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IONOMERIC BLENDS OF PYRIDINE CONTAINING POLYMERS WITH SULFONATED PET

A Dissertation Presented
by
MARTIN J. LINDWAY

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirement for the degree of

DOCTOR OF PHILOSOPHY

September 1992

Department of Polymer Science and Engineering

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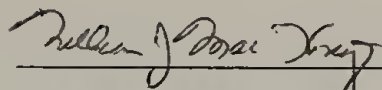
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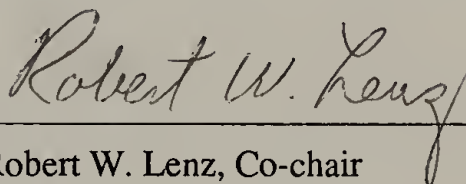
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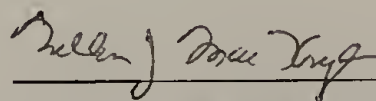
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Dedicated to my wife, through her comfort, love and support,
she has harmonized a great age of discovery for me.

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I would finally like to attempt to express my deepest appreciation to my wife. You are truly God-sent. Our relationship has been truly blessed. You have made countless sacrifices in support of my aspirations, always making sure my cup was full. You asked for little and gave much more, so moment by moment in the years to come I hope to give back all that you've given in devotional love.

ABSTRACT

IONOMERIC BLENDS OF PYRIDINE CONTAINING POLYMERS WITH SULFONATED PET

SEPTEMBER 1992

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An investigation of acid-base interactions and zinc transition-metal complexations in ionomeric blends of sulfonated poly(ethylene terephthalate) (PET) with pyridine containing polymers will be discussed in relation to the level of specific intermolecular interactions, as measured with FTIR, and the degree of compatibilization, as observed from DSC and DMTA. Two pyridine containing polymer systems were evaluated: (1) a novel main-chain thermotropic liquid crystalline polyester containing pyridine dicarboxylate units, and (2) poly(ethyl acrylate-co-4-vinyl pyridine).

Model thermotropic liquid crystalline polyester systems were developed and screened based on a set of macromolecular structure requirements directed toward future blends studies with PET and PBT. The first investigation discussed the preparation and characterization of TLCPs based on the biphenyl mesogen, 4,4'-bis(6-hydroxyhexoxy)-biphenyl, BHHBP. Two series of TLCPs were prepared and characterized by CPOM, DSC, and WAXD. Both series of polymers exhibited smectic A phase types.

The second investigation discussed the preparation and characterization of thermotropic liquid crystalline polyester based on the triad mesogen monomer, 4,4'-(terephthaloyldioxy)dibenzoyl dichloride, (ClH₂THCl). Various dihydroxy flexible spacers having chemical substituents similar in structure to the repeat units of PET and/or PBT were copolymerized with ClH₂THCl and evaluated by CPOM, DSC, and WAXD. From this investigation, a series of polymers were characterized as an enantiotropic nematics. From this series, a candidate was selected as a model system, where the composition of flexible spacers was: 75% bis(4-hydroxybutyl) terephthalate and 25% 1,6-hexanediol.

The flexible spacers of the model system was then modified to contain pyridine dicarboxylate units. This modified model system (TLCP_N) was characterized as having a similar phase and phase-temperature relationship when compared to the model system.

Upon development and characterization of TLCP_N, ion exchange procedures were developed to exchange the sodium ions of PET-SO₃Na for hydrogen and subsequently hydrogen ions for zinc. Stoichiometric blends of both the free acid and zinc neutralized form of sulfonated PET were prepared and characterized by FTIR, DSC, and DMTA. For both these blends there was no evidence for specific intermolecular interactions or compatibilization.

In the final investigation, both the free acid and zinc neutralized forms of sulfonated PET were blended with poly(ethyl acrylate-co-4-vinyl pyridine). The stoichiometric blends were prepared and characterized similar to the previous study. A zinc blend containing 77% sulfonated PET (7% SO₃Zn) and 23 % poly(ethyl acrylate-co-4-vinyl pyridine) (10.6 % VP) appeared to be predominately single phase by DSC and partially phase separated by DMTA. Where similar blends containing 58 % poly(ethyl acrylate-co-4-vinyl pyridine) (5.2 % VP) appear partially phase separated by both DSC and DMTA.

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CHAPTER 1

INTRODUCTION

The development of new high performance thermoplastics has become increasingly challenged by the demands of advanced material requirements and cost-effectiveness. The ability to tailor to these stringent material requirements of high tensile strength, modulus, heat distortion temperature, and lower thermal expansion can be satisfied by utilizing composite materials. Through greater understanding and control of the components microstructure, composition and morphology, predicted properties could synergistically solve the needs of these advanced applications. To remain cost-effective, there is a strong industrial interest for enhancing the specific properties of existing systems and satisfying new material requirements for the changing market.

In the area of engineering thermoplastics, TPs, the common means for improving mechanical properties has been with fillers such as glass-chopped fibers. Glass fiber-reinforced thermoplastic composites actually have been seen as a short term solution to cost-effective property improvements, but problematic in respect to processing. Some of the difficulties in processing glass fibers include increased energy consumption, increased wear on equipment, and utility to process films, foams, and by thermoforming. In the search for alternative means for reinforcing TPs, there has been a number of industrial and academic research groups, who have investigated the utilization of single organic crystals¹⁻⁸ and liquid crystals.⁹⁻¹⁹ These investigations centered

around the theme of in situ formation (via crystallization) of the reinforcing agent during processing.

Through these investigations, there has been a greater focus on utilizing the liquid crystalline polymers as reinforcing agents. These homogenous composites would circumvent the processing difficulty associated with chopped glass fibers, and offer both rheological and mechanical property enhancement.

Liquid crystalline polymer/TP blend systems have been described as potential candidates for "molecular composites". Appreciation for the initial theoretical development for molecular composites can be attributed to Flory's evaluation of binary/ternary systems consisting of single polymer rigid rods.²⁰ Through his evaluation, he constructed phase diagrams in which a critical region of a single isotropic phase consisting of rigid rods is randomly dispersed in a random coil matrix. Therefore, if one were to control the kinetics of phase separation, the resulting material should possess a high level of specific mechanical properties as predicted from an extension of a classical composite principle. The principle predicts fibers (rods) dispersed in a matrix having widths on a molecular or supermolecular level would be in theory much stronger than fibers having widths on a macromolecular level. This viewpoint is presented based on fracture mechanics, where one has higher fiber content utilization efficiency, or simply using the analogous argument that a rope is stronger than a rod of similar size and material. The concept of molecular composites was first described by Takayanagi's²¹ study of aramid/nylon systems, along with Helminiak, Hwang, and Wiff^{22,23} who developed improved methods of processing these "molecular composites". These molecular composite systems, which are associated more directly with lyotropic liquid crystalline polymers, resulted in significant increases in mechanical properties. Unfortunately, these systems require certain exotic and highly corrosive solvents for processing. A more desirable situation would be a melt processable liquid crystalline polymer,²⁴⁻²⁶ which could be incorporated to greater extent (in comparison to glass-

fiber reinforced TPs) into the conventional processing technology of TPs. These aspects were realized in the commercial development of thermotropic liquid crystalline polymers, TLCPs, as pure materials. TLCPs are characterized by their unique high local (microscopic) orientationally ordered domains at specific temperature regimes in the melt. When these domains are oriented in an elongation flow field and retained in the solid state, they exhibit high specific tensile strength and modulus. The alignment in the direction of the flow field also offers a unique reduction in melt viscosity, as reviewed by Wissbrun.²⁷ Commercialization of TLCPs as pure materials has had limited success, mainly inhibited by the high cost of aromatic monomer synthesis, and lack of a thorough understanding of their flow properties in controlling the unfavorable high anisotropy at weld lines. Therefore, there has been an increased interest in utilizing these unique high anisotropic materials as "in situ composites" through blending with conventional TPs,²⁸ and utilizing these blends in applications where glass-fiber reinforcing additives could not be used during processing. The new class of self-reinforced composite materials would be an attractive means of balancing both properties and cost-effectiveness. Additionally, the TP blended with the TLCP has been proposed to reduce the typical problems associated with the high anisotropy found in injection molded parts of pure TLCPs,²⁹ but there have been few reported successes. Therefore, there will be greater emphasis on applications relating to extrusion of these blends.

For both cases, molecular or in situ composites, the difficulty lies in the method of dispersing the rigid molecules in the matrix of flexible molecules. When the interaction energy at the interface of both components is strong enough, the dispersion proceeds until the interfacial surface energy is balanced with the aggregation energy of rigid molecules. In the case of TLCP/TP blends, the resulting balance is in favor of aggregation of the *semi-rigid* molecules in domains larger than one would consider for molecular composites. Hence, these blends have been referred to as in situ composites.²⁸

The main body of research work has focused on the rheological and mechanical properties of various TLCP/TP systems. Rheological enhancement in these blends as mentioned above has been realized at low TLCP content (2-15%). Cogswell of ICI received a patent³⁰ based on his claims of TLCPs use as a processing aid with TPs. When 1-20% of various TLCPs were added to these blends there was a significant reduction in melt viscosity at shear rates between 100 and 1000 s⁻¹. Therefore, one would expect that this would be of great industrial importance in terms of increased production rate. But, this has not been the case, due to the resulting brittleness in materials found at even 3 % of TLCP content.³⁰ Siegmann and co-workers³¹ described polymer blends based on Vectra® with amorphous polyamide. They observed reduced viscosity in these blends which were lower than the individual components. They also discussed a two phase morphology which with increasing TLCP content acted as a reinforcing agent. The blends were considered immiscible in the injection molded parts. With increased TLCP content, the phase domains went from ellipsoidal to fibrous . Jackson and Kuhfuss also observed a similar skin-core morphology, for X7-G® (TLCP based on the incorporation 60% 4-hydroxybenzoic acid units into PET).²⁹ . This morphology exhibited better mechanical properties in the skin than in the core.

Joseph³² has studied the structure, thermal behavior, and mechanical properties of PET blends with X7-G® . He reported that the X7-G® acted as a nucleating agent for PET, significantly enhancing mechanical properties, and resulting in a skin-core morphology for injection molded parts. A number of groups^{28,31,33-36} have reported highly elongated LCP domains parallel to the flow field in blends with TPs. The effectiveness of this process is a function of the orientation imparted to the TLCP in the chosen process and the viscosity ratios ($\eta_{TLCP} < \eta_{TP}$) of the TLCP/TP blend. The matrix material, TP, should have a higher viscosity than the TLCP in order to transmit the elongation strain to the LCP domains. Most of the recent publications are concerned with optimizing the processing conditions with commercially available systems. There

are three good reviews concerning TLCPs and their blends with TPs.³⁷⁻³⁹ Kiss²⁸ of Celanese Corp. studied a variety of blends containing a confidential material related to Vectra®. In this study he evaluated a wide variety of TPs and had success in terms of improving mechanical properties in relation to the pure TLCP for blends of polymers with high T_g s and specific interaction. One consistent result was the brittleness of the blends due to poor interfacial adhesion of the TLCP phase. Kiss also felt that these types of blends would not solve the weld line problem, caused by the inherently high anisotropy of TLCPs. Therefore, pure TLCP materials are typically filled to reduce this problem as well as their cost. The mechanical property enhancement in his study was marginal for a variety of systems, specifically PBT. The strength and modulus as measured by tensile and flex tests revealed reduction in properties in comparison to pure PBT. Again in relation to general composite principles, adhesion with the matrix is the key to property enhancement. Even with the success Kiss had with certain systems, the benefit at that time could not balance their cost. For these blends to be useful commercially, the issue of adhesion and control of morphology must be resolved. Concluding this review of the literature, non-structural properties have only been sparsely examined for TLCP/TP composite blends.

The PSE department at UMASS is involved in a multi-group effort to investigate the principles of in situ composites for the AKZO Corporation. Based on their commercial TPs: polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and nylon 6, the strategy has been to develop novel TLCP/TP blends with enhanced mechanical and rheological properties. This dissertation contains the following objectives; (1) the preparation and characterization of novel TLCPs, (2) modification of selected candidates from (1) in order to investigate ionomeric TLCP/TP blends with sulfonated PET and (3) investigation of ionomeric blends of poly (ethyl acrylate-co-vinyl pyridine) with sulfonated PET. The motivation for investigating specific intermolecular

interactions of ionomeric blends will be the central theme through out the rest of this chapter. The general concept of TLCP/TP ionomeric blends was disclosed in a memorandum by MacKnight.⁴⁰ He discussed the use of specific interactions to induce an increased compatibility between the immiscible phases of TLCP/TP blends. This enhanced compatibility would offer greater interfacial adhesion between phases which in theory should result in improved mechanical properties.

The degree of interfacial adhesion has been a concern for these blends warranting further investigation. Based on findings in the open literature, TLCP/TP blends have not yet offered the desired improvements in mechanical properties. In composite and blend theory, if there is sufficient interfacial adhesion between the reinforcing component and the matrix, there should be enhancement of mechanical properties following at least a rule of mixture. The strategy of the AKZO project has been to investigate novel TLCPs which would offer greater compatibility and thus greater interfacial adhesion between these blends. The focus of the synthesis group has been to prepare blocks, grafts, and ionogenic TLCPs with ester or ester/amide linkages which would enhance compatibility with AKZO's TPs.

High molecular weight polymer pairs are typically immiscible due to unfavorable thermodynamics, specifically relating very small combinatorial entropy of mixing and positive enthalpy of mixing. If one considers a polymer pair, where all independent variables are equal (temperature, pressure, molecular weight, chain structure, physical mixing, etc.), the interfacial properties of the pairs will determine the relative compatibility. Therefore, one means of compatibilizing two immiscible polymer pairs has been through the use of specific intermolecular interactions. There are various types of specific interactions which have been utilized to promote compatibility in blends: hydrogen bonding,^{41,42} π -electron systems,^{43,44} charge-transfer,^{45,46} ion-ion,^{47,48} dipole-dipole,^{49,50} ion-dipole,⁵¹⁻⁵³ acid-base,^{54,55} and metal complexes.⁵⁶⁻⁶⁰

I would like to cite some of the recent advancements in the area of ionomeric blends

involving ionic interactions. Eisenberg and co-workers have conducted a number of fundamental studies relating to the use of ionic interactions as a means of compatibilizing polymer pairs.⁶¹⁻⁸¹ The unmodified polymer pairs of these systems would be considered immiscible. Incorporation of a minimal content of ionogenic moiety of 5 mole% into these systems was found sufficient to enhance miscibility. Some of the systems investigated included polystyrene with poly(ethyl acrylate),^{62,63} polystyrene with polyisoprene,⁶⁴ and polyphenylene with poly(ethyl acrylate).⁶⁶ The techniques used to quantify the nature and the level of specific interaction in these blends included FT-IR and COSY NMR experiments.^{54,55} There are a variety of techniques used to characterize the level of compatibility^{84,85}, these techniques utilize a certain dynamic range to resolve domain sizes ranging from 5- 2000 Å. The degree of miscibility in relation to distribution of charged complexes has been under close evaluation. Brereton and Vilgis have recently proposed a theoretical model of mixing in such a system.⁸⁶ They concluded that blends containing charged complexes will appear mixed on a scale greater than the distance between interacting groups, and phase separated on a scale less than the distance between interacting groups. Supportive evidence for this model would greatly enhance the scientist's ability to control the degree of miscibility.

Dissertation Prospectus Summary

The initial focus of this research project was in relation to the "Molecular Composite Project" funded by the AKZO Corporation. The main objective of the entire project has been the investigation into blend additives which would enhance both mechanical and rheological properties of the commercial AKZO resins; PET, PBT, and nylons. The general strategy of the group has been the investigation of blends of novel TLCPs with their resins at low TLCP content (5-30%). These blends were then

evaluated as potential "molecular composites" or "in situ composites", which should enhance the mechanical and rheological properties of their resins. The area of concern in these types of blends has been the resulting brittleness and marginal property enhancement. Poor interfacial adhesion in these types of blends continues to be targeted as one of the major deficiencies, which is caused by poor mixing of the polymer pairs at the interface. The use of specific intermolecular interactions, as in the case of ionomeric blends, was considered as one route for enhanced mixing between polymer pairs at the interface.

The main objective was to investigate the use of acid-base and transition-metal (Zn) complexes in polymer blends of sulfonated PET with pyridine containing polymers. The initial research objective involved the synthesis and characterization of novel nematic TLCPs which contained repeat units similar in molecular structure to PET and PBT and were liquid crystalline during the processing of PET. These system requirements were expected to yield improved compatibility when blended with PET and PBT and utilize the inherently good mechanical and rheological properties observed in TLCPs. Once a system was screened, the research prospectus then focused on the incorporation of an ionogenic moiety (pyridine dicarboxylate) into a selected TLCP which would promote specific intermolecular interactions in an ionomeric blend containing AKZO's sulfonated PET (with 7% sulfonation). Sulfonated PET was received from AKZO in the sodium neutralized form, therefore the procedures for the ion exchange of sodium sulfonated PET were developed in order to study both free-acid and zinc blends. Once the individual polymers were characterized, the procedure for solution blending was developed. These blends were evaluated in terms of the level of specific intermolecular interactions and degree of compatibilization.

A second approach for enhancing the properties of AKZO's PET was also considered using blends of sulfonated PET with poly(ethyl acrylate-co-4-vinyl pyridine),

EA VP. These blends offer a potentially interesting biphasic material of a rubbery EA VP phase ($T_g = -7^\circ\text{C}$) and a semi-crystalline sulfonated PET phase ($T_g = 70^\circ\text{C}$ and $T_m = 228^\circ\text{C}$) which could be further explored as an impact modifier or as a compatibilizing agent upon blending with PET.

Hence, the goal of this research was the investigation into the use of specific intermolecular interactions of ionomeric blends containing sulfonated PET. Although, ionomeric blends have been studied by a variety of groups for a number of years, there has been no reported study of ionomeric blends with polyesters and only a few as previously cited multi-phase components. Therefore, developments in this area should reveal important insights to the use of specific interactions as a means of controlling compatibility and properties of immiscible polymeric blends.

The following will outline the objectives of the next four core chapters (2-5) for the dissertation. These core chapters are laid out in form similar for future manuscripts to be published. The objective of Chapter 2 and 3 is to present the preparation and characterization of novel TLCPs in support of the synthesis strategy mentioned for the above AKZO "Molecular Composite Project". The objective of Chapter 4 is to present the preparation and characterization of a modified candidate selected from Chapter 3 and the study of ionomeric blends of this modified TLCP with the free acid and zinc neutralized form of sulfonated PET. Finally, the objective of Chapter 5 is to present the preparation and characterization of ionomeric blends of poly(ethyl acrylate-co-vinyl pyridine) with the free acid and zinc neutralized form of sulfonated PET.

References

1. Joseph, J.R., Kardos, J.L., and Nielsen, L.E., *J. Appl. Polym. Sci.*, **12**, 1151 (1968)
2. Kardos, J.L., McDonnell, W.L., and Raison, J., *J. Macromol. Sci., Phys.*, **B6**, 397 (1972)
3. Kardos, J.L. and Raison, J., *Polym. Eng. Sci.*, **15**, 1975 (1972)
4. Kiss, G., Kovacs, A.J., and Wittmann, J.C., *J. Appl. Polym. Sci.*, **26**, 2665 (1981)
5. Narkis, M., Siegmann, A., Dagan, A., and DiBenedetto, A.T., *J. Appl. Polym. Sci.*, **21**, 989 (1977)
6. Shaw, M. T. and Chen, J.H., *Proc. International Conf. Rhel. 8th*, **3**, 99-108 (1980)
7. Siegmann, A., Narkis, M., Puterman, M., and DiBenedetto, A.T., *Polymer*, **20**, 89 (1979)
8. Siegmann, A., Narkis, M., Puterman, M., and DiBenedetto, A.T., *J. Polym. Sci. Phys.*, **17**, 225 (1979)
9. Noel, C. and Billard, J., *Molec. Cryst. Lett.*, **6**, 269 (1978)
10. Noel, C., Fayolle, B., and Billard, J., *J. Physique*, **4063**, 485 (1979)
11. Kronberg, B., Bassignana, I., and Paterson, D., *J. Phys. Chem.*, **82**, 1714 (1978)
12. Griffin, A.C. and Havens, S.J., *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 259, (1980)
13. Ringsdorf, R., Schmidt, H.W., and Schneller, A., *Macromol. Chem., Rapid Commun.*, **3**, 745 (1982)
14. Dubault, A., Casagrande, C., and Vegssie, M., *Mol. Cryst. Liq. Cryst.*, **72**, 189 (1982)
15. Cser, F., Nyitrai, K., Hardy, G., Menzel, J., and Varga, J., *J. Polym. Sci., Polym. Symp.*, **69**, 91 (1981)
16. George, E.R., Porter, R.S., and Griffin, A.C., *Mol. Cryst. Liq. Cryst.*, **110**, 27 (1984)
17. Buckley, A., Conciatori, A. B., and Calundann, G.W., *U.S. Patent*, 4,434,262 (1984)

18. Kayiyama, T., Washizu, S., and Takayanagi, M., *J. Appl. Polym. Sci.*, **29**, 3955 (1984)
19. Huh, W., Weiss, R. A., and Nicolais, L., *Polym. Eng. Sci.*, **23**, 779 (1983)
20. Flory, P.J., *Macromol.*, **11**, 1138 (1978)
21. Takayanagi, M., Ogata, T., Morifawa, M., and Kai, T., *J. Macromol. Sci., Phys.*, **B17**, 591 (1980)
22. Hwang, W.F., Wiff, D.R., Helminiak, T.E., Verschoore, C., Price, G.E., and Adams, W.W., *Polym. Eng. Sci.*, **23**, 879 (1983)
23. Hwang, W.F., Wiff, D.R., Helminiak, T.E., and Benner, C.L., *J. Macromol. Sci., Phys.* **B22**, 231 (1983)
24. Calundann, G.W. and Jaffe, M., *Proc. Robert A. Welch Conferences on Chemical REsearch XXVI, Synthetic Polymers*, 247 (1982)
25. Chung, T.S., *Polym. Eng. Sci.*, **26**, 901 (1986)
26. Demartino, R.N., *J. Appl. Polym. Sci.*, **28**, 1805 (1983)
27. Wissbrun, K.F., *J. Rheol.*, **25**; 619 (1981)
28. Kiss, G., *Polym. Eng. Sci.*, **27**, 410 (1987)
29. Jackson, W.J. and Kuhfuss, H.F., *J. Polym. Sci. Phys.*, **14**, 2043-2058 (1976)
30. Cogswell, F.N., Griffin, B.P. and Rose, J.B., U.S. Patent 4,386,174 (1981)
31. Siegmann, A., Dagan, A., and Kenig, S., *Polymer*, **26**, 1325 (1985)
32. Joseph, E.G., Wilkes, G.L., and Baird, D.G., *Polymer Liquid Crystals*, Blumstein, A., ed., (New York: Plenum Press) 197 (1984)
33. Isayev, A. I. and Modic, M.J., *Polym. Compos.*, **8**, 158 (1987)
34. Weiss, R.A., Huh, W., and Nicolais, L., *Polym. Eng. Sci.*, **27**, 684 (1987)
35. Blizard, K.G. and Baird, D.G., *Polym. Eng. Sci.*, **27**, 653 (1987)
36. Michiyuki, A. and Nakagawa, K., *Polymer*, **28**, 263 (1987)
37. Brostow, W., *Kunststoffe*, **78**, 411 (1988)
38. National Materials Advisory Board Commission on Eng. & Tech. Systems National Research Council, *Liquid Crystalline Polymers*, (Washington D.C.: National Academy Press) (1990)
39. Dutta, D., Fruitwala, H., Kohli, A., and R.A. Weiss, *Polymer Engineering and Science*, **30** (17), 1005-1018, (1990)

40. MacKnight, W.J. , Pat. Appl. (AKZO ACR 5484), (1989)
41. Otocka , E.P. and Eirich, F.R., J. Polym. Sci., Part A-2, **6**, 895 (1968)
42. Otocka, E.P. and Eirich, F.R., J. Polym. Sci., Part A-2, **6**, 913 (1968)
43. Cruz, C.A., Barlow, J.W. and Paul, D.R., Macromolecules, **12**, 726 (1979)
44. Djordjevic, M. B. and Porter, R.S., Polym. Eng. Sci., **23**, 650 (1983)
45. Schneider, H.A., Cantow, J.J. and Percec, V., Polymer Bulletin, **6**, 617 (1982)
46. Schneider, H.A., Cantow, J.J., Massen, U. and Northfleet-Neto, H., Polymer Bulletin, **7**, 263 (1982)
47. Otocka , E.P. and Eirich, F.R., J. Polym. Sci., Part A-2, **6**, 921 (1968)
48. Otocka , E.P. and Eirich, F.R., J. Polym. Sci., Part A-2, **6**, 933 (1968)
49. Prud'homme, R.E., Polym. Eng. Sci., **22**, 90 (1982)
50. Allard, D. and Prud'homme, R.E., J. Appl. Polym. Sci., **26**, 559 (1982)
51. Belorgey, G., Aubin, M. and Prud'homme, R.E., Polymer, **23**, 1051 (1982)
52. Hara, M., Smith,P., and Eisenberg, A., ACS Polymer Preprint, **51**, 726 (1984)
53. Hara, M. and Eisenberg, A., Macromolecules, **17**, 1335 (1984)
54. Hara, M., Wollmann,D., and Eisenberg, A., ACS Polymer Preprints, **25**, 280 (1984)
55. Hara, M., and Eisenberg, A., Polym. Eng.Sci., **24**, 1306 (1984)
56. Eisenberg, A. and Natansohn, A., Macromolecules, **20**, 323 (1987)
57. Eisenberg, A., and Natansohn, A., ACS Polym. Prep., **27**(1), 349 (1986)
58. Lundberg, R.D., Peiffer, D.G., Duvdevani , I. and Agarwal, P.K., J. Polym. Sci.: Letters, **24**, 581 (1986)
59. Lundberg, R.D., Peiffer, D.G., Duvdevani , I. and Agarwal, P.K., J. Polym. Sci.: Part B: Phys., **25**, 839 (1987)
60. Lundberg, R.D., Peiffer, and Phillips, R.R., J. Polym. Sci.: Part B: Phys., **27**, 245 (1989)
61. Weiss, R.A., Li, C., Sen, A., Register, R.A., and Cooper, S., J. Polym. Sci.: Part B: Phys., **27**, 1911 (1989)
62. Aouadj, O., Lassoued, A., and Djadoun, S., Phys. Opt. Dyn. Phen. Proc. in Macrom. Sys., 525 (1985)

63. Hara, M., Smith, P., and Eisenberg, A., Current Topics in Polymer Science, Vol. II, R.M. Ottenbrite, L.A. Ultracki and S. Inoue eds., (New York: Carl Hanser Verlag), 256-283 (1987)
64. Eisenberg, A. and Smith, P., J. Poly. Sci.: Letters, **21**, 223 (1983)
65. Eisenberg, A., Smith, P. and Zhou, Z.-L., Poly. Eng. Sci., **22**, 1117 (1982)
66. Eisenberg, A. and Murali, R., J. Poly. Sci.: Part B: Phys., **26**, 1385 (1988)
67. Eisenberg, A. and Zhou, Z.-L., J. Poly. Sci. Phys., **21**, 595 (1983)
68. Eisenberg, A. and Simmons, A., ACS Polym. Prep., **27**(1), 341 (1986)
69. Eisenberg, A. and Murali, R., ACS Polym. Prep., **27**(1), 343 (1986)
70. Eisenberg, A. and Natansohn, A., ACS Polym. Prep., **27**(1), 349 (1986)
71. Eisenberg, A. and Hara, M., Macromolecules, **20**, 2160 (1987)
72. Eisenberg, A. and Hara, M., Macromolecules, **17**, 1335 (1984)
73. Eisenberg, A. and Hara, M., Polym. Eng. Sci., **24**, 1306 (1984)
74. Eisenberg, A. and Natansohn, A., Macromolecules, **20**, 323 (1987)
75. Eisenberg, A., Natansohn, A. and Rutkowska, M., Polymer, **28**, 885 (1987)
76. Eisenberg, A., Natansohn, A., and Rutkowska, M., Poly. Eng. Sci., **27**, 1504 (1987)
77. Eisenberg, A. and Rutkowska, M., Macromolecules, **17**, 821 (1984)
78. Eisenberg, A. and Rutkowska, M., J. Appl. Polym. Sci., **30**, 3317 (1985)
79. Eisenberg, A. and Rutkowska, M., J. Appl. Polym. Sci., **33**, 2833 (1987)
80. Eisenberg, A. and Rutkowska, M., J. Appl. Polym. Sci., **29**, 755 (1984)
81. Eisenberg, A. and Zhang, X., Polym. Adv. Tech., **1**, 9 (1990)
82. Eisenberg, A. and Zhang, X., J. Polym. Sci.: Part B: Phys., **28**, 1841 (1990)
83. Eisenberg, A., Natansohn, A., and Murali, R., Makromol. Chem., Macromol. Sym., **16**, 175 (1988)
84. Walsh, D.J. and Rostani, S., Adv. Polym. Sci., **70**, 119 (1985)
85. Walsh, D.J., Comprehensive Polymer Science, Vol.2, Booth, C. and Price, C. eds., (New York: Pergamon Press), 135-154 (1989)
86. Brereton, M.G. and Vilgis, T.A., Macromolecules, **23**, 2044 (1990)

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS CONTAINING BIPHENYL MESOGEN

Introduction

The scientific and technological interest in defining the phase behavior of main chain thermotropic liquid crystalline polymers, TLCPs, over the past decade has allowed for great strides in understanding structure-property relationships of these unique materials. Therefore, current research efforts are able to focus on specific aspects influencing mesophase stability and structure. A number of research groups have conducted investigations which have focused on liquid crystalline polymers containing the biphenyl mesogenic monomer 4,4'-bis(6-hydroxyhexoxy)-biphenyl,¹⁻¹³ BHHBP, shown in Figure 2.1. BHHBP exhibits a highly ordered, stable, smectic phase.¹

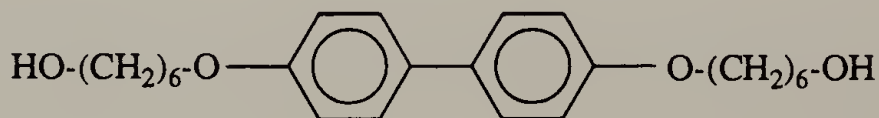


Figure 2.1: Mesogenic monomer 4,4'-bis(6-hydroxyhexoxy)-biphenyl, BHHBP

BHHBP has been incorporated into polyesters,²⁻⁵ polycarbonates,⁶⁻⁸ polyurethanes,⁹⁻¹² and polyethers.¹³ A comprehensive investigation in the re-orientational dynamics of BHHBP in the melt has indicated that the rotational freedom about the biphenyl linkage is only observed in the isotropic state.¹ The formation of the mesophase is predominately observed upon cooling from the isotropic state. The mesophase has been typically viewed as being unstable and crystallizes spontaneously on further cooling or upon annealing to produce a crystal phase with a higher melting point than the isotropization temperature of the mesophase.¹⁰⁻¹² Therefore, the mesophase is classified as being monotropic. The objective of this chapter is to evaluate various comonomer compositions which would "frustrate" or destroy the tendency for these BHHBP containing thermotropic liquid crystalline polyesters to crystallize. This investigation would give information of the relative stability of the mesophase and relate this stability to the influence of structure. The first approach, Scheme I, is represented on the next page in Figure 2.2.

The incorporation of isophthaloyl units as a comonomer with terephthaloyl units along with its non-linear "kinked" structure should both "frustrate" or destroy the tendency for crystallization, allowing the mesophase to be readily discerned from the crystalline phase. The mole ratios of isophthaloyl units to terephthaloyl copolymerized with BHHBP is represented on the next page in Table 2.1.

Scheme I

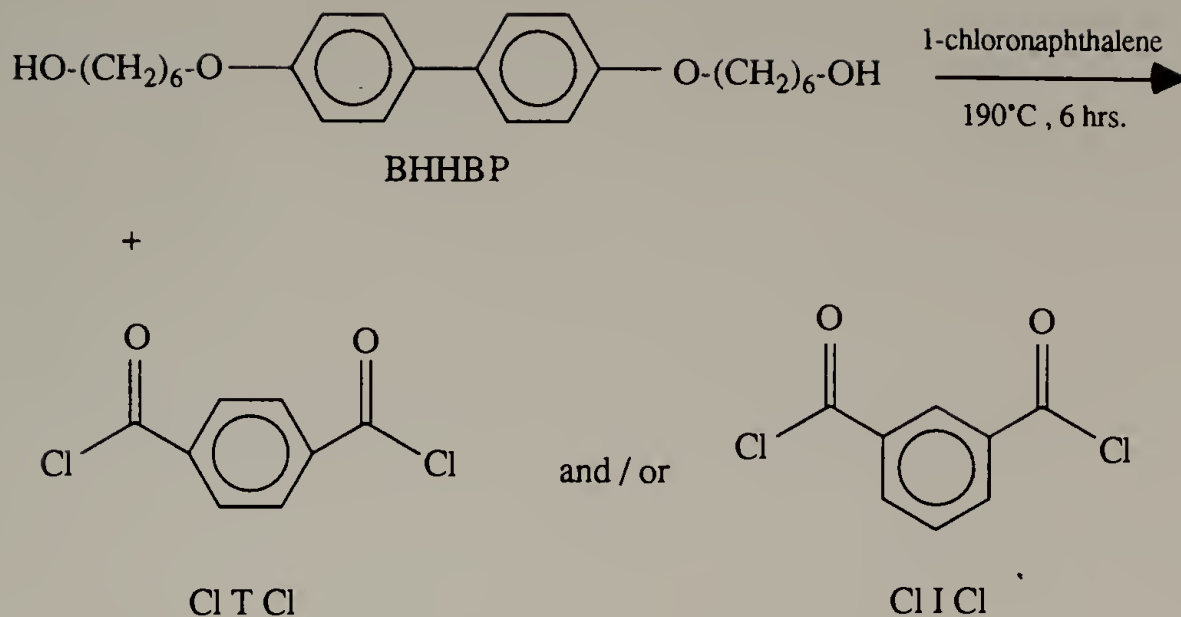


Figure 2.2: Scheme I, the copolymerization of BHHBP with terephthaloyl chloride and/or isophthaloyl chloride

Table 2.1: Mole ratios of diacid chloride to BHHBP (0.5) for polymers prepared following Scheme I

Polymer	Mole ratio of Cl T Cl	Mole ratio of Cl I Cl
I 1	0.5	0.0
I 2	0.33	0.17
I 3	0.17	0.33
I 4	0.0	0.5

The second approach evaluates the copolymerization of a second mesogenic monomer, 4,4'-(terephthaloyldioxy)dibenzoyl dichloride with BHHBP, Scheme II, as represented on the next page in Figure 2.3. The influence of a second mesogen on the relative stability of the highly ordered smectic phase observed for BHHBP was also examined.

The thermal and morphological characterization of these polymers by cross-polarized optical microscopy (CPOM) and differential scanning calorimetry (DSC) will be discussed in relation to wide-angle X-ray diffraction (WAXD) data obtained on drawn fibers.

Scheme II

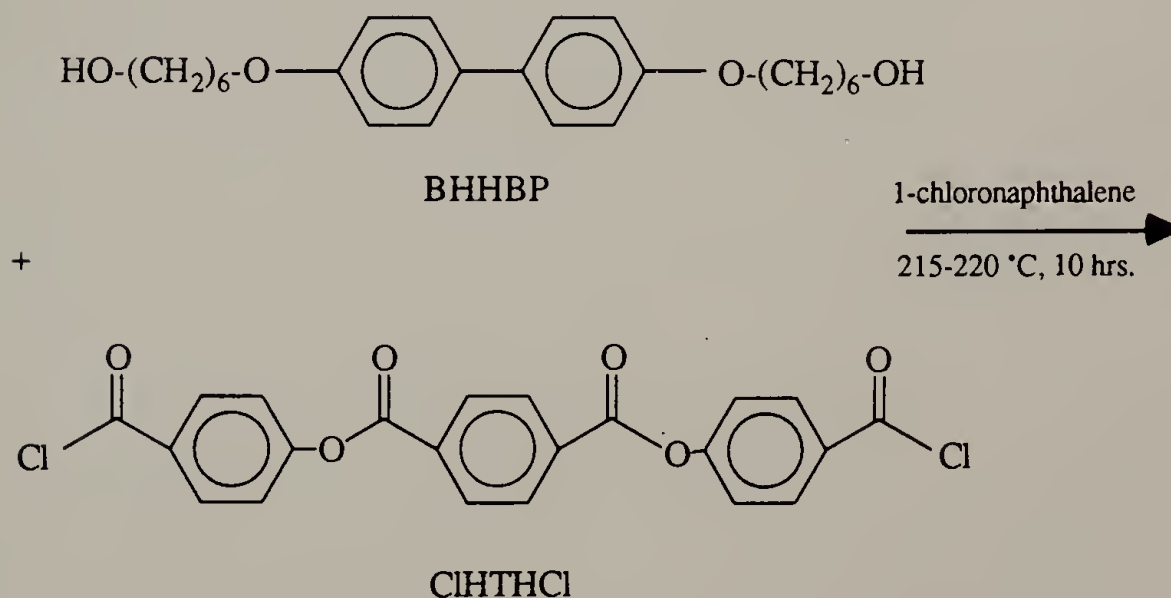


Figure 2.3: Scheme II, the copolymerization of BHHBP with mesogenic monomer 4,4'-(terephthaloyldioxy)dibenzoyl dichloride, ClHTHCl

Experimental

Materials

All chemicals were obtained from the Aldrich Chemical Co.. Isophthaloyl chloride was vacuum distilled and terephthaloyl chloride was sublimed before using. The reaction solvent, 1-chloronaphthalene, was vacuum distilled over CaH_2 . Other reagents and recrystallization solvents were previously stored over activated 3-4 Å molecular sieves.

Monomer Synthesis

Synthesis of 4,4'-bis(6-hydroxyhexoxy)-biphenyl,¹⁴: In a 1 l three neck round-bottom flask fitted with a condenser, pressure equalizing addition funnel, inert gas inlet and magnetic stirrer, was added 0.5 l of absolute ethanol and 32.0 g (0.8 moles) of NaOH. Purified Ar was bubbled through the solution for 15 minutes. Subsequently 37.2 g (0.2 moles) of 4,4'-dihydroxy biphenyl was added maintaining the bubbling of Ar for 15 more minutes at ambient temperature to prevent oxidation. The resulting slurry is heated to reflux, and 122.2 g (0.88 moles) of 6-chlorohexanol previously purged with Ar is added slowly. The reaction mixture is refluxed for 24 hours, cooled to room temperature and poured into 1 l of distilled ice water. The crude solid was washed twice with distilled water, acidified to pH=5-6 with HCl and filtered. The solid product was washed with distilled water to pH=7, dried and recrystallized twice from dioxane. The recrystallized product was then vacuum dried at 110 °C for 24 hours. m.p.=179 °C, yield 70%. Elemental analysis; Calculated for $\text{C}_{24}\text{H}_{34}\text{O}_4$: C, 74.57% ; H, 8.87%. Found: C, 74.53% ; H, 8.85%.

Synthesis of 4,4'-(terephthaloyldioxy)dibenzoyl dichloride:¹⁵ In a 2 l three neck round-bottom flask fitted with a pressure equalizing addition funnel, gas inlet, and mechanical stirrer was added 0.8 l of 0.4 N Na_2CO_3 and 52.48 g (0.38 moles) of *p*-

hydroxybenzoic acid. The pH of the solution was adjusted with 0.4 N Na_2CO_3 to a pH ≈ 8 . A solution of 32.48 g (0.16 moles) of terephthaloyl chloride in 0.35 l of CHCl_3 was sequentially added, via a addition funnel, dropwise into a vigorously stirred reaction pot over a 1 hour period. The reaction solid was then filtered and washed with distilled water several times. The solid was then placed in a 2 l Erlenmeyer flask and was acidified with 1 N HCl to pH=3-4. The mixture was then filtered, washed with distilled water, and dried in vacuum at 110°C overnight. The yield for preparation 4,4'-(terephthaloyldioxy)dibenzoic acid was 95%.

In a 1 l three neck round-bottom flask fitted with a condenser, inert gas inlet, and magnetic stirrer, was added 20 g (0.492 moles) of 4,4'-(terephthaloyldioxy)dibenzoic acid, 0.4 l anhydrous toluene, 0.12 l thionyl chloride, and 3 ml of dimethyl formamide. The solution was allowed to reflux for 2 hours or until dissolution. The yellow solution was cooled to room temperature, filtered, washed with excess toluene, and dried in a dessicator under vacuum overnight. The white powder was then recrystallized in CHCl_3 . m.p. 224°C , yield 74%. ^1H NMR (d-DMSO ppm): 7.47 (d, 4H), 8.05 (d, 4H), 8.33 (s, 4H). Elemental analysis; Calculated for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Cl}_2$: C, 59.61%; H, 2.73%; Cl, 16.00%. Found: C, 59.54%; H, 2.71%; Cl, 15.92%.

Polymer Synthesis

All polymers were prepared in a dry Schlenk tube fitted with a condenser and magnetic stirrer. The concentration of monomers to reaction solvent, 1-chloronaphthalene, was 0.1 g/ml. An example of a polymer prepared from Scheme I (I 2), involved charging a 50 ml Schlenk tube with 0.5000 g (1.2935 mmole) of BHHBP, 0.1746 g (0.8602 mmole) of terephthaloyl chloride, 0.0880 g (0.4333 mmole) of isophthaloyl chloride and 7.6 ml of 1-chloronaphthalene. The reaction mixture was maintained between $190\text{-}200^\circ\text{C}$ under a slow stream of dry Ar for 6 hrs. and

precipitated in toluene. The solid was redissolved in CHCl_3 and reprecipitated in MeOH followed by Soxhlet extraction in refluxing MeOH for 2 days, vacuum dried at $110\text{ }^\circ\text{C}$ for 2 days, giving a yield of 85%, and inherent viscosity for I 2 in trifluoroacetic acid at $30\text{ }^\circ\text{C}$ was 1.50 g/dl, I 1 1.62 g/dl; I 3 1.53 g/dl; I 4 1.58 g/dl. ^1H NMR (CDCl_3 ppm) for I 1-4 had many similar resonance peaks except for the peaks associated with aromatic protons, therefore frequency, (multiplicity, integration) for I 2 - I 4 will be for these aromatic protons; I 1 1.60 (m, 9H), 1.82 (m, 7H), 4.05 (m, 4H), 4.38 (m, 4H), 6.97 (d, 4H) 7.46 (d, 4H), 8.05 (s, 4H); I 2 6.97 (d, 4H) 7.46 (m, 5H), 8.05 (s, 4H) 8.19 (d, 2H), 8.71 (s, 1H); I 3 6.97 (d, 4H) 7.46 (m, 5H), 8.05 (s, 4H) 8.19 (d, 2H), 8.71 (s, 1H); I 4 6.97 (d, 4H) 7.46 (m, 5H), 8.19 (d, 2H), 8.71 (s, 1H); Elemental analysis; Calculated for (I 2) $\text{C}_{32}\text{H}_{36}\text{O}_6$: C, 74.39%; H, 7.02%. Found: C, 74.27%; H, 6.98%; Cl, 0.0%.

The polymer prepared in Scheme II (I-2), involved charging a 50 ml Schlenk tube with 0.5000 g (1.2935 mmole) of BHHBP, 0.5733 g (1.2935 mmole) of ClHTHCl, and 11 ml of 1-chloronaphthalene. The reaction mixture was maintained between $215\text{-}220\text{ }^\circ\text{C}$ under a slow stream of dry Ar for 10 hrs. and precipitated in toluene. The solid was redissolved in trifluoroacetic acid and reprecipitated in acetone followed by Soxhlet extraction in refluxing acetone for 2 days, vacuum dried at $110\text{ }^\circ\text{C}$ for 2 days, giving a yield of 87%, and inherent viscosity in trifluoroacetic acid at $30\text{ }^\circ\text{C}$ was 1.05 g/dl. ^1H NMR (CF_3COOD ppm): 2.17 (s, 16H), 4.68 (s, 8H), 7.03 (d, 4H), 7.50 (m, 8H), 8.33 (d, 4H), 8.55 (s, 4H) 4. Elemental analysis; Calculated for $\text{C}_{46}\text{H}_{44}\text{O}_{10}$: C, 72.99%; H, 5.86%. Found: C, 72.85%; H, 5.84%; Cl, 0.0%.

Characterization Methods

The elemental analysis was performed by the Microanalysis Laboratory at the University of Massachusetts. Inherent viscosities, IVs, for all polymers were determined at $30\text{ }^\circ\text{C}$ in trifluoroacetic acid, using a Cannon-Ubbelohde viscometer. The

polymer concentration was 0.5 g/dl. Proton nuclear magnetic resonance, ^1H NMR, spectra for all compounds were recorded on a Varian XL-200 operating at 200 MHz in deuterated solvents. ^1H NMR spectra for polymer solutions in CF_3COOD were recorded with the spectral width set at -900. CPOM was performed on a Carl Zeiss Ultraphoto II polarizing microscope equipped with a Linkham Scientific Instruments TMS 90 temperature controller and a TMH 600 hot stage. The hot stage temperature was calibrated with vanillin and potassium nitrate melting point standard. DSC measurements were conducted with a Perkin-Elmer DSC-7 on samples ranging from 7-10 mg. The temperature and power ordinates of the DSC were calibrated with respect to the known melting point and heat of fusion of a high purity indium standard supplied by Perkin-Elmer. For exothermic and endothermic processes the peak temperatures were taken as the transition temperatures. WAXD data were obtained with a fine-focusing X-ray tube equipped with a graphite monochromator and a pinhole collimator or a collimator with two pairs of crossed slits. The detection device used was a Xentronics area detector from Nicolet-Siemens interfaced with a PC for collecting, storing, and analyzing X-ray images.

Results and Discussion

The synthesis of BHHBP, as earlier described by Sato¹⁴, was prepared using a Williamson ether synthesis. This mesogenic monomer has been characterized to exhibit a very stable smetic phase¹. All polymers were prepared in solution of 1-chloronaphthalene (b.p. 259 °C) containing no acid-accepting reagent, but were slowly purged with Ar. The high boiling solvent permitted higher reaction temperature (215-220 °C) than conventional reactions containing a low-boiling acid-accepting reagent. The use of high boiling solvents to yield polymers with high molecular weights was first

described by Billibin¹⁵. The polymers prepared by Scheme I had relatively high inherent viscosity values, greater than 1.5 g/dl and were easily fiber forming. The polymer prepared by Scheme II was also fiber forming with a inherent viscosity value of 1.05 g/dl.

Analysis of Thermotropic Liquid Crystalline Phase Behavior

Cross-Polarized Optical Microscopy. The resulting textures for polymer prepared from Scheme I were difficult to discern from composition I 1 to I 4. The resulting textures appear thread-like, to the eye, as typically observed for other liquid crystalline BHHBP polymers¹. The photographs were less distinctive and were not submitted. The combination of having both a crystalline phase along with a mesophase and a threaded texture which can be similar in nature to a crystalline phase with dense spherulitic structure made the optical characterization difficult. The relative high values for inherent viscosity in combination with the probable existence of a highly ordered phase could account for the observed highly viscous melts when sheared between microscope slides. Although these conditions are not considered advantageous for the development of clear smectic phase types, a highly viscous melt is indicative of a smectic phase type. With the observed threaded texture and high viscous melt under shear correlated with a basic phase-temperature behavior of these materials, we employed differential scanning calorimetry to provide more detailed information about the phase transitions in relation to chemical structure.

Differential Scanning Calorimetry. The second heating and cooling traces recorded by DSC for Scheme I and Series II polymers, Figure 2.4-2.8, are collected in at the end of this Chapter. The resulting transition temperatures and values for enthalpy and entropy associated with the formation mesophase or crystalline phase recorded at 10 °C/min. from the isotropic state are tabulated on the following page in Table 2.2. We

must emphasize that the results are based on scan rate of 10 °C/min., and the measured transitions should be considered dependent on this rate. Evaluation of this rate dependency along with other thermal aging experiments were beyond the scope of this investigation.

The objective of the DSC evaluation was to determine the influence of a kink structure for Series I polymers on the formation of a mesophase relative to a crystalline phase. Polymers I 1 and 2 exhibit only one endothermic transition and a lower temperature endothermic tail indicative of crystalline melt-perfection. The measured value of under cooling ($\Delta (T_C - T_{i-C})$) 30 and 42 respectively, are representative of a crystallization process. The ΔS_{i-C} values for polymer I 1 and 2 indicate a strong tendency for crystallization. Polymer I 2 displayed a significant cold crystallization at 125 °C or a cold "liquid" crystallization and subsequent isotropization with further heating. Polymer I 3 displays two endothermic peaks, the larger peak represents a significant reduction in the melting point in comparison to I 1 and 2. In relation to the smaller endotherm, representing a smectic isotropic transition, is a shallow exotherm depicting cold "liquid" crystallization. The two endothermic peaks are similar to what have been typically observed for other BHHBP containing polymers⁹⁻¹². This particular results is the evidence for the classification of this polymer as monotropic. The observed undercooling is more representative of the formation of a mesophase than that observed for polymer I 1 and 2. The tendency of I 3 to crystallize under these conditions is significantly hindered. This condition is even better represented in polymer I 4, which has an $\Delta (T_C - T_{i-S})$ value of 8 °C. The relatively high ΔS_{i-S} values for polymers I 3 and 4 indicate the formation of a highly ordered phase. We speculated that perhaps the lower value is associated with an increase in the percentage of mesophase formation relative to crystallization. Based on these results, we conclude that the incorporation of

Table 2.2: Results of the thermal transitions for the Series I and II as recorded by DSC at 10 °C/min

Polymer	T _{S-i}	T _C	T _{i-s}	T _{i-c}	$\Delta(T_C - T_{i-s})$	$\Delta(T_C - T_{i-c})$	ΔH_{i-s} (kJ/mol)	ΔS_{i-s} (J/mol*K)
I 1	—	149	—	119	—	30	13.3	33.9
I 2	—	146	—	104	—	42	13.1	34.6
I 3	111	118	104	—	14	—	6.0	15.9
I 4	121	—	115	—	6	—	7.3	18.9
II	—	116,126	—	89	—	31*	16.6	45.8

ΔH and calculated ΔS values are associated with the exothermic peak observed on cooling

* T_C was taken as the median between the two endothermic peaks.

isophthaloyl units into BHHBP polymer based on I 1 "frustrate" or weaken the dominate crystallization process allowing for stabilization of the mesophase. These conclusions are not all inclusive and more detailed evaluation would appear to be necessary.

The DSC trace for Series II polymer was very similar in nature to polymer I 1. The second heating trace displays two unresolved endothermic peaks, similar to the main endothermic peak and shoulder of polymer I 1. These endothermic peaks being representative of two different crystalline morphologies. For polymer II the amount of undercooling seems equal in proportion, yet the melting temperature is reduced by nearly 30 °C. The melting temperature for a polymer containing the HTH mesogen connected to 1,6-hexanediol spacers, having a similar inherent viscosity, melts at approximately 260 °C. The melting behavior of the polymer II therefore seems to be dominated by the influences of BHHBP mesogen, yet the packing appears to be frustrated relative to T_C value of polymer I 1. The tendency for crystallization of polymer II seems on the same order as for polymer I 1, based on the $\Delta(T_C - T_{i,S})$ value of 31 °C. In terms of the objective, Scheme I and II seem to shed light on structural aspects which influence the two opposing ordering processes that are occurring in these BHHBP containing polymers. We therefore, turned to the evaluation of these materials by WAXS for more detailed information of the influence Scheme I and II has on ordering of BHHBP mesogen.

Wide-Angle X-Ray Scattering. Scheme I and II polymers were melt drawn into fibers suitable WAXD. These fibers were drawn by hand at a temperature just above the exothermic peak observed on cooling by DSC. The resulting X-ray diffraction patterns for the drawn fibers, Figures 2.10 - 2.13, were obtained at room temperature and are collected at end of this Chapter. The X-ray diffraction patterns for polymers I 1 - I4 showed intense layer reflections of the first and second order. For polymers I 1 and I 4, the diffraction patterns were representative of a smetic A phase. The X-ray diffraction patterns of polymer I 2 showed a tilted highly ordered smetic phase, which has a tilt

angle of about 12 - 13 degrees (ϕ). The tilt angles for the polymer I 3 were calculated by two methods in collaboration with Fisher⁵. In the first method, he measured directly the azimuthal angle of the layer reflection. The second method, he calculated a molecularly simulated length of the BHHBP molecule and then compared this data with the measured *d*- spacing.

The introduction of isophthaloyl units in Scheme I has influenced the tendency for BHHBP polymer, such as polymer I 1, to crystallize. The DSC results indicate lower melting points for polymers I 2 - I4 and a greater tendency for the formation of the highly ordered mesophase. From the WAXD data, we mainly observed smetic A phase type, with the exception of the tilted reflections observed for polymer 2. The assignment of the phase type for polymer 2 would require further investigation, but incorporation of a small percentage of isophthaloyl units appears to allow for a greater degree of ordering. The X-ray diffraction pattern for polymer I 3 was similar to that of I 4 and was not submitted.

The X-ray diffraction pattern for polymer II is shown in Figure 2.14. This pattern is similar to those shown for the other polymers in Series I representing a smetic A phase. The results of both WAXD and DSC seem to indicate a subsequent mesophase which is influenced by the BHHBP mesogen.

Conclusions

Polymers based on BHHBP were prepared following Scheme I and II and were characterized as smetic thermotropic liquid crystalline polyesters. Scheme I: The incorporation of nonlinear isophthaloyl units significantly decreased the strong tendency for crystallization and increased the stability for mesophase formation. The evidence for these tendencies are represented in the DSC traces shown in Figures 2.5 - 2.8. The

resulting WAXD patterns shown in Figure 2.9 - 2.11 reveal predominately smetic A phase types, with the exception of a slightly tilted smetic phase for polymer I 2.

Based on our finding there are certain aspects relating to the thermodynamics of Series I and II polymer which warrants future consideration. Therefore, kinetic and isothermal studies would be recommended, these studies should give us a better handle on the relative mesophase stability of BHHBP in relation to chemical structure.

Figure 2.4: DSC traces for polymer I 1 recorded at 10°/min.: (a) heating; (b) cooling

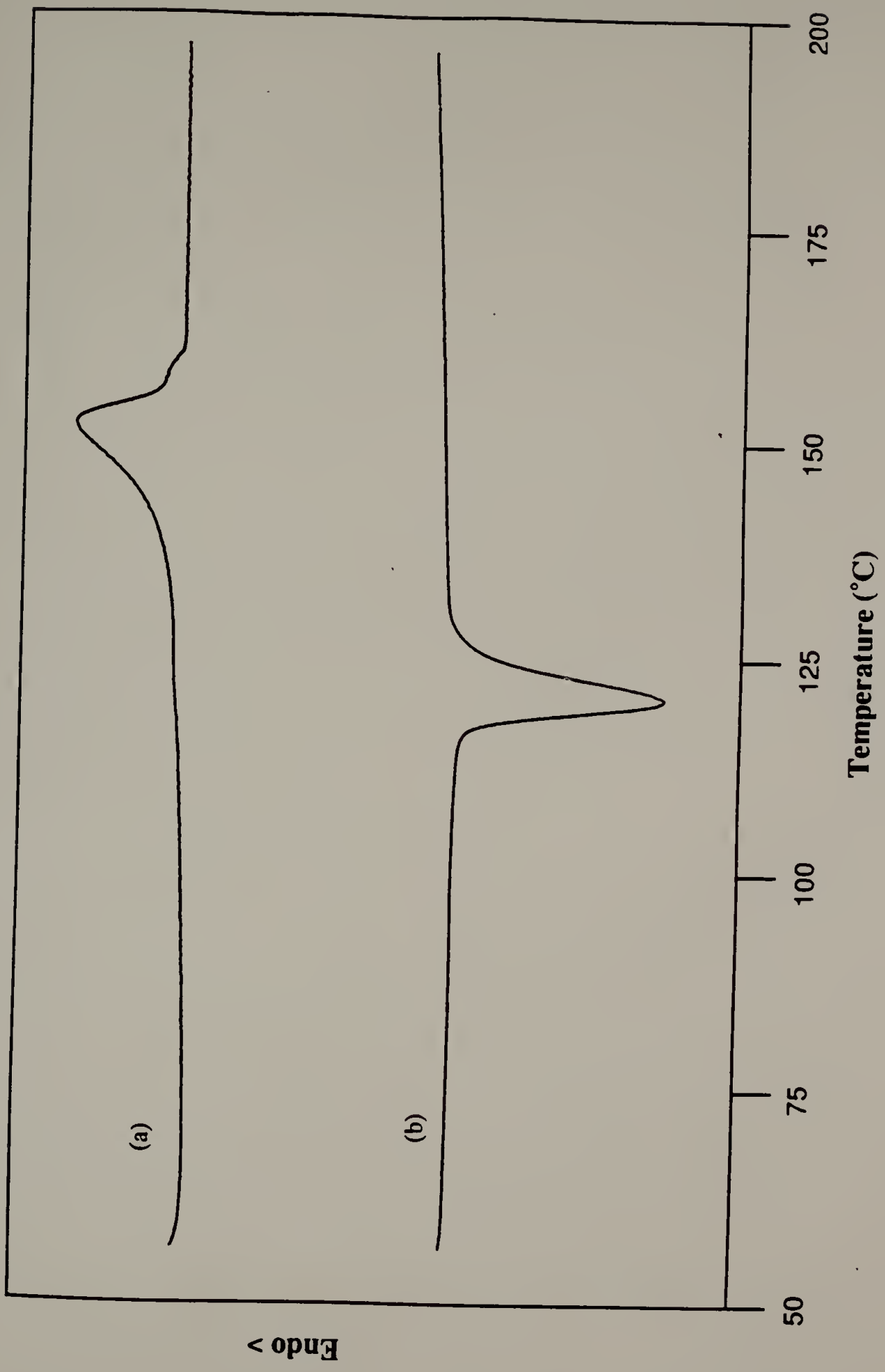


Figure 2.5: DSC traces for polymer 1 2 recorded at 10°/min.: (a) heating; (b) cooling

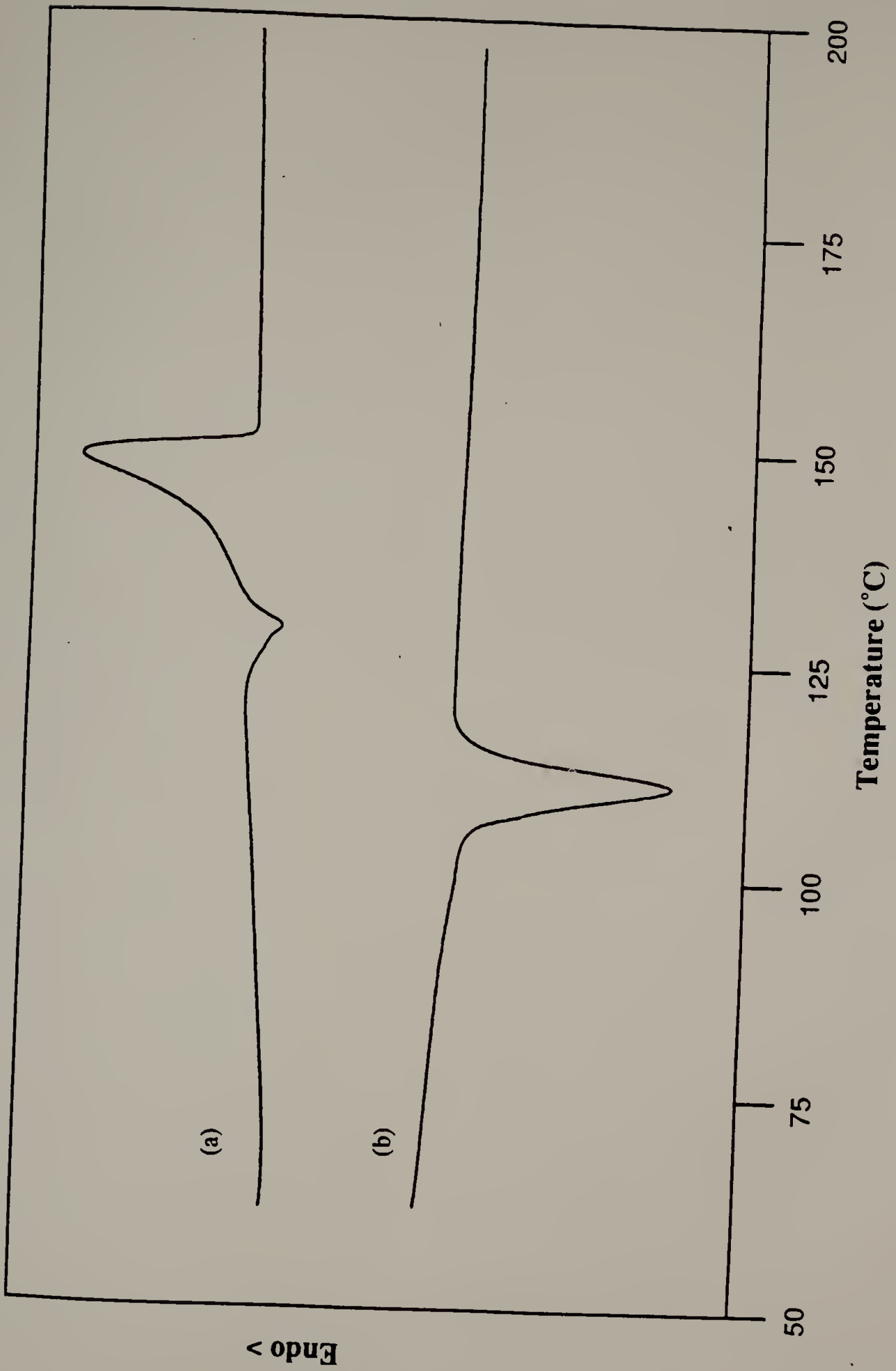


Figure 2.6: DSC traces for polymer I 3 recorded at 10°/min.: (a) heating; (b) cooling

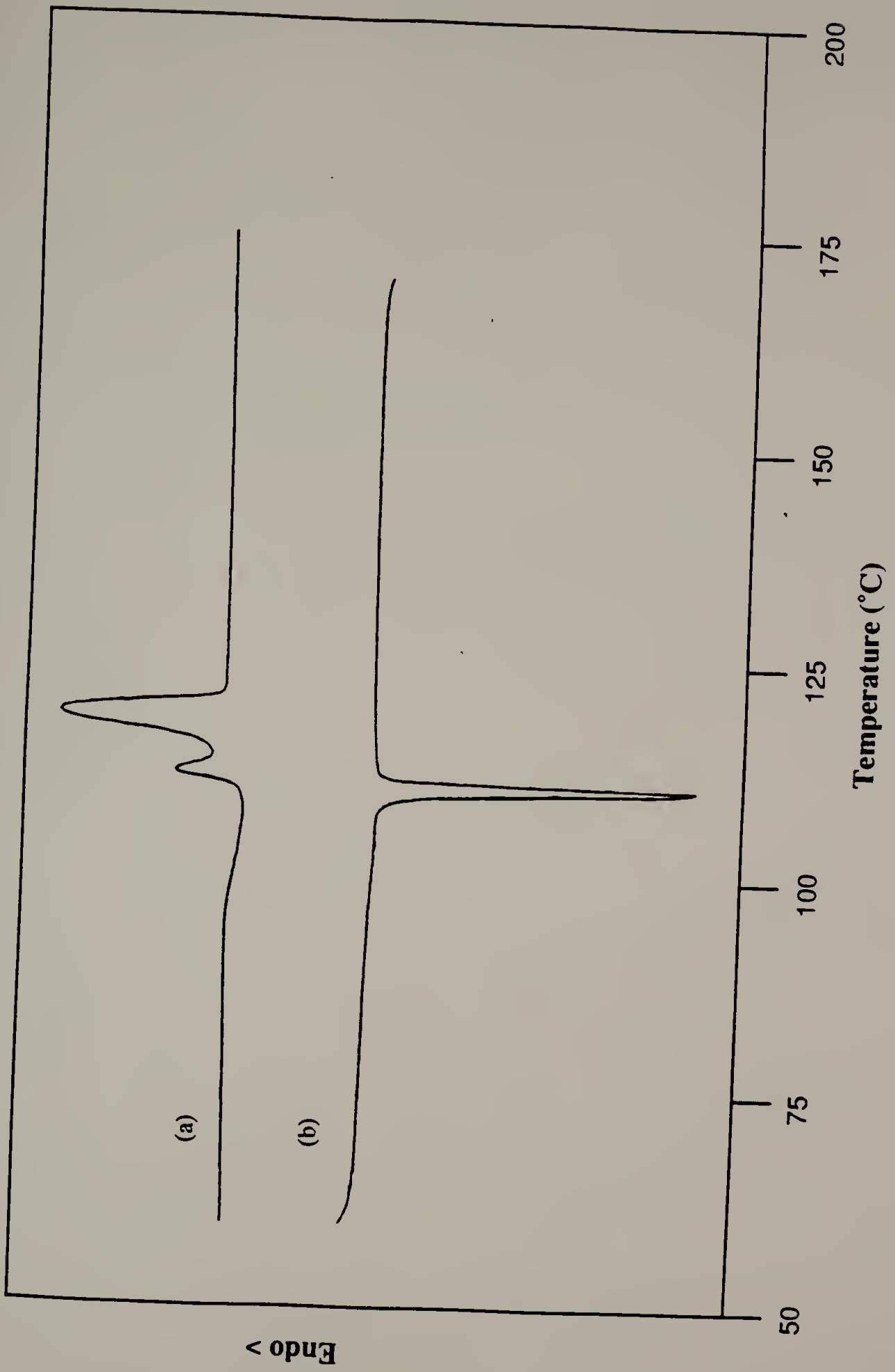


Figure 2.7: DSC traces for polymer I 4 recorded at 10°/min.: (a) heating; (b) cooling

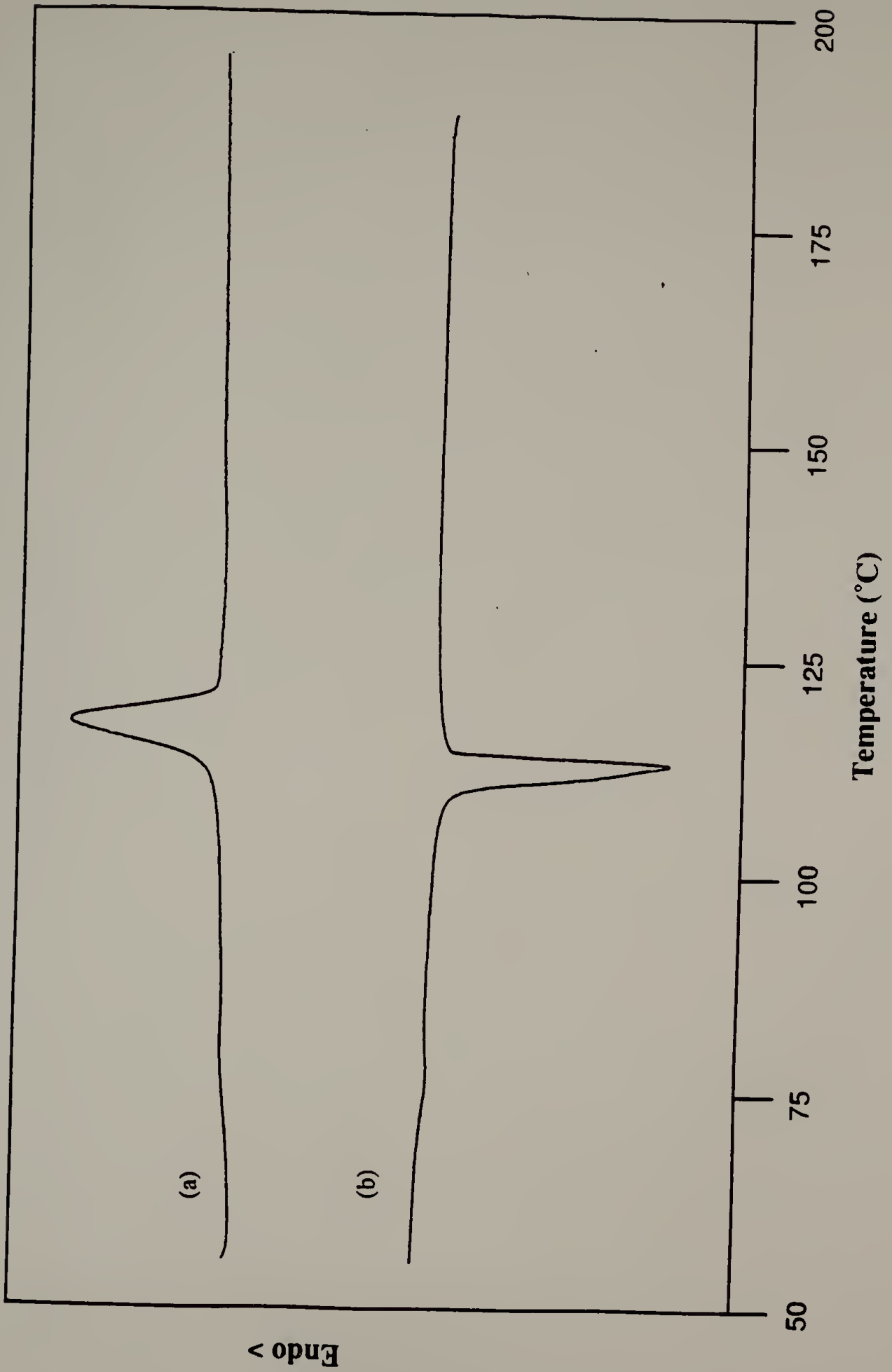


Figure 2.8: DSC traces for polymer II recorded at 10°/min.: (a) heating; (b) cooling

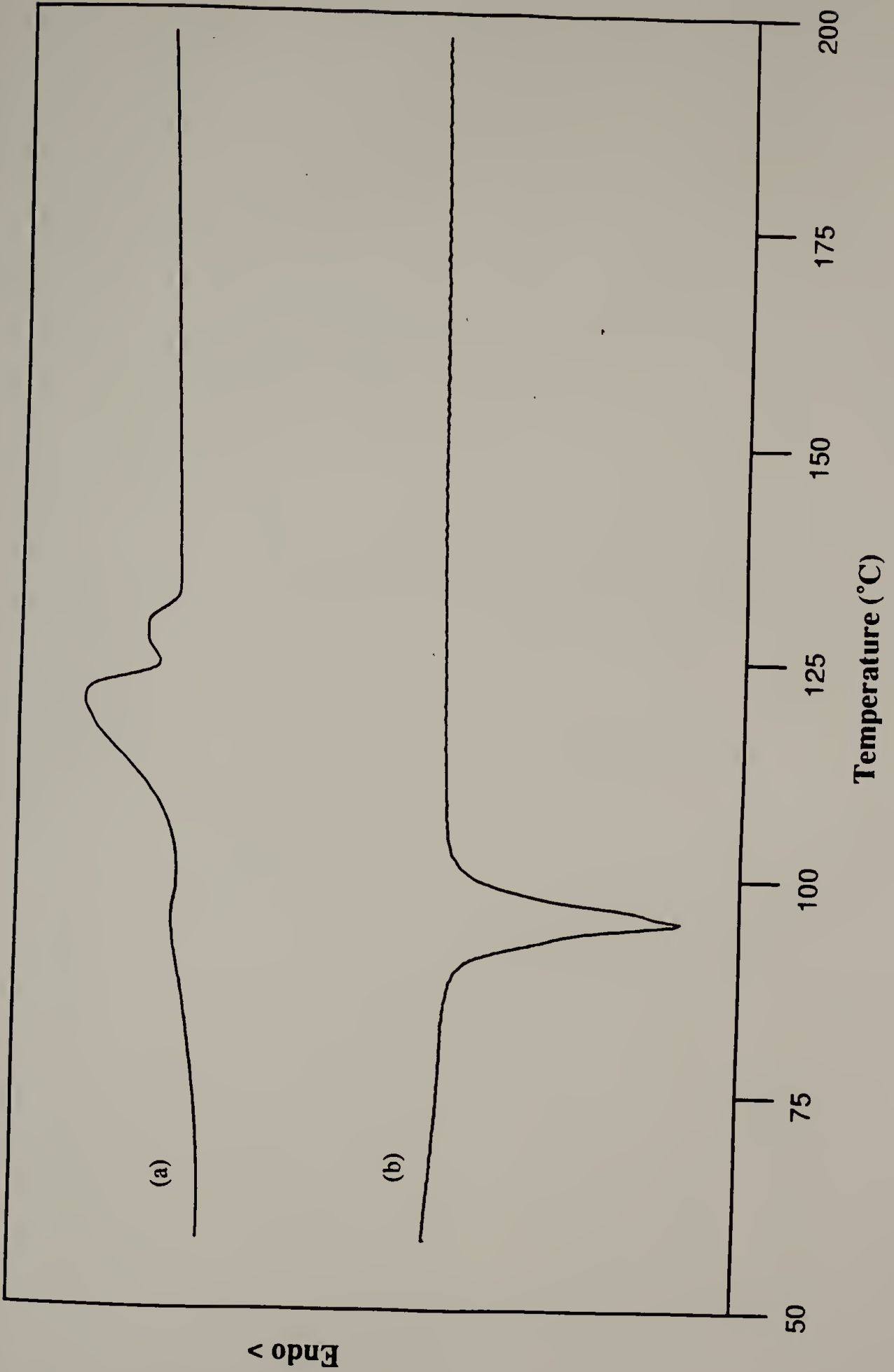




Figure 2.9: WAXD pattern for a drawn fiber of polymer I 1; smetic A

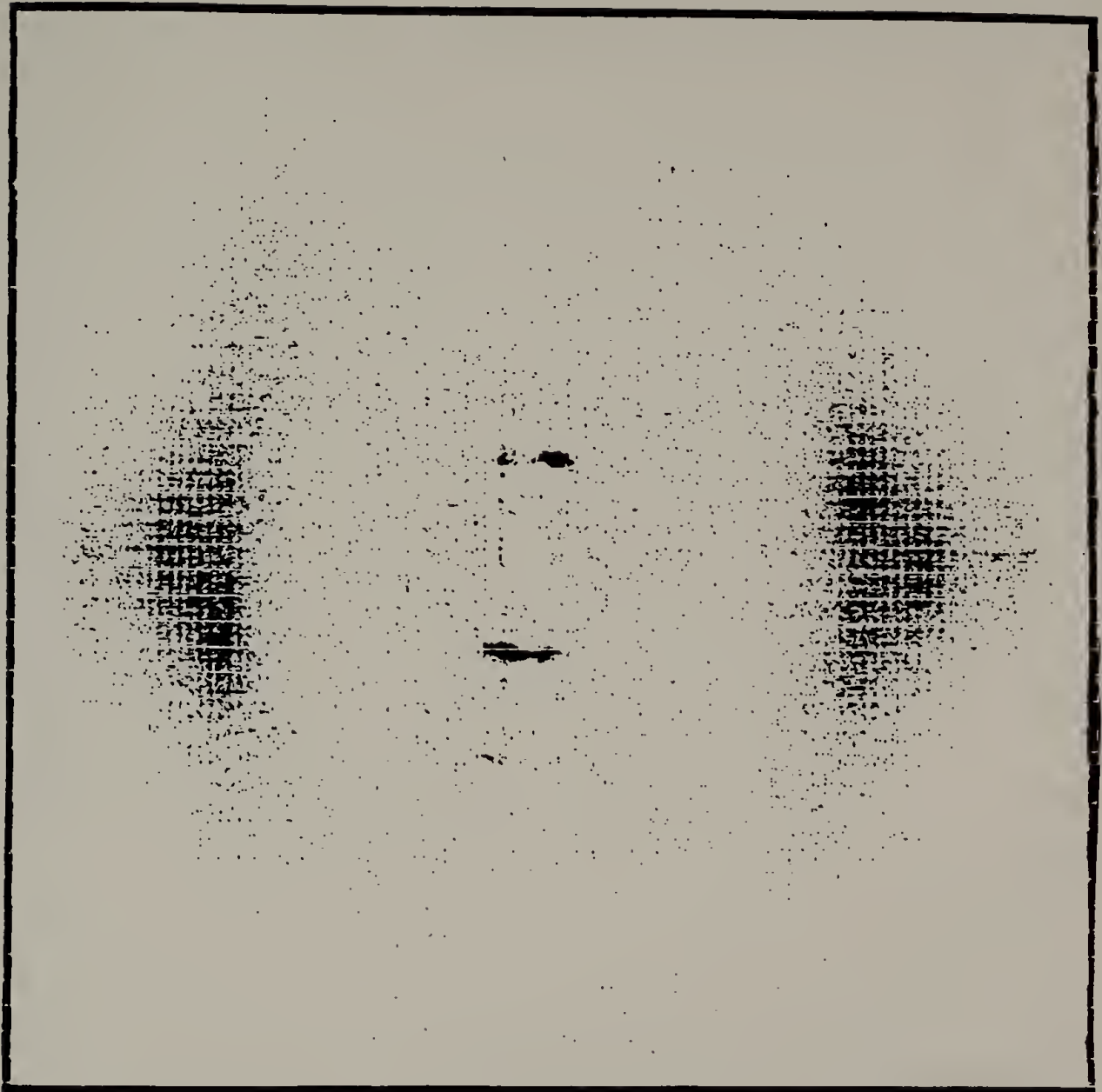


Figure 2.10: WAXD pattern for a drawn fiber of polymer I 2;
undetermined smetic phase type

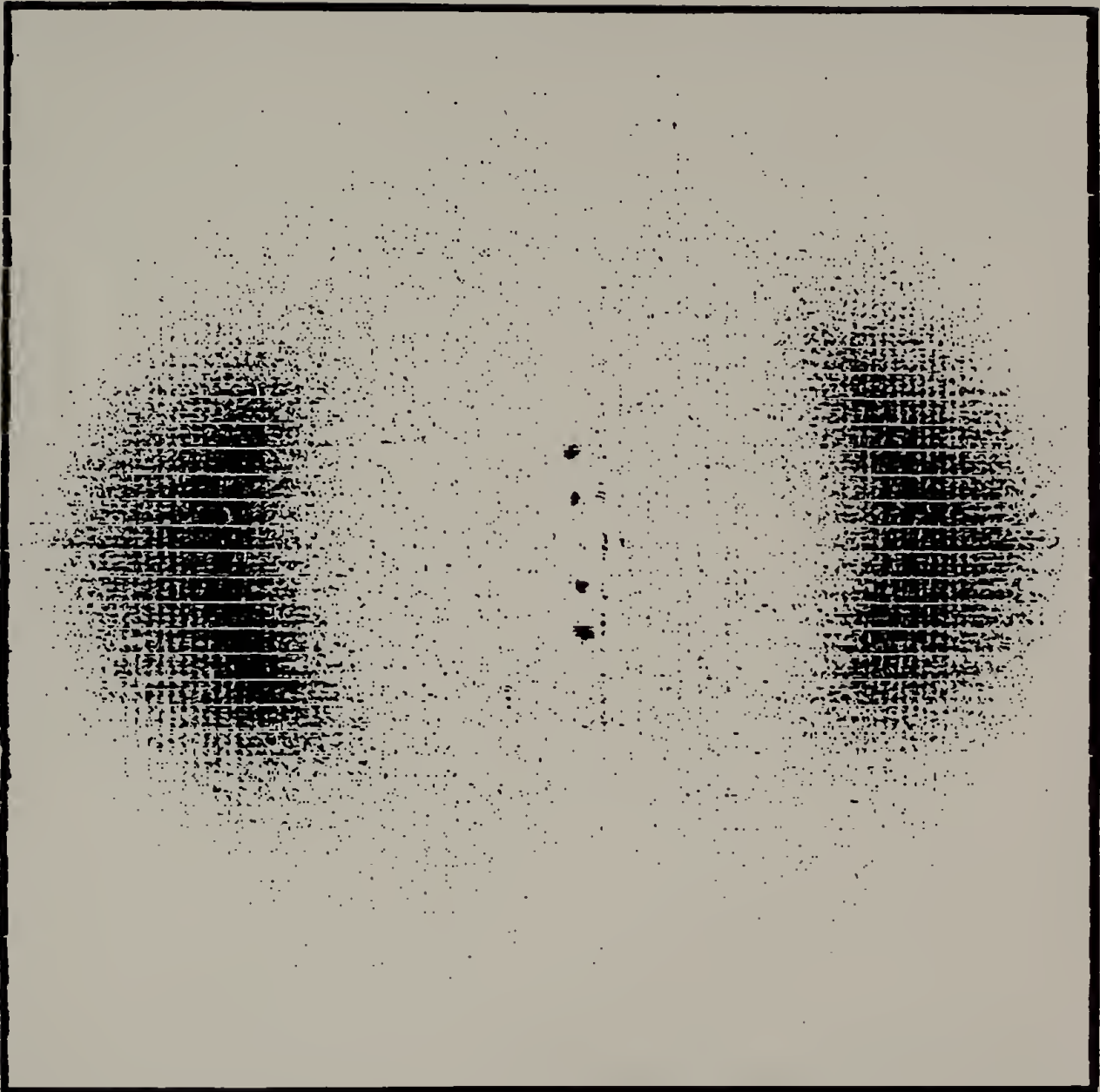


Figure 2.11: WAXD pattern for a drawn fiber of polymer I 4; smetic A

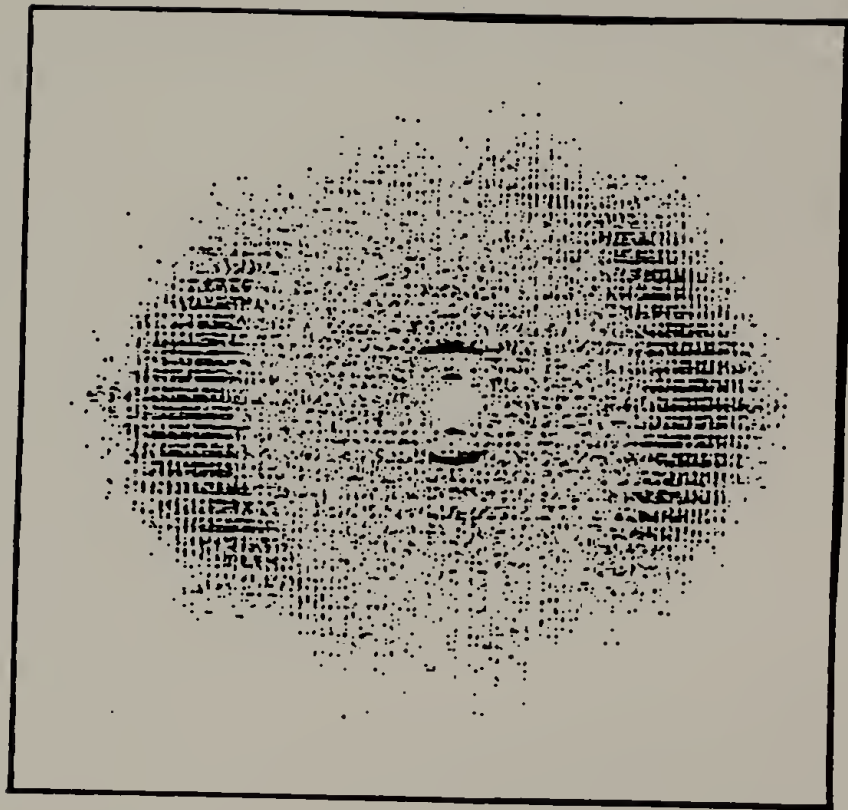


Figure 2.12: WAXD pattern for a drawn fiber of polymer II; smectic A

References

1. Smyth, G., Pollack, S.K., Hsu, S.L., and MacKnight, W.J., *Mol. Cryst. Liq. Cryst.*, **7**(6), 839-861 (1990)
2. Reck, B. and Ringsdorf, H., *Makromol. Chem., Rapid Commun.*, **6**, 291 (1985)
3. Zentel, R. and Reckert, G., *Makromol. Chem.*, **187**, 1915 (1986)
4. Bualek, S. and Zentel, R., *Makromol. Chem.*, **189**, 791 (1988)
5. Fisher, H., Karasz, F.E., and MacKnight, W.J., To be published.
6. Sato, M., Nakatsuchi, K., and Ohdatsu, Y., *Makromol. Chem. Rapid Commun.*, **7**, 231-234 (1986)
7. Sato, M., Nakatsuchi, K., and Ohdatsu, Y., *Makromol. Chem. Rapid Commun.*, **8**, 383-386 (1987)
8. Sato, M., Nakatsuchi, K., and Ohdatsu, Y., *J. Polym. Sci., Part A: Polym. Chem.*, **26**(11), 3077-?? (1988)
9. Smyth, G., Valles, E.M., Pollack, S.K., Grebowicz, J., Stenhouse, P.J., Hsu, S.L., and MacKnight W.J., *Macromolecules*, **23**, 3389 (1990)
10. Pollack, S.K., Shen, D.Y., Hsu, S.L., Wang, Q., and Stidham, H.D., *Macromolecules*, **22**, 551 (1989)
11. Stenhouse, P.J., Valles, E.M., MacKnight, W.J., and Kantor, S.W., *Macromolecules*, **22**, 1467 (1989)
12. Pollack, S.K., Smyth, G., Stenhouse, P.J., Papadimitrakopoulos, F., Hsu, S.L., and MacKnight, W.J., Submitted for publication.
13. Shaffer, T.D., and Percec, V., *J. Polym. Sci., Lett. Ed.*, **23**, 185 (1985)
14. Sato, M., Jadhav, J.Y., Mallon, J.J., and Kantor S.W., to be published.
15. Bilibin, A.Yu., Schepelevsky, A.A., Frenkel, S.Ya., and Skorokhodov, S.S., *MACRO IUPAC, Florence, Preprints*, **2**, 232-233 (1980)

CHAPTER 3

PREPARATION AND CHARACTERIZATION OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS CONTAINING TRIAD MESOGEN

Introduction

For more than a decade thermotropic main chain liquid-crystalline polymers, TLCPs, with alternating semi-rigid and flexible units along the backbone have drawn considerable attention. The preparation and characterization of these polymers are well documented in numerous reviews.¹⁻³

TLCPs are characterized by their unique high local (microscopic) orientational ordered domains at specific temperature regimes in the melt. When these domains are oriented in an elongation flow field and retained in the solid state, they exhibit high specific tensile strength and modulus. The alignment in the direction of the flow field also offers a unique reduction in melt viscosity, as reviewed by Wissbrun.⁴ The commercialization of TLCPs as pure materials has had limited success, mainly inhibited by the high cost of aromatic monomer synthesis, and lack of a thorough understanding of their flow properties in controlling the unfavorable high anisotropy at weld lines. Therefore, there has been an increased interest in utilizing these unique high anisotropic materials as "in situ composites" through blending with conventional thermoplastics, TPs,⁵ and utilizing these blends in applications where glass-fiber reinforcing additives could not be used during processing. The new class of self-reinforced composite

materials would be an attractive means of balancing both properties and cost-effectiveness.

The research efforts to date have naturally focused on blends containing commercially available TLCP systems (Vectra[®], X-7G[®], and Xydar[®]) and have recently been reviewed.⁶⁻⁸ One consistent result has been the brittleness of these blends due to their poor interfacial properties. Poor interfacial adhesion is an inherent quality in all blends containing TLCPs, which is considered detrimental for obtaining enhanced mechanical properties in a multicomponent system. For these blends to be useful commercially, the issue of adhesion and control of the resulting morphology must be resolved.

The commercially available TLCPs are comprised of mainly aromatic random copolyesters prepared in melt at temperature exceeding 300 °C. At these temperatures, transesterification is prevalent and the resulting pseudo equilibrium structure is ill defined having a distribution of mesogenic segment lengths. These materials are also characterized by high melt flow temperature, low solubility, and decomposition before isotropization. For a more fundamental investigation into TLCP/TP blends, we preferred the evaluation of a more defined TLCP structure, fiber forming qualities, and phase transition temperatures below 300 °C.

The main objective of this chapter is to discuss the preparation and characterization of TLCPs which would promote greater interfacial adhesion in blends with PET and PBT. The synthesis strategy was to copolymerize the triaromatic "triad" mesogenic monomer, 4,4'-(terephthaloyldioxy)dibenzoyl dichloride shown on the next page in Figure 3.1, with the various flexible spacers also listed on the next page in Table 3.1.

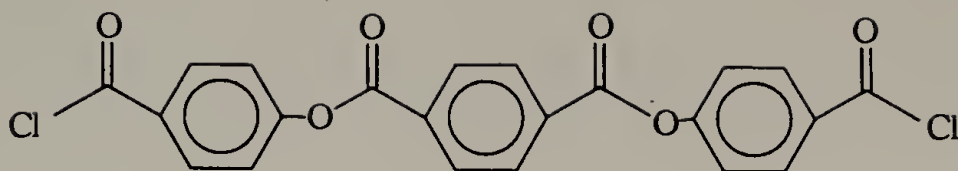


Figure 3.1: Mesogenic monomer 4,4'-(terephthaloyldioxy)dibenzoyl dichloride, ClHTHCl

Table 3.1: Flexible spacers to be copolymerized with ClHTHCl

Flexible Spacer	Abbr.
bis(2-hydroxyethyl)terephthalate	BHET
bis(4-hydroxybutyl)terephthalate	BHBT
1,4-butanediol	BDO
1,6-hexanediol	HDO
1,10-decanediol	DDO

Polymers were prepared in solution following Scheme I, as represented in Figure 3.2, where the composition of flexible spacers evaluated are listed on the following page in Table 3.2.

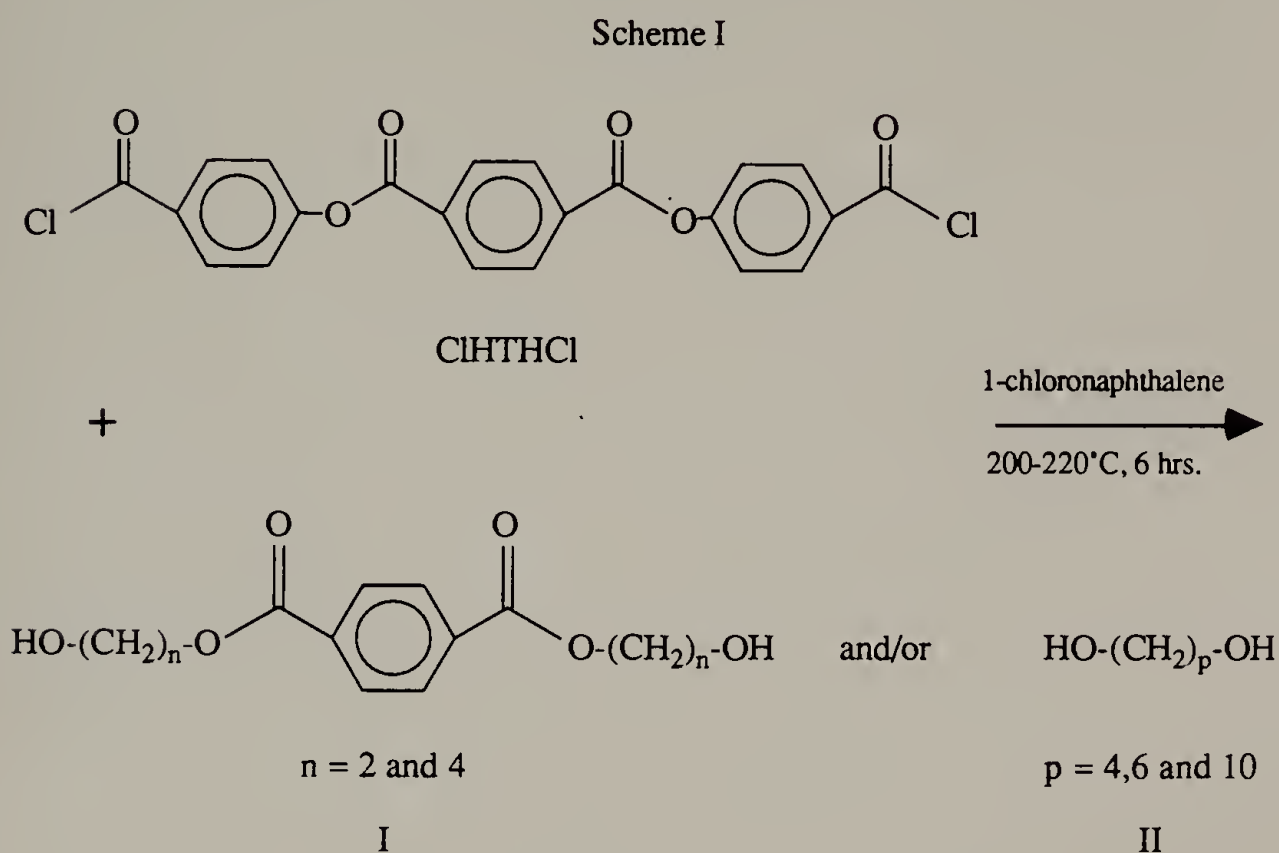
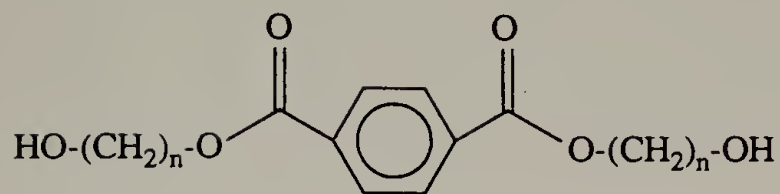


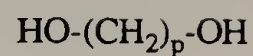
Figure 3.2: Scheme I, evaluation of various flexible spacers with ClHTHCl

Table 3.2: Polymers (A-H) prepared following Scheme I



$n = 2$ and 4

I



$p = 4, 6,$ and 10

II

Polymer	n	p	% I	% II
A	2	0	100	0
B	4	0	100	0
C	2/4	0	50/50	0
D	4	4	75	25
E	4	6	75	25
F	4	10	75	25
G	4	4	50	50
H	4	6	50	50

This "triad" mesogenic structure has been incorporated into a variety of TLCPs as previously reported in our laboratory.⁹ Therefore, the objective was to use this well studied mesogen and evaluate flexible spacers possessing a chemical structure, which would promote enhanced interfacial adhesion and be considered liquid crystalline in the processing temperature window of PET and PBT (250-300 °C).

The thermal and morphological characterization of these polymers by cross-polarized optical microscopy (CPOM) and differential scanning calorimetry (DSC) constitute the primary screening program. From these results, candidates were selected and will be further discussed in relation to wide-angle X-ray diffraction (WAXD) data obtained on drawn fibers.

Experimental

Materials

All chemicals were obtained from the Aldrich Chemical Co. The aliphatic diols were distilled over CaH₂ and then previously stored over activated 4 Å molecular sieves. Terephthaloyl chloride was purified by sublimation. Bis(2-hydroxyethyl)terephthalate was purchased from Polyscience Inc. and was twice recrystallized from ethyl acetate. 1-Chloronaphthalene was vacuum distilled over CaH₂. THF was pre-dried over CaCl₂ and then distilled over sodium-benzophenone. Other reagents and recrystallization solvents were previously stored over activated 3-4 Å molecular sieves.

Monomer Synthesis

Synthesis of 4,4'-(terephthaloyldioxy)dibenzoyl dichloride:¹⁰ In a 2 l three neck round-bottom flask fitted with a pressure equalizing addition funnel, gas inlet, and mechanical stirrer was added 0.8 l of 0.4 N Na₂CO₃ and 52.48 g (0.38 moles) of *p*-

hydroxybenzoic acid. The pH of the solution was adjusted with 0.4 N Na_2CO_3 to a pH ≈ 8 . A solution of 32.48 g (0.16 moles) of terephthaloyl chloride in 0.35 l of CHCl_3 was sequentially added, via a addition funnel, dropwise into a vigorously stirred reaction pot over a 1 hour period. The reaction solid was then filtered and washed with distilled water several times. The solid was then placed in a 2 l Erlenmeyer flask and was acidified with 1 N HCl to a pH=3-4. The mixture was then filtered, washed with distilled water, and dried in vacuum at 110°C overnight. The yield for preparation 4,4'-(terephthaloyldioxy)dibenzoic acid was 95%.

In a 1 l three neck round-bottom flask fitted with a condenser, inert gas inlet, and magnetic stirrer, was added 20 g (0.492 moles) of 4,4'-(terephthaloyldioxy)dibenzoic acid, 0.4 l anhydrous toluene, 0.12 l thionyl chloride, and 3 ml of dimethyl formamide. The solution was allowed to reflux for 2 hours or until dissolution. The yellow solution was cooled to room temperature, filtered, washed with excess toluene, and dried in a desiccator under vacuum overnight. The white powder was then recrystallized in CHCl_3 . m.p. 224°C and yield 74%. ^1H NMR (d-DMSO ppm): 7.47 (d, 4H), 8.05 (d, 4H), 8.33 (s, 4H). Elemental analysis; Calculated for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Cl}_2$: C, 59.61%; H, 2.73%; Cl, 16.00%. Found: C, 59.54%; H, 2.71%; Cl, 15.92%.

Synthesis of bis(4-hydroxybutyl)terephthalate:¹¹ In a 1 l three neck round-bottom flask fitted with condenser/reflux column, pressure equalizing addition funnel, inert gas inlet, and mechanical stirrer, was added 100 g (1.11 moles) of 1,4 -butanediol, 35 ml (0.43 moles) of pyridine, and 200 ml THF. The solution was purged with purified N_2 for 15 minutes. Subsequently 60 g (0.30 moles) of terephthaloyl chloride in 100 ml of THF was added dropwise over a 30 minute period into a vigorously stirred reaction pot.

The cloudy yellow solution was brought to reflux for 1 hr at which time the solution cleared. The yellow solution was then distilled by rotovap at 40°C until half the

original volume of THF remained. The remaining solution was poured over 1 l of ice water. The solid precipitate was then filtered off and dissolved in 300 ml of absolute ethanol. This solution was heated to reflux and hot filtered. The solution was cooled to 15 °C for 5 hrs. The resulting precipitate represented crude product of the 2.5 mer, m.p. 138 °C. The filtrate was further cooled to 0 °C for 12 hrs., filtered, and was then poured over ice water. The resulting precipitate was filtered, dried, and recrystallized twice with ethyl acetate. m.p. 72 °C and yield 65 %. ¹H NMR (CDCl₃ ppm): 1.87 (m, 4H), 1.95 (m, 4H), 3.73 (t, 4H), 4.39 (t,4H), 8.09 (s, 4H). Elemental analysis; Calculated for C₁₆H₂₂O₆: C, 61.92%; H, 7.15%. Found: C, 61.96%; H, 7.15%.

Polymer Synthesis

All polymers were prepared in a dry Schlenk tube fitted with a condenser and magnetic stirrer. The concentration of monomers to reaction solvent, 1-chloronaphthalene, was 0.1 g/ml. An example of a polymer prepared from Scheme I, involved charging a 50 ml Schlenk tube with 0.3500 g (1.1278 mmole) of BHBT, 0.0443 g (0.3748 mmole) of HDO, 0.6665 g (1.5804 mmole) of ClHTHCl, and 7.6 ml of 1-chloronaphthalene. The reaction mixture was maintained between 200-220 °C under a slow stream of dry Ar for 6 hrs. and precipitated in toluene. The solid was redissolved in trifluoroacetic acid and reprecipitated in acetone followed by Soxhlet extraction in refluxing acetone for 2 days, vacuum dried at 110 °C for 2 days, giving a yield of 89%, and inherent viscosity for this polymer in trifluoroacetic acid at 30 °C was 1.34 g/dl. ¹H NMR (CF₃COOD ppm): 2.22 (s, 16H), 4.70 (s, 12H), 7.50 (d, 4H), 8.33 (d, 4H), 8.55 (s, 8H). Elemental analysis; Calculated for C_{35.5}H₃₀O₁₁: C, 67.50%; H, 4.79%. Found: C, 67.41%; H, 4.77%; Cl, 0.0%.

Characterization Methods

The elemental analysis was performed by the Microanalysis Laboratory at the University of Massachusetts. Inherent viscosities, IVs, for all polymers were determined at 30 °C in trifluoroacetic acid, using a Cannon-Ubbelohde viscometer. The polymer concentration was 0.5 g/dl. Proton nuclear magnetic resonance, ^1H NMR, spectra for all compounds were recorded on a Varian XL-200 operating at 200 MHz in deuterated solvents. ^1H NMR spectra for polymer solutions in CF_3COOD were recorded with the spectral width set at -900. CPOM was performed on a Carl Zeiss Ultraphoto II polarizing microscope equipped with a Linkham Scientific Instruments TMS 90 temperature controller and a TMH 600 hot stage. The hot stage temperature was calibrated with vanillin and potassium nitrate melting point standard. DSC measurements were conducted with a Perkin-Elmer DSC-7 on samples ranging from 7-10 mg. The temperature and power ordinates of the DSC were calibrated with respect to the known melting point and heat of fusion of a high purity indium standard supplied by Perkin-Elmer. For exothermic and endothermic processes the peak temperatures were taken as the transition temperatures. WAXD patterns were obtained with a Statton X-ray camera using Ni filtered $\text{Cu K}\alpha$ radiation on drawn fibers.

Results and Discussion

The synthesis of ClHTHCl and the use of high boiling solvents to yield polymers with high molecular weights was first described by Billbin¹⁰. All polymers were prepared in solution of 1-chloronaphthalene (b.p. 259 °C) containing no acid-accepting reagent, but were slowly purged with Ar. The high boiling solvent permitted higher reaction temperature (200-220 °C) than conventional reactions containing a low-boiling acid-accepting reagent. Conditions did permit sufficient removal of HCl to subsequently

yield polymers having high inherent viscosity values ranging from 0.56 to 1.34 dl/g. Polymers having inherent viscosity values greater than 0.7 dl/g were found to be fiber forming, and therefore this value was considered as one of the system requirements for the primary screening program. Polymers prepared with BHET as a monomer or comonomer exhibited inherent viscosity values less than 0.4 dl/g. Reasonable inherent viscosity values for polymers containing BHET were not attainable even with ultra pure monomer and tight stoichiometric control. These findings were similar to the original work of Billibin and co-worker,¹⁰ who could not obtain even moderate inherent viscosity values for HTH copolymers containing ethylene glycol units. In consideration of "induction effects", one would anticipate that the reacting hydroxyl group of ethylene glycol would be more nucleophilic adjacent to another hydroxyl group than to an adjacent ester group. The initial esterification reaction of ethylene glycol can also be represented as a six member ring intermediate structure which would reduce its nucleophilicity due to intramolecular hydrogen bonding. Unfortunately, a detailed investigation towards justifying these explanations for BHET monomer/comonomer systems were beyond the scope of this work.

Analysis of Thermotropic Liquid Crystalline Phase Behavior

The proposed main objective of this chapter, as previously stated, is the preparation and characterization of TLCPs which would promote greater interfacial adhesion in blends with PET and PBT. The purpose for the analysis is to screen various flexible spacers copolymerized with the triad mesogenic monomer, CIHTHCl, which have similarities in chemical structure and satisfy macromolecular structure requirements. These requirements stated below constitute an outline for the primary screening program:

- (1) nematic thermotropic liquid crystalline phase behavior
- (2) nematic in the processing window of PET/PBT (250-300 °C)
- (3) $\Delta(T_i - T_{C-N})$ should be greater than 30 °C

- (4) pure TLCP must be fiber forming, i.e. has IV greater than 0.7 dl/g
- (5) T_i should be less than T_{dec} (where T_{dec} is consider to be 350 °C)

Nematic TLCPs are desirable materials for in situ composites because of their outstanding mechanical and rheological properties, as recently reviewed.^{12,13}

Commercially available nematic TLCPs are characterized by tensile and flexural moduli between 8 to 22 GPa, low melt viscosities in the 100 -1000 s⁻¹ shear regime, and low linear coefficients of thermal expansion on the order of 6 ppm/°C. Nematic TLCPs appear to be more desirable than smetic TLCPs, since the mesogenic units have no translational order and are easily oriented in elongational and high shear flow fields.

Along with the unique properties of TLCPs previously stated, investigators have also observed relatively long relaxation times in comparison to their isotropic counterpart.^{14,15} To utilize these unique properties in blends with thermoplastics, there must be sufficient control over the ability to orient and retain the resulting highly order domains into the solid state. Therefore, the TLCPs to be blended with thermoplastics (e.g. PET and PBT) should at least be nematic within the processing window of the blends and should have a relatively broad temperature range for the nematic phase.

Values for molecular weights and molecular weight distributions are difficult to determine for these predominately aromatic polyesters due to their relative poor solubility in practical organic solvents. Therefore inherent viscosity measurements are made to give an indication of their molecular weight values. Empirically, we have observed that polymers with IVs greater than 0.7 dl/g as measured at 30 °C in trifluoroacetic acid are fiber forming and yield suitable mechanical properties when fabricated by fiber spinning.¹⁶

One interesting aspect for future blend studies would be the evaluation of TLCP/TP blends mixed in the isotropic state. Therefore the desired isotropization temperature, T_i , will be targeted sufficiently lower then the ensuing onset of decomposition temperature (T_{dec} being associated with 5% wt. loss). A temperature of

300 °C was considered the upper limit to minimize changes in chemical structure due to thermal degradation or transesterification. This requirement cannot be obtained with commercially available TLCPs, but was possible with the TLCPs discussed in this chapter.

In the primary screening program, candidates were evaluated based on the previously stated macromolecular structure requirements, as characterized by elemental analysis, solution viscometry, cross-polarized optical microscopy, and differential scanning calorimetry. The secondary screening program included the confirmation of a nematic phase of selected candidates by wide angle X-ray scattering (WAXS) conducted on hand drawn fibers.

Cross-Polarized Optical Microscopy. The light microscope, equipped with a polarizer and analyzer, has the capacity to reveal phase types, molecular order, and defect distributions. In the initial stages of this investigation, hot stage cross-polarizing microscopy was used to characterize the temperatures at which various phase transitions occurred and to observe the resulting microstructure or "texture". The observed texture was cross referenced against an atlas of standard monomeric and polymeric liquid crystals.¹⁷ All polymers were taken through a standard evaluation routine: (1) a melt cast film was prepared by shearing a thin film between two cover slips at 20-25 °C above T_m ; (2) cooled at 10 °C/min. to 50 °C; (3) heated at 10 °C/min. to 10 ° above the extinction of birefringence, T_i ; (4) cooled at 10 °C/min. to 50 °C; (5) repeated steps 3 and 4, but at temperature rate of 2 °C/min. around the temperature of each phase transition.

A common feature for all polymers revealed a "classical" dense thread-like texture, which clearly developed on both the heating and cooling scans 10-20 ° lower than T_i and T_d (where T_d is the temperature of deisotropization), respectively. Upon cooling from the isotropic state, nematic droplets quickly formed at T_d and upon further

cooling coalesced into the dense thread-like texture. The final texture of polymer E quenched from the nematic phase to 25 °C is shown in Figure 3.3.

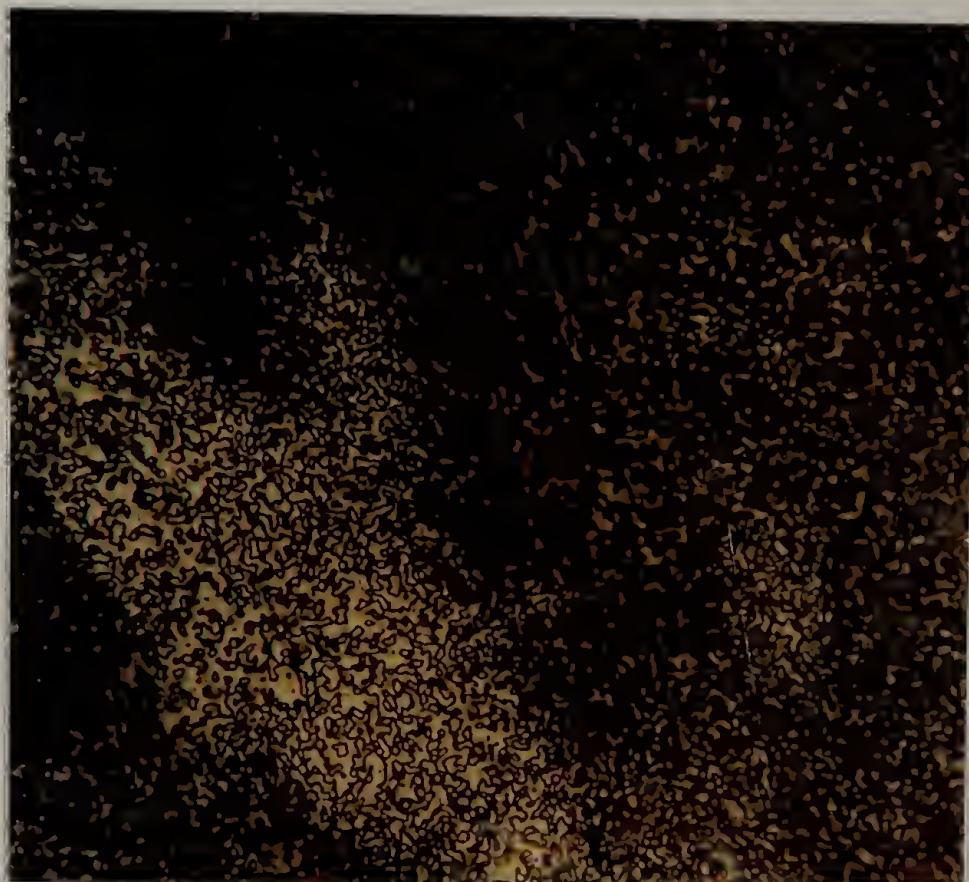


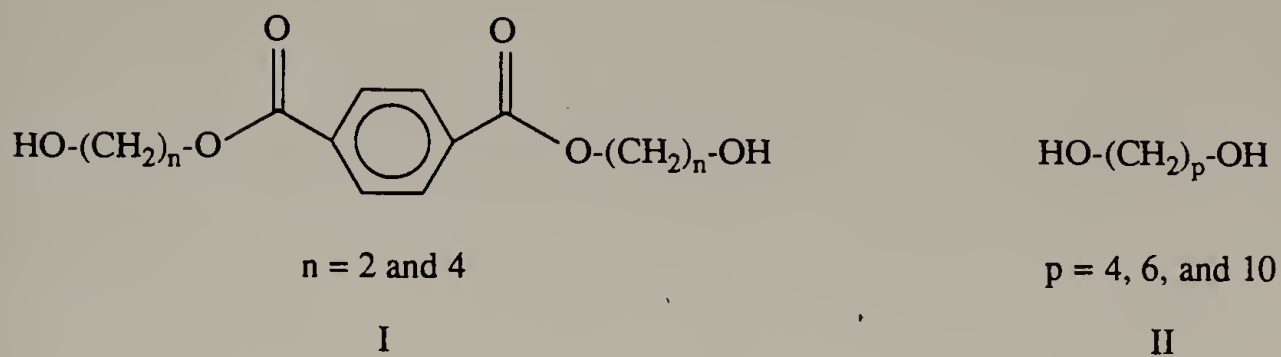
Figure 3.3: Optical micrographs depicting the observed mesophase of the polymer E quenched to 25 °C from the nematic phase, a dense thread-like texture which is representative of the series of polymer evaluated. Magnification equals 250x.

With the observed thread-like textures, representative of nematic TLCPs, correlated with a basic phase-temperature behavior for this series of polymers, we employed differential scanning calorimetry to provide more detailed information about the phase transitions in relation to chemical structure.

Differential Scanning Calorimetry. Heating and cooling scans at 10 °C/min. were conducted on polymers A-H. DSC traces for polymers B, D, and E, Figure 3.4 - 3.6, are collected at the end of this Chapter. For all the polymers prepared, a summary of the third heating and cooling scans at 10 °C/min. and the measured inherent viscosity values in trifluoroacetic acid at 30 °C are listed in Table 3.3 on page 57. Based on the macromolecular structure requirements for the primary screening program, polymer E was selected. The details of the thermal analysis by DSC for polymer E are listed in Table 3.4 on page 58. These results were consistent with the other polymers evaluated in this series: the calculated values for entropy of deisotropization, ΔS_{di} , were in the range of -8 to -10 J/mol*K. These values should be viewed as representative of the degree of ordering observed on cooling, since this value would be dependent on the rate of cooling. These results are in the range of ΔS_i values observed by Ober,⁹ for his initial study on triad polyester with various methylene spacers. The degree of undercooling into the nematic phase ($\Delta (T_i - T_d)$) was in the range of 10-15 °, and the degree of undercooling into the crystalline phase ($\Delta (T_N - T_C)$) was in the range of 30-40 °. These values are again dependent on the cooling rate, but are indicative of degree of undercooling typically observed for their respective phases.⁹

Based on these DSC results and the previously discussed optical micrographs, this series of polymers appear to have a similar phase behavior which depicts a nematic enantiotropic TLCP. A correlation of ΔS_{di} with the average distance between mesogenic units for this series was not considered due to the significant difference in their measured IVs

Table 3.3: Summary of DSC and IV results for the evaluation of flexible spacers



Polymer	n	p	% I	% II	T _m (°C)	T _i (°C)	IV (dl/g)
A	2	0	100	0	290	345	0.24
B	4	0	100	0	275	288	0.89
C	2/4	0	50/50	0	282	343	0.28
D	4	4	75	25	249	300	1.12
E	4	6	75	25	249	288	1.34
F	4	10	75	25	266	310	0.61
G	4	4	50	50	224	327	0.56
H	4	6	50	50	211	301	0.61

DSC results are based on the 3rd heating scan at 10 °C/min.

IVs were measured in trifluoroacetic acid at 30 °C

Table 3.4: Summary of DSC results from the 3rd heating and cooling scan at 10°C/min for polymer E, Poly(75%BHBT-co-25%HDO/HTH)

T_{C-N}	ΔH_{C-N}	T_i	ΔH_i (kJ/mol)	ΔS_i (J/mol*K)	$\Delta (T_i - T_{C-N})$	T_{i-N}	ΔS_{di} (J/mol*K)	T_{N-C}
249	19.8	288	5.44	9.7	31	279	-9.2	215

The major difference found between polymers in this series was the phase transition temperatures and the breadth of each transition. Polymers containing BHET as a monomer or comonomer had transitions which were significantly broader. This increase in the breadth of the thermal transitions was associated with the lower inherent viscosity values, but more specifically could be related to the distributions of molecular weights which were not measured. We turn now to the evaluation of polymer E by wide-angle X-ray scattering to confirm the existence of a nematic phase type.

Wide-Angle X-Ray Scattering. The evaluation of TLCPs by WAXS in the molten state greatly complements thermal and morphological investigations, which cannot always be counted on to produce an unambiguous determination of the mesophase type present. WAXS is necessary for the determination of smectic phase types, which produce both a diffuse ring at 4-5 Å relating to the interchain spacings, and sharp rings between 15 and 50 Å, which relates to the layer spacing of mesogens.^{9,18,19} Nematic structures naturally have less order and form a diffuse ring at 4-5 Å, which again relates to the interchain spacing of mesogens.²⁰ This diffuse ring for a nematic "melt" is similar to the diffuse halo that is typically observed for an amorphous "solid", relating to the remaining local degree of order observed in the melt.

The WAXD patterns for the powders and fibers of polymer A-H showed a considerably larger number of clearly defined spacings, because of their strong tendency to crystallize. These diffraction patterns revealed rings (arcs) in the 2.9 to 6.5 Å range for polymers A-H which were associated with the interchain spacing of the crystal repeat units. Typically, TLCPs crystallize at a slow enough rate in which the mesomorphic order can be maintained at low temperatures by quenching-in of the mesophase for X-ray studies. But, the "triad" polymers in this study and another⁹ have shown a strong tendency to crystallize and therefore the study was carried out in the molten state for a better determination of the phase type. An example of the WAXD patterns recorded for these polymers is represented at the end of the chapter in Figure 3.7 for polymer E, in

which hand drawn fibers were placed in a capillary and heated into the anticipated nematic state. At 270 °C, the sample was annealed for 4 hrs. during which the diffraction pattern was recorded, as shown in Figure 3.7 (the fiber axis is vertical to the page). The diffuse arcs superimposed on a diffuse ring at d - spacing of 4.5 Å is indicative of a oriented nematic melt with some loss of orientation due to relaxation.

Conclusions

The main objective of this chapter was the preparation and characterization of TLCPs which would promote greater interfacial adhesion in blends with PET and PBT. The synthesis strategy was to copolymerize the triaromatic "triad" mesogenic monomer, ClHTHCl, with various flexible spacers possessing a similar chemical structure to the repeat units of PET and PBT, as shown in Scheme I. The polymers prepared, as listed in Table 3.2, were screened based on specific macromolecular structure requirements for future blends studies with PET and PBT. A summary of the DSC and IV results for this series of polymers are listed in Table 3.3. At this point in the screening program polymer E, poly(75%BHBT-co-25%HDO/HTH), was identified as a potential candidate for future blends studies.

The series of polymers (A-H) were evaluated by WAXD on drawn fibers at a temperature between T_m and T_i . The compilation of results from CPOM, DSC, and WAXD indicate that the polymers prepared were all nematic enantiotropic TLCPs. The evaluation of a variety of flexible spacers allowed us to tailor the temperature window of the TLCP's liquid crystallinity to overlap the processing temperatures for PET and PBT.

This investigation has produced a potential candidate(s) for future studies involving in-situ composites with polyesters. The similarity in chemical structure of the

flexible spacers incorporated into these TLCPs should promote enhance interfacial adhesion which is essential for obtaining desired increases in mechanical properties.

Figure 3.4: DSC traces for polymer B recorded at 10°/min.: (a) heating; (b) cooling

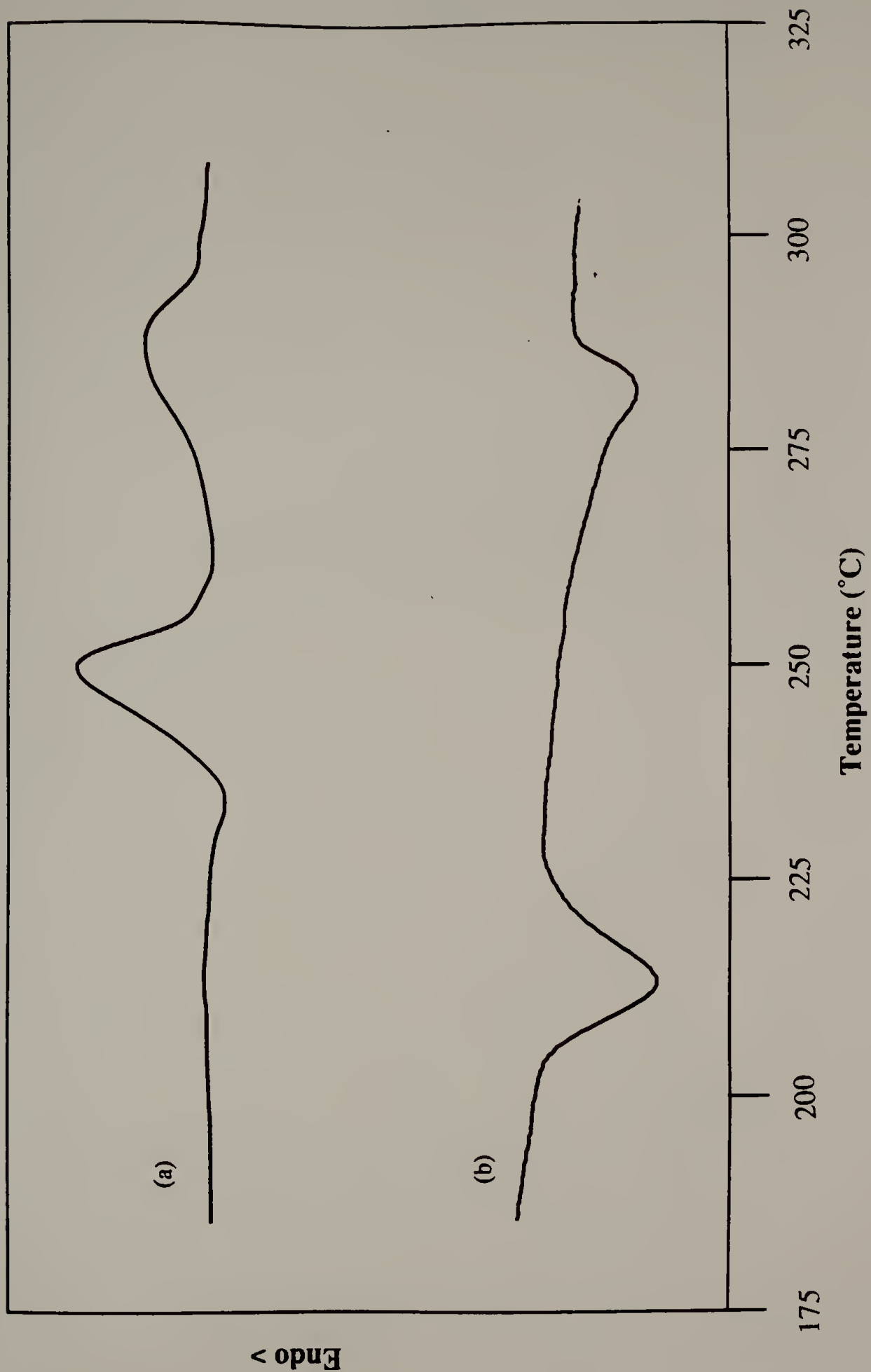


Figure 3.5: DSC traces for polymer D recorded at 10°/min.: (a) heating; (b) cooling

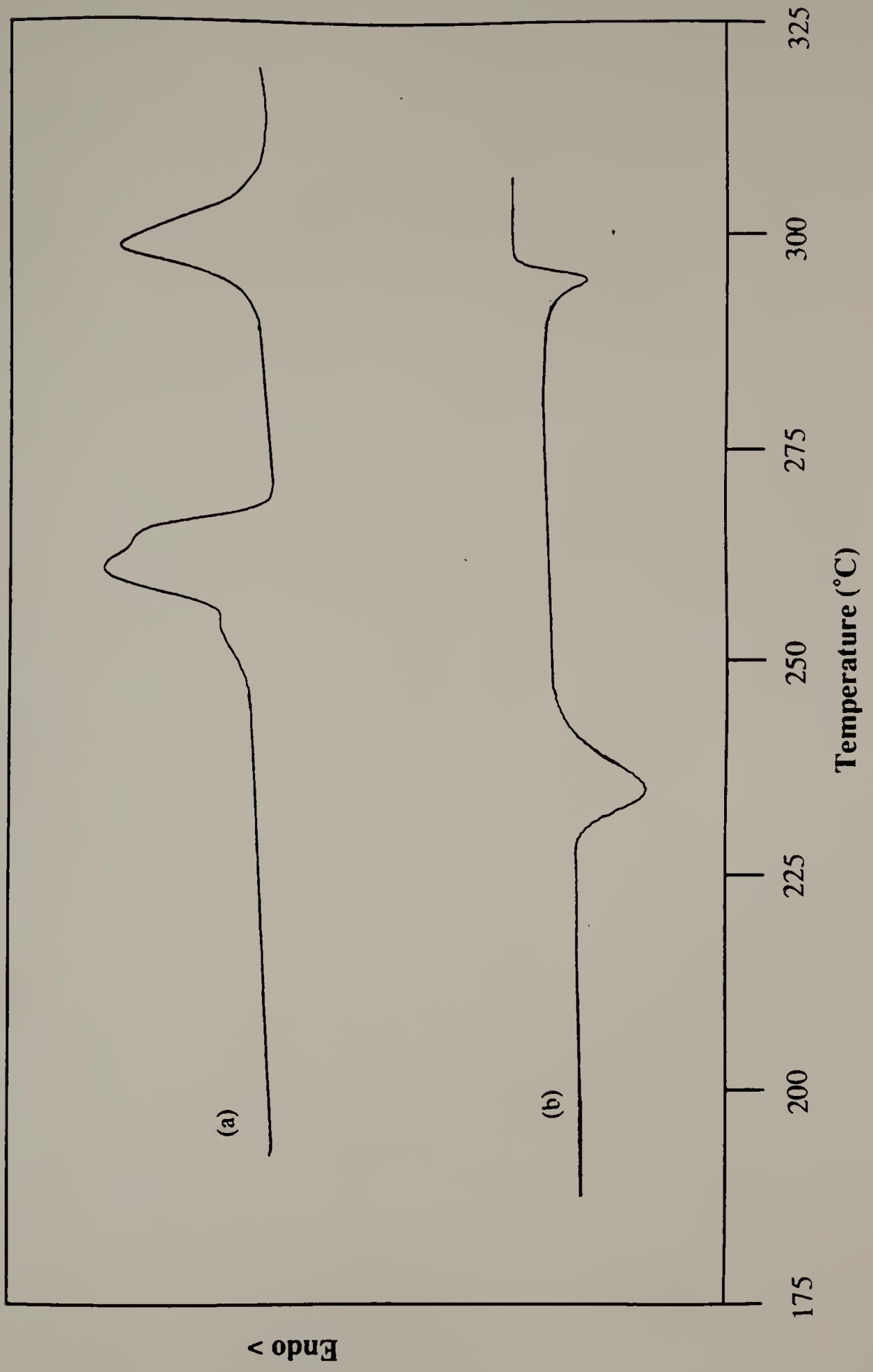
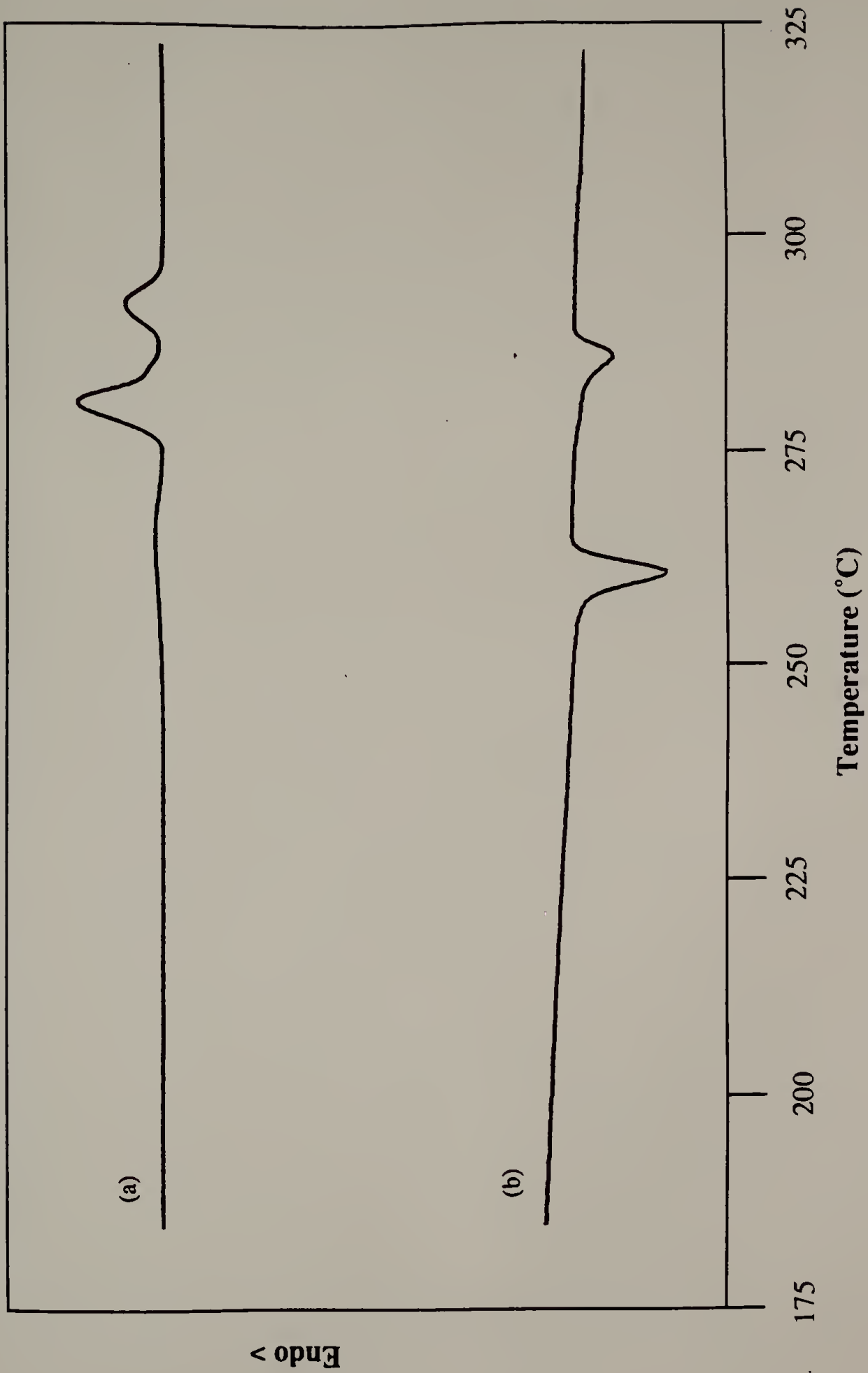


Figure 3.6: DSC traces for polymer E recorded at 10°/min.: (a) heating; (b) cooling



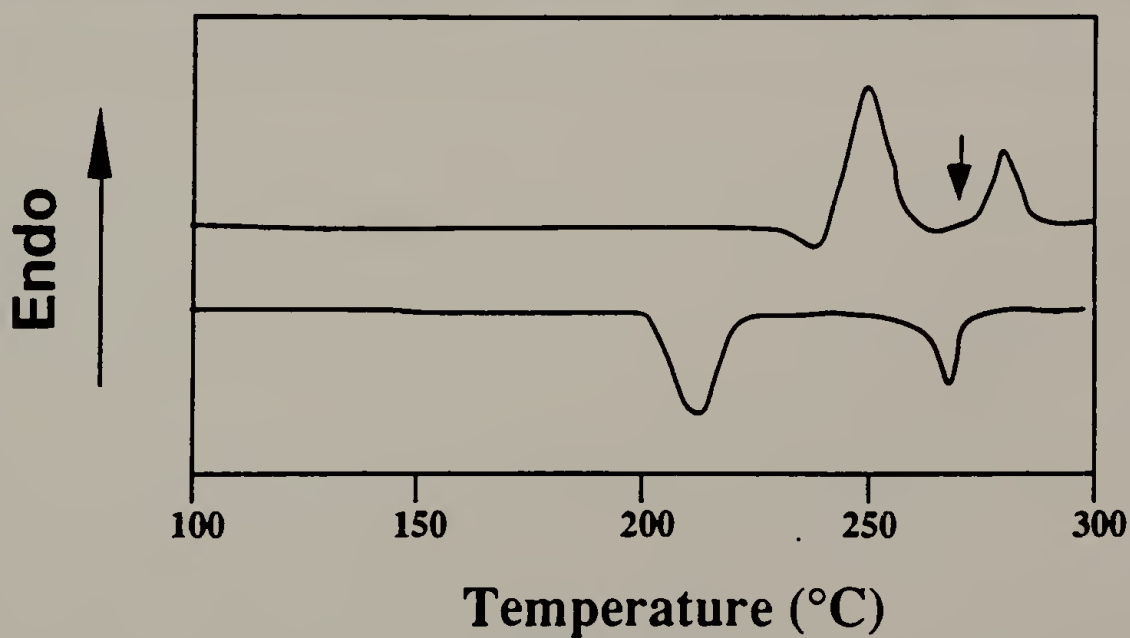


Figure 3.7: WAXD pattern for a drawn fiber of polymer E annealed at 270 °C for 4hrs. and a schematic of the DSC trace at 10 °C/min.

References

1. Ober, C.K., and Bluhm, T.L., Current Topics in Polymer Science: Volume 1, Ottenbrite, Ultracki, Inoue, eds. (Munich, Vienna, and New York: Hanser Publishers), 249 (1987)
2. Chapoy, L.L., ed., Recent Advances in Liquid Crystalline Polymers, (New York: Elsevier Appl. Sci.), (1985)
3. Blumstein, A., ed., Polymeric Liquid Crystals, (New York: Academic Press), (1985)
4. Wissbrun, K.F., *J. Rheol.*, **25**, 619 (1981)
5. Kiss, G., *Polym. Eng. Sci.*, **27**, 410 (1987)
6. Brostow, W., *Kunststoffe*, **78**, 411 (1988)
7. National Materials Advisory Board Commission on Eng. & Tech. Systems National Research Council, Liquid Crystalline Polymers, (Washington D.C.: National Academy Press) (1990)
8. Dutta, D., Fruitwala, H., Kohli, A., and Weiss, R.A., *Polymer Engineering and Science*, **30** (17), 1005-1018, (1990)
9. Ober, C.K., The Synthesis and Characterization of Some Liquid Crystalline Polyesters based upon the Oxybenzoate-terephthalate Mesogenic Unit, PhD Thesis, University of Massachusetts, Amherst (1982)
10. Bilibin, A.Yu., Schepelevsky, A.A., Frenkel, S.Ya., and Skorokhodov, S.S., *MACRO IUPAC, Florence, Preprints*, **2**, 232-233 (1980)
11. Hasslin, H-W., Droscher, M., and Wegner, G., *Makromol. Chem.*, **181**, 301 (1980)
12. Jaffe, M., Calundann, G., and Yoon, H., Handbook of Fiber Science and Tehcnology: Volume III, 83 (1989)
13. MacDonald, W.A., High Value Polymers, 428 (1990)
14. Wissbrun, K.F., *Br. Polym. J.*, **12**, 163 (1980)
15. Ide., Y. and Chung, T., *J. Macromol. Sci. Phys.*, **B23(4-6)**, 497 (1984)

16. Farris, R.J. and Joslin, S., in a private communication
17. Demus, D. and Richter, L., Textures of Liquid Crystals, (Weinheim: Verlag Chemie), (1978)
18. Lieber, L., Strzelecki, D. van Luyen and Levelut, A.M., *Europ. Polym. J.*, **17**, 71 (1982)
19. Blumstein, A., Sivaramakrishnan, K., Blumstein, R.B., and Clough, S.B., *Polymer*, **23**, 47 (1982)
20. DeVries, A., *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970) .

CHAPTER 4

PREPARATION AND CHARACTERIZATION OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS CONTAINING PYRIDINE DICARBOXYLATE AND THEIR BLENDS WITH SULFONATED PET

Introduction

Investigations into the use of polymer blends as a cost-effective means of satisfying essential property requirements has resulted in materials with the desirable combination of properties or even synergistically enhanced properties. However, the development of new miscible or compatible polymer blend systems has been significantly challenged by the unfavorable thermodynamics typically possessed by high molecular weight polymer pairs. Since the mixing of these pairs leads to a very small combinatorial entropy of mixing, one has had to focus on factors controlling the enthalpy of mixing, such as specific intermolecular interactions. Therefore, there has been a number of investigations into the enhancement of polymer pairs miscibility by the incorporation of moieties having specific sites for intermolecular interaction promoting a favorable negative enthalpy of mixing.^{1,2} An example of this approach considers ionic moieties incorporated into a polymeric backbone, an approach not necessarily novel since ion-containing polymers or ionomers have been investigated for nearly 60 years.³ But, only in the past decade have ionomeric blends (polymer pairs possessing less than 15% of complementary ionogenic moieties along their backbone) been intensely

investigated as a means of compatibilizing polymer pairs, which left unmodified would remain immiscible.

In terms of the thermodynamic considerations discussed, the enthalpy of mixing controls the degree of miscibility or compatibility. This term relates to the temperature and composition dependent attractive forces between two polymer pairs, which dictates interfacial properties of a properly mixed blend. The interfacial mixing or the degree of interfacial adhesion is ultimately responsible for the resulting mechanical properties of the system, especially in the case of compatibilized multiphase blends. Further experimental evidence which could demonstrate how applicable the incorporation of ionogenic moiety into the backbone of immiscible polymer pairs should greatly enhance the polymer scientist's ability to control the degree of miscibility and develop new materials. These aspects will be examined in this chapter for blends of thermotropic liquid crystalline polymers (TLCPs) with engineering thermoplastics (TPs).

In the previous chapter, TLCPs were developed to be blended with TPs, such as PET and PBT. These types of blends have attracted much attention recently⁴⁻⁶ as a means of utilizing the expensive, but unique mechanical and rheological properties of TLCPs in applications where glass-fiber reinforcing additives could not be used during processing. This new class of self-reinforced composite or "in situ composite" would be an attractive means of balancing both properties and cost-effectiveness.

Unfortunately, there are further thermodynamic considerations to contend with in blends of LCP/TP, as realized by Flory's lattice model,⁷ and later by Ballauff.^{8,9} They have demonstrated that, in a ternary athermal (i.e. $\chi = 0$) system of rigid rods, coils, and solvent, the random-coil component is strongly excluded from the anisotropic phase and this phase separation persists in the solvent-free mixtures. Experimentally, one investigator has even demonstrated that a polyester based TLCP blended with PBT resulted in a brittle material having mechanical properties which deviated negatively from a simple rule of mixtures.¹⁰ The morphological investigation further indicated a lack of

interfacial adhesion between the two developed phases, which accounted for the poor mechanical properties.

The main objective of this chapter was to explore the utility of specific interactions as a means of compatibilizing thermotropic liquid crystalline polyesters with poly(ethylene terephthalate). The specific interactions considered for this investigation were acid base and zinc transition metal complexations. Eisenberg and co-workers¹¹ have demonstrated that the pairwise attraction of a minimum of 5 mole% ionogenic moieties incorporated along the polymer backbone was necessary for compatibilization of immiscible pairs (polystyrene and poly(ethyl acrylate)), by dynamic mechanical thermal analysis (DMTA). The ionogenic moieties evaluated in this study consisted of the free acid form of sulfonated polystyrene and poly(ethyl acrylate-co-4-vinyl pyridine). The improved compatibility of the ionomeric blend was achieved by proton transfer of the sulfonic acid functional group to the basic vinyl pyridine, which led to the formation of complementary ionic pairs. Lundberg and co-workers¹² studied the solution behavior of stoichiometric blends of zinc sulfo EPDM and poly(styrene-co-4-vinyl pyridine) and observed nearly a decade increase in viscosity, relating to the degree of intramolecular interactions.

Investigations into TLCP/TP blends have indicated a significant enhancement in mechanical properties when the TLCP content is greater than 20%.^{10,13} When the TLCP content reaches this level, assuming the dispersed phase-to-matrix viscosity ratio is close to or greater than 1, fibril formation of LC domains appears favorable. Under these conditions, an optimized elongation flow field can easily orient LCP fibrils enough to produce a self-reinforced material having enhanced mechanical properties.

The sulfonated PET contained 7% sodium, 5-sulfo isophthalate units.¹⁴ The desired content of TLCP to be blended was set to be greater than 20%, and therefore, the stoichiometric level of Lewis-base units to be incorporated into the TLCP was predetermined, 0.35 meq/g of polymer. The type of Lewis-base units to be employed

was based on derivatives of pyridine dicarboxylate since this structure could be easily incorporated into typical polyester synthetic methods. This is the first reported investigation into ionomeric blends of thermotropic liquid crystalline polymers and of blends containing sulfonate poly(ethylene terephthalate). Hence, both of these components were developed and their blends were then characterized.

The Lewis-base modified TLCP, hereafter written as TLCP_N, prepared and characterized for this study was modeled after a selected candidate from a screening program designed specifically for investigations of TLCP/PET blends, as discussed in the previous chapter.¹⁵ The strategy for the preparation of TLCP_Ns was based on the synthesis of the triaromatic "triad" mesogenic monomer, 4,4'-(terephthaloyldioxy)-dibenzoyl dichloride (ClHTHCl), with bis(4-hydroxybutyl) 2,5-pyridinedicarboxylate (BHBP_{2,5}) or bis(4-hydroxybutyl) 3,5-pyridinedicarboxylate (BHBP_{3,5}). The monomer BHBP_{2,5} was considered to be very similar in structure to bis(4-hydroxybutyl) terephthalate, a flexible spacer successfully utilized in Chapter 3.

The preparation and the isolation of the monomer BHBP_{2,5} will be discussed. Polymers were prepared in solution following Scheme I, as represented in Figure 4.1. Compositions of BHBP_{2,5} evaluated are listed in Table 4.1.

Several attempts were made to synthesize BHBP_{3,5}, but the resulting oily products could not be adequately isolated. Instead, Scheme II, as represented in Figure 4.2, was utilized in order to incorporate 3,5-pyridine dicarboxylate units into a TLCP_N of similar structure as to be prepared in Scheme I.

Scheme I

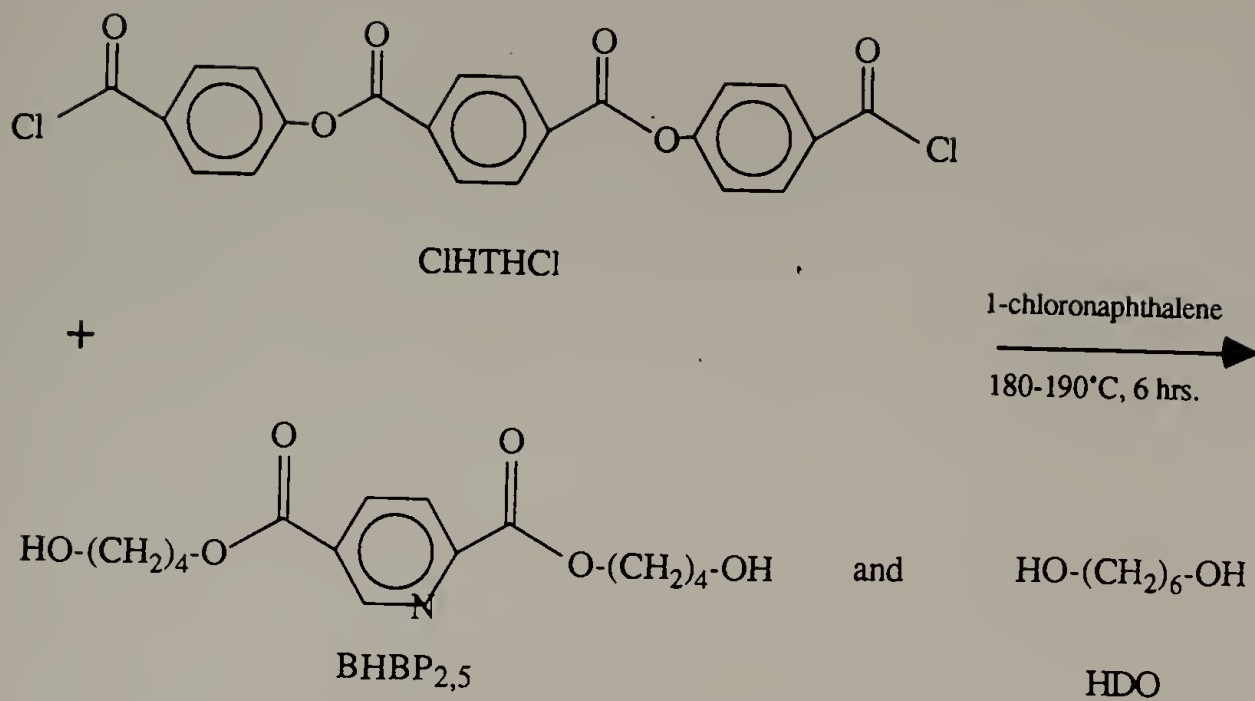


Figure 4.1: Scheme I, evaluation of BHP_{2,5} and HDO with ClHTHCl

Table 4.1: Composition of BHP_{2,5} and HDO copolymerized with ClHTHCl

Polymer	% BHP _{2,5}	% HDO
I 1	75	25
I 2	50	50

Scheme II

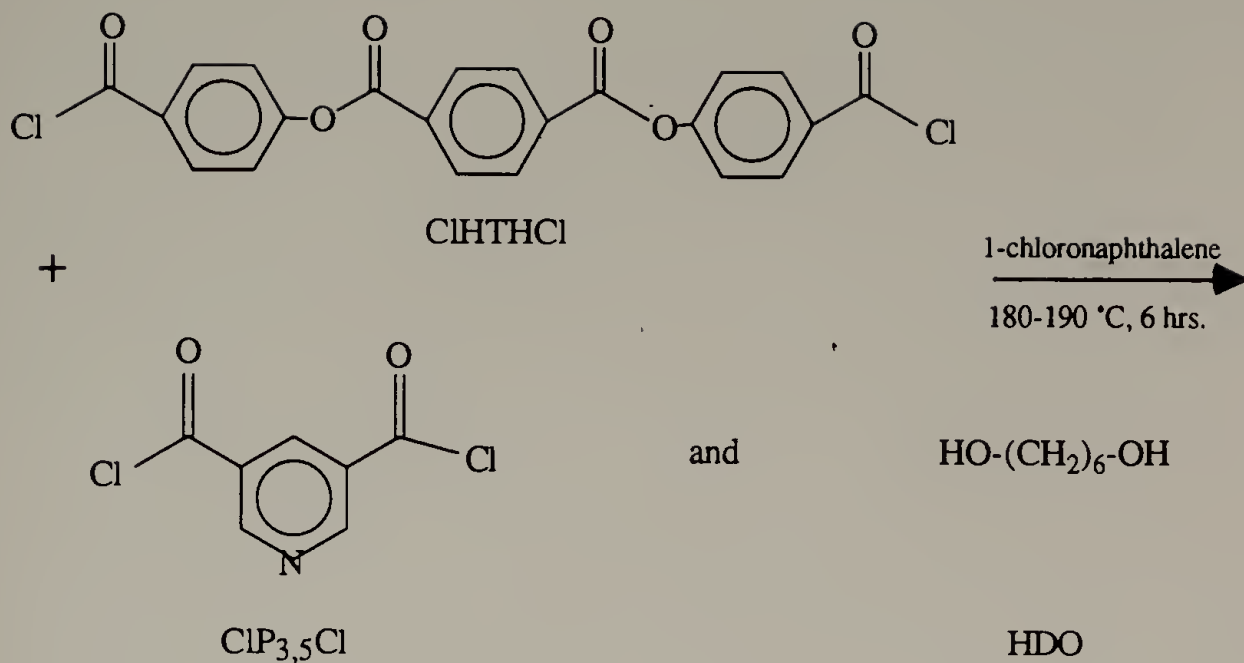


Figure 4.2: Scheme II, incorporation of 3,5-pyridine dicarboxylic acid dichloride, CIP_{3,5}Cl, into a triad TLCP_N

The composition of 3,5-pyridine dicarboxylate units evaluated are listed in Table 4.2. The molar equivalence of pyridine dicarboxylate units for polymer II 1-2 are the same as listed in Table 4.1 for polymers I 1-2, respectively. BHBP_{3,5}* depicts the ideal case in which BHBP_{3,5} would be formed in situ, but is merely represented here for sake of clarity.

Table 4.2: Compositions of ClP_{3,5}Cl and HDO copolymerized with ClHTHCl in Scheme II

Polymer	% ClP _{3,5} Cl	% HDO	% BHBP _{3,5} *
II 1	25	75	75
II 2	17	83	50

The characterization of the thermotropic liquid crystalline phase behavior of polymers prepared in Scheme I and II by cross-polarized optical microscopy (CPOM) and differential scanning calorimetry (DSC) will be discussed in relation to the unmodified TLCP systems developed in Chapter 3, poly(75%BHBT-co-25%HDO/HTH). Isothermal studies were conducted on the TLCP_Ns by thermal gravimetric analysis (TGA) and their relative thermal stability will also be discussed in relation to poly(75%BHBT-co-25%HDO/HTH).

The procedures developed for the ion exchange of the sodium ions of sulfonated PET for hydrogen and subsequently hydrogen ions for zinc will be presented, along with preparation and characterization of their blends with TLCP_Ns. Fourier transform infrared (FTIR) spectroscopy was used to probe the level of specific intermolecular interactions present. The degree of compatibilization was examined by both DSC and dynamic mechanical thermal analysis (DMTA).

Experimental

Materials

Poly(ethylene terephthalate) modified with 7 mole% of sodium, 5-sulfo isophthalate units was received from AKZO Corporate Research, Arnhem Holland, ($\eta_{inh} = 0.44$; inherent viscosity of a solution in trifluoroacetic acid at a concentration of 0.50 g/dl at 30 °C). All other chemicals were obtained from the Aldrich Chemical Co. The aliphatic diols were distilled over CaH_2 and then previously stored over activated 4 Å molecular sieves. Terephthaloyl chloride was purified by sublimation. 2,5-pyridine dicarboxylic acid was purified by dissolution with 0.5 N Na_2CO_3 to a pH \approx 9-10, decolorized twice with charcoal, and then acidified with 1 N HCl. 1-Chloronaphthalene was vacuum distilled over CaH_2 . THF was pre-dried over CaCl_2 and then distilled over sodium-benzophenone. *m*-Cresol was pre-dried over CaCl_2 and then distilled. Amberlyst 15[®], a non-aqueous cationic exchange resin, was purified with multiple washing in 1 N H_2SO_4 , deionized water, and toluene. The resin was then dried in an azeotropic distillation of toluene. Trifluoroacetic acid was purchased at 99% purity and was used without further purification. CHCl_3 was pre-dried over 4 Å molecular sieves and then distilled over P_2O_5 . Other reagents and recrystallization solvents were previously stored over activated 3-4 Å molecular sieves.

Monomer Synthesis

Synthesis of 4,4'-(terephthaloyldioxy)dibenzoyl dichloride:¹⁵ In a 2 l three neck round-bottom flask fitted with a pressure equalizing addition funnel, gas inlet, and mechanical stirrer was added 0.8 l of 0.4 N Na_2CO_3 and 52.48 g (0.38 moles) of *p*-hydroxybenzoic acid. The pH of the solution was adjusted with 0.4 N Na_2CO_3 to a pH \approx 8. A solution of 32.48 g (0.16 moles) of terephthaloyl chloride in 0.35 l of CHCl_3 was sequentially added, via an addition funnel, dropwise into a vigorously stirred

reaction pot over a 1 hour period. The reaction solid was then filtered and washed with distilled water several times. The solid was then placed in a 2 l Erlenmeyer flask and was acidified with 1 N HCl to a pH \approx 3-4. The mixture was then filtered, washed with distilled water, and dried in vacuum at 110°C overnight. The yield for preparation of 4,4'-(terephthaloyldioxy)dibenzoic acid was 95%.

In a 1 l three neck round-bottom flask fitted with a condenser, inert gas inlet, and magnetic stirrer, was added 20 g (0.492 moles) of 4,4'-(terephthaloyldioxy)dibenzoic acid, 0.4 l anhydrous toluene, 0.12 l thionyl chloride, and 3 ml of dimethyl formamide. The solution was allowed to reflux for 2 hours or until dissolution. The yellow solution was cooled to room temperature, filtered, washed with excess toluene, and dried in a desiccator under vacuum overnight. The white powder was then recrystallized in CHCl_3 . m.p. 224°C and yield 74%. ^1H NMR (d-DMSO ppm): 7.47 (d, 4H), 8.05 (d, 4H), 8.33 (s, 4H). Elemental analysis; Calculated for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Cl}_2$: C, 59.61%; H, 2.73%; Cl, 16.00%. Found: C, 59.54%; H, 2.71%; Cl, 15.92%.

Synthesis of 3,5-pyridine dicarboxylic diacid chloride: In a 1 l three neck round-bottom flask fitted with a condenser, inert gas inlet, and magnetic stirrer, was added 30 g (0.18 moles) of 3,5-pyridine dicarboxylic acid, 90 ml (1.26 moles) of thionyl chloride, and 2 ml of dimethyl formamide. The solution was refluxed for 1.5 hours or until dissolution. The thionyl chloride was primarily removed by distillation and then further removed in a desiccator under vacuum overnight. The diacid chloride was then recrystallized from anhydrous hexane. The resulting crystals were white. m.p. 61 °C and yield 60%. Elemental analysis; Calculated for $\text{C}_7\text{H}_3\text{NO}_2\text{Cl}_2$: C, 41.21%; H, 1.48%; N, 6.87%; Cl, 34.76%. Found: C, 41.12%; H, 1.41%; N, 6.86%; Cl, 34.69%.

Synthesis of 2,5-pyridine dicarboxylic diacid chloride: In a 1 l three neck round-bottom flask fitted with a condenser, inert gas inlet, and magnetic stirrer, was added 40 g

(0.24 moles) of 2,5-pyridine dicarboxylic acid, 100 ml (1.4 moles) of thionyl chloride, and 2 ml of dimethyl formamide. The solution was refluxed for 1.5 hours or until dissolution. The thionyl chloride was primarily removed by distillation and then further removed in a desiccator under vacuum overnight. The residual amber solid was dissolved in THF and decolorized twice with charcoal. The THF was then removed by distillation. The diacid chloride was then recrystallized from anhydrous hexane. The resulting crystals were yellow. m.p. 54 °C and yield 55%. Elemental analysis; Calculated for $C_7H_3NO_2Cl_2$: C, 41.21%; H, 1.48%; N, 6.87%; Cl, 34.76%. Found: C, 41.01%; H, 1.32%; N, 6.72%; Cl, 34.81%.

Synthesis of bis(4-hydroxybutyl 2,5-pyridinedicarboxylate): In a 500 ml three neck round-bottom flask fitted with condenser/reflux column, pressure equalizing addition funnel, inert gas inlet, and mechanical stirrer, was added via syringe 61 ml (0.69 moles) of 1,4 -butanediol, 14 ml (0.17 moles) of pyridine, and 75 ml THF. The solution was purged with purified Ar for 15 minutes. Subsequently 14 g (0.69 moles) of 2,5-pyridine dicarboxylic diacid chloride in 270 ml of THF was added dropwise over a 30 minute period into a vigorously stirred reaction pot. The yellow solution was refluxed for 1 hr.. The yellow solution was then distilled by rotovap at 50 °C until essentially all of the THF and pyridine was removed. The remaining 1,4-butanediol in the solution was then removed by vacuum distillation. The resulting oily product was poured into 50 ml of ethanol and cooled to 10 °C for 5 hrs. The solid precipitate, containing the 2.5 mer (m.p. 125 °C), was filtered off and the remaining ethanol was removed by distillation. The crude oily product was recrystallized twice with a solution of toluene:ethyl ether (50:50 by volume) and dried under vacuum at 40 °C for 48 hrs. m.p. 72 °C and yield 65 %. 1H NMR ($CDCl_3$ ppm): 1.75 (m, 4H), 1.95 (m, 4H), 3.74 (t, 4H), 4.45 (t,4H), 8.21 (d, 1H), 8.43 (d, 1H), 9.32 (s, 1H). Elemental analysis; calculated for $C_{15}H_{21}O_6N$: C, 57.86%; H, 6.80%; N, 4.50%. Found: C, 57.81%; H, 6.78%, N, 4.46%.

Polymer Synthesis

All polymers were prepared in a dry Schlenk tube fitted with a condenser and magnetic stirrer. The concentration of monomers to reaction solvent, 1-chloronaphthalene, was 0.1 g/ml. An example of the preparation of polymer I 1 following Scheme I, involved charging a 50 ml Schlenk tube with 0.3113 g (1.0000 mmole) of BHBP_{2,5}, 0.0394 g (0.3333 mmole) of HDO, 0.5623 g (1.3333 mmole) of ClHTHCl, and 8 ml of 1-chloronaphthalene. The reaction mixture was maintained between 180-190 °C under a slow stream of dry Ar for 6 hrs. and precipitated in toluene. The solid was Soxhlet extracted in refluxing toluene for 2 days, vacuum dried at 110 °C for 2 days, giving a yield of 89%, and inherent viscosity for polymer I 1 in trifluoroacetic acid at 30 °C was 0.87 g/dl. ¹H NMR (CF₃COOD ppm): 2.24 (s, 16H), 4.71 (s, 12H), 7.50 (d, 4H), 8.33 (d, 4H), 8.55 (s, 4H), 8.72 (d, 1H), 9.62 (s, 1H). Elemental analysis; Calculated for C_{34.75}H_{29.25}O₁₁N_{7.75}: C, 65.89%; H, 4.65%; N, 1.66%. Found: C, 65.78%; H, 4.60%; N, 1.58%; Cl, 0.0%.

Ion Exchange Procedure

Ion exchange of sodium for free-hydrogen: In a 250 ml three neck round-bottom flask fitted with a condenser, inert gas inlet, and mechanical stirrer, was added 10 g (3.5 meq of Na) of 7% sodium, sulfonated PET, 42 g (175 meq of H) of Amberlyst 15[®], and 50 ml of trifluoroacetic acid. The solution was gently stirred for 3 hrs. The slurry was then filtered through a buchner funnel fitted with a low porosity, glass-fiber filter paper. The resin was collected in the funnel and was further washed with small portions of trifluoroacetic acid totaling 100 ml. The volume of the resulting filtrate was then reduced to approximately 75 ml by distillation under aspirator pressure at 30 °C. The filtrate was then precipitated in acetone and followed by Soxhlet extraction in refluxing acetone for 2 days. The white solid was then vacuum dried at 70 °C for 2 days, giving a

yield of 80%. Elemental analysis; Calculated for $C_{10}H_{8.07}O_{3.79}S_{.07}$: C, 62.84%; H, 4.26%; S, 1.17%. Found: C, 62.81%; H, 4.22%; S, 1.06%; Na, 0.0%.

Ion exchange of free-hydrogen for zinc: In a 175 ml chromatographic column (3 cm x 25 cm, D x L) fitted with coarse-grade glass frit, was added a slurry, composed of 10 g (3.5 meq of H) of the free-acid form of 7% sulfonated PET as a fine powder (mesh size 50) in a saturated aqueous solution of zinc acetate. To this packed column, 5 bed volumes equaling 600 ml of a saturated solution of zinc acetate was subsequently passed through the column at an output rate of 10 ml/min.. The slurry was then placed in a 500 ml Erlenmeyer flask with 350 ml of deionized water, vigorously stirred for 1 hr., and filtered. The filter cake was further washed with deionized water until no detectable trace of zinc acetate was observed by the evaluation of aliquots of the filtrate with 1 N NaOH for the formation of zinc hydroxide. The powder was then vacuum dried at 70 °C for 2 days. Elemental analysis; Calculated for $C_{10}H_{8.07}O_{3.79}S_{.07}Zn_{.035}$: C, 62.14%; H, 4.13%; S, 1.16%; Zn, 1.18%. Found: C, 62.02%; H, 4.15%; S, 1.07%; Zn, 1.09%.

Solution Blend Preparation

All polymer blends were prepared in a *m*-cresol:chloroform solution (70:30 by volume) under similar conditions. The following is an example of the preparation of the acid-blend of sulfonated PET with polymer I 1, poly(75%BHBP_{2,5}-co-25%HDO/HTH). In a 500 ml Erlenmeyer flask fitted with a condenser, inert gas inlet, and magnetic stirrer, 7.5 g (2.625 meq of H) of the 7% free-acid form of sulfonated PET was dissolved in 175 ml of *m*-cresol:chloroform solution heated to 60 °C. In a separate 125 ml Erlenmeyer flask fitted with a condenser, inert gas inlet, and magnetic stirrer, 2.5 g (2.625 meq of N) of polymer I 1, was dissolved in 75 ml of *m*-cresol:chloroform solution. This second solution containing polymer I 1 was then slowly added dropwise to a vigorously stirred solution of sulfonated PET at 25 °C over a period of 30 min.. The concentration of polymer for both acid and zinc blends was adjusted with the *m*-

cresol:chloroform solution to prevent gelation and to ensure proper mixing. A final concentration of 0.4 g/ml was found to be sufficient to prevent gelation. The solution was continuously stirred for 5 hrs to ensure proper mixing. The solution of polymer blend was then precipitated in hexane, followed by Soxhlet extraction in refluxing hexane for 2 days, and vacuum dried at 70 °C for 3 days. The yield was 93%.

Characterization Methods

The elemental analysis was performed by the Microanalysis Laboratory at the University of Massachusetts. Inherent viscosities (IVs) for all polymers were determined at 30 °C in trifluoroacetic acid, using a Cannon-Ubbelohde viscometer. The polymer concentration was 0.5 g/dl. Proton nuclear magnetic resonance (^1H NMR) spectra for all compounds were recorded on a Varian XL-300 operating at 300 MHz in deuterated solvents. ^1H NMR spectra for polymer solutions in CF_3COOD were recorded with the spectral width set at -900. CPOM was performed on a Carl Zeiss Ultraphoto II polarizing microscope equipped with a Linkham Scientific Instruments TMS 90 temperature controller and a TMH 600 hot stage. The hot stage temperature was calibrated with vanillin and potassium nitrate melting point standard. FTIR spectra for all compounds were recorded on an IBM 30 with the resolution of 1 cm^{-1} . A minimum of 128 scans were signal averaged. The samples were cast on KBr plates from a solution of hexafluoroisopropanol.

DSC measurements were conducted with a Perkin-Elmer DSC-7 on samples ranging from 7-10 mg. The temperature and power ordinates of the DSC were calibrated with respect to the known melting point and heat of fusion of a high purity indium standard supplied by Perkin-Elmer. The glass transition temperature (T_g) was defined as the midpoint of the change in the specific heat, and for exothermic and endothermic processes the peak temperatures were taken as the transition temperatures. TGA measurements were conducted with a Perkin-Elmer TGA-7 on samples ranging from 5-7

mg. DMTA measurements were conducted with a Polymer Laboratories PL-DMTA on compression molded films in the single-cantilever mode at 1 Hz.

Results and Discussion

The previous chapter¹⁶ discussed a screening program, which evaluated a variety of dihydroxy flexible spacers copolymerized with the mesogenic monomer ClHTHCl. The objective was to tailor the liquid crystalline phase behavior to a set of macromolecular structure requirements which would promote greater interfacial adhesion for "in situ composite" blends with PET and PBT. The requirements stated below constitute an outline for that screening program:

- (1) nematic thermotropic liquid crystalline phase behavior
- (2) nematic in the processing window of PET/PBT (250-300 °C)
- (3) $\Delta(T_i - T_{C-N})$ should be greater than 30 °C
- (4) pure TLCP must be fiber forming (i.e. has IV greater than 0.7 dl/g)
- (5) T_i should be less than T_{dec} (where T_{dec} is considered to be 350 °C)

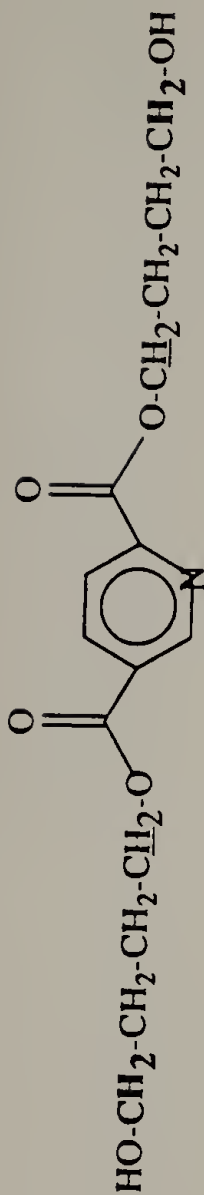
From this study, the candidate selected was poly(75%BHBT-co-25%HDO/HTH)¹⁴, a TLCP composed primarily of a flexible spacer, bis(4-hydroxybutyl) terephthalate (BHBT). The synthesis objective of the present investigation was the incorporation of pyridine dicarboxylate units into a TLCP_N, similar in structure and in liquid crystalline phase behavior. By considering a TLCP in a series, where only the flexible spacers are varied, the factors which control the temperature range for the observed nematic phase are generally the average distance between mesogenic units, molecular weights (i.e. IVs), and relative stability imparted on the crystalline phase by the spacer. Therefore, the initial focus of this investigation was the synthesis and characterization of BHBT-

type monomers containing pyridine dicarboxylate units. The methodology for the synthesis of BHBP_{2,5} and BHBP_{3,5} naturally followed the one previously discussed for the preparation of BHBT.¹⁷

Analysis of Monomer Molecular Structure

The synthesis of BHBP_{2,5} under similar conditions as described for BHBT¹⁷ resulted in primarily 2.5 mer of BHBP_{2,5}. The fact, that the acid chlorides groups for ClP_{2,5}Cl are asymmetric could account for a significant difference in their relative reactivity toward BDO. This difference in reactivity in combination with (1) the ratio ClP_{2,5}Cl:BDO and (2) the initial concentration of ClP_{2,5}Cl in THF could account for the low production of BHBP_{2,5}. Therefore, these two parameters were then optimized and the highest yields of BHBP_{2,5} (65-70 %) were obtained for the following modified conditions: the ratio of ClP_{2,5}Cl:BDO was adjusted from 1:4 to 1:10 and the concentration of ClP_{2,5}Cl in THF was reduced from 60% to 5%.

Proton Nuclear Magnetic Resonance Spectroscopy. The techniques used to monitor the fractionation procedure was ¹H NMR and elemental analysis. As mentioned, the major product isolated from the original experimental conditions was the 2.5 mer of BHBP_{2,5}. The ratio of 1.5 mer (BHBP_{2,5}) to 2.5 mer was systematically monitored by ¹H NMR throughout the optimization process. Examination of the chemical structure of the 1.5 mer and 2.5 mer, as represented on the following page in Figure 4.3, indicates there are two types of oxymethylene units which could be distinguished with ¹H NMR. The oxymethylene units attached directly to hydroxy end groups are represented by CH₂s, and the oxymethylene units attached directly to ester groups are represented by CH₂s. The assigned resonance peaks for the two types of



(a) 1.5 mer of BHPBP_{2,5}



(b) 2.5 mer of BHPBP_{2,5}

Figure 4.3: Chemical structure of (a) 1.5 mer of BHPBP_{2,5}; and (b) 2.5 mer of BHPBP_{2,5}; representing the two types oxymethylene units

protons were sufficiently resolved in CDCl_3 at 300 MHz, so that subsequent integration of these peaks could be associated with the relative ratio of 1.5 mer to 2.5 mer. The error typically associated with the performed integration is approximately $\pm 5\%$. The ^1H NMR spectrum for a solution of the final isolated product of $\text{BHBP}_{2,5}$ in CDCl_3 , will be shown on the following pages in Figure 4.4 (a), along with Figure 4.4 (b), the enlarged region of the resonance peaks for oxymethylene protons.

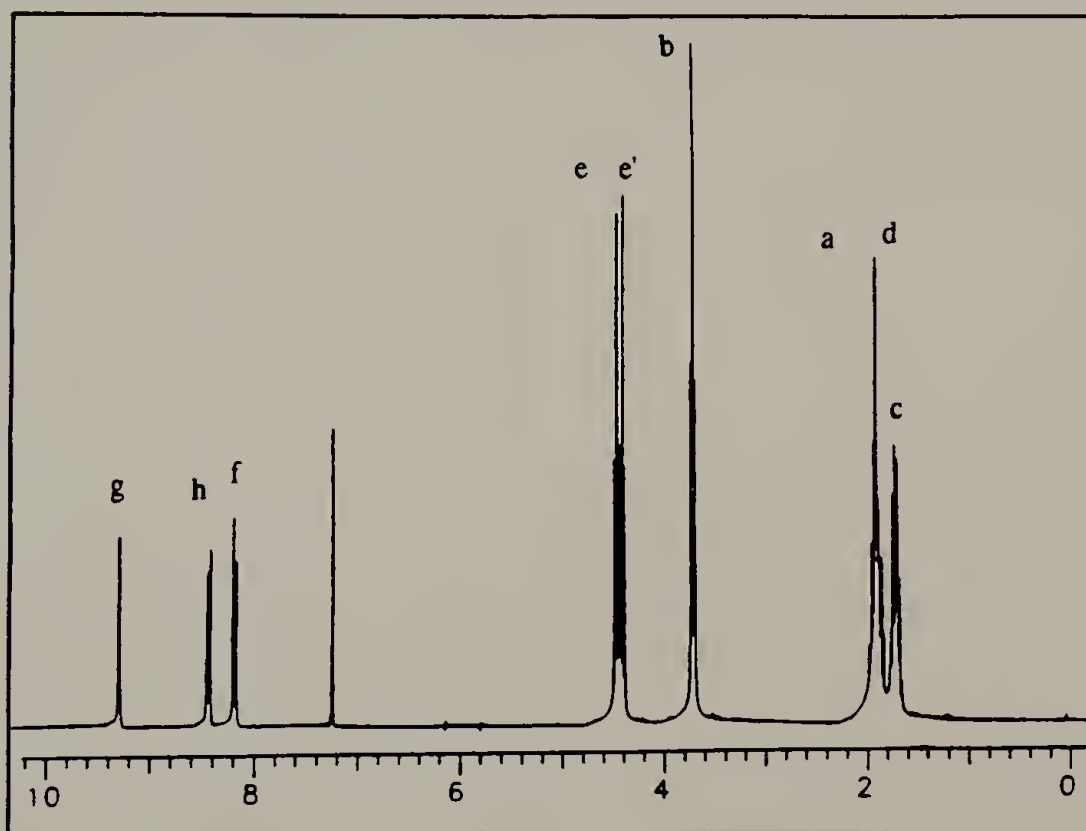
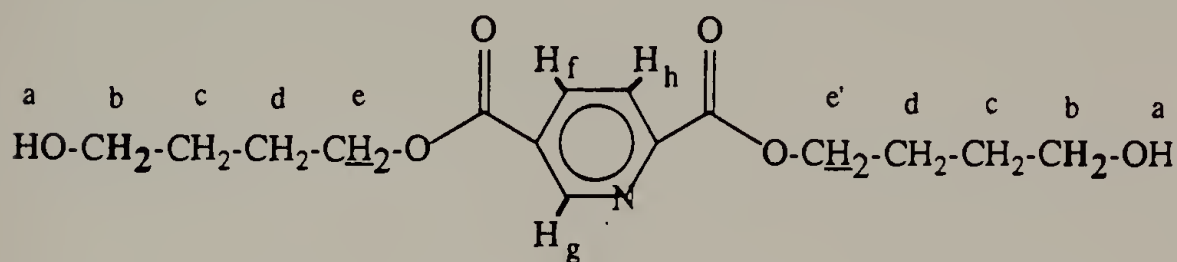


Figure 4.4: (a) ^1H NMR spectrum for a solution of $\text{BHBP}_{2,5}$ in CDCl_3 at 300 MHz
(continued next page)

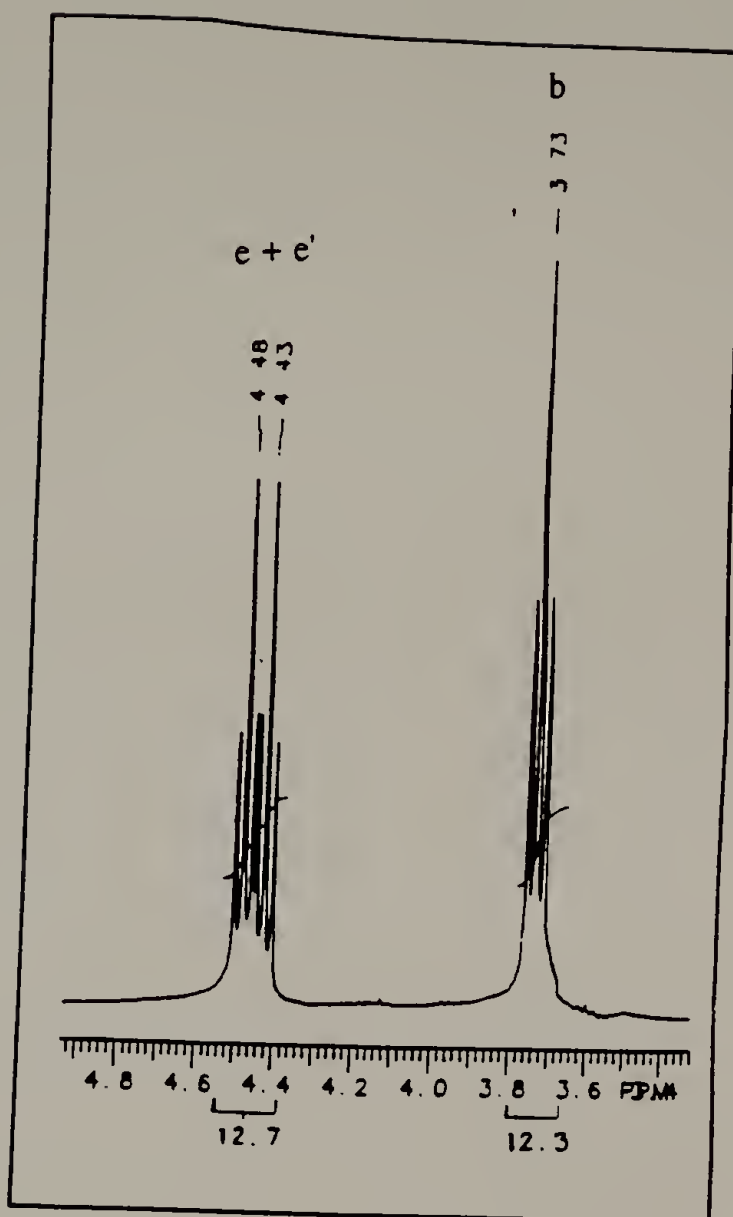


Figure 4.4: (continued)

(b) enlarged region of the ^1H NMR spectrum of BHBP_{2.5}; including the resonance peak frequencies (in ppm) and the area of integration for protons: e + e' and b

Elemental Analysis. There was a significant difference in the calculated weight percent of carbon, hydrogen, and nitrogen between the oligomeric products to permit an adequate assessment of the fractionated product. The error associated with this measurement is approximately $\pm 0.3\%$ for carbon, hydrogen and nitrogen. The calculated values for potential fractionated oligomeric products of BHBP_{2,5} from elemental analysis and their respective formula weights (F.W.s) are listed in Table 4.3.

Table 4.3: Calculated values for potential fractionated oligomeric products of BHBP_{2,5} from elemental analysis and their respective formula weights

# of repeat units	C%	H%	O%	N%	F.W.
1	55.45	5.08	33.59	5.88	238.18
1.5	57.86	6.80	30.84	4.50	311.33
2.5	58.75	5.88	30.10	5.27	531.52
3.5	58.95	5.50	29.80	5.59	751.72

The elemental analysis results of BHBP_{2,5} from the optimized fractionation process was the following: C, 57.94%; H, 6.74%; N, 4.50%.

¹H NMR and elemental analysis proved to be useful in monitoring the fractionation process. Other techniques, if made available, could have been more quantitative, such as high pressure liquid chromatography in combination with mass spectrometry. But, the most relative indicator of the purity of BHBP_{2,5} was the resulting IV values from the polycondensation of BHBP_{2,5} following Scheme I. The IV

values for polymers I 1 and I 2 in trifluoroacetic acid at 30 °C were 0.87 and 0.56 dl/g. As mentioned previously, IV values greater than 0.7 dl/g were considered sufficient for this investigation.

The relative high solubility of BHBP_{2,5} in relation to BHBT accounted for modifications of the original fractionation procedure. One interesting observation was the similarity of the melting point of BHBP_{2,5} and BHBT at 70-72 °C. The factors influencing the crystallization of both monomers appear to be similar, which should be advantageous for obtaining TLCPs with similar phase behavior.

Analysis of Thermotropic Liquid Crystalline Phase Behavior

Once the BHBP_{2,5} was isolated, polymers were prepared following Scheme I, and their LC phase behavior was characterized. Unfortunately, BHBP_{3,5} could not be sufficiently purified and therefore Scheme II was developed in order to incorporate 3,5-pyridine dicarboxylate units into a TLCP_N of similar structure and composition. All polymers prepared by both Scheme I and II were carried out in solution of 1-chloronaphthalene (b.p. 259 °C) containing no acid-accepting reagent, but were slowly purged with Ar. The high boiling solvent permitted higher reaction temperatures (180-190 °C) than conventional reaction conditions containing a low-boiling acid-accepting reagent. Conditions did permit sufficient removal of HCl to prevent high acid concentrations and to subsequently yield polymers having moderately high inherent viscosity values ranging from 0.56 to 1.01 dl/g.

Cross-Polarized Optical Microscopy. The light microscope, equipped with a polarizer and analyzer, has the capacity to reveal phase types, molecular order, and defect distributions. In the initial stages of this investigation, hot stage cross-polarizing microscopy was used to characterize the temperatures at which various phase transitions occurred and to observe the resulting microstructure or "texture". The observed texture

was cross referenced against the unmodified TLCPs of similar structure reported in the previous chapter.¹⁸ All polymers were taken through a standard evaluation routine under a slow stream of nitrogen: (1) a melt cast film was prepared by shearing a thin film between two cover slips at 20-25 °C above T_m ; (2) cooled at 10 °C/min. to 50 °C; (3) heated at 10 °C/min. to 10 ° above the extinction of birefringence, T_i ; (4) cooled at 10 °C/min. to 50 °C; (5) repeated steps 3 and 4, but at a temperature rate of 2 °C/min. around the temperature of each phase transition.

The polymers prepared in both Scheme I and II exhibited the common features observed for their unmodified counterpart.¹⁸ The developed microstructure was representative of the "classical" dense thread-like texture, common for nematic TLCPs. The texture of polymer I 1 developed after step 4 of the standard evaluation routine, is represented in the optical micrograph shown in Figure 4.5. With the observed thread-like texture, representative of nematic TLCPs, correlated with a basic phase-temperature behavior for the series I and II polymers, we used differential scanning calorimetry to provide more detailed information about the phase transitions in relation to the modification of chemical structure.



Figure 4.5: Final texture for polymer I 1 observed at room temperature

Differential Scanning Calorimetry. Heating and cooling scans at 10 °C/min. were conducted on polymers prepared from Scheme I and II. For all polymers prepared, a summary of the second heating and cooling scans at 10 °C/min. and the measured inherent viscosity values in trifluoroacetic acid at 30 °C are listed in Table 4.4. An example of the thermograms recorded for polymers I 1 and II 1 are shown on subsequent pages in Figure 4.6 and 4.7, respectively. Based on the macromolecular structure requirements, previously discussed, polymer I 1 and II 1 were selected for the ionomeric blends study with sulfonated PET.

The details of the thermal analysis by DSC for polymer I 1 are listed on page 98 in Table 4.5. These results were consistent with the unmodified nematic TLCP discussed in the previous chapter.¹⁴ These values should be viewed as representative of the degree of ordering observed on cooling, since this value would be dependent on the rate of cooling. These results are in the range of ΔS_i values observed by Ober,¹⁹ for his

initial study on triad polyester with various methylene spacers. The degree of undercooling into the nematic phase ($\Delta (T_i - T_d)$) was ca. 10 ° and the degree of undercooling into the crystalline phase ($\Delta (T_N - T_C)$) was ca. 50 °. These values are again dependent on the cooling rate, but are indicative of the degree of undercooling typically observed for their respective phases.²⁰ The incorporation of the linear 2,5-pyridinedicarboxylate units into a TLCP_N appears not to significantly change the crystalline or liquid crystalline phase behavior as observed for poly(75%BHBT-co-25%HDO/HTH). The phase relationship of polymer I 2 was also similar to the unmodified TLCP, which reinforces the finding for polymer I 1.¹⁴ Polymer I 2 was not considered a primary candidate for future blends studies, because of a low melting temperature of 195 °C.

Table 4.4: Summary of DSC and IV results for polymers prepared following Scheme I and II

Polymer	T _m (°C)	T _i (°C)	IV (dl/g)
I 1	238	283	0.87
I 2	195	292	0.56
II 1	209	255	0.93
II 2	220	275	1.01

DSC results are based on the 2nd heating scan at 10 °/min.

IVs were measured in trifluoroacetic acid at 30 °C

Figure 4.6: DSC traces for polymer I 1 recorded at 10°/min.: (a) heating; (b) cooling

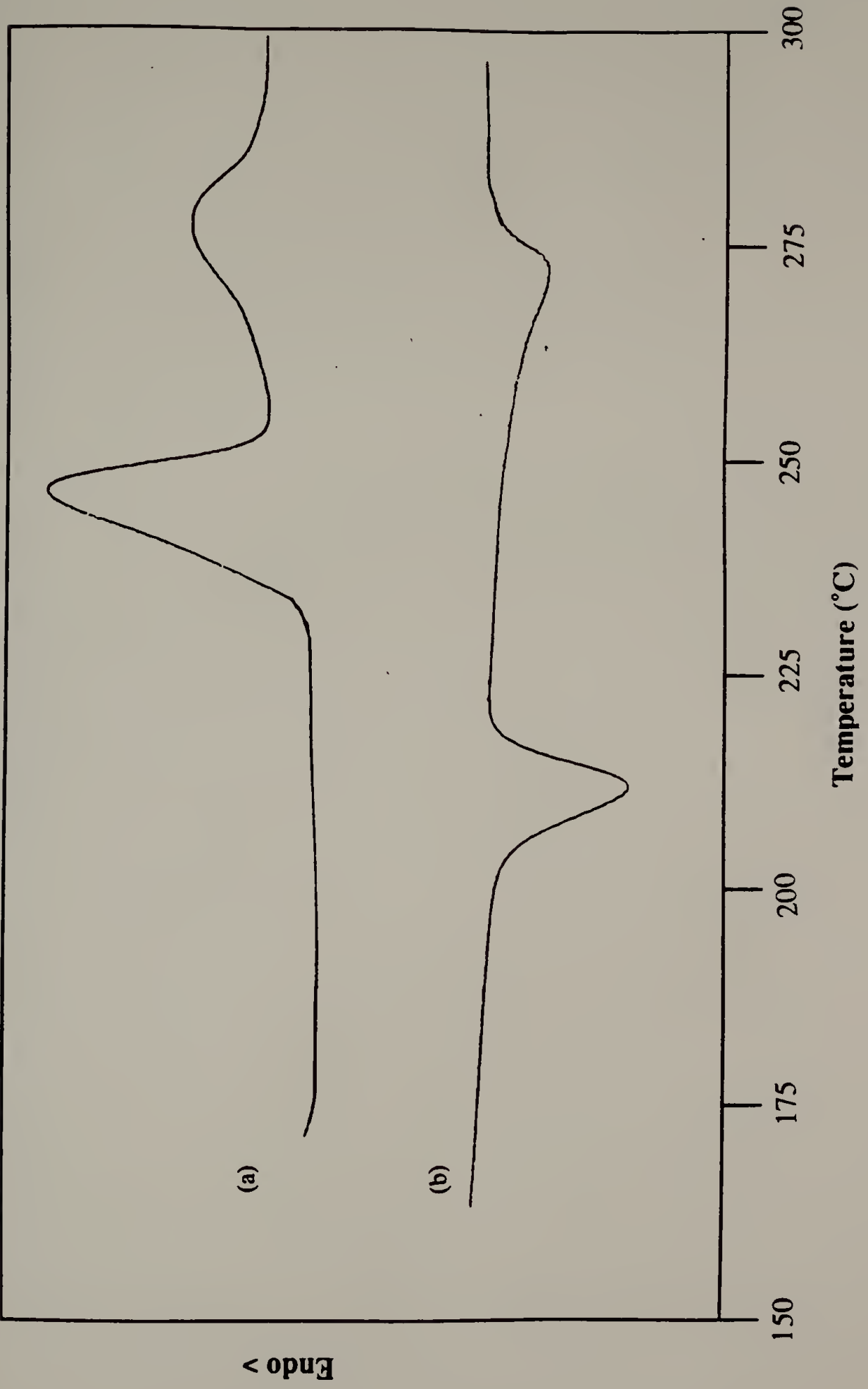


Figure 4.7: DSC traces for polymer II 1 recorded at 10°/min.: (a) heating; (b) cooling

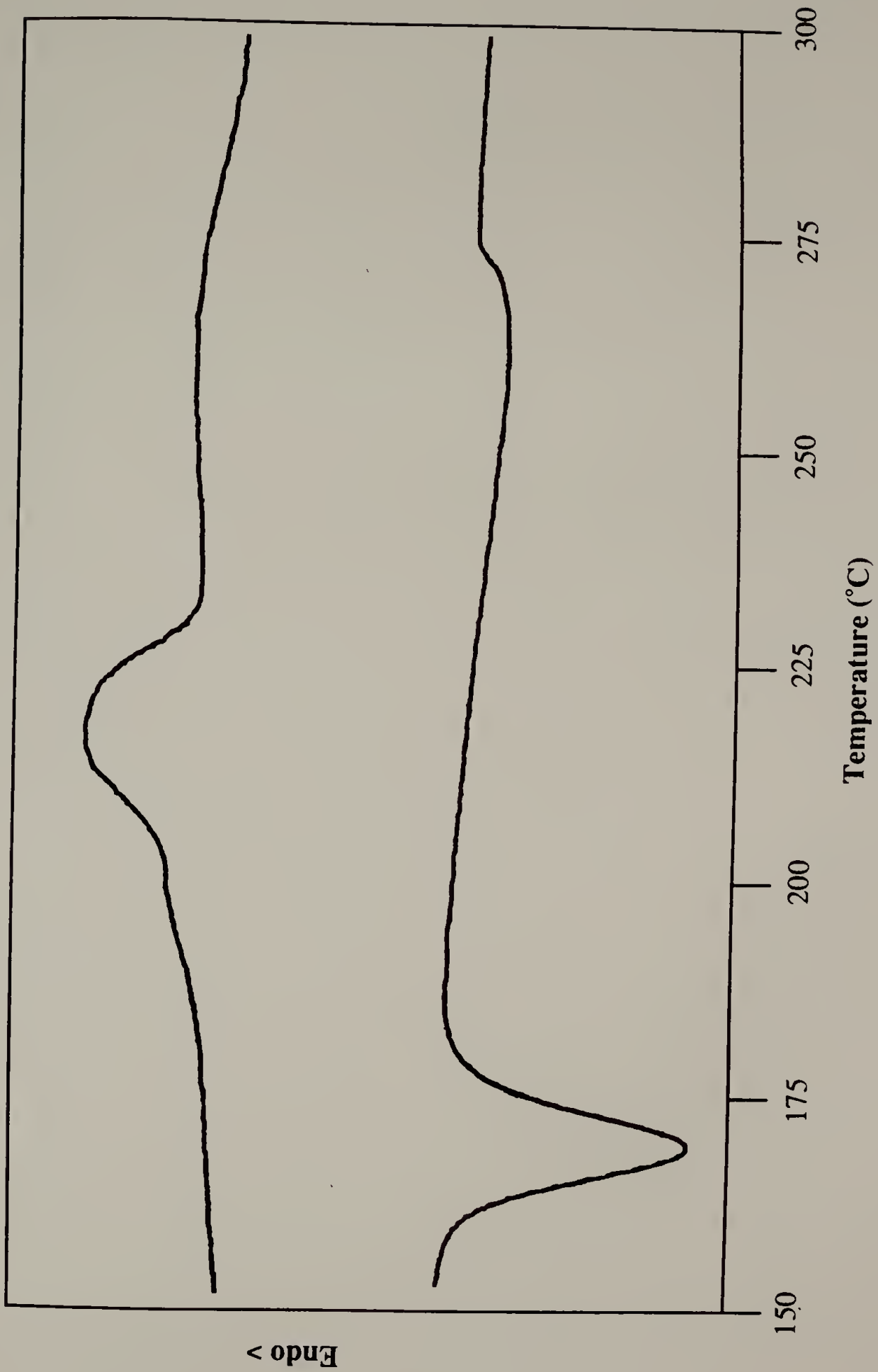


Table 4.5: Summary of DSC results from the 2nd heating and cooling scan at 10°C/min for polymer I 1,
Poly(75%BHBP_{2,5}-co-25%HDO/HTH)

T _{C-N}	ΔH _{C-N}	T _i	ΔH _i (kJ/mol)	ΔS _i (J/mol*K)	Δ(T _i -T _{C-N})	T _{i-N}	ΔS _{di} (J/mol*K)	T _{N-C}
238	18.2	283	4.75	8.5	45	276	8.3	187

Thermal Stability

Isothermal Thermal Gravimetric Analysis Studies. The relative thermal stability of TLCP_Ns prepared from Scheme I and II was investigated in relation to the unmodified model TLCP developed in the previous chapter.¹⁴ The incorporation of pyridine dicarboxylate units or any nitrogen containing moiety into a TLCP_N would be susceptible to oxidation or thermal molecular rearrangement during normal processing temperatures of PET (260 - 300 °C). The anticipated thermal conditions during the investigation of the ionomeric TLCP_N/PET-SO₃H(Zn) blends were considered to be temperatures between 250 - 275 °C for periods up to 15 minutes during which the blends could be fabricated into compression molded films or spun fibers. Therefore, isothermal experiments were carried out at 250 and 275 °C for a period of one hour under a nitrogen purge. The results of this isothermal study were compared to parallel experiments conducted on the unmodified model TLCP system, poly(75%BHBT-co-25%HDO/HTH). The specific mechanism for molecular decomposition was not explored at this time. The results of the isothermal study on 5 mg samples at 250 °C for 1 hour indicate no detectable percent weight loss outside of the estimated value for experimental error of ± 1 % weight loss/hour. The results of the isothermal study on 5 mg samples at 275 °C for 1 hour are listed in Table 4.6. The results indicate that at 275 °C thermal decomposition does become a factor for TLCP_N, with polymer I 1 having the highest level of instability. The rate of percent weight loss appears constant through out the isothermal experiments for both temperature studies. But, the amount of weight loss for the first 15 minutes was considered marginal for our investigation.

Table 4.6: TGA results from the isothermal study of polymers prepared from Scheme I and II at 275 °C for a period of 1 hr.

Polymers	% Wt. Loss/hr.	%Wt. Loss/15 mins.
I 1	3.2	0.8
I 2	2.75	0.7
II 1	2.25	0.6
II 2	1.1	0.3
P(75%BHBT-co-25%HDO/HTH)	0.5	0.05

The next isothermal study examined the relative stability of PET-SO₃H(Zn) and their ionomeric blends with polymer I 1. The experimental conditions for the analysis were the same as was previously discussed for the TLCP_N. The results of the isothermal study on 5 mg samples at 250 °C for 1 hour are listed in Table 4.7.

Table 4.7: TGA results from the isothermal study of sulfonate PET and their blends with polymer I 1 at 250 °C for a period of 1 hr

Polymer	% Wt. Loss/hr	% Wt. Loss/15mins
PET-SO ₃ Na	0.6	0.15
PET-SO ₃ H	3.1	0.86
PET-SO ₃ Zn	3.4	0.8
polymer I 1/PET-SO ₃ H	4.7	1.2
polymer I 1/PET-SO ₃ Zn	5.6	1.4

For PET-SO₃H(Zn) and their blends with polymer I 1, the results of the isothermal study conducted at 275 °C for a period of 1 hr. clearly indicated the onset of decomposition (% wt. loss > 5%) after approximately 15 minutes. Based on these results the thermal stability of the TLCP_N appears to be greater than both acid and zinc neutralized forms of sulfonated PET. These results indicate the thermal treatment of both components of the ionomeric TLCP_N/PET-SO₃H(Zn) blends could be considered up to 275 °C, but for less than a 15 minute period.

Ionomeric Blends Analysis

Optimization of the Ion Exchange Procedures for Sulfonated PET. With the development and characterization of novel TLCP_Ns, the focus of the investigation turned to the development of ion exchange procedures for PET-SO₃Na. The objective was to exchange sodium ions for hydrogen and hydrogen ions for zinc. The sulfonated PET used in this investigation was characterized as containing a sulfonation level of 7 mole%.¹⁴ The sulfonated groups were incorporated into PET by a standard two-step melt polycondensation reaction, in which 7 mole% of sodium, 5-sulfo-dimethyl isophthalate was substituted for the equivalent mole percent of dimethyl terephthalate. Direct sulfonation could not be considered, due to the relatively high reactivity of the ester linkages toward available sulfonation reagents.

The ion exchange of sodium ions for hydrogen in low molecular weight polar compounds is now considered trivial. But, due to the poor solubility of PET in practical organic solvents, the use of conventional ion exchange techniques is very restricted. The techniques developed were based on two fundamental concepts of ion exchange: (1) a batch process driven by the equilibrium principles, and (2) a column process driven by the laws of mass action.²¹

Three methods for the ion exchange of sodium for hydrogen were investigated. The first two methods involved the use of a non-aqueous ion exchange resin, Amberlyst

15[®] with 10% solutions of PET-SO₃Na in trifluoroacetic acid. The first method examined a batch process and the second method examined a column process, where naturally the Amberlyst 15[®] was considered the stationary phase and the polymeric solution was considered the mobile phase. Both processes were optimized to obtain quantitative exchanges of sodium ions for hydrogen by adjusting the excess of Amberlyst 15[®]. Both methods were successful, but the batch process was selected based on the minimum amount of solvent utilized in the process. For the batch process, Amberlyst 15[®] was used in a 50 fold excess. The third technique considered a finely milled powder of PET-SO₃Na (mesh size 50) as the stationary phase in a column process, where a 20% HCl solution was considered as the mobile phase. This process was also optimized for a quantitative exchange of sodium ions for hydrogen. The parameters controlling the ion exchange process were optimized, such as: (1) concentration of the mobile phase, (2) particle size, and (3) flow rate. Degree of neutralization was based on the elemental analysis results, which indicated no detectable trace of sodium and acceptable percentage of hydrogen with in ± 0.3 %.

Typically, ion exchange resins are characterized by their chemical structure, ion content, and the average molecular weight between crosslinks. These factors control the type of solvent which can be utilized and relative efficiency of ion exchange. The powdered sulfonated PET used in this investigation, was received having low crystallinity (ca. 8-10%), and this morphology was viewed as one of the contributing factors in the successful exchange of sodium for hydrogen ions.

The next ion exchange procedure to be developed was the exchange of hydrogen ions for zinc. Of the three methods previously discussed, the later method in which the powdered sulfonated PET was utilized as a stationary phase in a column process was the most successful. The mobile phase was a saturated solution of zinc acetate. Similar parameters were optimized to obtain quantitative neutralization to the zinc form. These results constitute the optimized procedure outlined in the experimental section, along

with the results of the elemental analysis. A variety of experiments were conducted to directly exchange sodium ions for zinc, such as: (1) the generation of Amberlyst 15[®] completely neutralized with zinc ions as a stationary phase, and (2) using powderized PET-SO₃Na as a stationary phase with a saturated solution of zinc acetate as the mobile phase. Unfortunately, both methods could not be optimized at this time to produce a quantitative exchange. Perhaps, if sodium 5-sulfo dimethyl isophthalate was neutralized with other alkali metals, such as potassium, the equilibrium constant for the direct exchange to zinc would be high enough to make these methods practical.

The main objective of this investigation was now examined: the use of specific intermolecular interactions as a means of compatibilizing a thermotropic liquid crystalline polyester with a semi-crystalline polyester. Ionomeric blends containing TLCP_N and sulfonated PET of both free-acid and zinc neutralized form were prepared and the level of specific interaction and the degree of compatibilization were characterized. The type of interactions to be examined were acid-base and zinc transition metal complexations.

Level of Specific Intermolecular Interactions between Ionogenic Pairs.

Stoichiometric acid and zinc blends were prepared containing 25% TLCP_N and 75% PET-SO₃H(Zn). The TLCP_Ns evaluated were polymer I 1 and II 2. All blends were prepared in solutions of *m*-cresol:chloroform (70:30 by volume). The concentrations were minimized to favor greater mixing, lower solution viscosities, prevent liquid crystalline phase separation, and reduce preferential polymer precipitation. The minimum concentration value was approximately a 4% solution by weight. Below this concentration, polymer precipitates were too difficult to be retained by filtration. One common observation was the significant increase in solution viscosity for the blends containing PET-SO₃Zn relative to the acid blends and the individual components of the blend. The existence of specific intermolecular interactions was promising. The lack of any gelation for the acid blends was a concern. Perhaps the high dielectric constants for *m*-cresol caused significant solvation of the ionogenic moiety hindering any proton

transfer. Unfortunately, the poor solubility of polyesters necessitates the use of solvents with high dielectric constants.

The level of specific intermolecular interactions was probed with the use of FTIR spectroscopy. Model compounds were prepared to assist in the identification of the pertinent resonance peaks associated with interacting pyridine dicarboxylate and sulfonate groups. These compounds were the dimethyl esters of 2,5 and 3,5-pyridine dicarboxylate, 5-sulfonic acid dimethyl isophthalate, and their mixed salts (acting as models for the blends). On subsequent pages, the FTIR spectrum of the dimethyl esters of 2,5-pyridine dicarboxylate and 3,5-pyridine dicarboxylate, and their mixed salts with 5-sulfonic acid dimethyl isophthalate in the region of 1550-1650 cm^{-1} are presented in Figure 4.8 and 4.9, respectively. In Figure 4.8 (a), the adsorption band at 1597 cm^{-1} represents the pyridine ring stretching. In Figure 4.8 (b), the adsorption band has broadened and shifted to 1610 cm^{-1} and a smaller second peak appears at 1635 cm^{-1} . The broadened adsorption band at 1610 cm^{-1} appears to indicate a composite of the pyridine ring stretching and a distribution of dipole-dipole interactions with the proton of the sulfonic acid group, which results in a shift in frequency of 13 cm^{-1} . The second peak at 1635 cm^{-1} appears to indicate pyridinium ring stretching. The existence of two peaks is believed to be representative of an acid-base equilibrium developed between pyridinium ion and pyridine, which does not favor either product. These results could indicate a few possible situations: (1) the base-dissociation constant is relatively low; (2) the Lewis basicity of the carbonyl-oxygens are able to compete with pyridine; or (3) combination of both (1) and (2). However, the objectives for the preparation of model compounds were accomplished: (1) aid in the peak assignments of the adsorption bands for pyridine and pyridinium ring stretching; and (2) qualitative evaluation of the base-dissociation constants.

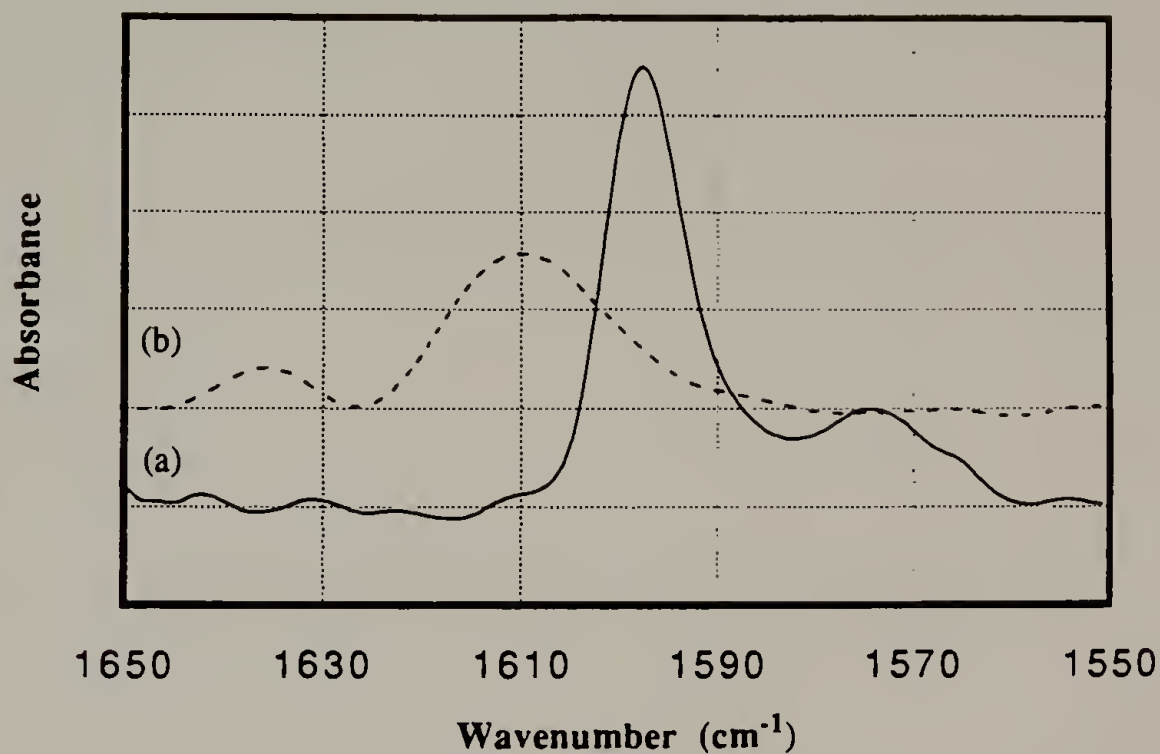


Figure 4.8: FTIR spectra of model compounds: (a) 2,5-dimethyl pyridine dicarboxylate (—); (b) and the mixed salt with 5 sulfonic acid dimethyl isophthalate(---)

In Figure 4.9, similar peak assignments can be made for 3,5-dimethyl pyridine dicarboxylate. The adsorption band at 1606 cm^{-1} appears to indicate the pyridine ring stretching and the broad adsorption band at 1625 cm^{-1} appears to indicate the pyridinium ring stretching, as discussed previously for 2,5-dimethyl pyridine dicarboxylate. The adsorption band at 1625 cm^{-1} appears to indicate a greater distribution of environments associated with the pyridinium ring stretching. The ratio of the two peak heights seem to indicate a base-dissociation constant significantly larger than was observed for 2,5-dimethyl pyridine dicarboxylate. Both observations appear to indicate, as would be expected, a greater Lewis basicity for 3,5-pyridine dicarboxylate unit which has no adjacent carbonyl group.

Figure 4.10, shows the FTIR spectrum of (a) poly(75%BHBP_{2,5}-co-25%HDO/HTH), polymer I 1, and (b) the ionomeric blend containing 25% polymer I 1 with 75% PET-SO₃H in the $1550\text{-}1650\text{ cm}^{-1}$ region. In both spectra, the adsorption band at 1606 cm^{-1} , which corresponds to the pyridine dicarboxylate ring stretching, is a dominate feature. In Figure 4.10 (b), the 1606 cm^{-1} band appears to be slightly broadened and there also appears to be a slight shoulder at 1612 cm^{-1} . The FTIR spectra for polymer II 2 also indicated no shift in the absorbance band for pyridine ring stretching as was observed in the model compounds. These results were only considered to be qualitative, and thus a relative comparison of absorbance bands of interacting species. Proper normalization was hindered by the close similarities in molecular structures of the blend components. Based on the speculations made for the FTIR spectrum of the model compounds, these results seem to indicate very small levels of specific interaction present in these ionomeric blends, even for the TLCP_N containing 3,5-pyridine dicarboxylate units. Unfortunately, these results were very similar in the zinc blends, where there was no observed shift in pyridine ring stretching for polymers I 1 and II 2.

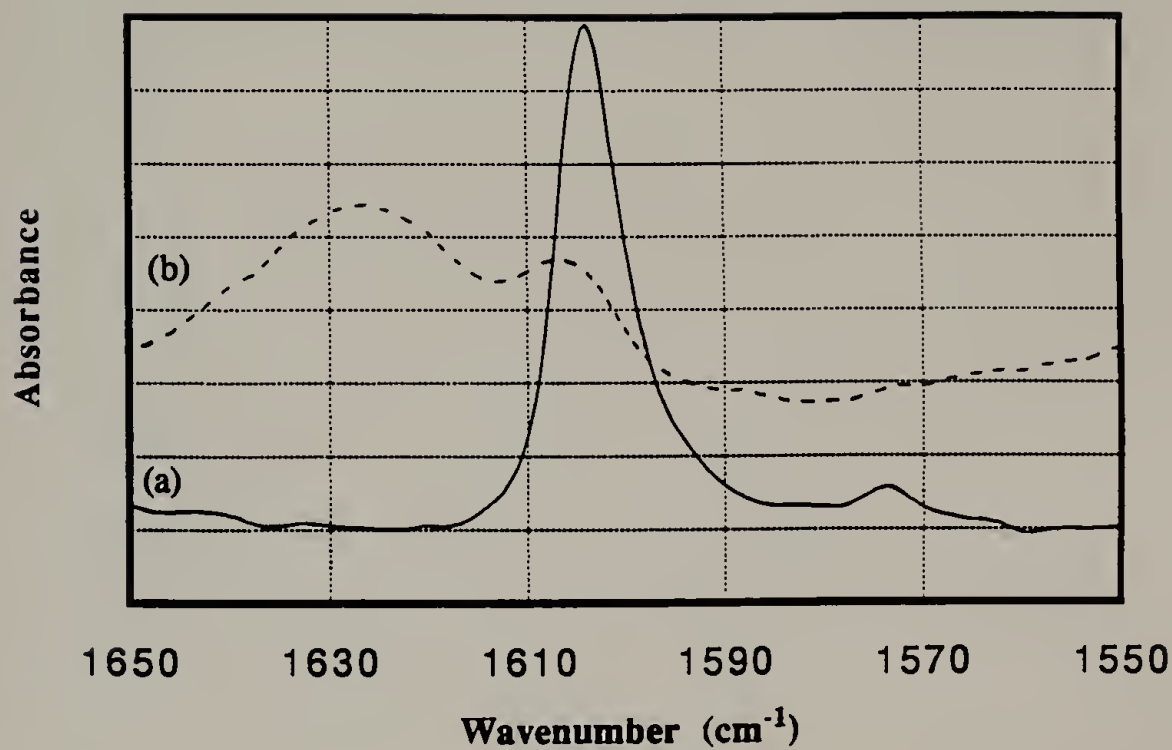


Figure 4.9: FTIR spectra of model compounds: (a) 3,5-dimethyl pyridine dicarboxylate (—); (b) and the mixed salt with 5 sulfonic acid dimethylisophthalate (—)

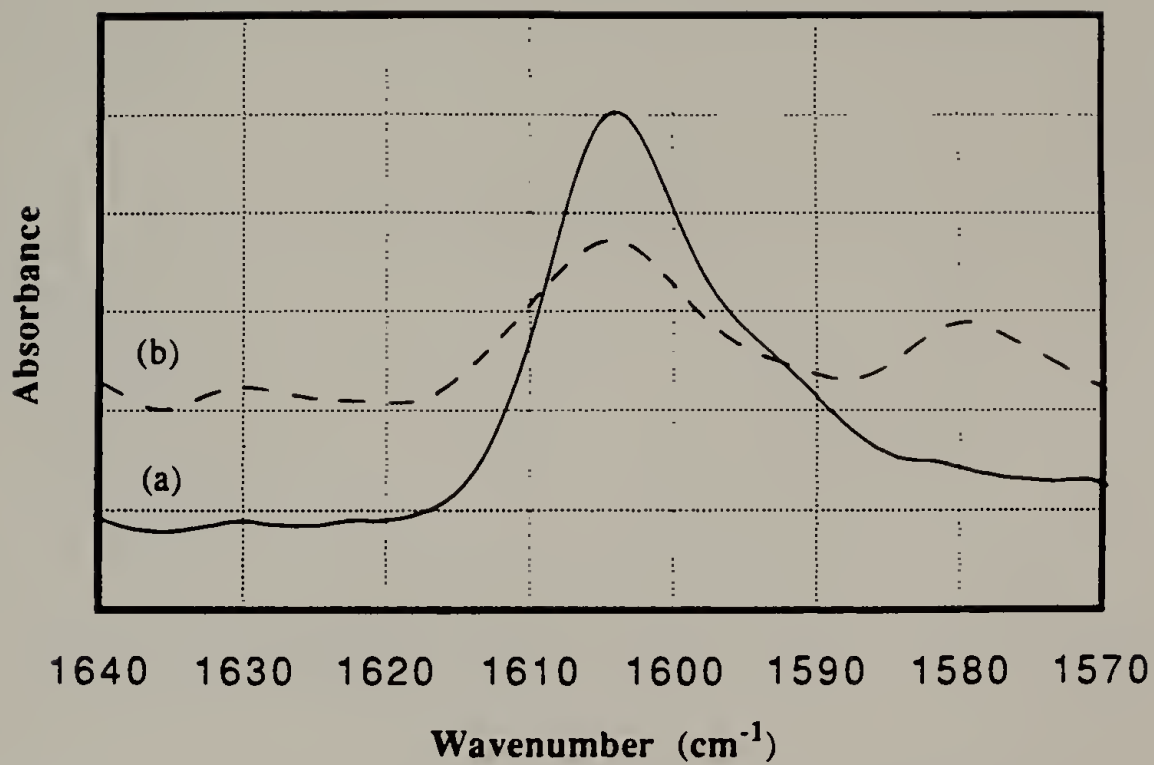


Figure 4.10: FTIR spectra: (a) poly(75%BHBP_{2.5}-co-25%HDO/HTH), polymer I 1, and (b) the acid blend of polymer I 1 with 75% PET-SO₃H

The assignment of resonance peaks associated with stretching vibrations of sulfonic acid, zinc sulfonate, and sulfonate anion, in the region of 1000 -1150 cm^{-1} could not be clearly resolved due to the multiple frequency overlaps of aromatic and alkoxy (C—O) groups associated with the highly aromatic polyester, TLCP_N.

Degree of Compatibilization. The degree of compatibilization for TLCP_N/PET-SO₃H(Zn) blends was evaluated, where the TLCP_N selected was polymer I 1. The degree of compatibilization was characterized by DSC and DMTA. The DSC results for the individual components of the blends are listed in Table 4.8. These results were based on the second heating and cooling scans at 10 °C/min.. The tabulated value for the T_g of polymer I 1 was based on the DMTA , since the T_g could not be detected by DSC.

Table 4.8: DSC results for the individual components of TLCP_N/PET-SO₃H(Zn) blends, as recorded on second heating and cooling scans at 10 °C/min.

Polymer	T _g (°C)	Δ T _g (°C)	T _m (°C)
I 1	56	—	238
PET-SO ₃ H	69	6	222
PET-SO ₃ Zn	73	6	225

The compression molded films of both the acid and zinc blends were prepared. These films were evaluated by both DSC and DMTA. The DSC scans were recorded at 10 °C/min, and the resulting T_gs for sulfonated PET component, T_{g2}s, are listed in Table 4.9. Again, the T_gs of polymer I 1, T_{g1}s, could not be detected by DSC. Therefore values as listed were recorded by DMTA. The melting transition temperatures for

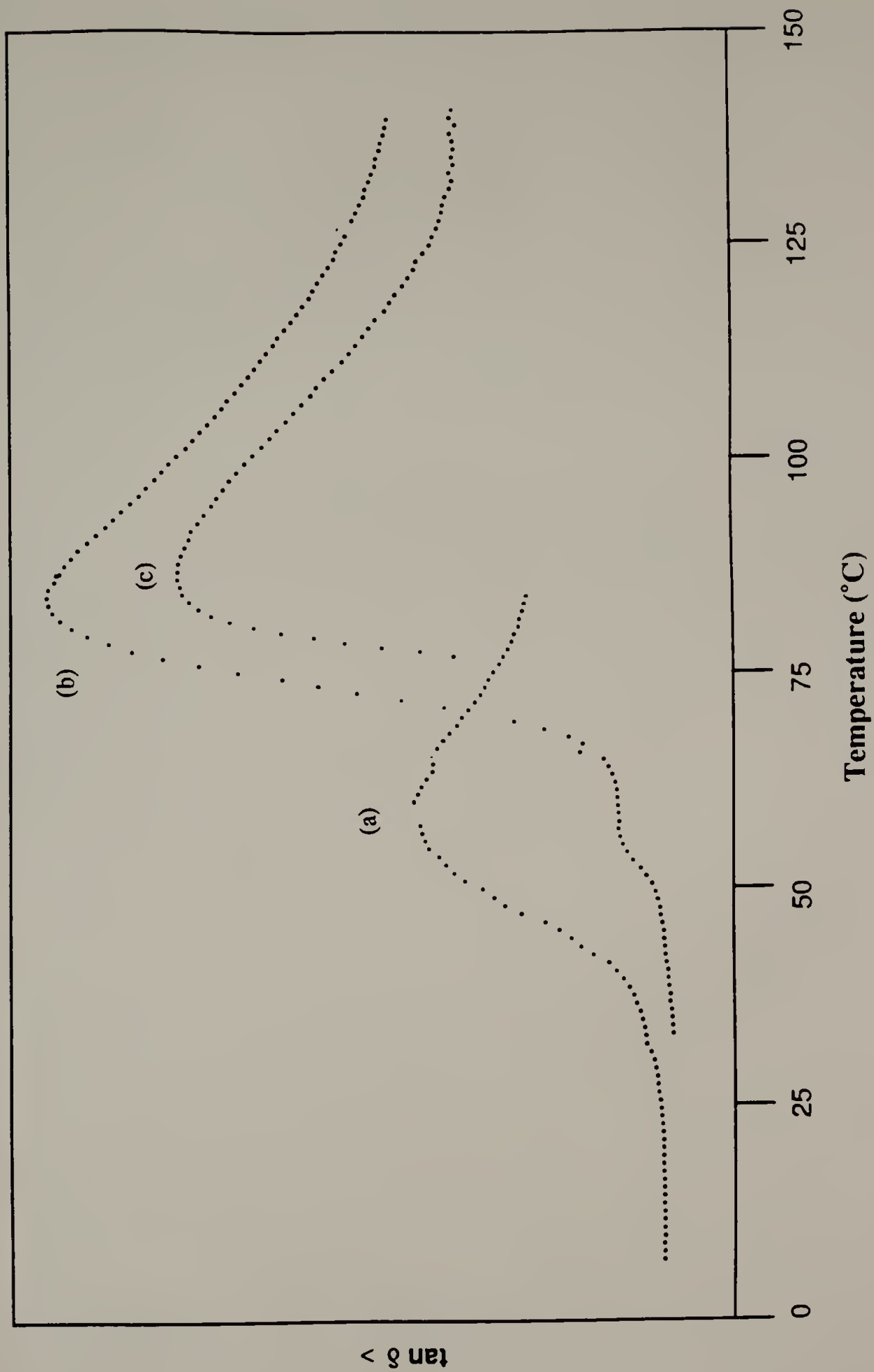
components of the blend differed by only 10°, which resulted in endothermic transitions appearing to coalesce. The T_m s values for both blends were 224-228 °C.

Table 4.9: Summary of the DSC results for the TLCP_N/PET-SO₃H(Zn) blends, where the TLCP_N evaluated is polymer I 1

Blends	T_{g1} (°C)	ΔT_{g1} (°C)	T_{g2} (°C)	ΔT_{g2} (°C)
(25/75) I 1/PET-SO ₃ H	56	—	69	10
(25/75) I 1/PET-SO ₃ Zn	56	—	69	9

The $\tan \delta$ vs. temperature plots for polymer I 1, PET-SO₃Zn, and their blends were run in the single cantilever mode at 1 Hz, and are shown in Figure 4.11. The DMTA experiments were conducted on the same compression molded films used in the DSC analysis. The $\tan \delta$ maxima indicates a minimum shift in temperature upon blending. The $\tan \delta$ values for polymer I 1 are considerably low because of the composition in the blend and perhaps the composition of the amorphous phase. These results appear to indicate no compatibilization resulting from the incorporation of either ionogenic moiety. The films evaluated were very brittle, which could be due to their poor interfacial adhesion or the low IV values of the sulfonated PET.

Figure 4.11: The $\tan \delta$ vs. temperature plots for (a) polymer I 1, (b) the zinc blend, and (c) PET-SO₃Zn, recorded in the single cantilever mode at 1 Hz



Conclusions

The main objective of this chapter was to explore the utility of specific interactions as a means of compatibilizing thermotropic liquid crystalline polyesters with poly(ethylene terephthalate). The initial strategy focused on the incorporation of derivatives of pyridine dicarboxylate units into a thermotropic liquid crystalline polyester, TLCP, previously developed for blends studies with PET or PBT. The screening program and the development of this model system were presented in the previous chapter.¹⁵ The selected candidates were based on the copolymerization of bis(4-hydroxybutyl) terephthalate, BHBT, with triaromatic "triad" mesogenic monomer, CIHTHCl. Therefore, Scheme I and II, as shown in Figure 4.1 and 4.2, respectively, were designed to incorporate derivatives of pyridine dicarboxylate into monomers of similar chemical structure as BHBT. The monomers, BHBP_{2,5} and CIP_{3,5}Cl were prepared and characterized in order to prepare polymers following Scheme I and II. The liquid crystalline phase behavior for this series of polymers was then examined by CPOM and DSC. The summary of the DSC and IV results for this series of polymers are listed in Table 4.4. Based on the comparison of these results with the model TLCP system,¹⁶ all polymers exhibited a similar nematic enantiotropic phase behavior.

With the development and characterization of novel TLCP_{NS}, the focus of the investigation turned to the development of the necessary ion exchange procedures for PET-SO₃Na. The objective was to exchange the initial sodium ions for hydrogen and then hydrogen ions for zinc. Two procedures were developed and optimized to obtain the desired quantitative ion exchange.

The main objective of this investigation was then examined. Stoichiometric acid and zinc blends were prepared in solution and characterized. First, the level of specific intermolecular interactions were evaluated with FTIR. The FTIR spectrum revealed no significant specific interactions for the blends, when compared to the spectrum recorded

for model compounds. The initial criteria considered the development of a TLCP similar in molecular structure to PET or PBT in order to promote greater compatibility, but this significantly complicated any quantitative evaluation of their recorded FTIR spectrum. However, the adsorption bands for the pyridine ring stretching were clearly resolved. Future exploratory studies should make proper adjustments for the similarity in chemical structure before considering FTIR as a technique to probe the level of specific interactions.

The degree of compatibilization was characterized by DSC and DMTA. The DSC results presented in Table 4.9 and the $\tan \delta$ vs. temperature traces shown in Figure 4.10 indicated no significant compatibilization, as anticipated from the previous FTIR results.

Although no significant specific intermolecular interactions or compatibilization was evident, the exploratory study had produced some significant findings: (1) ion exchange procedures for sulfonated PET, which could be utilized for a variety of alkali, alkaline earth, or transition metals, and (2) the development of novel TLCP_{Ns} with similar phase behavior to their unmodified counterparts.

This initial study was restricted to the investigation of aromatic-polyester based TLCP/TP blend systems. The systems, as previously mentioned, were initially designed to be very similar in chemical structure as to enhance the intermolecular Van der Waals forces and thus greater interfacial adhesion for the enhancement of the physical properties of PET. But, these intentions prevented any thorough characterization of these blends by almost all common techniques, as seen in the difficulty in resolving specific IR absorbance bands, T_g s, T_m s, and $\tan \delta$ s. Stress-strain analysis would not be consider sensitive to these similarities in structure, and fibers were prepared. These results were not presented in this chapter, because the fibers were considerably brittle and were not analyzed. From the outset, selection of the ionogenic moiety to be incorporated into TLCP_{Ns} required rather high thermal stability, and thus moderate to

low Lewis basicity. Future ionomeric TLCP/TP system should consider temperature regimes below 200 °C, so as to maintain greater thermal stability and to utilize ionogenic moieties with greater Lewis basicity.

References

1. Paul, D. R. and Newman, S., Polymer Blends, (New York: Academic Press), (1978)
2. Olabisi, O., Robeson, L. M., and Shaw, M. T., Polymer-Polymer Miscibility, (New York: Academic Press), (1979)
3. MacKnight, W. J., Lantman, C. W., and Lundberg, R. D., "Ionomers", eds. Booth, C. and Price, C., Comprehensive Polymer Science: The Synthesis, Characterization, Reactions, and Applications of Polymer, 2, (New York: Pergamon Press), (1987)
4. Brostow, W., *Kunststoffe*, **78**, 411 (1988)
5. National Materials Advisory Board Commission on Eng. & Tech. Systems National Research Council, Liquid Crystalline Polymers, (Washington D.C.: National Academy Press (1990)
6. Dutta, D., Fruitwala, H., Kohli, A., and Weiss, R.A., *Polymer Engineering and Science*, **30** (17), 1005-1018, (1990)
7. Flory, P. J., *Macromolecules*, **21**, 66 (1988)
8. Balluaff, M., *J. Polym. Sci., Part B, Phys.*, **25**, 739 (1987)
9. Balluaff, M., *Mol. Cryst. Liq. Cryst.*, **136**, 175 (1986)
10. Kiss, G., *Polym. Eng. Sci.*, **27**, 410 (1987)
11. Eisenberg, A, Smith, P., and Zhou, Z.L., *Polym. Eng. Sci.*, **22**, 1117 (1982)
12. Lundberg, R. D., Phillips, R. R., and Peiffer, D. G., *J. of Polym. Science: Part B: Polymer Physics*, **27**, 245-260 (1989)
13. Beery, D, Kenig, S., and Siegmann, A., *Polym. Eng. Sci.*, **31**(6), 465 (1991)
14. 7% sulfonated PET was received as a gift from the AKZO Corporate Reserch, Arnhem, Holland. (IV = 0.44; inherent viscosity of a solution in trifluoroacetic acid at a concentration of 0.5 g/dl at 30 °C)
15. Chapter 3: page 66, Table 3.3
16. Chapter 3: page 52
17. Chapter 3: pages 49
18. Chapter 3: pages 51-70

19. Ober, C.K., The Synthesis and Characterization of Some Liquid Crystalline Polyesters based upon the Oxybenzoate-terephthalate Mesogenic Unit, PhD Thesis, University of Massachusetts, Amherst (1982)
20. Chapter 3: pages 54-58
21. Ringbom, A., Complexation in Analytical Chemistry: a guide for the critical selection of analytical methods based on complexation reactions, (New York: Interscience Publisher), (1963)

CHAPTER 5

PREPARATION AND CHARACTERIZATION OF IONOMERIC BLENDS OF POLY(ETHYL ACRYLATE-CO-VINYL PYRIDINE) WITH SULFONATED PET

Introduction

Multi-phase polymer systems have been of considerable scientific and technological interest, as can be seen in some of the more recent monographs and reviews.¹⁻¹¹ The term "multi-phase polymer system" is a very broad classification of materials, including: segmented polymers, block copolymers, composites, immiscible polymers, partially compatible polymers, liquid crystalline polymers, semi-crystalline polymers and ionomers. These materials have received considerable attention because of their unique morphologies and the wide range of mechanical properties which have been observed.

The well-known challenges confronting the development of multi-phase polymer systems or polymer blends have been in relation to the thermodynamics of the system, which typically favors polymer pair immiscibility. The unfavorable thermodynamic conditions of high molecular weight pairs are typically associated with low entropy of mixing and a positive enthalpy of mixing. The enthalpy term relates to the temperature and composition dependent attractive forces between two polymer pairs, which also dictates interfacial properties of a properly mixed blend. The interfacial mixing or the degree of interfacial adhesion is ultimately responsible for the resulting mechanical properties of the system, especially in the case of multi-phase polymer blends. In a

practical sense, only the enthalpy term can be influenced towards an enhanced degree of compatibilization or interfacial adhesion between polymer pairs. One general approach, which has been recently reviewed,^{9,11} has been the incorporation of ionogenic moieties to act as specific sites for intermolecular interactions between established immiscible polymer pairs causing a favorable decrease in the enthalpy of mixing.

Eisenberg and co-workers¹² have demonstrated that pairwise attraction of a minimum of 5 mole% of ionogenic moieties along a polymer backbone was necessary for compatibilization of immiscible pairs of polymer blend containing polystyrene and poly(ethyl acrylate), as concurred from dynamic mechanical thermal analysis (DMTA). The ionogenic moieties evaluated in this study consisted of the free acid form of sulfonated polystyrene and poly(ethyl acrylate-co-4-vinyl pyridine). The improved compatibility of the ionomeric blend was achieved by proton transfer of the sulfonic acid functional group to the basic vinyl pyridine, which led to the formation of complementary ionic pairs.

Peiffer and coworkers¹³ examined transition metal complexations formed between the zinc and copper melt salts of sulfonated EPDM with poly(styrene-co-4-vinyl pyridine), as a means of enhancing the enthalpy of mixing and controlling the melt viscosity, in relation to the unmodified blend (EPDM/PS). The authors observed significantly higher melt viscosities for stoichiometric blends along with Fourier transform infrared (FTIR) spectroscopy results which indicated a complexation involving a 1:1 stoichiometry of sulfur and nitrogen.

MacKnight and coworkers¹⁴⁻¹⁶ have examined both acid-base interactions and zinc transition metal complexations of sulfonated poly(styrene) and poly(ethyl acrylate-co-4-vinyl pyridine) blends. They have thoroughly characterized the degree of compatibilization in relation to ionic contents up to 10 mole%, and have observed various degrees of compatibilization. Their results indicate a predominately immiscible

two phase system existed below ionic contents of less than 5 mole% and a single mixed phase system becomes the dominate phase above 5 mole%, as concluded by DMTA.

The ionomeric blend systems, which have been cited or previously discussed, contained predominately non-crystalline components. For the initial investigations into the structure-property relationships of ionomeric blends, these systems offered the desired simplicities of having single-phase components. Further experimental evidence which could demonstrate how applicable the incorporation of ionogenic moiety into the backbone of immiscible polymer pairs should greatly enhance the polymer scientist's ability to control the degree of miscibility and develop new materials. Therefore, the present investigation explores acid-base interactions and zinc transition metal complexation of ionomeric blends containing a multi-phase (semi-crystalline) component. The semi-crystalline component selected for this study was sulfonated poly(ethylene terephthalate). The level of sulfonation was 7 mole% and the degree of crystallinity was approximately 35%, as determined by differential scanning calorimetry (DSC).

Ion exchange procedures were developed, which exchange the initial sodium ions of sulfonated PET for hydrogen and subsequently hydrogen ions for zinc. Both components, the free acid and the zinc neutralized form of sulfonated PET were then used to prepare acid and zinc blends with poly(ethyl acrylate-co-4-vinyl pyridine) (p(EA-co-VP)). The level of acid-base interactions and zinc transition metal complexations was probed by FTIR spectroscopy. The degree of compatibilization was examined by both DSC and DMTA in respect to blends containing unmodified poly(ethyl acrylate) and zinc neutralized sulfonated PET.

Experimental

Materials

Poly(ethylene terephthalate) modified with 7 mole% of sodium, 5-sulfo isophthalate units was received from AKZO Corporate Research, Arnhem Holland, ($IV = 0.44$; inherent viscosity of a solution in trifluoroacetic acid at a concentration of 0.50 g/dl at 30 °C). Poly(ethyl acrylate) ($M_n = 230,000$ and $M_w/M_n = 3.87$) and poly(ethyl acrylate-co-4-vinyl pyridine) modified with 5.2 and 10.6 mole% of 4-vinyl pyridine ($M_n = 201,000$, $M_w/M_n = 2.02$ and $M_n = 161,000$ and $M_w/M_n = 1.96$, respectively) used in this study was prepared and characterized in our research group, as previously reported.¹⁴ The average molecular weight values were determined by GPC and were based on polystyrene standards. All other chemicals were obtained from the Aldrich Chemical Co. *m*-Cresol was pre-dried over $CaCl_2$ and then distilled. Amberlyst 15[®], a non-aqueous cationic exchange resin, was purified with multiple washing in 1 N H_2SO_4 , deionized water, and toluene. The resin was then dried in an azeotropic distillation of toluene. Trifluoroacetic acid was purchased at 99% purity and was used without further purification. $CHCl_3$ was pre-dried over 4 Å molecular sieves and then distilled over P_2O_5 .

Ion Exchange Procedure

Ion exchange of sodium for free-hydrogen: In a 250 ml three neck round-bottom flask fitted with a condenser, inert gas inlet, and mechanical stirrer, was added 10 g (3.5 meq of Na) of 7% sodium, sulfonated PET, 42 g (175 meq of H) of Amberlyst 15[®], and 50 ml of trifluoroacetic acid. The solution was gently stirred for 3 hrs. The slurry was then filtered through a buchner funnel fitted with a low porosity, glass-fiber filter paper. The resin was collected in the funnel and was further washed with small portions of trifluoroacetic acid totaling 100 ml. The volume of the resulting filtrate was then

reduced to approximately 75 ml by distillation under aspirator pressure at 30 °C. The filtrate was then precipitated in acetone and followed by Soxhlet extraction in refluxing acetone for 2 days. The white solid was then vacuum dried at 70 °C for 2 days, giving a yield of 80%. Elemental analysis; Calculated for $C_{10}H_{8.07}O_{3.79}S_{.07}$: C, 62.84%; H, 4.26%; S, 1.17%. Found: C, 62.81%; H, 4.22%; S, 1.06%; Na, 0.0%.

Ion exchange of free-hydrogen for zinc: In a 175 ml chromatographic column (3 cm x 25 cm, D x L) fitted with coarse-grade glass frit, was added a slurry, composed of 10 g (3.5 meq of H) of the free-acid form of 7% sulfonated PET as a fine powder (mesh size 50) in a saturated aqueous solution of zinc acetate. To this packed column, 5 bed volumes equaling 600 ml of a saturated solution of zinc acetate was subsequently passed through the column at an output rate of 10 ml/min.. The slurry was then placed in a 500 ml Erlenmeyer flask with 350 ml of deionized water, vigorously stirred for 1 hr., and filtered. The filter cake was further washed with deionized water until no detectable trace of zinc acetate was observed by the evaluation of aliquots of the filtrate with 1 N NaOH for the formation of zinc hydroxide. The powder was then vacuum dried at 70 °C for 2 days. Elemental analysis; Calculated for $C_{10}H_{8.07}O_{3.79}S_{.07}Zn_{.035}$: C, 62.14%; H, 4.13%; S, 1.16%; Zn, 1.18%. Found: C, 62.02%; H, 4.15%; S, 1.07%; Zn, 1.09%.

Solution Blend Preparation

All polymer blends were prepared in a *m*-cresol:chloroform solution (70:30 by volume) under similar conditions. The following is an example of the preparation of the acid-blend of sulfonated PET with p(EA-co-VP). In a 500 ml Erlenmeyer flask fitted with a condenser, inert gas inlet, and magnetic stirrer, 7.50 g (2.625 meq of H) of the 7% free-acid form of sulfonated PET was dissolved in 175 ml of *m*-cresol:chloroform solution heated to 60 °C. In a separate 125 ml Erlenmeyer flask fitted with a condenser, inert gas inlet, and magnetic stirrer, 2.36 g (2.625 meq of N) of p(EA-co-VP), was dissolved in 75 ml of *m*-cresol:chloroform solution. This second solution containing

p(EA-co-VP) was then slowly added dropwise to a vigorously stirred solution of sulfonated PET at 25 °C over a period of 30 min.. The concentration of polymer for both acid and zinc blends was adjusted with the *m*-cresol:chloroform solution to prevent gelation and to ensure proper mixing. A final concentration of 0.4 g/ml was found to be sufficient to prevent gelation. The solution was continuously stirred for 5 hrs to ensure proper mixing. The solution of polymer blend was then precipitated in hexane, followed by Soxhlet extraction in refluxing hexane for 2 days, and vacuum dried at 70 °C for 3 days. The yield was 97%.

Characterization Methods

The elemental analysis was performed by the Microanalysis Laboratory at the University of Massachusetts. Inherent viscosities (IVs) for all polymers were determined at 30 °C in trifluoroacetic acid, using a Cannon-Ubbelohde viscometer. The polymer concentration was 0.5 g/dl. FTIR spectra for all compounds were recorded on an IBM 30 with the resolution of 1 cm⁻¹. A minimum of 128 scans were signal averaged. The samples were cast on KBr plates from a solution of hexafluoroisopropanol.

DSC measurements were conducted with a Perkin-Elmer DSC-7 on samples ranging from 7-10 mg. The temperature and power ordinates of the DSC were calibrated with respect to the known melting point and heat of fusion of a high purity indium standard supplied by Perkin-Elmer. The glass transition temperature (T_g) was defined as the midpoint of the change in the specific heat, and for exothermic and endothermic processes the peak temperatures were taken as the transition temperatures. DMTA measurements were conducted with a Polymer Laboratories PL-DMTA on compression molded films in the single-cantilever mode at 1 Hz.

Results and Discussion

The initial focus of the investigation was to develop sufficient ion exchange procedures to quantitatively exchange sodium ions for hydrogen and subsequently hydrogen ions for zinc. Once the ion exchange processes were optimized, the main objective of this investigation, the preparation and characterization of acid and zinc blends of sulfonated poly(ethylene terephthalate) with poly(ethyl acrylate-co-4-vinyl pyridine) was examined. For the acid blend, the speculation of ion-ion pairwise interaction via proton transfer mechanism can easily be visualized. For the zinc blend, a schematic representation of the zinc complexation is shown on next page in Figure 5.1.

Optimization of the Ion Exchange Procedures for Sulfonated PET

The initial objective was to exchange sodium ions for hydrogen and hydrogen ions for zinc. The sulfonated PET used in this investigation was characterized as containing a sulfonation level of 7 mole%.¹⁷ The sulfonated groups were incorporated into PET by a standard two-step melt polycondensation reaction, in which 7 mole% of sodium, 5-sulfo-dimethyl isophthalate was substituted for the equivalent mole percent of dimethyl terephthalate. Direct sulfonation could not be considered, due to the relatively high reactivity of the ester linkages toward available sulfonation reagents.

The ion exchange of sodium ions for hydrogen in low molecular weight polar compounds is now considered trivial. But, due to the poor solubility of PET in practical organic solvents, the use of conventional ion exchange techniques is very restricted. The techniques developed were based on two fundamental concepts of ion exchange: (1) a batch process driven by the equilibrium principles, and (2) a column process driven by the laws of mass action.¹⁷

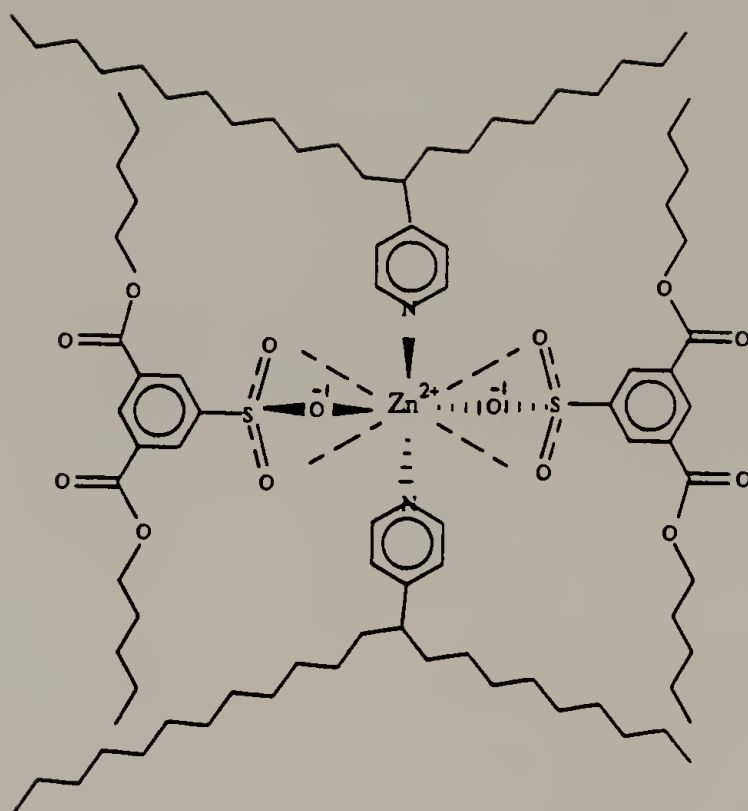


Figure 5.1: Schematic representation of the zinc blend of PET- SO_3Zn and poly(ethyl acrylate-co-4-vinyl pyridine)

Three methods for the ion exchange of sodium for hydrogen were investigated. The first two methods involved the use of a non-aqueous ion exchange resin, Amberlyst 15[®] with 10% solutions of PET-SO₃Na in trifluoroacetic acid. The first method examined a batch process and the second method examined a column process, where naturally the Amberlyst 15[®] was considered the stationary phase and the polymeric solution was considered the mobile phase. Both processes were optimized to obtain quantitative exchanges of sodium ions for hydrogen by adjusting the excess of Amberlyst 15[®]. Both methods were successful, but the batch process was selected based on the minimum amount of solvent utilized in the process. For the batch process, Amberlyst 15[®] was used in a 50 fold excess. The third technique considered a finely milled powder of PET-SO₃Na (mesh size 50) as the stationary phase in a column process, where a 20% HCl solution was considered as the mobile phase. This process was also optimized for a quantitative exchange of sodium ions for hydrogen. The parameters controlling the ion exchange process were optimized, such as: (1) concentration of the mobile phase, (2) particle size, and (3) flow rate. Degree of neutralization was based on the elemental analysis results, which indicated no detectable trace of sodium and acceptable percentage of hydrogen with in $\pm 0.3 \%$.

Typically, ion exchange resins are characterized by their chemical structure, ion content, and the average molecular weight between crosslinks. These factors control the type of solvent which can be utilized and relative efficiency of ion exchange. The powdered sulfonated PET used in this investigation, was received having low crystallinity (ca. 8-10%), and this morphology was viewed as one of the contributing factors in the successful exchange of sodium for hydrogen ions.

The next ion exchange procedure to be developed was the exchange of hydrogen ions for zinc. Of the three methods previously discussed, the later method in which the powdered sulfonated PET was utilized as a stationary phase in a column process was the most successful. The mobile phase was a saturated solution of zinc acetate. Similar

parameters were optimized to obtain quantitative neutralization to the zinc form. These results constitute the optimized procedure outlined in the experimental section, along with the results of the elemental analysis. A variety of experiments were conducted to directly exchange sodium ions for zinc, such as: (1) the generation of Amberlyst 15® completely neutralized with zinc ions as a stationary phase, and (2) using powdered PET-SO₃Na as a stationary phase with a saturated solution of zinc acetate as the mobile phase. Unfortunately, both methods could not be optimized at this time to produce a quantitative exchange. Perhaps, if sodium 5-sulfo dimethyl isophthalate was neutralized with other alkali metals, such as potassium, the equilibrium constant for the direct exchange to zinc would be high enough to make these methods practical. Investigation for direct ion exchange to zinc or any other transition metal such as copper or cobalt was outside the scope of this investigation, yet will be explored in future work.

Level of Specific Intermolecular Interactions between Ionogenic Pairs

Stoichiometric acid and zinc blends were prepared containing p(EA-co-VP) and PET-SO₃(H)Zn. The stoichiometry was based on a 1:1 ratio of sulfur to nitrogen. The composition of the blends evaluated are listed in Table 5.1.

All blends were prepared in solutions of *m*-cresol:chloroform (70:30 by volume) under similar conditions. The concentrations were minimized to favor greater mixing, lower solution viscosities, and reduce preferential polymer precipitation. The minimum concentration value was approximately a 4% solution by weight. Below this concentration, the resulting polymer precipitate was too difficult to be retained by filtration. One common observation was the significant increase in solution viscosity for the blends containing PET-SO₃Zn relative to the acid blends and the individual components of the blend. For the zinc blends, the temperature was raised to 60 °C, which significantly reduced the solution viscosity to ensure proper mixing.

Table 5.1: The compositions of p(EA-co-VP)/PET-SO₃H(Zn) blends and their respective ionogenic content

Blend	% p(EA-co-VP)	% (VP)	% (7% PET-SO ₃ H)	% (7% PET-SO ₃ Zn)
A	23	0	—	77
B	23	10.6	—	77
C	23	10.6	77	—
D	58	0	—	42
E	58	5.2	—	42

The existence of specific intermolecular interactions in these blends was promising. The lack of any gelation for the acid blends was a concern. Perhaps the high dielectric constant for *m*-cresol caused significant solvation of the ionogenic moiety hindering any proton transfer. Unfortunately, the poor solubility of polyesters necessitates the use of solvents with high dielectric constants.

The level of specific intermolecular interactions was probed with the use of FTIR spectroscopy. Films were cast from 1% polymer solution in hexafluoroisopropanol on to KBr disks. Figure 5.2 shows the resulting FTIR spectra: (a) p(EA-co-VP) % VP 10.6; (b) zinc blend B; (c) acid blend C in the 1550-1650 cm⁻¹ region. In Figure 5.1 (a), the broad absorbance peak at 1600 cm⁻¹ corresponds to the pyridine ring stretching. In Figure 5.2 (b), the 1618 cm⁻¹ band corresponds to a pyridine ring stretching as a result of the formation of the zinc-pyridine complexes. In Figure 5.2 (c), a bimodal peak appears with a maximum absorbance at 1615 cm⁻¹, yet retaining the initial absorption of pyridine ring stretching at 1600 cm⁻¹ as a shoulder. The 1615 cm⁻¹ band is believed to correspond to formation of hydrogen bonds. If a proton transfer were to occur, the

corresponding pyridinium ring stretching would result in a peak shift to 1640 cm^{-1} , as well as having an extinction coefficient significantly higher than for initial pyridine ring stretching. These speculations were supported by similar findings of two separate FTIR spectroscopic study of ionomeric blends containing p(EA-co-VP). In the first study, Peiffer and coworkers¹³ examined a blend p(EA-co-VP) with zinc neutralized sulfonated EPDM. They assigned the absorbance band at 1618 cm^{-1} to correspond to pyridine stretching as a result of the formation of zinc-pyridine complexes. In the second study, MacKnight and coworkers^{15,16} examined both the acid and zinc blends of sulfonated polystyrene with p(EA-co-VP) and their respective model compounds. They assigned an absorbance band at 1640 cm^{-1} to correspond to pyridinium ring stretching as a result of a proton transfer mechanism and an absorbance band at 1620 cm^{-1} to correspond to pyridine ring stretching as a result of the formation of zinc-pyridine complexes.

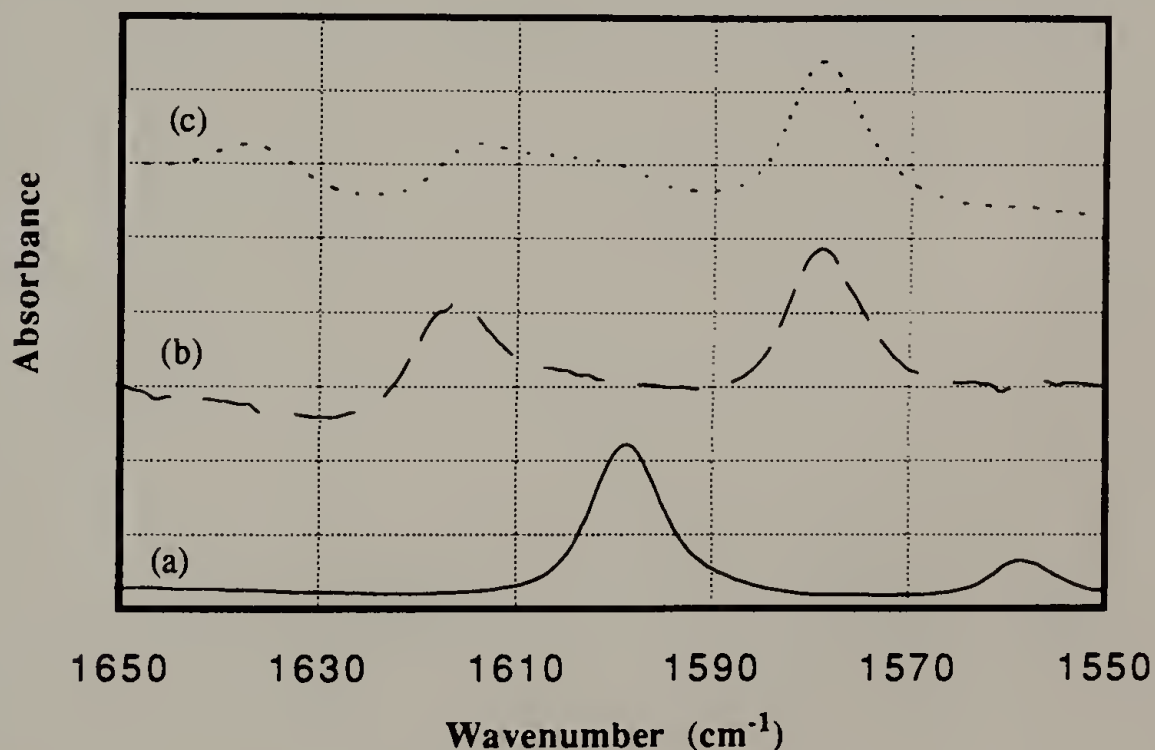


Figure 5.2: FTIR spectra: (a) p(EA-co-VP), %VP 10.6 (—); (b) zinc blend B (---); (c) acid blend C (...)

Quantitative analysis of the level of zinc complexation or hydrogen bonding was hindered by the lack of an isolated reference absorbance band. Normalization of the blends spectrum were approximated by the neighboring absorbance band at 1580 cm^{-1} , which corresponded to aromatic ring stretching associated with the terephthalate units. The C—H stretching of the ethyl group of p(EA-co-VP) was difficult to resolve from methylene groups of PET-SO₃H(Zn). Therefore, the results are a qualitative representation of the level of specific interactions. Based on Figure 5.2 (a)-(c), the formation of zinc-pyridine complexes seems to be significantly favored in comparison to the formation of hydrogen bonds. There was no evidence of the formation of pyridinium ions by the means of a proton transfer mechanism. As mentioned, the number of solvent systems suitable for the blends preparation prevented any further investigation of solvent effects. Melt mixing was not considered a potential option, due to the relatively poor thermal stability at temperatures which would insure proper mixing.

Blend E (58% p(EA-co-VP) % VP 5.2 and 42% PET-SO₃Zn) was also evaluated by FTIR under the same conditions previously described. The same batch of 7 mole% zinc neutralized PET was used in the preparation of blend E and blend B. Figure 5.3 shows the resulting FTIR spectrum: (a) p(EA-co-VP) % VP 10.6; (b) zinc blend B; (c) zinc blend E in the $1550\text{-}1650\text{ cm}^{-1}$ region. The spectra for blend E contains a bimodal peak corresponding to a mixture of two types of pyridine ring stretching. In Figure 5.3 (c) the absorbance band at 1618 cm^{-1} corresponds again to pyridine ring stretching as a result of the formation of zinc-pyridine complexes as primarily observed for blend B Figure 5.3 (b), and also contains an absorbance band at 1598 cm^{-1} which corresponds to free pyridine ring stretching. This bimodal peak represents an equilibrium of these two types of ring stretching, the relative ratios could not be determined quantitatively, for reasons previously mentioned. One general explanation could be the lack of interfacial mixing due to an increase in phase separation, preventing appropriate conditions for complexation. Probable causes for an increase in phase separation are: (1) the increase

in distance between VP groups; (2) the increase in the blended composition of p(EA-co-VP); (3) compositional drift, caused by higher conversion (25% increase in M_n) and lower initial concentration of VP. These are based on the following assumptions (1) milliequivalent ionogenic moiety per gram of component was accurately determined, (2) weight % of components measured remained in the blend during solution blending and precipitation, and (3) blend was properly mixed in hexafluoroisopropanol. There are many factors which could account for the lack of complexation in blend E, and these types of experiments were not within the scope of this initial study.

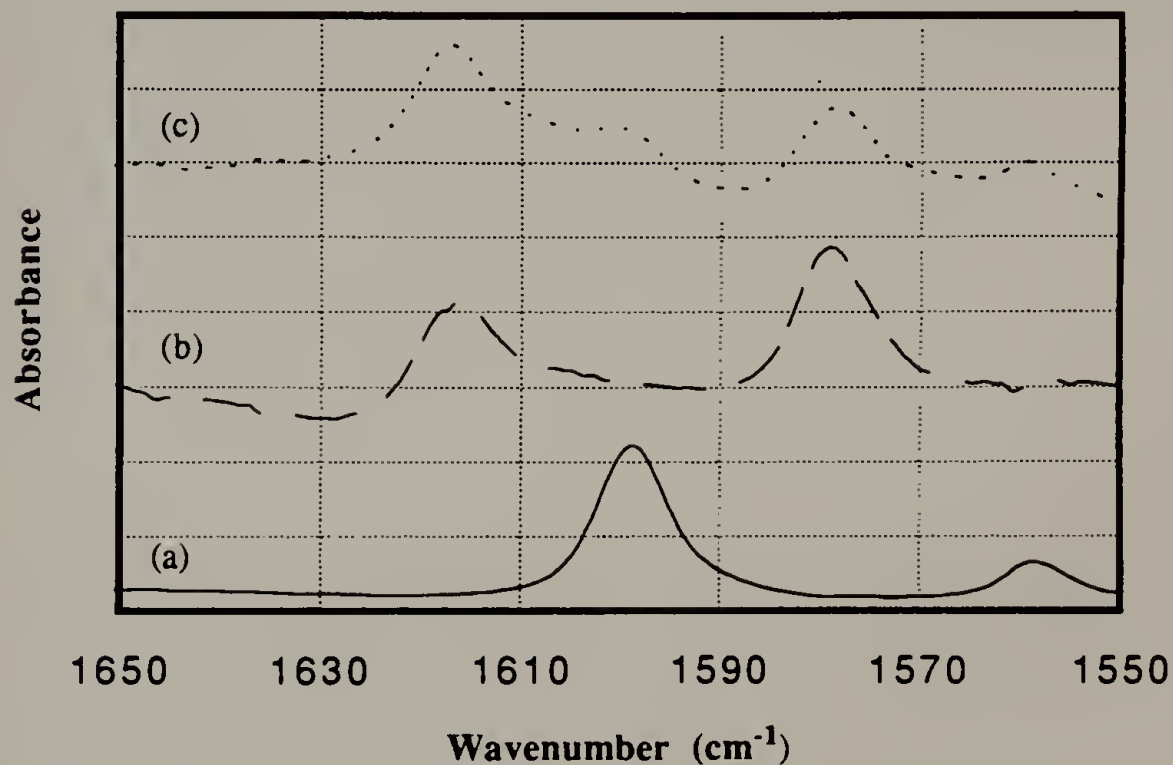


Figure 5.3: FTIR spectra: (a) p(EA-co-VP), %VP 10.6 (—); (b) zinc blend B (---); (c) zinc blend E (...)

Degree of Compatibilization

The main objective of this investigation was to examine an ionomeric blend system containing a multi-phase (semi-crystalline) component. Therefore, the degree of crystallinity of sulfonated PET was optimized and the influence on the degree of compatibilization was evaluated by DSC and DMTA. The optimum annealing temperatures from the solid state for PET-SO₃Zn and blend B were determined with DSC by the evaluation of ΔH_m vs. temperature, at which point a ΔH_m (maximum) was observed at 170 and 150 °C, respectively. The optimum annealing time at these selected temperatures in relation to ΔH_m (maximum) was 60 minutes, at which point $\Delta (\Delta H_m/\text{min.})$ had significantly decreased. The calculated percentage of crystallinity was based on $\Delta H_{\text{fus}}^\circ$ value for PET of 113 J/g¹⁹. The DSC heating scans of annealed PET films revealed the classical multi-endothermic transitions, the lower endotherm ($\Delta H_m'$) being approximate 10-20 °C above the set annealing temperature. The overall % crystallinity was based on the ΔH_m of both endothermic transitions. The lower endotherm has been associated with a discontinuous crystallite size distribution, which was very sensitive to the annealing conditions.^{20,21} Roberts demonstrated evidence for a reorganization mechanism, as the set annealing temperature approached the higher endothermic transition, only a single endothermic transition was observed, which melted at a higher T_m . The optimum annealing conditions for pure PET has been observed for considerably longer time periods (>16 hrs) at temperatures very close to the T_m .²¹ For this investigation, similar conditions would not be practical due to the thermal stability of the ionomeric systems. The optimized conditions were then applied from the solid state to films of PET-SO₃Zn and to all the blends listed in Table 5.1, the degree of compatibilization was examined. The summary of the DSC results will be presented in subsequent tables. Pertinent DSC traces which support the text of the following results and discussion section, are collected at the end of this chapter in Figures 5.4 -5.11. The summary of the DSC results for the individual components of the blends are listed in

Table 5.2. These results were based on heating scans at 10 °C/min. The DSC heating scans for films of PET-SO₃Zn and p(EA-co-VP) (10.6% VP) are presented in Figure 5.4-5.6.

Table 5.2: Summary of DSC results for the homopolymers; results are based on heating scans at 10 °C/min.

Polymer	T _g (°C)	Δ T _g (°C)	T _m (°C)	Δ H _m (J/g)
PET-SO ₃ H	69	20	222	39
PET-SO ₃ Zn	69	22	225	43
p(EA-co-VP) (10.6% VP)	-7	11	—	—
p(EA-co-VP) (5.2% VP)	-18	9	—	—
p(EA)	-20	9	—	—

In determining the degree of compatibility for multiphase blends by DSC, a general limitation occurs when the T_gs of the components are too similar. A difference in T_gs between 30-50 °C can usually be resolved by DSC with a significant degree of confidence. In Table 5.2, the difference in T_gs for the individual components was greater than 70 °C. The summary of the evaluation of T_gs for the annealed blends by DSC are listed in Table 5.3. These results were based on the heating scans at 10 °C/min.. Blends A and D represent the unmodified blends containing 23 and 58% p(EA), respectively. The DSC heating scans for compression molded films of blends A and D are presented in Figure 5.7 and 5.8. These blends were considered immiscible, since there was no measurable shift in their T_gs and the value for Δ T_gs remained constant in comparison to the transitions of their respective homopolymers. Blend B,

containing 77% PET-SO₃Zn, displayed the highest degree of compatibilization based on the coalescence to a single T_g at 39 °C, as shown in Figure 5.9. Blend C, the acid blend, also displayed compatibilization but not to the same degree that was observed for

Table 5.3: Summary of the evaluation of T_gs for the annealed blends; results are based on DSC heating scan at 10 °C/min

Blend	T _g 1 (°C)	Δ T _g 1 (°C)	T _g 2 (°C)	Δ T _g 2 (°C)
A	-18	13	70	25
B	39	40	—	—
C	10	16	42	38
D	-18	12	68	28
E	-2	18.5	44	30

T_g1 represent the lower glass transition temperature

T_g2 represent the higher glass transition temperature

the zinc blend. Blend E, containing 42% PET-SO₃Zn, displayed a moderate degree of compatibilization based on the relative shift of both T_gs and the moderate increase in Δ T_gs.

The summary of the evaluation of the endothermic transitions for the annealed blends are listed in Table 5.4. Blend C was not evaluated with this series, due to the low relative thermal stability in the blend with p(EA-co-VP) at the set annealing conditions, as observed by optical microscopy. Therefore, the investigation focused on the zinc blends of both modified and unmodified poly(ethyl acrylate).

Table 5.4: Summary of the evaluation of the endothermic transitions for the annealed films of PET-SO₃Zn and their blends; results are based on the DSC heating scans at 10 °C/min.

Sample	T _m (°C)	Δ H _m ' (J/g)	Δ H _m (J/g)	% Cryst.*
PET-SO ₃ Zn	225	22	21	35
Blend A	219	6	30	32
Blend B	205	8	35	37
Blend D	221	2	12	29
Blend E	216	2.5	15.5	36

* Normalized value for the overall % crystallinity for the blends, where Δ H_{fus}° for PET used in the calculation was 113 J/g¹⁹

The overall % crystallinity for PET-SO₃Zn was 35%. The overall crystallinity appears to have an equal contribution from both of the endothermic transitions. For the blends, only 14 - 18% of the crystallinity could be associated with the lower endothermic transition. Annealing studies conducted on pure PET²¹, observed a similar trend of increase contribution to the higher Δ H_m when the set annealing temperature was increased. But, in the case of PET the value for T_m also increased. In the modified blends B and E, both T_m values were lower than for PET-SO₃Zn. For all blends, the greater contribution to the higher endothermic transition can be associated with an overall increase in molecular mobility of the system, a classical response similar to an increase in annealing temperature for pure PET. The modified blend B and E had a slightly higher value for the overall crystallinity in comparison to their unmodified counterpart, blend A and D, but have lower values for T_m. The increase in crystallinity and the decrease in T_m could be explained by an increase in the rate of heterogeneous nucleation. The

increase in the number of sites for nucleation could be a result of a decrease in size of the dispersed p(EA-co-VP) phase, which was seen by cross-polarized optical microscopy. The optical micrographs of blends A and B are present at the end of this chapter in Figure 5.12 (a) and (b), respectively. The phase separation of p(EA) from PET-SO₃Zn is apparent, the size of the dark spheres are on the order of 12 μ m in diameter. Figure 5.12 (b) by comparison show a considerable degree of compatibilization, which corresponds to the results with DSC. Obviously these conclusions are solely based on this preliminary investigation into the effect of compatibility on crystallization. A thorough characterization of blends containing a semi-crystalline component warrants detailed investigations of phase equilibria, crystallization kinetics, and morphology. Therefore, these aspects will have to be encompassed in future studies.

The DSC results for the annealed samples of PET-SO₃Zn and blend B were compared to quenched samples. The DSC heating scans for the quenched and annealed films of PET-SO₃Zn are shown in Figure 5.4 - 5.5, respectively. The DSC heating scan for the quenched and annealed films of blend B are shown in Figure 5.9 - 5.10, respectively. The DSC curves for PET-SO₃Zn reveal the anticipated decrease in T_g with respect to a significant increase in cooling rate. The measured T_g for PET-SO₃Zn decreased from 69 °C to 56 °C. The effects of an enhanced crystalline phase on the T_g for blend B was difficult to discern. The T_g for the quenched PET-SO₃Zn was considerably close to the T_g of the blend, and appeared to be only a small shift in T_g of 5°C.

The degree of compatibilization was further probed with DMTA. Films were compression molded and annealed under the same conditions as previously discussed. Pertinent $\tan \delta$ vs. temperature traces, which support the text of the following results and discussion section, are collected at the end of this chapter. Figure 5.13 represents the $\tan \delta$ vs. temperature traces of: (a) p(EA-co-VP) (10.6% VP); (b) an annealed film of blend

B; (c) an annealed film of PET-SO₃Zn. Experiments were conducted in the single cantilever mode at 1 Hz with a heating rate of 3°C/min.. Examination of Figure 5.13 (b) indicated phase separation into a p(EA-co-VP) rich phase with a maximum in tan δ value at 23 °C and a PET-SO₃Zn rich phase with a maximum in tan δ value at 68 °C. The corresponding shifts in tan δ for the p(EA-co-VP) rich phase were approximately 20 °C and 22 °C for the PET-SO₃Zn rich phase. Annealed films of blend B were compared to compression molded films with no further thermal treatment. In the preparation of compression molded films, the average cooling rate was measured at 25 °C/min.. Figure 5.14 represents the tan δ vs. temperature traces for annealed and compression molded films of blend B. There appears to be a significant shift in the tan δ corresponding to PET-SO₃Zn rich phase (68 °C to 55 °C). The tan δ peak associated with p(EA-co-VP) has disappeared or has been incorporated in the tan δ response for PET-SO₃Zn rich phase. The explanation for the disappearance of the shoulder peak of p(EA-co-VP) rich phase is difficult to discern. The DMTA trace for the compression molded film appears to be single phase and rather broad, indicative of a miscible phase with some remaining microheterogeneity. Upon annealing a shift is observed, possibly related to stiffening of the amorphous phase due to an increase in crystallinity. But at this point in the investigation, we can only conclude that both films appear to be significantly compatibilized in the dynamic range of DMTA.

Figure 5.15 represents the tan δ vs. temperature trace for blend E. The trace indicates a certain degree of compatibilization. The bimodal response was indicative of a p(EA-co-VP) rich phase associated with the tan δ maximum at 14 °C and a PET-SO₃Zn rich phase associated with the tan δ maximum at 70 °C. The corresponding shifts in tan δ for the p(EA-co-VP) rich phase is approximately 16 °C and 17 °C for the PET-SO₃Zn rich phase. This preliminary study has indicated the utility of incorporating ionogenic

moieties capable of forming zinc transition metal complexes to compatibilize blends of sulfonated PET and poly(ethyl acrylate-co-4-vinyl pyridine).

Conclusions

Ion exchange procedures were developed, which exchange the initial sodium ions of sulfonated PET for hydrogen and subsequently hydrogen ions for zinc. The level of sulfonation evaluated was 7 mole%. This ionic content was considered an optimal balance between an adequate level of specific interactions and a significant degree of crystallinity (35%). The free acid and zinc neutralized form of sulfonated PET was then solution blended with p(EA-co-VP) containing 5.2 and 10.6% VP.

The level of specific interactions were probed by FTIR. For the both the acid and zinc blends, the absorbance band corresponding to the pyridine ring stretching was used to measure the level of interactions. Qualitatively, the zinc blends demonstrated the highest level of interactions. This was demonstrated by the formation of a new absorbance band at 1618 cm^{-1} which corresponded to the formation of zinc-pyridine complexes and the disappearance of the pyridine ring stretching at 1600 cm^{-1} . The blend containing 77% PET-SO₃Zn and 23% p(EA-co-VP) (10.6 % VP), blend B, demonstrated the highest degree of zinc-pyridine complexation, while the zinc blend containing 58% p(EA-co-VP) (5.2 % VP), blend E, displayed an equilibrium mixture of absorbance bands related to zinc-pyridine complexation and free pyridine ring stretching. For the acid blend C, there appeared to be no proton transfer mechanism present, but rather a partial shift of an absorbance band to higher wavenumbers corresponding to hydrogen bonding.

The degree of crystallinity of the sulfonated PET and their blends was optimized. The degree of compatibilization and crystallinity was then evaluated by DSC and DMTA. The unmodified blends containing poly(ethyl acrylate) with PET-SO₃Zn were shown to be immiscible by DSC. The modification of poly(ethyl acrylate) with 4-vinyl pyridine proved to compatibilize the blends by both DSC and DMTA. The highest degree of compatibilization was observed for blend B, which contained the highest ionic content and thus the smallest distance between charge complexes. The degree of phase separation which occurred upon annealing was difficult to discern from the stiffening of the amorphous phase due to an increase in crystallization. Further studies appear to be necessary which would encompass the characterization phase equilibria, crystallization kinetics and morphology.

The main objective of this investigation was to explore acid-base interactions and zinc transition metal complexations of ionomeric blends containing sulfonated PET. Previous investigations of ionomeric blends have concentrated on predominately amorphous-amorphous blends. This study considered ionomeric blends containing a multi-phase (semi crystalline) component, which has further demonstrated the utility of ionogenic moieties as a means of compatibilizing immiscible polymer blends.

Figure 5.4: DSC trace for a compression molded film of PET-SO₃Zn, recorded at 10 °/min.

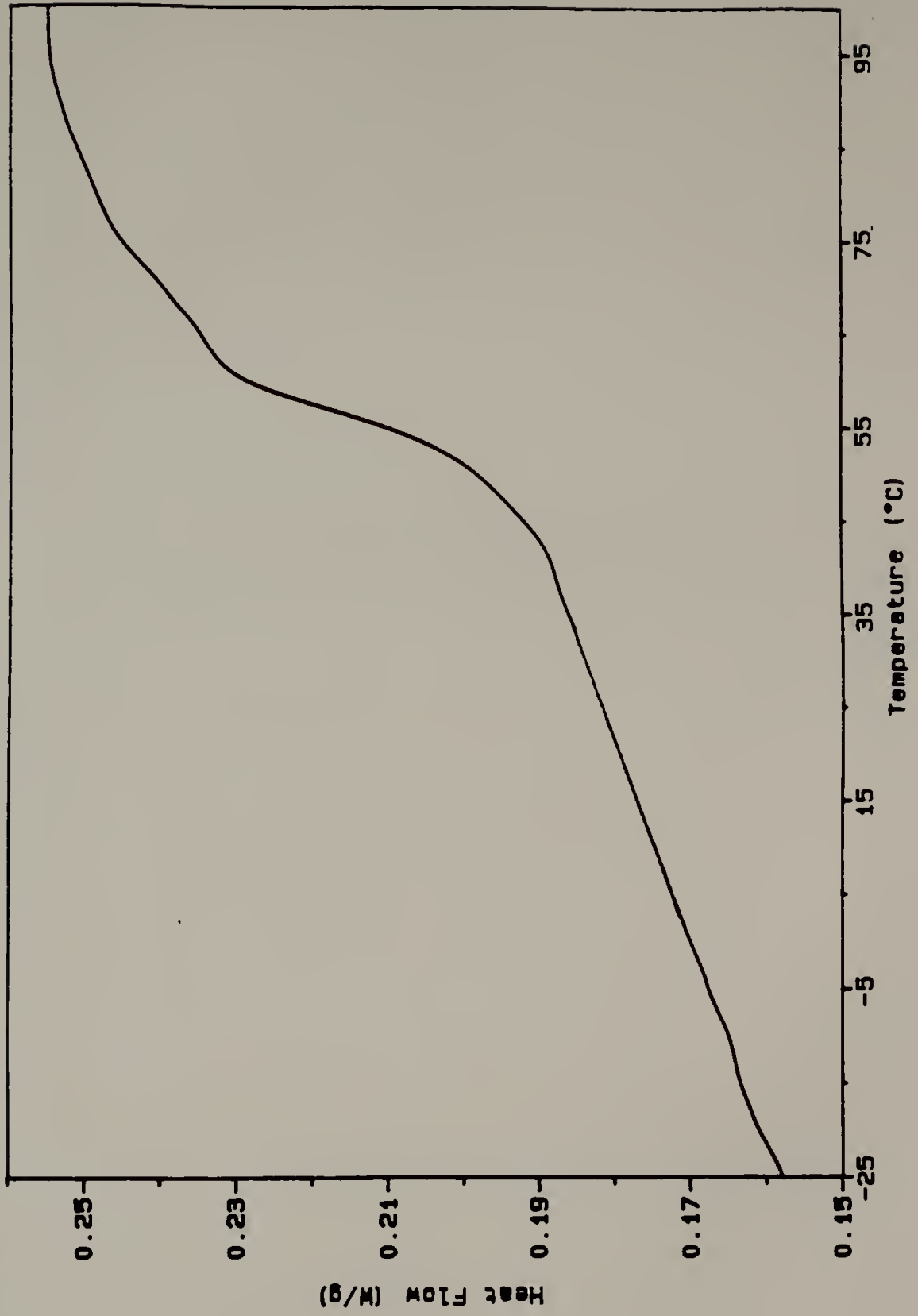


Figure 5.5: DSC trace for an annealed film of PET-SO₃Zn, recorded on the second heating at 10 °/min.

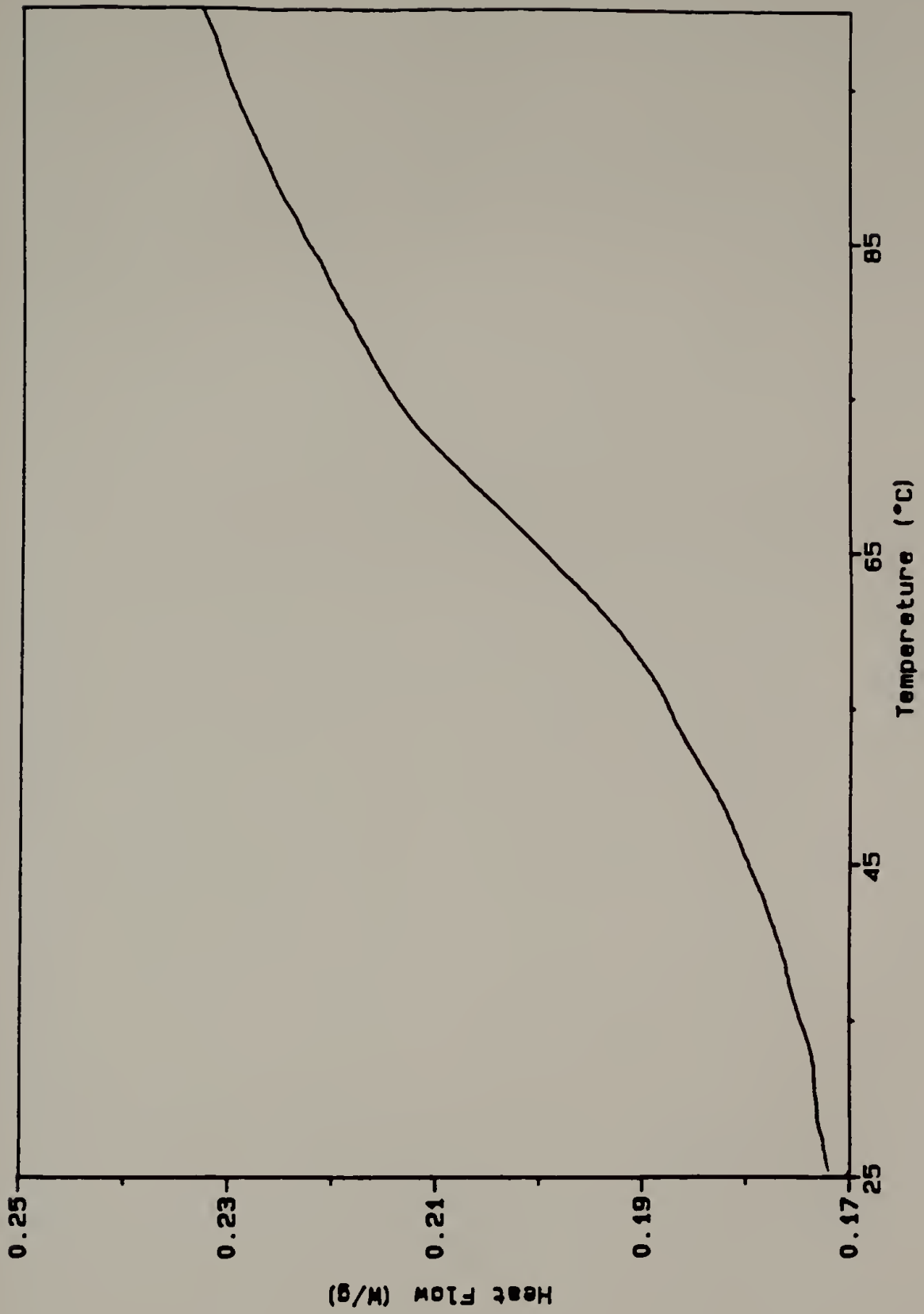


Figure 5.6: DSC trace for a compression molded film of p(EA-co-VP) (10.6% VP), recorded on the second heating at 10 °/min.

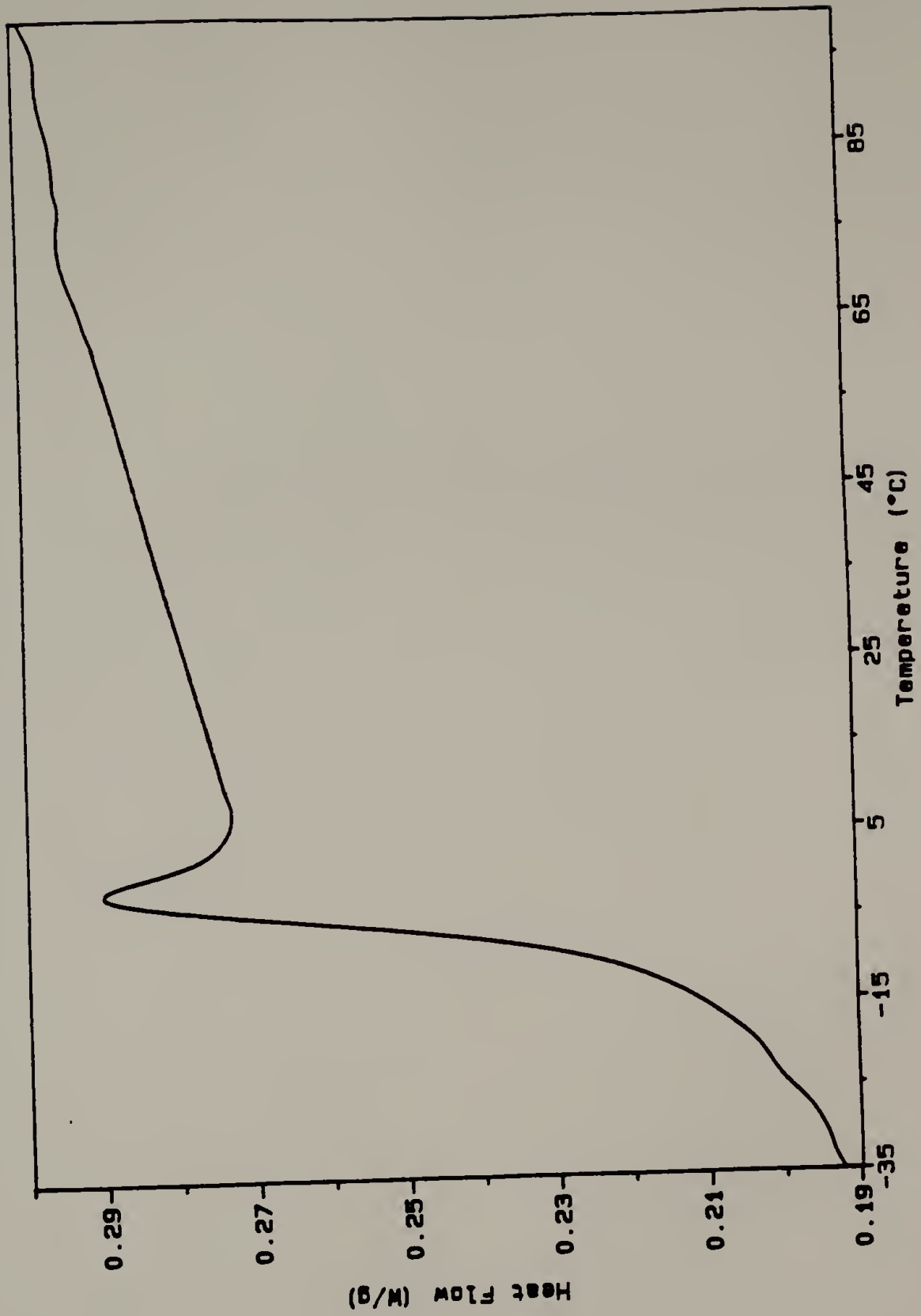


Figure 5.7: DSC trace for a compression molded film of blend A, recorded on the second heating at 10 °/min.

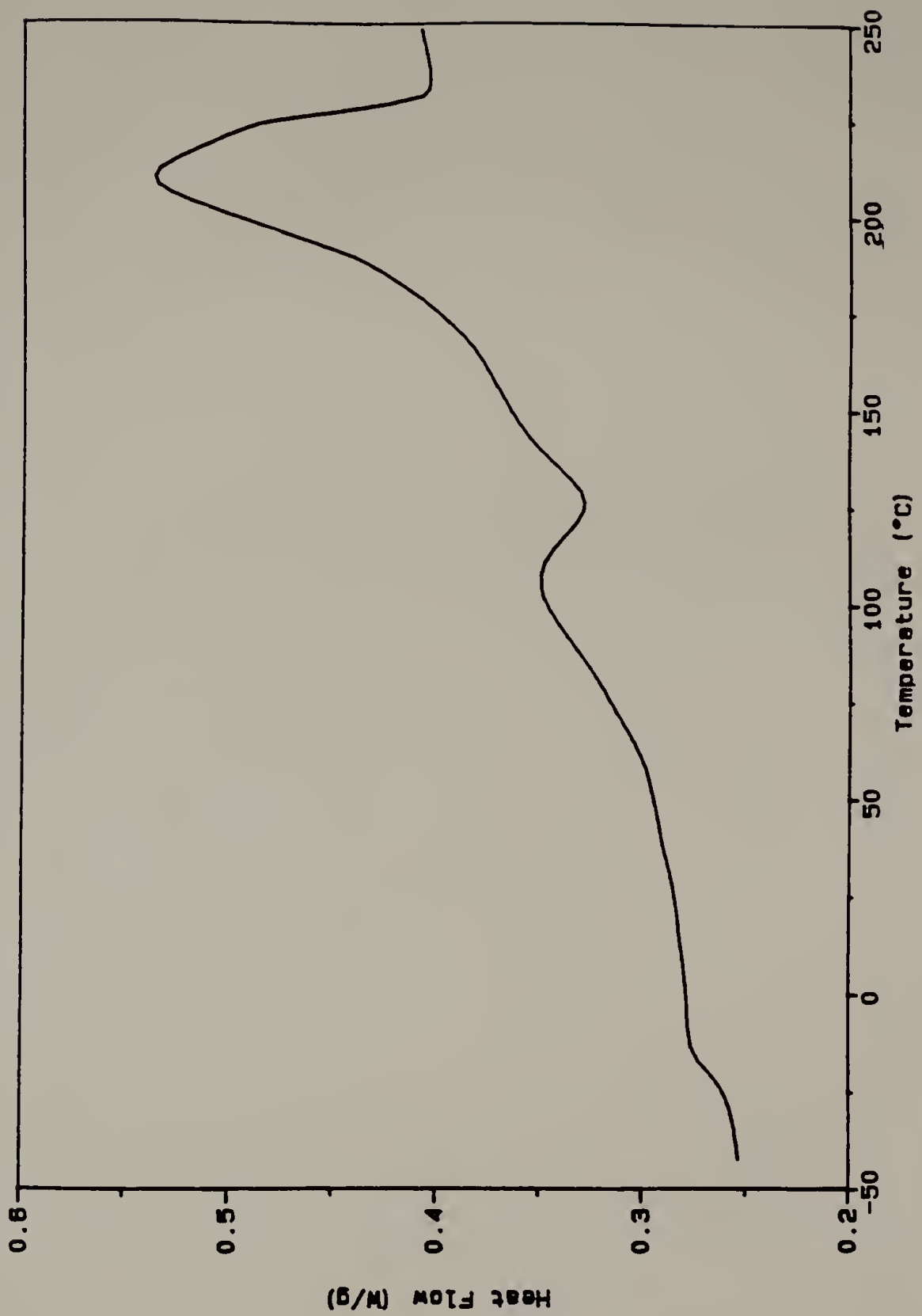


Figure 5.8: DSC trace for a compression molded film of blend D, recorded on the second heating at 10 °/min.

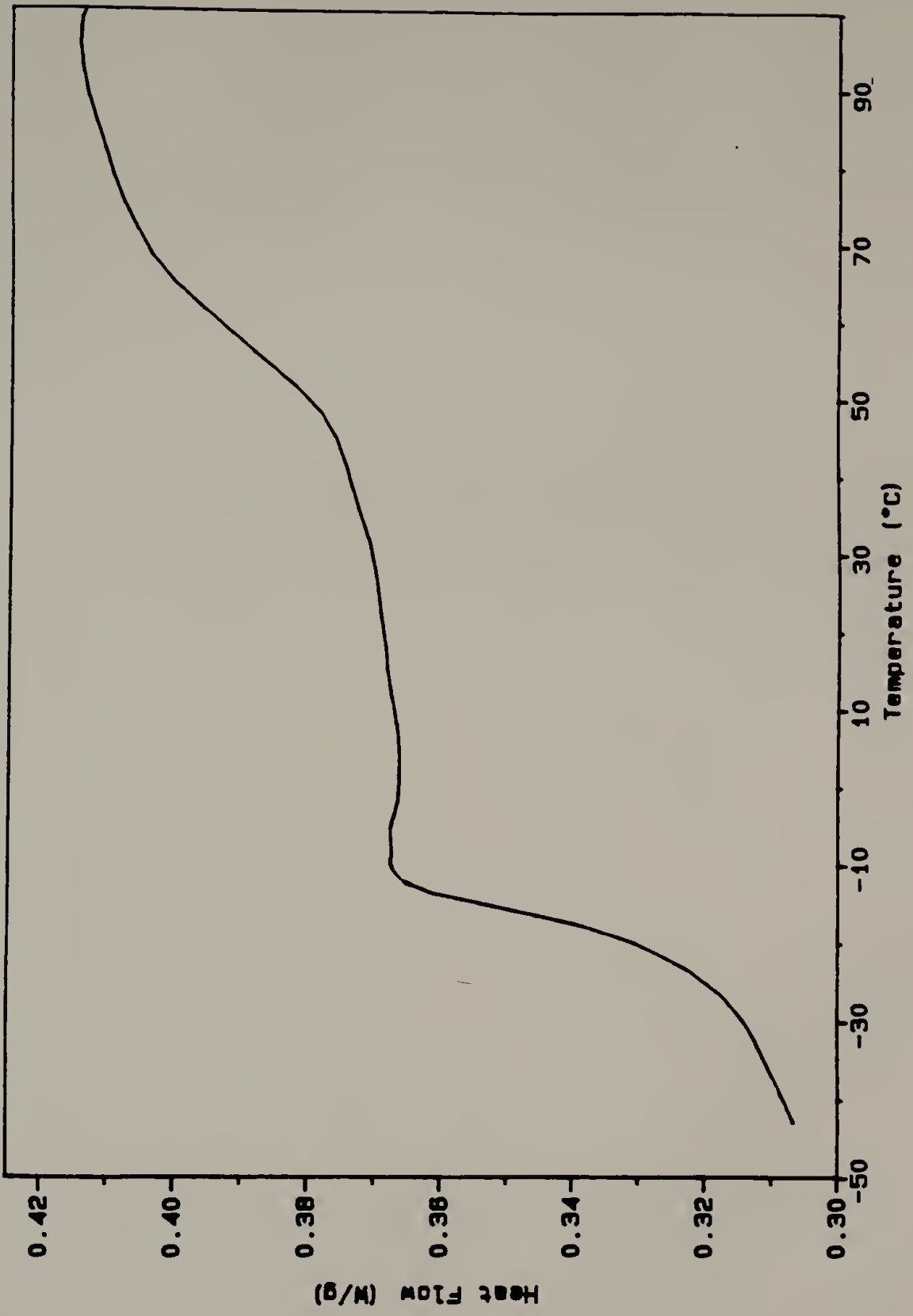


Figure 5.9: DSC trace for an annealed film of blend B, recorded at 10 °/min.

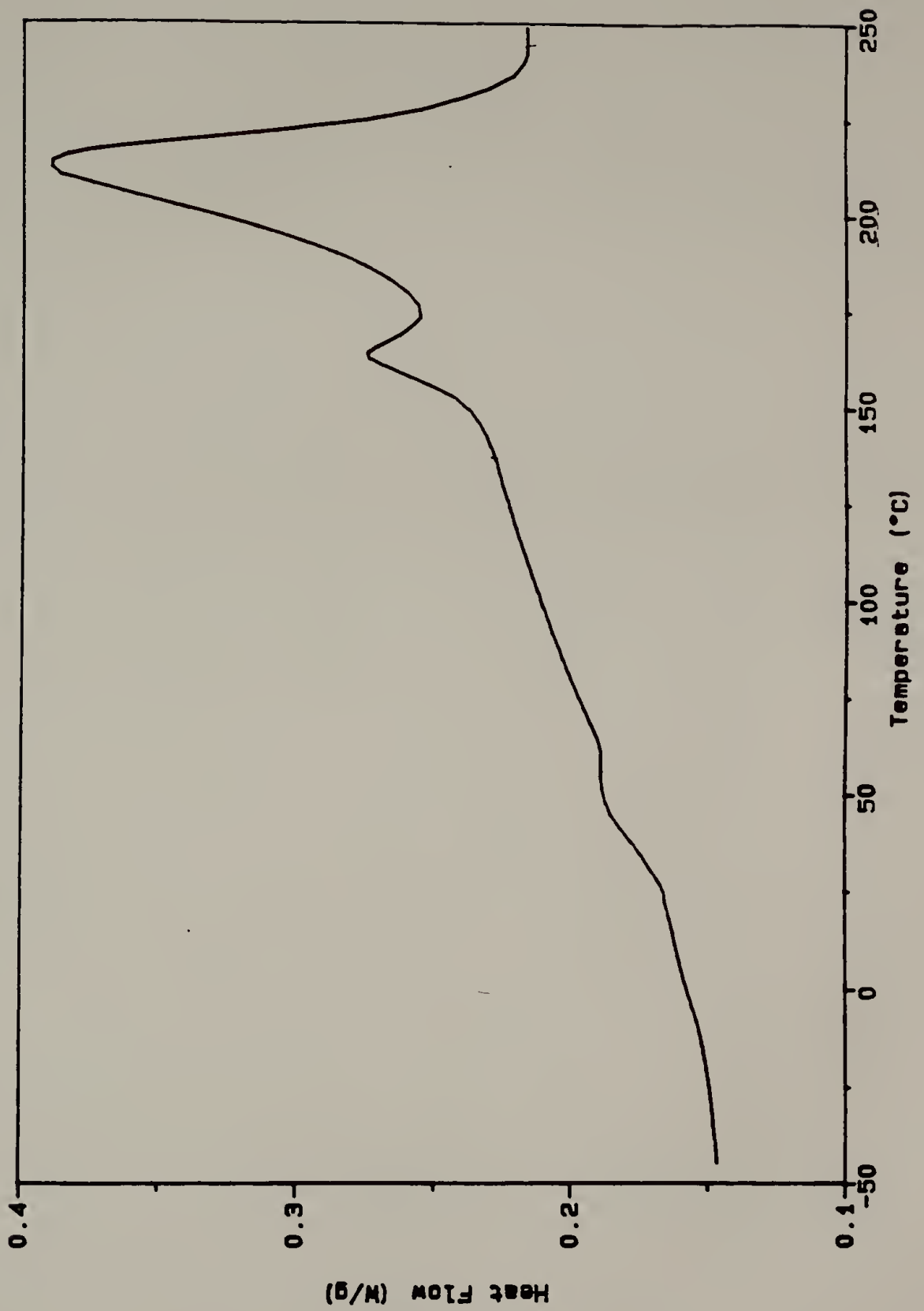


Figure 5.10: DSC trace for a compression molded film of blend B, recorded on the second heating at 10 °/min.

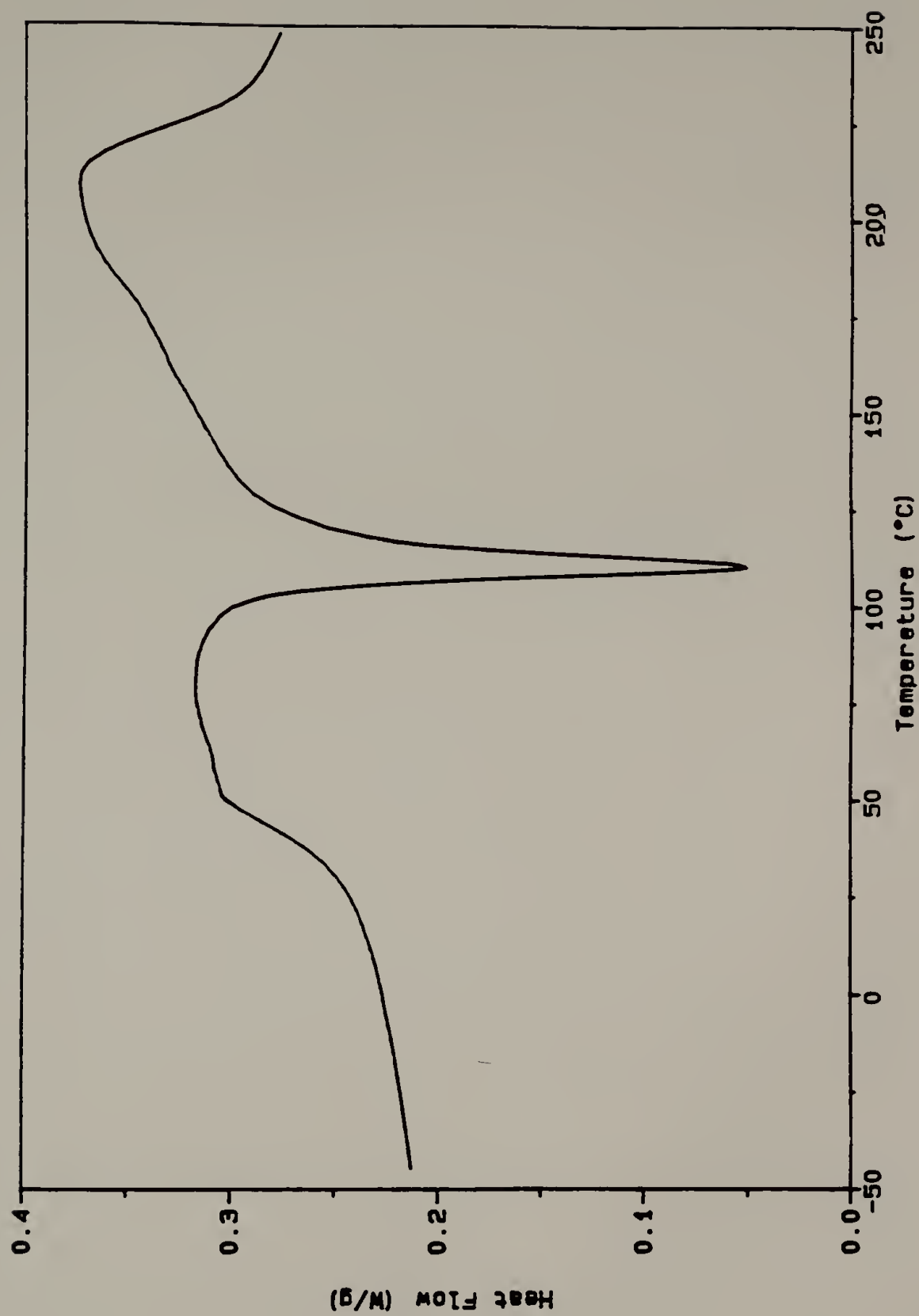


Figure 5.11: DSC trace for an annealed film of blend E, recorded at 10 °/min.

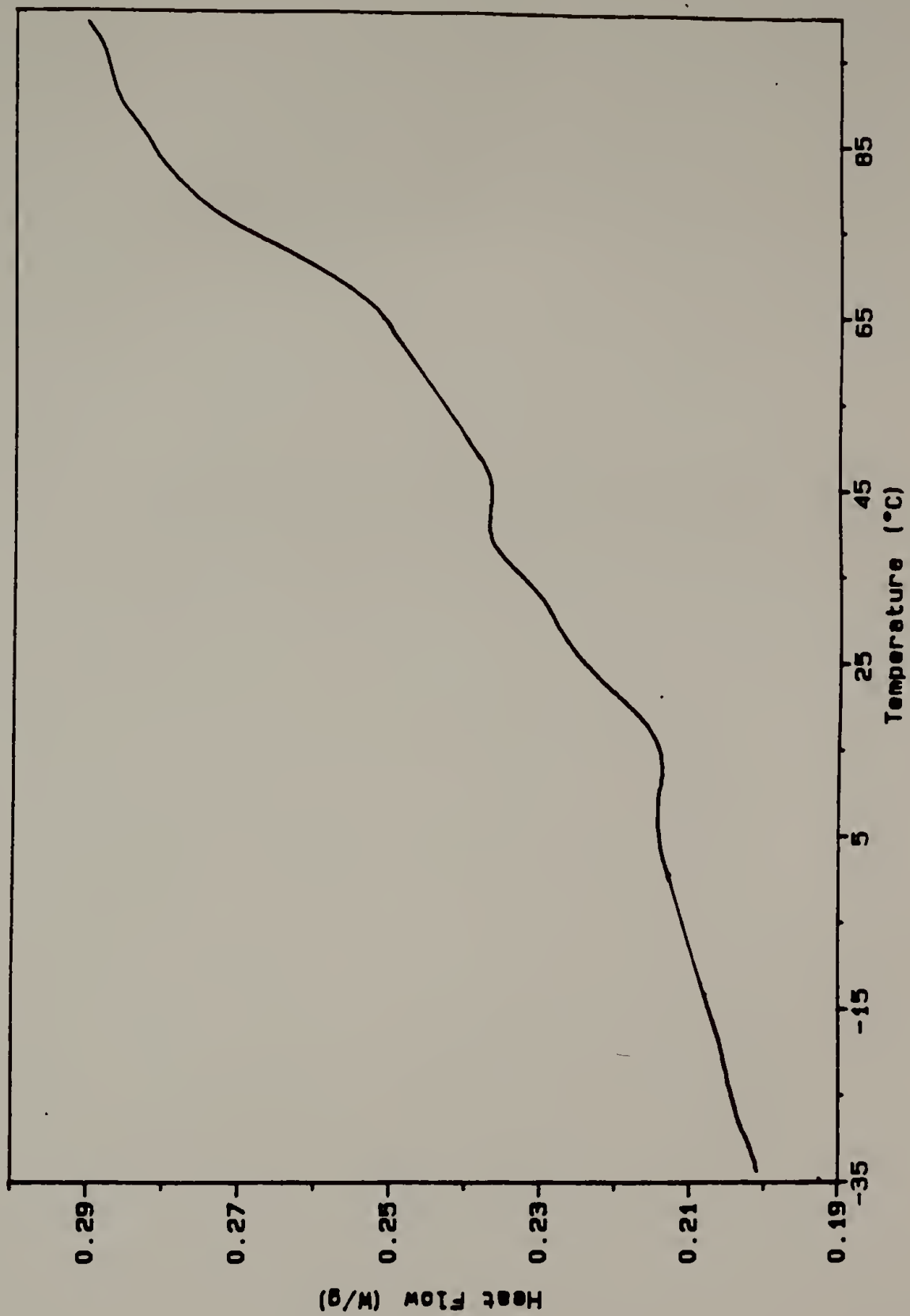




Figure 5.12: Optical micrographs of blend A and B: (a) optical micrograph of an annealed sample of blend A, where the size of the dark spheres are on the order of $12\mu\text{m}$ in diameter (mag. 125X)

(continued next page)



Figure 5.12: (continued)

(b) optical micrograph of an annealed sample of blend B (mag. 125X)

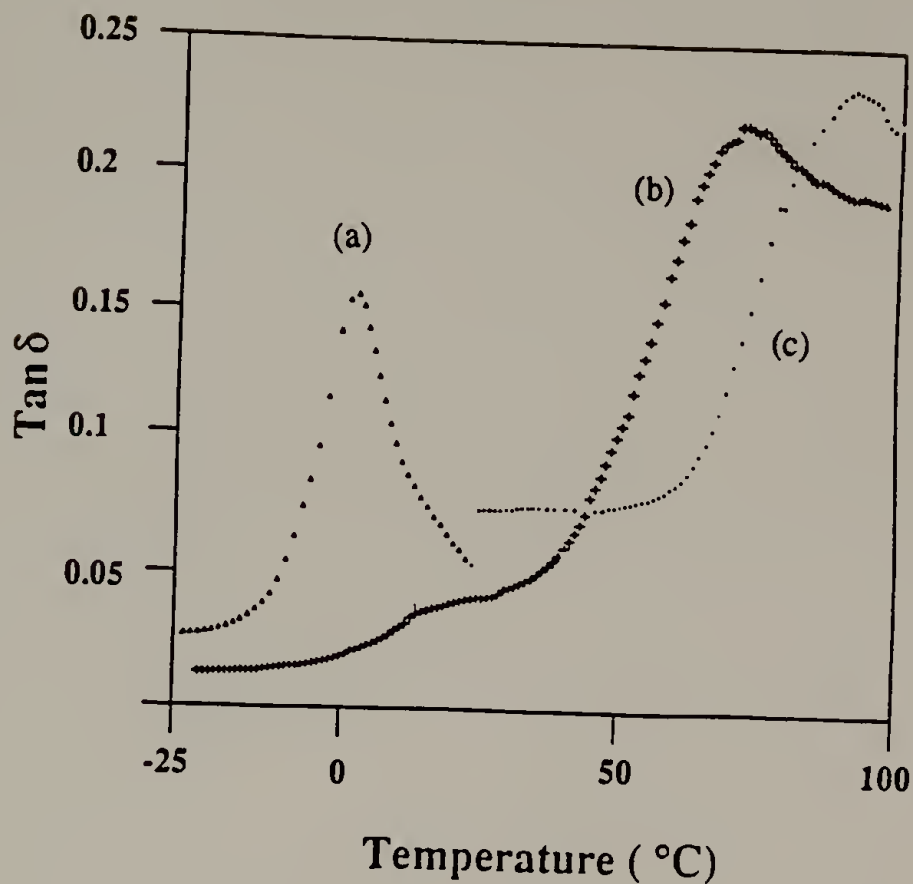


Figure 5.13: The $\text{tan } \delta$ vs. Temperature plots for (a) p(EA-co-VP) (10.6% VP), (b) blend B, and (c) PET-SO₃Zn, recorded in the single cantilever mode at 1 Hz.

Figure 5.14: The $\tan \delta$ vs. Temperature plots for blend B: (a) compression molded film; and (b) annealed film, recorded in the single cantilever mode at 1 Hz

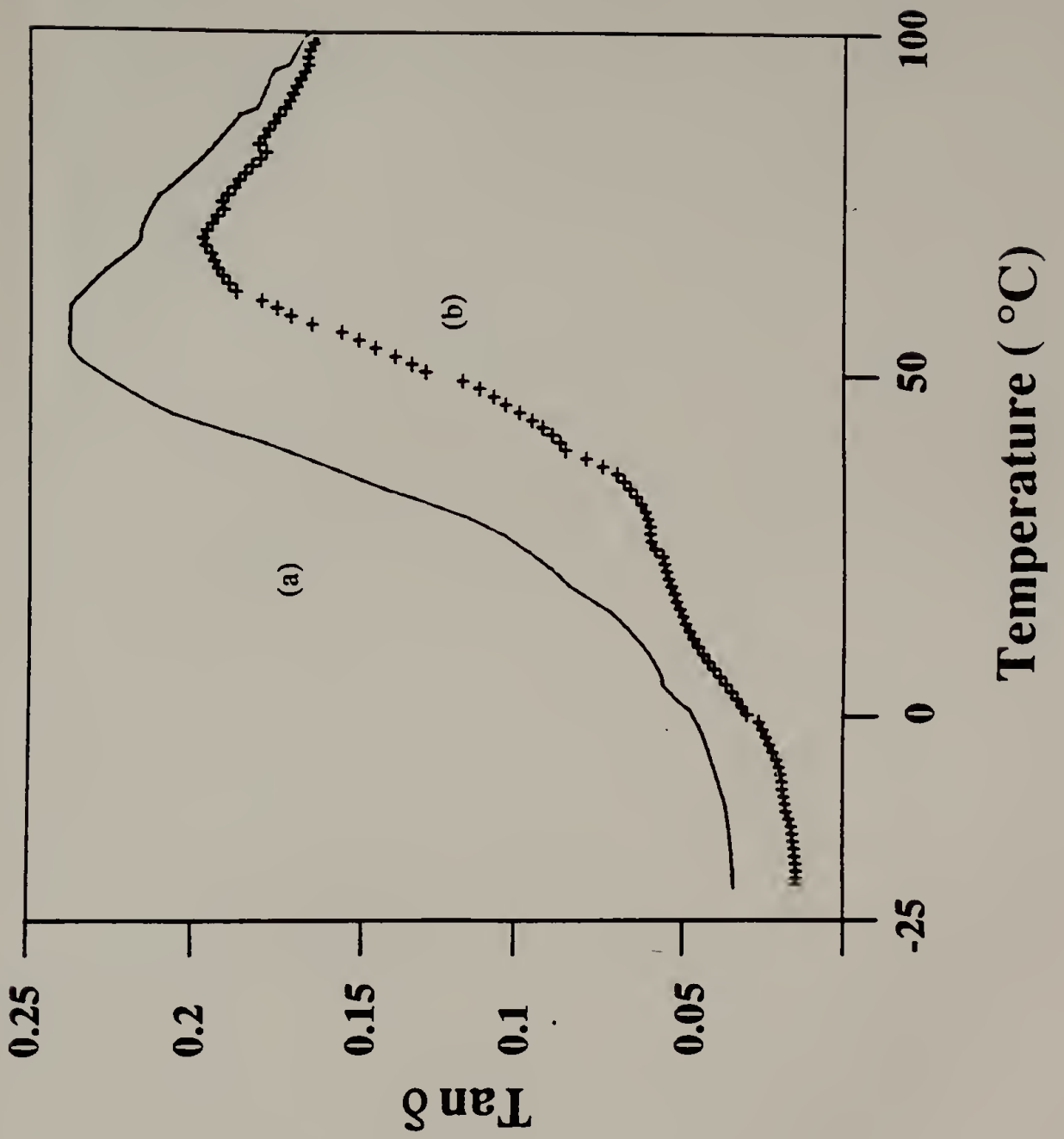
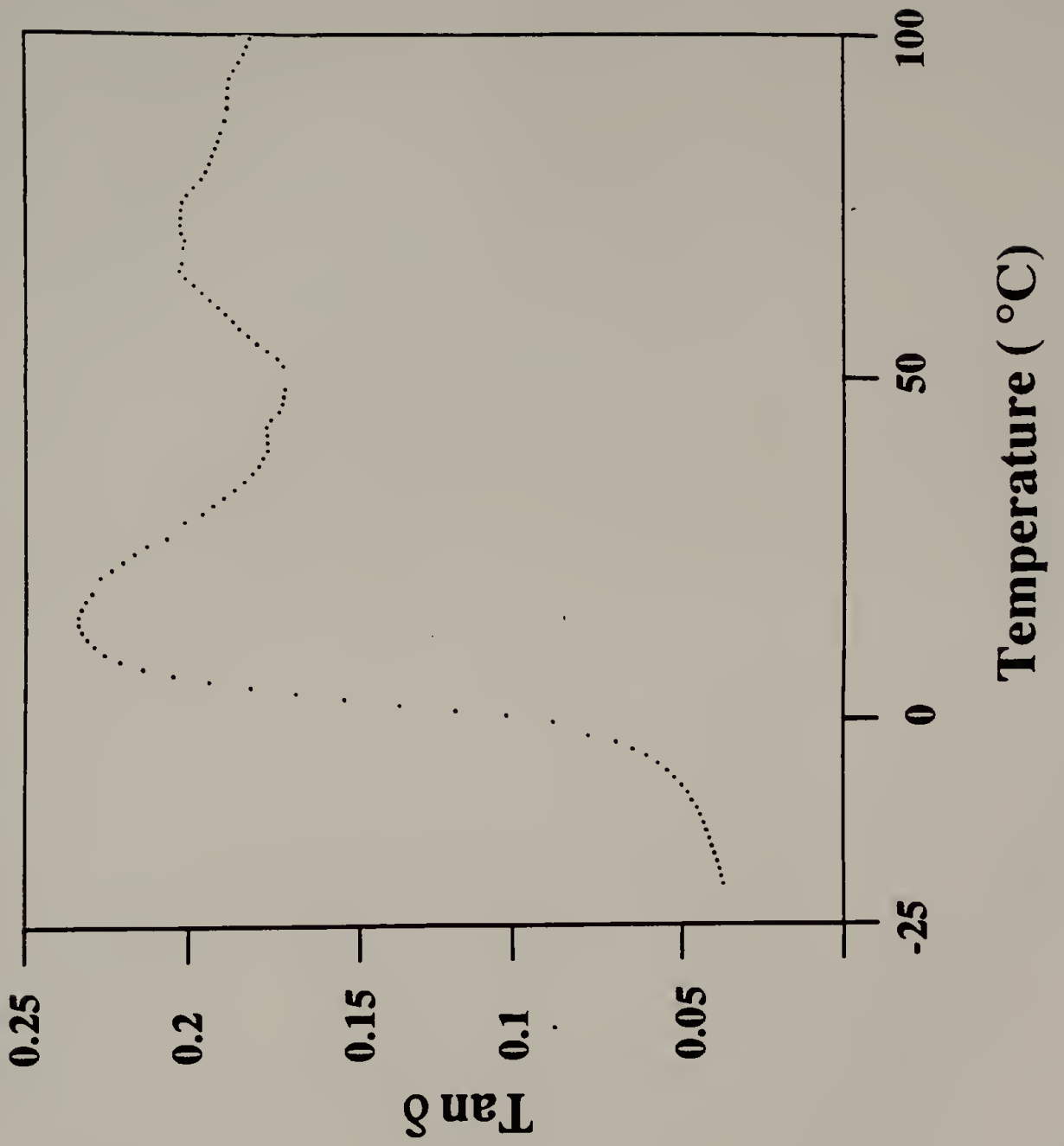


Figure 5.15: The $\tan \delta$ vs. Temperature plot for blend E, recorded in the single cantilever mode at 1 Hz.



References

1. Cooper, S. J., Estes, G. M., eds., Multiphase Polymers, ACS Adv. Chem. Series No. 176: Washington D.C., (1979)
2. Olabisi, O, Robeson, L. M., Shaw, M. T., Polymer-Polymer Miscibility, (New York:Academic Press), (1979)
3. Han, C. D., Multiphase Flow in Polymer Processing, (New York:Academic Press) (1981)
4. Solc, K., eds., Polymer Compatibility and Incompatibility, (Chur:MMI Press) (1982)
5. Han, C. D. eds., Polymer Blends and Composites in Multiphase Systems, ACS Adv. Chem. Series No. 206: Washington D.C., (1984)
6. Walsh, D. J., Higgins, J. S., and Maconnachie, A., eds., Polymer Blends and Mixtures, NATO Series E. No. 89, (Dordrecht:Martinns Nijhoff), (1985)
7. Kleintjens, L. A. and Lemstra, P., eds., Integration of Fundamental Polymer Science Technology, (New York:Elsevier), (1985)
8. Paul, D. R. and Sperling, L. H., Multicomponent Polymer Materials, ACS Adv. Chem. Series No. 211: Washington D.C., (1986)
9. Ottenbrite, R. M., Utracki, L. A., Inoue, S., eds., Current Topics in Polymer Science, (Munche:Hanse Ver.), (1987)
10. Utracki, L. A., Industrial Polymer Alloys and Blends, (Munche:Hanse Ver.), (1989)
11. Utracki, L. A. and Weiss, R. A., Multiphase Polymers: Blends and Ionomers, ACS Adv. Chem. Series No. 395: Washington D.C., (1989)
12. Eisenberg, A, Smith, P., and Zhou, Z.L., Polym. Eng. Sci., **22**, 1117 (1982)
13. Peiffer, D. G., Duvdevani, I., Agarwal, P. K., and Lundberg, J. Polym. Sci., Polym. Lett. Ed., **24**, 581 (1986)
14. MacKnight, W. J., Douglas, E., and Sakurai, K., Macromolecules, **24**, 6776 (1991)
15. MacKnight, W. J., Douglas, E., and Sakurai, K., submitted for publication in Macromolecules
16. MacKnight, W. J., Douglas, E., and Sakurai, K., submitted for publication in Macromolecules

17. 7% sulfonated PET was received as a gift from the AKZO Corporate Reserch, Arnhem, Holland. (IV = 0.44; inherent viscosity of a solution in trifluoroacetic acid at a concentration of 0.5 g/dl at 30 °C)
18. Ringbom, A., Complexation in Analytical Chemistry: a guide for the critical selection of analytical methods based on complexation reactions, (New York:Interscience Publisher), (1963)
19. Brandrup, J. and Immergut, E. H., Polymer Handbook, Third Edition, (New York:John Wiley & Sons,Inc.) (1989)
20. Gray, A. P. and Casey, K., J. Polym. Sci., **2B**, 381 (1964)
21. Roberts, R. C., Polymer, **10**, 117, (1969)

CHAPTER 6

CONCLUSIONS AND SUGGESTED FUTURE WORK

Conclusions

The long range goal of this dissertation was to develop ionomeric blends which could act as a property enhancing additives when blended with PET. The prospectus of this dissertation was the investigation of acid-base interactions and zinc transition-metal complexations in polymer blends of sulfonated PET with pyridine containing polymers. Incorporation of sites for specific intermolecular interactions into immiscible polymer pairs has been successfully demonstrated as a route for enhanced compatibilization via a favorable decrease in the enthalpy of mixing. In open literature, the main body of research has mainly focused on amorphous-amorphous ionomeric blends. Therefore, these developments of ionomeric blend systems containing a semi-crystalline component has further demonstrated the utility of specific interactions for controlling compatibility.

The strategy involved the development of two systems to be blended with sulfonated PET. The first system involved the synthesis of novel thermotropic liquid crystalline polyesters containing pyridine dicarboxylate units (TLCP_N), which upon blending with sulfonated PET could act as an "in situ composite", enhancing both mechanical and rheological properties of PET. The second system involved the preparation of an ionomeric blend containing poly(ethyl acrylate-co-4-vinyl pyridine), which upon blending with sulfonated PET could act as an impact modifier to PET.

The synthesis strategy was to develop TLCPs systems which satisfied a set of macromolecular structure requirements directed toward future blends studies with PET or PBT. The initial investigation (Chapter 2) discussed the preparation and characterization of TLCPs having the biphenyl mesogen, 4,4'-bis(6-hydroxyhexoxy)-biphenyl, BHHBP. This mesogen has a strong tendency to form highly ordered phases, namely smectic phase types and crystalline. The objective was to increase the stability for mesophase formation over the competing crystallization process. The significant results of this investigation demonstrated that increasing substitution of isophthaloyl units for terephthaloyl units significantly decreased the strong tendency for crystallization and increased the stability for mesophase formation. The resulting WAXD patterns revealed predominately smectic A phase types for polymers evaluated. This series of TLCPs were all isotropic above 170 °C, which would prevent their use in future blends studies, as previously discussed. A second TLCP system was prepared and characterized which copolymerized BHHBP with another mesogenic monomer, 4,4'-(terephthaloyldioxy)dibenzoyl dichloride, ClHTHCl. The goal was to evaluate the influence of a mixed mesogenic system on the strong tendency for the biphenyl mesogen to form smectic phase types and perhaps increase the temperature of isotropization. The results indicated that HTH mesogen had no significant influence on the overall phase behavior or the temperature in which the transitions occurred.

The next investigation (Chapter 3) evaluated TLCP systems based on ClHTHCl. The structure property relationships between this mesogen and various flexible spacer units were initially established in Professor Lenz's laboratory. Therefore, a screening program was developed which could easily evaluate a variety of flexible spacer having chemical substituents similar in structure to the repeat units of PET and/or PBT. The candidate, poly(75%BHBT-co-25%HDO/HTH), was selected and characterized as an enantiotropic nematic. The similarity in chemical structure of the flexible spacers should

promote enhanced interfacial adhesion which is essential for obtaining desired increases in mechanical properties.

This selected candidate was then used as reference structure for the investigation of the ionomeric blends containing a Lewis-base modified TLCP_N with sulfonated PET (Chapter 4). The initial strategy focused on the incorporation of pyridine dicarboxylate units into a TLCP_N based on the previous selected candidate(s) (Chapter 3). Pyridine dicarboxylate was successfully incorporated into a flexible spacer similar to BHBT. The resulting TLCP_N, poly(75%BHBP_{2,5}-co-25%HDO/HTH), was characterized as an enantiotropic nematic TLCP with phase transition temperatures similar to poly(75%BHBT-co-25%HDO/HTH).

Upon development and characterization of TLCP_N, ion exchange procedures were developed to exchange the sodium ions of PET-SO₃Na for hydrogen and subsequently hydrogen ions for zinc. Stoichiometric blends of both the free acid and zinc neutralized form of sulfonated PET were prepared in solution with selected TLCP_Ns. Acid-base interactions and transition metal complexations were evaluated by FTIR, DSC, and DMTA.

For these blends, there were no significant level of specific interactions or compatibilization evident, although the exploratory study had produced some significant findings: (1) ion exchange procedures for sulfonated PET, which could be utilized for a variety of alkali, alkaline earth, or transition metals, and (2) the development of novel TLCP_Ns with similar phase behavior to their unmodified counterparts.

In the final investigation (Chapter 4), both the free acid and zinc neutralized form of sulfonated PET were blended with poly(ethyl acrylate-co-4-vinyl pyridine). The stoichiometric blends were prepared and characterized similar to the previous study. The level of acid-base interactions and zinc complexations was measured by a shift in frequency of the absorbance band corresponding to pyridine ring stretching. The zinc blend containing 23% of p(EA-co-VP) with 10.6% VP appeared to have the greatest

level of interactions. The interactions observed for the acid blend appeared to be related to the formation of hydrogen bonds instead of a proton transfer mechanism. An equilibrium mixture of hydrogen bonded pyridine and non-interacting pyridine was established, which favored neither species. A zinc blend containing 58% of p(EA-co-VP) with 5.2% VP also appeared to develop an equilibrium mixture of zinc-pyridine complexes with non-interacting pyridine, which appear to favor complexation. Factors accounting for the observed equilibrium mixtures were discussed. A thorough investigation was not within the scope of this dissertation.

The degree of crystallinity of the sulfonated PET and their blends was optimized. The degree of compatibilization and crystallinity was then evaluated by DSC and DMTA. The unmodified blends containing poly(ethyl acrylate) with PET-SO₃Zn were shown to be immiscible by DSC. The modification of poly(ethyl acrylate) with 4-vinyl pyridine proved to compatibilize the blends by both DSC and DMTA. The highest degree of compatibilization was observed for blends containing 23% of p(EA-co-VP) with 10.6% VP, which contained the highest ionic content and thus the smallest distance between charged complexes. The degree of phase separation which occurred upon annealing was difficult to discern from the stiffening of the amorphous phase due to an increase in crystallization. The other ionomeric blends appear to be less compatible, which was expected from the results of the previous FTIR investigations.

In previous studies on amorphous-amorphous ionomeric blends, a minimum of 5 mole percent ionogenic moieties was adequate for enhanced compatibilization of immiscible pairs. In this investigation of ionomeric blends containing a semi-crystalline component, the threshold distance between charge complexes appears to be smaller, but there remains many factors still to be considered. The level of complexity of having a semi-crystalline component in these type of systems warrants further studies which encompasses the characterization of phase equilibria in relation to crystallization kinetics and morphology.

Suggested Future Work

This dissertation was set up to explore the utility of specific interactions as a means of enhancing compatibility and interfacial adhesion of immiscible blends containing a thermotropic liquid crystalline polyester and semi-crystalline polyester. This dissertation hopefully presented further evidence which demonstrates how applicable these types of interactions can be used to control the degree of compatibility. Naturally, there are still many issues that need to be further examined, and which are being addressed by Chui-Wah Ng (graduate student of Professor MacKnight). Some of these issues and suggested future work will be highlighted in the following outline.

The physical properties of the ionomeric blends were not presented in the dissertation. The inherent viscosity of the sulfonated PET received from the AKZO corporation were considerably low in comparison to fiber grade PET. The IV value of 0.44 g/dl in trifluoroacetic acid at 30 °C resulted in materials which were inherently brittle. The effects of molecular weight on compatibility and physical properties needs to be addressed. Therefore steps should be taken to prepare or receive sulfonated PET with significantly higher IV values. Perhaps, the research effort at Eastman Kodak on sulfonated PET could supply some materials or technical assistance.

The ion exchange procedures developed could be expanded to include other metal salts of sulfonated PET for two specific reasons: (1) permit direct metal ion - metal ion exchange, which would eliminate the current two step process ($M_1 \rightarrow H \rightarrow M_2$) and the need for exotic solvents; (2) examination of metal salts which could enhance thermal stability and compatibility of the blends.

Future development of TLCPs containing ionogenic moieties should consider systems which are less thermally liable and whose structure and property relationships

can be clearly resolved from the blended polymer by standard characterization techniques.

Future work on the p(EA-co-VP)/PET-SO₃Zn blends should establish the relationship of phase equilibria, crystallization kinetics, and morphology. Preliminary work by SALS, CPOM, SEM, and TEM on these systems have all shown promising results as a method of characterization. Once these blends have been sufficiently characterized, they should be incorporated into PET or PBT and evaluated as potential impact modifiers.

BIBLIOGRAPHY

- Allard, D. and Prud'homme, R.E., *J. Appl. Polym. Sci.*, **26**, 559 (1982)
- Aouadj, O., Lassoued, A., and Djadoun, S., *Phys. Opt. Dyn. Phen. Proc. in Macrom. Sys.*, 525 (1985)
- Balluaff, M., *J. Polym. Sci., Part B, Phys.*, **25**, 739 (1987)
- Balluaff, M., *Mol. Cryst. Liq. Cryst.*, **136**, 175 (1986)
- Beery, D, Kenig, S., and Siegmann, A., *Polym. Eng. Sci.*, **31**(6), 459 (1991)
- Belorgey, G., Aubin, M. and Prud'homme, R.E., *Polymer*, **23**, 1051(1982)
- Bilibin, A.Yu., Schepelevsky, A.A., Frenkel, S.Ya., and Skorokhodov, S.S., *MACRO IUPAC, Florence, Preprints*, **2**, 232-233 (1980)
- Blizard, K.G. and Baird, D.G., *Polym. Eng. Sci.*, **27**, 653 (1987)
- Blumstein, A., ed., *Polymeric Liquid Crystals*, (New York: Academic Press) 44 (1985)
- Blumstein, A., Sivaramakrishnan, K., Blumstein, R.B., and Clough, S.B., *Polymer*, **23**, 47 (1982)
- Brandrup, J. and Immergut, E. H., *Polymer Handbook, Third Edition*, (New York:John Wiley & Sons,Inc.) (1989)
- Brereton, M.G. and Vilgis, T.A., *Macromolecules*, **23**, 2044 (1990)
- Brostow, W., *Kunststoffe*, **78**, 411 (1988)
- Bualek, S. and Zentel, R., *Makromol. Chem.*, **189**, 791 (1988)
- Buckley, A., Conciatori, A. B., and Calundann, G.W., U.S. Patent, 4,434,262 (1984)
- Calundann,G.W. and Jaffe, M., *Proc. Rober A. Welch Conferences on Chemical Research XXVI, Synthetic Polymers*, 247 (1982)
- Chapoy, L.L., ed., *Recent Advances in Liquid Crystalline Polymers*, (New York: Elsevier Appl. Sci.), (1985)
- Chung, T.S., *Polym. Eng. Sci.*, **26**, 901 (1986)
- Cogswell, F.N., Griffin, B.P. and Rose,J.B., U.S. Patent 4,386,174, (1981)

- Cooper, S. J., Estes, G. M., eds., Multiphase Polymers, ACS Adv. Chem. Series No. 176: Washington D.C., (1979)
- Cruz, C.A., Barlow, J.W. and Paul, D.R., *Macromolecules*, **12**, 726 (1979)
- Cser, F., Nyitrai, K., Hardy, G., Menzel, J., and Varga, J., *J. Polym. Sci., Polym. Symp.*, **69**, 91 (1981)
- Demartino, R.N., *J. Appl. Polym. Sci.*, **28**, 1805 (1983)
- Demus, D. and Richter, L., Textures of Liquid Crystals, (Weinheim: Verlag Chemie), 126 (1978)
- DeVries, A., *Mol. Cryst. Liq. Cryst.*, **10**, 219 (1970)
- Djordjevic, M. B. and Porter, R.S., *Polym. Eng. Sci.*, **23**, 650 (1983)
- Dubault, A., Casagrande, C., and Vegssie, M., *Mol. Cryst. Liq. Cryst.*, **72**, 189 (1982)
- Dutta, D., Fruitwala, H., Kohli, A., and R.A. Weiss, *Polymer Engineering and Science*, **30** (17), 1005-1018 (1990)
- Dutta, D., Fruitwala, H., Kohli, A., and Weiss, R.A., *Polymer Engineering and Science*, **30** (17), 1005-1018, (1990)
- Eisenberg, A, Smith, P., and Zhou, Z.L., *Polym. Eng. Sci.*, **22**, 1117 (1982)
- Eisenberg, A. and Hara, M , *Macromolecules*, **17**, 1335 (1984)
- Eisenberg, A. and Hara, M, *Polym. Eng. Sci.*, **24**, 1306 (1984)
- Eisenberg, A. and Hara, M., *Macromolecules*, **20**, 2160 (1987)
- Eisenberg, A. and Natansohn, A., *ACS Polym. Prep.*, **27**(1), 349 (1986)
- Eisenberg, A. and Natansohn, A., *Macromolecules*, **20**, 323 (1987)
- Eisenberg, A. and Rutkowska, M., *J. Appl. Polym. Sci.*, **29**, 755 (1984)
- Eisenberg, A. and Rutkowska, M., *J. Appl. Polym. Sci.*, **30**, 3317 (1985)
- Eisenberg, A. and Rutkowska, M., *J. Appl. Polym. Sci.*, **33**, 2833 (1987)
- Eisenberg, A. and Rutkowska, M., *Macromolecules* , **17**, 821 (1984)
- Eisenberg, A. and Simmons, A., *ACS Polym. Prep.*, **27**(1), 341 (1986)
- Eisenberg, A. and Zhang, X., *J. Polym. Sci.: Part B: Phys.*, **28**, 1841 (1990)
- Eisenberg, A. and Zhang, X., *Polym. Adv. Tech.*, **1**, 9 (1990)
- Eisenberg, A. and Zhou, Z.-L., *J. Poly. Sci. Phys.*, **21**, 595 (1983)

- Eisenberg, A., and Natansohn, A., ACS Polym. Prep., **27**(1), 349 (1986)
- Eisenberg, A., Natansohn, A., and Murali, R., Makromol. Chem., Macromol. Sym., **16**, 175 (1988)
- Eisenberg, A., Natansohn, A., and Rutkowska, M., Poly. Eng. Sci., **27**, 1504 (1987)
- Eisenberg, A., Smith, P. and Zhou, Z.-L., Poly. Eng. Sci., **22**, 1117 (1982)
- Eisenberg, A., Natansohn, A. and Rutkowska, M., Polymer, **28**, 885 (1987)
- Eisenberg, A. and Murali, R., J. Poly. Sci.: Part B: Phys., **26**, 1385 (1988)
- Eisenberg, A. and Smith, P., J. Poly. Sci.: Letters, **21**, 223 (1983)
- Farris, R.J. and Joslin, S., in a private communication
- Fisher, H., Karasz, F.E., and MacKnight, W.J., To be published.
- Flory, P. J., Macromolecules, **21**, 66 (1988)
- Flory, P. J., Macromolecules, **21**, 66 (1988)
- Flory, P.J., Macromol., **11**, 1138 (1978)
- George, E.R., Porter, R.S., and Griffin, A.C., Mol. Cryst. Liq. Crysts., **110**, 27 (1984)
- Gray, A. P. and Casey, K., J. Polym. Sci., **2B**, 381 (1964)
- Griffin, A.C. and Havens, S.J., J. Polym. Sci., Polym. Lett. Ed., **18**, 259, (1980)
- Han, C. D. eds., Polymer Blends and Composites in Multiphase Systems, ACS Adv. Chem. Series No. 206: Washington D.C., (1984)
- Han, C. D., Multiphase Flow in Polymer Processing, (New York:Academic Press) (1981)
- Hara, M. and Eisenberg, A., Macromolecules, **17**, 1335 (1984)
- Hara, M., and Eisenberg, A., Polym. Eng.Sci., **24**, 1306 (1984)
- Hara, M., Smith,P., and Eisenberg, A., ACS Polymer Preprint, **51**, 726 (1984)
- Hara, M., Smith,P., and Eisenberg, A., Current Topics in Polymer Science. Vol. II, R.M. Ottenbrite, L.A. Ultracki and S. Inoue eds., (New York:Carl Hanser Verlag), 256-283 (1987)
- Hara, M., Wollmann,D., and Eisenberg, A., ACS Polymer Preprints, **25**, 280 (1984)
- Hasslin, H-W., Droscher, M., and Wegner, G., Makromol. Chem., **181**, 301 (1980)

- Huh, W., Weiss, R. A., and Nicolais, L., *Polym. Eng. Sci.*, **23**, 779 (1983)
- Hwang, W.F., Wiff, D.R., Helminiak, T.E., and Benner, C.L., *J. Macromol. Sci., Phys.* **B22**, 231 (1983)
- Hwang, W.F., Wiff, D.R., Helminiak, T.E., Verschoore, C., Price, G.E., and Adams, W.W., *Polym. Eng. Sci.*, **23**, 879 (1983)
- Ide., Y. and Chung, T., *J. Macromol. Sci. Phys.*, **B23(4-6)**, 497 (1984)
- Isayev, A. I. and Modic, M.J., *Polym. Compos.*, **8**, 158 (1987)
- Jackson, W.J. and Kuhfuss, H.F., *J. Polym. Sci. Phys.*, **14**, 2043-2058 (1976)
- Jaffe, M., Calundann, G., and Yoon, H., *Handbook of Fiber Science and Tehcnology: Volume III*, 83 (1989)
- Joseph, E.G., Wilkes, G.L., and Baird, D.G., *Polymer Liquid Crystals*, Blumstein, A., ed., (New York: Plenum Press) 197 (1984)
- Joseph, J.R., Kardos, J.L., and Nielsen, L.E., *J. Appl. Polym. Sci.*, **12**, 1151(1968)
- Kardos, J.L. and Raison, J., *Polym. Eng. Sci.*, **15**, 1975 (1972)
- Kardos, J.L., McDonnell, W.L., and Raison, J., *J. Macromol. Sci., Phys.*, **B6**, 397 (1972)
- Kayiyama, T., Washizu, S., and Takayanagi, M., *J. Appl. Polym. Sci.*, **29**, 3955 (1984)
- Kiss, G., Kovacs, A.J., and Wittmann, J.C., *J. Appl. Polym. Sci.*, **26**, 2665 (1981)
- Kiss, G., *Polym. Eng. Sci.*, **27**, 410 (1987)
- Kleintjens, L. A. and Lemstra, P., eds., *Integration of Fundamental Polymer Science Technology*, (New York: Elsevier), (1985)
- Kronberg, B., Bassignana, I., and Paterson, D., *J. Phys. Chem.*, **82**, 1714 (1978)
- Lieber, L., Strzelecki, D. van Luyen and Levelut, A.M., *Europ. Polym. J.*, **17**, 71 (1982)
- Lundberg, R.D., Peiffer, and Phillips, R.R., *J. Polym. Sci.: Part B: Phys.*, **27**, 245 (1989)
- Lundberg, R.D., Peiffer, D.G., Duvdevani, I. and Agarwal, P.K., *J. Polym. Sci.: Letters*, **24**, 581 (1986)
- Lundberg, R.D., Peiffer, D.G., Duvdevani, I. and Agarwal, P.K., *J. Polym. Sci.: Part B: Phys.*, **25**, 839 (1987)
- MacDonald, W.A., *High Value Polymers*, 428 (1990)

- MacKnight, W. J., Douglas, E., and Sakurai, K., *Macromolecules*, **24**, 6776 (1991)
- MacKnight, W. J., Douglas, E., and Sakurai, K., submitted for publication in *Macromolecules*
- MacKnight, W. J., Lantman, C. W., and Lundberg, R. D., "Ionomers", eds. Booth, C. and Price, C., *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions, and Applications of Polymer*, **2**, (New York:Pergamon Press), (1987)
- MacKnight, W.J. , Pat. Appl. (AKZO ACR 5484), (1989)
- Michiyuki, A. and Nakagawa, K., *Polymer*, **28**, 263 (1987)
- Narkis, M., Siegmann, A., Dagan, A., and DiBenedetto, A.T., *J. Appl. Polym. Sci.*, **21**, 989 (1977)
- National Materials Advisory Board Commision on Eng. & Tech. Systems National Research Council, *Liquid Crystalline Polymers*, (Washington D.C.:National Academy Press) (1990)
- Noel, C. and Billard, J., *Molec. Cryst. Lett.*, **6**, 269(1978)
- Noel, C., Fayolle, B., and Billard, J., *J. Physique*, **40**, 485 (1979)
- Ober, C.K., and Bluhm, T.L., *Current Topics in Polymer Science: Volume 1*, Ottenbrite, Ultracki, Inoue, eds. (Munich, Vienna, and New York: Hanser Publishers), 249 (1987)
- Ober, C.K., *The Synthesis and Characterization of Some Liquid Crystalline Polyesters based upon the Oxybenzoate-terephthalate Mesogenic Unit*, PhD Thesis, University of Massachusetts, Amherst (1982)
- Olabisi, O., Robeson, L. M., and Shaw, M. T., *Polymer-Polymer Miscibility*, (New York: Academic Press), (1979)
- Olabisi, O., Robeson, L. M., and Shaw, M. T., *Polymer-Polymer Miscibility*, (New York: Academic Press), (1979)
- Otocka , E.P. and Eirich, F.R., *J. Polym. Sci., Part A-2*, **6**, 895 (1968)
- Otocka , E.P. and Eirich, F.R., *J. Polym. Sci., Part A-2*, **6**, 921 (1968)
- Otocka , E.P. and Eirich, F.R., *J. Polym. Sci., Part A-2*, **6**, 933 (1968)
- Otocka, E.P. and Eirich, F.R., *J. Polym. Sci., Part A-2*, **6**, 913 (1968)
- Ottenbrite, R. M., Utracki, L. A., Inoue, S., eds., *Current Topics in Polymer Science*, (Munchen:Hanser Ver.), (1987)
- Paul, D. R. and Newman, S., *Polymer Blends*, (New York: Academic Press), **20** (1978)

- Paul, D. R. and Sperling, L. H., Multicomponent Polymer Materials, ACS Adv. Chem. Series No. 211: Washington D.C., (1986)
- Peiffer, D. G., Duvdevani, I., Agarwal, P. K., and Lundberg, J. Polym. Sci., Polym. Lett. Ed., **24**, 581 (1986)
- Pollack, S.K., Shen, D.Y., Hsu, S.L., Wang, Q., and Stidham, H.D., Macromolecules, **22**, 551 (1989)
- Pollack, S.K., Smyth, G., Stenhouse, P.J., Papadimitrakopoulos, F., Hsu, S.L., and MacKnight, W.J., Submitted for publication.
- Prud'homme, R.E., Polym. Eng. Sci., **22**, 90 (1982)
- Reck, B. and Ringsdorf, H., Makromol. Chem., Rapid Commun., **6**, 291 (1985)
- Ringbom, A., Complexation in Analytical Chemistry: a guide for the critical selection of analytical methods based on complexation reactions, (New York: Interscience Publisher), (1963)
- Ringsdorf, R., Schmidt, H.W., and Schneller, A., Macromol. Chem., Rapid Commun., **3**, 745 (1982)
- Roberts, R. C., Polymer, **10**, 117, (1969)
- Sato, M., Jadhav, J.Y., Mallon, J.J., and Kantor S.W., to be published.
- Sato, M., Nakatsuchi, K., and Ohdatsu, Y., J. Polym. Sci., Part A: Polym. Chem., **26**(11), 3077 (1988)
- Sato, M., Nakatsuchi, K., and Ohdatsu, Y., Makromol. Chem. Rapid Commun., **7**, 231-234 (1986)
- Sato, M., Nakatsuchi, K., and Ohdatsu, Y., Makromol. Chem. Rapid Commun., **8**, 383-386 (1987)
- Schneider, H.A., Cantow, J.J. and Percec, V., Polymer Bulletin, **6**, 617 (1982)
- Schneider, H.A., Cantow, J.J., Massen, U. and Northfleet-Neto, H., Polymer Bulletin, **7**, 263 (1982)
- Shaffer, T.D., and Percec, V., J. Polym. Sci., Lett. Ed., **23**, 185 (1985)
- Shaw, M. T. and Chen, J.H., Proc. International Conf. Rhel. 8th, **3**, 99-108 (1980)
- Siegmann, A., Dagan, A., and Kenig, S., Polymer, **26**, 1325 (1985)
- Siegmann, A., Narkis, M., Puterman, M., and DiBenedetto, A.T., J. Polym. Sci. Phys., **17**, 225 (1979)
- Siegmann, A., Narkis, M., Puterman, M., and DiBenedetto, A.T., Polymer, **20**, 89 (1979)

- Smyth, G., Pollack, S.K., Hsu, S.L., and MacKnight, W.J., *Mol. Cryst. Liq. Cryst.*, **7**(6), 839-861 (1991)
- Smyth, G., Valles, E.M., Pollack, S.K., Grebowicz, J., Stenhouse, P.J., Hsu, S.L., and MacKnight W.J., *Macromolecules*, **23**, 3389 (1990)
- Solc, K., eds., *Polymer Compatibility and Incompatibility*, (Chur:MMI Press) (1982)
- Stenhouse, P.J., Valles, E.M., MacKnight, W.J., and Kantor, S.W., *Macromolecules*, **22**, 1467 (1989)
- Takayanagi, M., Ogata, T., Morifawa, M., and Kai, T., *J. Macromol. Sci., Phys.* **B17**, 591 (1980)
- Utracki, L. A. and Weiss, R. A., *Multiphase Polymers: Blends and Ionomers*, ACS Adv. Chem. Series No. 395: Washington D.C., (1989)
- Utracki, L. A., *Industrial Polymer Alloys and Blends*, (Munche: Hanser Ver.), (1989)
- Walsh, D.J., *Comprehensive Polymer Science, Vol.2*, Booth, C. and Price, C. eds., (New York: Pergamon Press), 135-154 (1989)
- Walsh, D. J., Higgins, J. S., and Maconnachie, A., eds., *Polymer Blends and Mixtures*, NATO Series E. No. 89, (Dordrecht: Martinus Nijhoff), (1985)
- Walsh, D.J. and Rostani, S., *Adv. Polym. Sci.*, **70**, 119 (1985)
- Weiss, R.A., Huh, W., and Nicolais, L., *Polym. Eng. Sci.*, **27**, 684 (1987)
- Weiss, R.A., Li, C., Sen, A., Register, R.A., and Cooper, S., *J. Polym. Sci.: Part B: Phys.*, **27**, 1911 (1989)
- Wissbrun, K.F., *Br. Polym. J.*, **12**, 163 (1980)
- Wissbrun, K.F., *J. Rheol.*, **25**, 619 (1981)
- Zentel, R. and Reckert, G., *Makromol. Chem.*, **187**, 1915 (1986)

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