Eastman Chemical Co. Dimethyl isophthalate, sodium acetate (ACS reagent grade, 99.5 + %), and 1-dodecanol were purchased from Aldrich. In addition, phosphoric acid (crystals, 98 %), cobalt acetate (99 %), antimony (III) oxide (99 %), manganese acetate (99 %) and titanium isopropoxide were all purchased from Aldrich and were used directly.

3.2.2 Preparation of Catalyst Solutions

Sb catalyst: Sb_2O_3 (3.00 g) solid was dissolved in 250 mL ethylene glycol (EG). The mixture was heated at 100 °C and stirred for 24 hours under nitrogen purge. The mixture was then filtered and a clear solution was obtained at a concentration of 0.012 g / mL based on Sb.

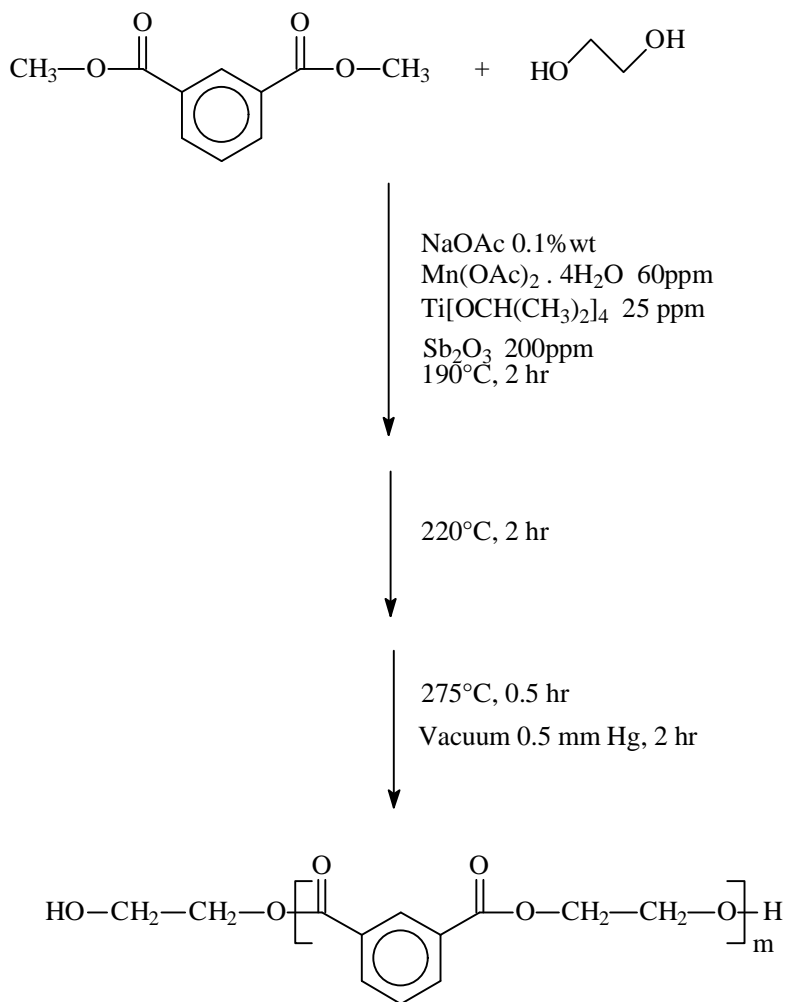
Mn catalyst: $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.685 g) and pure HOAc (1.319 g) were added to 125 mL of EG and heated to produce the catalyst solution at a concentration of 0.0215 g / mL based on Mn.

Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g) with 62.5 mL of n-BuOH in a dry bottle under nitrogen at a concentration of 0.055 g / mL based on Ti.

3.2.3 Synthesis of Non-Terminated High Molecular Weight Poly(Ethylene Isophthalate) (PEI)

To a mixture of 48.5 g of DMI and 31 g of EG (100 % excess), manganese catalyst (2.31 mL), antimony catalyst (3.8 mL) and titanium catalyst (0.51 mL) were

added under nitrogen (Scheme 3.1). A multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. The final product was obtained by breaking the reaction flasks. Since no solvent was involved in the reaction, no further purification was performed.

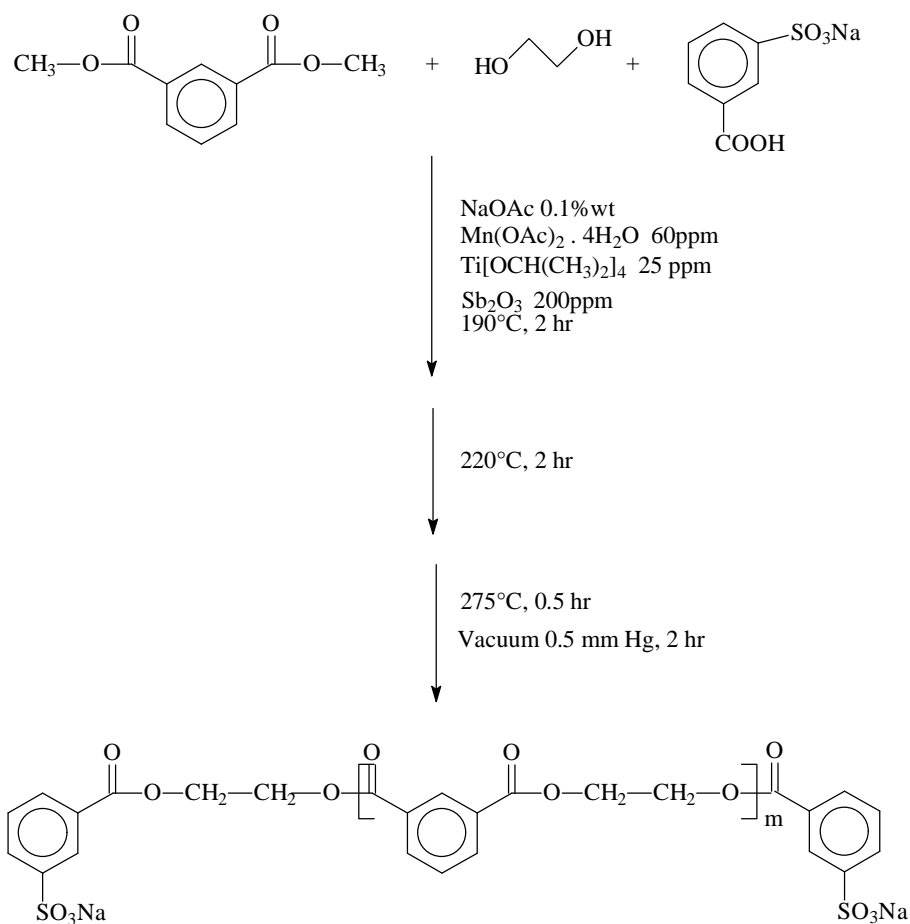


Scheme 3.1. Synthesis of non-terminated PEI polymers by melt polymerization

3.2.4 Synthesis of Sulfonate Terminated PEI Ionomers (PEI-SSBA)

To a mixture of DMI (48.5 g, 0.25 mol) and EG (31 g, 0.5mol, 100 % excess), varying amounts of end capper, SSBA (PEI-xSSBA, x = 1 mol %, 3 mol %, 5 mol %

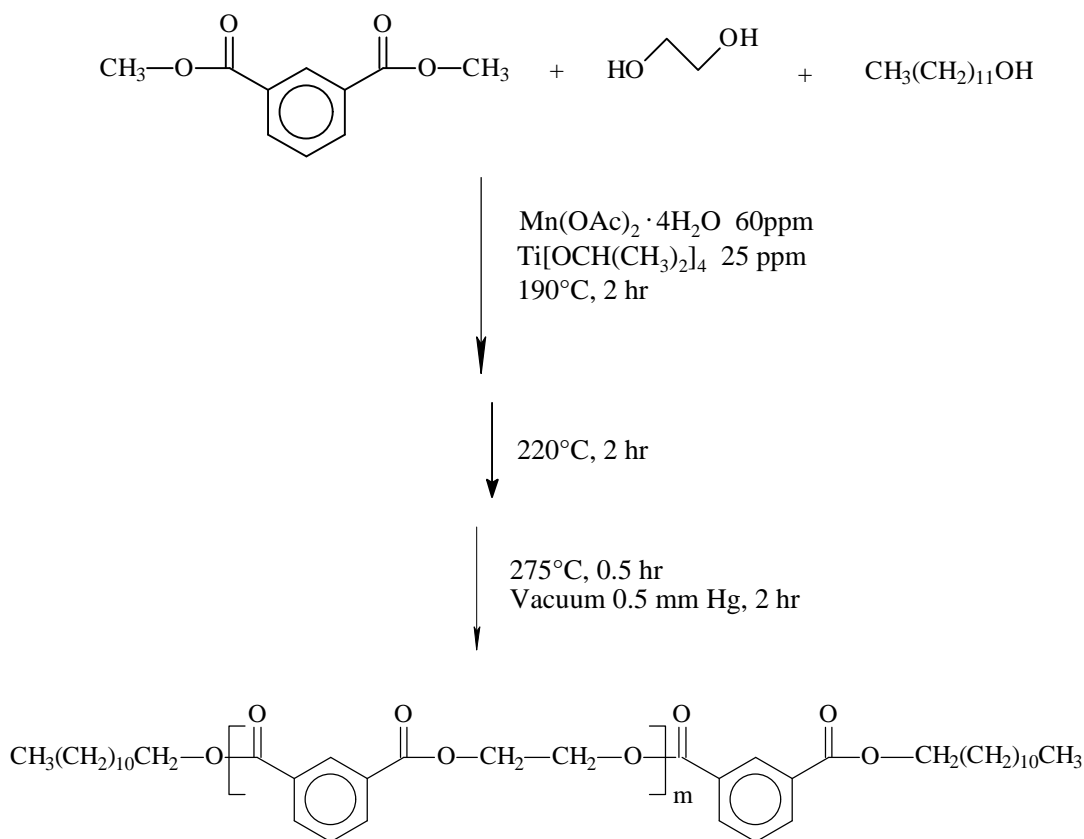
compared to DMI) were added to obtain a series of PEI ionomers with different molecular weights (Scheme 3. 2). Manganese catalyst (2.31 mL), antimony catalyst (3.8 mL) and titanium catalyst (0.51 mL) were charged under nitrogen. A multi-step temperature procedure was used for the reaction, i.e. the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours, and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. The final product was obtained by breaking the reaction flasks. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.



Scheme 3.2. Synthesis of sulfonate terminated PEI ionomers by melt polymerization

3.2.5 Synthesis of Dodecanol Terminated Poly(ethylene isophthalate) (PEI-Dode-OH)

In order to obtain PEI with controlled molecular weights, 1-dodecanol (b.p. = 262 °C) was utilized. To the mixture of dimethyl isophthalate (48.5 g, 0.25 mol), ethylene glycol (31 g, 0.5 mol, 100 % excess) and dodecanol (PEI-yDode-OH, y = 5 mol %, 10 mol %, 15 mol %, 20 mol %, 30 mol % and 40 mol %) were added (Scheme 3. 3). Manganese catalyst (2.31 mL), and titanium catalyst (0.51 mL) were added under nitrogen. The same multi-step temperatures were used for the reaction, i.e. the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. The final product was obtained by breaking the reaction flasks. No further purification was needed.



Scheme 3.3. Synthesis of dodecanol terminated poly(ethylene isophthalate) (PEI-Dode-OH)

3.2.6 Polymer Characterization

A 400 MHz NMR (Varian-400) was used to characterize all the PEI samples. The solvent used was CDCl_3 . FTIR spectra were collected on an infrared spectrometer (Perkin Elmer, 283B) to detect the sulfonate end group. Gel permeation chromatography (GPC) was performed to obtain the molecular weights and molecular weight distributions using a Waters 2690 chromatograph equipped with a differential refractive index detector (Viscotek Laser Refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel, using polystyrene standards. Chloroform was utilized as the mobile phase and the data were recorded at 25 °C at a flow rate of 1.0 mL / min. Melt rheology behavior was analyzed using a melt rheometer (TA Instruments, Advanced Rheometer AR 1000). DSC (Perkin Elmer, Pyris 1) was used to study glass transition temperatures. All the samples were kept at 290 °C for 3 min to eliminate any thermal history, then quenched from 290 °C to room temperature at a rate of 200 °C/min, and finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen and all the data collected were from the second scan. TGA (Thermal Analyst 2100, Du Pont Instruments) was used to study the thermal stability of the polymers. The solution behavior of the PEI samples was studied using an Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$. The solvent used was chloroform.

3.3 Results and Discussions

3.3.1 GPC and NMR Analysis

Amorphous polyester systems were selected as a model for our initial studies because of their high solubility in CHCl_3 , which enables them to be easily characterized. PEI-SSBA ionomers with varying amounts of a sodium sulfonate end capper (1 mol %, 3 mol %, 5 mol % of SSBA) were synthesized to study the effect of ionic interactions on polymer properties. A matched set of dodecanol terminated PEI polymers were also synthesized for comparison. For all of the reactions, ethylene glycol was used at 100 mol % excess.

NMR spectroscopy of PEI-5%SSBA indicated the disappearance of the hydroxyl ethyl groups at 3.9 and 4.2 ppm, suggesting that the $\text{CH}_2\text{CH}_2\text{-OH}$ end groups in the oligomer (Figure 3.1, top) were replaced with SSBA (Figure 3.1, bottom). In contrast, the non-terminated polyester displayed hydroxyl ethyl end groups (Figure 3.1, top). Figure 3.2 shows the NMR spectrum of dodecanol terminated PEI-12%Dode-OH. Dodecanol connected to the polymer chain end was observed at 4.3 ppm (2 H, *t*), 1.7 ppm (2 H, *m*), 1.3 ppm (18 H, *m*) and 0.8 ppm (3 H, *t*). No free dodecanol was identified in any of the polymer samples. The amount of dodecanol remaining in the polymer chain ends was 4.8 mol %. It should be noted that the polymer chain displayed a significantly reduced amount of dodecanol than had originally been charged into the reaction flask. This is due to the fact that dodecanol has a boiling point of 260-262 °C, and thus most of it was lost during the lengthy, high temperature reaction procedure, as only a portion of it reacted with the polymer chains. The relationship of molecular weight to amount of dodecanol charged into the reaction is plotted in Figure 3.3. This curve was obtained from experimental data, which usefully reveals the amount of dodecanol that should be used to obtain a desired molecular weight. GPC was also employed for the characterization of the synthesized dodecanol terminated polyesters and non-terminated polyesters exhibited high molecular weights (around 37,000 g/mol) (Figure 3.4). Unfortunately, the exact molecular weights of PEI-SSBA ionomers could not be determined by GPC due to the strong interaction between the ionic end cappers and the GPC column. Table 3.2 gave the calculated number average molecular weights of the ionomers as determined using Carothers' Equations:

where

m_e = the molar mass of the combined end group

m_u = the molar mass of an internal repeat unit

$N(A)$ = moles of monofunctional end capping reagent

x = the number of internal repeat units

The number-average molar weight of the reaction product is then:

$\langle Mn \rangle = (\text{total mass of product molecules}) / (\text{moles of product molecules})$

$$= [\Sigma (m_e + x * m_u)] / (N(A)/2)$$

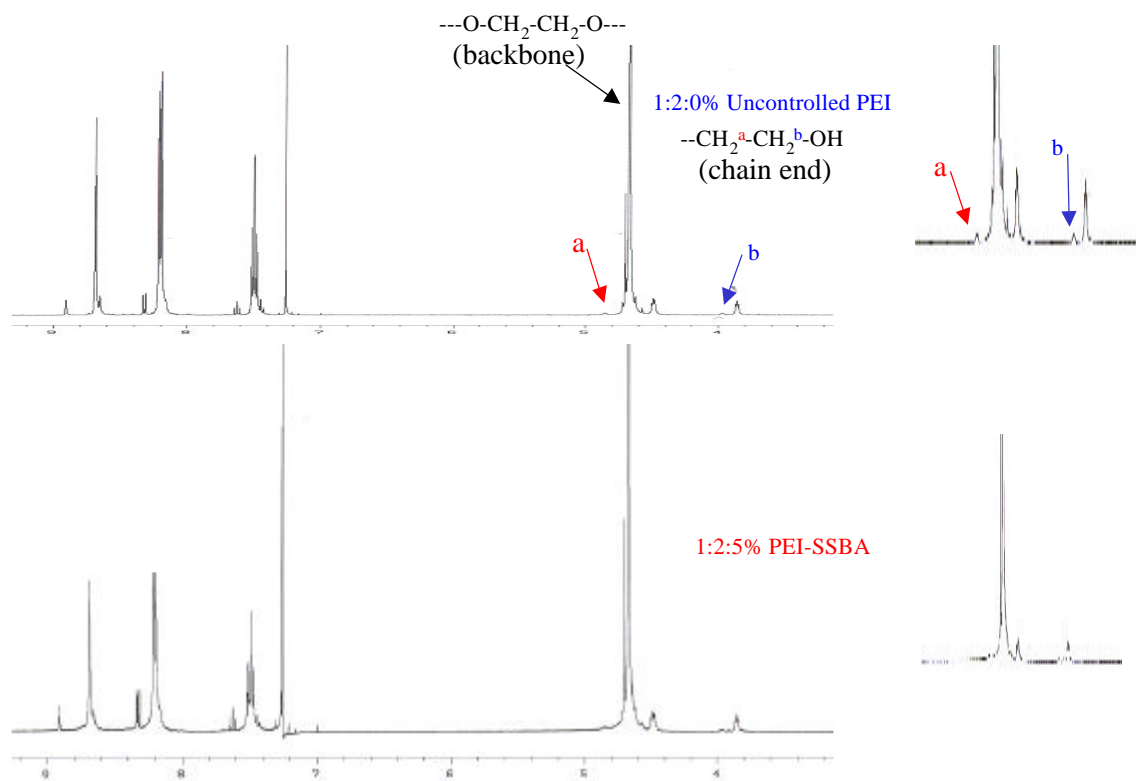


Figure 3.1. ^1H NMR spectra of non-terminated poly(ethylene isophthalate) (top) and sulfonate terminated PEI-5%SSBA (bottom) in CDCl_3 at room temperature

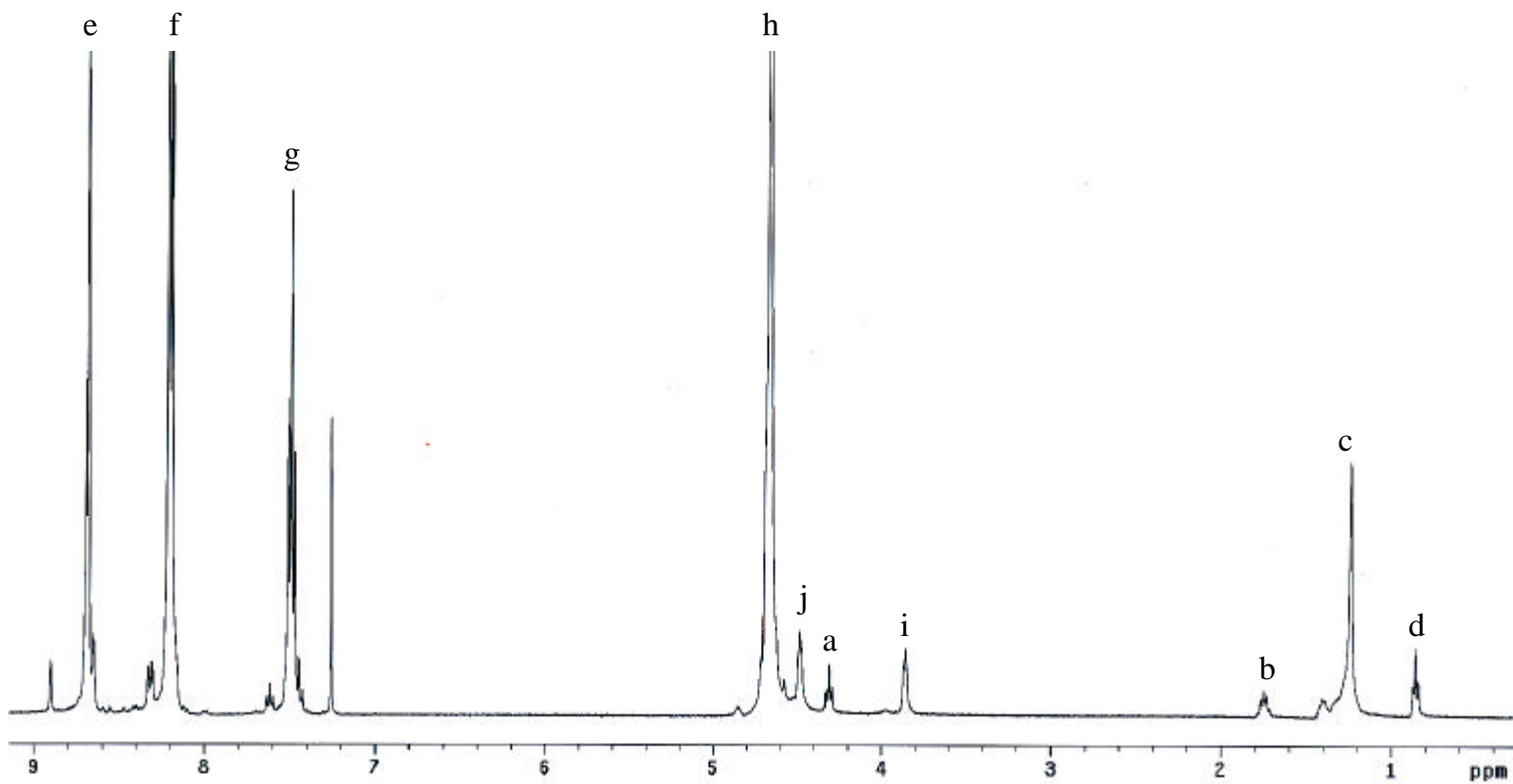
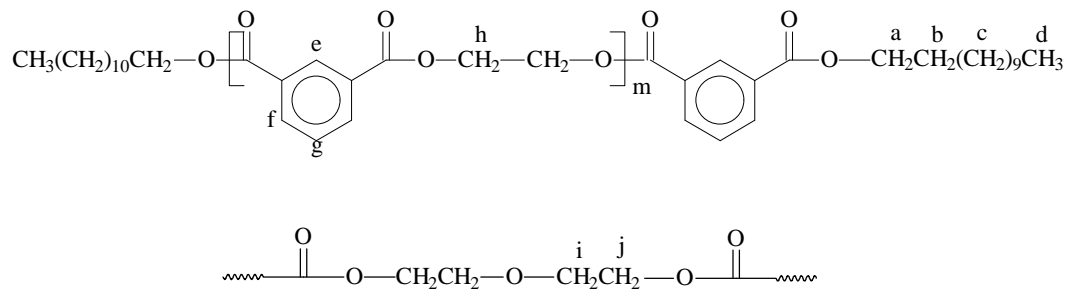


Figure 3.2. ¹H NMR spectrum of dodecanol terminated PEI with 12 mol % of dodecanol (PEI-12%Dode-OH), CDCl₃, room temperature

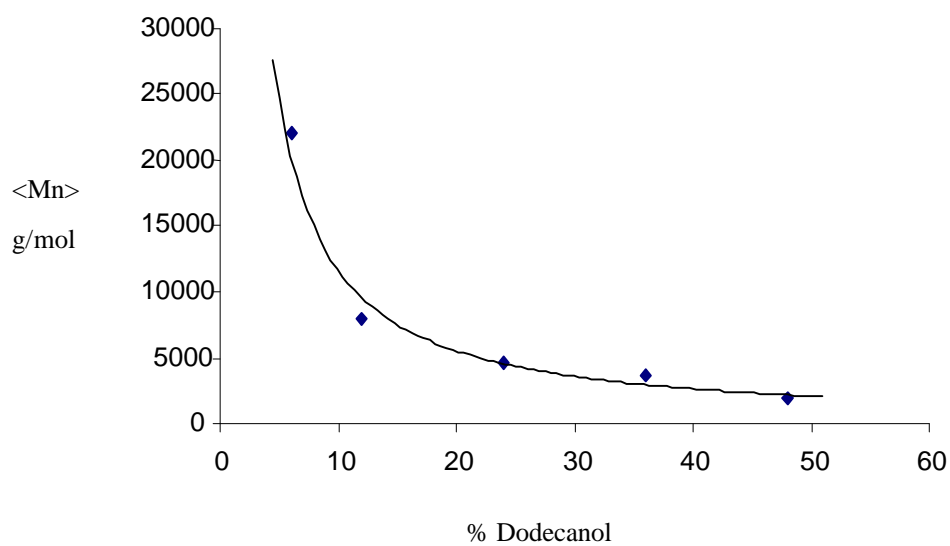


Figure 3.3. Relationship of number average molecular weight vs amount of charged dodecanol of PEI-xDode-OH (GPC in CDCl_3 , room temperature)

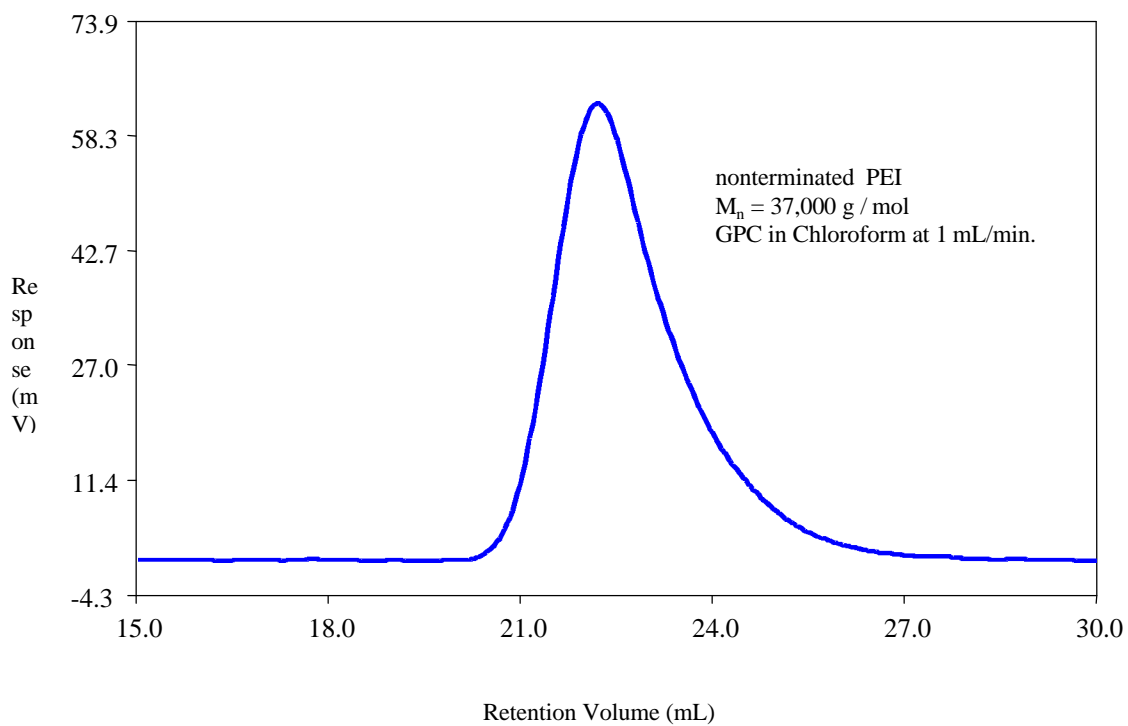
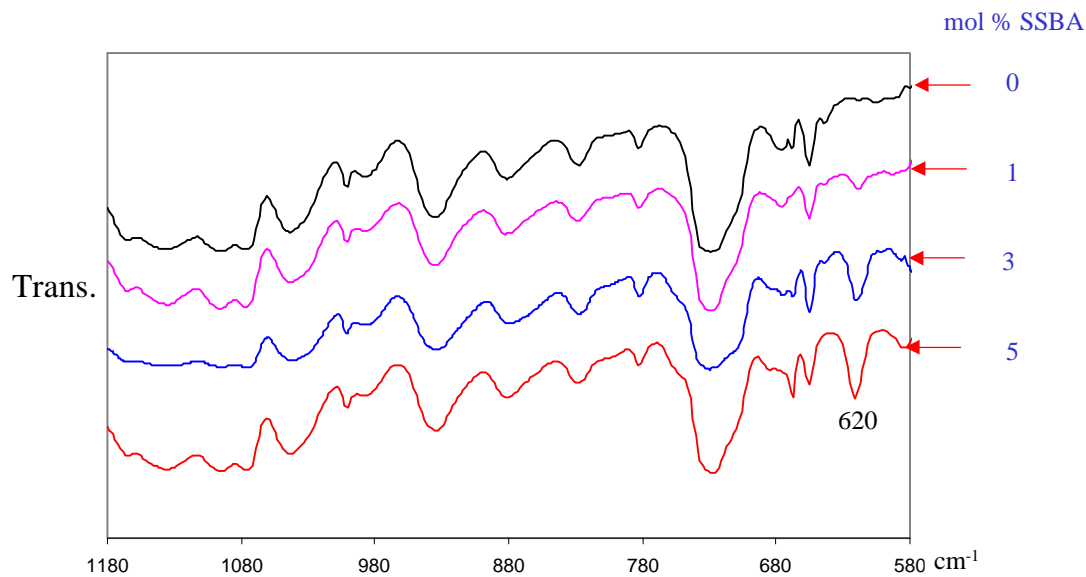


Figure 3.4. GPC trace of non-terminated high molecular weight PEI; chloroform, 1 mL/min, room temperature

3.3.2 FTIR Analysis

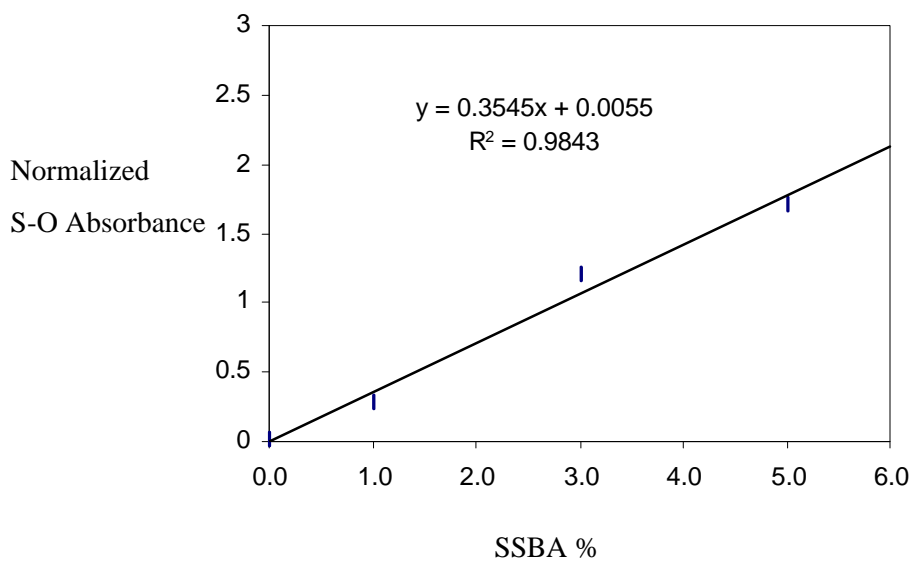
In the FTIR spectrum, the peak for the S-O stretching mode, which normally appears between 600-700 cm^{-1} for organic sulfonates¹⁸ was used to identify the sulfonate groups of ionic oligomers. The IR spectra of the PEI and PEI-SSBA are shown in Figure 3.5a. As expected, no S-O stretching mode was observed for the non-terminated polyester. For PEI-SSBA, however, the peaks observed at 620 cm^{-1} due to S-O stretching mode are very clear. Furthermore, as the ionic group content in the ionomers increased, the peak intensity increased correspondingly. This correlation, which was nearly linear as estimated by the plot of peak area vs. ionic group content (Figure 3.5b), indicated the successful incorporation of SSBA end cappers in the ionomers. These results also confirmed that FTIR is a reliable indicator of the presence of sulfonate groups.

¹⁸ Nakanishi, K. Infrared Absorption Spectroscopy (Practical); Holden-Day Inc.; San Francisco, 1962; p54



FTIR - MIDAC, M2004 series, under N_2 , 25°C.

(a)



(b)

Figure 3.5. a) FTIR spectra of non-terminated PEI and sulfonate terminated PEI-SSBA; b) Normalized S-O absorbance peak area from SSBA vs ionic group content in PEI-SSBA, bending 1,3 substituted benzene ring at 730 cm^{-1} was used as internal standard

3.3.3 DSC and TGA Analysis

DSC and TGA measurements were performed to study the effect of counterions and chain backbone structure on thermal properties of the PEI polymers. As revealed by DSC, all the PEI samples were amorphous with no detectable melting or crystallization phenomena. With regard to the PEI-Dode-OH, increasing the content of the dodecanol end group resulted in lower molecular weight polymers and more dominant plasticizing effect, thus lower glass transition temperatures as expected (Table 3.1). Interestingly, the T_g s of all the PEI-SSBA polymers were approximately 60 °C, indicating that they were not sensitive to varying ionic group (SSBA) content (Table 3.2). Two factors are associated with these results. With higher ionic group (SSBA) content, the PEI ionomer displays lower molecular weight as a result of the successful incorporation of the ionic end groups to the ionomers – thus decreasing the T_g . Conversely, higher SSBA content results in stronger ionic interactions and the formation of more ionic aggregates. It is the formation of these ionic crosslinks that restricts polymer chain mobility, which in turn increases the T_g of the ionomer.^{19, 20} As a result of the two factors described above, the observed T_g s were relatively unchanged (58 ~ 60 °C) when the SSBA content in PEI-SSBA was varied. It is believed that all of the ionic aggregates in the PEI ionomers were multiplets (2-8 ion pairs, < 50 Å), rather than ionic clusters (phase separation, > 50 Å), since only one glass transition temperature was observed for every ionomer.⁵ As shown in DSC curves, the crystallization peaks and melting point were unremarkable, indicating that the ionic PEI polymers possessed relatively low crystallinity. As such, they are good candidates for amorphous materials (Figure 3.6).

¹⁹ Ogura, K.; Sobue, H.; Nakamura, S. *J. Polym. Sci. Polym. Phys.* **1973**, 11, 2079

²⁰ Otocka, E. P.; Kwei, T. K. *Macromolecules* **1968**, 1, 401

⁵ Greener, J.; Gillmor, J. R.; Daly, R. C. *Macromolecules* **1993**, 26, 6420

Table 3.1. DSC and TGA results of non-terminated and dodecanol terminated (PEI-Dode-OH) polymers

PEI-Dode-OH (DMI : EG : Dode-OH)	M_n (g / mol)	PDI	% DEG	T_g (°C), DSC	5% wt loss T (°C) TGA, N ₂
1 : 2 : 0 %	37,800	2.11	2.1	59	350
1 : 2 : 5 %	22,300	2.12	2.7	54	356
1 : 2 : 12 %	8,400	2.33	2.5	49	360
1 : 2 : 24 %	5,200	2.53	2.4	42	355
1 : 2 : 36 %	4,400	2.44	2.3	33	353
1 : 2 : 48 %	2,600	2.18	2.6	24	355

Table 3.2. DSC results of sulfonate terminated PEI-SSBA, N₂, second heat, heating rate is 10 °C/min

DMI : EG : SSBA	M_n (g / mol)	T_g (°C), DSC	5% wt loss T (°C) TGA, N ₂
1 : 2 : 0 %	37,800	59	350
1 : 2 : 1 %	38,100	58	378
1 : 2 : 3 %	13,300	58	374
1 : 2 : 5 %	8,400	60	365

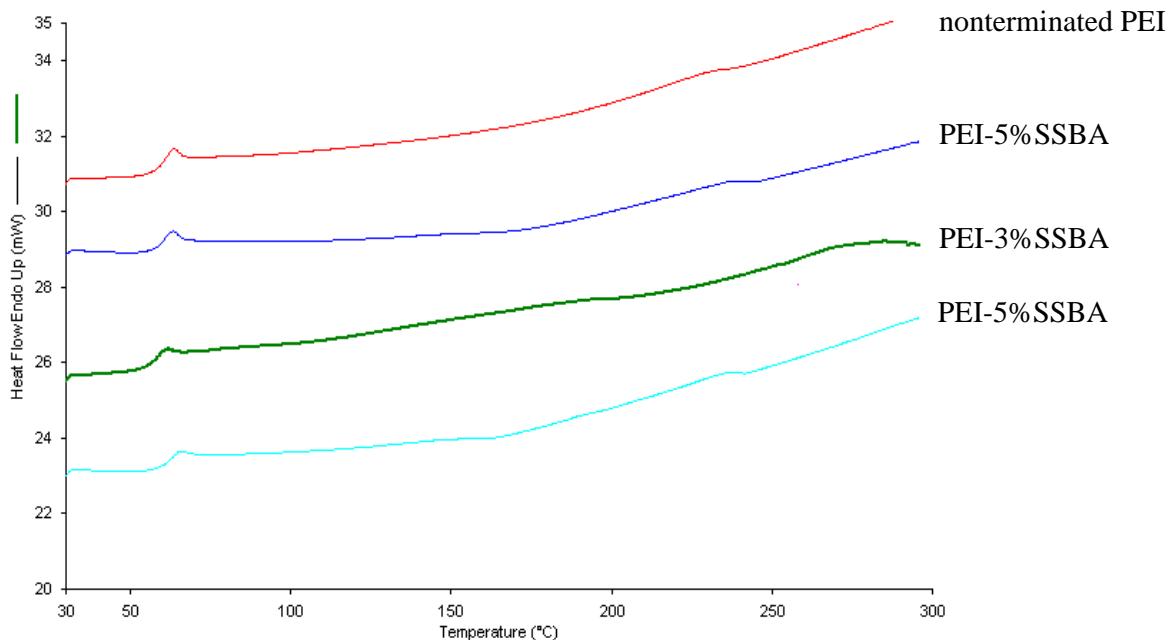


Figure 3.6. DSC curves of sulfonate terminated PEI-SSBA, N₂, second heat, 10 °C/min heating rate

A summary of the thermal properties of the ionic and non-ionic PEI samples is provided in Table 3.3. Low molecular weight ionic PEI with 5 mol % SSBA (PET-5%SSBA, $M_n = 8,400$ g / mol), displayed a higher glass transition temperature ($T_g = 62$ °C) comparable to that of the non-terminated high molecular weight PEI ($M_n = 37,100$ g / mol, $T_g = 57$ °C) (Table 3.3, first two samples). This is due to the fact that an ionic interaction tends to be quite strong and helps to maintain the structural integrity of the polymer chain, thus limiting the mobility of the polymer chain and producing a high glass transition temperature. The second and third samples shown in Table 3.3 displayed the same low molecular weight, however the PEI-12%Dode-OH showed a much lower glass transition temperature (as expected), while the PEI-5%SSBA ionomer had a much higher glass transition temperature due to the strong ionic interaction. Benzoic acid and benzyl alcohol were also studied as end cappers to control the molecular weight of the PEI, however, it is presumed that volatility prevented their utility.

Table 3.3. Summary of DSC, GPC and NMR results for polyester prepared using different end capping agents

PEI with different end cappers	T _g (°C), DSC	M _n (g/mol) GPC ^a , NMR ^b , or Calculation ^c
non-terminated PEI	57	37,000 ^{a, b}
PEI-5%SSBA	62	8,400 ^{b, c}
PEI-12%Dode-OH	41	8,400 ^{a, b}
PEI-5%Benzoic Acid	57	37,000 ^{a, b}
PEI-5%Benzyl Alcohol	57	32,000 ^{a, b}

TGA showed that all samples were thermally stable up to 400 °C (Table 3.1, table 3.2, Figure 3.7).

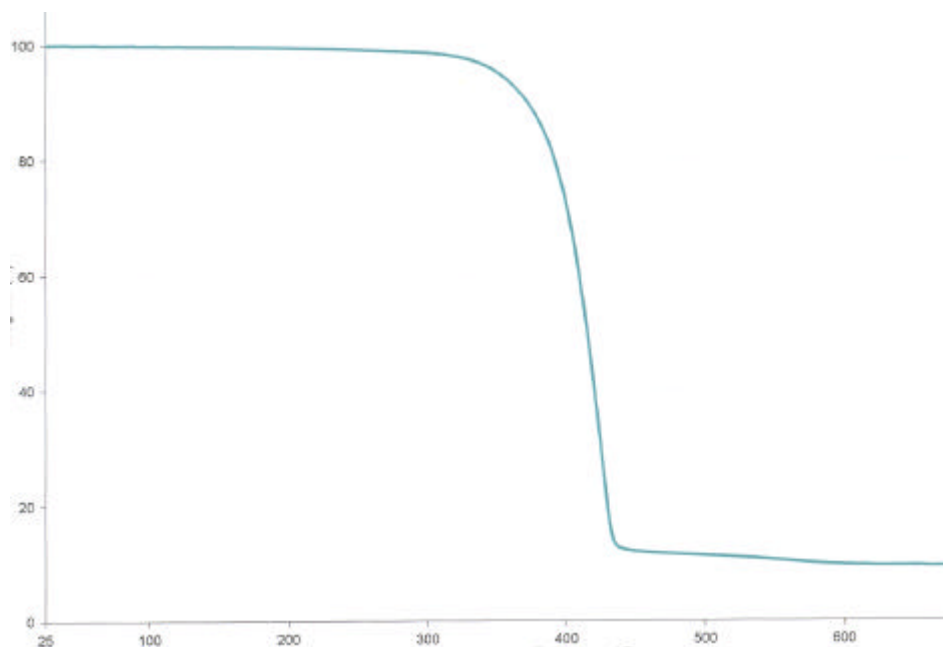


Figure 3.7. TGA trace of non-terminated high molecular weight PEI, N₂, heating rate 10 °C/min

3.3.4 Solution Viscometry Study

Solution viscometry was used to study the solution behavior of the PEI samples. For the non-terminated low molecular weight PEI, Huggins and Kramer equations were employed,²¹ and two straight lines were obtained (Figure 3.8a). For the ionomers, however, two curves with upward curvatures were noted (PEI-3%SSBA, Figure 3.8b). The observed non-linear relation between solution viscosity and (dilute) polymer concentration is believed to arise from the ionic interactions in the solutions. With the existence of ionic groups within the polymer chains, the aggregation level varies as a result of different ionic association at different dilute solution concentrations. Considering this added factor, it is reasonable to expect that the dilute solution viscosity behavior of the ionomers would not resemble the linear behavior of non-ionic polymers. Further experimental and theoretical studies of these non-linear relationships should be carried out. It should be noted, however, that the results described above are consistent with the previous literature for telechelic sulfonated ionic liquid crystalline systems.²²

²¹ Joseph C. Salamone, *Polymeric Materials Encyclopedia*; Boca Raton: CRC Press; 1996, Vol 6, 3473

²² B. Zhang and R. A. Weiss, *J. of Polymer Science: Part A: Polymer Chemistry* **1992**, 30, 989

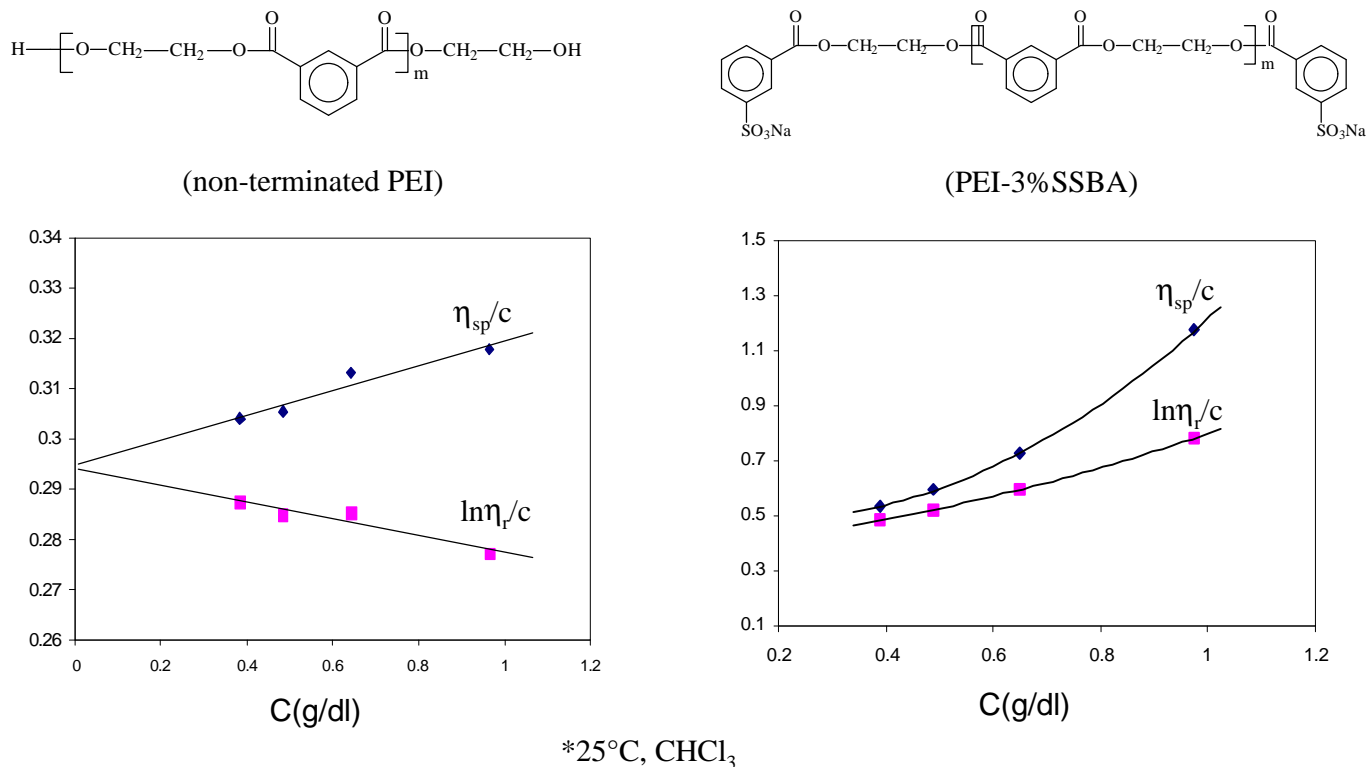


Figure 3.8. Solution behavior of the non-terminated low molecular weight PEI (left) and sulfonate terminated PEI-3%SSBA (right) samples, CHCl₃, 25°C

3.3.5 Melt Rheology Study

Although melt rheology is not an efficient way of determining the structure and organization of the ionic aggregates, it is quite efficient for identifying the size and number of aggregates.²³ As such, it effectively complements other, more direct, characterization techniques and provides useful insights.^{2, 3, 4} Any factor affecting the ionic associations and their interaction with the surrounding organic matrix, e.g., the structure of the ionic moiety, the counterion type, the degree of neutralization, and the flexibility of the polymer backbone, will also influence the melt rheology of the ionomers.^{24, 25, 26, 27, 28, 29} The melt rheological behavior of an ionomer can be investigated

²³ Greener, J.; Gillmor, J. R.; Daly, R. C. *Macromolecules* **1993**, 26, 6416

²⁴ Weiss, R. A.; Agarwal, P. K. *J. Appl. Polym. Sci.* **1981**, 26, 449

²⁵ Weiss, R. A.; Agarwal, P. K. J.; Lundburg, R. D. SPE ANTEC Proc. 1984, 468

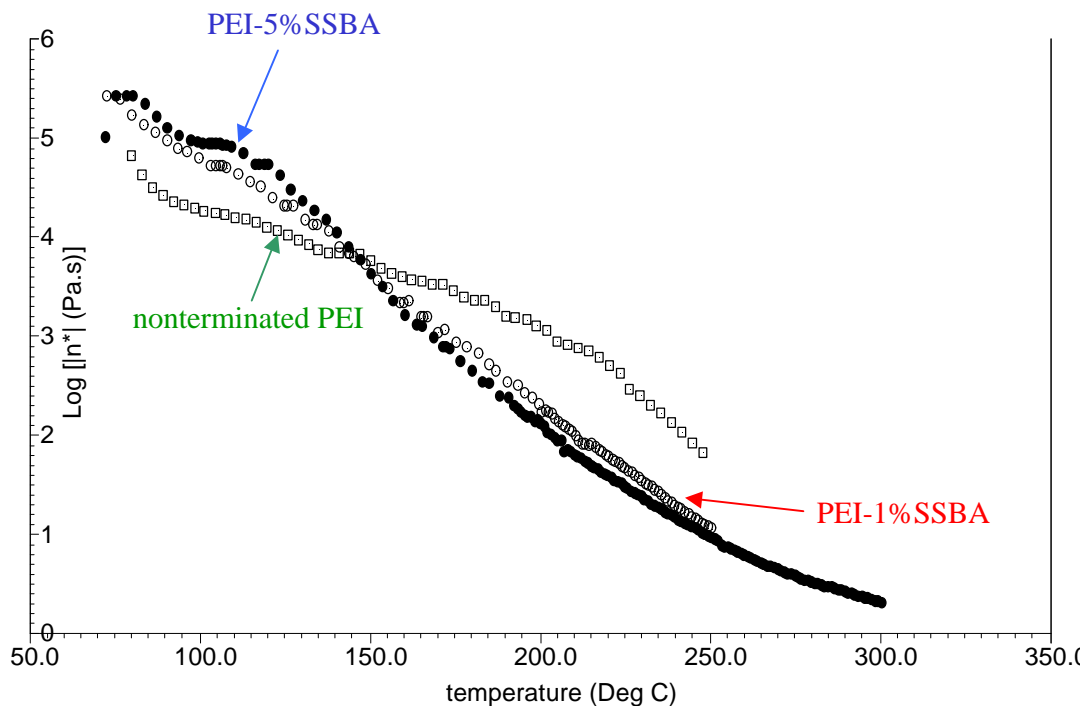
²⁶ Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, 24, 1071

²⁷ Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. In *Ions in Polymers*; Eisenberg, A. Ed.; ACS Polymer Preprints: American Chemical Society: Washington, DC, 1980; p 3

using a conventional melt rheometer. Figure 3.9 shows the results of non-terminated high molecular weight PEI and sulfonate terminated PEI-1%SSBA and PEI-5%SSBA polymers. At lower temperatures (<150 °C), PEI-1%SSBA and PEI-5%SSBA displayed higher viscosity than that of the non-terminated PEI, which behaved similarly to a higher molecular weight polymer. The formation of ionic aggregates at these lower temperatures (<150 °C) is probably responsible for the apparent molecular weight increase in these samples. Thus, the observed high melt viscosities (<150 °C) are attributed to ionic interactions. At higher temperatures (>150 °C), however, the ionic clusters dissociated, and the ionomers behaved as low molecular weight oligomers. This argument can be used to explain the dramatically decreased melt viscosity for both ionomers (>150 °C). These attractive ionomer characteristics (high MW polymer melt behavior at low temperature and low MW oligomer melt behavior at high temperature) may benefit processing (high temperature), while maintaining strong mechanical properties at typical application temperatures. Thus, the effective molecular weight of an ionomer, which also determines viscosity, is thermally reversible as a result of the thermal ionic aggregate association / dissociation mechanism.

²⁸ Lundburg, R. D.; Makowski, H. S. In *Ions in Polymers*; Eisenberg, A. Ed.; ACS Polymer Preprints: American Chemical Society: Washington, DC, 1980; p 21

²⁹ Bagrodia, S.; Pisipati, R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1984**, 29, 306



N_2 , 1 rad/sec, step isothermal

Figure 3.9. Melt rheological behavior of high molecular weight non-terminated PEI and sulfonate terminated PEI-1%SSBA and PEI-5%SSBA, N_2 , 1 rad/sec, step isothermal

In summary, the existence of ionic groups on polyester chain ends did affect the physical and mechanical properties of the materials. The ionic PEI displayed relatively higher viscosity and higher glass transition temperatures than their non-ionic PEI counterparts, primarily due to the formation of ionic aggregations that limited the mobility of the polymer chains. The higher the ionic group content, the more ionic aggregation and the stronger the ionic interaction. This association was confirmed by systematic studies on the various physical properties of the ionomers and dodecanol terminated analogs.

3.4 Conclusions

Novel sulfonate terminated amorphous polyester ionomers (PEI-SSBA) were synthesized using DMI and EG (100 % excess) with varying amounts of sodium sulfonate end capper. Dodecanol terminated non-ionic PEI-Dode-OH polymers were also successfully synthesized as the comparison.

We have shown that by using melt polymerization, a sulfonate end cap could be successfully introduced to a polymer chain end to form a telechelic ionic polymer. NMR, FTIR and solution viscometry confirmed the ionic and nonionic polymer structure, as well as the existence of the ionic end caps. Glass transition temperatures, as shown by DSC, revealed that the low molecular weight ionomers displayed characteristics comparable to those of high molecular weight non-terminated polyesters. With regard to the PEI ionomers, melt rheology results demonstrated that at lower temperatures (<150 °C), they displayed rheological properties characteristic of higher molecular weight materials. Above 150 °C, the ionic aggregates were destroyed and the melt viscosities decreased dramatically to levels typical of non-ionic polymer materials of similar molecular weight, thus possibly facilitating their melt processibility.

CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF TELECHELIC SEMI-CRYSTALLINE POLYESTERS

4.1 Introduction

Semi-crystalline polyesters are an important class of materials that are widely used in industry, especially in comparison to amorphous aromatic polyester systems. Poly(ethylene terephthalate) (PET) is one of the most significant semicrystalline polyesters, with an annual world wide production of approximately 6.7 million tons. PET, which can be processed by melt spinning, injection molding, blow molding or film extrusion,¹ is widely used as textile filaments and packaging materials, and in bottle production. Recently, PET has also been considered for many other applications, such as optical and electronic materials, adhesives and coatings, high performance materials, and in biotechnology applications. Highly versatile, PET can be easily modified to meet different application requirements, either by changing the monomer structure or by introducing additional functional groups.

Since 1953, when PET was well established as a textile fiber, attempts have been made to overcome some of the problems associated with it. A small amount of ionic third component has been added to get copolyester and in turn a fiber to eliminate/minimize the limitations of PET fiber, particularly those related to coloring.

It is known that ionic bonding materials, such as metal sulfonates and carboxylates, can aid in the synthesis of reversible polymer structures. By introducing even a small amount of covalently bonded ionic moieties into a polyester, its physical and rheological properties can be profoundly affected.^{2, 3, 4, 5, 6, 7} Even at low ion

¹ Rao, B. R.; Datye, K. V. *Textile Chemist and Colorist* **1996**, 28, 17

² Eisenberg, A.; King, M. *Ion-containing Polymers*; Academic Press: New York, 1977; p15

³ Greener, J.; Gillmor, J. R.; Daly, R. C. *Macromolecules* **1993**, 26, 6420

⁴ Zhang, B.; Weiss, R. A. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, 30, 91

⁵ MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, 16, 41

⁶ Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Macromol. Chem Phys.* **1988**, C28, 99

⁷ Tant, M. R.; Wilkes, G. L. *J. Mater. Sci. Macromol. Chem Phys.* **1988**, C28, 1

concentrations, ionic interactions permit control of the physical properties of many polymers,⁸ including modulus, glass transition temperature, viscosity, melt strength, fatigue, and mass transport. Most of the semicrystalline ionic polyesters that have been studied were either random liquid crystalline ionic copolyesters,^{9, 10, 11} or random PET ionomers,^{1, 3} in which the ionic groups were introduced to the polymer backbone as pendent groups. Many studies of random PET ionomer blends have also been reported.^{12, 13, 14} However, little work has been done on telechelic ionic PETs. Compared with random ionic polyesters, telechelic ionic polyesters possess a better controlled polymer pseudo-network structure than that of random ionomers due to the uniform length of polymer chains and fixed number of ionic end groups. As previously discussed, the reversible polymer concept can reduce polymer melt viscosity, minimize polyester degradation during processing, and facilitate the molding of miniaturized polyester products.

This chapter will discuss the synthesis of novel telechelic semi-crystalline PET ionomers, as well as the synthesis of non-ionic PET with controllable molecular weights. The chemical structures, thermal and rheological properties of the polymers were well characterized and the influence of the ionic functionality is reported below.

4.2 Experimental

4.2.1 Materials

All reagents were used without further purification. Ethylene glycol and 3-sulfobenzoic acid, sodium salt (SSBA, 97 %) were generously donated by Eastman Chemical Co. Dimethyl terephthalate, sodium acetate (ACS reagent grade, 99.5 + %), and 1-dodecanol were purchased from the Aldrich. Also phosphoric acid (crystals, 98

⁸ Eisenberg A.; Kim J.-S. Introduction to ionomers; John Wiley & Sons, Inc: New York, 1998; Chapter 1.

⁹ Xue Y.; Hara M. *Macromolecules* **1997**, 30, 3803

¹⁰ Xue Y.; Hara M.; Yoon, H. N.; *Macromolecules* **1998**, 31, 7806-7813

¹¹ Hara, M.; Sauer, J. A., *J. Macro. Sci. Rev. in Macro. Chem. and Phys. C34*: **1994**, 3, 325-373

¹² Ng, C. W. A.; MacKnight, W. J. *Macromolecules* **1996**, 29, 2412

¹³ Boykin, T. L.; Moor, R. B. *Polym. Eng. Sci.* **1998**, 38, 1658

¹⁴ Ng, C. W. A.; Lindway, M. G.; MacKnight, W. J. *Macromolecules* **1994**, 27, 3027

%), cobalt acetate (99 %), antimony (III) oxide (99 %), manganese acetate (99 %) and titanium isopropoxide were purchased from Aldrich and were used directly.

4.2.2 Preparation of Catalysts Solutions

Sb catalyst: Sb_2O_3 (3.00 g) solid was dissolved in 250 mL ethylene glycol (EG). The mixture was heated at 100°C and stirred for 24 hours under nitrogen purge. The mixture was then filtered and a clear solution was obtained at a concentration of 0.012 g / mL based on Sb.

Mn catalyst: $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.685 g) and pure HOAc (1.319 g) were added to 125 mL of EG and heated to give a catalyst solution at a concentration of 0.0215 g / mL based on Mn.

Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g) with 62.5 mL of n-BuOH in a dry bottle under nitrogen at a concentration of 0.055 g / mL based on Ti.

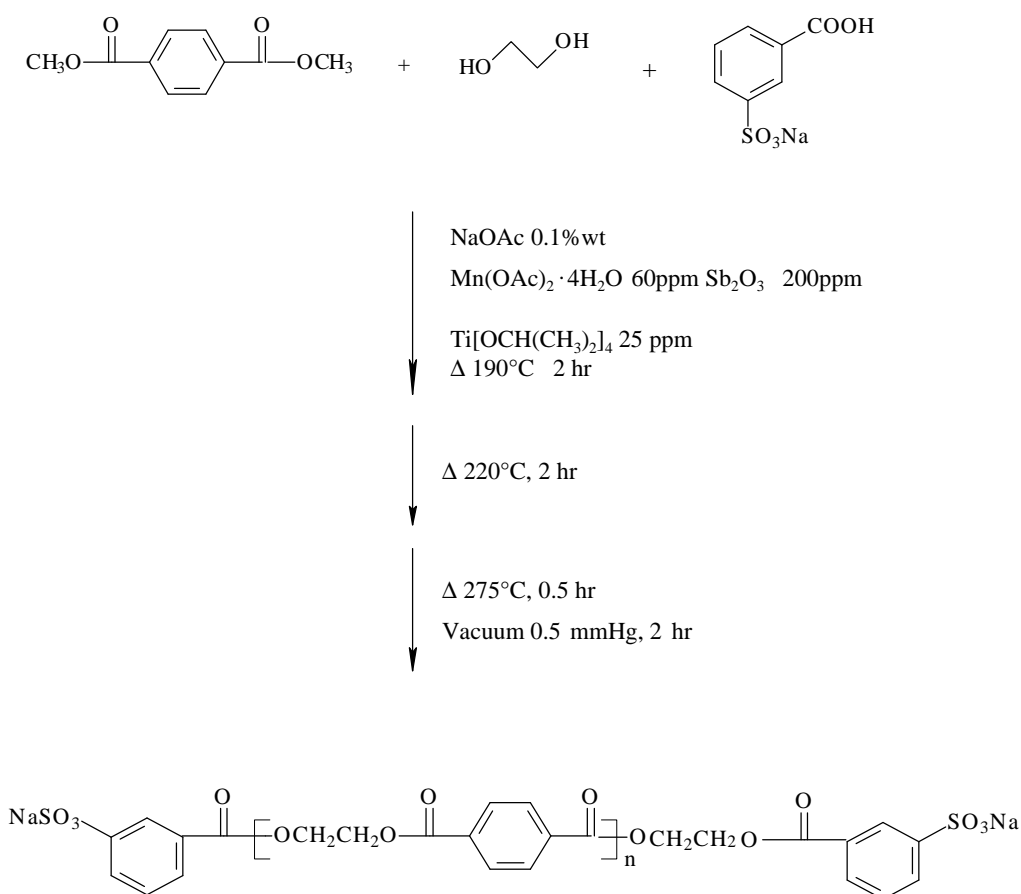
Co catalyst: Cobalt acetate (2.025 g) was mixed with ethylene glycol (125 mL) to obtain a catalyst solution with a concentration of 0.02 g / mol based on Co.

P catalyst: Phosphoric acid (99 %, 3.48 g) was dissolved in n-BuOH (12.5 g, 15.43 mL) and then mixed with ethylene glycol (125 mL) to obtain the catalyst at a concentration of 0.025 g / mol based on P.

4.2.3 Synthesis of Telechelic Semi-crystalline PET Ionomers (PET-SSBA or PET-xSSBA)

To a mixture of dimethyl terephthalate (DMT, 48.5 g, 0.25 mol) and ethylene glycol (EG, 31 g, 0.5 mol, 100 % excess), varying amounts of an end capper, SSBA (x = 1 mol %, 3 mol %, 5 mol %, 10 mol % compared to DMT) were added to obtain PET ionomers (Scheme 4.1). Two series were made based on different catalyst systems. The first series was synthesized with manganese catalyst (2.31 mL), antimony catalyst (3.8

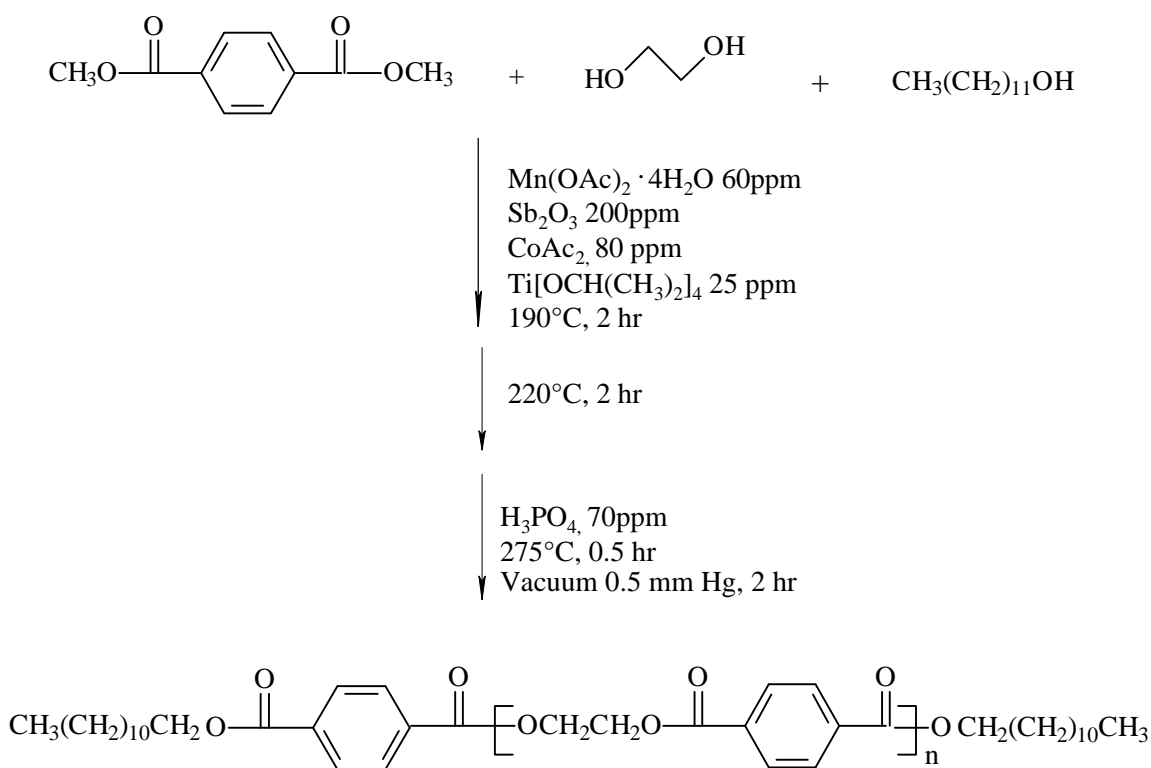
mL) and titanium catalyst (0.51 mL). The second series was synthesized with manganese catalyst (2.31 mL), antimony catalyst (3.8 mL), titanium catalyst (0.51 mL), cobalt catalyst (3.0 mL) and finally, just prior to the vacuum, phosphoric acid (2.1 mL) was added. All of the PET ionomers contained this 5-catalyst system. In a similar fashion to the PEI polymers, a multi-step temperature procedure was used for the reaction, i.e., the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an extra 2 hours. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.



Scheme 4.1. Synthesis of PET-SSBA ionomers using melt polymerization

4.2.4 Synthesis of Dodecanol Terminated Semi-crystalline PET (PET-Dode-OH or PET-yDode-OH)

To a mixture of dimethyl terephthalate (48.5 g, 0.25 mol), ethylene glycol (31 g, 0.5 mol, 100 % excess), varying amounts of dodecanol ($y = 5$ mol %, 10 mol %, 12 mol %, and 15 mol %) were added (Scheme 4.2). Manganese catalyst (2.31 mL), antimony catalyst (3.8 mL), titanium catalyst (0.51 mL) and cobalt catalyst (3.0 mL) were used. Just prior to applying vacuum, phosphoric acid (2.1 mL) was added under nitrogen. The same multi-step temperatures were used for the reaction, i.e. the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. No further purification was needed.



Scheme 4.2. Synthesis of dodecanol terminated semi-crystalline PET using melt polymerization

4.2.5 Polymer Characterizations

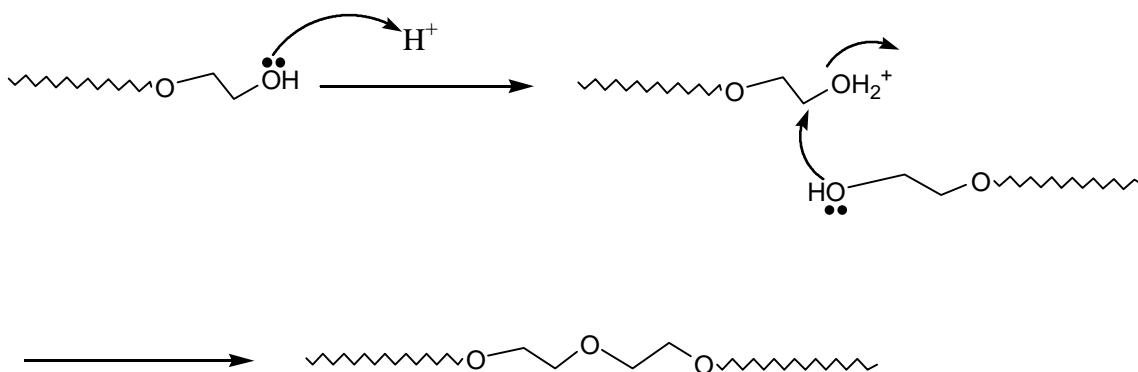
A 400 MHz NMR (Varian-400) was used to characterize all PET samples. The solvent used was TFA/CDCl₃ (2:1, v/v). FTIR spectra were collected on an infrared spectrometer (Perkin Elmer, 283B) to detect the sulfonate end group of the PET ionomers. Gel permeation chromatography (GPC) was performed to obtain the molecular weights and molecular weight distributions of the dodecanol terminated PET samples. The mobile phase was phenol/tetrachloroethane (60/40, w/w) at 25 °C. Melt rheology was analyzed using a melt rheometer (TA Instruments, Advanced Rheometer AR 1000). DSC (Perkin Elmer, Pyris 1) was used to study glass transition temperatures and crystallization behavior. All the samples were kept at 290 °C for 3 min to eliminate any thermal history, then quenched from 290 °C to room temperature at a rate of 200 °C/min, and finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen and all the data collected were from the second scan. The solution behavior of the samples was studied using an Ubbelohde viscometer at 25 ± 0.1°C. The solvent used was the mixture of phenol and tetrachloroethane (60/40, w/w).

4.3. Results and Discussion

4.3.1 NMR Analysis

NMR was used to confirm the chemical structure of the PET-SSBA ionomers. Figure 4.1 reveals the spectra of PET-5%SSBA. The solvent used was CF₃COOD/CDCl₃, 2:1 (v/v) at room temperature (22 °C). Peaks c (8.1 ppm, aryl hydrogens in benzene ring) and d (4.8 ppm, aliphatic hydrogens) are associated with the polymer backbone. Peaks a (8.6 ppm) and b (7.6 ppm) resulted from the aryl hydrogens in the SSBA end group. After integration, the percentage of SSBA that was found to be present in the polymer was about 4.3 mol %, which is very close to the initial feed (5.0 mol %). This shows that the SSBA end group was very stable and very little was lost as a result of the relatively high temperature and vacuum used during the melt polymerization. The percentage of DEG (4.15 and 4.55 ppm), which results from an inherent side reaction, is 5.7 mol %. It was found that the percentage of DEG was determined by the purity of SSBA. If there was insufficient NaOAc to maintain the end capper in completely sodium form, a side

reaction occurred (Scheme 4.3). Following the addition of sufficient NaOAc, however, the percentage of DEG was reproducibly lower than 3 mol %.



Scheme 4.3. Proposed mechanism of side reaction of hydroxyl group of growing polymer chain with the acidic form of the SSBA component¹⁵

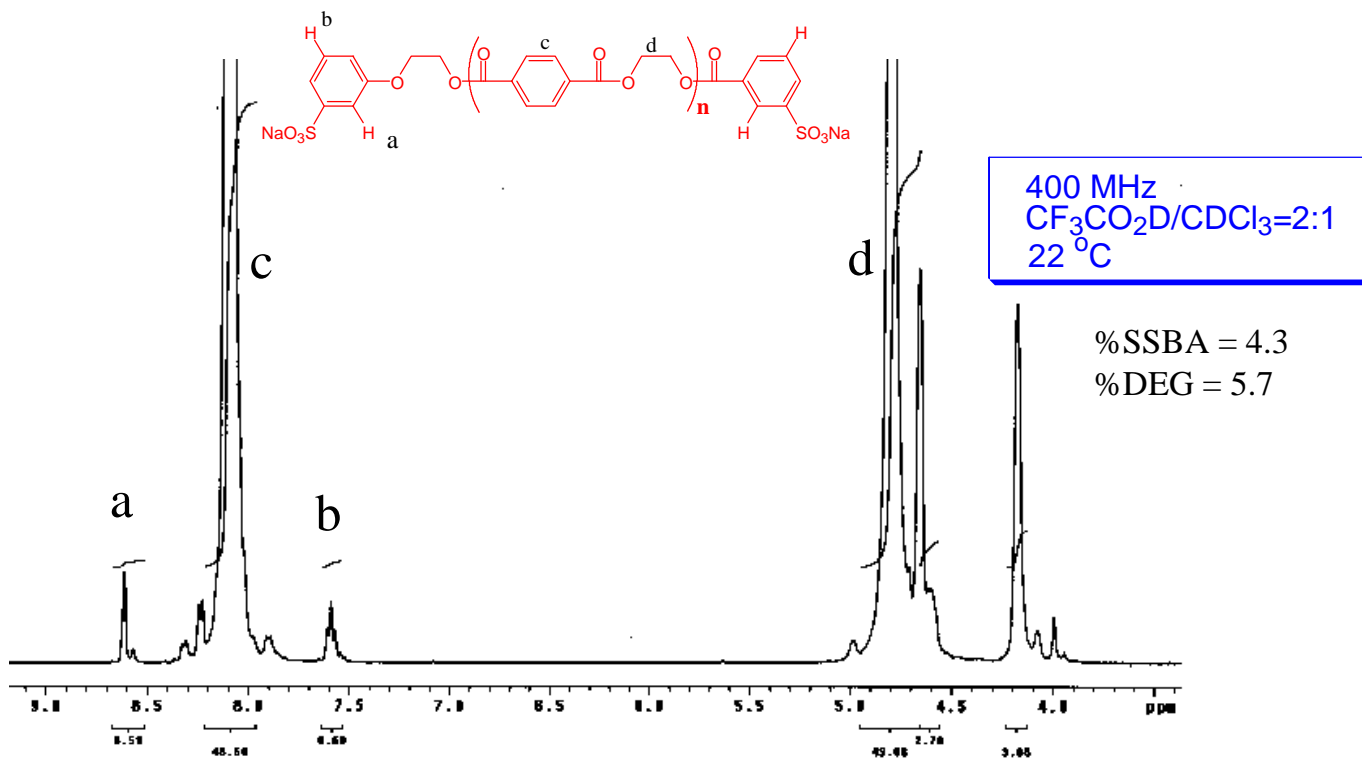


Figure 4.1. ^1H NMR spectrum of PET-5%SSBA, $\text{CF}_3\text{COOD}/\text{CDCl}_3$, 2:1 (v/v), room temperature, $\langle M_n \rangle$ (NMR) = 9100g/mol, $\langle M_n \rangle$ (Calculation) = 8400g/mol

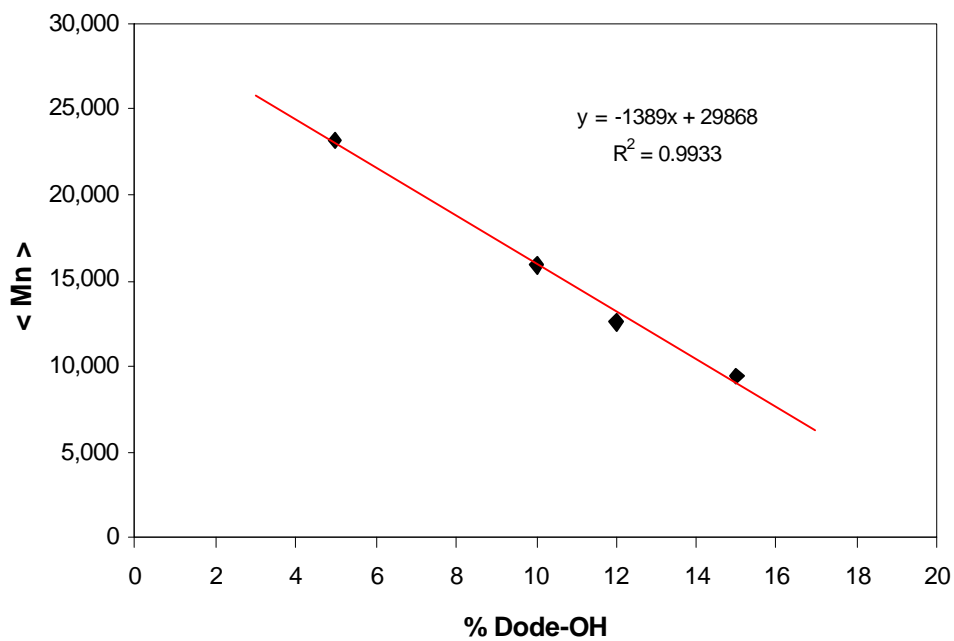
¹⁵ Joseph C. Salamone, *Polymeric Materials Encyclopedia*; Boca Raton: CRC Press; 1996, vol. 8, p6078

4.3.2 GPC Analysis

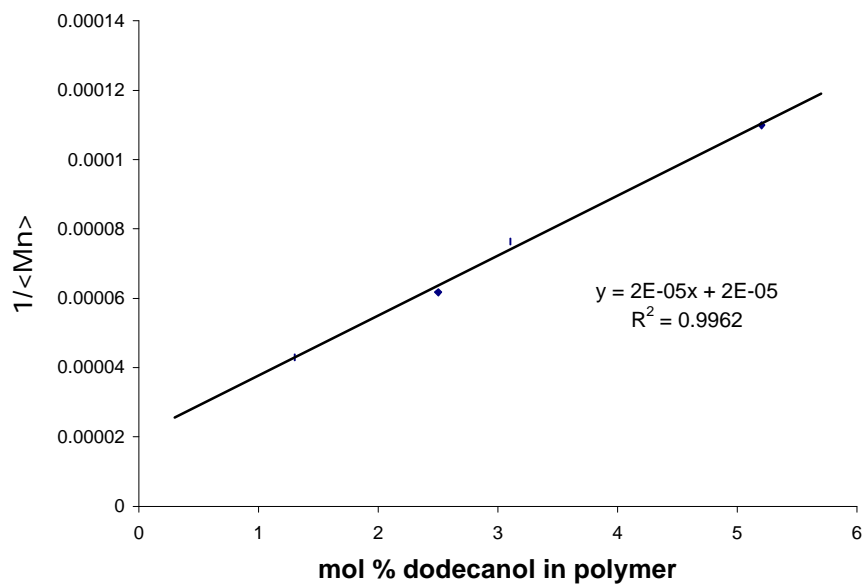
GPC was used to obtain the molecular weights of the PET-Dode-OH samples. The solvent used in the GPC experiments was a mixture of phenol and tetrachloroethane (60/40, w/w), at a temperature of 25 °C. GPC results (Table 4.1) showed that all $\langle M_w \rangle / \langle M_n \rangle$ values were between 2.0 ~ 2.5, which could be expected from a traditional polycondensation reaction. By comparing the data listed in Table 4.1, an inverse correlation between the amount of dodecanol charged and molecular weight was observed and illustrated in Figure 4.3a. A straight line was obtained by fitting the data, which confirmed that dodecanol was an efficient reagent for controlling the molecular weight of PET under the polymerization conditions. The simple linear relationship between molecular weight and the approximate amount of dodecanol allows one to predict and control the desired molecular weight of a given PET-Dode-OH sample. Figure 4.3b showed the linear relationship of $1/\langle M_n \rangle$ vs mol% dodecanol in polymer.

Table 4.1. GPC results of PET-Dode-OH with different amounts of dodecanol. Solvent: phenol / tetrachloroethane (60/40, w/w), room temperature

PET-xDode-OH	Catalyst	M_n (g/mol)	M_w (g/mol)	mol % dodecanol in polymer	PDI
PET-5%Dode-OH	Ti/Mn/Sb/Co/P	23,300	57,300	1.3	2.46
PET-10%Dode-OH	Ti/Mn/Sb/Co/P	16,200	35,800	2.5	2.21
PET-12%Dode-OH	Ti/Mn/Sb/Co/P	13,100	28,800	3.1	2.20
PET-15%Dode-OH	Ti/Mn/Sb/Co/P	9,100	19,300	5.2	2.13



(a)



(b)

Figure 4.3. (a) Number average molecular weight vs percentage of dodecanol employed in the synthesis of PET-Dode-OH; (b) $1/\langle M_n \rangle$ vs percentage of dodecanol in polymers

4.3.3 Solution Viscometry Study

Solution viscometry was used to study the dilute solution behavior of the PET samples. The solvent of choice was a mixture of phenol and tetrachloroethane (60/40, w/w, 25 °C). For PET-SSBA samples, two upward curvatures were observed by analyzing the data using Huggins and Kreamer equations. These non-linear relationships between solution viscosity and (dilute) polymer concentration are characteristic behaviors of telechelic ionomers, and are believed to arise from the ionic interactions in solution.¹⁶ With regard to the dodecanol terminated PET-Dode-OH polymers, Huggins and Kreamer equations were also employed, and two straight lines were obtained (Figure 4.4). The viscosity molecular weight ($\langle M_v \rangle$) of PET-12%Dode-OH was 19,000 g/mol, and 16,000 g/mol for the PET-15%Dode-OH. All of the constants needed to calculate the viscosity average molecular weights were obtained from the earlier literature.¹⁷ Solution viscometry studies confirmed that dodecanol proved to be an effective end capper for controlling molecular weight.

¹⁶ B. Zhang and R. A. Weiss, *J. of Polymer Science: Part A: Polymer Chemistry* **1992**, 30, 989

¹⁷ Rosu, R. F.; Shanks, R. A.; Bhattacharya, S. N. *Polymer International*, 1997, **42**, 267-275

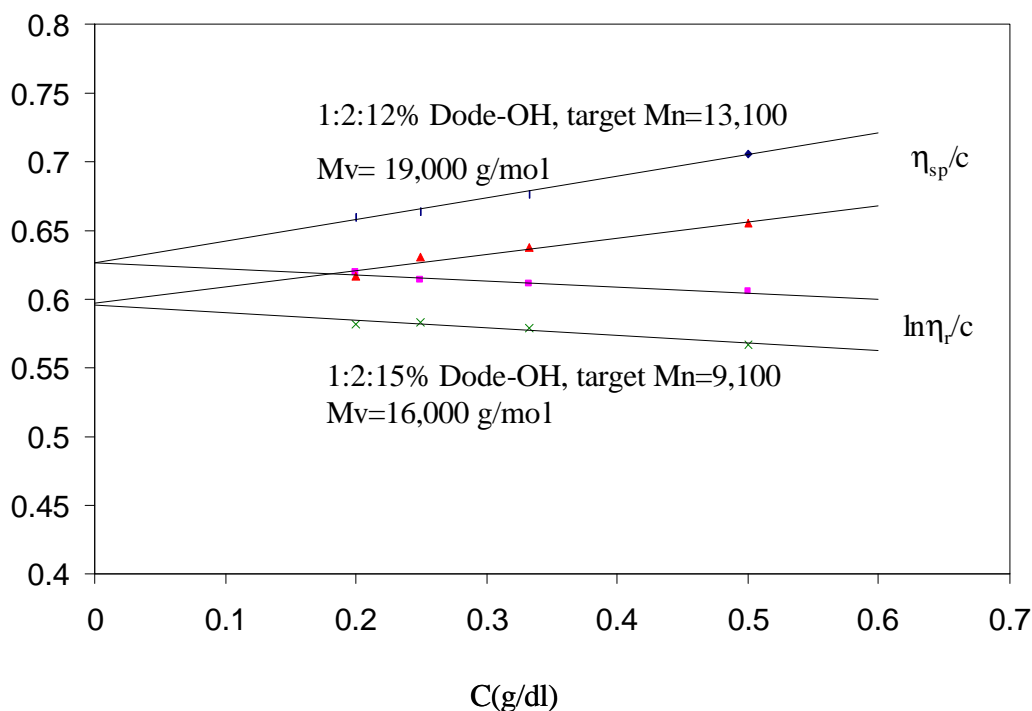


Figure 4.4. Solution viscosity of PET-12%Dode-OH and PET-15%Dode-OH, Mark-Houwink Eq: $[\eta] = kM_w^\alpha$, $k = 2.10 \times 10^{-4} \text{ dl g}^{-1}$, $\alpha = 0.82$. Phenol : Tetrachloroethane (60/40, w/w), 25°C¹⁶

4.3.4 FTIR Analysis

As expected, all of the PET ionomers were typically opaque due to crystallinity. In the FTIR spectrum, the peak for the S-O stretching mode, which normally appears between 600-700 cm^{-1} for organic sulfonates,¹⁸ was used to identify the sulfonate groups of the PET-SSBA oligomers. The IR spectra of PET-1%SSBA and PET-5%SSBA are shown in Figure 4.5. Although there is no S-O stretching mode observed for the nonionic PET, the peaks at 630 cm^{-1} due to S-O stretching mode are quite evident in ionic PET samples. Furthermore, a positive correlation was observed between higher ionic content and increased peak intensity.

¹⁸ Nakanishi, K. Infrared Absorption Spectroscopy (Practical); Holden-Day Inc.; San Francisco, 1962; p54

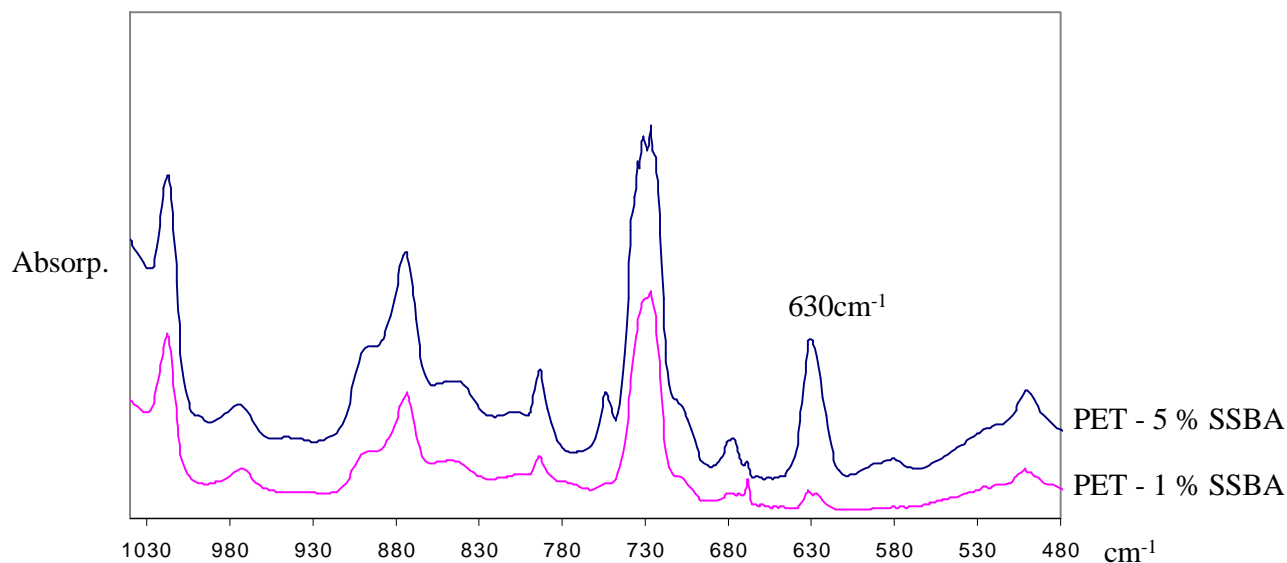


Figure 4.5. FTIR spectra of sulfonate terminated PET-1%SSBA and PET-5%SSBA

4.3.5 DSC Analysis

As shown in Figure 4.6 and Table 4.2, DSC revealed that all of the telechelic ionic PET-SSBA polyesters had only one glass transition temperature. Moreover, “cluster T_g s”^{19, 20} were not observed, suggesting that the ionic aggregates in these ionomers were multiplet type as discussed in Chapter 2 (2.3.2). Low molecular weight ionic PET-5%SSBA ($\langle M_n \rangle = 8,400$ g/mol), displayed a relatively high glass transition temperature ($T_g = 77$ °C), which was analogous to that of non-terminated high molecular weight PET ($M_n = 27,000$ g/mol, $T_g = 77$ °C, Table 4.2). This is attributed to the fact that the ionic interactions in ionomers are sufficiently strong to maintain the structural integrity of the polymer chain, thus limiting its mobility and affording a high glass transition temperature.

Considering PET-5%SSBA and PET-15%Dode-OH in Table 4.2, although they displayed similarly low molecular weights, PET-15%Dode-OH had a significantly lower

¹⁹ Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, 23, 4098

²⁰ Eisenberg, A.; King, M. *Ion-Containing polymers, Physical Properties and Structure*; Academic: New York, 1977

and broad glass transition ($T_g = 66$ °C). This could be due to the fact that the crystallization rate of the PET-15%Dode-OH was quite rapid. Thus, the degree of crystallinity was very high even after the very fast quenching, resulting in a broad glass transition in the amorphous phase and almost undetectable crystallization temperature of the amorphous phase. The low T_g value is believed to have resulted from the low molecular weight due to the absence of ionic interactions. Conversely, the PET-5%SSBA had a much higher glass transition temperature due to the strong ionic interactions. The higher crystallization temperature of the higher ionic content is believed due to the harder to crystallize for the larger amount of ionic aggregates and stronger ionic interactions.

Table 4.2. DSC results of non-terminated PET, PET-xSSBA and PET-15%Dode-OH, N_2 , second heat with heating rate at 10 °C/min

Polymers	T_g (°C)	T_c (°C)	T_m (°C)
non-terminated PET (high molecular weight)	77	137	244
PET-1%SSBA	78	142	234
PET-3%SSBA	76	147	231
PET-5%SSBA	77	151	212
PET-15%Dode-OH	66 (broad)	not detected	249

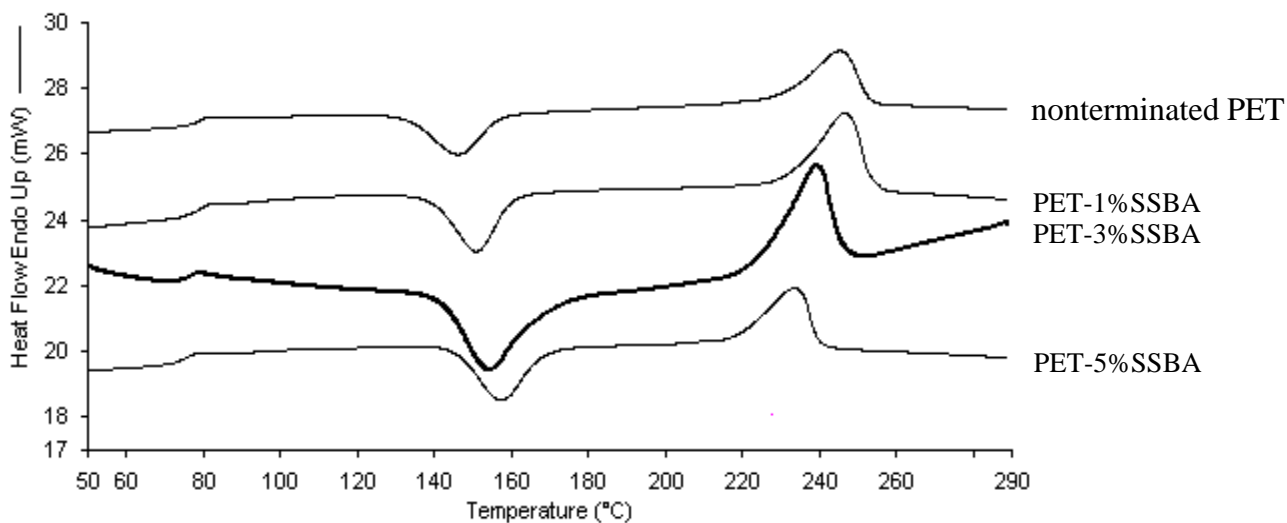


Figure 4.6. DSC results of non-terminated PET and PET- x SSBA ($x = 1, 3, 5$ mol % compared to DMT)

The similar glass transitions observed for the PET-SSBA samples with different SSBA ionic group content can be explained by the same argument applied to the PEI-SSBA samples, as discussed in Chapter 3. Again, it would appear that the restricted chain mobility as a result of ionic interactions equalized the molecular weight factor. All the PET-SSBA samples were quenched from their melt states, so very little or no crystallinity was present in the samples prior to the second heating scan. The similar T_c and T_m peak areas for each sample supported this conclusion (Figure 4.6). As a result, the influence of the crystallinity on T_g can be minimized here.

On the other hand, the impact of ionic interactions on the crystallization and melting temperatures of the PET-SSBA samples was dramatic (Table 4.2 and Figure 4.7). As SSBA content increased from 0 mol % to 5 mol %, the crystallization temperature (T_c) increased from 137 °C to 151 °C, while the melting temperatures (T_m) decreased from 244 °C to 212 °C. It is believed that the ionic interactions influenced the chain packing mechanism, and more kinetics details will be discussed in Chapter 8.

Compared with PET-SSBA polyesters, dodecanol terminated PET-Dode-OH rendered the expected correlation between glass transition temperature and molecular weight. There is a general relationship between glass transition temperature and number average molecular weight, which is shown in the following equation,

$$T_g = T_{g, \infty} - K/\langle M_n \rangle$$

where $T_{g, \infty}$ is the glass transition temperature when the molecular weight of a polymer is infinitely large, K is a constant. In other words, when a higher content of dodecanol was used, a lower molecular weight was obtained, which in turn resulted in a lower glass transition temperature. As previously discussed, when the dodecanol amount was as high as 15 mol % compared to the DMT monomer, the polymer chains were sufficiently short to recrystallize quickly during the quenched cooling process. Thus, these materials not only displayed lower glass transition temperatures, but also showed a very broad temperature range (Figure 4.8).

As seen from DSC results (Table 4.3 and Figure 4.7), T_c and T_m values were influenced by dodecanol content – i.e., higher levels of dodecanol resulted in lower T_c values and higher T_m values. This trend contrasts with that of the ionic PET samples, wherein higher dodecanol content was associated with lower molecular weight. In addition, shorter polymer chains resulted in easier packing (lower T_c) and fewer crystalline defects (higher T_m).^{21, 22, 23} Kinetics studies can provide a clearer picture of the crystallization behavior and will be discussed in greater detail in Chapter 8.

²¹ Wunderlich, B. *Macromolecular Physics*, Vol. 1 - Crystal Structure, Morphology, Defects; Academic Press, New York, 1973

²² Wunderlich, B. *Macromolecular Physics*, Vol. 2 - Crystal Nucleation Growth, Annealing; Academic Press, New York, 1976

²³ Wunderlich, B. *Macromolecular Physics*, Vol. 3; Academic Press, New York, 1980

Table 4.3. DSC results of dodecanol terminated PET (PET-yDode-OH, y = 5 mol %, 10 mol %, 15 mol %); N₂, second heat with heating rate at 10 °C/min

PET-xDode-OH	T _g (°C)	T _c (°C)	T _m (°C)	T _{m, onset} (°C)
PET-5%Dode-OH	75	147	243	223
PET-10%Dode-OH	70	131	244	227
PET-15%Dode-OH	66 (broad)	N/A	249	238

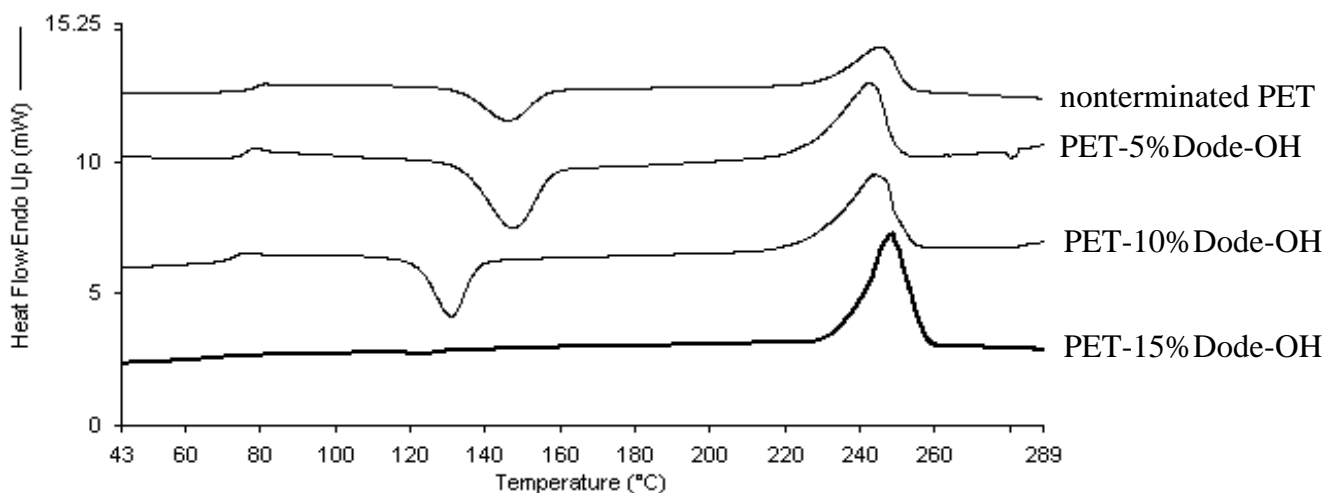
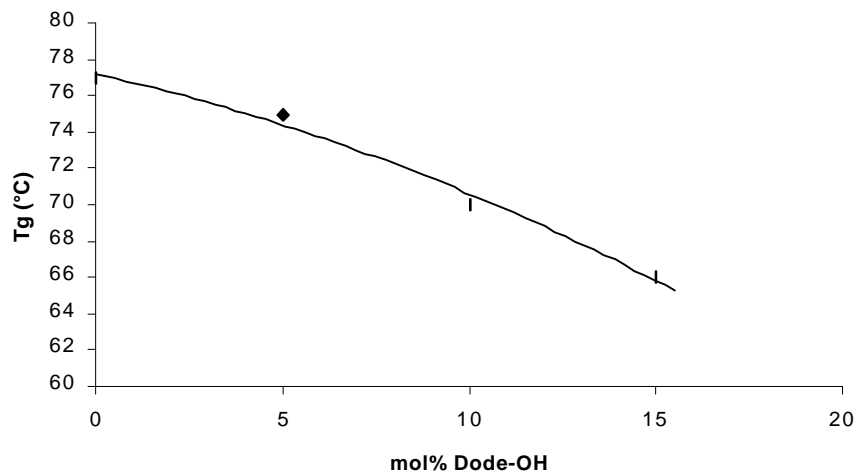


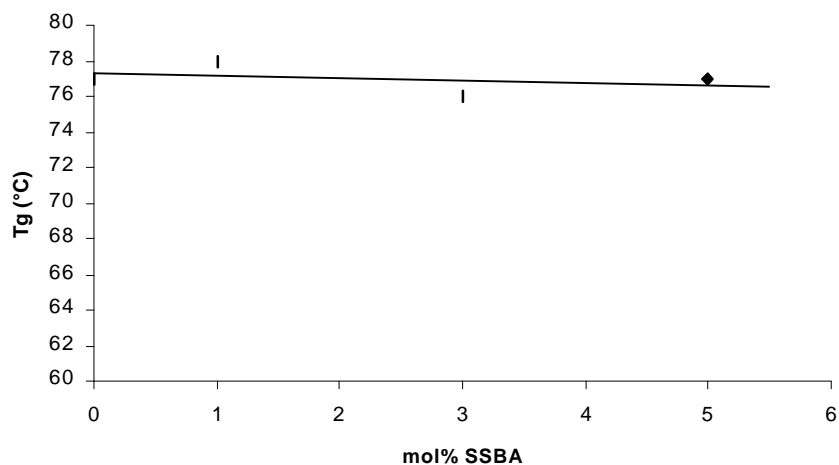
Figure 4.7. DSC curves of non-terminated PET and dodecanol terminated PET (PET-yDode-OH, y = 5 mol %, 10 mol %, 15 mol %); N₂, second heat with heating rate at 10 °C/min

More clearly, the dependence of glass transition temperatures (T_g) with different amount (mol%) of dodecanol in PET-Dode-OH and SSBA ionic groups in PET-SSBA samples were illustrated in Figure 4.8. From the comparison between Fig. 4.8 (a) and Fig. 4.8 (b), the influence of the ionic end groups in the ionomers (PET-SSBA) was

demonstrated, which the glass transition temperature didn't change a lot with the decrease of molecular weight, while for dodecanol terminated PET, glass transition temperature decreased with the decrease of molecular weight. The mechanism of the relatively unchanged T_g values among the ionomers was previously discussed in this section.



(a)



(b)

Figure 4.8. (a) The relationship between glass transition temperatures (T_g) and the content of dodecanol in PET-Dode-OH polyesters; (b) the relationship between glass transition temperatures (T_g) and the content of SSBA ionic groups in PET-SSBA polyesters

4.3.6 Melt Rheology Study

Melt rheology studies were carried out on PET-Dode-OH polyesters. For PET-Dode-OH samples, melt rheology experiments were performed at temperatures ranging from 210 °C to 290 °C, at 1 rad/sec under nitrogen (Figure 4.9). Resulting data showed that melt viscosity decreased with an increase in dodecanol content. This, of course, was expected, as molecular weight also decreased when increased levels of the dodecanol end capper were used. Additionally, it was observed that the transition temperature of melt flow (T_{flow}) increased with a decrease in molecular weight. According to the literature,^{20, 21, 22} shorter polymer chains are positively correlated to easier chain packing. As a result, better regularity resulted in fewer defects in the polymer crystalline structures, thus resulting in a higher transition temperature of melt flow. This trend was confirmed by DSC (Table 4.3 and Figure 4.7), which showed that both the melting peak temperature (T_m) and melting onset temperature ($T_{m, \text{onset}}$) increased with an increase of dodecanol, which is also corresponds to a decrease in molecular weight. Interestingly, the $T_{m, \text{onset}}$ and T_{flow} were very close to each other for all the three dodecanol terminated PETs as demonstrated in Figure 4.10.

²⁰ Wunderlich, B. *Macromolecular Physics*, Vol. 1 - Crystal Structure, Morphology, Defects; Academic Press, New York, 1973

²¹ Wunderlich, B. *Macromolecular Physics*, Vol. 2 - Crystal Nucleation Growth, Annealing; Academic Press, New York, 1976

²² Wunderlich, B. *Macromolecular Physics*, Vol. 3; Academic Press, New York, 1980

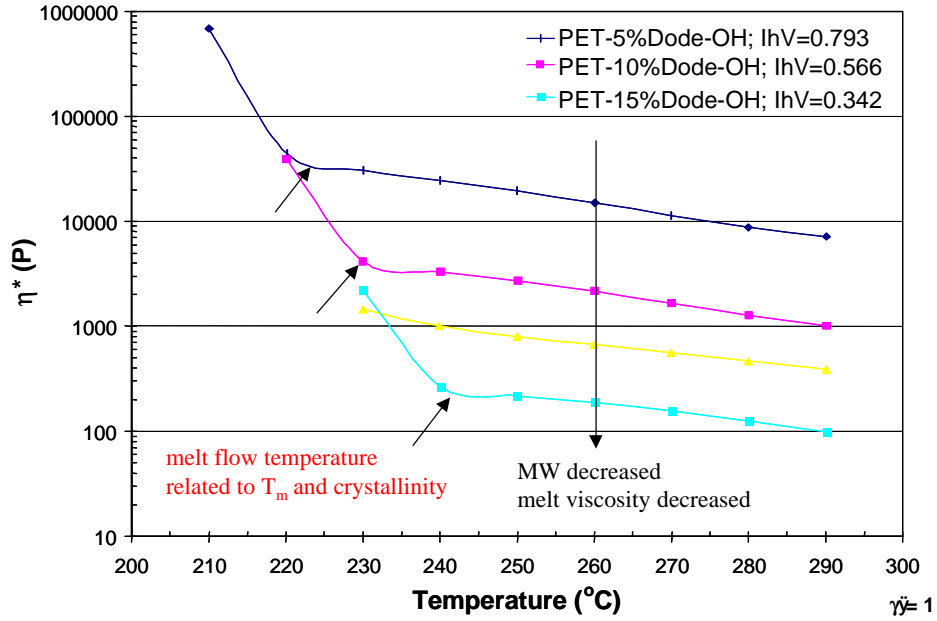


Figure 4.9. Melt rheology of dodecanol terminated PET (PET-5%Dode-OH, PET-10%Dode-OH, PET-15%Dode-OH), $\dot{\gamma} = 1$

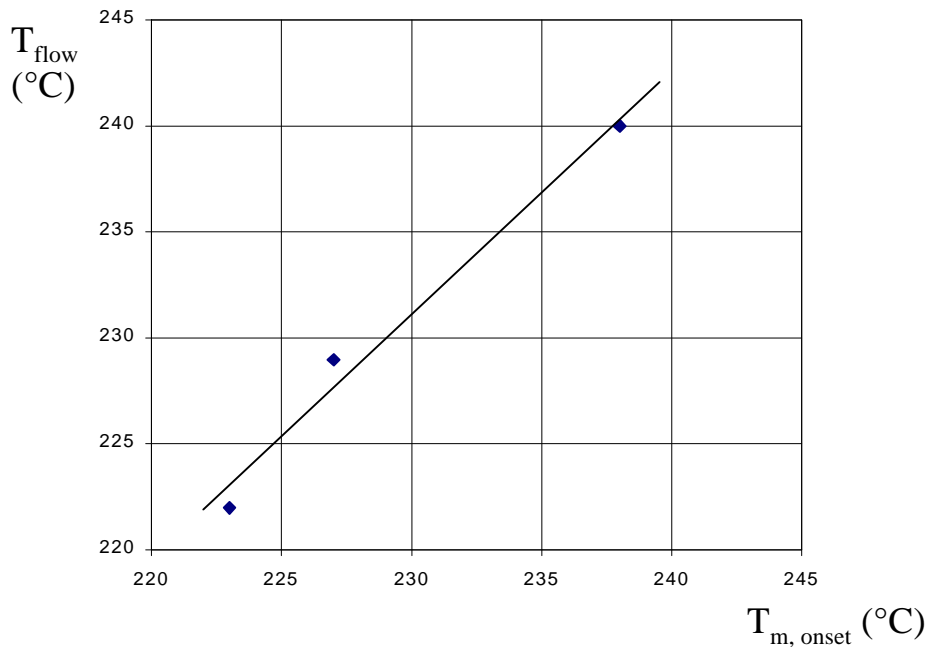


Figure 4.10. Relationship between the onset melt temperatures ($T_{m, \text{onset}}$) from DSC (Table 4.3) and the melt flow transition temperatures (T_{flow}) from melt rheology (Figure 4.8) of the dodecanol terminated PET samples (PET-5%Dode-OH, PET-10%Dode-OH, PET-15%Dode-OH)

The presence of an antimony catalyst in the polymerizations also affected the melt rheology of the PET ionomers (Figure 4.11 & Figure 4.12). Figure 4.11 depicts two samples of PET-10%Dode-OH with and without antimony catalyst. The two polymers displayed similar inherent viscosities, which suggests that they possessed similar molecular weights. However, with regard to PET-10%Dode-OH with antimony catalyst, the transition temperature was 242 °C, as compared to PET-10%Dode-OH without antimony catalyst whose transition temperature was 232 °C. The 10 °C difference is attributed to the fact that the antimony catalyst served as a nucleating agent, resulting in different levels of crystallinity. Figure 4.12 depicts two samples of PET-5%SSBA polymers with nearly identical molecular weights – one with the antimony catalyst and the other without it. Unlike the previously compared PET-10%Dode-OH, the transition temperature difference between these latter samples was on the order of 20 °C, which was presumably due to the residue of antimony catalyst that interacted with the ionic aggregations in the ionomers. Indeed, previously published results^{24, 25} indicate that the presence of an antimony catalyst could affect the crystallization process. A more detailed study of this topic will be discussed in Chapter 8.

²⁴ Jabrain, S. A. *J. Appl. Polym. Sci.* **1987**, 34, 85

²⁵ Lawton, E. L. *Polym. Eng. Sci.* **1985**, 25, 348

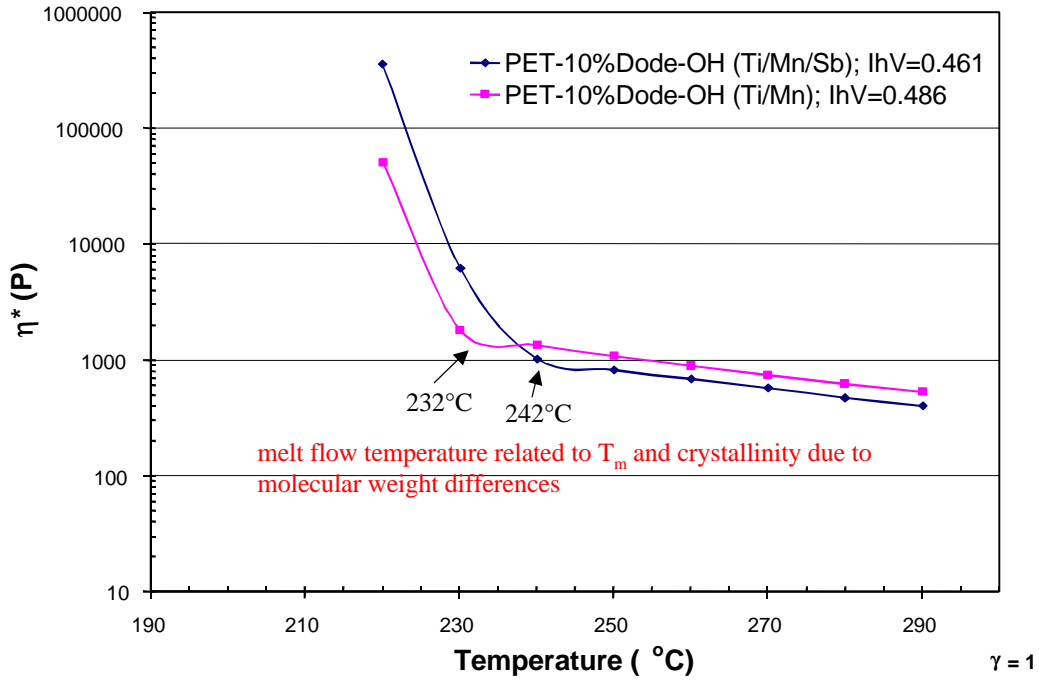


Figure 4.11. Melt rheology of PET-10%Dode-OH with and without antimony trioxide catalyst, $\gamma = 1$

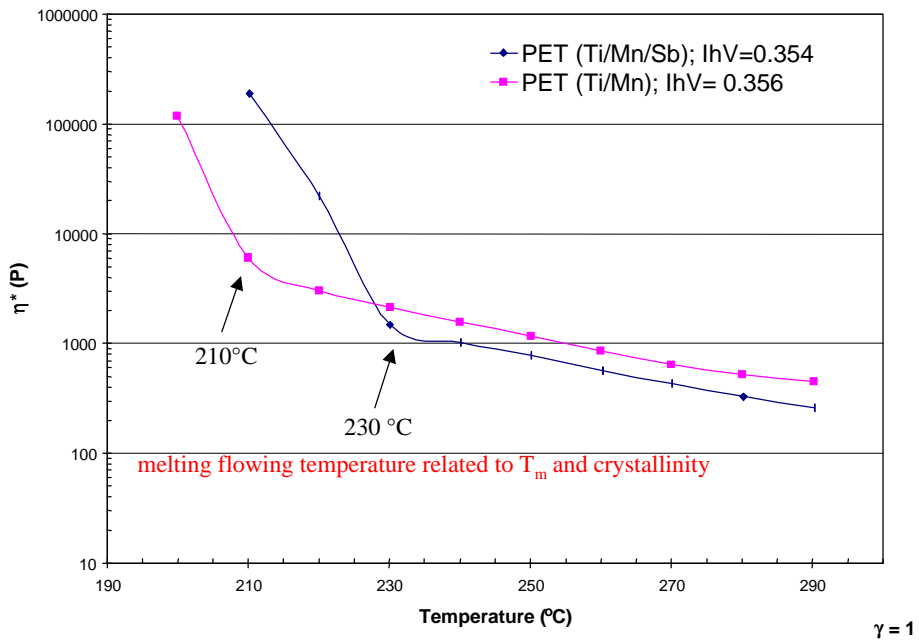
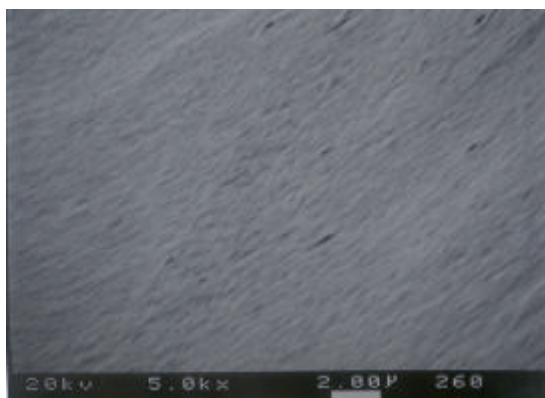


Figure 4.12. Melt rheology of PET-5 %SSBA with and without antimony trioxide catalyst, $\gamma = 1$

4.3.7 Morphology Study

SEM is a very useful tool for studying the morphology of a polymer material. PET-5%SSBA ($\langle M_n \rangle = 8,400$ g/mol) and non-terminated PET ($M_n = 27,000$ g/mol) were placed in two aluminum pans on a hot plate. After the samples had completely melted, fibers were drawn using spatulas. Figure 4.13 depicts the skin surfaces of the ionic and non-ionic PET fibers. Induced by ionic aggregation, the skin surface of the PET-5%SSBA was rougher than that of the normal PET. These varying surface properties may have potential industrial applications, perhaps in the area of adhesives.

Surface of PET 5%SSBA



Surface of PET



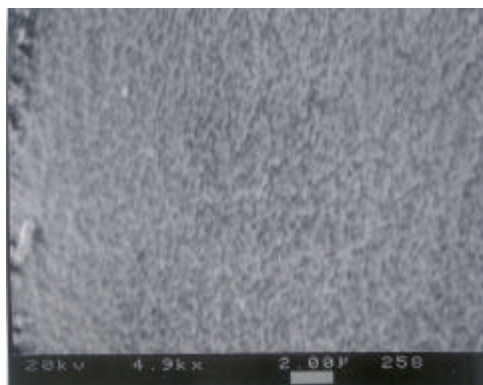
Figure 4.13. SEM of outside skin surface of non-terminated PET and PET-5%SSBA, 5.0K x

Furthermore, once the fibers had been broken in liquid nitrogen, the fracture surfaces were also examined by SEM (Figure 4.14). Distinct morphologies with very different domain sizes were observed for the two samples. Specifically, the domain size of the non-terminated PET was larger than $2 \mu\text{m}$, which is believed to be due to normal crystalline/amorphous phase separation.^{26, 27} On the other hand, the domain size of the PET-5%SSBA polymers was only about 100-200 nm, most likely due to ionic aggregation, wherein the larger crystalline/amorphous domains were destroyed, leaving

²⁶ Pecorni, T. J.; Hertzberg, R. W. *Polymer* **1993**, 34, 5053

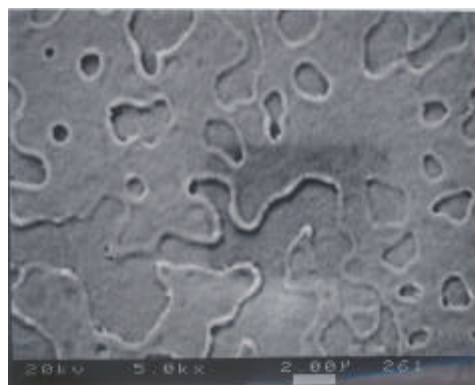
only smaller observable features. It should also be noted that during the preparation of the PET fibers, it was not possible to draw a fiber from PET-15%Dode-OH sample (molecular weight 8,400 g/mol). This contrasts with the ionic PET samples of similar molecular weight, from which fibers could be drawn. Once again, this was attributed to strong ionic interactions. More studies are needed to explore the industrial potential of PET ionomers.

Cross section of PET 5%SSBA



Ionic aggregation
Domain Size: 100 ~ 200 nm

Cross section of PET



Crystalline / Amorphous
Domain Size: > 2 µm

Figure 4.14. SEM of fracture surfaces of non-terminated PET and PET-5%SSBA, 5.0K x

4.4 Conclusions

Novel ionic and non-ionic poly(ethylene terephthalate) polyester were successfully synthesized and characterized. NMR was employed to confirm the polymer structures, as well as the existence of SSBA and dodecanol end groups. FTIR was also used to confirm the incorporation of SSBA end groups by monitoring the characteristic absorption of S-O stretching at 630 cm^{-1} . NMR results showed DEG side reactions could only be controlled when SSBA was in 100 % of sodium salt formation. GPC was used to obtain the molecular weights of the non-ionic controlled PET polymers. In combination, GPC and NMR results revealed that only a portion of the dodecanol was used to form polymer chain ends, and thus control molecular weight. In fact, most of the dodecanol

²⁷ Foot, J. S.; Ward, I. M. *J. Materials. Sci.* **1972**, 7, 367

was lost during the reaction due to the relatively low boiling temperature of this material, in conjunction with the high polymerization temperature.

Solution behavior studies revealed that the PET-Dode-OH samples agreed well to the Mark-Houwink equation, while the ionic PET-SSBA samples showed upward curvatures in the η_{sp}/c and η_r/c vs. c plots due to strong ionic interaction. Only one glass transition temperature was observed for all of the ionic PET polyesters, which indicates that the ionic aggregates in these ionomers were multiplets, instead of clusters. The very strong ionic interaction in the ionomers limited the mobility of the polymer chains, which helped to maintain the glass transition at a relatively high temperature, despite the fact that molecular weights were much lower. Melt rheology studies revealed the influence of ionic interactions, molecular weights and antimony catalyst on the melt behaviors of the polymers. Furthermore, very different morphological behavior was observed between the ionic and non-ionic PET fibers on both their outside skin surfaces and their fracture surfaces.

CHAPTER 5. MODIFICATION OF TELECHELIC PEI AND PET IONOMERS: TELECHELIC POLY(ETHYLENE ISOPHTHALATE-co-trans-1,4-DIMETHYL CYCLOHEXANE DICARBOXYLATE) (PEI-CHDC) AND POLY(ISOPHTHALATE-CO-TEREPHTHALATE) (PEIT) IONOMERS

5.1 Introduction

Amorphous and semicrystalline polyesters are important materials that are widely used for a number of industrial applications. As such, a tremendous body of work exists that demonstrate the properties of the two homopolymers (1) amorphous poly(ethylene isophthalate) (PEI) and (2) semicrystalline poly(ethylene terephthalate) (PET).^{1, 2, 3, 4} Despite their many attractive properties, there are a number of drawbacks associated with PET and PEI homopolymers, such as poor dyeability, low moisture regain, poor adhesion to metals and poor processability as a result of their high melting temperature. Generally, copolymerization affords an effective means of modifying the crystallinity, morphology, melting point, glass transition temperature, solubility, and permeability of these materials.⁵ Thus, the copolymerization of PEI and PET with other monomers of varying chemical structures has been studied and is now commonly employed in industrial processes.^{6, 7, 8, 9}

For example, the polarity and crystallinity of the polymer backbone can be modified by introducing comonomers with more or less polarity, or by modifying the polymer main chain using ionic components.^{10, 11, 12} Furthermore, *trans*-cyclohexyl

¹ Eliasson, H.; Mellander, B. E. *J. Phys-condens. Mat.* **1999**, 11, 8807

² Sekelik, D. J.; Stepanov, E. V.; Nazarenko, S. J. *Polym. Sci. Polym. Phys.* **1999**, 37, 847

³ Song, M.; Hourston, D. J. *J. Therm. Anal. Calorim.* **1998**, 54, 651

⁴ Bai, S.; Hu, J. Z.; Pugmire, R. J. *Macromolecules* **1998**, 31, 9238

⁵ Lee S. W. Ree. W.; Park, C. E.; *Polymer* **1999**, 40, 7137

⁶ Grag, S. N.; Misra, A. *Makromol. Chem. Rapid Commun.* **1981**, 2, 241

⁷ Misra, A.; Grag, S. N. *J. Polym. Sci. Polym. Phys. Ed.* **1986**, 24, 983

⁸ Varma, D. S.; Agarwal, R.; Varma, I. K. *Text. Res. J.* **1986**, 56, 364

⁹ Varma, D. S.; Agarwal, R.; Varma, I. K. *Text. Res. J.* **1986**, 56, 438

¹⁰ Rao, B. R.; Datye, K. V. *Text. Chem. Color* **1996**, 28, 17

¹¹ Boykin, T. L.; Moor, R. B. *Polym. Eng. Sci.* **1998**, 38, 1658

¹² Ng, C. W. A.; MacKnight, W. J. *Macromolecules* **1996**, 29, 2412

moieties can be used to replace aromatic rings in mesogens in low molecular weight liquid crystals to both lower the crystal melting point and increase the breadth of the nematic phase.¹³ Cyclohexyl moieties have also been used in the formation of block copolyesters.¹⁴ The literature also reports the use of semi-flexible polyesters containing mesogens and flexible spacers to increase the solubility and decrease the melting point.¹⁵ ¹⁶ Moreover, *trans*-1,4-cyclohexane dicarboxylate (*trans*-CHDC) is a commercially available material that can be used as a comonomer to adjust the polarity and crystallinity of the polyester backbone. With respect to PEI homopolymers, the introduction of *trans*-cyclohexane dicarboxylate (*trans*-CHDC) decreases both the polarity and crystallinity of the PEI chain, thus increasing its solubility in organic solvents, as well as decreases the melting point, which can enhance processability.

Poly(ethylene isophthalate-co-terephthalate) (PEIT) random copolyesters have also been widely studied, particular for their industrial potential.^{17, 18, 19} PEIT copolyesters have a crystallizing component and a poorly or non-crystallizing component.²⁰ The incorporation of dimethyl isophthalate changes the morphology (i.e., crystallinity and crystal size) and properties (i.e., T_m , T_g , thermal and mechanical properties) of PET homopolymers, possibly improving their low temperature processability, as well as their ability to adhere to substrates such as metal and ceramic. PEIT copolyesters are currently widely used in industry as thermally shrinkable package films and as heat-sealable laminating films for steel cans and metal and ceramic sheets.^{21, 22, 23, 24, 25, 26} Nonetheless, little work has been done on ionic PEIT copolyesters. This

¹³ Gray, G. In *Polymer Liquid Crystals*; Ciferri, A., Ed.; Academic Press: New York, 1982; p13

¹⁴ Polk, M.; Bota, K.; Akubiro, E.; Phingbodhipakkiya, M. *Macromolecules* **1981**, 14, 1626

¹⁵ Braun, D.; Schulke, U. *Makromol. Chem.* **1986**, 187, 1145

¹⁶ Clausen, K.; Kops, J.; Rasmussen, K.; Rasmussen, K. H.; Sonne, J. *Macromolecules* **1987**, 20, 2660

¹⁷ de Hardura, A. M.; Kint, A. P. R.; Monoz-Guerra, S. *Macromolecules* **2000**, 33, 4596

¹⁸ Spera, S.; Po, R.; Abis, L. *Polymer* **1996**, 37, 729

¹⁹ Abis, L. Po, R.; Bacchilega, G.; Occiello, E.; Garbassi, F. *Makromol. Chem.* **1992**, 193, 1859

²⁰ Ha, W. S.; Chun, Y. K.; Jang, S. S.; Rhee, D. M.; Park, C. R. *J. Polym. Sci. Polym. Part B: Polymer Physics* **1997**, 35, 309

²¹ Goodman, I. In: Mark, H. F.; Gaylord, N. G.; Bikales, N. M., editors. *Encyclopedia of polymer science and technology*, 11. New York: Wiley, 1969, p. 1

²² Hsiue, G-H.; Yeh, T-S.; Chang, S. *J. Appl. Polym. Sci.* **1989**, 37, 2803

²³ Kanda, K.; Okamura, Y. Minamiki, T.; Inoue, T.; Kondoo, Y. Korean Patent, No. 85 1958

²⁴ Ooniwa, N.; Kato, H. Kondoo, T. Korean Patent, No. 93-19864

²⁵ Matsui, K.; Natakawa, Y.; Tanaka, A.; Inoue, T. Korean Patent, No. 92-9046

chapter will address the synthesis and characterization of novel sulfonate terminated telechelic ionic PEI-co-trans-CHCD-SSBA and PEIT-SSBA copolyesters, which heretofore has not been addressed.

5.2 Experimental

5.2.1. Materials

All reagents were used as received without further purification. Ethylene glycol, *trans*-1,4-cyclohexane dicarboxylate (*trans*-CHDC) and 3-sulfobenzoic acid, sodium salt (SSBA, 97 %) were generously donated by Eastman Chemical Co.. Dimethyl isophthalate, dimethyl terephthalate, sodium acetate (ACS reagent grade, 99.5 + %), and 1-dodecanol were purchased from Aldrich, as were phosphoric acid (crystals, 98 %), cobalt acetate (99 %), antimony (III) oxide (99 %), manganese acetate (99 %) and titanium isopropoxide.

5.2.2. Preparation of Catalyst Solution

Mn catalyst: $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.685 g) and pure HOAc (1.319 g) were added to 125 mL of EG and heated to render a catalyst solution in a concentration of 0.0215 g / mL based on Mn.

Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g) with 62.5 mL of *n*-BuOH in a dry bottle under nitrogen at a concentration of 0.055 g / mL based on Ti.

Sb catalyst: Sb_2O_3 (3.00 g) solid was dissolved in 250 mL ethylene glycol (EG). The mixture was heated at 100°C and stirred for 24 hours under nitrogen purge. Then the mixture was filtered and a clear solution was obtained in a concentration of 0.012 g / mL based on Sb.

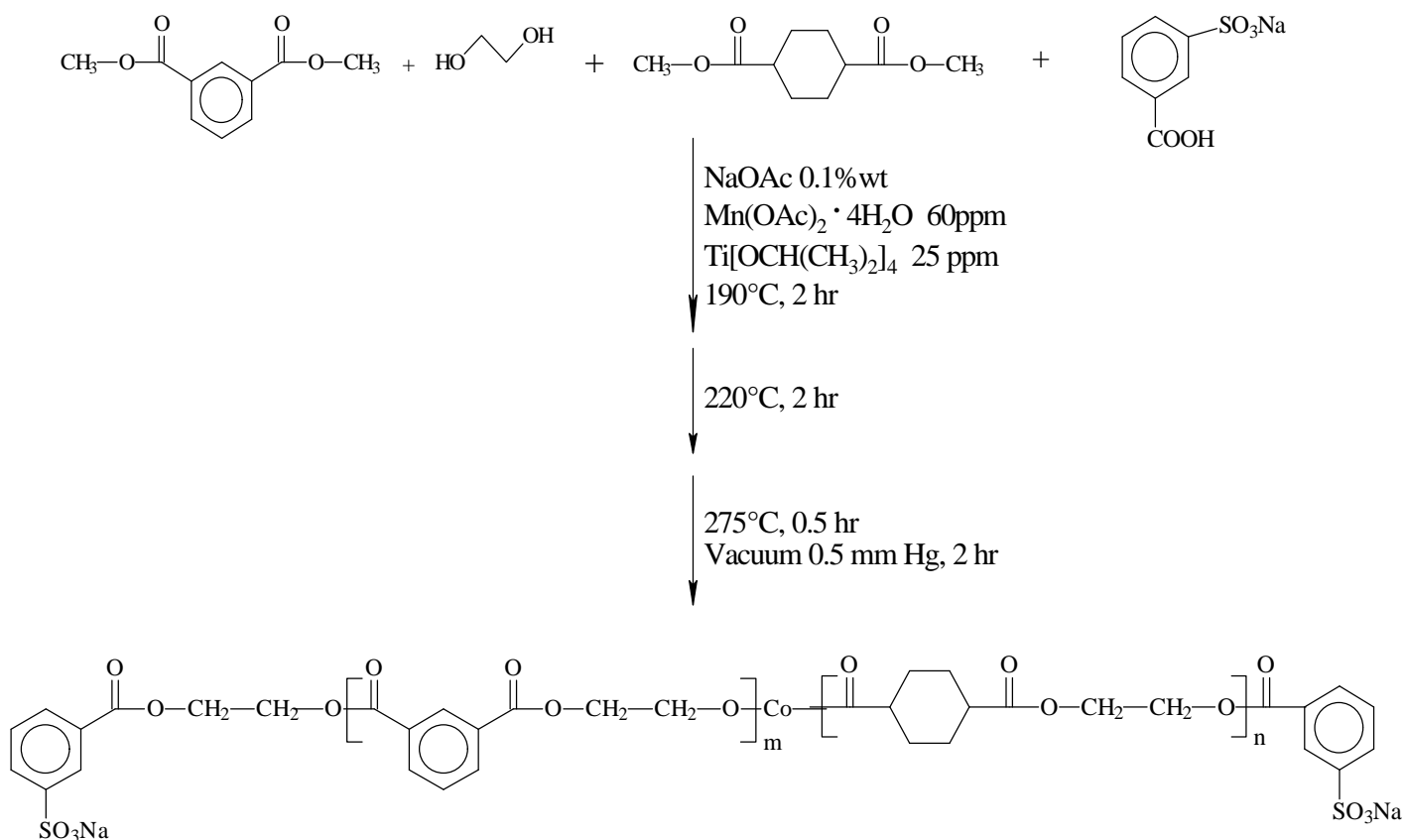
²⁶ Heyes, P. J.; White, C. H.; Singh, H. European Patent, No. 384 606

Co catalyst: Cobalt acetate (2.025 g) was mixed with ethylene glycol (125 mL) to obtain a catalyst solution with a concentration of 0.02 g / mol based on Co.

P catalyst: Phosphoric acid (99 %, 3.48 g) was dissolved in n-BuOH (12.5 g, 15.43 mL) and then mixed with ethylene glycol (125 mL) to obtain a catalyst with a concentration of 0.025 g / mol based on P.

5.2.3 Synthesis of Sulfonate Terminated Poly(ethylene isophthalate –co- *trans*-1,4-cyclohexane dicarboxylate) Ionic Copolymers (PEI-*trans*-CHDC-SSBA or DMI/*trans*-CHDC-SSBA)

To a mixture of EG (31 g, 0.5mol, 100% excess), SSBA (ionic end capper, 5 mol % compared to DMI and *trans*-CHDC), different molar ratios of DMI and *trans*-1,4-CHDC (0% : 100%, 25% : 75%, 50% : 50%, 75% : 25% and 100% : 0 %) were added to obtain a series of ionic DMI/*trans*-CHDC-5%SSBA (Scheme 5.1). Manganese catalyst (2.31 mL), and titanium catalyst (0.51 mL) were charged under nitrogen. A multi-step temperature process was used for the reaction, i.e., the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. The final product was obtained by breaking the reaction flask. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.

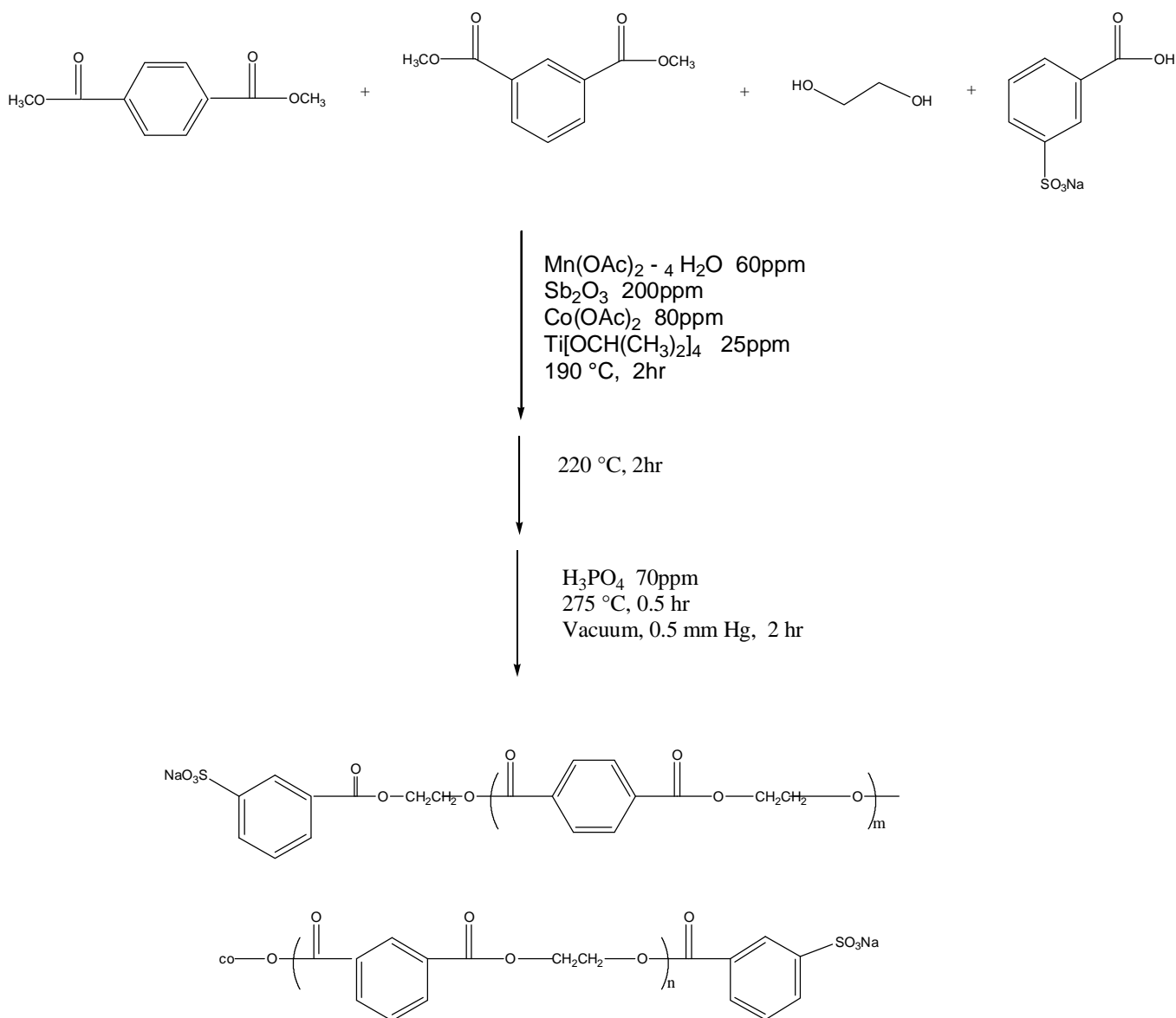


Scheme 5.1. Synthesis of DMI/*trans*-CHDC-5%SSBA using melt polymerization

5.2.4 Synthesis of Sulfonate Terminated Telechelic Ionic Poly(ethylene isophthalate-co-terephthalate) (PEIT-SSBA) Copolymers

To a mixture of EG (31 g, 0.5 mol, 100 % excess), SSBA (ionic end capper, 5 mol % compared to DMI and DMT), and different molar ratio of DMI and DMT (0% : 100%, 25% : 75%, 50% : 50%, 75% : 2% and 100% : 0%) were added to obtain a series of ionic DMI/DMT copolymers with 5 mol % the SSBA end capper (Scheme 5.2). Manganese catalyst (2.31 mL), antimony catalyst (3.8 mL), titanium catalyst (0.51 mL), cobalt catalyst (3.0 mL) and finally (just prior to introducing a vacuum), phosphoric acid (2.1 mL) were sequentially added. A multi-step temperature ramp was used for the reaction, i.e., the reaction mixture was heated and stirred at 190°C for 2 hours, 220°C for 2 hours and 275°C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2

hours. The final product was obtained by breaking the reaction flask. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.



Scheme 5.2. Synthesis of sulfonate terminated poly(ethylene isophthalate-co-terephthalate) (PEIT-SSBA) copolymers using melt polymerization

5.2.5 Polymer Characterization

A 400 MHz NMR (Varian-400) was used to characterize all of the non-ionic PEI and PET copolymers. The solvents of choice were CDCl_3 for the PEI-co-*trans*-CHDC samples, and $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (2:1, v/v) for the PEIT copolymers. FTIR spectra were collected on an infrared spectrometer (PE, 283B) to detect the sulfonate end group in the PEI-co-*trans*-CHDC copolymers. DSC (PE, Pyris 1) was used to study glass transition temperatures. All the samples were kept at 290 °C for 3 min to eliminate any thermal history, then quenched from 290°C to room temperature at a rate of 200 °C/min, and finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen and all the data collected were from the second scan. TGA (Thermal Analyst 2100, Du Pont Instruments) was used to study the thermal stability of the polymers. The solution behavior of the samples was studied using an Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$. The solvent used was chloroform.

5.3 Results and Discussion

5.3.1 NMR Analysis

All of the synthesized polymers were clear with a yellow cast. NMR (400 MHz) was employed to characterize the structure of all the ionomers. Ionic PEI-*trans*-CHDC copolymers were readily dissolved in CDCl_3 at room temperature for NMR analysis (Figure 5.1). PEIT-SSBA copolymers were dissolved in $\text{CDCl}_3/\text{CDCl}_3$ (2:1, v/v) at room temperature for NMR analysis. Figure 5.2 depicts the spectrum of PEIT-SSBA copolyester with DMI/DMT at 1:1 mol ratio. Peaks at 8.8 ppm (1H, *s*), 8.4 ppm (2H, *t*) and 7.7 ppm (1H, *s*) were attributed to the aryl hydrogens in the isophthalate component, while the peak at 8.2 ppm (4H, *m*) was attributed to the aryl hydrogens in the terephthalate component. The peak at 4.9 ppm (4H, *m*) resulted from the aliphatic hydrogens of the ethylene glycol. From these data, we determined that the composition of the copolymer had the same ratio of DMI and DMT as what was initially charged, namely a 1:1 ratio. Again, SSBA end capper was not observed due to very low concentration, as well as overlapping with isophthalate in the polymer chain.

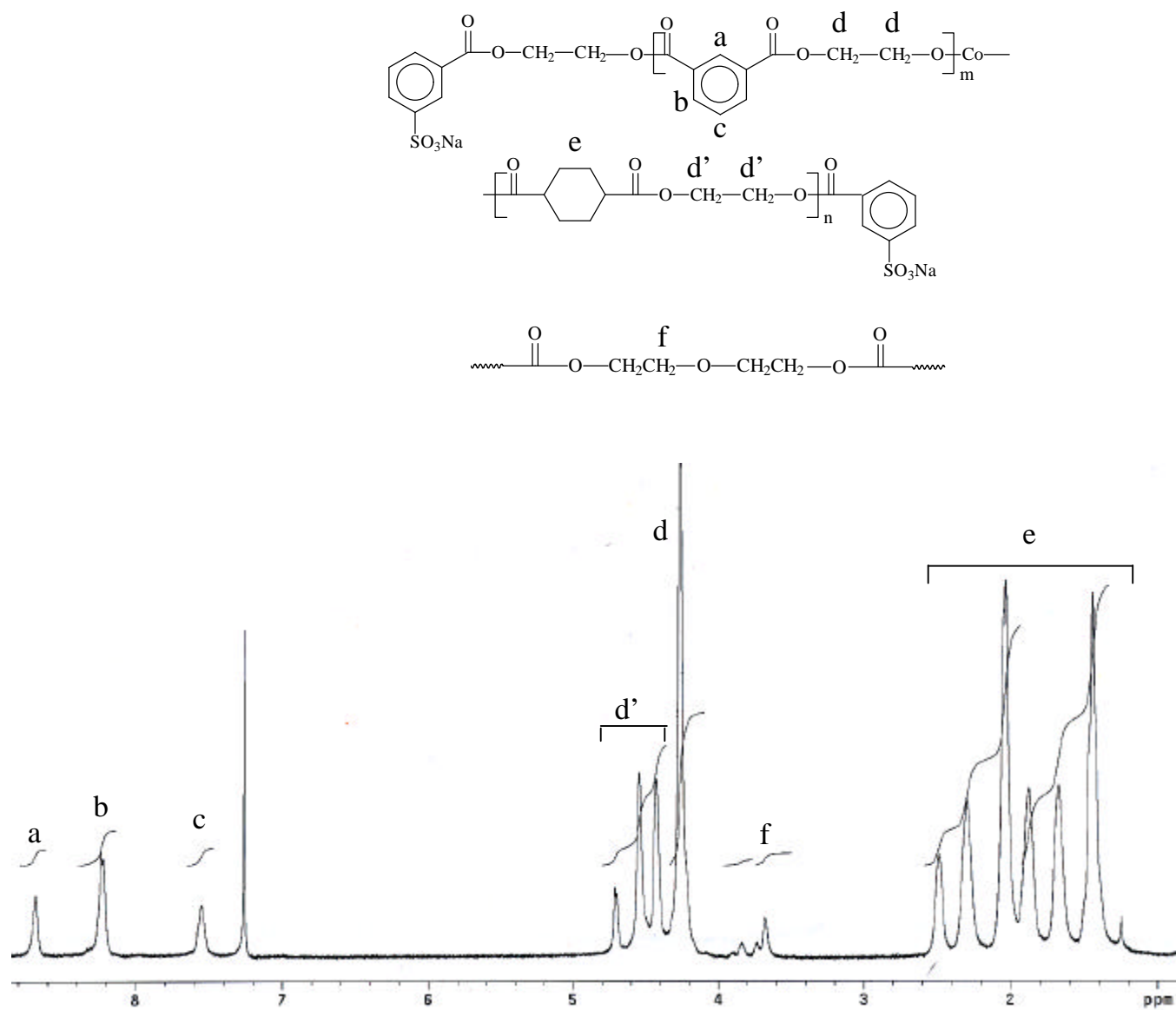


Figure 5.1. ^1H NMR spectrum of PEI-co-*trans*-1,4-CHDC-SSBA copolyester, DMI: *trans*-1,4-CHDC = 1:1 mol ratio, CDCl_3 , room temperature

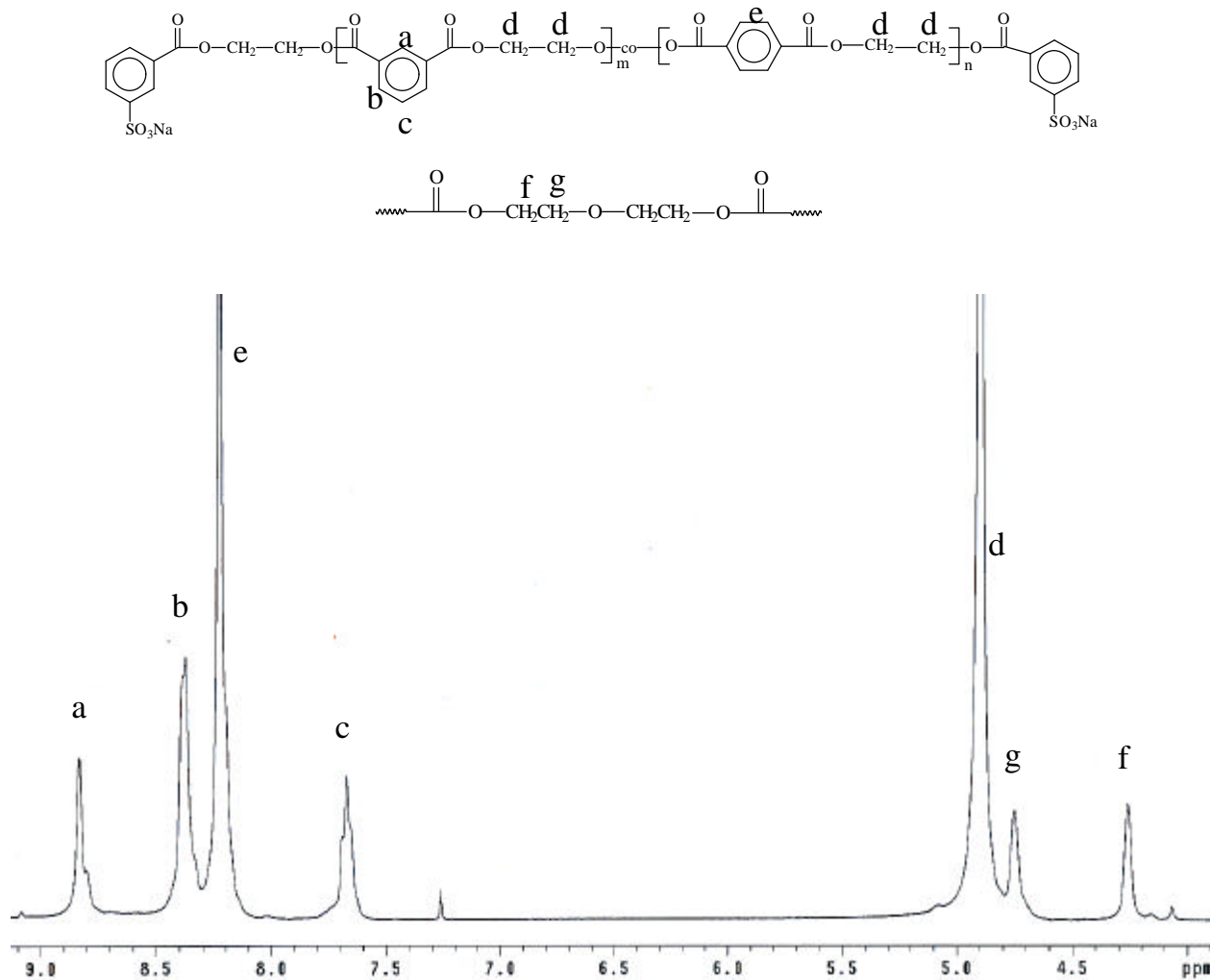


Figure 5.2. ^1H NMR spectrum of PEIT-5%SSBA, DMI : DMT = 1:1 mol ratio, 5 mol % of SSBA, $\text{CF}_3\text{COOD}/\text{CDCl}_3 = 2:1$, v/v; room temperature

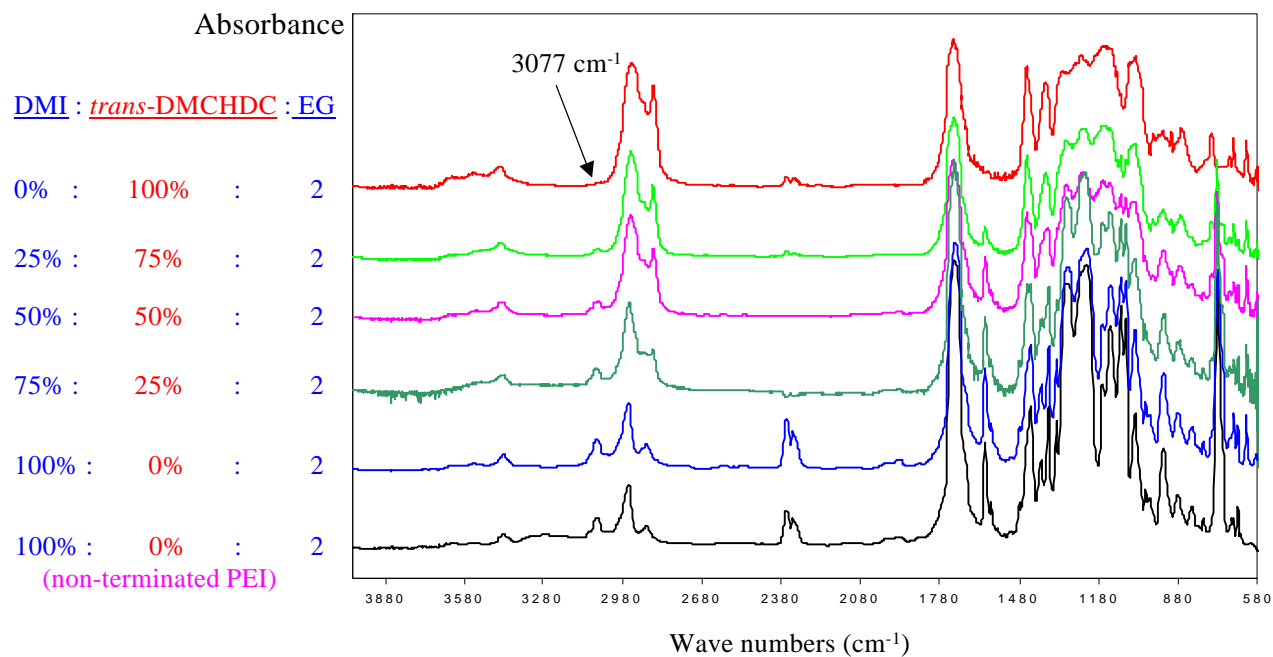
5.3.2 FTIR Analysis

As previously demonstrated, FTIR is a useful and reliable tool to verify both the composition of copolymers and the presence of ionic end groups. From FTIR spectra of ionic PEI-*trans*-CHDC-5%SSBA copolymers, a peak at 3077 cm^{-1} was observed due to the C-H stretching vibration of the benzene ring in the dimethyl isophthalate (DMI)

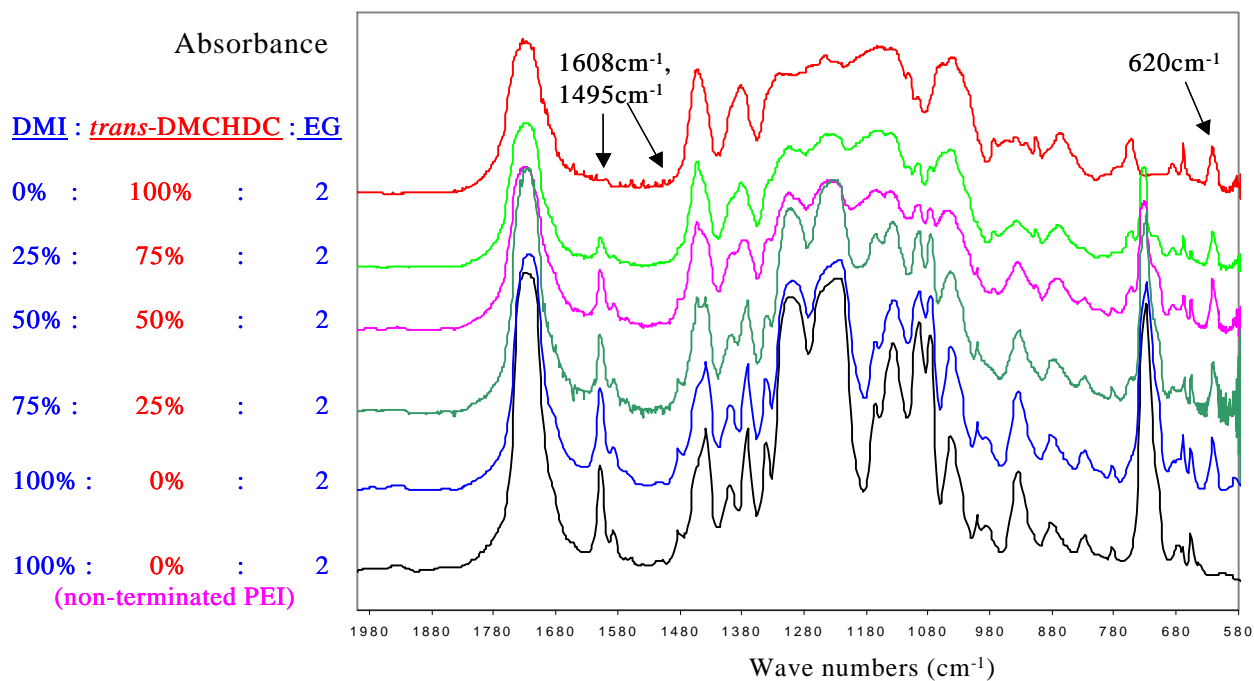
component (Figure 5.3).²⁷ The peak height decreased as a result of a reduction in DMI and an increase in the CHDC component. When the content of the DMI was zero, a pure CHDC ionomer resulted, and the peak disappeared. Peaks at 1608 and 1495 cm^{-1} resulted from benzene ring vibration in the DMI component. And as previously noted, when the DMI content was zero, both those peaks were not observed. From FTIR spectra, the characteristic absorption of S-O at 620 cm^{-1} was observed, which was due to the SSBA end group.²⁸ At the same time, no such peak was observed in non-terminated PEI sample.

²⁷ Silverstein, R. M. Webster, F. X. in: Spectrometric Identification of Organic Compounds, 6th Ed., John Wiley & Sons, Inc. 1998, Chap. 3

²⁸ Nakanishi, K. Infrared Absorption Spectroscopy (Practical); Holden-Day Inc.; San Francisco, 1962; p54



* 3077 cm^{-1} : C-H stretching of benzene ring



* 1608, 1495 cm^{-1} : C-H vibration of benzene ring

Figure 5.3. FTIR spectrum of PEI-*trans*-CHDC-5%SSBA copolymers, 3077 cm^{-1} : C-H stretching of benzene ring; 1608, 1495 cm^{-1} : C-H vibration of benzene ring

5.3.3 DSC and TGA Analysis

DSC and TGA were used to study the thermal properties of sulfonate terminated PEI- *trans*-CHDC copolymers and PEIT copolymers. TGA results showed that all of the samples were very stable below 350 °C under nitrogen (Table 5.1), while DSC results revealed that the glass transition temperatures decreased when the content of *trans*-CHDC increased. Regardless of ionic end group content, introducing *trans*-CHDC to polymer chain uniformly decreased the rigidity of the polymer chain. Additionally, it was demonstrated that the *trans*-CHDC structure provided more free volume in the polymers.²⁹ All these factors contributed to the lower glass transition temperatures that were observed.

Table 5.1. DSC and TGA results of PEI-*trans*-CHDC-5%SSBA copolyesters, N₂, heating rate at 10°C, second heat was used for DSC

PEI- <i>trans</i> -CHDC-5%SSBA (DMI: <i>trans</i> -1,4-CHDC:EG:SSBA)	T _g (°C) DSC, N ₂	5 % wt loss T (°C), TGA, N ₂
0: 100%: 2: 5%	24	382
25%: 75%: 2: 5%	32	383
50%: 50%: 2: 5%	39	378
75%: 25%: 2: 5%	48	369
100%: 0: 2: 5%	62	360
100%: 0: 2: 5%	58	350

Compared with PET-SSBA homopolymers, all of the PEIT-SSBA ionomers were clear and amorphous. From DSC curves in Figure 5.4, only glass transition temperatures were only observed for the PEIT-SSBA; no crystallization or melting peaks were noted.

²⁹ Domszy, R. C.; Shannon, P. J. *Macromolecules* **1990**, 23, 2790

This is attributed to the fact that the kinked meta-linkage of the DMI structure completely destroyed the regularity of the polymer chain, thus making the copolymer completely amorphous. All of the PEIT-SSBA ionomers exhibited single T_g s, and the glass transition temperatures decreased with increasing DMI content (Table 5.2).

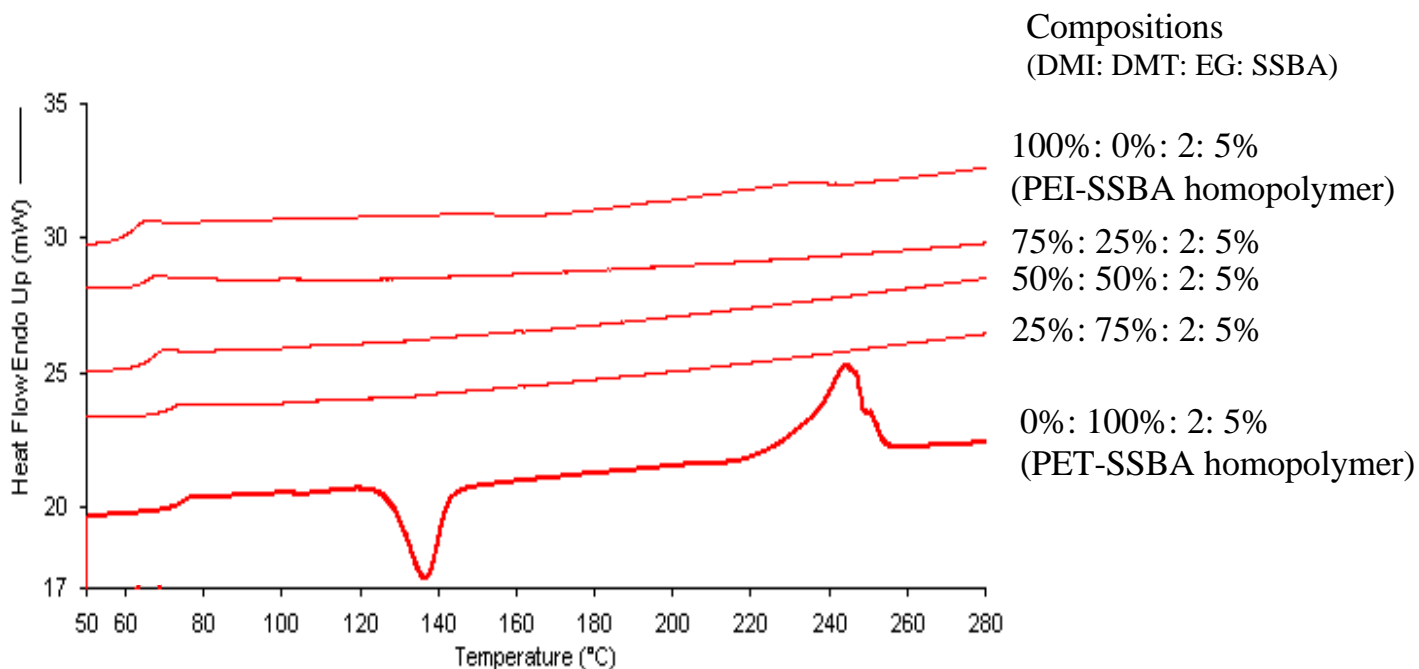


Figure 5.4. DSC curves of ionic poly(ethylene isophthalate –co- terephthalate) (PEIT-SSBA) copolymers; N_2 , second heat, heating rate: 10 °C/min

Table 5.2. DSC and TGA results of ionic poly(ethylene isophthalate –co- terephthalate) (PEIT-5%SSBA) copolymers; N₂, second heat, heating rate: 10 °C/min

PEIT-5%SSBA compositions (DMI: DMT: EG: SSBA, mol ratio)	T _g (°C) N ₂ , DSC	5 % wt loss T _g (°C), N ₂ , (TGA)
100%: 0%: 2: 5%	60	378
75%: 25%: 2: 5%	63	375
50%: 50%: 2: 5%	66	368
25%: 75%: 2: 5%	70	370
0%: 100%: 2: 5%	75	388

5.3.4 Solution Viscometry Study

Solution viscometry was used to study the solution behavior of PEI-*trans*-CHDC-SSBA copolymers. All of the samples were dissolved in chloroform at room temperature. Upward curvatures were observed for η_{sp}/c vs. c for these ionomers (Figure 5.5), which did not conform to the Huggins and Kreamer equation. Conversely, for the non-ionic oligomers, Huggins and Kreamer equations were obeyed, and two straight lines were obtained (Figure 5.5). The observed non-linear relationship between solution viscosity and (dilute) polymer concentration is believed to have arisen from the ionic interactions in solution. With the existence of ionic groups at the polymer chain end, it is known that the aggregation level varies due to solution concentrations. Considering this factor, it is reasonable to expect that the dilute solution viscosity behavior of the ionomers would not correspond to the linear behavior of non-ionic polymers. It should be pointed out that these results are consistent with existing literature concerning other sulfonated ionic liquid crystalline systems.³⁰ However, additional experimental and theoretical studies of these non-linear relationships will be valuable.

³⁰ B. Zhang and R. A. Weiss, *J. of Polymer Science: Part A: Polymer Chemistry* **1992**, 30, 989

terephthalate) (PEIT-SSBA) were successfully synthesized. NMR was used to determine the structure of the copolyester ionomers. FTIR was used to confirm the composition of these novel ionic poly(ethylene isophthalate-co-*trans*-CHDC) copolymers, as well as to identify the ionic end groups. TGA results showed that all of the ionic copolyesters had very good thermal stability, displaying only 5 % wt loss at 350 °C under nitrogen. With regard to the PEI-*trans*-CHDC-SSBA copolymers, DSC results showed that by introducing a *trans*-CHDC comonomer, the polarity and chain packing regularity decreased due to the *trans* structure of the CHDC. Correspondingly, this also resulted in more free volume for polymer chain mobility and lower glass transition temperature. For ionic poly(ethylene isophthalate-co-terephthalate) (PEIT-SSBA), DSC results indicated that the new copolyester materials were soft, clear and almost totally amorphous, due to the kinked-structure of DMI, which reduced the regularity of the polymer chains and made crystallization less likely to occur. As telechelic ionomers, all of the samples produced upward curvatures in η_{sp}/c vs. c plots in dilute solution. This is a characteristic behavior of an ionomer.

CHAPTER 6. SYNTHESIS AND CHARACTERIZATION OF BRANCHED TELECHELIC POLYESTER IONOMERS

6.1 Introduction

The engineering thermoplastic, poly(ethylene terephthalate) (PET), is superior to general purpose thermoplastics in terms of thermal stability, ease of processing, chemical resistance and attractive mechanical properties at higher temperatures. These characteristics make it possible to utilize PET for a number of industrial uses, such as injection-molded engineering components, injection blown-molded soft drink containers, films for recording tapes, and synthetic fibers. Manipulating the polymer backbone is one way in which mechanical properties can be influenced. Recently, a considerable effort to control the backbone architecture of PET star polymers and dendrimers has been reported,^{1, 2, 3, 4} especially since highly branched backbones can enhance solubility and reduce viscosity in solvents compared to linear analogues.^{5, 6, 7}

Early work by Manaresi *et al.*⁸ established a solid foundation for the study of branched PET and the correlation of experimental data with theory. Additional efforts to produce and characterize branched PETs have also been reported.^{9, 10, 11, 12, 13} In addition to their improved properties in solution, branched PETs also have superior melt strength and extensional viscosity, compared with linear PET.^{10, 11} This is analogous to the

¹ Tomallia, D. A.; Baker, J.; Dewald, R.; Hal, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, 17, 117

² Feast, W. J. Stainton, N. M. *J. Mater. Chem.* **1994**, 4, 1159

³ Newkome, G. R.; *J. Org. Chem.* **1985**, 50, 2003

⁴ Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, 143, 1

⁵ Tomalia, D. A.; Hall, V. B. M.; Hedstrand, D. M.; *Macromolecules* **1987**, 20, 1164

⁶ Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J.; *Macromolecules* **1993**, 26, 1514

⁷ Mournay, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Wooley, K. L.; Hawker, C. J. *Macromolecules* **1992**, 25, 2401

⁸ Manaresi, P.; Parrini, P.; Semeghini, G. L.; de Fonasari, E. *Polymer* **1976**, 17, 595

⁹ Langla, B.; Strazielle, C.; *Makromol. Chem.* **1986**, 187, 591

¹⁰ Manaresi, P.; Munari, A.; Pilati, F. *Polymer* **1986**, 17, 955

¹¹ Rosu, R. F.; Shanks, R. A.; Bhattacharya, S. N.; *Polym. Int.* **1997**, 42, 267

¹² Jaykannan, M.; Ramakrishnan, S. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 309

¹³ Hess, C.; Hirt, P.; Oppermann, W. *J. Appl. Polym. Sci.* **1999**, 74, 728

properties of low density polyethylenes vs. high density polyethylenes.¹¹ It is thought that branched PETs may be useful in preparing many blow-molded or extruded products, either by itself or as an additive to a linear PET. Introducing a branched structure to a recycled PET may improve flow properties and broaden the range of products for which it may be suitable.^{14,15} Alternatively, recycled PET may also be modified by blending it with branched PET to enhance its properties.

This chapter describes the melt polymerization and physical characterization of novel ionic and non-ionic branched PEI and PET by melt polymerization.

6.2 Experimental

6.2.1 Materials

All reagents were used without further purification. Ethylene glycol and 3-sulfobenzoic acid, sodium salt (SSBA, 97 %) were generously donated by Eastman Chemical Co. Dimethyl isophthalate (99 %), terephthalate (99 %), trimellitic anhydride (TMA, 97 %), sodium acetate (ACS reagent grade, 99.5 + %), and 1-dodecanol were purchased from Aldrich, as were phosphoric acid (crystals, 98 %), cobalt acetate (99 %), antimony (III) oxide (99 %), manganese acetate (99 %) and titanium isopropoxide.

6.2.2 Preparation of Catalyst Solutions

Sb catalyst: Sb_2O_3 (3.00 g) solid was dissolved in 250 mL ethylene glycol (EG). The mixture was heated at 100°C and stirred for 24 hours under nitrogen purge. The mixture was then filtered and a clear solution was obtained at a concentration of 0.012 g / mL based on Sb.

¹¹ Rosu, R. F.; Shanks, R. A.; Bhattacharya, S. N.; *Polym. Int.* **1997**, 42, 267

¹⁴ Barrett, L. W.; Sperling, L. H. *Polym. Mater. Sci. Eng.* **1991**, 65, 180

¹⁵ Rebeiz, S. K.; Iyer, V. S.; Fowler, W. D.; Paul, D. R. *ANTEC* **1990**, 90, 1459

Mn catalyst: $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.685 g) and pure HOAc (1.319 g) were added to 125 mL of EG and heated to render a catalyst solution in a concentration of 0.0215 g / mL based on Mn.

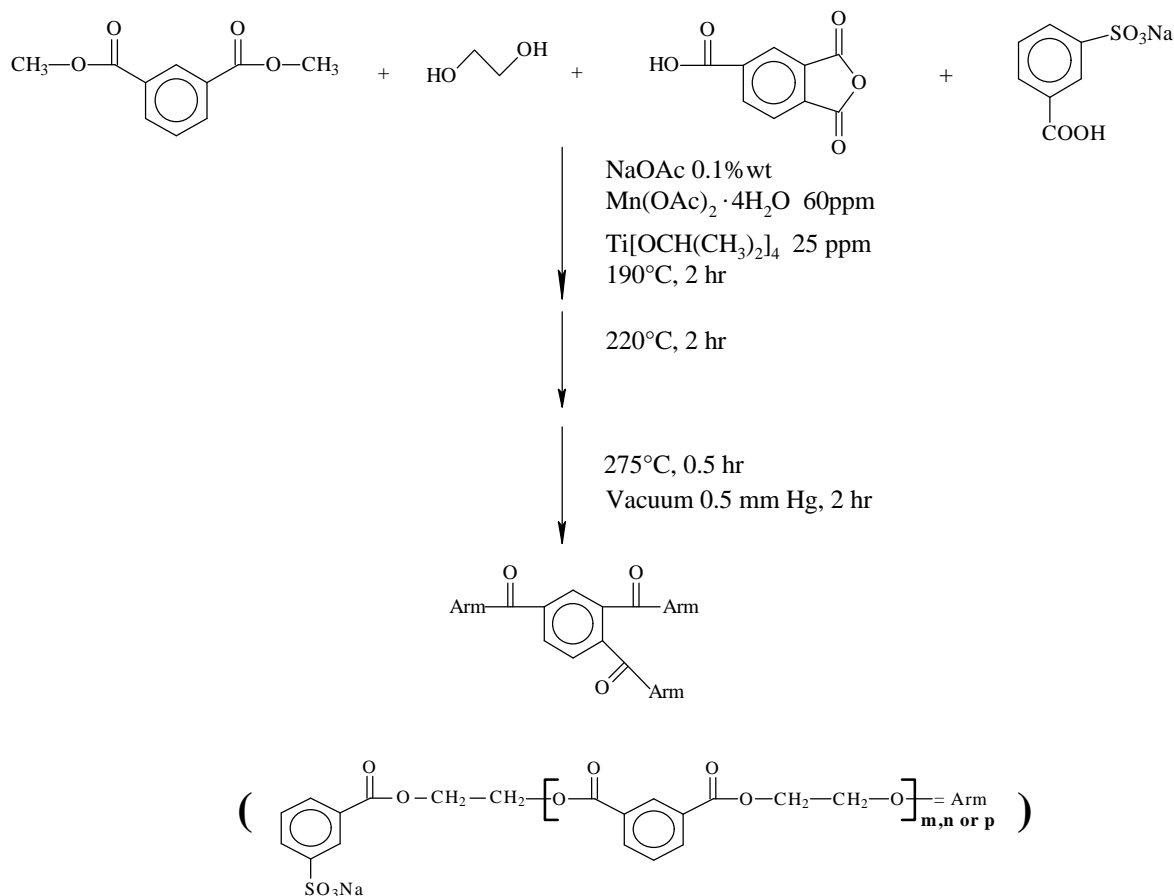
Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g) with 62.5 mL of n-BuOH in a dry bottle under nitrogen at a concentration of 0.055 g / mL based on Ti.

Co catalyst: Cobalt acetate (2.025 g) was mixed with ethylene glycol (125 mL) to obtain a catalyst solution with a concentration of 0.02 g / mol based on Co.

P: Phosphoric acid (99 %, 3.48 g) was dissolved in n-BuOH (12.5 g, 15.43 mL) and then mixed with ethylene glycol (125 mL) to obtain the catalyst with a concentration of 0.025 g / mol based on P.

6.2.3 Synthesis of Sulfonate Terminated Amorphous Branched PEI Ionomers (bPEI-SSBA/TMA)

To a mixture of DMI (48.5 g, 0.25 mol), EG (31 g, 0.5 mol, 100% excess) and TMA (0.1 mol % compared to DMI), and varying amounts of the end capper, SSBA (1 mol %, 3 mol %, 5 mol % compared to DMI) were combined to obtain a series of PEI ionomers with different molecular weights (Scheme 6.1). Both manganese catalyst (2.31 mL), and titanium catalyst (0.51 mL) were charged under nitrogen. A multi-step temperature process was used for the reaction, i.e., the reaction mixture was heated and stirred at 190°C for 2 hours, 220°C for 2 hours and 275°C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an additional 2 hours. The final product was obtained by breaking the reaction flask. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.

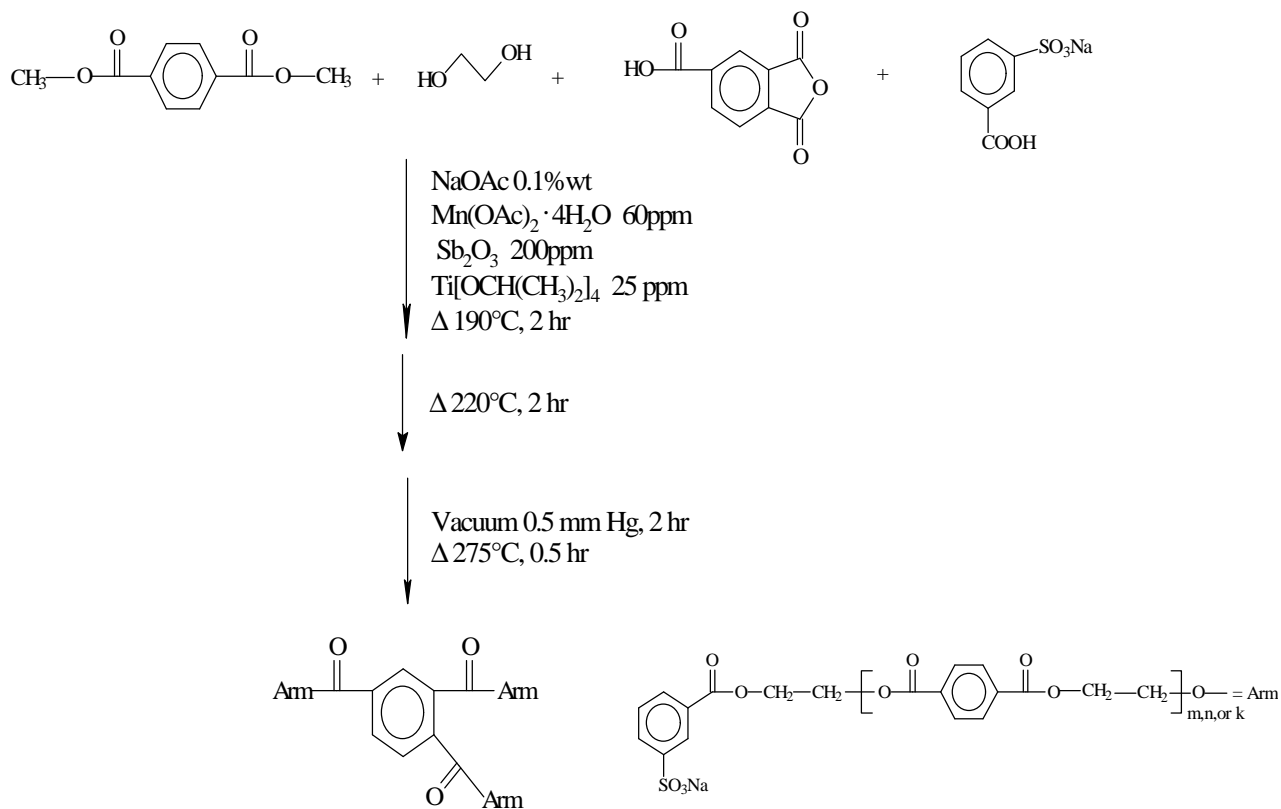


Scheme 6.1. Synthesis of sulfonate terminated branched PEI using TMA as branching agent via melt polymerization

6.2.4 Synthesis of Sulfonate Terminated Semi-crystalline Branched Polyester Ionomers (bPET-SSBA/TMA)

Two series of branched PET ionomers were synthesized. One series was synthesized with a fixed amount of ionic end group and a varying amount of branching agent (Scheme 6.2, Table 6.2.); while the second series used a fixed amount of branching reagent and varied the amount of SSBA end group (Scheme 6.2, Table 6.3.). For the first series of bPET-5%SSBA/xTMA (Table 6.2), a mixture of dimethyl terephthalate (DMT, 48.5 g, 0.25 mol), ethylene glycol (EG, 31 g, 0.5 mol, 100% excess), varying amounts of trimellitic anhydride (TMA, 0.1 mol %, 0.3 mol %, 0.5 mol %, 1 mol %, compared to DMT), and the end capper, SSBA (5 mol % compared to DMT) were added to obtain

PET ionomers. For the second series bPET-xSSBA/1%TMA (Table 6.3), a mixture of dimethyl terephthalate (DMT, 48.5 g, 0.25 mol), ethylene glycol (EG, 31 g, 0.5 mol, 100 % excess) and trimellitic anhydride (TMA, 1 mol % compared to DMT), and differing amounts of end capper, SSBA (1 mol %, 3 mol %, 5 mol %, compared to DMT) were added to obtain PET ionomers. Manganese catalyst (2.3 mL), antimony catalyst (3.8 mL), titanium catalyst (0.5 mL), cobalt catalyst (3.0 mL) were added initially and finally, just before the vacuum, phosphoric acid (2.1 mL) was charged. The same catalyst system was used for the preparation of all of the bPET-SSBA/TMA polymers. A multi-step temperature procedure was used for all reactions, i. e., the reaction mixture was heated and stirred at 190 °C for 2 hours, 220 °C for 2 hours and 275 °C for 0.5 hour. At the end, vacuum (0.5 mm Hg) was applied for an extra 2 hours. Since no solvent was involved in the reaction, no further purification was needed. Since SSBA was 97 % purity, NaOAc (0.1 wt %) was used to react with the non-sulfonated component in SSBA to help maintain SSBA in the sodium salt form. Future efforts should maintain a constant 0.1:1 mol ratio of NaOAc to SSBA.



Scheme 6.2. Synthesis of sulfonate terminated branched PET using TMA as branching agent via melt polymerization

6.2.5 Polymer Characterization

A 400 MHz NMR (Varian-400) was used to characterize the sulfonate terminated branched PEI-SSBA and PET-SSBA ionomers. CDCl₃ was used as the solvent for the branched PEI ionomers, while CF₃COOD/CDCl₃ (2:1, v/v) was the solvent of choice for the branched PET ionomers. Melt rheology behavior was analyzed using a melt rheometer (TA Instruments, Advanced Rheometer AR 1000). DSC (Perkin Elmer, Pyris 1) was used to study glass transition temperatures and crystallization processes. All the samples were kept at 290 °C for 3 min to eliminate any thermal history, then quenched from 290 °C to room temperature at a rate of 200 °C/min, finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen and the data collected were from the second scan. TGA (Thermal Analyst 2100, Du Pont Instruments) was used to study the thermal stability of the polymers. The solution

behavior of the samples was studied using an Ubbelohde viscometer at 25 ± 0.1 °C. The solvent used was the mixture of phenol and tetrachloroethane (60/40, w/w).

6.3. Results and Discussion

Branched telechelic ionic PEI (Table 6.1) and PET (Table 6.2 and Table 6.3) copolymers were synthesized via a standard melt polycondensation reaction. The branched PEI ionomers resulted in clear amorphous polymers, while the branched PET ionomers were opaque until the branching agent reached 1 mol % (compared to DMT), when it became a clear amorphous polymer. Polymer yields were about 100 %.

6.3.1. NMR Analysis

Figure 6.1 depicts the ^1H NMR spectrum of bPEI-SSBA/TMA polymer with the composition of 1 : 2 : 0.5 % : 5 % (DMI : EG : TMA : SSBA). Aryl hydrogens of the polymer backbone can be found at 8.7 ppm (1H, *d*), 8.2 ppm (2H, *d*) and 7.5 ppm (1H, *t*). Aliphatic hydrogens can be found at 4.65 ppm (4H, *s*). An SSBA end group of branched PEI ionomer could not be detected because of the overlapping with the DMI component in the polymer backbone. Branched ionic PET polyesters were dissolved in $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (2:1, v/v) solvent. Backbone: aryl hydrogens were (4H, *s*) at 8.2 ppm; aliphatic hydrogens (4H, *s*) were found at 4.7 ppm; SSBA end groups were found at 8.7 ppm (1H, *d*), 8.2 ppm (2H, *m*) and 7.6 ppm (1H, *t*). It was not possible to detect the presence of the branching units from the NMR spectrum.¹⁶

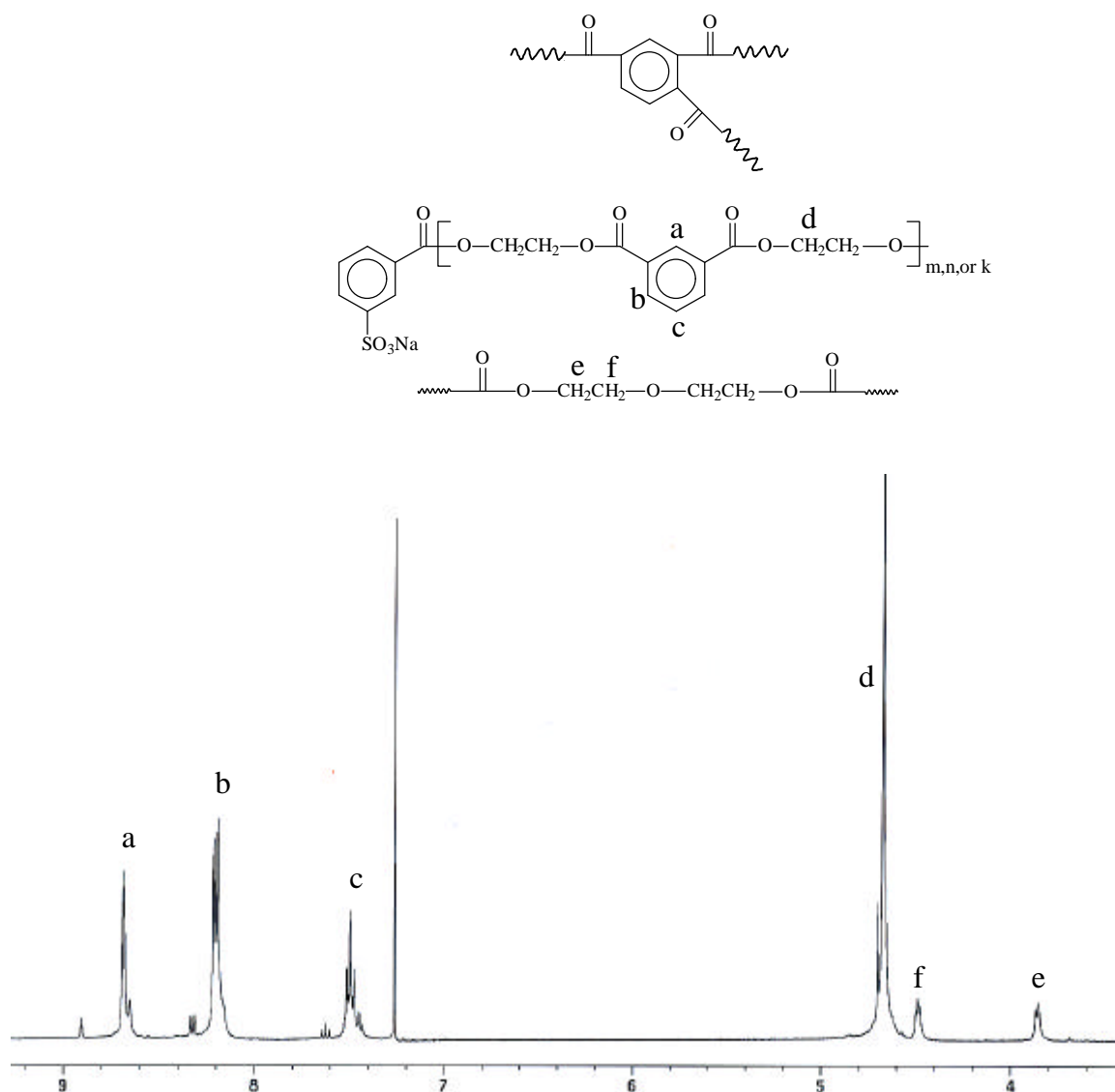


Figure 6.1. ^1H NMR spectrum of branched PEI-5%SSBA ionomers with 0.5 mol % TMA, in CDCl_3 , room temperature

6.3.2. Solution Viscometry Study of Branched PEI Ionomers

Solution viscometry of sulfonate terminated amorphous branched PEI ionomers was studied in chloroform solution at 25 °C. Figure 6.2 shows that all of the ionomers produced upward curvatures in the η_{sp}/c vs. c plot, which is characteristic behavior of a linear telechelic PEI ionomer. Compared with non-ionic PEIs, the linear deviation is more obvious for sample bPEI-5%SSBA/0.3%TMA than for sample bPEI-

5%SSBA/0.2%TMA. The bPEI-5%SSBA/0.5%TMA ionomer, which contained the highest content of the branching agent, deviated most dramatically from a linear relationship. Different molecular chain topologies caused by the different amounts of the branching agent, TMA, in the ionomers, which could affect the effective ionic interactions among the polymer chains, could attribute to the observed trend. Further study is needed to clarify this behavior.

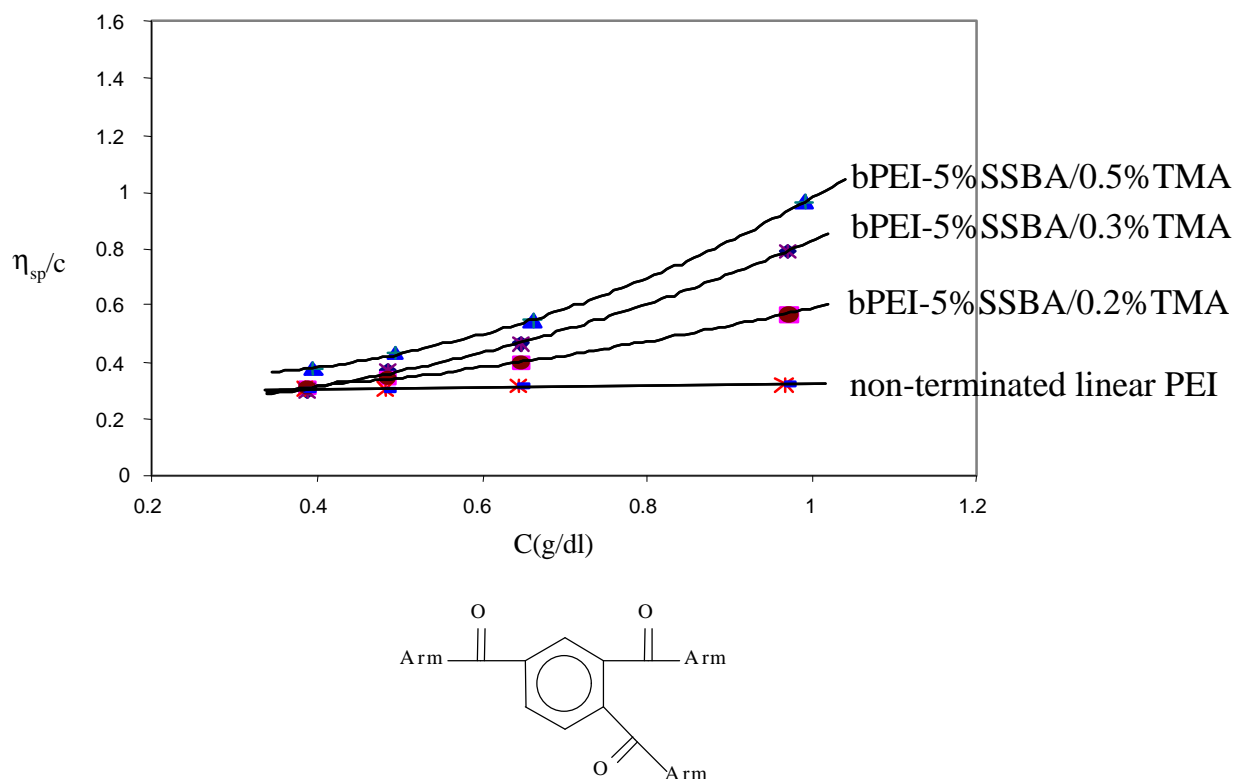


Figure 6.2. Solution behavior of non-terminated PEI and sulfonate terminated branched PEI-5%SSBA ionomers in chloroform at 25 °C

6.3.3 Thermal Analysis of Branched PEI Ionomers

DSC and TGA were used to study the thermal properties of branched telechelic PEI ionomers, and the results are summarized in Table 6. 1. TGA analysis revealed that all the polyesters showed good thermal stability up to 360 °C (Table 6.1), and no crystalline behavior was observed.

When a branching reagent (such as TMA) is introduced into a polymer, the polymer's chain will become shorter with the more amount of TMA, thus lowering glass transition temperature. However, our DSC results revealed that with TMA contents varying between 0 – 0.5 mol %, the four resulting PEI ionomers (with 5 mol % SSBA) had identical glass transition temperatures (~ 57 °C), which is very close to that of the non-terminated PEI sample (Table 6.1, $T_g = 58$ °C). This is very likely due to the strong ionic interaction of the ionomers, as previous discussed (Chapter 3), whereby polymer chain mobility was hindered and less endgroup effects, thus displayed high molecular weight characteristics. Despite these seemingly opposite effects as a result of branching and ionic interaction, the overall glass transition temperatures did not change.

Table 6.1. DSC and TGA of branched PEI-5%SSBA with different amounts of branching agent, heating rate is 10 °C/min

Branched PEI-5%SSBA/xTMA	T_g (°C) N ₂ , DSC	5 % wt loss N ₂ , TGA
bPEI-5%SSBA/0.1%TMA	57	367
bPEI-5%SSBA/0.2%TMA	57	370
bPEI-5%SSBA/0.3%TMA	57	369
bPEI-5%SSBA/0.5%TMA	57	370
PEI-5%SSBA (linear)	60	360
non-terminated linear PEI	58	350

6.3.4 Glass Transition Behaviors in Branched PET Ionomers

When examining sulfonate terminated semicrystalline branched telechelic PET ionomers, the effect of branching on glass transition temperature is more complex. From DSC results, we can see that for the PET ionomers with the same ionic end group (5%SSBA, Figure 6.3 and Table 6.2), when branching reagent content was increased, the glass transition temperature decreased. Several factors are believed to contribute to this

phenomenon. First, more free volume is created by the local structure irregularity around the branch point,¹⁶ which is known to decrease the glass transition temperature of a polymer. Secondly, as was discussed in relation to the PEI ionomers, ionic end groups tend to aggregate the polymer chain through ionic interaction, which can increase glass transition temperature. Also importantly, because they are semicrystalline polymers, the degree of crystallinity can influence the glass transition temperature in the amorphous region. Thus, the overall T_g trend for these materials must be determined in relation to all of these factors. Though more study is needed to clarify the relative importance of these factors, the decreasing of T_g with increasing TMA is probably due to the decreasing of crystal content. Highly crystalline PET has higher T_g due to restriction of mobility in the amorphous chains by the crystals.

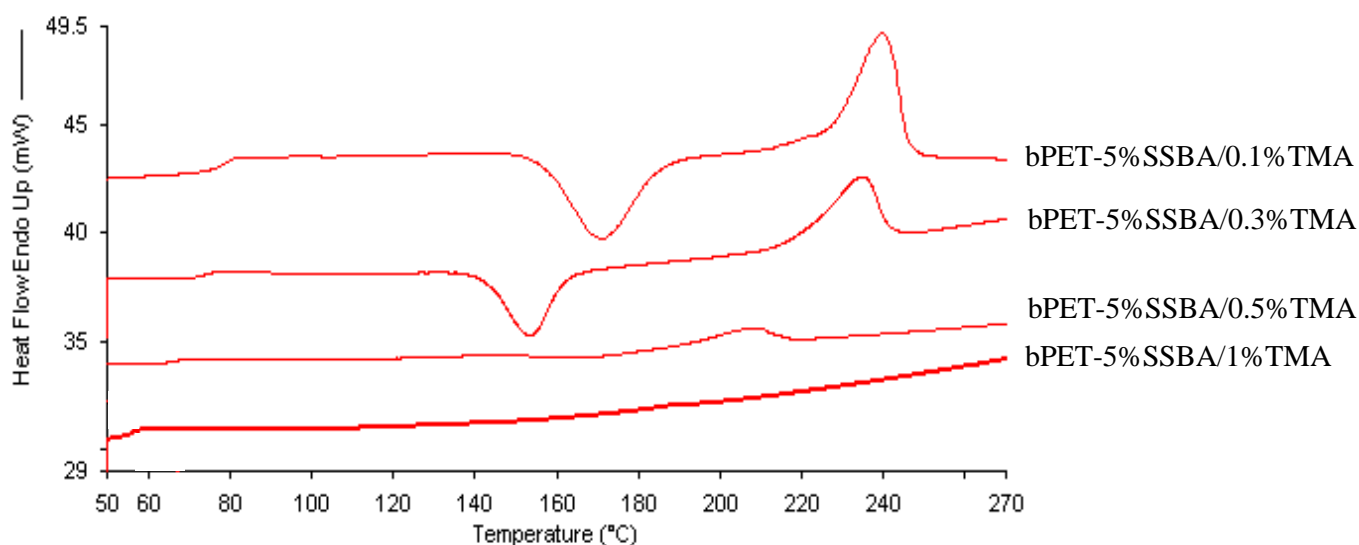


Figure 6.3. DSC curves of sulfonate terminated branched PET-5%SSBA ionomers with different amounts of branching agent (0.1, 0.2, 0.3, 1 mol % of TMA compared to DMT)

¹⁶ Hudson N.; MacDonald, W. A.; Neilson, A.; Richards, R. W.; Sherrington, D. C. *Macromolecules* **2000**, *33*, 9255

Table 6.2. DSC results of sulfonate terminated branched PET-5%SSBA with different amounts of branching agent (TMA, 0.1, 0.2, 0.3, 1% compared with DMT), heating rate is 10 °C/min

Branched PET-SSBA/xTMA	T _g (°C)	T _c (°C)	T _m (°C)
bPET-5%SSBA/0.1%TMA	79	192	240
bPET-5%SSBA/0.3%TMA	74	153	235
bPET-5%SSBA/0.5%TMA	64	not detectable	205
bPET-5%SSBA/1%TMA	56	not detectable	not detectable

Sulfonate terminated branched PET ionomers, which have the same amount of branching agent, but varying amounts of end capper (Figure 6.4 and Table 6.3), were also studied. For the first two samples (bPET-1%SSBA/1%TMA and bPET-3%SSBA/1%TMA), although they possess different molecular weights, their ionic interactions are still strong enough to hold the polymer chains together, thus resulting in relatively unchanged glass transition temperatures. The decrease of the glass transition temperature of bPET-5%SSBA/1%TMA is probably also due to the very low crystallization degree (Figure 6.4), as discussed above.

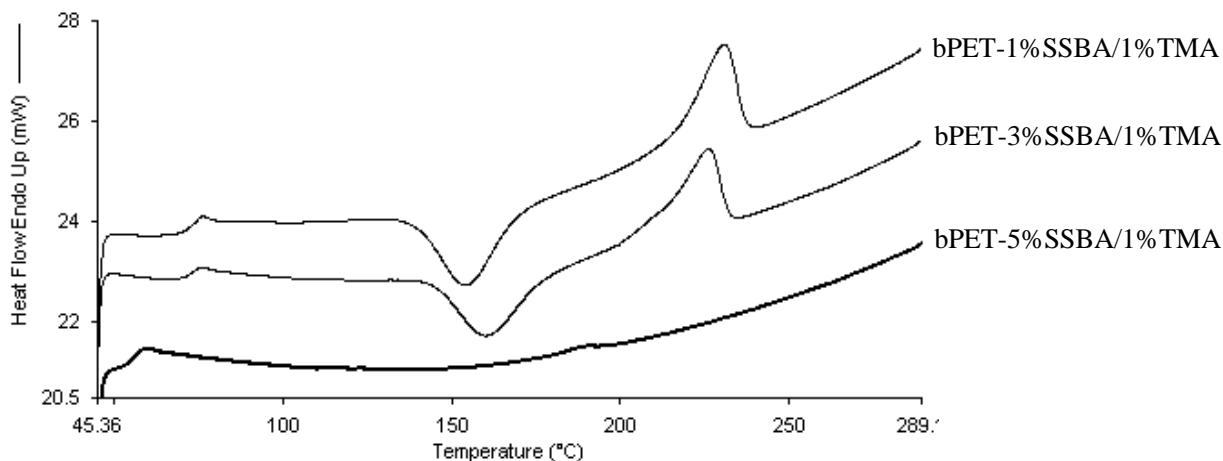


Figure 6.4. DSC curves of branched PET-xSSBA/TMA ionomers (TMA is 1mol % compared to DMT and SSBA, x = 1, 3, 5 mol %); N₂, heating rate is 10 °C/min

Table 6.3. DSC results of branched PET-xSSBA/TMA ionomers (TMA is 1mol % compared to DMT and SSBA, x = 1, 3, 5 mol %); N₂, heating rate is 10 °C/min

Branched PET-xSSBA/TMA	T _g (°C)	T _c (°C)	T _m (°C)
bPET-1%SSBA/1%TMA	74	153	231
bPET-3%SSBA/1%TMA	73	160	226
bPET-5%SSBA/1%TMA	56	not detectable	not detectable

6.3.5 Crystallization Behaviors in Branched PET Ionomers

With different amounts of SSBA and TMA, two parameters, the branching degree and ionic interaction strength, were changed to study their influence on the crystallization behaviors of the branched PET ionomers using DSC.

First, the effect of the different branching degree was investigated with a fixed amount of SSBA content (5 mol% SSBA). The crystallization temperature (T_c), determined from the amorphous region of samples of bPET-5%SSBA/yTMA (Figure 6.3

and Table 6.2), showed a tendency to decrease with increased branching degree caused by higher TMA content. An increase in branching alone, with the same amount of end capper, might be expected to shorten the polymer chains, thus accelerating the onset of crystallization from the amorphous state. It has been shown that percent crystallinity decreases with an increase in polymer chain irregularity.¹² Thus, an increase in branching agent, coupled with the very strong ionic holding interactions among polymer chains, weakens the packing ability of the polymer chain arms. When the branching agent was present in sufficient quantity, i.e., bPET-5%SSBA/1%TMA, the ionomers were completely amorphous, optically clear, unable to crystallize.

Secondly, keeping the branching agent (TMA) content unchanged, the relationship between the ionic interaction and the crystallization behavior was also illustrated as the following. Using the uncrystallizable bPET-5%SSBA/1%TMA sample as reference, the amount of SSBA was decreased to 3% and 1%, and their crystallization behaviors were examined using DSC. As discussed above, the strong ionic interaction and high irregularity in bPET-5%SSBA/1%TMA contributed to the poor crystallization capability of the sample. With lower ionic interaction strength in bPET-3%SSBA/1%TMA and bPET-1%SSBA/1%TMA, the molecular mobility is expected to be relatively higher, which facilitates the chain packing for crystallization. So it is possible to observe certain degree of crystallization in the latter two samples (with 3% and 1% SSBA), and this prediction was confirmed by the DSC results as shown in Figure 6.4. Furthermore, a lower crystallization temperature (T_c) was observed in the bPET-1%SSBA/1%TMA sample than that of bPET-3%SSBA/1%TMA, which suggests a relatively easier crystallization process. Again, this result can be explained with the same argument as discussed above.

Additionally, a tendency of increasing melting temperatures (T_m), which reflects better packed crystalline structures (for polymers with similar backbones), was observed for the PET ionomers with either decreasing branch degrees (lower TMA contents,

¹² Jaykannan, M.; Ramakrishnan, S. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 309

Figure 6.3 and Table 6.3) or decreasing ionic interactions (lower SSBA contents, Figure 6.4 and Table 6.3). This is consistent with the change of the crystallization temperatures with the different ionomer chemical structures, and can be explained in a similar manner as before.

6.4 Conclusions

Novel telechelic branched PEI and PET ionomers were synthesized and characterized. NMR results confirmed the presence of polymer chains and SSBA end groups, but the branching agent, TMA, could not be detected by NMR because of the extremely low concentration. All of the samples showed the characteristic behavior of ionomers in solution. The results indicated that once the branching agent was introduced, glass transition temperatures, crystallinity, crystallization and melting temperatures, and solution viscosity were all affected. It was also visually observed that all of the branched ionic polyesters showed much higher melt viscosity and melt strength than the corresponding linear telechelic polyester ionomers.

CHAPTER 7. PREPARATION AND CHARACTERIZATION OF PET IONOMER/ZINC STEARATE BLENDS

7.1 Introduction

In order to enhance the processibility of a PET ionomer, a plasticizer is often introduced. Other additives, however, have the potential to weaken or disassociate the ionic interactions at melt processing temperatures, thus interfering with network formation. They would, however, allow re-establishment of the ionic interactions at application temperatures.¹

Conventionally, the addition of a plasticizer has been considered as a means of increasing the free volume available to the polymer segments, thereby lowering both the glass transition temperature and the melt viscosity of the polymer. Lundberg *et al.*² showed that there are two fundamentally different types of plasticizers that can be used to plasticize ionomers: those that uniformly increase the free volume of the backbone (“backbone plasticizers”), and those that act selectively to diminish the interchain association of the ionic groups on the polymer chain (“ionic plasticizer”). However, ionic plasticizers have been shown to be more effective in lowering melt viscosity than the “backbone” variety. It is possible to selectively plasticize either the ion-rich phase or the nonpolar hydrocarbon phase of sulfonated polystyrene (SPS) ionomers.

Much work has been done on the effect of conventional plasticizers. Recently, Wiss *et al.* examined the plasticization of dioctyl phthalate (DOP) and glycerol in sodium-neutralized sulfonated polyesters using dynamic mechanical analysis. They reported that DOP lowered the T_g of the backbone polymer and shifted the entire modulus versus temperature curve to lower temperature ranges, which is typical of a

¹ Duvdevani, I.; Lundberg, R. D.; Wood-lordova; Wilkes, G. L., in *Columbic Interactions in Macromolecular System*, A. Eisenberg, A. Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1986, p, 184

² Lundberg, R. D.; Makowski, H. S.; Westerman, M. L. *Ions in Polymers*, A. Eisenberg, A. Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980, Chap. 5

conventional plasticizer. The glycerol, on the other hand, substantially decreased the softening temperature while having little or no effect on T_g . The DMA curves also indicated that the rubbery plateau and the high temperature loss peak disappeared with glycerol addition.³ These results clearly support the preferential plasticization of the two phases of an ionomeric reaction by polar and nonpolar diluents, as suggested earlier by Lundberg.² Bagrodia et al. have also studied the effect of plasticizers on the rheological behavior of ionomers.^{4, 5} Tong and Bazuin reported the plasticization of a poly(ethyl acrylate) ionomer by an alkyl aniline.⁶

One convenient way of shielding the ionic interaction is by using a polar additive that is highly crystalline in nature, such as stearate. Agarwal *et al.*⁷ proposed that zinc stearate above its melting point solvates or “dissolves” the ionic interactions, permitting the flow of polymer segments at high temperature. Makowski et al. have shown that ionomers based on sulfonated ethylene-propylene-diene monomers (EPDM) containing zinc cations exhibited much lower melt viscosity than ionomers containing other cations such as Mg^{2+} , Ca^{2+} .⁸ The addition of zinc stearate lowers the melt viscosity of a Zn-SEPDM and polypropylene (PP) blend.⁹ Wilkes *et al.* prepared segmented thermoplastic ionene cationomers by reacting PTMO oligomers with various benzyl dihalide compounds. Melt rheology and solid state morphology studies clearly showed that zinc stearate was an effective ionic plasticizer for these different ionomers by lowering the softening temperatures from 180°C to 120°C, thereby permitting melt processability.¹⁰ In the work of De and coworkers,^{11, 12} blends of maleated ethylene-propylene-diene

³ Fitzgerald, J. J.; Kim, D.; Weiss, R. A. *J. Polym. Sci. Polym. Lett. Ed.* **1986**, 24, 263

² Lundberg, R. D.; Makowski, H. S.; Westerman, M. L. Ions in Polymers, A. Eisenberg, A. Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980, Chap. 5

⁴ Bagrodia, S.; Pisipati, R.; Wilkes, G. L.; Story, R. F.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1984**, 29, 3065

⁵ Bagrodia, S.; Wilkes, G. L.; Story, R. F.; Kennedy, J. P. *Polym. Eng. Sci.* **1986**, 26, 662

⁶ Tong, X.; Bazuin, C. G. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, 30, 389

⁷ Agarwal, P. K.; Makowski, H. S.; Lundberg, R. D. *Macromolecules* **1980**, 13, 1679

⁸ Makowski, H. S.; Lundberg, R. D.; Westerman, M. L. Ions in Polymers, A. Eisenberg, A. Ed., Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980, Chap. 1

⁹ Lundberg, R. D.; Duvdevani, I.; Piffer, D. G.; Agarwal, P. K.; in Kohudic MA, editor. Advances in polymer blends and alloys technology, Vol. 1. Lancaster: Technomic Publishing Co. Inc., 1988

¹⁰ Venkateshwaren, K.; Leir, C. E.; Wilkes, G. L. *J. Appl. Polym. Sci.* **1991**, 43, 951

¹¹ Antony, P.; De, S. K. *Polymer* **1999**, 40, 1487

¹² Datta, S.; De, S. K.; Kontos, E. G.; Wefer, J. M. *J. Appl. Polym. Sci.* **1996**, 61, 177

monomers (mEPDM) and maleated high density polyethylene (mHDPE) were synthesized. The addition of zinc stearate decreased the melt viscosity and increased tensile strength of the ionic polyblend. FTIR studies confirmed the existence of interionic interaction exist between the zinc stearate and the ionomer blend. In this chapter, some preliminary studies concerning the effect of zinc stearate on telechelic PET ionomers will be reported.

7.2 Experimental

7.2.1. Materials

All reagents were used without further purification. Ethylene glycol and 3-sulfobenzoic acid, sodium salt (SSBA, 97 %) were generously donated by the Eastman Chemical Co. Zinc stearate (ACS reagent grade, 99 %), dimethyl terephthalate, sodium acetate (ACS reagent grade, 99.5 + %), and 1-dodecanol were purchased from the Aldrich, as were phosphoric acid (crystals, 98 %), cobalt acetate (99 %), antimony (III) oxide (99 %), manganese acetate (99 %) and titanium isopropoxide, which were all used directly.

7.2.2 Preparation of Catalyst Solution

Sb catalyst: Sb_2O_3 (3.00 g) solid was dissolved in 250 mL ethylene glycol (EG). The mixture was heated at 100 °C and stirred for 24 hours under nitrogen purge. The mixture was then filtered and a clear solution was obtained at a concentration of 0.012 g / mL based on Sb.

Mn catalyst: $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (2.685 g) and pure HOAc (1.319 g) were added to 125 mL of EG and heated to render a catalyst solution at a concentration of 0.0215 g / mL based on Mn.

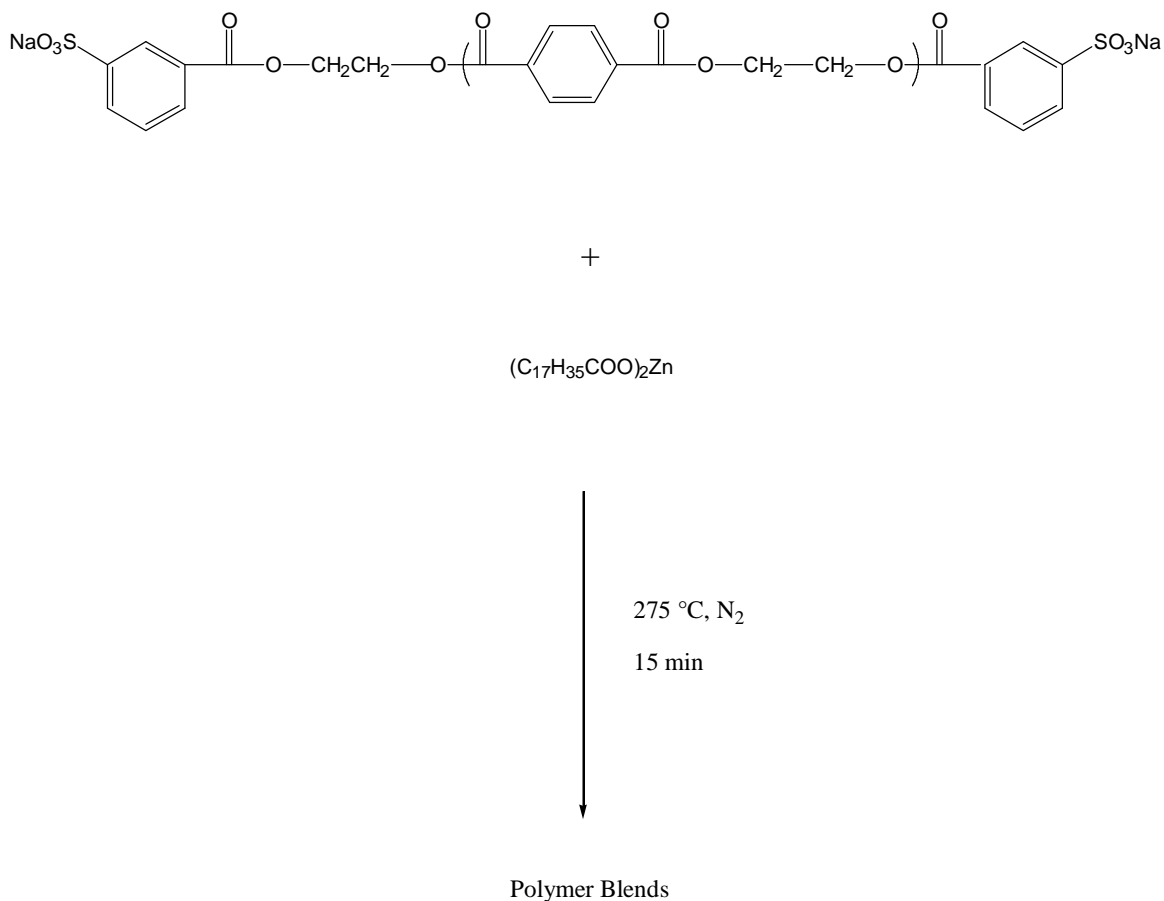
Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g) with 62.5 mL of n-BuOH in a dry bottle under nitrogen at a concentration of 0.055 g / mL based on Ti.

Co catalyst: Cobalt acetate (2.025 g) was mixed with ethylene glycol (125 mL) to obtain a catalyst solution with a concentration of 0.02 g / mol based on Co.

P catalyst: Phosphoric acid (99 %, 3.48 g) was dissolved in n-BuOH (12.5 g, 15.43 mL) and then mixed with ethylene glycol (125 mL) to obtain a catalyst with a concentration of 0.025 g / mol based on P.

7.2.3 Preparation of Blends(PET-SSBA-Zn) of Sulfonate Terminated Semi-crystalline Polyester Ionomers with Zinc Stearate

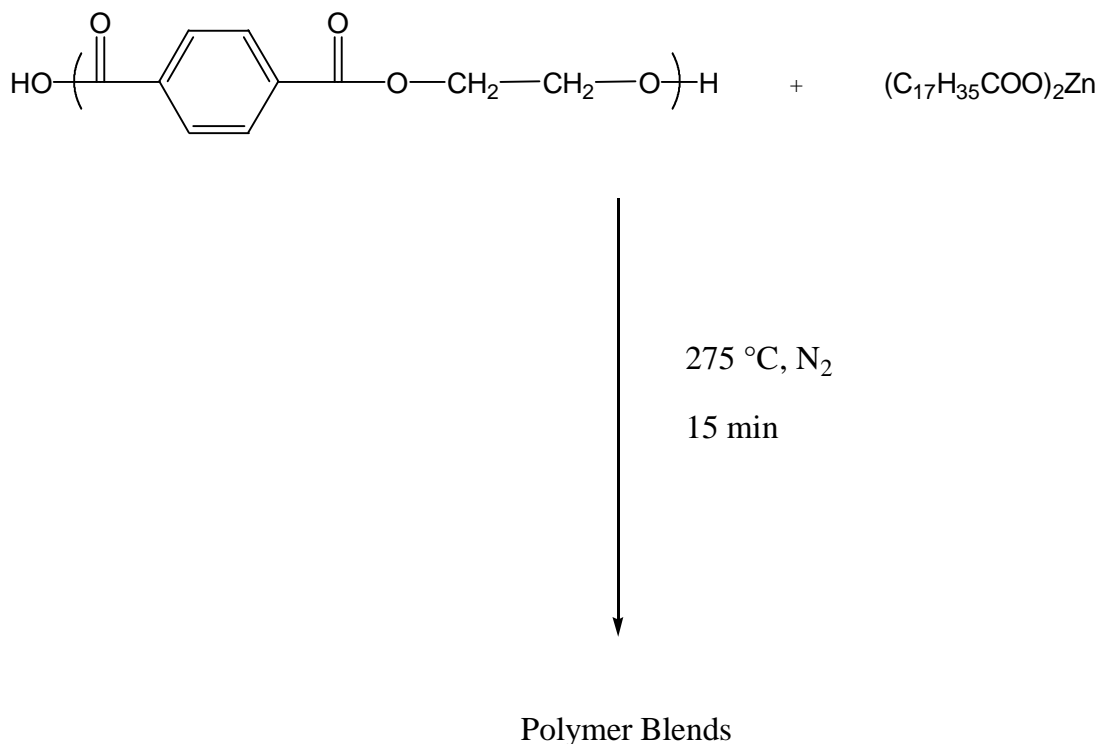
Telechelic PET ionomers (with 5 mol % SSBA) were synthesized as described in Chapter 5. Varying mole percentages of zinc stearate (0.1, 0.3, 0.5, 1 mol % compared to DMT) were added to 250 mL round bottom flasks at 275 °C under nitrogen (Scheme 7.1). After all the materials had melted, they were stirred for 15 minutes. The resulting products were isolated by breaking the flasks. Further purification was not necessary.



Scheme 7.1. Polymer blend of PET-5%SSBA with zinc stearate,
275°C, melt state, N_2

7.2.4 Preparation of Non-terminated PET Blends with Zinc Stearate

Non-terminated PET samples were synthesized as previously described in Chapter 5. Varying amounts of zinc stearate (the same amounts as used in the PET ionomer/zinc stearate blends) and non-terminated PET (I. V. = 0.744) were added to 250 ml round bottom flasks at 275°C under nitrogen (Scheme 7.2). After the materials had melted, they were stirred for 15 minutes. The final products were isolated by breaking the flasks. No further purification was necessary.



Scheme 7.2. Polymer blend of non-terminated PET with zinc stearate, 275°C , N_2

7.2.5 Polymer Characterization

A 400 MHz NMR (Varian-400) was used to characterize blended PET-SSBA-Zn ionomers. The solvent of choice was $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (2:1, v/v). Melt rheology behavior was analyzed using a melt rheometer (TA Instruments, Advanced Rheometer AR 1000). DSC (Perkin Elmer, Pyris 1) was used to investigate glass transition temperature and crystallization processes. All the samples were kept at $290\text{ }^\circ\text{C}$ for 3 min to eliminate any thermal history, quenched from $290\text{ }^\circ\text{C}$ to room temperature at a rate of $200\text{ }^\circ\text{C}/\text{min}$, and finally ramped to $290\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$. All DSC experiments were performed under nitrogen and the data of second scan was collected. All DSC results were from the second heat. TGA (Thermal Analyst 2100, Du Pont Instruments) was used to study the thermal stability of the polymer blends under nitrogen with the heating rate at $10\text{ }^\circ\text{C}/\text{min}$.

7.3 Results and Discussion

All of the samples were opaque. It was observed that the melt viscosity of the blends during mixing was much lower than that of original PET-SSBA ionomers, while the color of the samples changed from white to brownish at solid state.

7.3.1 NMR Analysis

NMR was used to characterize the composition of PET-SSBA-Zn polymer blends (Figure 7.1). Samples were dissolved in $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (2:1, v/v) at room temperature. Aryl hydrogens of polymer backbone were identified at 8.2 ppm (4H, *s*), while aliphatic hydrogens of ethylene glycol on the backbone were identified at 8.5 ppm (4H, *s*). SSBA end groups were observed at 8.65 ppm (1H, *d*), 8.2 ppm (2H, *m*) and 7.7 ppm (1H, *t*). Zinc stearate, however, was not observed in the spectrum because of the extremely low concentration. The NMR spectrum was quite similar to that of the originally charged ionomers.

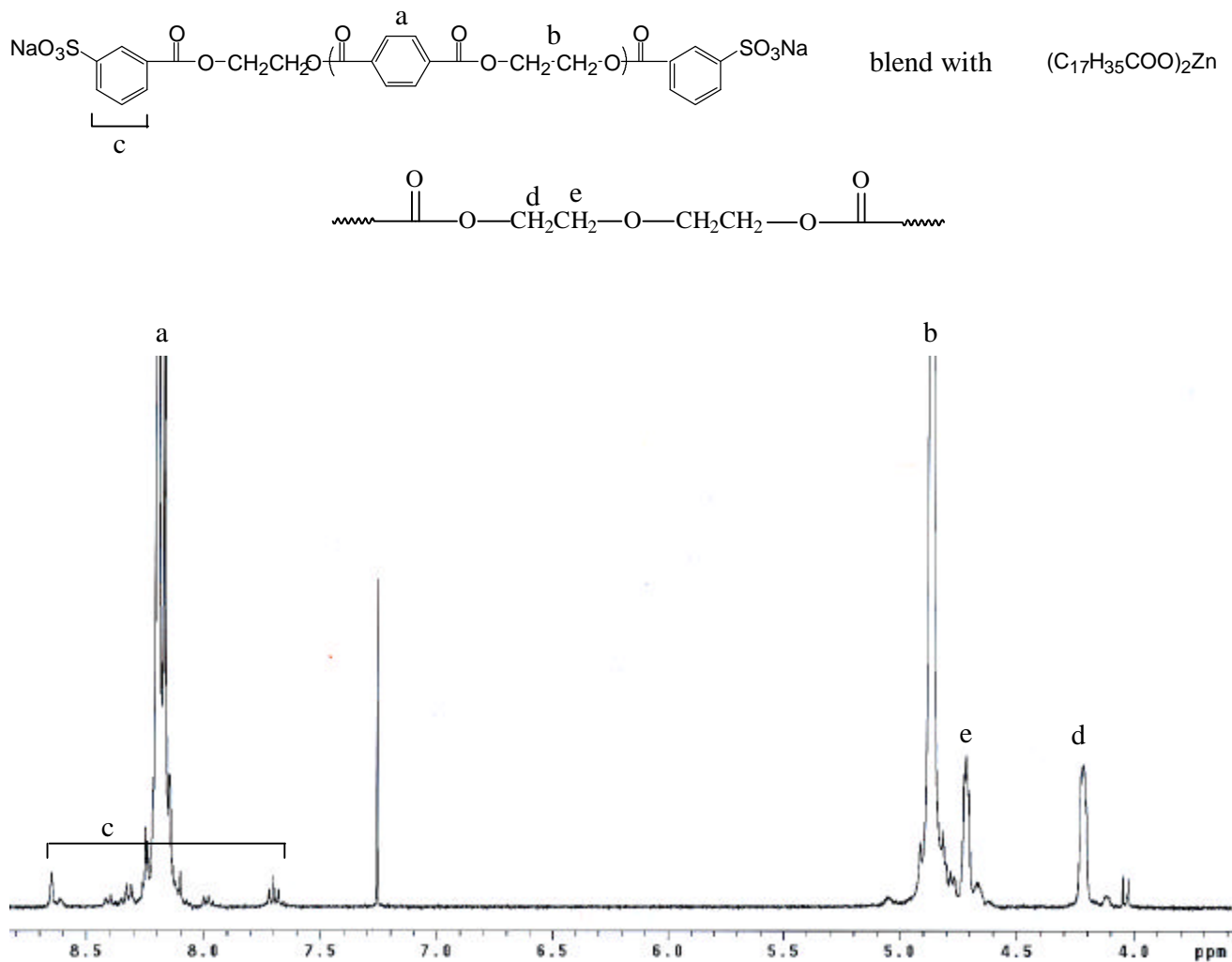


Figure 7.1. ^1H NMR spectrum of PET-5%SSBA blended with 0.1 mol % zinc stearate, $\text{CF}_3\text{COOD}/\text{CDCl}_3$, 2:1, v/v, room temperature

7.3.2 TGA Analysis

TGA was used to study the thermal stability of zinc stearate (Figure 7.2). From TGA results, it turned out that at lower temperatures (e.g., $<180\text{ }^\circ\text{C}$), zinc stearate is quite stable. However, when the temperature was increased to about $270\text{ }^\circ\text{C}$ (approximate melting point of a PET ionomer), the TGA curve dropped, indicating that a significant decrease in zinc stearate by weight began to occur. From this data, it can be inferred that zinc stearate is not particularly stable at blending temperatures, especially over longer

periods. The drop around 100 °C in the TGA data (Figure 7.2) was believed due to moisture loss.

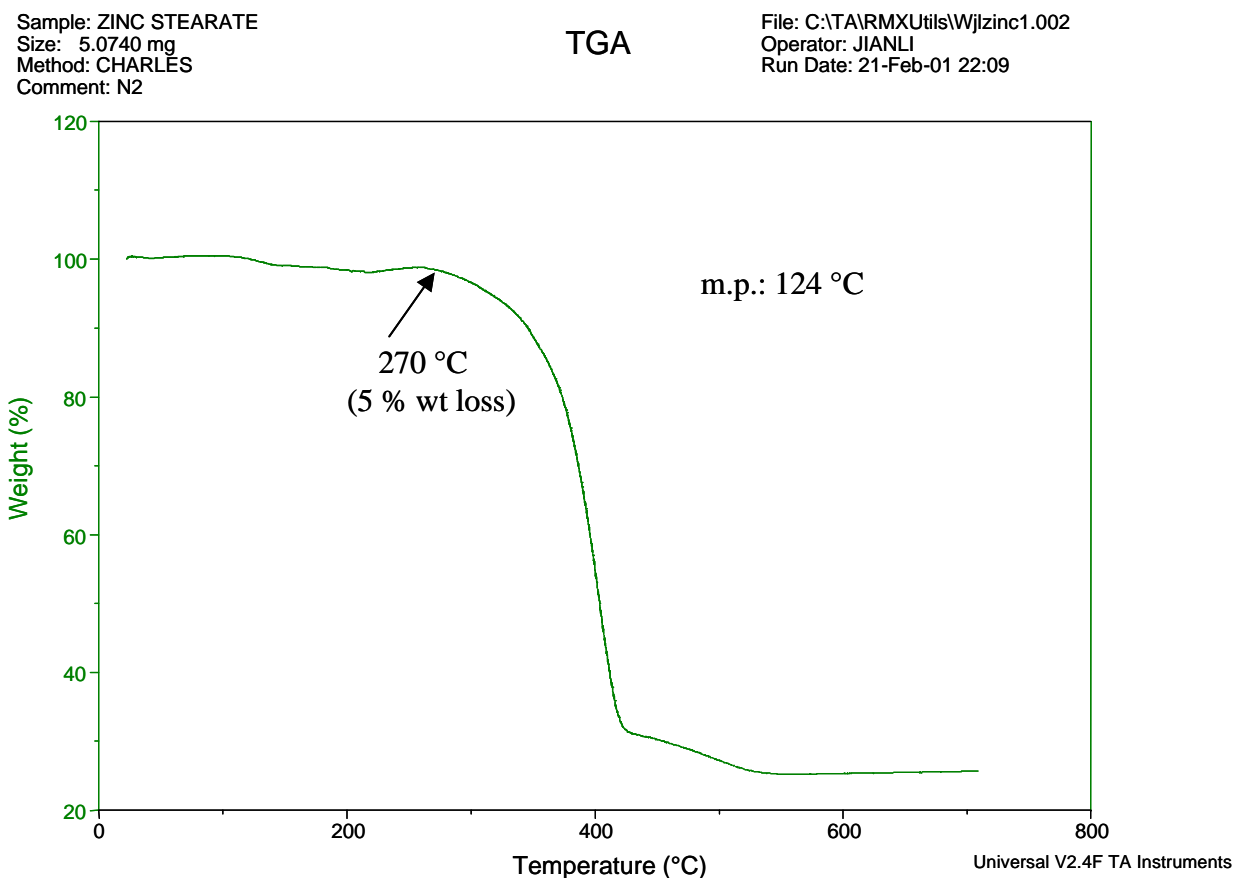


Figure 7.2. TGA graph of zinc stearate under nitrogen, heating rate: 10 °C/min

7.3.3 DSC Analysis

Figure 7.3 and Table 7.1 depicts the effect of zinc stearate incorporation on the glass transition temperature, crystallization temperature and melting transitions of various PET-5%SSBA with differing amounts of zinc stearate. All samples were scanned in a temperature range between 30 to 290 °C at a rate of 10 °C/min. Observable curves represent the second heating. According to the literature, for amorphous thermoplastic ionomers, the glass transition temperature of ionomer/zinc stearate blends is generally not affected by the addition of zinc stearate.¹⁰ Based on our DSC results, however, the glass

¹⁰ Venkateshwaren, K.; Leir, C. E.; Wilkes, G. L. *J Appl. Polym. Sci.* **1991**, 43, 951

transition temperature decreased with the increasing additions of zinc stearate. This phenomenon could be attributed to the fact that (1) a PET ionomer is a semicrystalline polymer, or (2) zinc stearate had already begun to decompose at blending temperatures, or (3) the PET ionomers degraded to lower molecular weight oligomers. A considerable depression of the crystallization peak temperature (T_c) and, with the higher of zinc stearate, in the onset temperature of melting of the polymer blends was observed. Furthermore, the melting peak broadened and melt viscosity decreased with an increase of zinc stearate. This is due to the fact that upon melting, zinc stearate shields the ionic interactions, resulting in a significant reduction in the melt viscosity of ionomers. Upon cooling, due to the strong tendency for zinc stearate to recrystallize below the melting point, there is impetus for the zinc stearate to migrate out of the ionic domains. This enables reformation of the ionic interactions, which results in the re-establishment of an ionic network.^{13, 14, 15, 16, 17, 18, 19, 20}

Non-terminated PET blended with varying amounts of zinc stearate were also synthesized in order to compare these materials with ionic PET/zinc stearate blends. The color of blends changed to brown. Results in Figure 7. 4 and Table 7.2 indicate that the addition of zinc stearate had very little effect on glass transition temperature, crystallization temperature, or melting point. This is attributed to the fact that because there was no ionic interaction in the polymer system, the usual shielding effect of zinc stearate on ionic aggregation did not occur.

¹³ Ghosh, S. K.; Bhattacharya, A. K.; De, P. P. *Plast. Rubber Compos.* **2001**, 30, 16

¹⁴ Ghosh, S. K.; De, P. P.; Khastgir, D. *J. Appl. Polym. Sci.* **2000**, 78, 743

¹⁵ Ghosh, S. K.; De, P. P.; Khastgir, D. *J. Appl. Polym. Sci.* **2000**, 78, 326

¹⁶ Ishioka, T.; Maeda, K.; Watanabe, I. *Spectrochim. Acta A* **2000**, 56, 1731

¹⁷ Jackson, D. A.; Kobertein, J. T.; Weiss, R. A. *J. Appl. Polym. Sci. Phys.* **1999**, 37, 3141

¹⁸ Kurian, T.; De, P. P.; Tripathy, D. K. *Kaut. Gummi. Kunstst* **1996**, 49, 755

¹⁹ Mandal, U. K.; Tripathy, D. K.; De, S. K. *Polym. Eng. Sci.* **1996**, 36, 283

²⁰ Xie, H. Q.; Ao, Z. P.; Guo, J. S. *J. Macromol. Sci. Phys.* **1995**, B34, 249

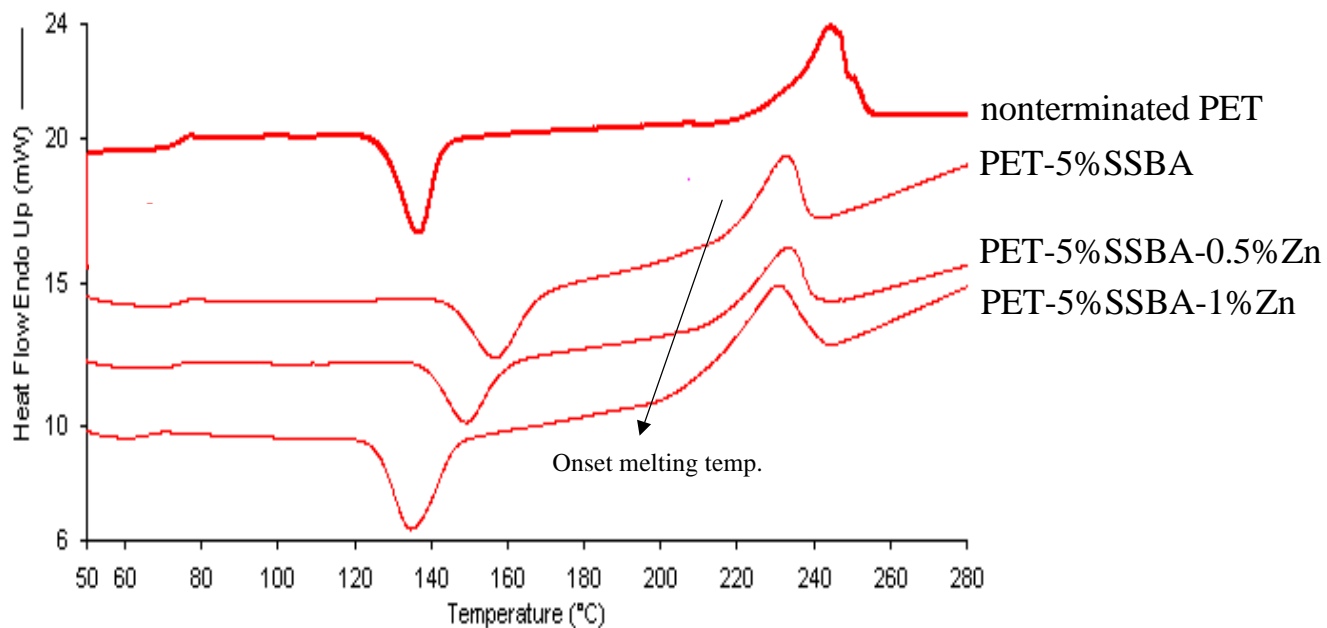


Figure 7.3. DSC curves of PET-5%SSBA and zinc stearate (0.5 mol % and 1 mol % compared to DMT) blends, under nitrogen, second heat, heating rate: 10°C/min

Table 7.1. DSC results of PET-5%SSBA and zinc stearate blends (zinc stearate: 0.1, 0.2, 0.3, 0.5, 1 and 5 mol % compared to DMT), under nitrogen, heating rate is 10°C/min

Polymer Blends (PET-5%SSBA-Zn Stearate)	T_g (°C)	T_c (°C)	T_m (°C, peak value)	T_m (°C, onset value)
PET- 5%SSBA-0% Zn	75	157	232	212
PET- 5%SSBA-0.1% Zn	73	149	233	208
PET- 5%SSBA-0.5% Zn	70	142	232	200
PET- 5%SSBA-1% Zn	66	135	230	192
PET- 5%SSBA-5% Zn	55	122	232	185

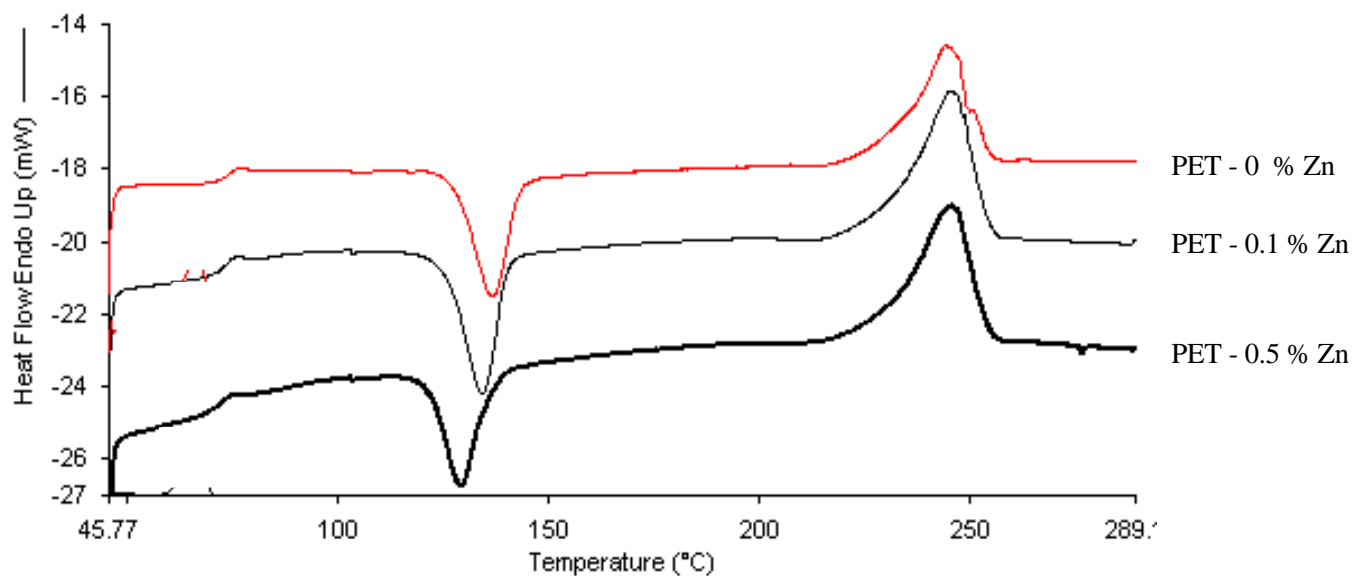


Figure 7.4. DSC curves of non-terminated PET and zinc stearate blends, under nitrogen, second heat, heating rate: 10 °C/min

Table 7.2. DSC results of non-terminated PET and zinc stearate blends (zinc stearate: 0.1, 0.5, 1 mol % compared to SSBA), under nitrogen, heating rate is 10 °C/min

Polymer Blends (PET-Zn Stearate)	T_g (°C)	T_c (°C)	T_m (°C, peak value)	T_m (°C, onset value)
PET-0% Zn	74	137	245	220
PET- 0.1% Zn	73	133	245	219
PET- 0.5% Zn	72	130	245	220
PET- 1% Zn	70	125	243	218

7.4 Conclusions

Ionic and non-ionic PET blends with zinc stearate were synthesized at 275°C under nitrogen for 15 minutes, during which the color of the sample changed from white to brownish. For the non-terminated PETs blended with zinc stearate, the onset crystallization temperature (softening temperature) did not change. On the other hand, when the ionic PET was blended with zinc stearate, the softening temperature decreased with increasing additions of zinc stearate. This may be due to the fact that zinc stearate destabilizes the ionic aggregates at melt processing temperatures, that are responsible for network formation, but allows re-establishment of ionic interactions at normal use temperatures. Thus, zinc stearate was found to be an effective ionic plasticizer in these ionomers by lowering the softening temperatures, thereby facilitating melt processing.

However, in our ionomer blending samples, the blending temperature was 275°C, which corresponds to the onset temperature of degradation of zinc stearate, according to TGA curves. Thus, the observed decrease in glass transition temperature for all the blending samples might be due to the degradation of zinc stearate. Further studies are needed to clarify this issue.

CHAPTER 8. DSC STUDY OF CRYSTALLIZATION BEHAVIOR OF SEMI-CRYSTALLINE POLYESTERS

8.1 Introduction

Poly(ethylene terephthalate) (PET) is a well known commercial polymer manufactured into fibers, films, and containers. The crystallization kinetics of these materials determine the physical end state of the polymer, which in turn influences the physical properties of the product. PET crystallization has been extensively studied. Thermally induced crystallization of PET results in a spherulitic structure, whose spherulitic radii typically vary from 6-50 μm , depending on crystallization conditions and the specific polymer sample.^{1, 2} The kinetics of PET crystallization is dependent upon many factors. Jackson and Longman³ studied the effects of molecular weight and catalyst residue on the rates of crystallization from the melt of PET and related copolymers. They discovered that for polymers of similar molecular weight, soluble polymerization catalyst systems exhibited lower rates of crystallization than insoluble catalysts. Gunther and Zachmann⁴ investigated the effects of the kind and/or amount of catalyst on the half time of crystallization ($t_{1/2}$) and on the orientation of PET. They found that under the same drawing conditions, increasing the molar mass of the catalyst system increased the degree of orientation. Among all the catalyst systems, the influence of antimony was especially important.^{1, 5, 6, 7} It was also recognized that the selective use of a catalyst system can have a greater impact on the rate and mechanism of crystallization of PET polymers than does molecular weight. Diethylene glycol (DEG), produced in a side reaction during the synthesis of PET, has also been found to affect crystallization kinetics.^{8, 9, 10, 11} Frank and Zachmann⁹ studied samples with DEG

¹ van Antwerpen, F.; van Krevelen, D. W. *J. Polym. Sci. Polym. Phys. Ed.*, **1972**, 10, 2423

² Sawyer, L. C.; Grubb, D. T. In: *Polymer Microscopy*, Chapman Hall, London 1987

³ Jacskon, G. B.; Longman, G. W. *Polymer*, **1969**, 10, 873

⁴ Gunther, B. Zachmann, H. G. *Polymer* **1983**, 24, 1008

⁵ Jabarain, S. A. *J. Appl. Polym. Sci.* **1987**, 34, 97

⁶ Jabarain, S. A. *J. Appl. Polym. Sci.* **1987**, 34, 85

⁷ Lawton, E. L. *Polym. Eng. Sci.* **1985**, 25, 348

⁸ Jabarin, S. A.; Patkar, M. *J. Appl. Polym. Sci.* **1993**, 47, 1749

⁹ Zachmann, H. G.; Frank, W. P. *Progr. Colloid Polym. Sci.* **1977**, 62, 88

¹⁰ Fakirov, S.; Seganov, I.; Schultz, J. M. *J. Appl. Polym. Sci.* **1986**, 32, 3371

¹¹ Fakirov, S. *Polymer* **1980**, 21, 373

contents up to 15 mol %. Their results showed that when crystallizing from the melt, increasing the DEG content increased the half time of crystallization, indicating a decrease in the rate of crystallization. These differences are also associated with the concurrent decrease of T_m and T_g , while at the same time increasing DEG concentration, as was confirmed by Farikov et al.¹⁰⁻¹¹ Much research has been done on increasing the crystallization rate of PET through the addition of nucleating agents and nucleating promoter additives in order to enhance its industrial applications, particularly as injection molding compounds.^{12, 13, 14, 15, 16, 17}

Polymer crystallization can be studied by a variety of methods, including dilatometry, calorimetry, x-ray diffraction, microscopy, light scattering, depolarized light intensity, and others as discussed by Price.¹⁸ The enthalpy involved during crystallization is readily measured by a differential scanning calorimeter (DSC). Isothermal crystallization measurements by DSC have been shown to be applicable and useful for studying the crystallization behavior of polymeric materials, since they are relatively easy to analyze and apply to theoretical models.

As to the novel telechelic PET ionomers synthesized in this research, it will be quite interesting to study the effects of ionic interaction on the rate of crystallization. The existence of ionic interactions and/or aggregations, which is highly temperature dependent, is expected to restrict polymer chain mobility. As is already well known, this factor can hinder a polymer chain from efficiently packing into an ordered state at a temperature within the crystallization window ($T_g < T < T_m$). However, the ionic aggregations themselves may also serve as nucleating agents, which in turn increase the rate of crystallization. Thus, this chapter explores the overall effects of ionic interaction,

¹² Jackson, J. B.; Longman, G. W. *Polymer*, **1968**, 10, 873

¹³ Toray, Industries Inc., JP 8214643, 1982, Jan. 25

¹⁴ Legras, R.; Biebuyck, J.; Meicier, J. P. USP 4393178, 1983, July 12

¹⁵ Wilders; Ray, C. EP 0388518, 1990, Sept. 26

¹⁶ Wang, X.; Zhu, H. S.; Bu, S. H. *Acta Polymerica* **1995**, 46, 163

¹⁷ Ye, M.; Wang, X., Huang, W.; Hu, J.; Bu, H. *J. Therm. Anal.* **1996**, 46, 905

¹⁸ Price, F. P. *Encyclo. Polym. Technol.* 1968, 8, 63

molecular weight, and antimony catalyst on the crystallization behaviors of PET ionomers.

8.2 Experimental

8.2.1 Materials

Ionic and non-ionic PET samples were prepared as previously discussed (Chapter IV). The following samples were used to study crystallization behavior:

- a) Ionic PET 1 (PET-SSBA-1): 1: 2: 5%SSBA, catalyst: Ti/Mn
- b) Ionic PET 2 (PET-SSBA-2): 1: 2: 5%SSBA, catalyst: Ti/Mn/Sb
- c) Ionic PET 3 (PET-SSBA-3): 1: 2: 5%SSBA, catalyst: Ti/Mn/Sb/Co/P
- d) Non-ionic PET 1 (PET-Dode-OH-1): 1: 2: 10% Dodecanol, catalyst: Ti/Mn
- e) Non-ionic PET 2 (PET-Dode-OH-2): 1: 2: 10% Dodecanol, catalyst: Ti/Mn/Sb
- f) Non-ionic PET 3 (PET-Dode-OH-3): 1: 2: 10% Dodecanol, catalyst: Ti/Mn/Sb/Co/P
- g) Non-ionic PET 4 (PET- Dode-OH-4): 1: 2: 15% Dodecanol, catalyst: Ti/Mn/Sb/Co/P

8.2.2 Polymer Characterization

A 400 MHz NMR (Varian-400) was used to characterize all PET samples. The solvent of choice was $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (2:1, v/v) at room temperature. FTIR spectra were collected on an infrared spectrometer (Perkin Elmer, 283B) to detect the presence of sulfonated end groups. Gel permeation chromatography (GPC) was performed to obtain the molecular weights and molecular weight distributions using a Waters 2690 chromatograph equipped with a differential refractive index detector (Viscotek Laser Refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel, using polystyrene standards. The mobile phase was chloroform and data were recorded at 25 °C at a flow rate of 1.0 mL / min.

Melt rheology behavior was analyzed using a melt rheometer (TA Instruments, Advanced Rheometer AR 1000). DSC (Perkin Elmer, Pyris 1) was used to measure glass transition temperatures and investigate isothermal crystallization behaviors. All the samples were maintained at 290 °C for 3 min to eliminate any thermal history, then quenched from 290 °C to room temperature at a programmed rate of 200°C/min, finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen and the data collected were the second scan. TGA (Thermal Analyst 2100, Du Pont Instruments) was used to study the thermal stability of the polymers.

8.2.3 Crystallization Study

DSC (PE, Pyris 1) was used to study the isothermal crystallization behaviors of the PET samples. All samples were dried in a vacuum oven prior to measuring. A typical procedure is described below. A sample (~ 10 mg) was weighed in an aluminum DSC sample pan. The calorimeter was operated with a stream of oxygen-free, dry nitrogen flowing through the chamber throughout the experiment. The sample was heated at a rate of 25 °C/min up to 290 °C and held for 20 minutes. The isothermal crystallization temperature was reached by rapidly cooling the sample (quenching) at 200 °C/min. The sample was then held at that temperature for 45 minutes to reach thermal equilibrium and ensure that the crystallization was complete. The sample was then heated again at 25 °C/min to 290 °C and held for an additional 20 minutes, then quenched to another isothermal crystallization temperature for 45 minutes to complete the crystallizing process. The entire procedure was repeated for a series of isothermal crystallization temperatures and crystallization peaks at the different crystallization temperatures were collected. A crystallization window for a PET sample can be constructed by plotting the half-time of crystallization vs. temperature.

8.3 Results and Discussion

8.3.1 Isothermal Study of PET with Dodecanol Terminated and Telechelic Sulfonate Terminated PET Ionomers by DSC

Figure 8.1 shows representative isothermal DSC curves of PET ionomers with 5% SSBA at varying temperatures (more than 20 temperatures were utilized). Each curve represents the entire crystallization process at a specific temperature. The sample temperature was first increased to 290 °C and maintained constant for 20 minutes to ensure the absence of crystallites. The sample was then quenched at 200 °C/min to the temperature of choice and held for 45 minutes to ensure complete the crystallization. A crystallization peak was recorded in this manner at each temperature. All of the curves rendered relatively symmetrical peaks. As seen from these curves, the crystallization exotherm peak narrowed when temperature was increased. Thus, crystallization occurred more rapidly at higher temperatures.

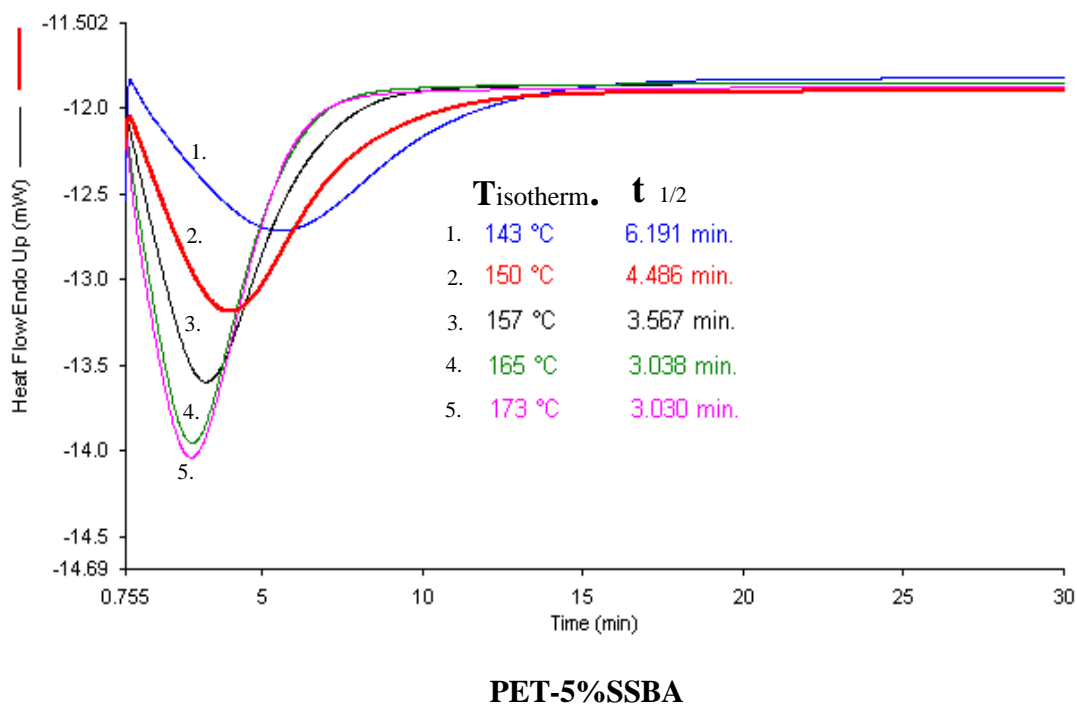


Figure 8.1. Isothermal DSC curves of PET ionomers with 5% SSBA at different temperatures. Half times of the crystallization are also given.

After obtaining the DSC curves of the crystallization peaks, the enthalpy of crystallization (ΔH) was calculated. Once this information was obtained, the time needed to complete half time of crystallization ($t_{1/2}$) was determined using a partial area software program. By comparing $t_{1/2}$, we were able to compare the relative crystallization rates of the polymers. By plotting $t_{1/2}$ vs. temperature, a crystallization window for rapid crystallization of the sample was constructed. Figure 8.2 shows the crystallization window of PET-SSBA-3. From this, we were able to ascertain that at temperatures between $160^{\circ}\text{C} \sim 185^{\circ}\text{C}$, the half time of crystallization was the smallest and remained relatively unchanged. Accordingly, the rate of crystallization occurred most rapidly within this temperature range. However, when the temperature was lower than 160°C or higher than 185°C , the crystallization half time increased, indicating that the rate of crystallization decreased at both lower and higher temperatures. This phenomenon was expected, since a polymer chain does not have sufficient energy to diffuse and organize orderly at lower temperatures (diffusion controlled crystallization rate). Conversely, when temperatures are too high, the crystallization process interferes with the melting process, thus inhibiting the formation of ordered polymer chains (nucleation controlled crystallization rate).

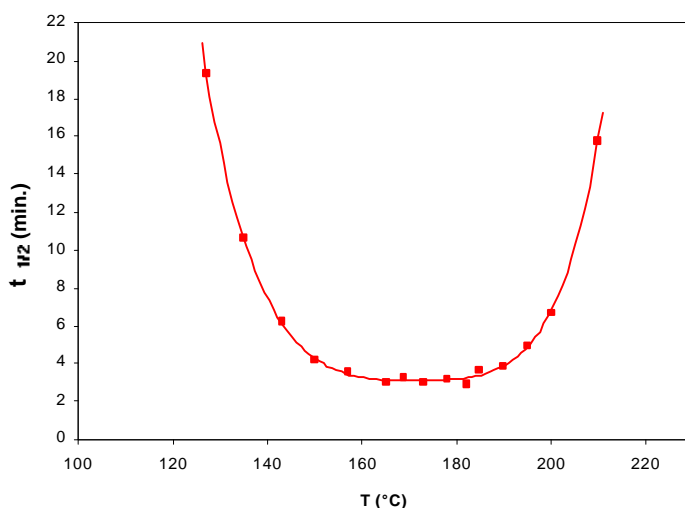


Figure 8.2. Crystallization window of PET-SSBA-3 (5 mol % of SSBA, 5 catalyst system) at different temperatures

8.3.2 Effect of Molecular Weight on Crystallization Behavior

The polymers that we used to study the effect of molecular weight on crystallization behavior were PET-Dode-OH-3 and PET-Dode-OH-4, which have the exactly same structure (except for chain length) and catalyst system (Table 8.1).

Table 8.1. Molecular weight, glass transition temperature and percentage DEG of PET-Dode-OH with 10 mol % and 15 mol % dodecanol

sample number	sample composition (DMT: EG: Dodecanol)	catalysts	M_n (g/mol, GPC)	T_g (°C)	DEG (%)
PET-Dode-OH-3	1: 2: 10%	Ti/Mn/Sb/Co/P	13,300	70	2.6
PET-Dode-OH-4	1: 2: 15%	Ti/Mn/Sb/Co/P	9,100	66	2.7

A crystallization window was easily constructed for the higher molecular weight PET-Dode-OH-3 (Figure 8.3), but not for PET-Dode-OH-4. Isothermal DSC curves of the PET-Dode-OH-4 revealed that the crystallization peaks of this sample were not symmetrical. This is due to the fact that the molecular weight of PET-Dode-OH-4 was much lower than of PET-Dode-OH-3. The crystallization rate of the PET-Dode-OH-4 was so rapid that crystallization occurred during quenching, prior to reaching thermal equilibrium at the specific isothermal temperature (Figure 8.4). In examining the non-isothermal DSC curves of the PET-Dode-OH-4, a similar phenomenon (Figure 8.5) was discovered. During the quenching process, a recrystallization peak appeared at 170 °C, and a very broad glass transition was observed in the second heat. It should also be noted that a crystallization peak was not observed during the second heat. These results indicate that most of the PET-Dode-OH-4 had already crystallized before the second heating process was initiated.

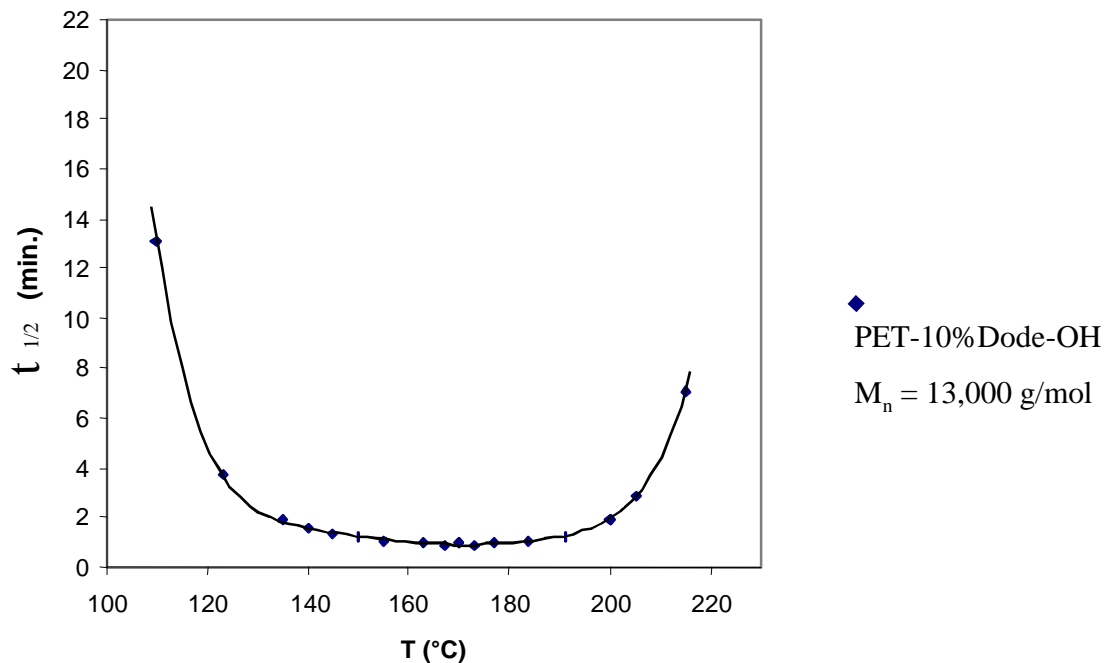


Figure 8.3. Isothermal crystallization window of PET-Dode-OH-3 (10 mol % dodecanol, $M_n = 13,000$ g/mol)

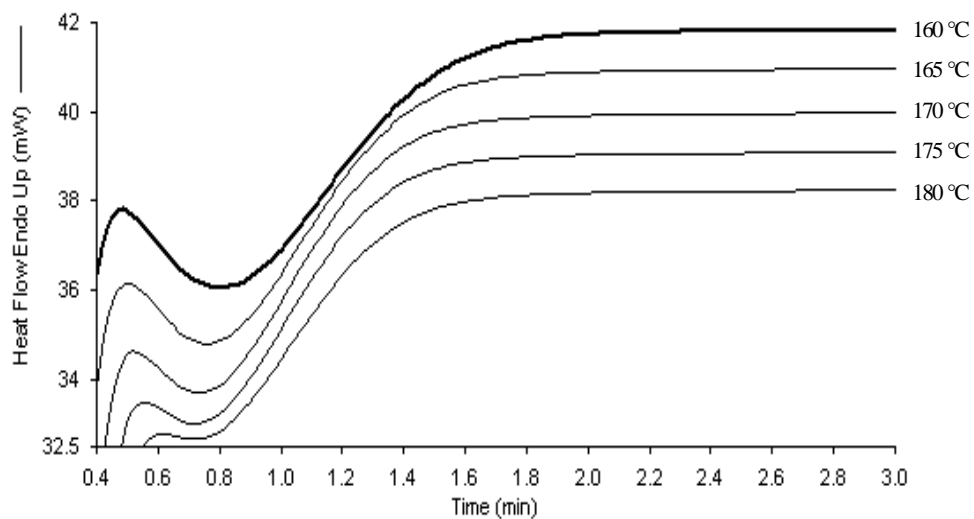


Figure 8.4. Isothermal crystallization curves of PET-Dode-OH-4 (15 mol % dodecanol) at temperatures of 160°C, 165°C, 170°C, 175°C and 180°C

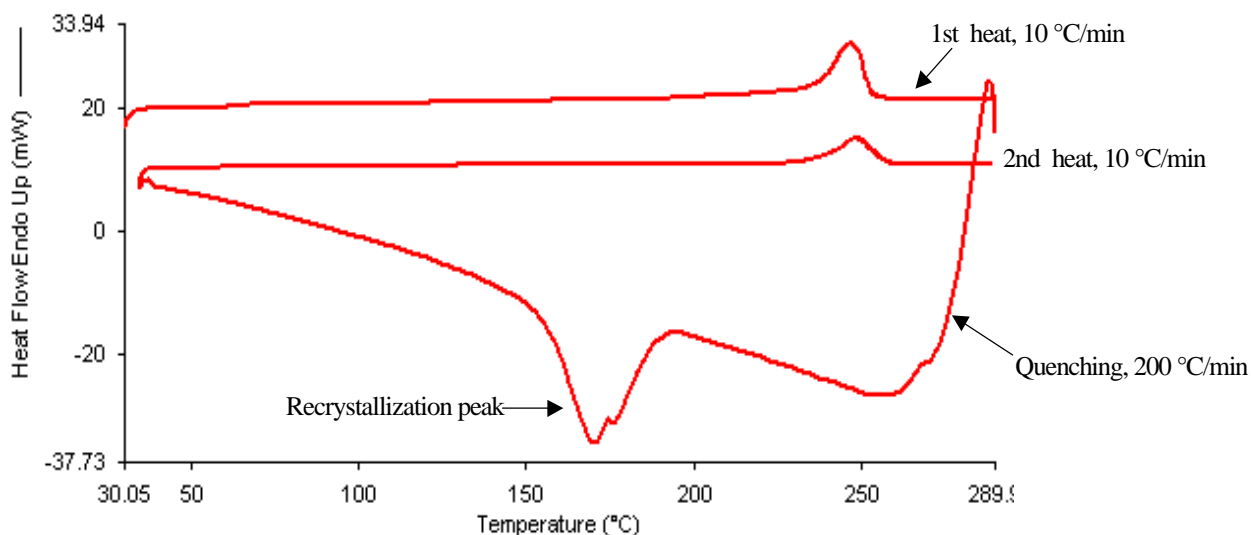


Figure 8.5. Non-isothermal DSC scan of PET-Dode-OH-4, N₂, heating rate is 10 °C/min, quenching rate is 200 °C/min

8.3.3 Effect of Ionic Interaction on Crystallization Behavior

The samples that were used to study the effect of telechelic ionic interaction on crystallization are listed in Table 8.2.

Table 8.2. Composition, molecular weight, solution viscosity and catalyst of sulfonate terminated and dodecanol terminated PET samples

sample number	sample composition (DMT: EG: end group)	catalysts	I. V. (Inherent Viscosity)	DEG (%)
PET-SSBA-3	1: 2: 5% (SSBA)	Ti/Mn/Sb/Co/P	0.354	2.5
PET-Dode-OH-3	1: 2: 10% (Dodecanol)	Ti/Mn/Sb/Co/P	0.556	2.6
PET-Dode-OH-4	1: 2: 15% (Dodecanol)	Ti/Mn/Sb/Co/P	0.342	2.7

Isothermal crystallization experiments by DSC were used to construct crystallization windows for ionic and non-ionic PET samples in order to investigate the

influence of ionic end groups on their crystallization behaviors. As noted previously, we were unable to construct crystallization windows for the molecular weight matched set of sulfonate terminated and dodecanol terminated PETs (PET-SSBA-3 and PET-Dode-OH-4) due to the rapid crystallization rate of the PET-Dode-OH-4. Therefore, we used the higher molecular weight non-ionic PET, PET-Dode-OH-3 ($M_n = 13,000$ g/mol), and compared it with the ionic PET, PET-SSBA-3 ($M_n = 8,000$ g/mol). In Figure 8.6, the crystallization windows of these two PET samples (PET-Dode-OH-3 and PET-SSBA-3) are depicted to illustrate the differences. While both of these samples had exactly the same polymer backbone, the PET-Dode-OH-3 with dodecanol had a much higher molecular weight (10 % dodecanol, $M_n = 13,000$ g/mol) than that of the PET-SSBA-3 (5 mol % SSBA, $M_n = 8,000$ g/mol). Generally, the higher the molecular weight, the slower the rate of crystallization. Our results, however, showed that the crystallization rate of PET-Dode-OH-3 was much faster than that of the ionic PET-SSBA-3. It is believed that the strong ionic interactions restricted the mobility of the polymer chains, which in turn made it more difficult for the chains to re-organize into an ordered state during crystallization.

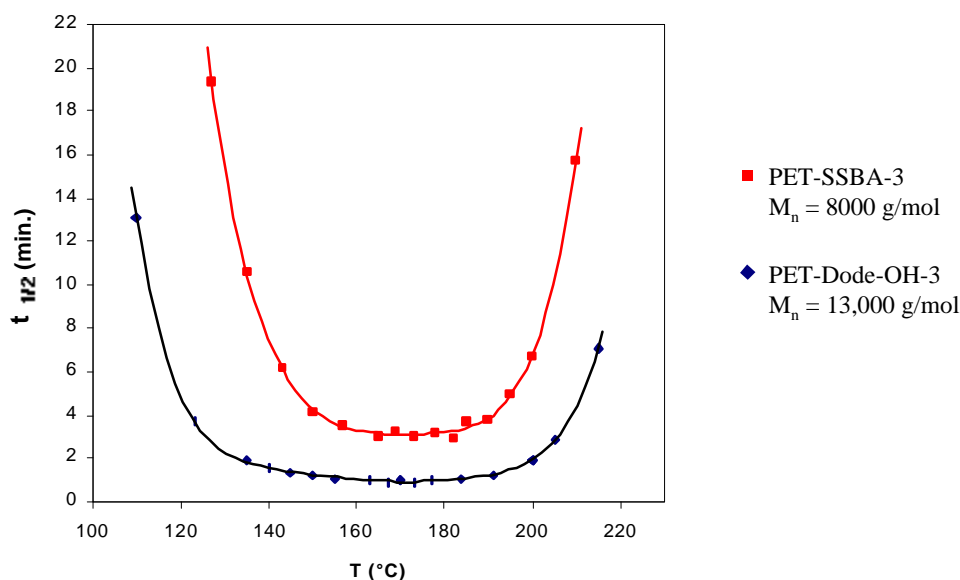


Figure 8.6. Isothermal crystallization windows of PET-SSBA-3 and dodecanol terminated PET (PET-Dode-OH-3), %DEG (PET-SSBA-3) = 5.7%, %DEG (PET-Dode-OH-3) = 2.6%

If the above assumption is correct, then it can be expected that this “ionic interaction slowdown” is temperature dependent, which means that the difference between the crystallization rates of non-ionic and ionic polymers should vary with different temperatures. Figure 8.7 shows a quantitative comparison between the rates for different samples. The crystallization rate ratio between the ionic and non-ionic PET samples is defined as $t_{1/2}$ (5 % SSBA) / $t_{1/2}$ (10 % dodecanol). Because the ratio is larger than 1 throughout the temperature range under consideration (125–220 °C), this indicates that the crystallization rate for the non-ionic PET sample is faster, which substantiates the conclusions drawn from Figure 8.6. Other important information is also revealed in Figure 8.7. At temperatures lower than 150 °C, the crystallization half time ratio of the ionic and non-ionic PET samples was relatively large. However, when the temperature was increased, the ratio became smaller until approximately 150 °C, after which the ratio was relatively constant (about 3). This trend is due to the fact that at lower temperatures, the ionic interactions are relatively strong, thereby slowing the rate of crystallization. At higher temperatures, however, the ionic interactions become weaker and more ionic aggregates dissociate. As a result, the polymer chains of the ionomer have greater mobility and can fold into an ordered state (crystallization) at higher temperatures with less ionic effect; this is reflected by a decreasing ratio value Figure 8.7 (<150 °C). When the temperature was above 150 °C, the dependence of ionic interaction on temperature was very small and, thus, the crystallization half time ratio was constant.

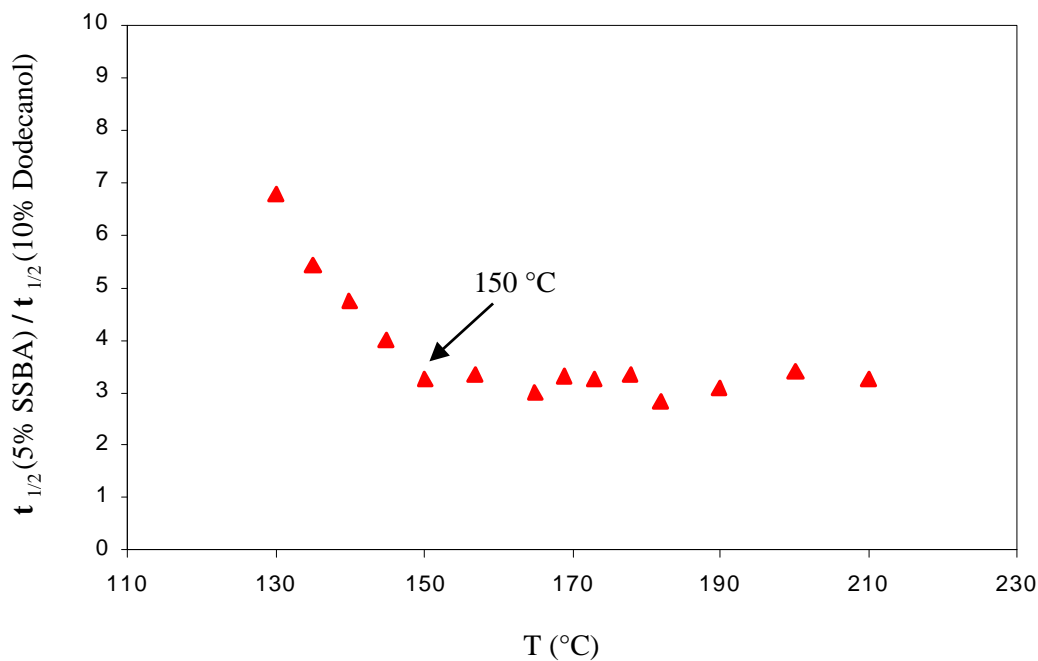


Figure 8.7. Ratio of the crystallization half times of ionic (PET-SSBA-4) and non-ionic (PET-Dode-OH-3) PET as a function of temperature

8.3.4 Effect of Catalyst on Crystallization Behavior

Catalyst residues also have a significant effect on the crystallization process of PET samples, especially with regard to the use of an antimony catalyst. Table 8.3 depicts some relevant data about the dodecanol terminated PETs, (PET-Dode-OH-1 and PET-Dode-OH-2) with and without antimony catalyst. Both of the samples had merely the same molecular weight and the same polymer structure. Table 8.4 provides useful information indicative of the molecular weight of the matched ionic PETs (PET-SSBA-1 and PET-SSBA-2) with and without antimony catalyst.

Table 8.3. Dedecanol terminated PET-Dode-OH (10 % of dodecanol) with and without antimony oxide catalyst

sample number	sample composition (DMT: EG: dodecanol)	catalysts	M _n (g/mol) (GPC)	T _g (°C)
PET-Dode-OH-1	1: 2: 10%	Ti/Mn	13,500	70
PET-Dode-OH-2	1: 2: 10%	Ti/Mn/Sb	13,100	71

Table 8.4. Sulfonate terminated PET-SSBA (5 mol % of SSBA) with and without antimony oxide catalyst

Sample number	sample composition (DMT: EG: SSBA)	catalysts	I. V. (Inherent Viscosity)	T _g (°C)
PET-SSBA-1	1: 2: 5%	Ti/Mn	0.354	77
PET-SSBA-2	1: 2: 5%	Ti/Mn/Sb	0.356	76

Much research has been conducted to study the influence of an antimony catalyst on the crystallization of PET.^{5, 6, 7, 19} This prior work uniformly confirms that the presence of an antimony catalyst residue acts as a nucleating agent to increase the crystallization rate. In fact, this thesis does not include a DSC isothermal study of PET-Dode-OH-1 and PET-Dode-OH-2 because of the well-established work already published. However, from the melt rheology studies that we performed earlier, it is evident that the presence of an antimony catalyst enhanced polymer chain packing and improved its regularity, thus resulting in a higher transition temperature to the melt phase (Figure 8.8).

⁵ Jabrain, S. A. *J. Appl. Polym. Sci.* **1987**, 34, 97

⁶ Jabrain, S. A. *J. Appl. Polym. Sci.* **1987**, 34, 85

⁷ Lawton, E. L. *Polym. Eng. Sci.* **1985**, 25, 348

¹⁹ di Fiore, C. Leone, B.; Guerra, G.; Petraccone, V.; di Dino, G.; Bianchi, R.; Vosa, R. *J. Appl. Polym. Sci.* **1993**, 48, 1997

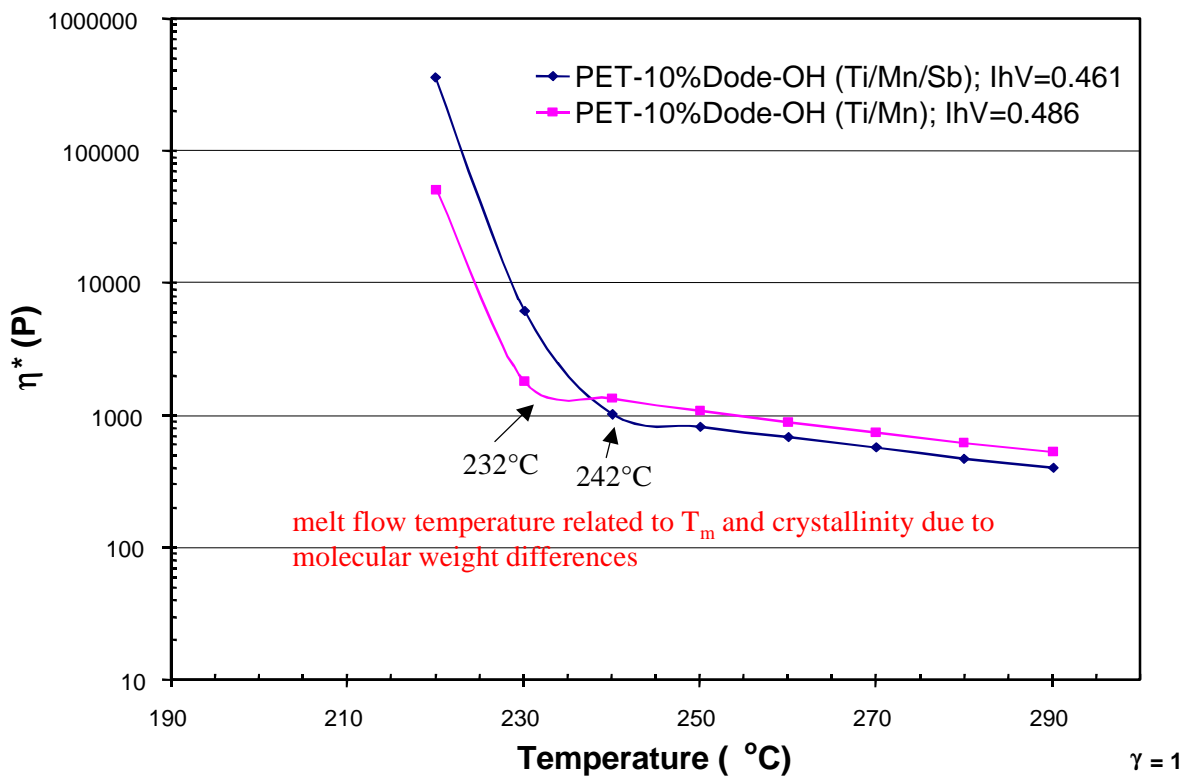


Figure 8.8. Melt rheology of dodecanol terminated PET-Dode-OH-1 (10 % Dodecanol) with and without antimony oxide catalyst, $\gamma=1$ Hz

More importantly, we investigated the isothermal crystallization behavior of ionic PET samples with and without antimony (PET-SSBA-1 and PET-SSBA-2). The isothermal crystallization windows of the two ionomers are shown in Figure 8.9.

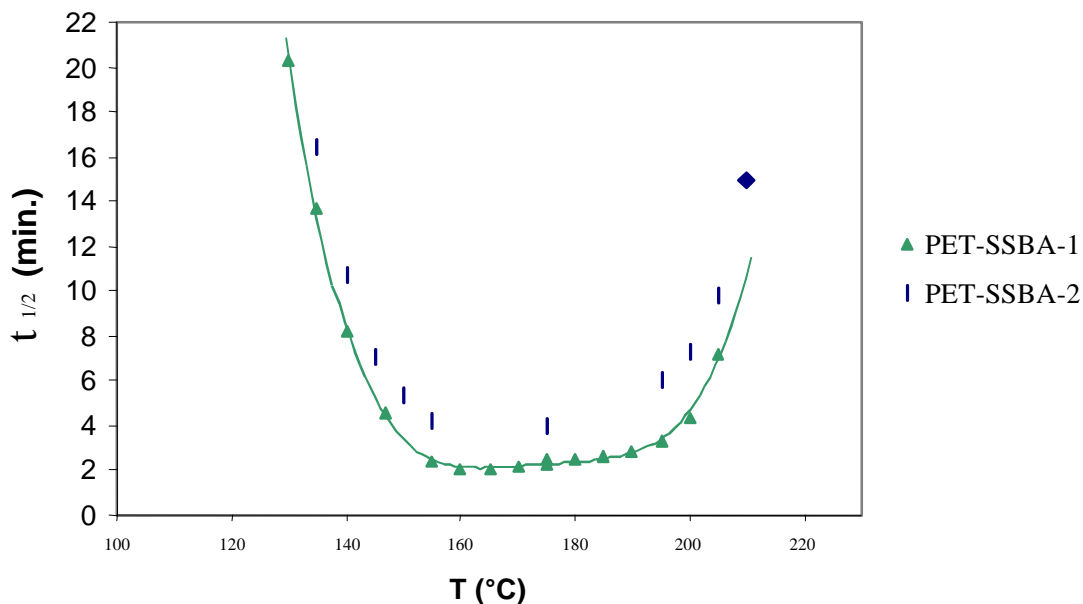


Figure 8.9. Isothermal crystallization windows of PET-SSBA-1 and PET-SSBA-2 with and without antimony oxide catalyst

It was quite evident that the $t_{1/2}$ of PET-SSBA-2 (with antimony) was shorter than that of PET-SSBA-1 (without antimony); indicating that the PET-SSBA-2 had a higher crystallization rate than the PET-SSBA-1 due to the high nucleating activity of the antimony catalyst. Non-isothermal DSC was performed to study the crystallization processes of ionic PET with and without antimony catalyst (Figure 8.10 and Figure 8.11). Figure 8.10 shows the second heat of PET-SSBA-1 and PET-SSBA-2, after cooling rates of 10 °C/min (cooling slowly) and 200 °C/min (quenching). This figure reveals that when both samples were quenched, then exposed to the second heat, the resulting DSC curves were quite similar (Figure 8.10, the bottom two curves). However, if both of the samples were cooled slowly, thus giving them more time to recrystallize, the second heating curves were quite different (Figure 8.10, top two curves). For PET-SSBA-2, which had antimony catalyst in the polymer, the second heat revealed a very broad glass transition temperature, and no crystallization peak was observed. This indicates that during the cooling process, the ionomer completely recrystallized with very little amorphous residue, and thus it was difficult to determine the obvious glass transition and crystallization transition. On the other hand, for the PET-SSBA-1 (which contained no

antimony catalyst), although the cooling process was quite lengthy, a crystallization peak was observed in the second heating curve. This demonstrates that without the presence of an antimony catalyst, the ionomer recrystallized very slowly, i.e., the antimony acted as a nucleating agent to increase the recrystallization of the ionomers.

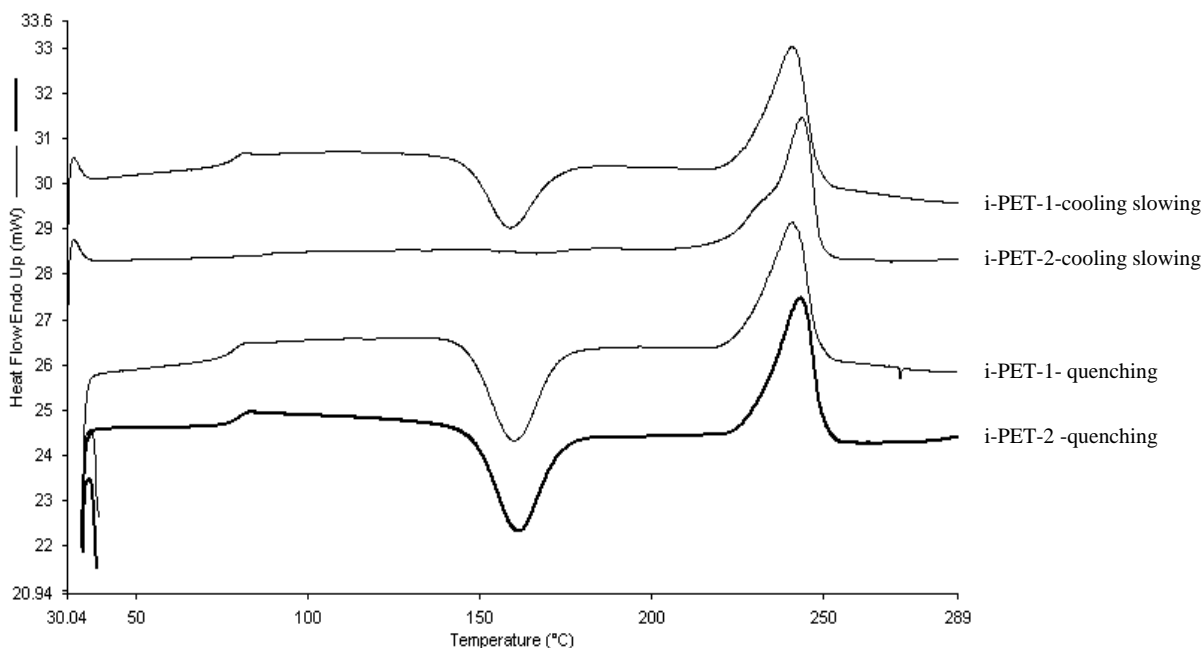


Figure 8.10. DSC curves of PET-SSBA-1 and PET-SSBA-2 with and without antimony catalyst, second heat; heating rate is 10 °C and cooling rates are either 10 °C/min (cooling slowly) or 200 °C/min (quenching), N₂

Figure 8.11 shows the heating and cooling curves of both samples using the same heating/cooling rate of 10 °C/min. It revealed that for the PET-SSBA-1 without antimony, very little recrystallization was observed during the cooling process; while for the PET-SSBA-2 with antimony catalyst, a significant recrystallization peak was observed. These results corroborate the conclusions noted above, namely that the presence of an antimony catalyst assists the polymer chains to recrystallize.

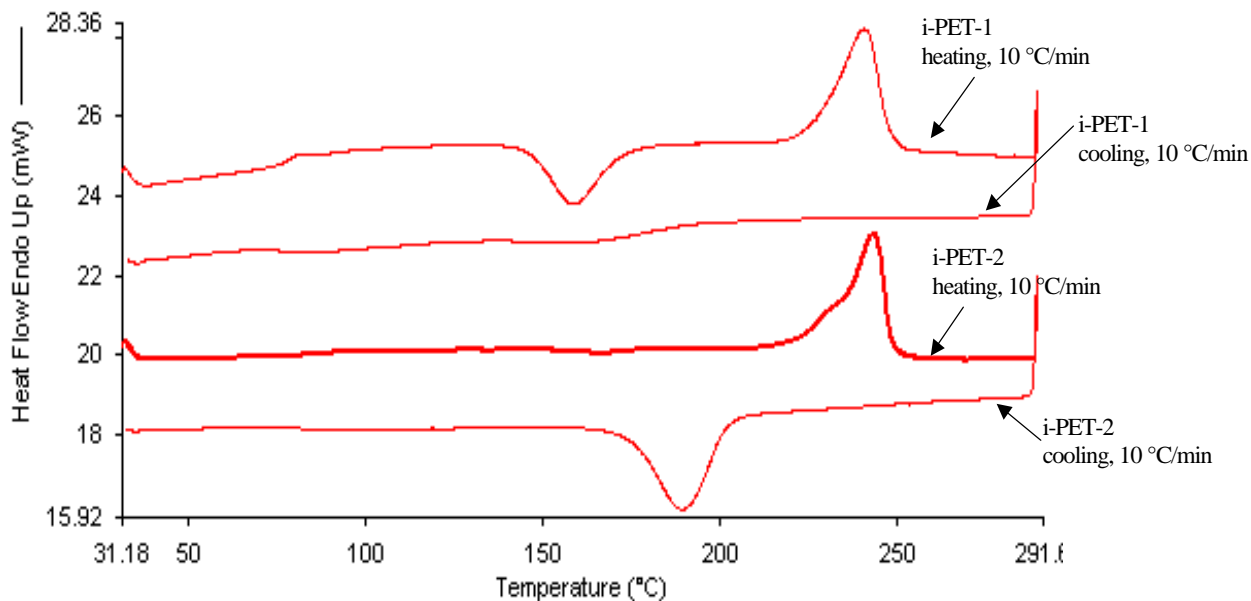


Figure 8.11. DSC curves of ionic PET with (PET-SSBA-2) and without (PET-SSBA-1) antimony oxide catalyst cooling and the second heat; both cooling rate and heating rate are 10°C/min, under N₂

Melt rheology results provided further information about the interaction of an ionic aggregate and an antimony catalyst (Figure 8.12). It was discovered that for the PET-SSBA-2 with antimony catalyst, the transition temperature to a melt flowing state was much higher than it was for the PET-SSBA-1 without antimony catalyst. The difference between these two transition temperatures was about 20 °C. For the non-ionic PETs (PET-Dode-OH-1 and PET-Dode-OH-2), however, in which there were no ionic aggregates, the transition temperature difference was only 10 °C. This difference is attributed to the interaction of the antimony catalyst and the ionic aggregates, thus enabling the polymer chains to pack easier and achieve better regularity.

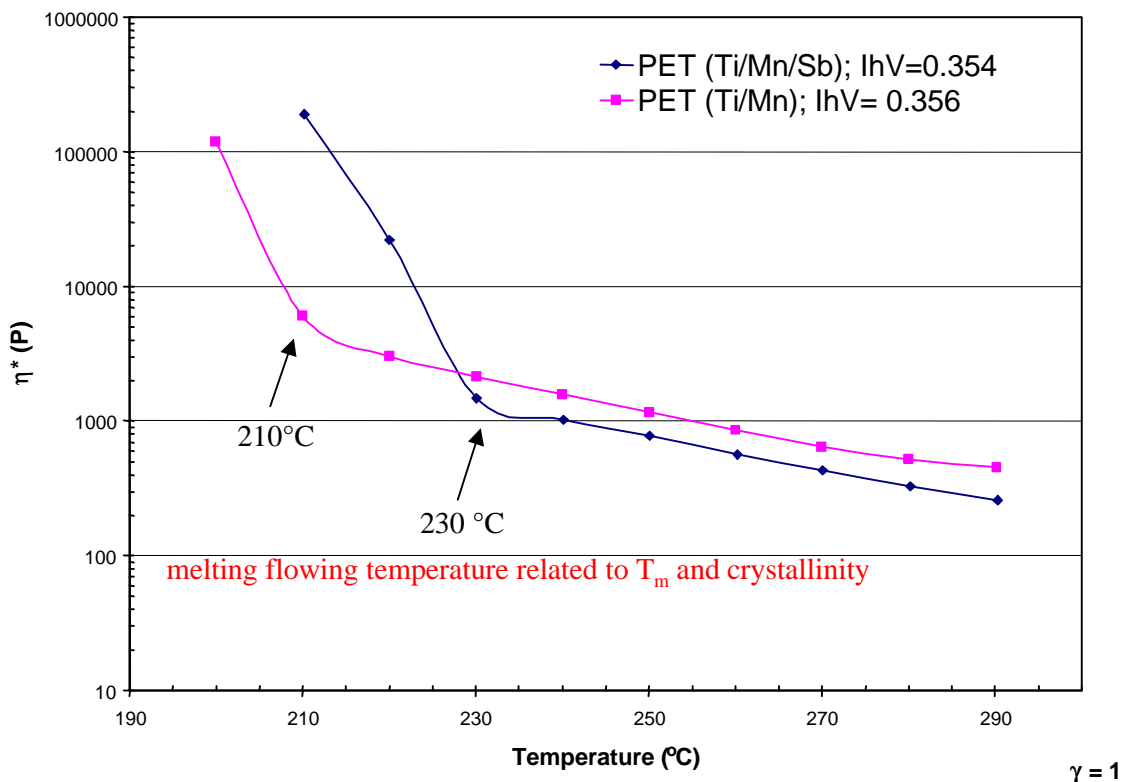


Figure 8.12. Melt rheology of PET-SSBA-1 and PET-SSBA-2 ionomers with and without antimony oxide catalyst, $\gamma = 1$ Hz

8.4 Conclusions

Isothermal and non-isothermal DSC studies were carried for both ionic and non-ionic PET samples. Isothermal crystallization studies showed that for the non-ionic PET samples with the same molecular structure, the crystallization rate decreased with an increase in molecular weight. It was also demonstrated that ionic interaction played an important role in controlling the crystallization process in ionomers. Both isothermal crystallization and non-isothermal crystallization studies showed that the crystallization rate of ionomers decreased dramatically, especially when compared to the non-ionic PET samples with the same molecular weight. Again, this phenomenon is attributed to the limited mobility of the polymer chains as a result of ionic interactions. Antimony catalyst helped to increase the crystallization rate of both ionic and non-ionic PET samples. At the same cooling rate (10°C/min), ionic PET with antimony catalyst

recrystallized completely, while the ionic PET without the catalyst could not crystallize efficiently at the same rate.

In addition, for the PET ionomers, the antimony catalyst residue was able to interact with ionic aggregates, thus increasing the crystallization rate to a greater extent than was observed for the non-ionic PET samples. Our melt rheology results were consistent with these DSC findings.

CHAPTER 9. SUMMARY AND FUTURE WORK

In order to overcome the disadvantages of traditional covalently bonded high molecular weight polymers, such as poor melt processability, low thermal stability and recycling difficulties associated with resulting fabricated materials, thermally reversible telechelic ionic groups were introduced to the chain ends of various polyesters using melt polymerization techniques.

Amorphous polyester ionomers, poly(ethylene isophthalate)s (PEI) were first synthesized using melt polymerization. NMR and FTIR confirmed the ionic and nonionic polymer structures and the existence of the ionic end caps. Solution behavior studies confirmed that the non-ionic PEI conformed to the Mark-Houwink equation quite well, while the ionic PEI produced upward curvature in the η_{sp}/c and $\ln(\eta_r/c)$ vs c plots due to the strong ionic interaction. DSC studies revealed that ionic interactions within the polymer system helped to maintain the structural integrity of the polymer chain, thus limiting the mobility of the polymer chains and maintaining a high glass transition temperature – similar, in fact, to that of the high molecular weight non-ionic PEI samples. Melt rheology results showed that at lower temperature (e.g., below 150°C), PEI ionomers demonstrated mechanical properties characteristic of high molecular weight materials. Above 150°C, however, the ionic aggregations were destroyed and the melt viscosity decreased dramatically to a level much lower than that of typical non-ionic high molecular polymeric materials. This unique melt behavior of the ionomers would facilitate their processability at high temperatures, as well as maintain high performance at application temperatures. Varying molecular weights of non-ionic PEI polyesters were also successfully obtained by using dodecanol as an end capper.

Novel telechelic ionic semi-crystalline poly(ethylene terephthalate) (PET) was synthesized with SSBA as an end capper, and non-ionic PET samples with controlled molecular weights using dodecanol were prepared for comparison. The chemical structures of the polymers were confirmed by NMR and FTIR. It was shown that ^1H NMR was able to detect SSBA or dodecanol end groups in the polymers. The existence

of SSBA end groups was also evidenced by the characteristic absorption of S-O stretching at 630 cm^{-1} in FTIR spectra. GPC was used to obtain molecular weight information of non-ionic controlled PET polymers. Similar solution behavior was observed for both the ionic and non-ionic PEI polymers. A single glass transition temperature was observed for all of the ionic PET polyesters, indicating that the ionic aggregates in these ionomers were multiplets, instead of clusters. The very strong ionic interaction in these ionomers limited the mobility of the polymer chains, thus helping to maintain the glass transition at relatively high levels despite the fact that the actual molecular weight was much lower.

In addition to the telechelic PEI and PET ionomers, novel telechelic ionic poly(ethylene isophthalate-co-*trans*-1,4-CHDC) and poly(ethylene isophthalate-co-terephthalate) (PEIT) copolymers were also prepared to study the effect of the polarity and rigidity of polymer chain backbones on ionic interaction. The successful synthesis of the copolymers was confirmed by NMR and FTIR data. TGA results showed that all of the ionic copolyesters had very good thermal stability. For sulfonated ionic poly(ethylene isophthalate-co-*trans*-1,4-CHDC), DSC results showed that the polarity and chain packing regularity decreased due to the *trans* structure of 1,4-CHDC, and this resulted in more free volume for the polymer chain, thus lowering the glass transition temperature. For ionic poly(ethylene isophthalate-co-terephthalate) (PEIT-SSBA), DSC indicated that the new copolyesters were almost totally amorphous, because the kinked-structure of DMI, reduced the regularity of the polymer chain and made crystallization more difficult. All of the samples were soft, clear and amorphous materials. And as telechelic ionomers, all of the samples exhibited upward curvature in their dilute solution (η_{sp}/c vs c and $\ln(\eta_r/c)$ vs c plots) is a characteristic behavior of an ionomers.

It is genererally believed that melt strength can be improved by introducing branching agents to a polyester system. After studying linear telechelic polyester ionomers, we investigated several branched polyester ionomer systems. Using trimellitic anhydride as the branching agent, novel telechelic branched PEI and PET ionomers were synthesized and characterized. NMR results confirmed the polymer chain structures and

the presence of the SSBA end groups. However, the branching agent, TMA, was not detected in NMR because of low concentration. All of the samples showed characteristic ionic behavior in solution. The melt strength of all the samples was much stronger than that associated with linear polyester ionomers. DSC results showed that after introducing a branching agent, the crystallinity, crystalline melting point, physical properties, solution viscosity, and melt viscosity of the polymers were all affected. However, it is difficult to predict the complex relationship between a branching agent and the resulting behavioral properties of the polymer because the branching reaction generally occurs in a random fashion.

Zinc stearate was an effective ionic plasticizer in these ionomer materials by lowering the softening temperature, thereby facilitating melt processability. A series of ionic and non-ionic PET blends with zinc stearate were prepared. Blending was carried out at 275°C under nitrogen for 15 minutes. It turned out that the softening temperature of non-ionic PET/Zn materials was not significantly affected, while the softening temperature of ionic PET/Zn materials dramatically decreased with an increase in zinc stearate. This may be due to the fact that zinc stearate might dissociate the ionic interactions at melt processing temperatures (the interactions that are responsible for network formation) but would allow re-establishment of these ionic interactions at lower temperatures. However, the blending temperature was 275°C, which corresponds to the degradation onset temperature of zinc stearate. Thus, the decrease in glass transition temperature of all the blend samples might be due to the degradation products of the zinc stearate. Further studies are needed to clarify this issue.

Crystallization behavior studies are very important for PET polymers. Crystallization kinetics, for example, determines the final physical state of the polymer, which in turn controls the physical properties of the resulting manufactured product. We studied the crystallization rates and processes associated with our novel ionic and non-ionic semi-crystalline PET samples by using isothermal and non-isothermal crystallization methods. DSC was a very powerful tool for this study. Determining the half time of the crystallization process was useful in representing the relative

crystallization rate. It was discovered that as the molecular weight of similar polymers increased, the crystallization rate decreased. The presence of antimony catalyst residue in the polymer had a more significant effect on improving the crystallization rate by acting as a nucleating agent. This is especially true for the ionic PET samples. Both DSC and melt rheology results indicated that the antimony catalyst reacted with the ionic aggregates to increase the crystallization rate even more dramatically.

Despite the extensive synthesis and characterization work done for this project, additional research is necessary. For example, the dilute solution behaviors of the PEI and PET ionomers at extremely low concentrations (i.e., < 0.3 g/dL) are interesting to study, which are expected to further illustrate the role of ionic functional groups in determining the physical properties of the ionomers. 500MHz NMR could be used to further detect the SSBA end group in PET-SSBA. The relationship of cyclic-trimer produced during melt polymerization of sulfonate terminated PEI and PET and the amount of SSBA end cappers could be established by running NMR of the distillate. Solid-state polymerization could be utilized in PET samples to increase the molecular weight. Besides SSBA, it would be useful to identify a new ionic end capper, such as a divalent salt, which might provide stronger ionic interactions. Additionally, it would be interesting to discover some other branching reagents to study the effect of branching reagent on the melt strength of the ionomers. Mechanical and adhesive testing of the new ionomers would also be very useful.

The crystallization behaviors in both PET-dode-OH and PET-SSBA model systems are also worth further investigation. It would be very interesting and important to find some other nucleating agents that might beneficially either increase or decrease the crystallization rate of our novel telechelic PET ionomers, depending on their proposed applications. Some examples in this area include (a) the molecular weight influence on the half time of crystallization ($t_{1/2}$) and crystallization degree in the model systems using isothermal DSC studies, and (b) the control of the crystallization window ($T_g - T_m$) with different amounts of dodecanol in PET. Determining the influence of dodecanol on the

hydrolytic stability of the polymer chains would also be a desirable extension of the study.

VITA

Huaiying Kang was born in Beijing, China, on March 15, 1972. She graduated from the Affiliated High School of the University of Science and Technology of China in 1989. She obtained her B.S. in polymer chemistry from the Department of Materials Science and Engineering of University of Science and Technology of China (USTC) in 1994. She then worked as a research assistant in the Nanotechnology Lab in USTC for one year. In 1995, she rejoined the Department of Materials Science and Engineering of USTC as a research assistant for another year. In 1996, she came to Virginia Polytechnic Institute and State University (Virginia Tech), where she worked for Dr. Paul Deck for the first two years. She then joined Dr. Timothy Long's research group in January, 1999, where she finished her M.S. in polymer chemistry in July, 2001. Huaiying Kang has been admitted by Pamplin College of Business of Virginia Tech as a MBA student, which will start in Fall, 2001.