1-1-1987

Rigid rod star-block copolymers :: synthesis and characterization of star-block liquid crystalline copolymers/

William Harve Dickstein
University of Massachusetts Amherst

Recommended Citation

Dickstein, William Harve, "Rigid rod star-block copolymers :: synthesis and characterization of star-block liquid crystalline copolymers/" (1987). *Doctoral Dissertations 1896 - February 2014*. 717.
https://scholarworks.umass.edu/dissertations_1/717

RIGID ROD STAR-BLOCK COPOLYMERS:
SYNTHESIS AND CHARACTERIZATION OF
STAR-BLOCK LIQUID CRYSTALLINE COPOLYMERS

A Dissertation Presented

By

WILLIAM HARVE DICKSTEIN

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

DOCTOR OF PHILOSOPHY

February, 1987

Polymer Science and Engineering

RIGID ROD STAR-BLOCK COPOLYMERS: SYNTHESIS AND CHARACTERIZATION OF STAR-BLOCK LIQUID CRYSTALLINE COPOLYMERS

A Dissertation Presented

by

William Harve Dickstein

Approved as to style and content by:

C. Peter Lillya

Professor C. P. Lillya, Chairperson of Committee

R S Porter

Professor R. S. Porter, Member

R.W. Lenz

Professor R. W. Lenz, Member

Edwin L Thomas

Professor E. L. Thomas, Head
Polymer Science and Engineering

To

Heidi and Catherine

ACKNOWLEDGEMENTS

I wish to express my deepest appreciation to my advisor, Professor C. P. Lillya. Dr. Lillya gave me the freedom to pursue challenging research along with the security of knowing that his support and knowledge were always behind me. I am also most grateful to the members of my committee, Professors Porter and Lenz. It was a rare and fortunate opportunity for me to be able to call upon committee members so knowledgeable in my field of research.

I should also like to acknowledge the many members of Dr. Lillya's research group. Their friendship and assistance added much to my stay. I would like to give a special acknowledgement to Kevin Sheehan. Kevin familiarized me with numerous synthetic techniques that proved so invaluable to my work.

The opportunity to work with Matt Muir in his ongoing rheological investigation of some of the new materials prepared in my work has been both informative and pleasurable. Matt's assistance almost overcomes having to listen to his jokes.

I would also like to express my thanks to the Polymer Science and Engineering Department and to my former advisor, Professor Vogl. The department provided the necessary environment to carry on research. The PSE department also provided me with the opportunity to engage in research without the burdens of teaching. Dr. Vogl was a large part of my decision to come to UMASS, and prior to his leaving for New York, I enjoyed very much the time that I had to work with him.

The IBM Corporation gave me the extraordinary opportunity to pursue my graduate work while still remaining in the employ of the corporation. I am extremely grateful for this opportunity and their support.

Finally, I would like to express my most heartfelt appreciation and thanks to my wife, Heidi, and daughter, Catherine. Heidi's encouragement, advise, and support are beyond my ability to express in words.

ABSTRACT

Rigid Rod Star-Block Copolymers: Synthesis and Characterization Of Star-Block Liquid Crystalline Copolymers

February 1987

William H. Dickstein

Ph.D., University of Massachusetts at Amherst

Directed by: Professor C.P. Lillya

The synthesis and characterization of rigid rod star-block copolymers is reported. These novel copolymers consist of flexible polymer chains radiating from a central point, at the ends of which are affixed liquid crystalline blocks. These copolymers are hypothetically designed for uses where high multi-dimensional strength and low weight are desired. A general synthetic procedure is reported where: 1) the arm number is variable, 2) the flexible arm length and polydispersity are controllable, and 3) both thermotropic and lyotropic mesogenic blocks are attached to the extremities of these star-block copolymers. The preparation of these new copolymers required the synthesis of novel intermediates. The synthesis and use of a new nonpolar solvent soluble blocked amine functional anionic initiator is described. Additionally, the preparation of novel amine telechelic poly(dimethylsiloxane) star and linear polymers is reported. Copolymers exhibiting a broad thermotropic liquid crystalline phase were prepared by attaching a low molecular weight, carboxylic acid functional, thermotropic mesogen to the ends of the telechelic star polymers via a quantitative amidation reaction. These thermotropic rigid rod star-block copolymers were characterized by qualitative and quantitative infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermal gravimetric analysis, and optical microscopy. Poly(*p*-benzamide) was grown from the aromatic amine end-groups of the telechelic siloxane polymers via the Yamazaki reaction. These copolymers were characterized by model reactions, infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, inherent viscosity, optical microscopy, and general solution properties. It was found that lyotropic liquid crystalline phases did occur in solutions of *N*,*N*-dimethylacetamide containing 2.85% lithium chloride if both the copolymer concentration and copolymer flexible arm length were sufficiently high. The radial nature of these copolymers apparently inhibits

their ability to form a liquid crystalline phase unless the flexible arm length is of a sufficient length to give the rigid blocks some degree of mobility. All copolymers were found to be highly phase separated and of high thermal stability.

TABLE OF CONTENTS

Chapter

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

DEFINITION, BACKGROUND, AND RATIONALE FOR RIGID ROD STAR-BLOCK COPOLYMERS

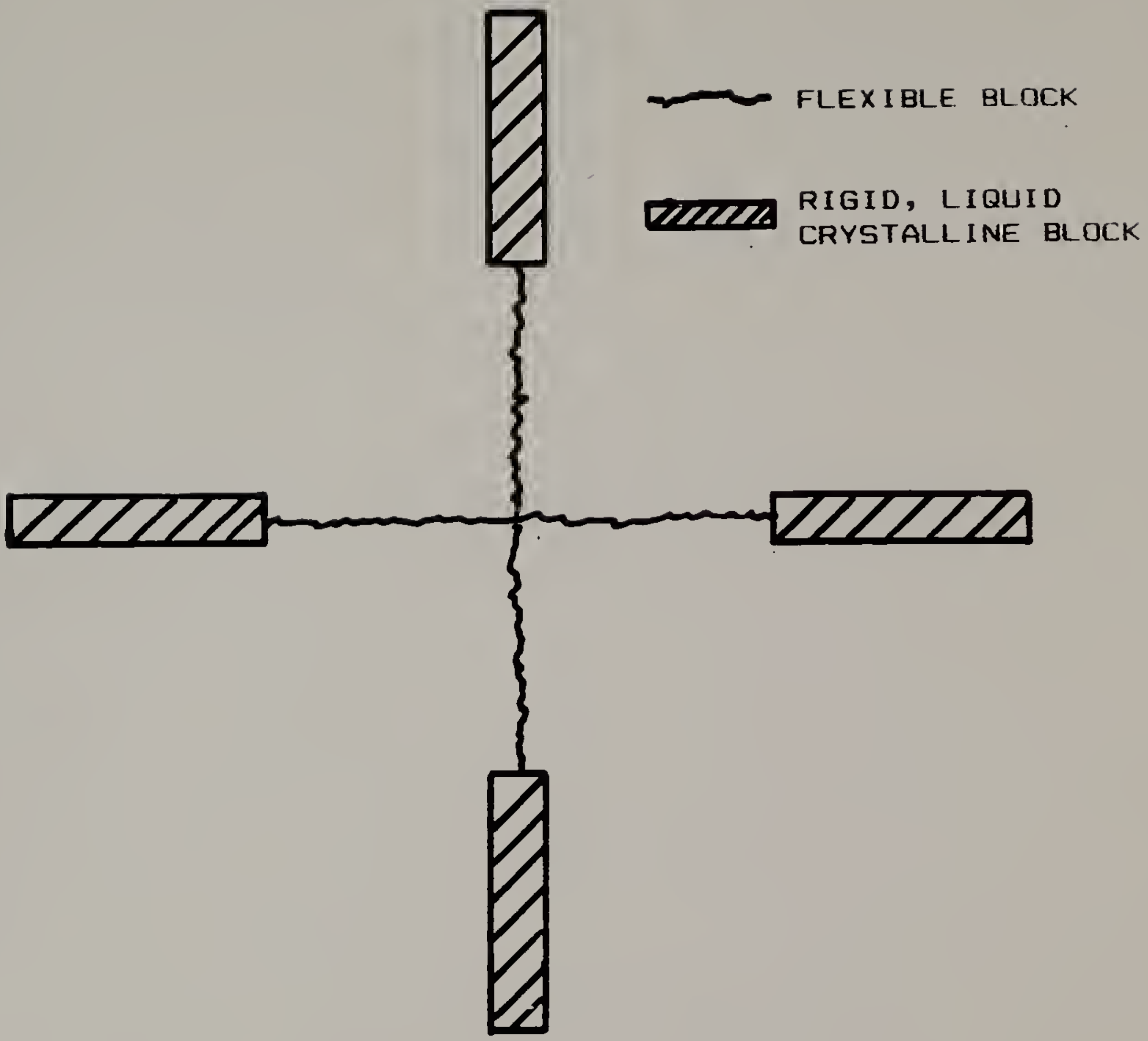
I. DEFINING THE PROJECT

The project described in this dissertation is the synthesis and characterization of rigid rod star-block copolymers. Figure 1.1 shows the general shape of these copolymers. As can be seen, these copolymers are comprised of a flexible core at the ends of which is attached a rigid, liquid crystalline mesogenic block. These copolymers may have any number of arms greater than two, and the liquid crystalline block attached at the end of the flexible core may be a thermotropic or lyotropic, low molecular weight or polymeric block.

This dissertation will describe the general synthesis of these new copolymers. This general synthesis requires that the parameters below be realizable using known polymer synthetic pathways. Although not all of these parameters will be exercised in the work described herein, the synthesis of these

Figure 1.1

The general structure of a rigid rod star-block copolymer. A flexible inner core of three arms or greater is capped at its ends with a rigid, mesogenic block that can be of any molecular weight and either thermotropic or lyotropic as a separate compound. This dissertation describes a completely general synthesis where the number of arms, the molecular weight of the flexible unit and its polydispersity are closely controlled, and where both thermotropic and lyotropic liquid crystalline blocks shall be attached at the ends of these flexible spacers.



General Synthesis Includes Control Of:

1. ARM NUMBER
2. FLEXIBLE ARM LENGTH AND POLYDISPERSITY
3. LYOTROPIC/THERMOTROPIC RIGID BLOCKS

copolymers must be sufficiently general so that the parameters below could be rationally exercised using known polymer synthetic techniques. The key parameters in Rigid Rod Star-Block Copolymers are:

1) Controlled Arm Number
2) Controlled Flexible Arm Length and Length Distribution
3) Both Lyotropic and Thermotropic Liquid Crystalline Blocks

In the work described in this dissertation, the arm number will be kept constant at four, however, the arm number could be readily increased to eighteen using known, literature practices. The flexible arm length will be varied over a great range while a narrow length distribution will be maintained. Finally, a low molecular weight thermotropic mesogen and a high molecular weight lyotropic mesogenic polymer will be attached at the ends of the flexible core.

The characterization of all polymers regarding their liquid crystalline properties will be included in this dissertation. The characterization will include optical, thermal, and rheological properties.

II. TOPIC BACKGROUND

The field of liquid crystalline polymers offers to the polymer scientist a unique area in which to modify the chain conformation of polymers. Since polymer properties are dependent upon the conformation of their chains, be they main or side chain, the synthesis and manipulation of liquid crystalline polymers presents itself as an exciting way to manipulate polymer properties. Two properties of particular, but not exclusive, interest currently in the field of liquid crystalline polymers are optical and mechanical properties.

Scientific exploration and subsequent technological exploitation of polymer liquid crystals is a recent development. Elliott and Ambrose first identified a separate anisotropic phase in a solution of poly(γ-benzyl-L-glutamate) in 1950 (1). Concomitant theoretical work by Onsager, Isihara, and Flory predicted that rigid entities in liquids could form separate anisotropic phases above a critical concentration (2-4).

It was not until the 1970's that systematic exploration of liquid crystalline polymers was widely reported. Brooks and Taylor in 1965 did report, that upon graphitization of carbon that a thermotropic mesophase did occur, however, it was a decade later before the field truly became active in synthetic polymers (5).

The field has developed along several lines, each of which will be discussed briefly in this introduction so as to lay a context for the work described in this dissertation. Generally, the field of liquid crystalline polymers has developed along the lines of thermotropic, polymers that melt into a liquid crystalline phase, and lyotropic, polymers that form a liquid crystalline phase in sufficiently concentrated solutions. Within the domain of thermotropic liquid crystalline polymers the field has divided itself into main chain and side chain polymers. The field of lyotropic liquid crystalline polymers has developed along the lines of extended main chain and rigid helical polymers. In neither general division have star shaped liquid crystalline polymers ever been reported until the work described in this dissertation.

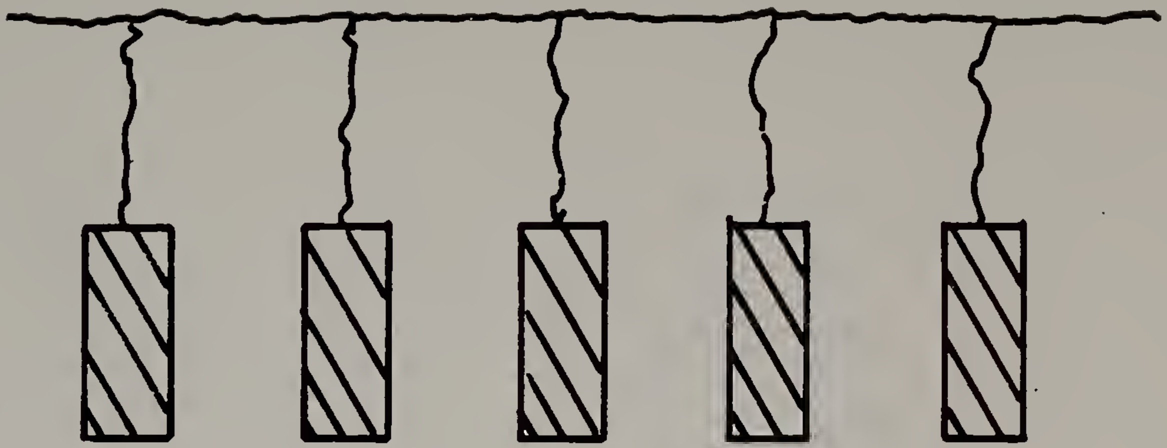
Thermotropic liquid crystalline polymers

As mentioned above, the domain of thermotropic liquid crystalline polymers has primarily divided itself on the general lines of side chain and main chain polymers. Recent work by Reck and Ringsdorf has described the synthesis of thermotropic liquid crystalline polymers with rigid, mesogenic groups in both the main and side chain, however, the field has been dominated to date by side and main chain polymers(6). Figure 1.2 shows the general topology of main chain and side chain thermotropic liquid crystalline polymers. As can easily be seen, these polymers are most frequently made by connecting rigid segments via flexible spacers, however, main chain thermotropic liquid crystalline polymers have been reported that do not require flexible spacers to melt without significant degradation (7). Generally, it has been the goal of the investigators in main chain thermotropic liquid crystalline polymers, in addition to the investigation of what molecular factors give rise to certain types of liquid crystalline behavior, to design liquid crystalline polymers that can be properly melt processed to achieve high strength/low weight materials, with most emphasis on fiber preparation (7). Investigators in side chain thermotropic liquid crystalline polymers have concentrated much less on ultimate strength mechanical properties, and turned their primary attention towards various potential optical and network properties (8).

The first reported main chain thermotropic liquid

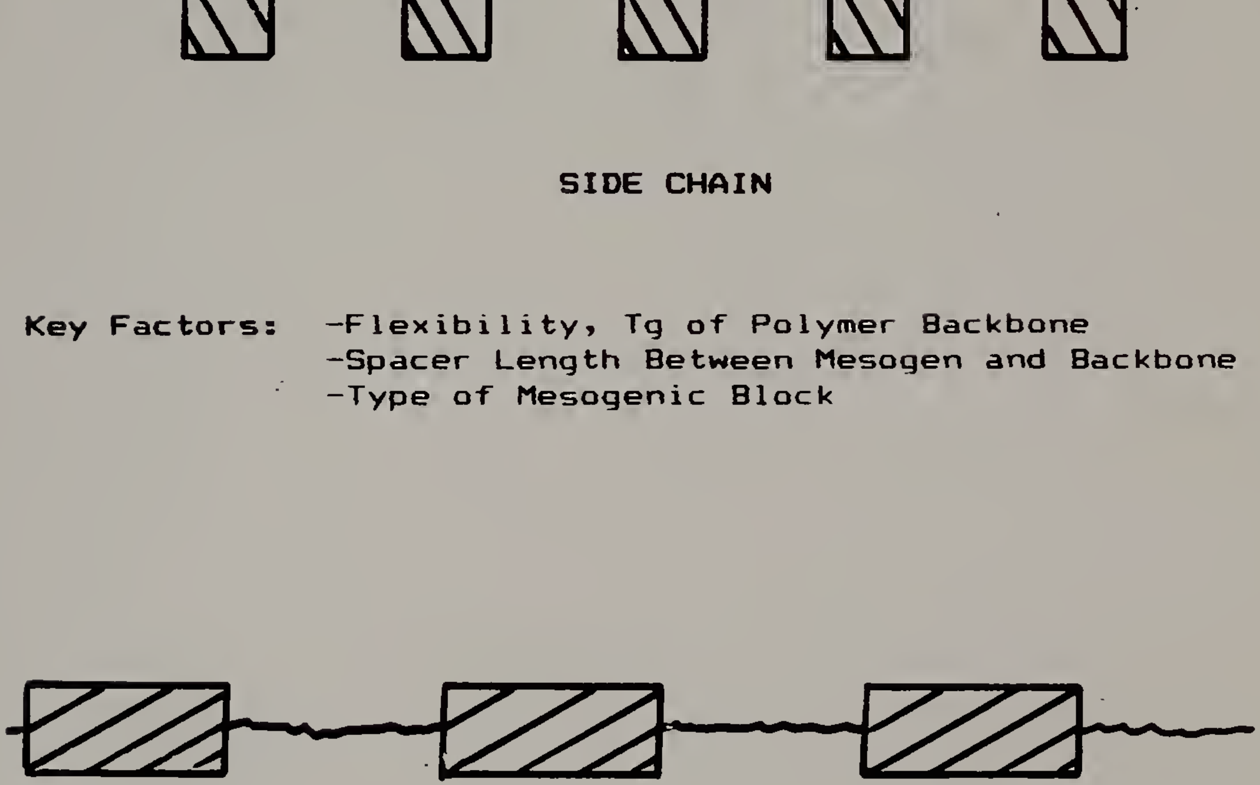
Figure 1.2

Diagrams of a side chain and main chain thermotropic liquid crystalline polymer. In both cases, rigid, thermotropic low molecular weight mesogenic blocks are attached via flexible spacers to achieve the appropriate structure. Although other types of thermotropic liquid crystalline polymers have been reported (see text), most thermotropic liquid crystalline polymers reported in the literature fall within these two general categories.



SIDE CHAIN

Key Factors: -Flexibility, Tg of Polymer Backbone
-Spacer Length Between Mesogen and Backbone
-Type of Mesogenic Block



MAIN CHAIN

Key Factors: -Presence of Flexible Spacers
-Length, flexibility, and regularity of spacer
-Axial Ratio, Regularity of Mesogenic Block

crystalline polymers were reported by Roviello and Sirigu in 1975 (9). Since that time the field has rapidly expanded so that only a brief background will be provided here; further information is available in the lengthy list of references that will be forthcoming.

For the most part, main chain thermotropic liquid crystalline polymers have been synthesized by connecting rigid, end reactive, low molecular weight, thermotropic liquid crystalline mesogens to various types and lengths of flexible spacers to form polyesters (7, 9, 10-37). The primary variables exercised in this work have been the type, flexibility, and length of the flexible spacer, and the axial ratio, regularity, and flexibility of the rigid, thermotropic mesogenic block. It has generally been found that the melting temperature and stability of the mesophase is decreased by increased spacer flexibility, odd lengths of the flexible spacer, and increased length of the flexible spacer as well as increased width, increased irregularity, and increased flexibility of the rigid, mesogenic block. Theoretical work on rigid/flexible main chain thermotropic liquid crystalline polymers has also been performed (11, 13). These rigid/flexible, polyester, main chain, thermotropic liquid crystalline polymers have primarily resulted in nematic mesophase morphologies, however, cholesteric (19, 29), smectic (27), and discotic (36, 37) mesophase morphologies have been reported. Unfortunately, most of these polymers have suffered from low molecular weights, due to their limited solubility which results in their early precipitation during preparation via solution polymerization. Additionally, the effort to lower the melting temperatures of these polymers to assist in processing and decrease degradation, also limits their use in applications requiring elevated temperatures.

Not all thermotropic main chain liquid crystalline polymers are synthesized by connecting rigid, thermotropic, end reactive, mesogenic blocks to flexible spacers via ester bonds. Other types of main chain thermotropic liquid crystalline polymers have been wholly aromatic polyesters (7, 16, 38-45), polyurethanes with flexible spacers (46), rigid/flexible polycarbonates (47), rigid, N-alkylated polyisocyanates (48,49), and poly(ester-amides) (50, 51). Roviello and Sirigu have synthesized liquid crystalline main chain thermotropic polyesters by connecting non-mesogenic blocks to flexible spacers (52). Theoretically this is due to the added restraint of the polymer on the rigid, non-mesogenic unit to result in a thermotropic liquid crystalline polymer. Recent work has described the synthesis of sequential block copolymer main chain thermotropic liquid crystalline polymers with thermoplastic poly(ether sulfone) blocks (53). Liquid crystalline main chain polymers have also been made by connecting divinyl thermotropic mesogens to poly(dimethylsiloxane) spacers via hydrosilation (54). The wholly aromatic, napthalene containing main chain thermotropic liquid crystalline polymers show the greatest potential technological use as high strength/low weight materials with good thermal stability.

Thermotropic side chain liquid crystalline polymers were first reported by Strzelecki in 1973 (55). As can be seen from Figure 1.2, these polymers are generally made by connecting low molecular weight, thermotropic liquid crystalline blocks to polymeric backbones via flexible spacers. This field has moved towards exploitation of three primary types of polymer backbones--poly(methacrylate) (56-59), poly(acrylate) (60), and poly(dimethylsiloxane) (61-69). A great number of thermotropic mesogens have been attached to these polymer backbones via flexible spacers to achieve many different properties and mesogenic morphologies. To date, nematic (60, 62, 67), smectic (56, 58, 60, 61, 62), and cholesteric (62, 65) mesogenic morphologies have been observed, and discotic low molecular weight mesogens have been attached to poly(dimethylsiloxane) backbones via flexible spacers to form thermotropic liquid crystalline polymers (66). However, the "discotic" side chain thermotropic liquid crystalline polymer mesophase has yet to be definitively determined.

The primary factors contributing to the attainment of liquid crystallinity in side chain thermotropic liquid crystalline polymers has been the flexibility of the polymer backbone, and the length of the flexible spacer between the polymer backbone and the attached thermotropic mesogenic block. The most flexible polymer backbone, poly(dimethylsiloxane), can be utilized to prepare room temperature side chain liquid crystalline polymers if the flexible spacer connecting the mesogenic unit to the polymer backbone is sufficiently long (69). Lengthening the flexible spacer between the mesogen and the polymer backbone decouples the motion of the mesogen from that of the main chain. Increasingly, the data suggests that side chain thermotropic liquid crystalline polymers are micro-heterogeneous (57, 58, 69). As the mesogenic block becomes more perfectly phase separated from the polymer backbone, the stability and order of the liquid crystalline phase is enhanced.

The primary potential technological utilization of side chain thermotropic liquid crystalline polymers is in the field of optical display devices (67). The polymer backbone acts like a matrix support to which the optically active thermotropic mesogenic unit is attached to allow for greater ease of display fabrication and decreased volatility. Other potential utilizations of side chain thermotropic liquid crystalline polymers mentioned have been uses as stationary phases in gas chromatography (61) and utilization as unique network materials (64, 68).

Lyotropic liquid crystalline polymers

The field of lyotropic liquid crystalline polymers has generally divided itself into the two primary areas of rigid, extended chain polymers and rigid, helical polymers. The first lyotropic liquid crystalline polymer reported by Elliott and Ambrose was a rigid, helical poly(γ-benzyl-L-glutamate) polypeptide (1). The first rigid, extended chain polymers were simultaneously developed in two industrial laboratories in the early 1970,s (70,71). Whether helical or extended chain, lyotropic liquid crystalline polymers form a liquid crystalline anisotropic phase in solutions above a critical polymer concentration. Extended chain lyotropic liquid crystalline polymers are presently commercially utilized as high modulus, high strength, and low weight fibers. The area continues to generate great scientific and technological interest.

As was mentioned above, rigid, helical polypeptides were the first liquid crystalline polymers to be reported (1). These materials are liquid crystalline due to the rigid, helical conformations they assume in certain solvents. At sufficiently high polymer concentrations the resulting rods organize themselves into a lyotropic liquid crystalline phase (72). Considerable work has been reported discussing the nature of the helix-coil transition in these polypeptides, with special attention paid to the high optical rotatory powers of these materials in solution (73, 74). Other work has delved into the potential role of liquid crystallinity in biological processes (75). The particular study of poly(γ-benzyl-L-glutamate) [PBLG] has been of great scientific utility due to the sensitivity of PBLG to helix-coil transitions that can be brought about easily by very small changes in the solvent (74), and due to the fact that PBLG can be synthesized to precise molecular weights with low polydispersity via Leuchs' anhydrides (76).

The field of extended chain lyotropic liquid crystalline polymers has been one of great advancement in the last fifteen years. The polymers of greatest impact in this area have been wholly aromatic, extended chain polyamides (77-87). However, extended chain poly(benzobisoxazole) (88-91), poly(benzobisthiazole) (89, 92), and poly(benzobisimidazole) (89) lyotropic liquid crystalline polymers have resulted in the highest modulus fibers. Remarkably, poly(benzobisthiazole) polymers of intrinsic viscosities as high as 30.3 dL/g have been reported, indicating both high molecular weight and extraordinarily high polymer rigidity (92). Both the wholly aromatic, extended chain polyamides, which have been reported to be actually worm like chains of high persistence length (86), and the more rigid poly(benzobisoxazole), poly(benzobisthiazole), and poly(benzobisimidazole) polymers go into solution with difficulty and degrade rather than melt upon heating. This combination of high strength, high modulus, low weight, and high temperature stability make these difficult to process polymers great materials for fibers, however, they do have some distinct disadvantages which the work in this dissertation will hypothetically address (83, 87, 89, 91, 92).

Other extended chain lyotropic liquid crystalline polymers have been reported. Included among these are block copolyesters (93, 94), *N*-substituted para-aromatic polyamides (95), block copolyamide polymers (96,97), and N-alkylated polyisocyanates (48). This area continues to be one of active synthetic, physical, scientific, and technological exploitation.

II. ADVANTAGES AND DISADVANTAGES OF POLYMER LIQUID CRYSTALS--RATIONALE FOR RIGID ROD STAR-BLOCK COPOLYMERS

Liquid crystalline polymers, in addition to their obvious scientific fascination, offer many technological uses. These technological advantages include the use of side chain liquid crystalline polymers in display devices (64, 67) and in gas chromatography (61). More significantly, the use of thermotropic main chain and lyotropic extended chain liquid crystalline polymers has resulted in exciting high strength, thermally stable, high modulus fibers (16,42, 87, 90, 92, 98-101). Fabrication and processing of liquid crystalline polymers into highly oriented, high strength, high modulus fibers is also aided by the low viscosities of thermotropic liquid crystalline nematic melts and lyotropic liquid crystalline nematic solutions (100, 102, 103).

Nonetheless, while liquid crystalline polymers can readily be processed to achieve the high one-dimensional orientation that leads to their high strength and high modulus in fiber use, liquid crystalline polymers suffer the distinct disadvantage of markedly poorer properties in the directions perpendicular to the direction of their chain extension. Halliday and White have discussed this problem theoretically, and state that the modulus perpendicular to the draw direction is roughly proportional to the cohesive energy density of the utilized polymer (104). Thus, the only forces opposing applied stress perpendicular to the draw direction are of a secondary nature, and, therefore, the polymer lacks strength in such directions. As a result, liquid crystalline polymers have been limited primarily to one-dimensional applications.

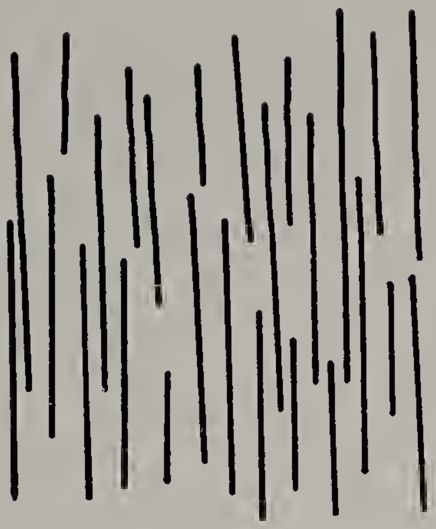
This problem has been recognized for a number of years, and efforts have been made to overcome this disadvantage of liquid crystalline polymers. The use of liquid crystalline block copolymers has shown potential in overcoming at least some of this problem (96, 97, 105). The excellent work of Takayanagi in the area of molecular composites has suggested that the use of liquid crystalline block copolymers can be employed to provide more than one-dimensional strength (105). The flexible blocks are hypothetically suggested to act as tie molecules to provide chemical bonds between the structurally supporting rigid blocks (105). Additionally, Takayanagi has suggested that liquid crystalline block copolymers would naturally phase separate to result in a heterogeneous structure which would inhibit crack propagation, a primary mode of polymer mechanical failure (105). Others have suggested that cholesteric polymer liquid crystals should be utilized to form biaxially oriented, chemically bond connected laminates (19, 106, 107). The work on cholesteric liquid crystalline polymers has been plagued by low molecular weights and a lack of potential for high temperature stability, therefore, no success has been reported in this area towards the goal of primary bond connected liquid crystalline biaxially oriented laminates. Work has been reported on attempts to biaxially orient liquid crystalline polymers (109), however, such materials will naturally prefer to form laminates which have very poor mechanical properties perpendicular to the direction of the biaxially extended chains.

The use of rigid rod star-block copolymers hypothetically could overcome these inherent difficulties in one-dimensionally and two-dimensionally extended chain liquid crystalline polymer applications. Figure 1.3 shows how the use of rigid rod star-block copolymers--

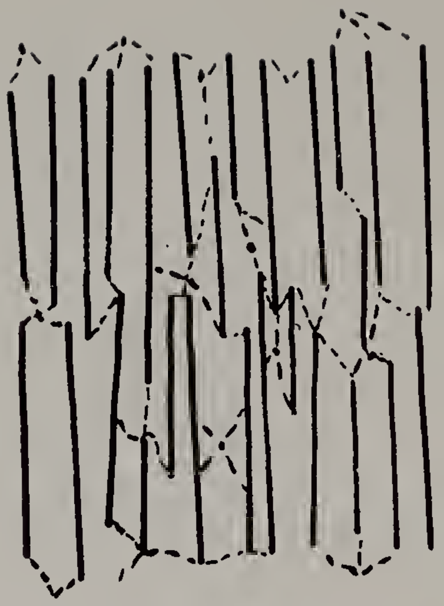
Figure 1.3

A pictorial explanation of the hypothetical advantage of using rigid rod star-block copolymers in one and two dimensional fiber applications. As can be seen, the flexible core of the rigid rod star-block copolymer connects uniaxially oriented rigid blocks, thus leading to improved mechanical properties in the direction perpendicular to the draw direction. Similarly, the flexible units of a rigid rod star-block copolymer could connect biaxially oriented laminates. Typical extended chain liquid crystalline polymers, ideally, could not take on a conformation to allow for good two-dimensional properties when uniaxially drawn or good three-dimensional properties when biaxially extended.

FIBERS



IDEALIZED NEMATIC
LINEAR FIBER



RIGID ROD STAR-
BLOCK COPOLYMER

2-D APPLICATIONS

TWO DIMENSIONAL APPLICATION
OF RIGID ROD STAR-BLOCK COPOLYMERS

either alone or blended with nematic polymer melts or solutions--could result in primary chemical bonding in directions perpendicular to the draw direction in fiber applications. Furthermore, rigid rod star-block copolymers, either alone or blended, could also provide tie molecules between biaxially oriented rigid laminates to result in good mechanical properties in the direction perpendicular to the plane of chain extension. Additionally, the heterogeneous nature of the rigid rod star-block copolymers would also inhibit crack propagation as suggested by Takayanagi (105).

So, in addition to the reporting of the first thermotropic and lyotropic star-block liquid crystalline copolymers, this dissertation will discuss the synthesis and initial characterization of rigid rod star-block copolymers that hold out the potential for significant scientific and technological importance. The next chapter will discuss the synthetic strategy employed and the specifics of that strategy for the synthesis of rigid rod star-block copolymers.

REFERENCES

1. A. Elliott and E.J. Ambrose. Discuss. Faraday Soc., 9, 246 (1950).

2. L. Onsager, Ann. N.Y. Acas. Sci., 51, 627 (1949).

3. A. Isihara, J. Chem. Phys., 19, 1142 (1951).

4. P.J. Flory, Proc. R. Soc. London, SerA234, 73 (1956).

5. J.D. Brooks and G.H. Taylor, Nature, 206, 697 (1965).

6. B. Reck and H. Ringsdorf, Makrom. Chem., Rapid Commun., 6(4), 291 (1985).

7. J.I. Jin, S. Antoun, C. Ober, and R.W. Lenz, Liquid Crystal Polymer Symposium, 16-17 July (1980).

8. H. Finkelmann, H.J. Kock, W. Gleim, and G. Rehage, Makrom. Chem., Rapid Commun., 5, 287 (1984).

9. A. Roviello and A. Sirigu, J. Polym. Sci., Letters Ed., 13, 455 (1975).

10. S. Antoun, R.W. Lenz, and J.I. Jin, J. Polym. Sci., Chem. Ed., 19, 1901 (1981).

11. P. Corradini and M. Vacatello, Mol. Cryst. Liq. Cryst., 97, 119 (1983).

12. A.C. Griffen and S.J. Havens, J. Polym. Sci., Phys. Ed., 19, 951 (1981).

13. P.G. deGennes, C.R. Acad. Sci. Paris, B281, 101 (1975).

14. K. Iiumura, N. Koide, R. Ohta, and M Takeda, Makrom. Chem., 182, 2563 (1981).

15. W.J. Jackson, Jr. and H.F. Kuhfuss, J. Polym. Sci., Chem. Ed., 14, 2043 (1976).

16. W.J. Jackson, Jr., British Polym. J., Dec., 154 (1980).

17. B.W. Jo and R.W. Lenz, Makrom. Chem., Rapid Commun., 3, 23 (1982).

18. B.W. Jo, J.I. Jin, and R.W. Lenz, Eur. Polym. J., 18, 233 (1982).

19. W.R. Krigbaum, A. Ciferri, and J. Asrar, Mol. Cryst. Liq. Cryst., 76, 79 (1981).

20. H.J. Lader and W.R. Krigbaum, J. Polym. Sci., Phys. Ed., 17, 1661 (1979).

21. A. Roviello and A. Sirigu, Makrom. Chem., 180, 2543 (1979).

22. A. Roviello and A. Sirigu, Makrom. Chem., 181, 1799 (1980).

23. A. Blumstein, S. Vilasager, S. Ponrathnam, S.B. Clough, and R.B. Blumstein, J. Polym. Sci., Phys. Ed., 20, 877 (1982).

24. W.R. Krigbaum and F. Salaris, J. Polym. Sci., Phys. Ed., 16, 883 (1978).

25. A. Blumstein, R.B. Blumstein, M.M. Gauthier, O. Thomas, and J. Asrar, Mol. Cryst. Liq. Cryst., 92, 87 (1983).

26. C. Ober, R.W. Lenz, G. Galli, and E. Chiellini, Macro., 16(7), 1034 (1983).

27. A.H. Al-Dujaili, A.D. Jenkins, and D.R.M. Walton, J. Polym. Sci., Chem. Ed., 22, 3129 (1984).

28. A.H. Al-Dujaili, A.D. Jenkins, and D.R.M. Walton, Makrom. Chem., Rapid Commun., 5, 33 (1984).

29. G. Chen and R.W. Lenz, J. Polym. Sci., Chem. Ed., 22, 3189 (1984).

30. C. Noel, F. Laupetere, C. Friedrich, B. Fayotte, and L. Bosio, Polymer, 25(6), 1808 (1984).

31. R.W. Lenz, Polymer J., 17(1), 105 (1985).

32. A. Blumstein, S. Vilasager, S. Ponrathnam, S.B. Clough, and R.B. Blumstein, J. Polym. Sci., Phys. Ed., 20, 877 (1982).

33. A. Blumstein and O. Thomas, Macro., 15(5), 1265 (1982).

34. A. Blumstein, K.N. Sivaramakrishnan, S.B. Clough, and R.B. Blumstein, *Molec. Cryst. Liq. Cryst.*, *49*, 255 (1979).

35. A. Blumstein and S. Vilasager, *Mol. Cryst. Liq. Cryst.*, *72*, 1 (1981).

36. W. Kreuder, H. Ringsdorf, and P. Tschirner, *Makrom. Chem., Rapid Commun.*, *6*, 367 (1985).

37. W. Kreuder, H. Ringsdorf, O. Hermann-Schoner, and J.H. Wendorff, *Makrom. Chem., Rapid Commun.*, *7*, 97 (1986).

38. W.J. Jackson, Jr., *Macro.*, *16(7)*, 1027 (1983).

39. G.W. Calundann, U.S. Patent 4,161,470 (July,17, 1979).

40. G.W. Calundann, U.S. Patent 4,279,803 (July 21, 1981).

41. G.W. Calundann, U.S, Patent 4,184,996 (Jan. 22, 1980).

42. J.R. Schaefgen, U.S. Patent 4,118,372 (Oct. 3, 1978).

43. C. Noel, C. Friedrich, F. Lauprete, J. Billard, L. Bosio, and C. Strazielle, *Polymer*, *25(2)*, 263 (1984).

44. W.J. Jackson, Jr., *Macro.*, *16(7)*, 1027 (1983).

45. J. Blackwell and G. Guiterrez, *Polymer*, *23(5)*, 671 (1982).

46. K. Iiumura, N. Koide, H. Tanabe, and M. Takeda, *Makrom. Chem.*, *182*, 2563 (1981).

47. A. Roviello and A. Sirigu, *Eur. Poly. J.*, *15*, 423 (1979).

48. S. M. Aharoni, *Macro.*, *12(1)*, 95 (1979).

49. S.M. Aharoni, *J. Polym. Sci., Phys. Ed.*, *18*, 1303 1980).

50. R.A. Vora and R.G. Patel, *Molec. Cryst. Liq. Cryst.*, *110(1-4)*, 109 (1984).

51. W.J. Jackson, Jr., J. Appl. Polym. Sci., 25, 1685 (1980).

52. A. Roviello, S. Santagatta, and A. Sirigu, Makrom. Chem., Rapid Commun., 4, 281 (1983).

53. T.D. Shaffer and V.Percec, ABS PAP ACS, 190(Sep.), 104 (1985).

54. C. Aguilera, J. Bartulin, B. Hisgen, and H. Ringsdorf, Makrom. Chem., 184, 253 (1983).

55. L. Strzelecki, Bull. Soc, Shim. Fr., 597 (1973).

56. V.V. Shilov, V.V. Tsukruk, and Y.S. Lipatov, J. Polym. Sci., Phys. Ed., 22(1), 41 (1984).

57. V.V. Shilov, V.V. Tsukruk, V.N. Bliznyak, and Y.S. Lipatov, Polymer, 23(4), 484 (1982).

58. V.V. Tsukruk, V.V. Shilov, I.I. Konstantinov, Y.S. Lipatov, and Y.B. Amerik, Eur. Polym. J., 18(11), 1015 (1982).

59. V.P. Shibaev, V.M. Moiseenko, T.S. Friedzon, and N.A. Plate, Eur. Polym. J., 16, 277 (1980).

60. P. Keller, Macro., 17(12), 2937 (1984).

61. B.A. Jones, J.S. Bradshaw, N. Nishioka, and M.L. Lee, J. Org. Chem., 49, 4947 (1984).

62. P.A. Gemmell, G. W. Gray, and D. Lacy, Molec. Cryst. Liq. Cryst., 122, 205 (1985).

63. H. Finkelmann and G. Rehage, Makrom. Chem., Rapid Commum., 1, 31 (1980).

64. H. Finkelmann, H.J. Kock, and G. Rehage, Makrom. Chem., Rapid Commun., 2, 317 (1981).

65. H. Finkelmann and G. Rehage, Makrom. Chem., Rapid Commun., 3, 859 (1982).

66. W. Kreuder and H. Ringsdorf, Makrom. Chem., Rapid Commun., 4, 807 (1983).

67. H.J. Coles, Faraday Discuss. Chem. Soc., 79, 1 (1985).

68. H. Finkelmann, H.J. Kock, W. Gleim, and G. Rehage, *Makrom. Chem., Rapid Commun.*, *5*, 287 (1984).

69. H. Ringsdorf and A. Schneller, *Makrom. Chem., Rapid Commun.*, *3*, 557 (1982).

70. J. Preston, B.K. Daniels, D.A. Zaukelies, U.S. Patent 3,600,269 (1971).

71. A.H. Frazer, U.S. Patent 3,536,651 (1970).

72. C. Robinson, J.C. Ward, and R.B. Beevers, *Discuss. Faraday Soc.*, *25*, 29 (1957).

73. C. Robinson, *Tetrahedron*, *13*, 219 (1961).

74. D.B. Dupre, R.W. Duke, W.A. Hines, and E.T. Samulski, *Mol. Cryst. Liq. Cryst.*, *40*, 247 (1977).

75. C. Robinson, *Molec. Cryst.*, *1*, 467 (1966).

76. R.W. Lenz, *Organic Chemistry of Synthetic High Polymers*, N.Y., Interscience Publ., p.467 (1967).

77. P.W. Morgan, *Macro.*, *10(6)*, 1381 (1977).

78. S.L. Kwolek, P.W. Morgan, J.R. Schaefgen, and L.W. Gulrich, *Macro.*, *10(6)*, 1390 (1977).

79. T.I. Bair, P.W. Morgan, F.L. Killian, *Macro.*, *10(6)*, 1396 (1977).

80. F. Higashi, M. Goto, Y. Nakano, and H. Kakinoki, *J. Polym. Sci., Chem. Ed.*, *18*, 851 (1980).

81. G.C. Alfonson, E. Bianchi, A. Ciferri, S. Russo, F.Salaris, and B. Valenti, *J. Polym. Sci., Polym. Symp. Ed.*, *65*, 213 (1978).

82. V.N. Tsvetkov, G.I. Kudryavtsev, I.N. Shtennikova, T.U. Peker, E.N. Zoklarova, V.D. Kalmykova, and A.V. Volokhina, *Eur. Polym. J.*, *12*, 517 (1976).

83. A.T. Kalashnik, N.P. Panikarova, E.V. Doubii, G.V. Kozhina, V.D. Kalmykova, and S.P. Papkov, *Vysokomol. Soedin, Ser. A*, *19(12)*, 2747 (1977).

84. M. Panar and L.F. Beste, *Macro.*, *10(6)*, 1401 (1977).

85. J. Asrar, J. Preston, A. Ciferri, and W.R. Krigbaum, *J. Polym. Sci., Chem. Ed.*, *20*, 373 (1982).

86. M. Arpin and C. Striazielle, *Polymer*, *18*, 591 (1977).

87. W.B. Black, *J. Macromol. Sci., Chem.*, *A7(11)*, 3 (1973).

88. D.B. Cotts and G.C. Berry, *Macro.*, *14*, 930 (1981).

89. R.C. Evers, F.E. Arnold, and T.E. Helminiak, *Macro.*, *14*, 925 (1981).

90. E.W. Choe and S.N. Kimm, *Macro.*, *14*, 920 (1981).

91. J.F. Wolfe and F.E. Arnold, *Macro.*, *14*, 909 (1981).

92. J.F. Wolfe, B.H. Loo, and F.E. Arnold, *Macro.*, *14*, 915 (1981).

93. M.B. Polk, K.B. Bota, M. Nandu, M. Phingbodhlipakkiya, and C. Edeogu, *Macro.*, *17*, 129 (1984).

94. M.B. Polk, K.B. Bota, E.C. Akubuiro, and M. Phingbodhlipakkiya, *Macro.*, *14*, 1626 (1981).

95. M. Takayanagi and T. Katayose, *J. Polym. Sci., Chem. Ed.*, *19*, 1133 (1981).

96. J. Preston, W.R. Krigbaum, and R. Kotek, *J. Polym. Sci., Chem. Ed.*, *20*, 3241 (1982).

97. S.M. Aharoni, *J. Polym. Sci., Phys. Ed.*, *19*, 281 (1981).

98. D. Acierno, F.P. LaMantia, G. Polizzotti, A. Ciferri, and B. Valente, *Macro.*, *15(6)*, 1455 (1982).

99. A. Ciferri, *Polym. Engin. and Sci.*, *15*, 191 (1975).

100. T.A. Hancock, J.E. Spruiell, and J.L. White, *J. Appl. Polym. Sci.*, *21*, 1227 (1977).

101. J. Preston, *Polym. Engin. and Sci.*, *15(3)*, 199 (1975).

102. A. Bickel, M.T. Shaw, and E.T. Samulski, *J. Rheol.*, *28(5)*, 647 (1984).

103. D.A. Simoff and R.S. Porter, Mol. Cryst. Liq. Cryst., 110, 1 (1984).

104. L. Halliday and J.W. White, Pure Applied Chem., 26, 545 (1971).

105. M. Takayanagi, T. Ogata, M. Morikaws, and T. Kai, J. Macromol. Sci., Phys., B17(4), 591 (1980).

106. W.R. Krigbaum, F.Salaris, and A. Ciferri, J. Polym. Sci., Letters Ed., 17, 601 (1979).

107. E. Chiellini, G. Galli, C. Malanga, and N. Spassky, Poly. Bull., 9, 336 (1983).

108. J.E. Flood, J.L. White, and J.F. Fellers, J. Appl. Polym. Sci., 27(8), 2965 (1982).

CHAPTER TWO

SYNTHETIC SCHEME FOR RIGID ROD STAR-BLOCK COPOLYMERS

I. INTRODUCTION

The synthesis of rigid rod star-block copolymers represents an advance in the area of synthesis of well defined polymers. To synthesize a copolymer in full accordance with the requirements presented in Chapter One, our scheme will have to take full advantage of existing methods in polymer synthesis and add some new methods as well. This chapter will explain a rational, general synthesis of rigid rod star-block copolymers and then discuss the specific initiators, monomers, and other reagents to be used in this work.

Prior to discussing the general synthetic scheme to be employed in this work, it will first be necessary to briefly provide a background into relevant synthetic areas. These areas include the synthesis of star, end-reactive, and end-reactive star polymers. After this background it will be clear that the synthetic scheme to be employed in this work is a truly general synthesis that completely satisfies the requirements presented in the first chapter of this dissertation.

II. SYNTHETIC BACKGROUND

The synthesis of rigid rod star-block copolymers utilizes several known polymer synthetic techniques. These synthetic techniques will be discussed in this section to provide a proper context for the general scheme to be presented subsequently. In accordance with this general synthetic scheme, the specific requirements of the chemical reagents will be outlined in the last section of this chapter. Following chapters will provide the detailed synthesis and characterization of all aspects of the synthetic scheme and the final synthesis and characterization of the rigid rod star-block copolymers.

Synthesis of Star Polymers

Over the last twenty years, several types of star (sometimes also referred to as radial polymers) polymers have been reported. Many synthetic pathways have been utilized, however as will be shown, only one method satisfies the strict requirements for the synthetic work to be discussed in this thesis.

Star polymers have been synthesized in two primary ways. One way reported has been to synthesize star polymers via multifunctional initiators from which the arms are grown as the polymerization proceeds. The other general method has been to terminate growing polymer chains with multifunctional terminating agents to form the star polymer. Both methods will be discussed in this section; however, only the latter method combined with anionic "living" polymerization can result in a star polymer of controlled arm length, narrow molecular weight distribution, and easily varied arm number.

Many types of star polymers have been prepared via the method of growing chains from a multifunctional initiator. These include styrene, isoprene, and butadiene polymers and block copolymers grown via living anionic polymerization from styrene/divinyl benzene gel multifunctional initiators (1-3). These polymers and block copolymers have been made with up to 56 arms, but it has proven difficult to control the arm number and polydispersity of the arms. A recent report has described the utilization of delocalized anions to grow star poly(styrene) via anionic living polymerization, however, a maximum of only three arms has been reported using this method (4). Cationic polymerization has also been used to grow star polymers from the inside out;

these methods include growing poly(tetrahydrofuran) from chloro-trimethylcellulose (5) and using Kennedy's inifer method (6). Both methods suffer from a lack of narrow molecular weight distributions as well as very limited arm numbers.

Preparing star polymers via termination of growing ends with multifunctional terminating agents is a much more general method. This method has typically involved terminating living anionic polymer chain ends with multifunctional silicon halides (7-11). This method has resulted in well-defined poly(styrene) and poly(diene) polymers and block copolymers of narrow molecular weight distributions, controlled arm numbers of up to eighteen (8), and theoretical arm lengths. Other multifunctional terminating agents have been used in anionic living polymerizations including styrene/divinyl benzene gels (12-15) and multifunctional esters (16), however, none of these terminating agents offer the control, precise reactivity, and easy change of arm number as do the silicon halides.

Other methods of a much less general sort have been used to prepare star polymers. These methods include the synthesis of star-block poly(styrene)-co-poly(4-vinylpyridine) by taking advantage of a side reaction in the anionic polymerization of 4-vinylpyridine (17), as well as termination of cationically growing poly(tetrahydrofuran) with a multifunctional terminating agent (18). Star poly(methylene) has also been reported (19). This polymer was simply made by hydrogenation of high 1,4 star poly(butadiene).

In summary, only the method of termination of living anionic polymer chain ends with multifunctional silicon halides will satisfy the requirements of the work to be described in this thesis. The next two sections will provide a background in telechelic polymers, which combined with information in this section, will lead to the rational synthesis of rigid rod star-block copolymers.

Synthesis of End-Reactive Polymers

The field of end-reactive polymers has been very active over the past twenty years. The varied and extensive work in this field has led to new possibilities in the control of macromolecular architecture. Many investigators, utilizing many polymerization techniques and pathways have made the field of end-reactive polymers an extremely dynamic area. As a result, the nomenclature of such polymers has as of yet not been standardized. For the purpose of this dissertation, the name semi-telechelic will refer to a polymer containing only one reactive end group, and the name telechelic will refer to a polymer containing a reactive end group at all of its extremities. The name macromolecular monomer will refer to a polymer containing an end group capable of taking part in a chain reaction polymerization. This section will provide a brief overview of this active area so as to lay a context for the forthcoming discussion of the general scheme to be used in the synthesis of rigid rod star-block copolymers.

End-reactive polymers have been prepared via cationic, anionic, and radical means. Of course all polymers prepared via step reaction polymerization means are typically end-reactive presuming that the growing polymer was not terminated due to an undesirable side-reaction leading to a loss of end group reactivity. As will be shown in this section, only telechelic polymers prepared via living anionic polymerization methods satisfy the strict requirements of monomer generality, narrow molecular weight distribution, and controlled functionality that will be needed to satisfy the forthcoming general synthetic scheme.

Many investigators have reported the synthesis of end-reactive polymers made via radical polymerization methods. These investigators generally prepare telechelic polymers by using functional radical initiators, which after propagation, transfer, and termination by radical coupling, reside at a certain amount of the polymer chain ends (20-28). Most reports have indicated that the average functionality of the polymer chains has been greater than two. Among the end group functionalities reported have been hydroxyl (20, 22, 23, 26, 28), carboxylic acid (24, 25, 27), ester (21, 24), and amine (24, 29, 30). Much of the work has concentrated on the synthesis of telechelic poly(butadiene)s. Needless to say, the difficulty in controlling the course of radical polymerizations makes the polymers made by these methods the least well-defined.

Cationic polymerization methods have been used to synthesize semi-telechelic polymers, telechelic polymers, and macromolecular monomers. The great bulk of this work has been carried out utilizing the initiator-transfer agents and "quasi-living" techniques pioneered by Kennedy over the last few years (31-51). This work involves the use of a cationic initiator that also acts as a transfer agent. By carefully controlling the reaction conditions, transfer to monomer is eliminated in favor of transfer to the initiator-transfer agent. The polymers prepared by this method feature nearly quantitative end functionalities, but have molecular weight distributions typically on the order of 1.5. Most of the work has utilized only one monomer, isobutylene, however, B-pinenes (36, 37) and indene (50) have also been explored with this method. Semi-telechelic (31) and telechelic (32-49) polymers have been prepared by this method with chloro (31, 36, 37, 39-41, 44, 49), hydroxyl (32, 42), allyl (32), oxirane (43, 46), phenol (45), Diels-Alder adduct (47), carboxylic acid, and ester functionalities (48). Macromolecular monomers have also been prepared via this procedure with acrylate and methacrylate functionalities attached to one end of poly(isobutylene) (50, 51). Although this method has very great utility, the limitations in monomer types and lack of a narrow molecular weight distribution disqualifies it for use in this thesis. Additionally, as will be discussed in the next section, this method has not been used to prepare star polymers of more than three arms.

Other cationic polymerization techniques have been used to prepare end-reactive polymers. Poly(tetrahydrofuran) telechelic (52) and macromolecular monomer (53-55) materials have been synthesized with ester and vinyl functionalities respectively. Other work has described the preparation of poly(2-methyl-2-oxazoline) macromolecular monomers with styrene functional groups at one end. Cationic polymerization methods remain an area of great activity in the synthesis of end-reactive polymeric materials.

Anionic polymerization methods offer the best means to attain quantitative functionalities, narrow molecular weight distributions, and monomer variability in the synthesis of end-reactive polymers. Recent reviews discuss the two primary anionic methods for the synthesis of end-reactive polymers (29, 30, 56, 57). These two primary methods are via functional initiators or via termination of living polymers to form a given functionality. The use of functional initiators and functional terminators combined with living anionic polymerization techniques have successfully been used to prepare semi-telechelic, telechelic, and macromolecular monomer materials.

Semi-telechelic polymers have been prepared via functional termination (55-61) and functional initiation methods (63-66). Most of this work has been performed on poly(styrene) and poly(dienes), however, other monomers such as the cyclic trimer of dimethylsiloxane, D3, have been used. Amongst the terminal functionalities are amine (58, 59, 64), hydroxyl (61, 62, 65), carboxylic acid (64), and many others (61). For the synthesis of semi-telechelic polymers the functional termination and functional initiation methods work equally well as long as the pertinent reagents are soluble in the reaction medium. Solubility has been a problem with functional initiators as they are typically insoluble in the nonpolar solvents that must be used in the synthesis of poly(dimethylsiloxane) and high 1,4-poly(dienes) (56, 57).

Telechelic polymers have been made utilizing the same general methods described above in the anionic synthesis of semi-telechelic polymers. The difference, of course, is that one must functionally terminate living polymers that have both ends living (66-69), or terminate living polymers initiated by functional initiators with multifunctional terminating agents (62-65). The monomers used and functionalities produced are as in the semi-telechelic polymers described above. The use of anionic functional initiators, however, in the case of telechelic polymer synthesis offers a distinct advantage over the use of functional termination methods. When more than one end of a growing polymer is living, particularly in nonpolar media, the possibility of gelation of the living ends is very great and this lead to obvious problems. The use of functional initiators alleviates this problem, however, the above mentioned solubility problems of most presently available functional anionic initiators leads to difficulties. The work described in this thesis will employ a unique non-polar soluble, blocked functional, anionic initiator which obviates the gelation problem without resulting in a solubility problem.

Macromolecular monomers have been prepared anionically via both the termination (61, 70, 74) and the functional initiation methods (75, 76). These one end-reactive polymers typically have styrene (70-72, 74-76) and methacrylic (75) functionalities. Such polymers can be utilized to prepare unique branched copolymers.

In summary, many polymerization methods have been utilized to prepare end-reactive polymers. Of the many methods utilized, anionic living polymerization techniques offer the best means of preparing well-defined, end-reactive polymers. Further, the use of the anionic functional initiator method is of particular utility when attempting to prepare telechelic polymers. The next section will describe the few methods available to prepare well-defined telechelic star polymers.

Preparation of Telechelic Star Polymers

Three methods for the preparation of telechelic star polymers have been reported. These are via cationic (36. 37, 45, 46, 77-80), delocalized anionic initiators (69), and the functional anionic initiator method (56). Only the latter method, pioneered by Schulz is appropriate for the work described in this thesis.

Cationic techniques based on Kennedy's initiator-transfer agents (36, 37, 45, 46, 77-80) have been used to prepare telechelic star polymers. However, this quasi-living method has been primarily limited to the use of the monomer isobutylene, results in polydispersities on the order of 1.5, and has never been used to prepare a star polymer of more than three arms.

The work of Gordon (69) utilizing delocalized anionic multifunctional initiators has resulted in three-armed poly(styrene) stars with carboxylic acid functionalities at the ends. This recent work has the potential for preparing well-defined telechelic stars, however, no star polymer of more than three-arms has been reported. Significant advances in the preparation and use of multifunctional delocalized anionic initiators would be necessary for this method to be appropriate for the work of this thesis.

The method of Schulz (56), where blocked functional anionic initiators in combination with multifunctional terminating agents are used, has resulted in telechelic star polymers. This method is a general type of telechelic star synthesis where polydispersity, molecular weight, and arm number can be readily controlled based on known literature techniques. The problem with this method is the limited solubility of presently available blocked functional anionic initiators (63-66). Chapter Three of this thesis will discuss the preparation of a new blocked functional anionic initiator that is soluble in non-polar solvents, thereby obviating the limitation of this method and extending it for use with additional monomers to make different and more well defined telechelic polymers. The next section of this chapter will describe the general scheme to be utilized in the synthesis of rigid rod star-block copolymers. This method will be an extension of the methods of Schulz.

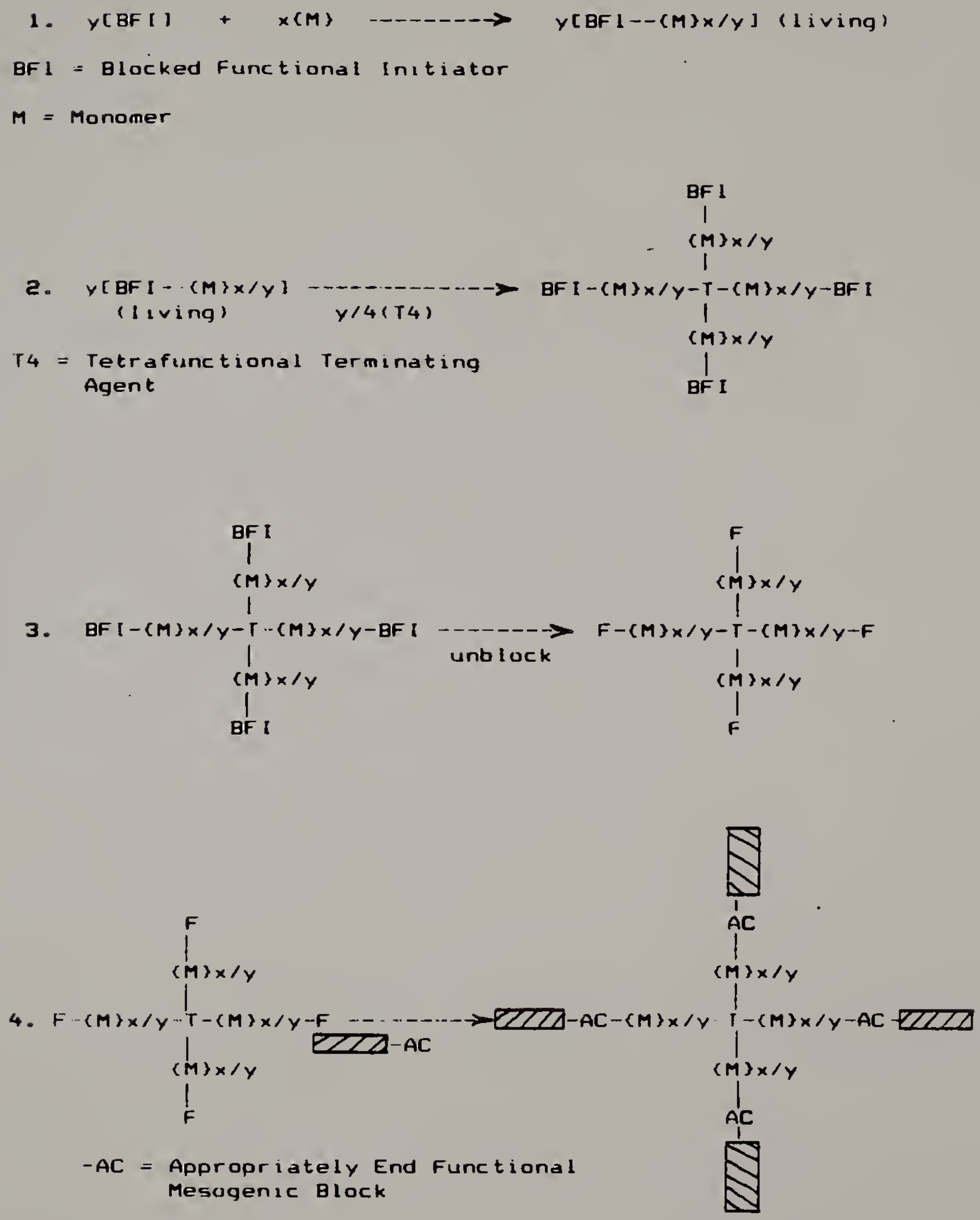
III. THE GENERAL SYNTHETIC SCHEME FOR THE SYNTHESIS OF RIGID ROD STAR-BLOCK COPOLYMERS

Figure 2.1 shows the general scheme for the synthesis of rigid rod star-block copolymers. As can be seen, a blocked functional anionic initiator will be used to initiate a living anionic polymerization. The polymerization will proceed to form a polymer of low polydispersity and controlled molecular weight. Upon termination with a multifunctional terminating agent, a star polymer will be formed with blocked functionality at

Figure 2.1

The general synthetic scheme for the synthesis of rigid rod star-block copolymers. This figure shows; (1) The blocked functional anionic initiator reacting with an appropriate monomer to form a living polymer. (2) By termination with a multifunctional terminating agent and (3) unblocking of the functional group, a telechelic star core is prepared. (4) Reaction with a rigid, liquid crystalline species gives a rigid rod star-block copolymer.

A GENERAL SYNTHETIC APPROACH TO THE SYNTHESIS OF RIGID ROD STAR-BLOCK COPOLYMERS



1. $y[\mathrm{BFI}] + x(\mathrm{M}) \longrightarrow y[\mathrm{BFI}\text{--}(\mathrm{M})x/y]$ (living)

BFI = Blocked Functional Initiator

M = Monomer

2. $\underset{\text{(living)}}{y[\mathrm{BFI}\text{--}(\mathrm{M})x/y]} \xrightarrow[y/4(\mathrm{T4})]{} \begin{array}{c} \mathrm{BFI} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{BFI\text{-}(M)}x/y\mathrm{\text{-}T\text{-}(M)}x/y\text{-}\mathrm{BFI} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{BFI} \end{array}$

T4 = Tetrafunctional Terminating Agent

3. $\begin{array}{c} \mathrm{BFI} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{BFI\text{-}(M)}x/y\mathrm{\text{-}T\text{-}(M)}x/y\text{-}\mathrm{BFI} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{BFI} \end{array} \xrightarrow[\text{unblock}]{} \begin{array}{c} \mathrm{F} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{F\text{-}(M)}x/y\mathrm{\text{-}T\text{-}(M)}x/y\text{-}\mathrm{F} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{F} \end{array}$

4. $\begin{array}{c} \mathrm{F} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{F\text{-}(M)}x/y\mathrm{\text{-}T\text{-}(M)}x/y\text{-}\mathrm{F} \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{F} \end{array} \xrightarrow[▨\text{-AC}]{} \begin{array}{c} ▨ \\ | \\ \mathrm{AC} \\ | \\ (\mathrm{M})x/y \\ | \\ ▨\mathrm{\text{-}AC\text{-}(M)}x/y\mathrm{\text{-}T\text{-}(M)}x/y\text{-}\mathrm{AC}\text{-}▨ \\ | \\ (\mathrm{M})x/y \\ | \\ \mathrm{AC} \\ | \\ ▨ \end{array}$

-AC = Appropriately End Functional Mesogenic Block each extremity. Although a four-armed star is shown in the figure, star polymers of up to eighteen arms could readily be made employing the method of multifunctional termination (8). After deblocking, a telechelic star polymer will have been formed.

The rigid rod star-block copolymers will be made by either growing a polymer from the ends of the telechelic star or by simply reacting a low molecular weight mesogen of appropriate functionality with the telechelic star polymers.

As can easily be seen, this general method fully satisfies the requirements outlined in Chapter One for the general synthesis of rigid rod star-block copolymers. The next section will discuss the specific requirements for the reagents, and the specific lyotropic and thermotropic liquid crystalline species to be utilized in the synthesis of the rigid rod star-block copolymers.

IV. SPECIFICS FOR THE PREPARATION OF THE RIGID ROD STAR-BLOCK COPOLYMERS

This section will describe the specific requirements for the blocked functional anionic initiator, the specific telechelic star core to be prepared, as well as the specific thermotropic and lyotropic liquid crystalline blocks to be utilized in the synthesis of the rigid rod star-block copolymers.

The blocked functional anionic initiator to be used in this work must satisfy a number of stringent requirements. The blocked functional group must be fully inert to the propagating anion. The nature of the initiator must also allow for the living polymerization of the cyclic trimer of dimethylsiloxane, D3, since that is the monomer of choice as described below. This requires that the initiator have a lithium counterion and be soluble in nonpolar solvents. Additionally, it is highly preferable that the blocked functionality be that of an aromatic amine for structural and reactivity concerns to be discussed below.

The flexible telechelic star core of choice is poly(dimethylsiloxane). It has been shown, that via the D3 monomer, a living anionic polymerization can be performed to prepare poly(dimethylsiloxane) of controlled molecular weight and low polydispersity (81-83). This, however, can only be performed utilizing the D3 monomer, a lithium counterion, and utilizing a nonpolar reaction medium with a very small amount of polar promoter. Utilization of the D4 monomer and/or a polar reaction medium will result in backbiting reactions to form cyclic products (84-86). The poly(dimethylsiloxane) polymer should be excellent for the flexible star core due to its extraordinary flexibility and its good thermal stability. Additionally, the living silanolate anion should react expeditiously with silicon chloride multifunctional terminating agents.

The thermotropic rigid rod star-block copolymers will be prepared by reacting a low molecular weight thermotropic mesogen with the end of the telechelic star cores. The actual thermotropic mesogen to be used will be described in Chapter Five.

The lyotropic rigid rod star-block copolymers will be made by growing poly(p-benzamide) off the ends of the telechelic star cores via the "Yamazaki" reaction. The Yamazaki reaction involves the preparation of certain polyamides via direct polycondensation by using phosphites in the presence of metal salts (87-90). This reaction has been shown to be particularly good in the preparation of poly(p-benzamide) homopolymers and block copolymers to useful and consistent molecular weights (87, 91, 92). It is important to point out that the Yamazaki reaction proceeds successfully only with aromatic amines and aliphatic and/or aromatic carboxylic acids; thus the requirement for an aromatic amine blocked functional anionic initiator.

The subsequent chapters of this thesis will present the detailed account of the preparation and characterization of the new blocked functional anionic aromatic amine initiator, the new telechelic poly(dimethylsiloxane) star polymers, and the thermotropic and lyotropic rigid rod star-block copolymers.

REFERENCES

1. R.N. Young and L.J. Fetters, Macro., 11(5), 899 (1978).

2. H. Eschwey, Polymer, 16(3), 180 (1975).

3. K. Ishizu, S. Gamoo, T. Fukutomi, and T. Kakurai, Polymer J., 12(6), 399 (1980).

4. B. Gordon III, M. Blumenthall, and J.E. Loftus, Poly. Bull., 11, 349 (1984).

5. H.J. Cantow, C. Feger, and T. Mezger, Int. Dissolving Pulps Confr., 5th, 184 (1980).

6. A. Nagy, R. Faust, and J.P. Kennedy, Poly. Bull., 13(2), 97 (1985).

7. N. Hadjichristidis, A. Guyot, and L.J. Fetters, Macro., 11(4), 668 (1978).

8. N. Hadjichristidis and L.J. Fetters, Macro., 13(1), 191 (1980).

9. N. Hadjichristidis and J.E.L. Roovers, J. Polym. Sci., Phys. Ed., 12(12), 2521 (1974).

10. S.M. Hirshfield, U.S. Patent 3,755,283 (May 19, 1971).

11. R.P. Zelinski and C.F. Wofford, J. Polym. Sci., A(3), 93 (1965).

12. G. Quack and L.J. Fetters, Ind. Eng. Chem. Prd. Res. Dev., 19(4), 587 (1980).

13. L.K. Bi and R. Milkovich, U.S. Patent 4,248,983 (Sept. 9, 1980).

14. L.K. Bi, R. Milkovich, and K.W. Poak, U.S. Patent 4,248,983 (Feb. 5, 1979).

15. L.K. Bi and L.J. Fetters, Macro., 9(5), 732 (1976).

16. P.A. Mancinelli, U.S. Patent 4,503,188 (March, 5, 1985).

17. A.P. Luyton, Polymer, 19(11), 1320 (1978).

18. L. Reibel, P. Lutz, A. Dondos, and E. Franta, Pap. Int. Symp. (1979).

19. V.R. Raju, J. Rheol., 25(4), 464 (1981).

20. N.D. Ghatge, S.P. Vernekar, and P.P. Wadgoank, J. Polym. Sci., Chem. Ed., 21(12), 3591 (1983).

21. W. Heitz and P. Ball, Ger. Patent 2,908,298 (Sept, 11, 1980).

22. D.M. White, U.S. Patent 4,146,697 (May 19, 1978).

23. K. Bouchal, E. Zurkova, and J. Kalas, Die Angewandte Chemie, 92, 107 (1980).

24. W. Konter, B. Bomer, and K.H. Kohler, Makrom. Chem., 182, 2619 (1981).

25. S.F. Reed Jr., J. Polym. Sci., A(8), 2147 (1971).

26. S.F. Reed Jr., J. Polym. Sci., A(9), 2029 (1971).

27. W.H. Stubbs, C.B. Gore, and C.S. Marvel, J. Polym. Sci., A(4), 1898 (1966).

28. K. Bouchal, E. Zurkova, J. Kalal, M. Sufcak, and O. Seycek, Die Angewandte Chemie, 86, 33 (1980).

29. S.F. Reed Jr., Poly. Prep., 15(2), 46 (1974).

30. R.D. Athey, Prog. Org. Coatings, 7, 289 (1979).

31. J.P. Kennedy and M. Hiza, Poly. Bull., 8, 557 (1982).

32. J.P. Kennedy, S.Y. Huang, and R.A. Smith, J. Macromol. Sci., Chem., A14(7), 1085 (1980).

33. J.P. Kennedy, Polymer J., 12(9), 609 (1980).

34. J.P. Kennedy, J. Macromol. Sci., Chem., A13(5), 695 (1979).

35. J.P. Kennedy and R. Santos, ABS PAP ACS, 186(Aug), 4 (1983).

36. J.P. Kennedy, T.P. Liao, S. Guhaniyogi, and V.S.C. Chang, J. Polym. Sci., Chem. Ed., 20, 3229 (1982).

37. J.P. Kennedy, T.P. Liao, S. Guhaniyogi, and V.S.C. Chang, J. Polym. Sci., Chem. Ed., 20, 3219 (1982).

38. V. Percec, S.C. Guhaniyogi, and J.P. Kennedy, Poly. Bull., 9, 27 (1983).

39. J.P. Kennedy and R.A. Smith, J. Polym. Sci., Chem. Ed., 18, 1523 (1980).

40. R.H. Wondraczek, J.P. Kennedy, and R.F. Storey, J. Polym. Sci., Chem. Ed., 20, 43 (1982).

41. A. Fehervari and J.P. Kennedy, J. Macromol. Sci., Chem., A15(2), 215 (1981).

42. B. Ivan, J.P. Kennedy, and V.S.C. Chang, J. Polym. Sci., Chem. Ed., 18, 3177 (1980).

43. J.P. Kennedy, V.S.C. Chang, and W.P. Francik, J. Polym. Sci., Chem. Ed., 20, 2809 (1982).

44. R. Santos, J.P. Kennedy, and M. Walters, Poly. Bull., 11, 261 (1984).

45. J.P. Kennedy, S.C. Guhaniyogi, and V. Percec, Poly. Bull., 8, 563 (1982).

46. J.P. Kennedy, S.C. Guhaniyogi, and V. Percec, Poly. Bull., 8, 571 (1982).

47. J.P. Kennedy, G.M. Carlson, and R. Riebel, Poly. Bull., 9, 268 (1983).

48. T.P. Liao and J.P. Kennedy, Poly. Bull., 5, 11 (1981).

49. R.H. Wondraczek, H.E. Hotzel, and G. Heubkin, Poly. Bull., 7, 377 (1982).

50. J.P. Kennedy and M. Hiza, J. Polym. Sci., Chem. Ed., 21, 1033 (1983).

51. T.P. Liao and J.P. Kennedy, Poly. Bull., 6, 135 (1981).

52. W. Stix and W. Heitz, Makrom. Chem., 180, 1367 (1979).

53. R. Asami, M. Takaki, K. Kyunda, and E. Asakura, Polymer J., 15(2), 139 (1983).

54. M. Takaki, R. Asami, and T Kawabara, *Poly. Bull.*, *7*, 521 (1982).

55. J. Sierra-Vargas, P. Masson, G. Beinert, P. Rempp, and E. Franta, *Poly. Bull.*, *7*, 277 (1982).

56. D.N. Schulz, J.C. Sanda, and B.G. Willoughby, *ACS Sym. Ser.*, *166*, 427 (1981).

57. D.N. Schulz, *Polym. Prep.*, *21(1)*, 32 (1980).

58. W.L. Hergenrotter, R.A. Schwarz, R.J. Ambrose, and R.A. Hayes, U.S. Patent 4,070,344 (May 5, 1975)

59. R.P. Quirk and P.L. Chang, *Polym. Prep.*, *24(2)*, 461 (1983).

60. A. Hirao, I. Hittori, T. Sasagawa, K. Yamaguchi, S. Nakahama, and N. Yamazaki, *Makrom. Chem., Rapid Commun.*, *3*, 59 (1982).

61. R. Milkovich, *Polym. Prep.*, *21(1)*, 40 (1980).

62. D.N. Schulz, A.F. Halasa, and A.E. Oberster, *J. Polym. Sci., Chem. Ed.*, *12*, 153 (1974)

63. D.N. Schulz and A.F. Halasa, *J. Polym. Sci., Chem. Ed.*, *15*, 2401 (1977).

64. G. Broze, R. Jerome, and P.H. Teyssie, *Makrom. Chem.*, *179*, 1383 (1978).

65. P.M. Lefebvre, R. Jerome, and P.H. Teyssie, *Macro.*, *10(4)*, 871 (1977).

66. G. Friedmann and J. Brossas, *Poly. Bull.*, *11(1)*, 25 (1984).

67. S.F. Reed Jr., *J. Polym. Sci.*, *A10*, 1087 (1972).

68. C.A. Wentz and E.E. Hopper, *Ind. Eng. Prd.*, *6*, 209 (1967).

69. B. Gordon III, M. Blumenthall, and J.E. Loftus, *Poly. Bull.*, *11*, 349 (1984).

70. R. Asami, M. Takaki, and H. Hanahata, *Macro.*, *16*, 628 (1983).

71. K. Hashimota, H. Sumitomo, and M. Kawasumi, *Poly. Bull.*, *11*, 121 (1984).

72. R. Milkovich, and M.T. Chang, U,S, Patent 3,989,768 (Nov. 3, 1976).

73. P. Rao, P. Masson, P. Lutz, G. Beinert, and P. Rempp, *Poly. Bull.*, *11*, 115 (1984).

74. Y. Kawakami, Y. Miki, T. Tsuda, R.A.N. Murthy, and Y. Yamashita, *Polymer J.*, *14(11)*, 913 (1982).

75. M. Maeda and S. Inoue, *Makrom. Chem., Rapid Commun.*, *2*, 537 (1981).

76. P. Masson, G. Beinert, E.Franta, and P. Rempp, *Poly. Bull.*, 7, 17 (1982).

77. J.P. Kennedy, L.R. Ross, and O. Nuyken, *Poly. Bull.*, *5*, 5 (1981).

78. V. Percek, S.C. Guhaniyogi, and J.P. Kennedy, *Poly. Bull.*, *8*, 25 (1982).

79. V. Percek, S.C. Guhaniyogi, and J.P. Kennedy, *Poly. Bull.*, *8*, 319 (1982).

80. R.H. Wondraczek and J.P. Kennedy, *J. Polym. Sci., Chem. Ed.*, *20*, 173 (1982).

81. H.J. Holle and B.R. Lehnen, *Eur. Poly. J.*, *11*, 663 (1975).

82. C.L. Lee and O.K. Johannson, *J. Polym. Sci., Chem. Ed.*, *14*, 729 (1976).

83. C.L. Lee, O.W. Marko, and O.K.Johannson, *J. Polym. Sci., Chem. Ed.*, *14*, 743 (1976).

84. M. Mazurek and J. Chojnowski, *Makrom. Chem.*, *178*, 1605 (1977).

85. M. Mazurek and J. Chojnowski, *Macro.*, *11(2)*, 347 (1978).

86. J.F. Brown, *J. Am. Chem. Soc.*, *87*, 931 (1965).

87. N. Yamazaki, M. Matsumoto, and F. Highashi, *J. Polym. Sci., Chem. Ed.*, *13*, 1373 (1975).

88. N. Yamazaki and F. Higashi, *J. Polym. Sci., Letters Ed.*, *12*, 185 (1974).

89. N. Yamazaki, F. Higashi, and J. Kawabata, *J. Polym. Sci., Chem. Ed.*, *12*, 2149 (1974).

90. N. Yamazaki and F. Higashi, *Tetrahedron Letters*, 49, 5047 (1972).

91. J. Asrar, J. Preston, A. Ciferri, and W.R. Krigbaum, *J. Polym. Sci., Chem. Ed.*, *20*, 373 (1982).

92. J. Asrar, J. Preston, and W.R. Krigbaum, *J. Polym. Sci., Chem. Ed.*, *20*, 79 (1982).

CHAPTER THREE

A BLOCKED AMINE FUNCTIONAL INITIATOR FOR ANIONIC POLYMERIZATION

I. INTRODUCTION

The field of end-reactive polymers has been an active one in polymer synthesis for more than twenty years. Several methods have been used to prepare end-reactive polymers including anionic (1-10), radical (11-14), cationic (15-21), and group-transfer polymerization 22). To date, anionic polymerization has been the most generally successful method to prepare end-reactive polymers from many monomers with resulting polymers of theoretical functionalities, narrow molecular weight distributions, and controlled molecular weights (8).

End-reactive polymers can be prepared via "living" anionic polymerization in two primary ways (8). To prepare telechelic polymers one can use multifunctional anionic initiators followed by functional termination (1-5, 8), or one can utilize blocked functional anionic initiators followed by multifunctional termination (6-10). The latter method pioneered by Schulz utilizing blocked functional initiators has a distinct advantage over the former method. Utilization of blocked functional anionic initiators alleviates the frequently encountered problem of gelation of multiple "living" ends found in anionic polymerizations with multifunctional initiators (8). This gelation problem is particularly troublesome when performing polymerizations in nonpolar solvents, however, in many cases nonpolar solvents are the solvents of choice to achieve well defined polymer microstructures.

Presently available blocked functional anionic initiators have, with varied levels of success, been able to prepare well-defined polymers with hydroxyl, carboxylic acid and amine end functionalities (6-10). However, the use of the blocked functional anionic initiator method has been limited due to the insolubility of most of the currently available blocked functional anionic initiators in nonpolar solvents (8). This nonpolar solvent insolubility of most presently available block functional anionic initiators prevents their use in the preparation of high 1,4 and high cis-1,4 polydienes and in the preparation of well-defined telechelic poly(dimethylsiloxane)s. Only a blocked hydroxyl functional anionic initiator has shown any solubility in benzene (10), however, this initiator is not soluble in hexanes (6), which limits its use to prepare high cis-1,4 polydienes.

This chapter will discuss the preparation and use of a new blocked amine functional anionic initiator that is soluble in nonpolar solvents. The preparation of well defined end-reactive amine functional poly(dimethylsiloxane)s will also be presented.

II. EXPERIMENTAL SECTION

Materials: *p*-Aminostyrene (PAS) was obtained from Polysciences and vacuum distilled from calcium hydride prior to use. Chlorotrimethylsilane and dichlorodimethylsilane were obtained from Aldrich Chemical Co. and distilled and then titrated prior to use. *N*,*O*-bis(trimethylsilyl)acetamide (BSA) was obtained from Sigma and used as received. *n*-Butyllithium and *sec*-butyllithium were obtained from Aldrich Chemical Co. in hexane and cyclohexane solutions respectively, and used as received after standardization as described in the measurements section. Ethylmagnesium bromide in tetrahydrofuran was obtained from Aldrich Chemical Co. and used as received. Molecular Sieves, 3 Angstrom, were obtained from MCB and activated as follows. After sitting under tetrahydrofuran for five days, the sieves were washed, the solvent was allowed to dry, and then the sieves were dried under vacuum ($\leq$ 0.005 mm Hg) for two days at 140°C; the sieves were stored under dry argon. Ionol, 2 6-di-tert-butyl-4-methylphenol, was obtained from Shell and recrystallized from Skelly F prior to use. Diphenylacetic acid was obtained from Aldrich Chemical Co. and was sublimed prior to use. Hexamethylcyclotrisiloxane (D3), was obtained from Petrarch Systems and purified by sublimation into a flask containing activated 3 Angstrom Molecular Sieves. This monomer was dispensed as a solution in dry benzene. Methyl violet was obtained from Eastman Kodak and used as received. Perchloric acid, 70%, was obtained from Eastman Kodak and used as received.

Hexane (HPLC grade) was obtained from Fisher Scientific, distilled from calcium hydride into a flask containing activated Molecular Sieves, and stored under argon prior to use. Cyclohexane was obtained from Fisher Scientific, stirred over sulfuric acid, washed and neutralized with distilled water and dilute aqueous sodium hydroxide, distilled from fresh phosphorus pentoxide, refluxed over sodium metal for two days, distilled under dry argon into a flask containing activated Molecular Sieves, and stored under argon prior to use. Benzene (spectroscopic grade) was obtained from Fisher Scientific, stirred over sulfuric acid, washed and neutralized with distilled water and aqueous sodium hydroxide, distilled from fresh phosphorus pentoxide, refluxed over sodium metal and benzophenone until free of both water and oxygen, distilled under dry argon into a flask containing activated Molecular Sieves, and stored under argon prior to use. Tetrahydrofuran (THF, spectroscopic grade) was obtained from Fisher Scientific, refluxed over sodium metal and benzophenone until free of both water and oxygen, distilled into a flask containing activated Molecular Sieves, and stored under argon prior to use. Hexamethylphosphoramide (HMPA) was obtained from Aldrich Chemical Co., stirred over anhydrous calcium oxide, fractionally vacuum distilled from calcium oxide into a flask containing sodium metal, refluxed two days over sodium, distilled under vacuum into a flask containing activated Molecular Sieves, and stored under argon in a refrigerator prior to use. Acetic acid was obtained from Fisher Scientific and distilled prior to use.

Preparation of p-N,N-Bis(trimethylsilyl)aminostyrene:

Into a clean, dry 100 mL round bottom flask containing a stirring bar and a small amount of ionol, was vacuum distilled 3.0 g (0.025 mol) of PAS. To this flask under argon at room temperature was added 25 mL of dry THF and 10mL (0.049 mol) of BSA. The reaction mixture was allowed to stir under argon for three days at room temperature. The N-monosilyllated PAS was isolated via vacuum distillation (0.01 mm Hg) at 59 - 63°C after the THF, unreacted BSA, and the trimethylsilylacetamide side product were removed by vacuum. The N-monosilyllated PAS was prepared in 97% yield and verified by NMR to be identical to that described previously (23). Then the 0.025 moles of N-monosilyllated PAS were cooled to -10°C and under argon was added 10 mL of THF and 25mL of 2M Ethylmagnesium bromide in THF (0.05 mol, 2 eq.). After its temperature had risen to ambient, the reaction mixture was stirred for three hours under argon and then 12.6 mL (0.10 mol, 4 eq.) of chlorotrimethylsilane was added. The reaction was allowed to proceed for seventeen hours after which the magnesium salts were filtered off in a glove bag, and the product was isolated by vacuum distillation (0.02 mm Hg) at 79 - 84°C after the THF and excess chlorotrimethylsilane were removed by vacuum. The overall preparation could be performed with a combined yield of 81% and the product was verified by NMR to be in agreement with literature values (23). The product was stirred over calcium hydride, vacuum distilled, and stored under argon in a refrigerator prior to use.

Reactions of Alkyllithiums with p-N,N-Bis(trimethylsilyl)aminostyrene; Generation of the Initiator: To a clean, dry, argon filled flask was added at room temperature 7 mL of dry benzene, 9.3 mL (0.00023 mol in cyclohexane) of *sec*-butyllithium, and then 3.7 mL (0.00024 mol in benzene) of *p*-*N*,*N*-bis(trimethylsilyl)-aminostyrene with vigorous stirring. The reaction mixture slowly became colored until an orange/red color persisted. The reaction was allowed to proceed under argon at room temperature for 1.5 hours at which time the reaction was terminated with dilute acetic acid. The termination with dilute acetic acid was a titration for living ends which along with gas chromatographic and NMR data indicated that the desired initiator species (DP = 1) was generated.

Polymerization of D3 with the Blocked Amine Functional Anionic Initiator: To a clean, dry, argon-filled flask was added 70 mL of dry benzene, 1.32 mL (0.00186 mol in cyclohexane) of *sec*-butyllithium, and then 3.76 mL (0.00186 mol in benzene) of *p*-*N*,*N*-Bis(trimethylsilyl)-aminostyrene at room temperature. After 1.2 hours, the initiator was formed as indicated by the persisting orange/red color. Then 2.00 mL (1.0 g in benzene) of D3 solution was added, followed by 1.0 mL of HMPA. Only after addition of HMPA did the characteristic color of the initiator immediately fade to the colorless appearance of the propagating silanolate. After 1.5 hours, 1.0 mL of the reaction was removed and terminated by 1.5 equivalents of chlorotrimethylsilane for use in gel permeation chromatography analysis; at the same time 0.46 mL (0.00095 mol in benzene) of dichlorodimethylsilane was added to form the blocked telechelic polymer. The coupling reaction was allowed to proceed for two days at room temperature under argon at which time the polymer was ready for unblocking of the amine functionality.

Unblocking of the Telechelic Blocked Amine Functional Poly(dimethylsiloxane): After infrared spectroscopy analysis, 10 mL of 2N aqueous HCl was added to the colorless solution containing the telechelic blocked amine functional poly(dimethylsiloxane). After thirty minutes, the now cloudy reaction mixture was investigated by infrared spectroscopy to insure total unblocking, then the colorless solution was transferred to a separatory funnel, neutralized with dilute aqueous sodium hydroxide, washed with distilled water, and filtered through a Whatman #1 filter into a round bottom flask from which the solvent was removed via rotary evaporation. Then the polymer was dried under vacuum (0.05 mm Hg) at 65°C for 65 hours to yield 1.22g (97.6% yield). The oily polymer was investigated by gel permeation chromatography, qualitative and quantitative infrared spectroscopy, and vapor phase osmommetry to determine its polydispersity and functionality.

Measurements: Titrations for living end concentration in the reactions of lithiumalkyls with *p*-*N*,*N*-bis(trimethylsilyl)aminostyrene were performed with known amounts of dilute aqueous acetic acid in benzene and based upon disappearance of the characteristic styryl anion color.

End-group analysis for the concentration of aromatic amine in the poly(dimethylsiloxane) polymers was performed by nonaqueous titrations as reported by Schulz (7), and by quantitative infrared analysis of the 1600 cm phenyl ring breathing peak in chloroform based on a Beer's law plot of *p*-*n*-butylaniline.

Gas chromatography was performed on a Hewlett/Packard 5790A gas chromatograph with an OV101 column, flame ionization detector, and Helium carrier gas. Infrared spectroscopy was performed on a Perkin-Elmer 1420 infrared spectrophotometer. NMR was performed on a T60 spectrophotometer. Vapor phase osmommetry was performed on a Knauer osmommeter in chloroform at 37°C with benzil as the standard. Gel permeation chromatography was performed on a Waters chromatogragh in THF.

Alkyllithiums were standardized for total base and total lithiumalkyl by the method of Kofron (24) utilizing diphenylacetic acid in THF.

III. RESULTS AND DISCUSSION

Attempts to prepare the mono-(trimethylsilyl)-aminostyrene in accordance with the literature procedure (23) failed due to formation of polymeric species. The literature procedure involved refluxing in hexamethyldisilazane, followed by addition of chlorotrimethylsilane. Therefore, milder conditions were sought to carry out the mono silylation. It has been reported, that silylation of hydroxyl, amine, and carboxylic acids under mild conditions has been accomplished using a number of special silylating agents (24 - 26). BSA was chosen to mono silylate the PAS due to a report that amines could be monosilylated by BSA in THF and/or dimethylacetamide at room temperature (26). The complete silylation of PAS was carried out as shown in Figure 3.1. The product was verified by NMR and Infrared spectroscopy to be in accordance with reported values, and gas chromatography indicated the product to be pure, see Figure 3.2.

The key step in the preparation of the new blocked amine functional anionic initiator was the generation of the anion by a clean reaction of an alkyllithium reagent quantitatively with *p*-*N*,*N*-bis(trimethylsilyl)-aminostyrene. Table 3.1 shows the many conditions under which *p*-*N*,*N*-bis(trimethylsilyl)aminostyrene was added to an equimolar amount of alkyllithium. As can be seen, only the addition of *p*-*N*,*N*-bis(trimethylsilyl)-aminostyrene to *sec*-butyllithium under totally nonpolar solvent conditions resulted in the generation of the desired initiator. Under no conditions was the desired one degree of polymerization achieved with *n*-butyllithium or in the presence of any polar promoter. Figure 3.2 shows the gas chromatography data from reactions 10 and 12 of Table 3.1. The data indicates the formation of one detectable species with no initial reactants left. The NMR and titration data also indicated that only in reactions 10 and 12 of Table 3.1 was the desired product exclusively formed.

Figure 3.1

The reaction scheme for the preparation of the new blocked amine functional anionic initiator. The *p*-*N*,*N*-bis(trimethylsilyl)aminostyrene can be prepared in an overall yield of 81%, and this styrene derivative reacts quantitatively with *sec*-butyllithium to form the initiator.

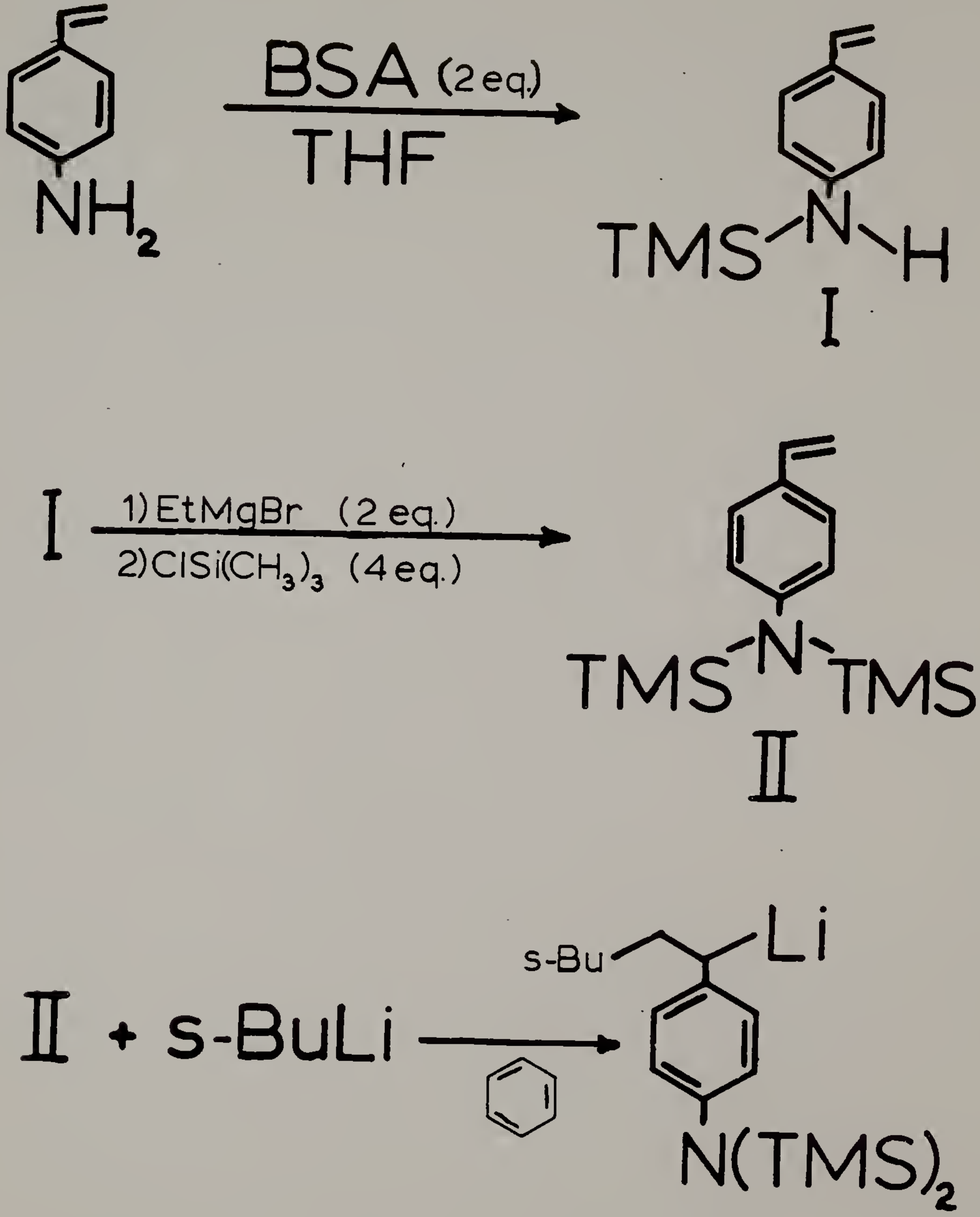
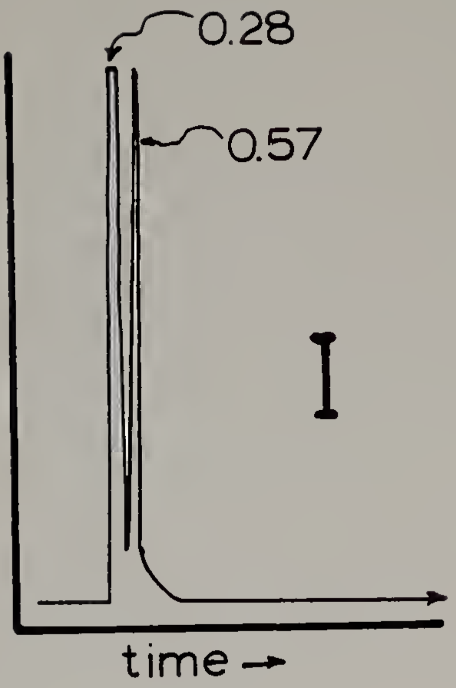
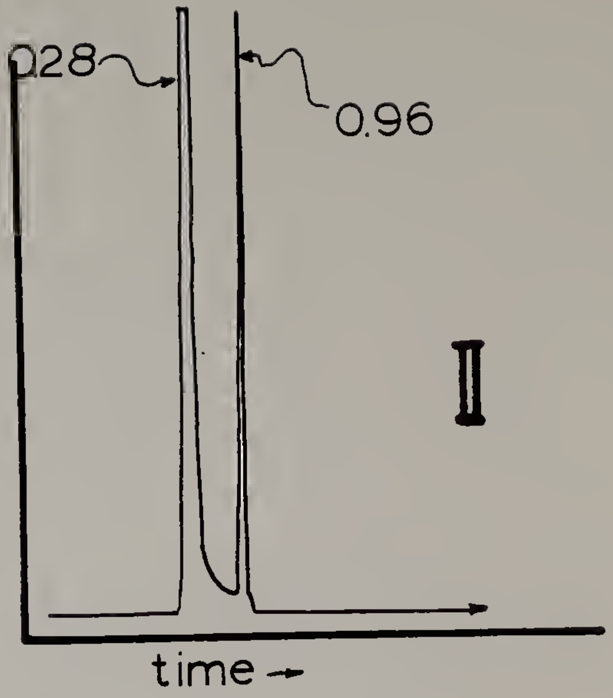

NH2
BSA (2eq.)
THF
TMS
N
H
I
I
1) EtMgBr (2 eq.)
2) ClSi(CH3)3 (4 eq.)
TMS
N
TMS
II
II + s-BuLi
s-Bu
Li
N(TMS)2

Figure 3.2

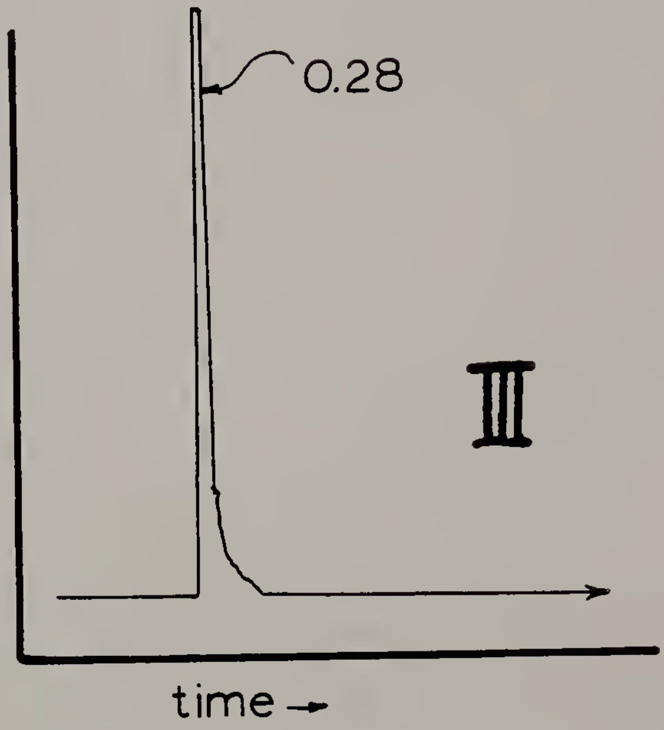
Gas chromatography data from the reactions of p-N,N-bis(trimethylsilyl)aminostyrene with alkyllithiums. Chromatograph I shows two peaks from the solvent and the p-N,N-(trimethylsilyl)aminostyrene at 0.28 and 0.57 minutes respectively. Chromatographs II and III show the results from reactions 10 and 11 respectively from Table 3.1. Only with sec-butyllithium and benzene as the exclusive solvent does one get the desired results as shown in chromatograph II.



I



II



III

Table 3.1

Reaction conditions and results of the reaction of *p*-*N*,*N*-bis(trimethylsilyl)aminostyrene with alkyllithiums. Only with *sec*-butyllithium and totally nonpolar conditions was the desired product formed exclusively.

REACTIONS OF ALKYLLITHIUMS WITH p-N,N-(TRIMETHYLSILYL)AMINOSTYRENE

REACTION	ALKYLLITHIUM	SOLVENT	TEMP	RESULT[i]
1	n-BuLi	benzene	25°C	oligimers
2	n-BuLi	benzene/HMPA[ii]	25°C	oligimers
3	n-BuLi	benzene/THF[iii]	25°C	oligimers
4	n-BuLi	benzene/THF[iii]	-78°C	olig[iv]
5	n-BuLi	benzene/THF[iii]	5°C	olig[iv]
6	n-BuLi	benzene/THF[iii]	25°C	olig[iv]
7	n-BuLi	benzene/THF[v]	25°C	olig[iv]
8	n-BuLi	benzene/THF[vi]	25°C	olig[iv]
9	n-BuLi	benzene/THF[vii]	25°C	olig[iv]
10	s-BuLi	benzene	25°C	DP=1[viii]
11	s-BuLi	benzene/THF[v]	25°C	olig[iv]
12	s-BuLi	benzene	25°C	DP=1[viii]

---

[i] The reported results are based on titration for living end concentration, gas chromatography, and NMR data.

[ii] HMPA was used at 2.5% by volume of total solvent.

[iii] THF was used at 45% by volume of total solvent.

[iv] Although mostly oligimer was formed, the reaction did take on a highly colored appearance indicative of styrl anion generation.

[v] THF was used at 5% by volume of total solvent.

[vi] THF was used at 14% by volume of total solvent.

[vii] THF was used at 33% by volume of total solvent.

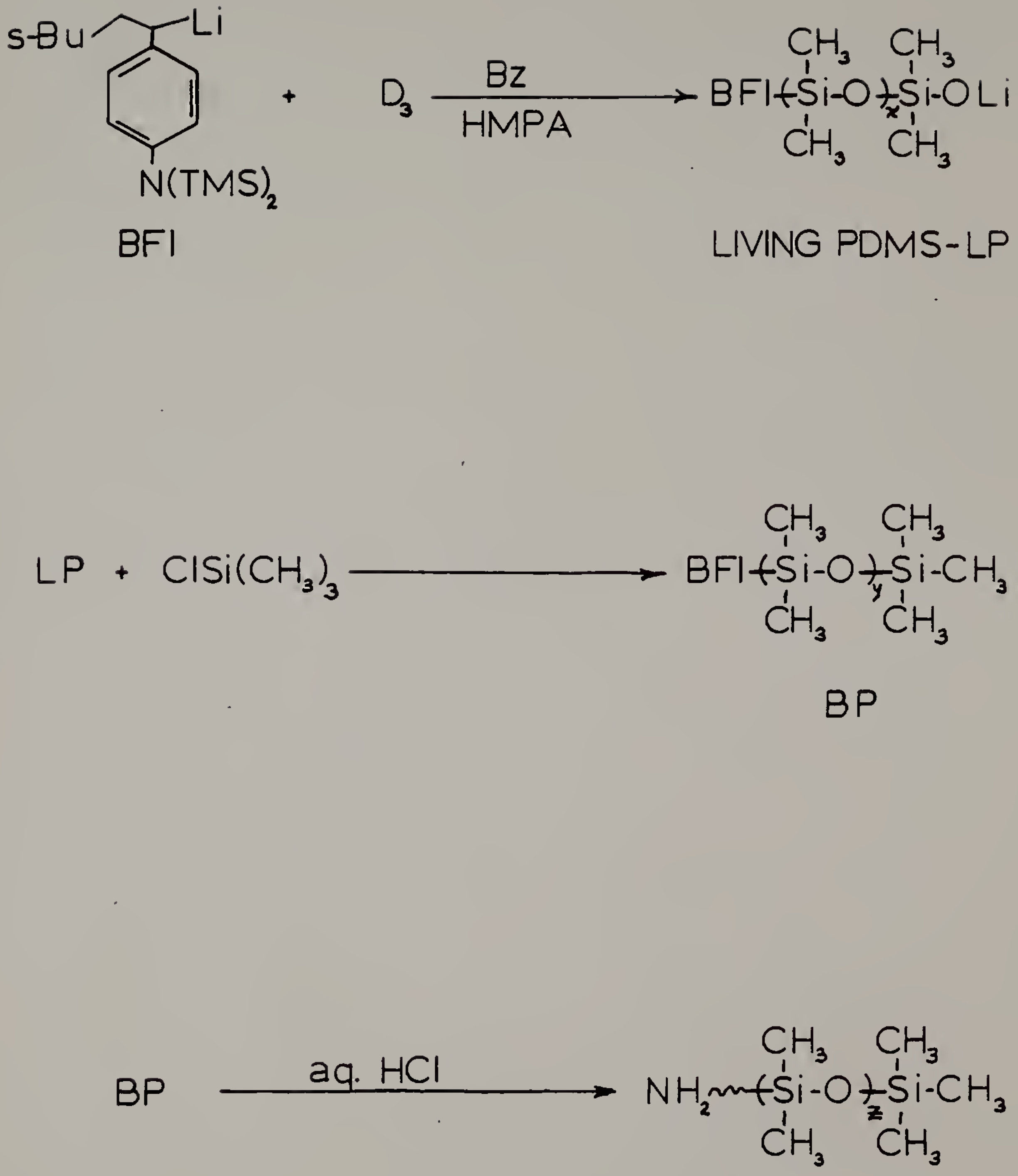
[viii] The desired product was generated.

The literature has reported mixed results in efforts to prepare nonpolar solvent soluble difunctional initiators by using reactions of alkyllithiums with divinyl and diisopropenyl benzenes (28, 29). Remmp (28) has reported the successful generation of a difunctional initiator by the addition of m-diisopropenylbenzene to two equivalents of sec-butyllithium, while Cameron (29) disputes this result. Cameron added the alkyllithium to the diisopropenyl benzenes, which encourages the oligimerization of the diisopropenyl compounds that he found. Cameron suggests that gel permeation chromatography be used in the analysis of any such reactions to insure that oligimerization does not take place.

Figure 3.3 shows the polymerization scheme to form a semi-telechelic amine functional poly(dimethylsiloxane) polymer via "living" anionic polymerization. It has been shown over the last fifteen years that low polydispersity, controlled molecular weight poly(dimethylsiloxane)s can be prepared without cyclic by products using living anionic polymerization techniques (30-32). This can only be accomplished with nonpolar reaction media and only a very slight amount of promoter; HMPA was used in this case although other promoters like THF and DMSO can be used. In our

Figure 3.3

The polymerization and unblocking scheme for the preparation of semi-telechelic poly(dimethylsiloxane) utilizing the new blocked amine functional anionic initiator. The living polymerization is commenced, terminated with chlorotrimethylsilane, and the amine functionality is unblocked to form the desired material.

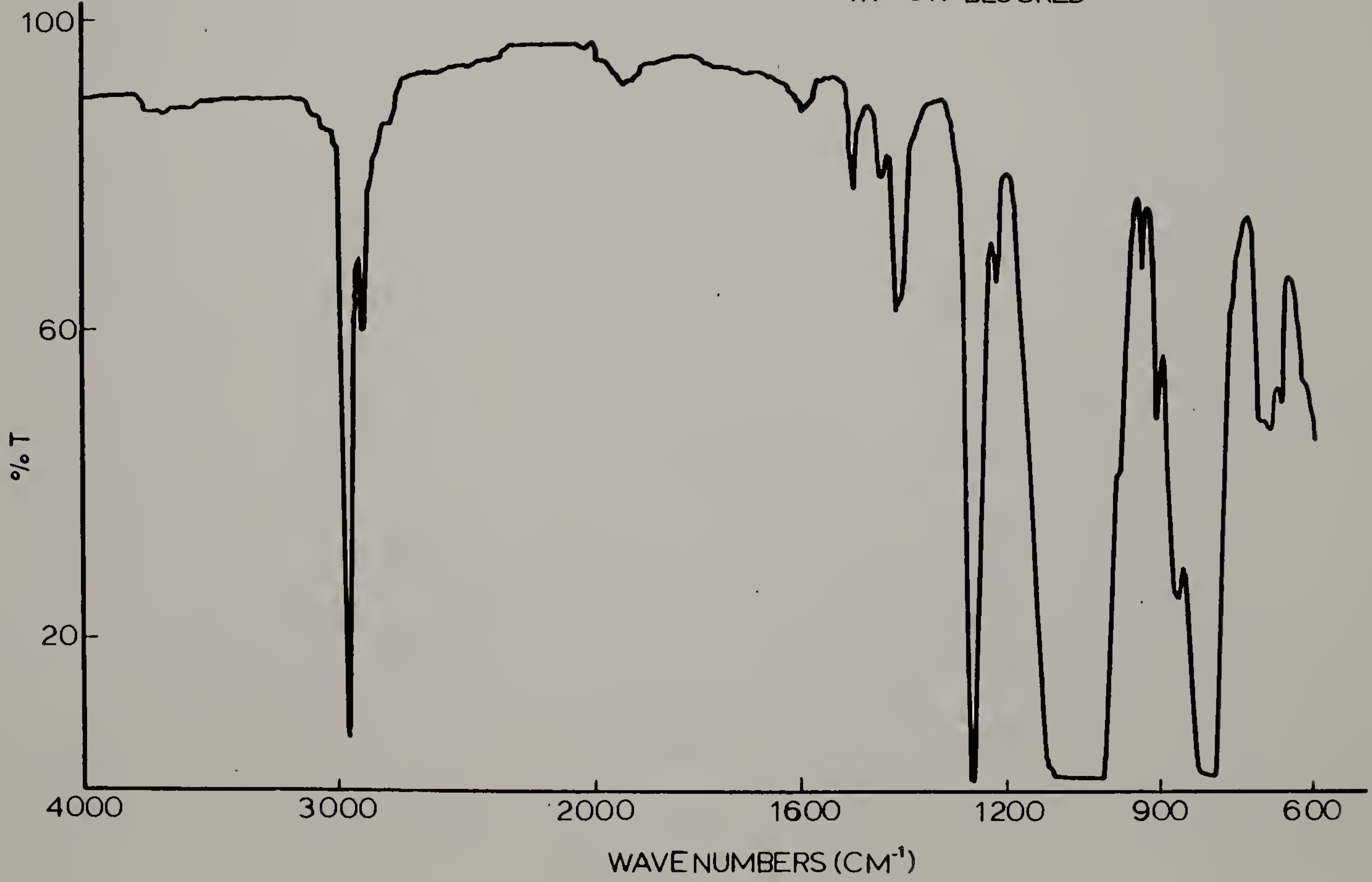

s-Bu
Li
N(TMS)₂
BFI
+
D₃
Bz
HMPA
BFI(Si(CH₃)₂-O)ₓSi(CH₃)₂-OLi
LIVING PDMS-LP
LP + ClSi(CH₃)₃
BFI(Si(CH₃)₂-O)ᵧSi(CH₃)₂-CH₃
BP
BP
aq. HCl
NH₂~(Si(CH₃)₂-O)_z Si(CH₃)₂-CH₃

reaction, the addition of D3 to the initiator solution does not cause the orange/red color of the reaction medium to change. Only upon the addition of HMPA does the initiator color vanish and the polymerization commence. Using this method several polymers of theoretical molecular weights of up to 6000 were prepared with molecular weight distributions of 1.07 to 1.25. Under no circumstances were lower molecular weight oligimers or bimodal distributions encountered as warned by Cameron.

The end-blocked poly(dimethylsiloxane)s can be unblocked easily by treatment with dilute aqueous hydrochloric acid as shown in Figure 3.3. This unblocking reaction is easily followed by observing the change in the infrared spectra as shown in Figures 3.4 and 3.5. In addition to the expected peaks from the siloxane polymer at 2960, 1260, 1000-1100, and 800 cm^{-1}, and the peaks from the phenyl fragment of the initiator at 1500 and 1600 cm^{-1}, one can easily see that in the blocked polymer spectrum no N-H absorption at 3350 and 3450 cm^{-1} can be observed. However, the silicon-nitrogen bond at 931 cm^{-1} can be seen easily. In the unblocked polymer spectrum the 931 cm^{-1} peak totally vanishes while the 3350 and 3450 cm^{-1} peaks indicative of free primary amine appear. Unblocking of the end-

Figure 3.4

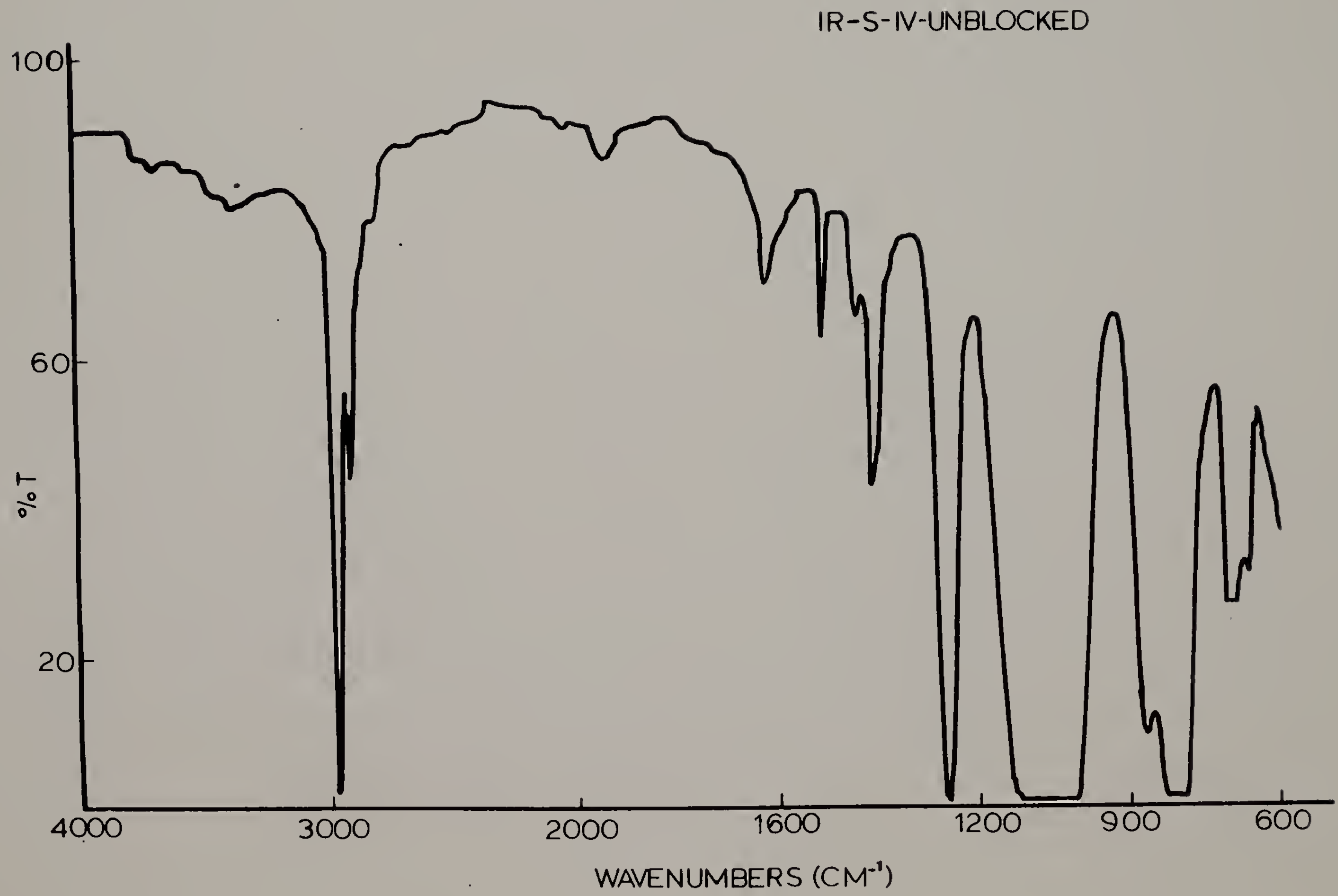
The infrared spectrum of a blocked poly(dimethylsiloxane) film. The typical absorption peaks for the siloxane at 2960, 1260, 1000-1100, and 800 cm^{-1} are present along with the phenyl peaks from the blocked initiator at 1500 and 1600 cm^{-1} . It is important to notice that there are no peaks from the free primary amine and that there is a distinct peak at 931 cm^{-1} indicating the presence of the silicon-nitrogen bond of the blocking group.



IR - S-IV-BLOCKED

Figure 3.5

The infrared spectrum of an unblocked poly(dimethylsiloxane) film. The typical absorption peaks for the siloxane at 2960, 1260, 1000-1100, and 800 cm^{-1} are present along with phenyl peaks from the initiator at 1500 and 1600 cm^{-1} . It is important to notice that the free primary amine peaks at 3350 and 3450 cm^{-1} are distinctly present, while the 931 cm^{-1} peak from the silicon-nitrogen bond of the blocking group is no longer present.


IR-S-IV-UNBLOCKED
100
60
20
%T
4000
3000
2000
1600
1200
900
600
WAVENUMBERS (CM⁻¹)

function of the siloxane polymers does not degrade the polymer as can be seen in Figure 3.6 showing gel permeation chromatography results of the blocked and unblocked polymer.

Table 3.2 shows the results of the synthesis of end -reactive poly(dimethylsiloxane) materials. As can readily be seen, the results show that low polydispersity, controlled molecular weight poly(dimethylsiloxane)s of theoretical functionalities can be prepared by the methods discussed in this chapter. The preparation of telechelic star poly(dimethylsiloxane)s utilizing this method will be discussed in the next chapter.

This work has several significant implications. Due to the favorable solubility characteristics of this new blocked amine functional anionic initiator, the possibility of preparing amine telechelic high 1,4 and high cis-1,4 linear and star type polydienes now seems reasonable. Additionally, it should be possible to prepare hexane soluble blocked hydroxyl functional anionic initiators by reacting silylated p-hydroxylstyrene with alkyllithiums. Furthermore, utilization of this work should assist in the expanding efforts of many groups to prepare increasingly well defined polymeric materials.

Figure 3.6

Gel permeation chromatography traces from a blocked and then unblocked poly(dimethylsiloxane) prepared with the new blocked amine functional anionic initiator. It is clearly shown that no degradation of the parent, blocked polymer is observable. Additionally, the resulting polymers show a unimodal distribution, low polydispersity, and no evidence for the formation of lower molecular weight oligimers.

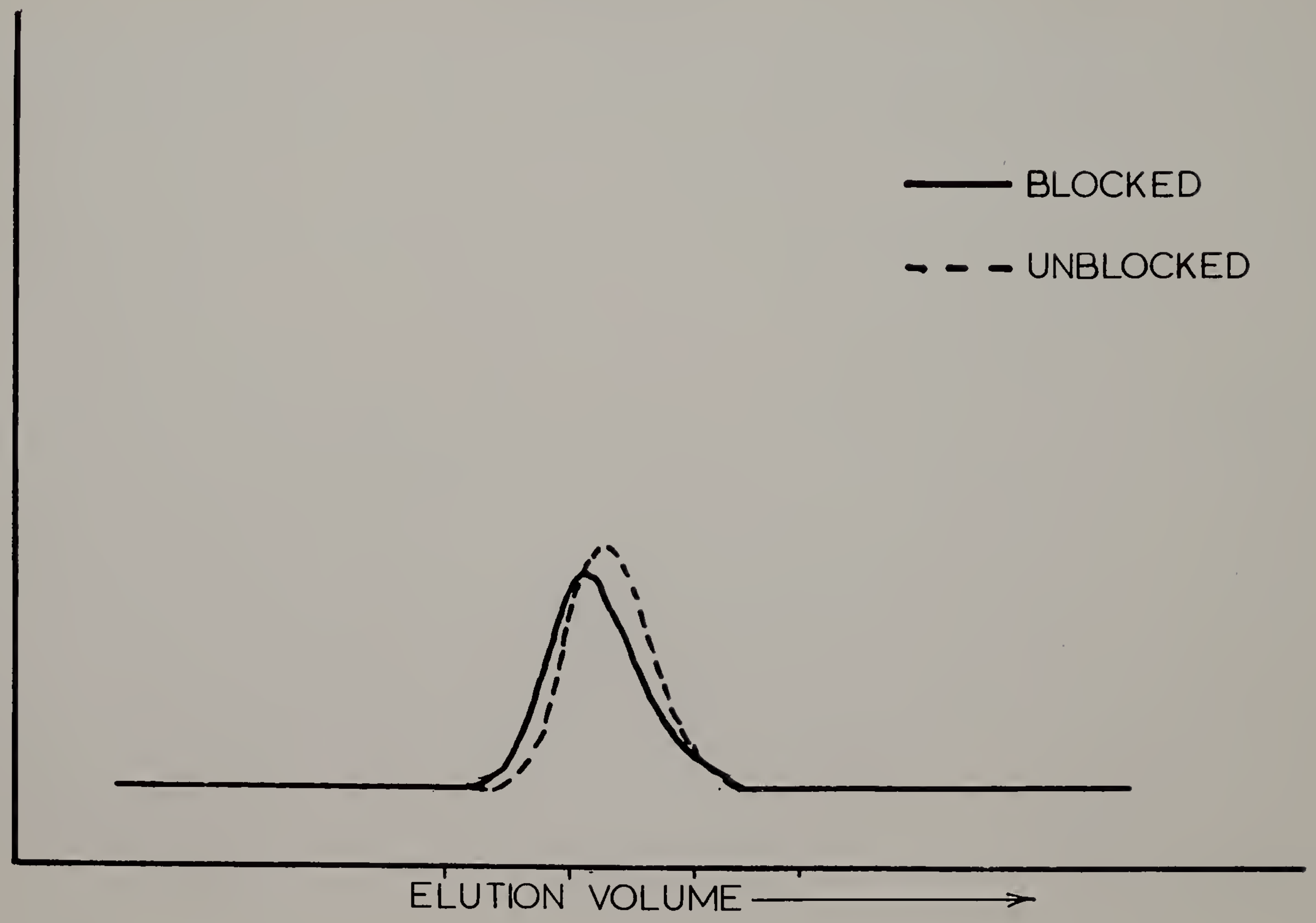

BLOCKED
UNBLOCKED
ELUTION VOLUME

Table 3.2

This table shows the complete results of the polymerization of D3 by the new blocked amine functional anionic initiator. The semi-telechelic and telechelic polymers formed are of low polydispersity, controlled molecular weight, and near theoretical functionalities.

SUMMARY OF TELECHELIC SILOXANES

Polymer	Mn(theo)*	Mn(found)#	Functionality+	Mw/Mn>
II	----	6000	0.97	1.26
III	----	780	0.94	1.14
IV	1500	1600 ± 200	1.9 ± 0.3	1.32

---

* Theoretical Mn based on (Monomer/(Initiator)x(Monomer MW)

#Mn found via vapor phase osmommetry, chloroform @ 37°C.

+Functionality found via infrared spectroscopy of 1600 cm phenyl ring vibration combined with Mn data.

>Mw/Mn based on polystyrene calibrated GPC in THF with no correction for broadening.

REFERENCES

1. S.F. Reed Jr., J. Polym. Sci., A-1, 10, 1087 (1972).

2. S.F. Reed Jr., J. Polym. Sci., A-1, 11(7), 1753 (1973).

3. C.A. Wentz and E.E. Hopper, Ind. Eng. Prd., 6. 209 (1967).

4. R.P. Quirk and P.L. Chang, Polym. Prep., 24(2), 463 (1983).

5. A. Hirao, I. Hittori, T. Sasagawa, K. Yamaguchi, and S. Nakahama, Makromol. Chem., Rapid Commun., 3, 59 (1982).

6. D.N. Schulz, A.F. Halasa, and A.E. Oberster, J. Polym. Sci., Chem. Ed., 12, 153 (1974).

7. D.N. Schulz and A.F. Halasa, J. Polym. Sci., Chem. Ed., 15, 240 (1977).

8. D.N. Schulz, J.C. Sanda, and B.G. Willoughby, ACS Symp. Ser., 166, 427 (1981).

9. G. Broze, R. Jerome, and P. Teyssie, Makromol. Chem., 179, 1383 (1978).

10. P.M. Lefebvre, R. Jerome, and P.H. Teyssie, Macro., 10(4), 871 (1977).

11. W. Konter, B. Bomer, and K.H. Kohle, Makrom. Chem., 182, 2619 (1981).

12. S.F. Reed Jr., J. Polym. Sci., A-1, 9, 2029 (1971).

13. S.F. Reed Jr., J. Polym. Sci., A-1, 8, 2147 (1971).

14. W.H. Stubbs, C.R. Gore, and C.S. Marvel, J. Polym. Sci., A-1, 4, 1898 (1966).

15. R. Santos, J.P. Kennedy, and M. Walters, Poly. Bull., 11, 261 (1984).

16. W. Stix and W. Heitz, Makrom. Chem., 180, 1367 (1979).

17. J.P. Kennedy, Polymer J., 12(9), 609 (1980).

18. J.P. Kennedy, T.P. Liao, S. Guhaniyogi, V.S.C. Chang, *J. Polym. Sci., Chem. Ed.*, *20*, 3229 (1982).

19. V. Percek, S.C. Guhaniyogi, and J.P. Kennedy, *Poly. Bull.*, *9*, 27 (1983).

20. J.P. Kennedy and R.A. Smith, *Poly. Bull.*, *8*, 1523 (1980).

21. M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macro.*, *18(2)*, 123 (1985).

22. D.Y. Sogah and O.W. Webster, *J. Polym. Sci., Letters Ed.*, *21*, 972 (1983).

23. K. Yamaguchi, A. Hirao, K. Suzuki, K. Takenaka, S. Nakamura, and N. Yamazaki, *J. Polym. Sci., Letters Ed.*, *21*, 395 (1983).

24. W.G. Kofron and L.M. Baclowski, *J. Org. Chem.*, *41(10)*, 1879 (1976).

25. J.F. Klebe, H. Finkbeiner, and D.M. White, *J. Am. Chem. Soc.*, *88(14)*, 3390 (1966).

26. S.V. Rogozhin, Y.A. Davidovich, and A.I. Yuntanov, *Synthesis*, 113 (1975).

27. L. Birkofer, *Chem. Ber.*, *93*, 424 (1960).

28. G.G. Cameron and G.M. Buchan, *Polymer*, *20*, 1129 (1979).

29. G. Beinert, P. Lutz, E. Franta, and P.Remmp, *Makromol. Chem.*, *179*, 551 (1977).

30. H.J. Holle and B.R. Lehnen, *Eur. Poly. J.*, *11*, 663 (1975).

31. C.L. Lee and O.K. Johannson, *J. Polym. Sci., Chem. Ed.*, *14*, 729 (1976).

32. C.L. Lee and O.K. Johannson, *J. Polym. Sci., Chem. Ed.*, *14*, 743 (1976).

CHAPTER FOUR

TELECHELIC STAR POLYMERS OF HIGHLY-DEFINED STRUCTURE

I. INTRODUCTION

A considerable body of work exists in the literature describing the preparation of increasingly well-defined polymers. Included in this body have been reports about advances in the synthesis of both end-reactive and star-type polymers. More recent work has combined these two areas of advancement such that ways now exist to prepare highly-defined, end-reactive star polymers (1-10). These telechelic star polymers have been prepared by the initiator-transfer methods pioneered by Kennedy (1-8), via multifunctional delocalized anionic initiators followed by functional termination (9), and by the method of blocked functional anionic initiators with multifunctional termination (10).

The above mentioned preparative methods all have their advantages and disadvantages with regard to their potential to prepare highly-defined telechelic star polymers. The "inifer" method of Kennedy has succeeded in the preparation of quantitatively functional three armed stars via cationic polymerization. However, this method is limited with regard to the types of monomers available for use, does not result in polymers of low polydispersity, and has never been utilized to prepare star polymers of more than three arms. The recent method of multifunctional delocalized anionic initiators can result in the preparation of star polymers of low polydispersity from potentially many monomers, however, this method has never been used to prepare star polymers of more than three arms (10).

The blocked functional anionic initiator method pioneered by Schulz offers the most advantages with the fewest disadvantages. Since this method involves the use of anionic "living" polymerization, the resulting star polymers have controlled molecular weight and low polydispersity (10). Additionally, since these star polymers are prepared by multifunctional termination of living polymer chain ends, the arm number of the resulting star polymers can be readily controlled as shown in the work of Fetters (11). Additionally, this method can potentially employ the many monomers available for use in anionic living polymerization. The disadvantage of this method lies in the lack of solubility of available blocked functional anionic initiators in nonpolar solvents as described in the previous chapters of this thesis. This limited solubility of available blocked functional anionic initiators results in limitations of this method in the preparation of siloxane polymers, and controlled microstructure diene polymers.

Chapter three described the synthesis and use of a new blocked amine functional anionic initiator that was soluble in nonpolar solvents. This new initiator extends the method of Schulz for the preparation of telechelic star polymers of controlled molecular weight, low polydispersity, controlled arm number, and quantitative end-reactivity. This chapter will describe the preparation of highly-defined telechelic star polymers of poly(dimethylsiloxane) using the new initiator described in Chapter Three.

EXPERIMENTAL SECTION

Materials: p-N,N-Bis(trimethylsilyl)aminostyrene was prepared as described in chapter three, distilled from calcium hydride, and stored in a refrigerator under argon prior to use. Chlorotrimethylsilane, dichlorodimethylsilane, and tetrachlorosilane were obtained from Aldrich Chemical Co. and were distilled and titrated prior to use. sec-Butyllithium was received from Aldrich Chemical Co. and titrated prior to use as described in Chapter Three. Three Angstrom Molecular Sieves were prepared as in Chapter Three. Ionol, diphenylacetic acid, and D3 were prepared as described in Chapter Three.

Hexane, cyclohexane, hexamethylphosphoramide(HMPA), and benzene were obtained and purified as described in Chapter Three.

Preparation of Amine End-Functional, Four-Armed, Star Poly(dimethylsiloxane): In a clean, dry, argon flushed round-bottom flask was generated 0.00093 moles of the blocked amine functional anionic initiator as described in Chapter Three. To this was then added 3.91 mL (2.0 grams) of the D3 solution followed by 0.60 mL of HMPA. After 2.5 hours of propagation at room temperature, one mL of the reaction mixture was removed and terminated by chlorotrimethylsilane for use in gel permeation chromatography, and then to the reaction mixture was added 0.23 mL (0.00024 mol) of tetrachlorosilane solution. After allowing termination to proceed for two days at room temperature, an infrared spectrum of the blocked polymer was recorded. The polymer was then unblocked as described in Chapter Three and finally transferred to a separatory funnel where the polymer was neutralized and washed with dilute aqueous sodium hydroxide and distilled water. After insuring that the polymer was fully unblocked by taking another infrared spectrum, the solution was filtered into a round-bottom flask, the solvent was removed by rotary evaporation, and the polymer was then dried under vacuum (0.05 mm Hg) for twenty hours at 65°C. A total of 2.08 grams of oily polymer was prepared (essentially quantitative yield), and the polymer was then characterized by gel permeation chromatography, vapor phase osmommetry, and infrared spectroscopy as described below.

Measurements: Infrared spectroscopy, gel permeation chromatography, vapor phase osmommetry, and appropriate titrations were performed as described in Chapter Three.

RESULTS AND DISCUSSION

Chapter Three of this thesis showed how the new blocked amine functional anionic initiator could be generated and used to prepare telechelic poly(dimethylsiloxane)s of controlled molecular weight, low polydispersity, and theoretical end-reactivities. This chapter extends this work to the preparation of equally well-defined telechelic star-type polymers.

The method of preparation of star polymers via living anionic polymerization followed by multifunctional termination with chlorosilanes has been shown to be an effective one (11-15). This method has been shown to give well-defined polymers of controlled arm number up to eighteen arms (11).

The star polymers prepared in this report were characterized by gel permeation chromatography(GPC), vapor phase osmommetry, and quantitative infrared spectroscopy. Figure 4.1 shows the gel permeation chromatography results of the coupling reactions of the living poly(dimethylsiloxane) polymers with chlorosilanes to prepare "one", "two", and four armed polymeric species. As can be seen, the coupling reaction results in the formation of higher molecular weight polymer cleanly, without broadening of the GPC peaks or any formation of multimodal distributions. An experiment was performed where a non-stoichiometric amount of tetrachlorosilane was added to the living polymer ends, and, as Figure 4.2 shows, the gel permeation chromatography results showed both significant broadening and asymmetry of the resulting GPC peak.

Table 4.1 shows a summary of the results of the star-type polymers prepared in this work. Clearly, the

Figure 4.1

Gel Permeation Chromatography Results for the polymerization of D3 by the new blocked amine functional anionic initiator terminated with three different chlorosilanes. As one terminates with stoichiometric amounts of the mono, di, and tetra chlorosilane, one sees the resulting polymer moving to lower elution volumes. Lower elution volumes indicate higher molecular weight, and the resulting unimodal distributions combined with maintenance of a narrow peak support the conclusion that quantitative coupling has taken place.

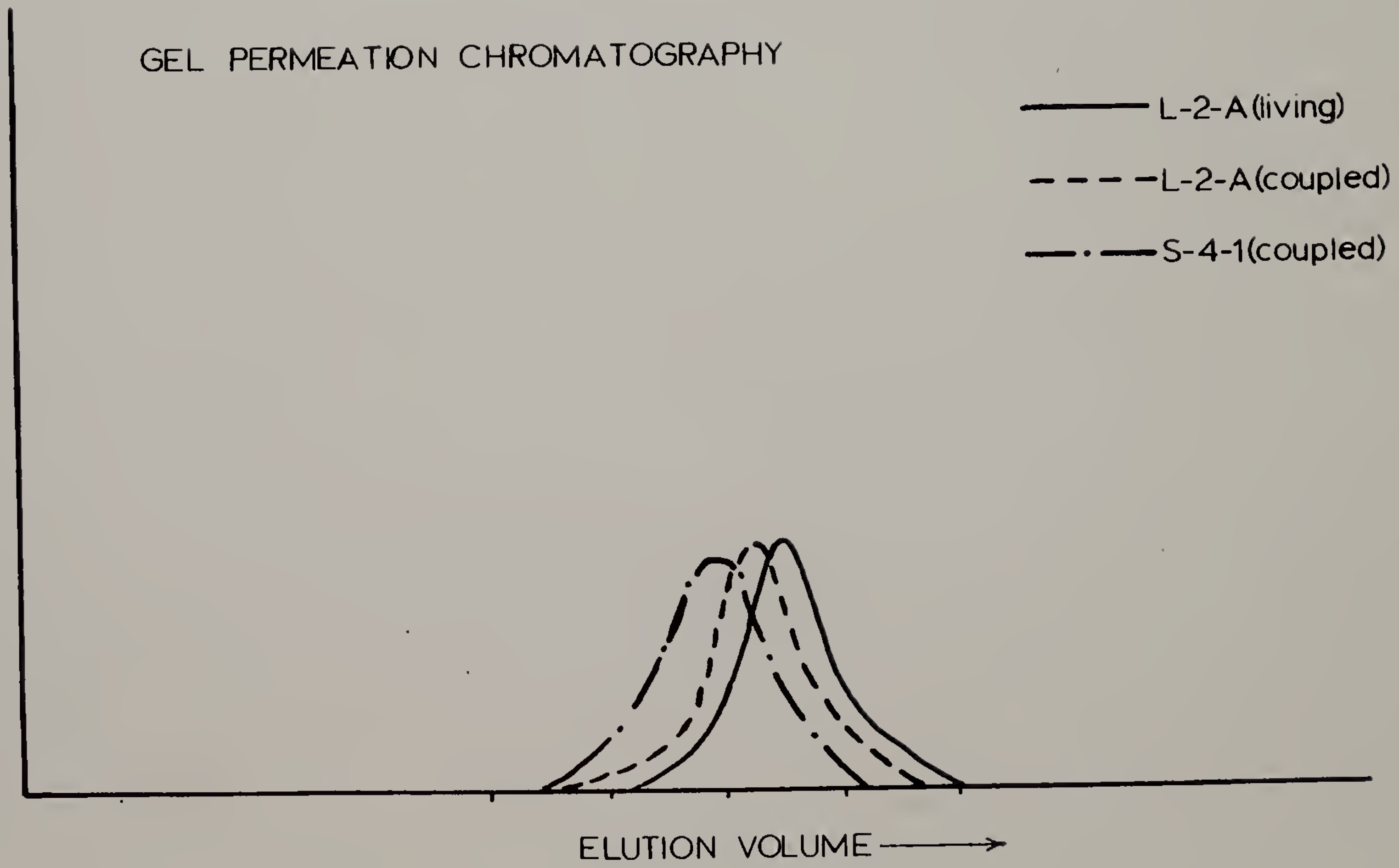

GEL PERMEATION CHROMATOGRAPHY
L-2-A (living)
L-2-A (coupled)
S-4-1 (coupled)
ELUTION VOLUME →

Figure 4.2

Gel permeation chromatography traces of precoupled and improperly coupled (0.8 eq. of tetrachlorosilane) poly(dimethylsiloxane)s. Coupling of the living polymer with a nonstoichiometric amount of the coupling agent results in a broadened and asymmetric GPC peak.

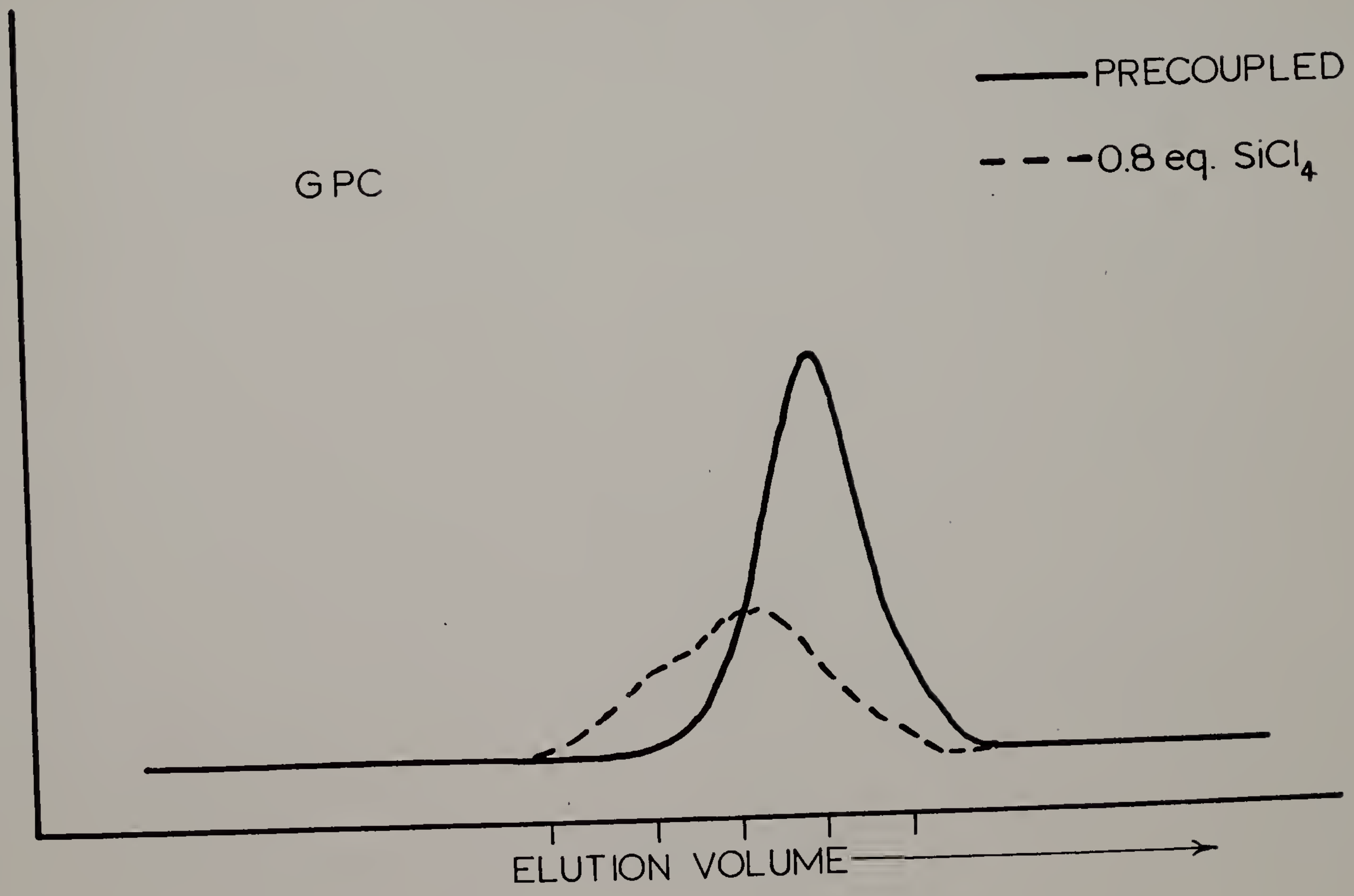

GPC
PRECOUPLED
0.8 eq. SiCl4
ELUTION VOLUME

Table 4.1

A Summary of the telechelic linear and star polymers prepared via initiation with the new functional initiator and termination by chlorosilanes. Clearly, this method does result in the preparation of low polydispersity, controlled molecular weight, and theoretically end-functional poly(dimethylsiloxane)s.

SUMMARY OF TELECHELIC SILOXANE SYNTHESIS

Polymer	Mn (theo)*	Mn (found)#	Functionality+	Mw/Mn>
L-I	1500	1600 ± 200	1.9 ± 0.3	1.32
L-II	1700	2100 ± 100	2.0 ± 0.2	1.13
ST-I	3200	2600 ± 200	4.1 ± 0.3	1.32
ST-II	5100	3900 ± 500	3.7 ± 0.4	1.20
ST-III	9000	6190 ± 1100	3.7 ± 0.5	1.31
ST-IV	16,000	17,000 ± 2000	4.1 ± 0.4	1.32
ST-V	24,000	24,000 ± 2000	4.3 ± 0.5	1.27

---

* Theoretical Mn based on [(Monomer/(Initiator)]x(Monomer MW)

#Mn found via vapor phase osmommetry, chloroform @ 37°C. Polymers ST-IV and ST-V Mn based on GPC extrapolation.

+Functionality determined via infrared spectroscopy of 1600 cm^{-1} phenyl ring vibration combined with Mn data.

>Mw/Mn based on polystyrene calibrated GPC in THF with no correction for broadening.

polymers formed are of low polydispersity, controlled molecular weight, and near theoretical functionality. Although only linear and four-arm star telechelic polymers were prepared, this method of synthesis of telechelic stars is clearly a general one which could achieve star polymers of various arm number as well as utilize other types of monomers.

This work has significant implications for the preparation of highly-defined polymer structures. First, this work represents the first preparation of well-defined star-poly(dimethylsiloxane)s. Second, due to the favorable solubility properties of the new initiator employed, the possibility of preparing well-defined high 1,4 and high 1,4-cis polydienes now exists. Finally, these new polymers open up the possibility of preparing well-defined model networks and novel star-block copolymers for new studies and uses.

REFERENCES

1. J.P. Kennedy, T.P. Liao, S. Guhaniyogi, and V.S.C. Chang, *J. Polym. Sci., Chem. Ed.,* *20*, 3229 (1982).

2. J.P. Kennedy, T.P. Liao, S. Guhaniyogi, and V.S.C. Chang, *J. Polym. Sci., Chem. Ed.*, *20*, 3219 (1982).

3. J.P. Kennedy, S.C. Guhaniyogi, and V. Percek, *Poly. Bull.*, *8*, 563 (1982).

4. J.P. Kennedy, S.C. Guhaniyogi, and V. Percek, *Poly. Bull.*, *8*, 571 (1982).

5. J.P. Kennedy, L.R. Ross, and O. Nuyken, *Poly. Bull.*, *5*, 5 (1981).

6. V. Percek, S.C. Guhaniyogi, and J.P. Kennedy, *Poly. Bull.*, *8*, 25 (1982).

7. V. Percek, S.C. Guhaniyogi, and J.P. kennedy, *Poly. Bull.*, *8*, 319 (1982).

8. R.H. Wondraczek and J.P. Kennedy, *J. Polym. Sci., Chem. Ed.*, *20*, 173 (1982).

9. B. Gordon III, M. Blumenthall, and J.E. Loftus, *Poly. Bull.*, *11*, 349 (1984).

10. D.N. Schulz, J.C. Sanda, and B.G. Willoughby, *ACS Sym. Ser.*, *166*, 427 (1981).

11. N. Hadjichristidis and L.J. Fetters, *Macro.*, *13(1)*, 191 (1980).

12. N. Hadjichristidis, A. Guyot, and L.J. Fetters, *Macro.*, *11(4)*, 668 (1978).

13. N. Hadjichristidis and J.E.L. Roovers, *J. Polym. Sci., Phys. Ed.*, *12(12)*, 2521 (1974).

14. S.M. Hirshfield, U.S. Patent 3,755,283 (May 19, 1971).

15. R.P. Zelinski and C.F. Wofford, *J. Polym. Sci.*, *A-1(3)*, 93 (1965).

CHAPTER FIVE

SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

I. INTRODUCTION

The field of thermotropic liquid crystalline polymers has developed primarily along the paths of main chain (1-6) and side chain polymers (7-12). These polymers have generally been prepared by reacting low molecular weight, end-functional thermotropic mesogens with end-reactive flexible spacers to result in the appropriate topology. A number of variables have been exercised in these studies including type and length of the flexible spacer, axial ratio and regularity of the mesogen, and the type of backbone in side chain polymers.

More recent work has reported the preparation of thermotropic liquid crystalline polymers with mesogenic units in both the side and main chains (13). Other work has reported the termination of oligimeric end-functional polyglycols with aromatic diester and diacid mesogenic units (14). Both of these works have resulted in novel liquid crystalline polymers.

This chapter will report the synthesis of the first star-block thermotropic liquid crystalline polymers. These star-block copolymers, see Figure 5.1, are comprised of a four-arm poly(dimethylsiloxane) star core at the extremities of which are attached amide/ester mesogenic units. Although only four-armed stars have been prepared in this study, the synthesis of the poly(dimethylsiloxane) star core has been shown to be of sufficient generality such that the arm number could be readily varied up to eighteen using known methods (15). In this chapter, the preparation of several four arm star-block materials and one linear-block material of low polydispersity is reported. These materials are also characterized as to their general polymer and liquid crystalline properties.

II. EXPERIMENTAL SECTION

Materials: The telechelic poly(dimethylsiloxane) intermediates were prepared in previously reported work (15). Table 5.1 shows the pertinent properties of these intermediates. p-Hydroxybenzoic acid was obtained from Aldrich Chemical Co., recrystallized twice from methanol, dried exhaustively under vacuum, and stored under argon prior to use. p-Anisoyl chloride was obtained from Aldrich Chemical Co., vacuum distilled, and stored under

Figure 5.1

A schematic of a thermotropic rigid rod star-block copolymer. This new class of liquid crystalline polymers is comprised of a flexible star-core at the extremities of which are attached the thermotropic mesogens.

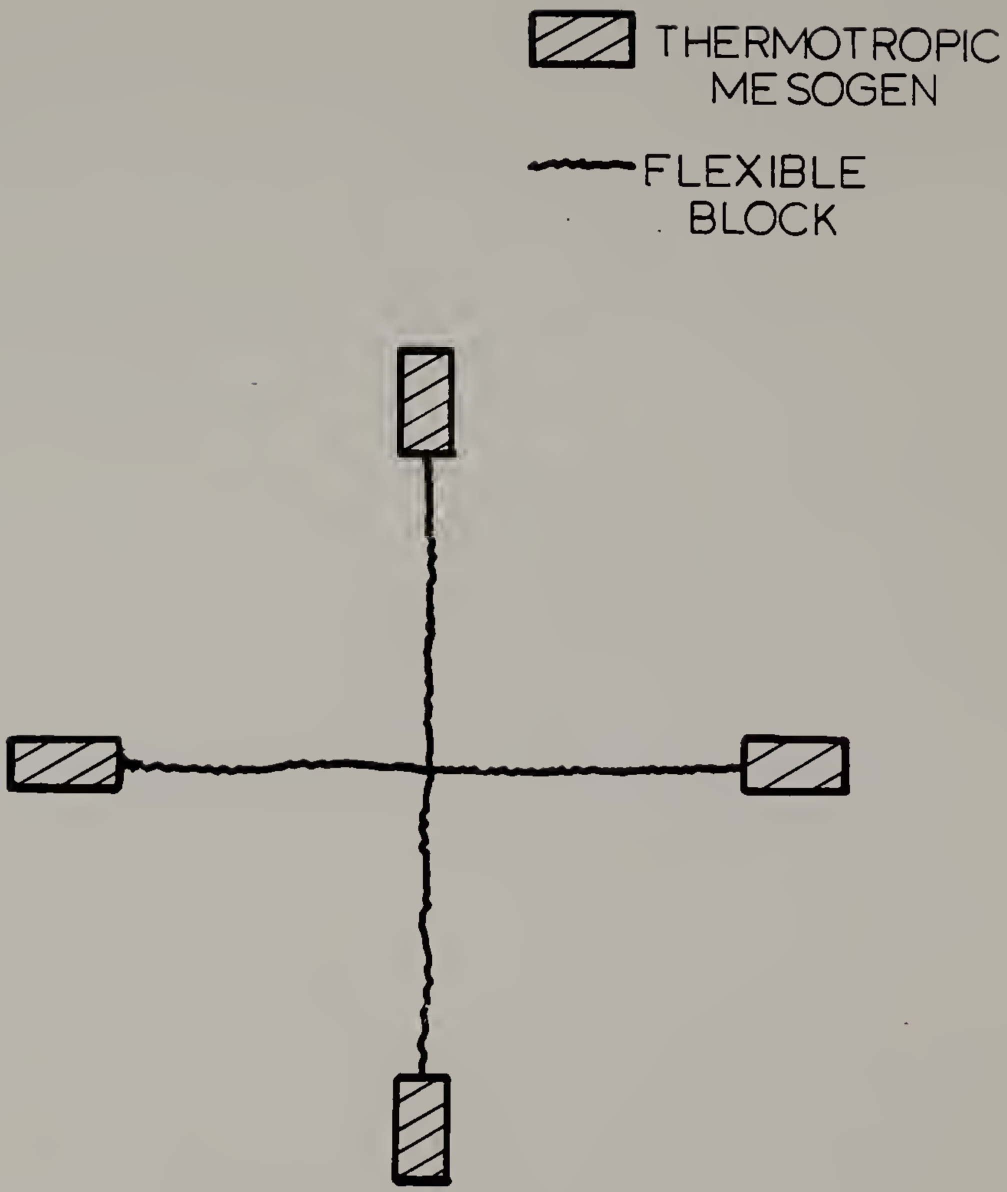

THERMOTROPIC MESOGEN
FLEXIBLE BLOCK

Table 5.1

The pertinent data concerning the previously reported (15) telechelic poly(dimethylsiloxane) intermediates. These well-defined telechelic flexible star-cores were the substrates to which the thermotropic mesogens were attached.

SUMMARY OF TELECHELIC SILOXANES

Polymer	Mn (theo)*	Mn (found)#	Functionality+	Mw/Mn>
L-I	1500	1600 ± 200	1.9 ± 0.3	1.32
ST-I	3200	2600 ± 200	4.1 ± 0.3	1.32
ST-II	5100	3900 ± 500	3.7 ± 0.4	1.20
ST-III	9000	6190 ± 1100	3.7 ± 0.5	1.31
ST-IV	16,000	17,000 ± 2000	4.1 ± 0.4	1.32
ST-V	24,000	24,000 ± 2000	4.3 ± 0.5	1.27

---

* Theoretical Mn based on [(Monomer/(Initiator)]x(Monomer MW).

#Mn found via vapor phase osmommetry, chloroform @ 37°C. Polymers ST-IV and ST-V Mn based on GPC extrapolation.

+Functionality found via infrared spectroscopy of 1600 cm^{-1} phenyl ring vibration combined with Mn data.

>Mw/Mn based on polystyrene calibrated GPC in THF with no correction for broadening.

argon prior to use. 4-Butylaniline was obtained form Aldrich Chemical Co., vacuum distilled into activated three Angstrom molecular sieves, and stored away from light under argon prior to use.

Thionyl chloride was obtained from Aldrich Chemical Co. and used as received. Benzene was purified as previously reported (16). Pyridine was obtained from Fisher Scientific, distilled from calcium hydride into activated 3 Angstrom Molecular Sieves, and stored under argon prior to use. Chloroform (Spectroscopic grade) was obtained from Fisher Scientific and used as received.

Preparation of 4-(4'-methoxybenzoyloxy)benzoic acid: This thermotropic liquid crystalline mesogen was prepared by a method similar to that of Young (17). This compound, once prepared, was not rigorously purified, just recrystallized from a suitable solvent to a m.p. of 221°C as compared to a reported value of 223°C (18). Upon melting this compound entered a nematic liquid crystalline phase which persisted until the onset of degradation.

Preparation of 4-(4'-methoxybenzoyloxy)benzoyl chloride: This compound was prepared from the above described acid using thionyl chloride as reported by Young (17). The acid chloride was prepared and used without further purification.

Preparation of 4-(4'-methoxybenzoyloxy)-4-n-butylbenzamide: Into an argon filled, clean, dry 250 mL round bottom flask containing 0.0041 moles of 4-(4'-methoxybenzoyl)benzoyl chloride was added 35 mL of pyridine and 2 mL (0.0127 mol) of 4-butylaniline. The reaction proceeded under argon for 21 hours at 65°C at which point 80 mL of distilled water was added to yield much white precipitate. The precipitate was gathered by filtration, and the product was then dissolved in 400 mL of boiling acetone, and finally precipitated by addition to distilled water. Collected by filtration, the product was purified by column chromatography, and was finally recrystallized several times until pure to thin layer chromatography. The product acquired at 45% yield was a white microcrystalline solid which melted at 213°C by differential scanning calorimetry (DSC) to form an apparently nematic liquid crystalline phase which persisted until the onset of degradation.

Preparation of p-N-butylphenyl-4'-anisamide: Into an argon filled, clean, dry 250 mL round bottom flask was added 40 mL of pyridine, 5 mL (0.0377 mol) of 4-

butylaniline, and 2 mL (0.0148 mol) of p-anisoyl-chloride. The reaction proceeded with stirring under argon for 18 hours at 75°C at which time the reaction was terminated by the addition of distilled water which resulted in the precipitation of much white product. The product was collected by filtration, washed thoroughly with distilled water to remove the excess unreacted 4-butylaniline, and then recrystallized to yield 4.0 g (96% yield) of white crystalline product. The product was pure to thin layer chromatography (TLC) and had a melting point of 144.0 -144.5°C (19). The yield was considerably higher than that previously reported (19).

Preparation of a four-arm star thermotropic rigid rod star-block copolymer: Into an argon filled, clean, dry 250 mL round bottom flask containing 0.0184 moles of 4-(4'-methoxybenzoyloxy)benzoyl chloride was added 20 mL of pyridine. After heating to 65°C in an oil bath, 14 mL of a benzene solution containing 2.92 grams of ST-V (see Table 5.1) telechelic poly(dimethylsiloxane) was added with vigorous stirring. The reaction proceeded under argon for 45 hours at 65°C at which time 10 mL of distilled water was added to insure total precipitation of the copolymer product. The precipitate was collected by filtration, the product was taken up in 100 mL of boiling tetrahydrofuran (THF), filtered to remove the excess acid, and then condensed by removing the solvent via rotary evaporation. The resulting material was then dissolved into THF and reprecipitated into methanol several times to yield 2.92 grams (93% yield) of a rubbery solid. The copolymer was then characterized by qualitative and quantitative infrared spectroscopy, gel permeation chromatography, differential scanning calorimetry, thermal gravimetric analysis, and optical microscopy. This copolymer was found to melt at 201°C into a liquid crystalline phase which persisted to at least 300°C above which optical microscopy was not performed.

Measurements: Qualitative and quantitative infrared spectroscopy were performed on a Perkin-Elmer 1420 spectrometer. The quantitative infrared spectroscopy was performed in spectroscopic grade chloroform and measured the extent of amidation of the amine telechelic poly(dimethylsiloxane)s based on a Beer's law plot of the model compound p-N-butylphenyl-4'-anisamide.

Gel permeation chromatography was performed on a Waters chromatograph with tetrahydrofuran as the solvent. The gel permeation chromatograph was standardized with polystyrene standards. Optical microscopy was performed by placing a sample mounted between cover slips onto a hot stage between crossed polarizers. Low temperature differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-II equipped with a nitrogen filled hood. Higher temperature DSC was performed on a Perkin-Elmer DSC-IV. Thermal gravimetric analysis was performed on a Perkin-Elmer TGS-II.

III. RESULTS AND DISCUSSION

The thermotropic rigid rod star-block copolymers were prepared from the previously reported, well-defined poly(dimethylsiloxane) telechelic linear and star-polymers shown in Table 5.1. The synthesis, shown in Figure 5.2, simply involved the reaction of the pendant aromatic amines of the telechelic poly(dimethylsiloxane)s with the acid chloride shown. Figures 5.3 and 5.4 show the infrared spectra of a telechelic poly(dimethylsiloxane) and a final copolymer product. The spectrum shown in Figure 5.4 is fully consistent with the complete amidation of the telechelic poly(dimethylsiloxane). Quantitative infrared spectroscopy indicated that the amidation reaction proceeded to at least 95% completion for the reactions of the one linear and five star block copolymers reported in this work. This was expected due to the highly favorable

Figure 5.2

This figure shows the synthesis of the thermotropic rigid rod linear and star-block copolymers discussed in this work. As can be seen, the final copolymers are simply prepared by reaction of the telechelic siloxane intermediates with the acid chloride shown to attach the ester/amide rigid unit to the extremities of the copolymers.

THERMOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

Synthesis

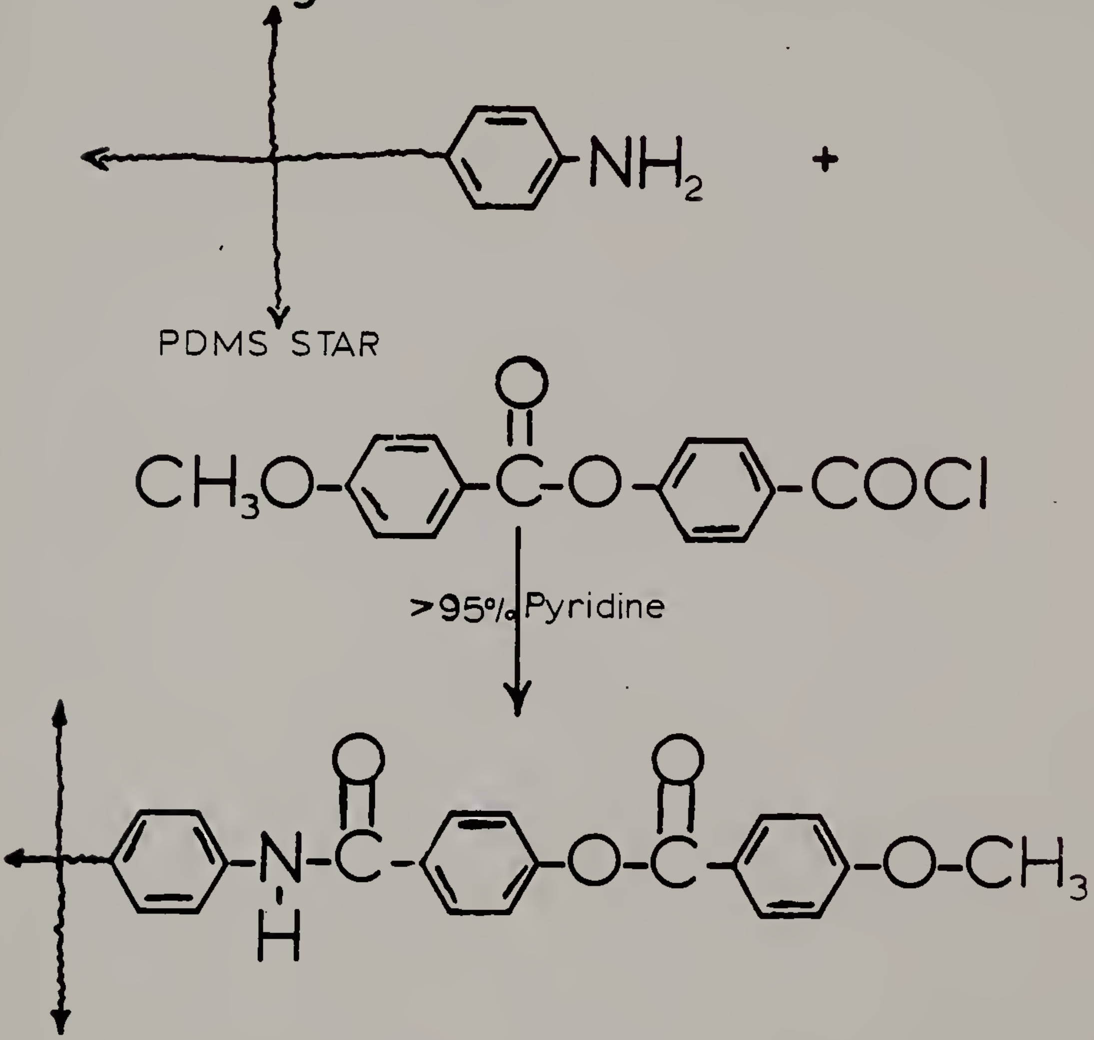


Figure 5.3

The infrared spectrum of a telechelic poly(dimethylsiloxane) intermediate. The bands typical of siloxanes can be seen in addition to the phenyl and primary amine absorptions due to the attached aromatic amine function at the siloxane's extremities.

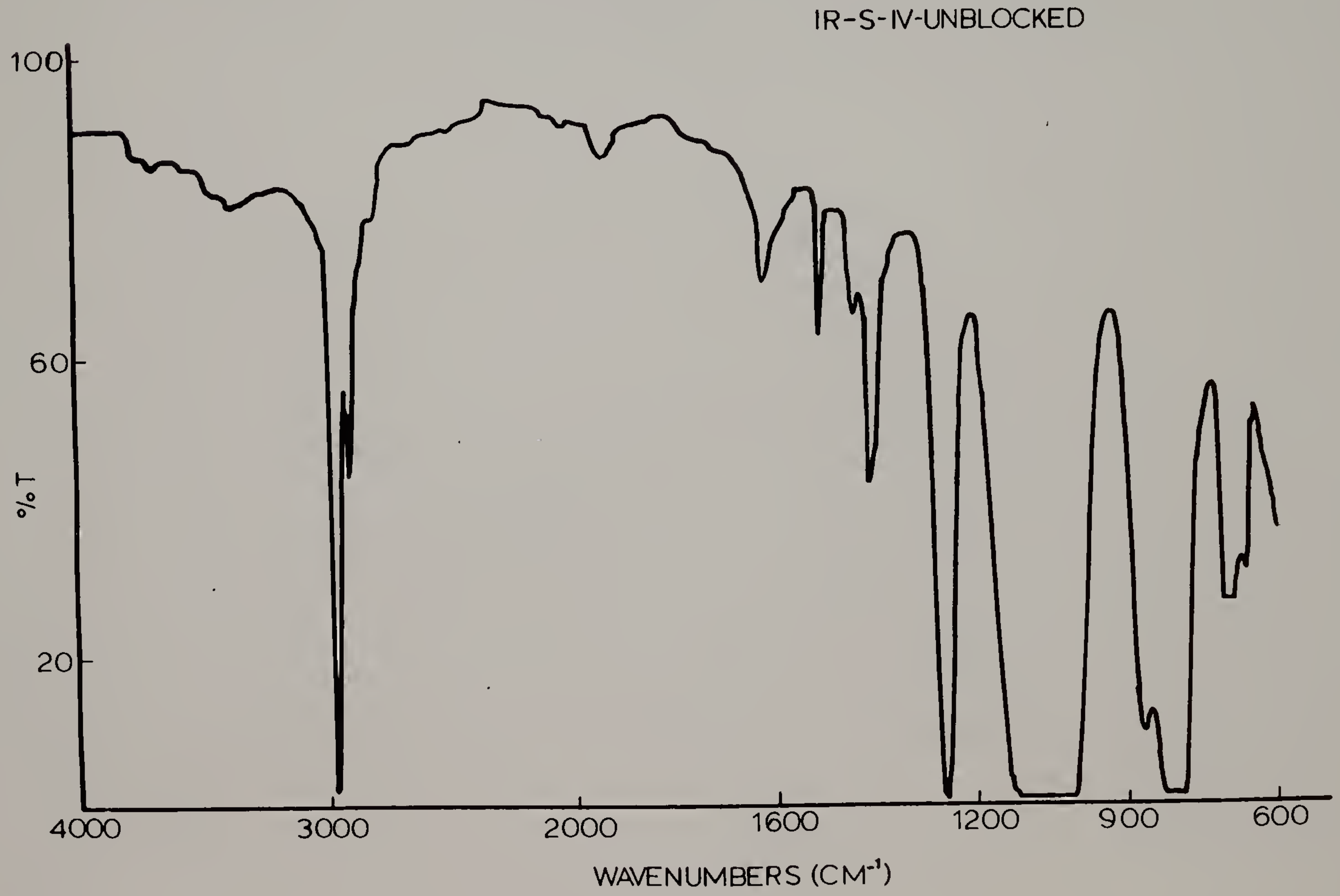
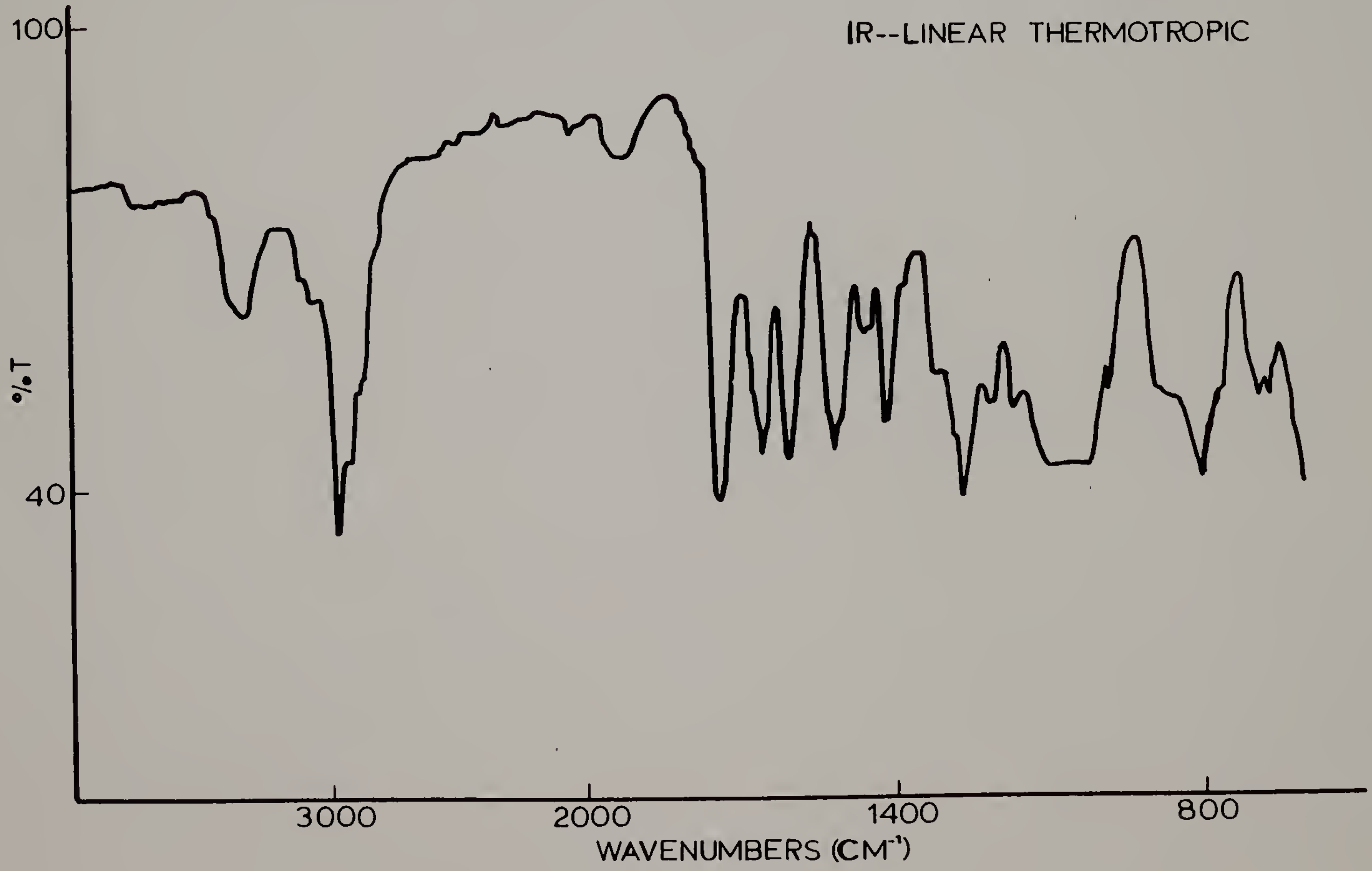

IR-S-IV-UNBLOCKED
100
60
20
%T
4000
3000
2000
1600
1200
900
600
WAVENUMBERS (CM^{-1})

Figure 5.4

The infrared spectrum of L-T-I, a final thermotropic rigid rod block copolymer. Compared to Figure 5.3, one can easily observe the formation of strong secondary amine and strong amide carbonyl absorptions at 3350 and 1650 cm^{-1} respectively. Quantitative infrared spectroscopy based on the amide carbonyl absorption indicated that the extent of amidation of the siloxane supports was virtually quantitative.


IR--LINEAR THERMOTROPIC
100
40
%T
3000
2000
1400
800
WAVENUMBERS (CM⁻¹)

reactivity of the amine with acid chlorides. Quantitative infrared analysis was possible using p-N-butylphenyl-4'-anisamide as the model compound due to the lack of other bands in the amide carbonyl region of the spectra of these materials.

All six of the copolymers prepared in this work were solids ranging from waxy to rubbery materials as the length of the flexible poly(dimethylsiloxane) spacer increased. Gel permeation chromatography, see Figure 5.5, indicated that the preparation of the copolymers did not degrade the siloxane substrates. Similarly, Table 5.2 shows that the low polydispersity of the siloxane substrates was maintained in the final copolymers. Although the attachment of the mesogenic unit could arguably alter the hydrodynamic properties of these copolymers, the gel permeation chromatography data still supports strongly our proposed structure for the final copolymers.

As expected, all of the copolymers showed clear evidence for phase separation of the siloxane segments from the rigid units. Figure 5.6 shows a low temperature DSC scan typical of all of the materials except the two lowest molecular weight star-block copolymers. These two materials, Star-1 and Star-2, failed to show crystallinity of the siloxane units under the conditions

Figure 5.5

Gel permeation chromatographs showing a poly(dimethylsiloxane) intermediate and the block copolymer formed from it. Clearly, the formation of the copolymer did not result in degradation of the siloxane substrate, and the final copolymer maintained the same low polydispersity of the siloxane intermediate.

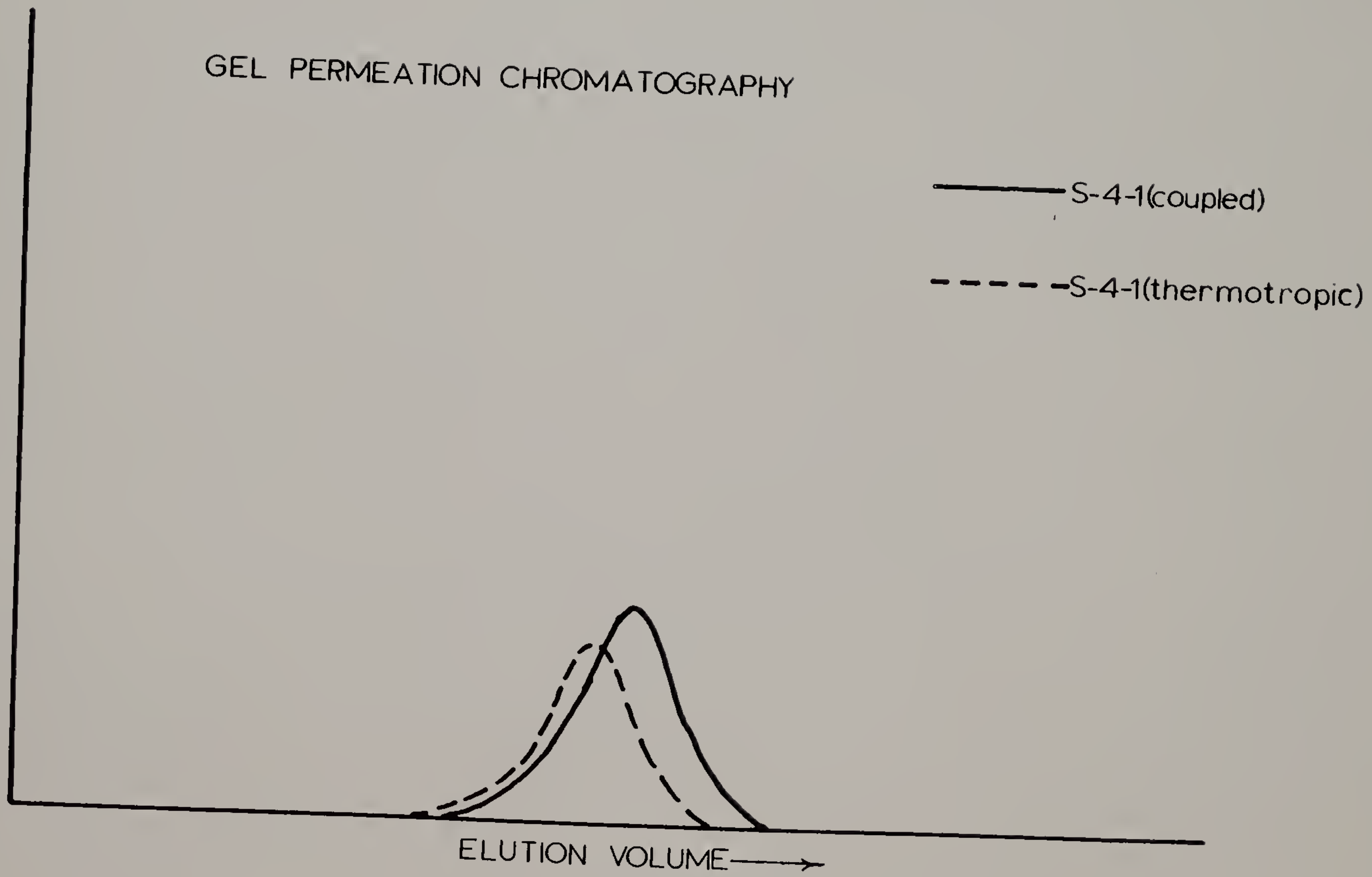

GEL PERMEATION CHROMATOGRAPHY
S-4-1(coupled)
S-4-1(thermotropic)
ELUTION VOLUME

Table 5.2

A summary of the molecular weight distributions of the poly(dimethylsiloxane) intermediates and their corresponding copolymer products. The minor variations in the before and after products could be due to irregular broadening of the gel permeation chromatograph as well as the fact that the Mw/Mn values were calculated based on polystyrene standards. Nonetheless, the values are similar indicating both intermediates and copolymer products to be of low polydispersity.

MOLECULAR WEIGHT DISTRIBUTIONS OF THE POLY(DIMETHYLSILOXANE) INTERMEDIATES AND THEIR CORRESPONDING COPOLYMER PRODUCTS

SAMPLE*	FLEXIBLE ARM LENGTH	Mw/Mn#
Linear-1-S	800	1.32
Linear-1-C		1.18
Star-1-S	650	1.32
Star-1-C		1.24
Star-2-S	975	1.20
Star-2-C		1.25
Star-3-S	1550	1.31
Star-3-C		1.31
Star-4-S	4250	1.32
Star-4-C		1.15
Star-5-S	6000	1.27
Star-5-C		1.40

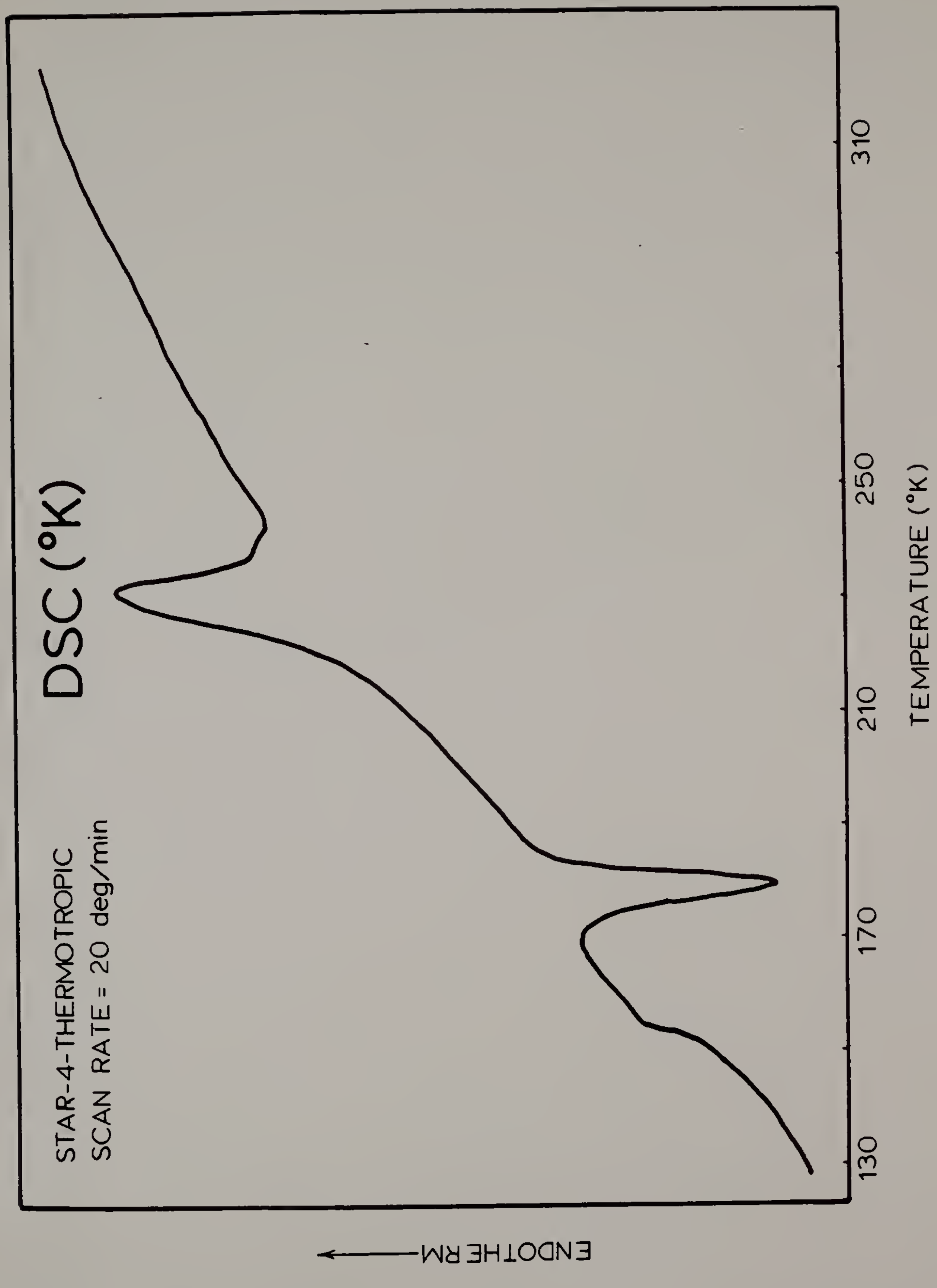
---

* The S and C suffixes on the sample designations stand for the telechelic siloxane and final copolymer respectively.

The molecular weight distributions were found through gel permeation chromatography in tetrahydrofuran based on polystyrene standards. The calculated figures were not corrected for broadening, and in no cases were other than unimodal distributions found.

Figure 5.6

A low temperature DSC thermogram of a block copolymer product. A low temperature glass transition typical of siloxanes is clearly visible along with cold crystallization and melting of the siloxane segment of the copolymer.


DSC (°K)
STAR-4-THERMOTROPIC
SCAN RATE = 20 deg/min
130
170
210
250
310
TEMPERATURE (°K)
ENDOTHERM

of the experiment, however, all six of the copolymers did show a low temperature glass transition typical for poly(dimethylsiloxane)s as can be seen in Table 5.3. Also included in Table 5.3 are the glass transition temperatures of two of the poly(dimethylsiloxane) telechelic stars. The similarity of the glass transition temperatures of the siloxane segments of the copolymers observed under identical experimental conditions to those of the telechelic siloxanes indicates a high degree of phase separation of the siloxane blocks in the final copolymer products.

As mentioned above, all copolymers, with the exception of the two lowest molecular weight star shaped materials, showed cold crystallization and melting of their siloxane segments. The occurrence of crystallintity of the siloxane segment in the low molecular weight linear block copolymer, suggests that the star topology inhibits crystallinity when the flexible arms are too short. Figure 5.7 shows a graph of the enthalpy of melting of the siloxane segment of the star-block copolymers versus the siloxane arm length normalized for the amount of siloxane in the copolymers. Clearly, as tabulated in Table 5.4, as the siloxane arm length increases, the extent to which crystallinity of the siloxane segment occurs likewise increases. Further,

Table 5.3

The glass transition temperatures of the siloxane segments of the product copolymers. Comparing the glass transition temperatures of the copolymers to the glass transition temperatures of the two telechelic siloxanes indicates that the the siloxane segment of the copolymers is distinctly phase separated from the rigid segment.

GLASS TRANSITION TEMPERATURES OF SILOXANE SEGMENT OF COPOLYMERS

POLYMER	Mn/arm	Tg (°C)
L-T-I	800	-118.5
ST-T-I	650	-117.4
ST-T-II	975	-120.7
ST-T-III	1550	-119.5
ST-T-IV	4250	-119.6
ST-T-V	6000	-120.5
ST-I*	650	-115.2
ST-IV*	4250	-119.3

---

* Signifies that these polymer samples are unreacted telechelic siloxane amines, not copolymers.

Figure 5.7

A graph of the enthalpy of melting of the siloxane segment of the star-block copolymers versus the siloxane arm lengths normalized for the siloxane content. As the arm length increases, the ability of the siloxane segment to crystallize under the identical conditions of this DSC experiment increases.

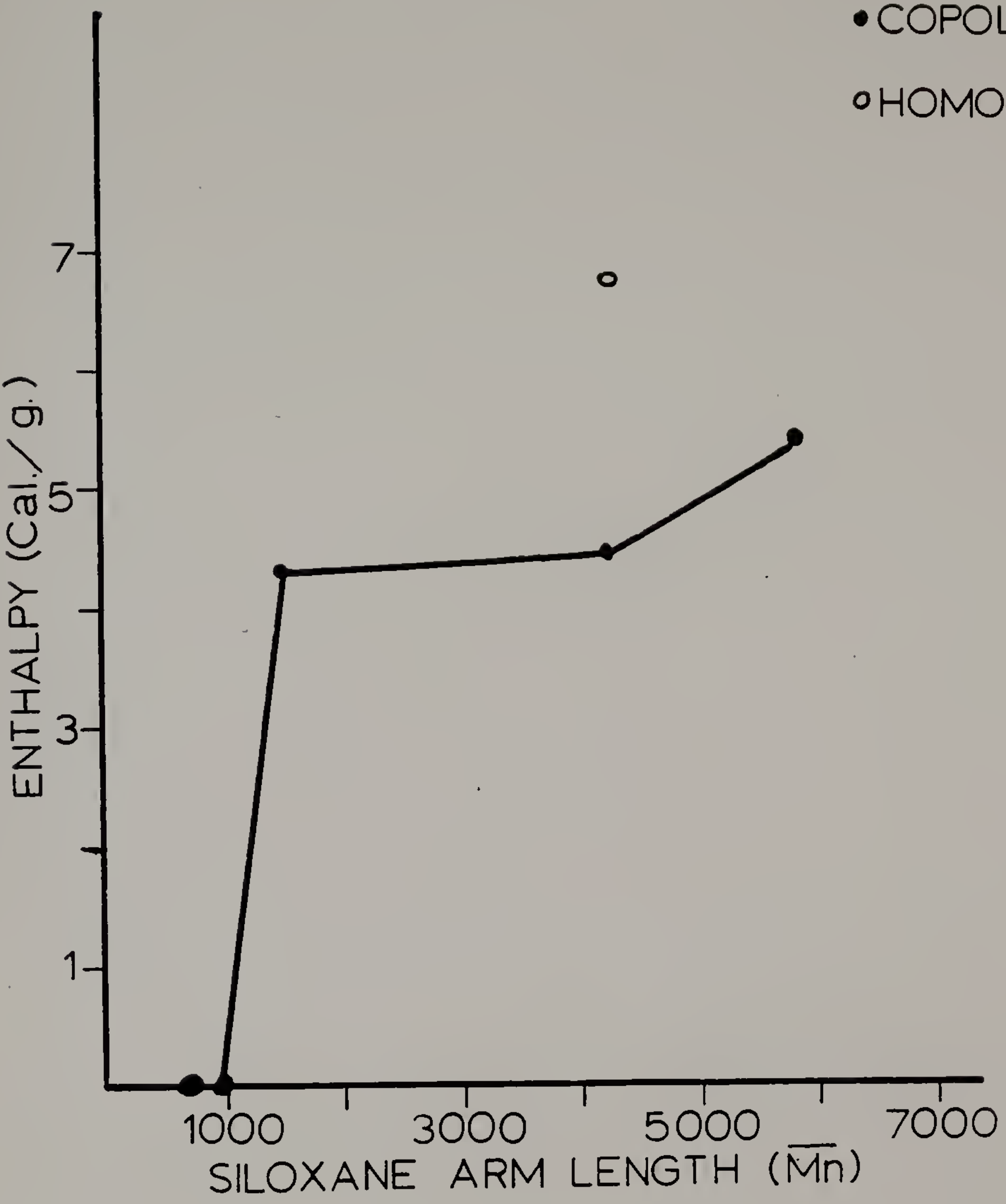

● COPOLYMERS
○ HOMO-PDMS
ENTHALPY (Cal./g.)
7
5
3
1
1000
3000
5000
7000
SILOXANE ARM LENGTH ($\overline{Mn}$)

Table 5.4

The melting temperatures and enthalpies of melting of the siloxane segment of the block copolymers. With increasing arm length, the ability of the siloxane segments to crystallize increases under the identical conditions of this DSC experiment.

MELTING TEMPERATURES AND ENTHALPIES OF MELTING OF THE SILOXANE SEGMENT OF THE THERMOTROPIC BLOCK COPOLYMERS

Polymer	Mn/arm	Tmax (°C)*	Enthalpy (cal/g)
L-T-I	800	-39.5	0.55
ST-T-I	650	none	----
ST-T-II	975	none	----
ST-T-III	1550	-47.1	3.53
ST-T-IV	4250	-42.1	3.93
ST-T-V	6000	-37.9	5.14
ST-I#	650	none	----
ST-IV#	4250	-38.3	6.67

---

* All runs performed on a Perkin-Elmer DSC-II at a heating rate of 20°C/min on samples quenched to -150°C from 50°C at a cooling rate of 320°C/min. Tmax is the maximum temperature of the peak of the melting endotherm.

These polymers are telechelic amine siloxanes; they are not thermotropic copolymers.

as shown in Figure 5.8, the temperature at the maximum of the melting endotherm also mirrors the trend of siloxane arm length in the star-block copolymers. A similar trend will be shown later for the melting of the rigid units in the star-block copolymers.

Prior to doing higher temperature DSC, scanning thermal gravimetric analysis (TGA) was performed to insure that high temperature endotherms were not the result of degradation. Table 5.5 gives the results of the TGA analysis of the six copolymers as well as two of the telechelic poly(dimethylsiloxane)s. As expected, all of these materials showed good resistance to thermal degradation. It also appears that the thermal stability of the copolymers increases with increased length of the poly(dimethylsiloxane) flexible arms.

The liquid crystallinity of the copolymers was explored by DSC and optical microscopy. Prior to preparing the copolymers, a suitable model compound for the rigid segment had to be prepared so that the final copolymer would qualify as a thermotropic rigid rod star-block copolymer. The model compound, 4-(4'-methoxybenzoyloxy)-4-n-butylbenzamide, was prepared to duplicate the ester/amide rigid unit that would be at the extremities of the copolymer chains. The model ester/amide was shown by optical mixing studies to go

Figure 5.8

A graph of the temperature of the maximum of the melting endotherms versus the flexible arm lengths for the siloxane segment of the star-block copolymers. As the arm lengths increase, the temperature of the maximum of the melting endotherms likewise increase.

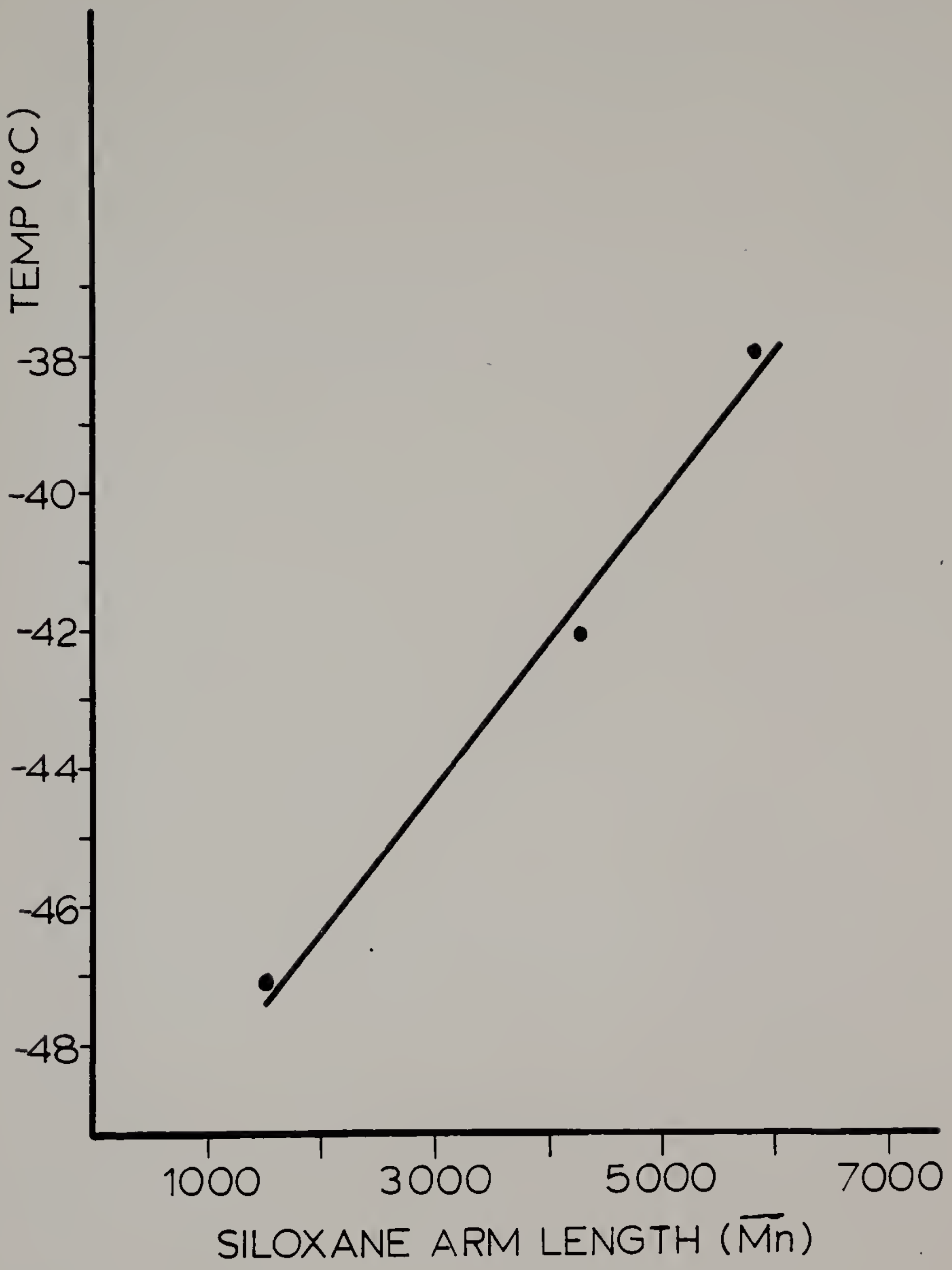

TEMP (°C)
-38
-40
-42
-44
-46
-48
1000
3000
5000
7000
SILOXANE ARM LENGTH ($\overline{Mn}$)

Table 5.5

Thermal gravimetric analysis of the block copolymers. The expected thermal stablility of these mostly siloxane copolymers was achieved.

THERMAL GRAVIMETRIC ANALYSIS OF THE THERMOTROPIC BLOCK COPOLYMERS

Polymer>	5% wt. loss(°C)	Max. Degrad.+(°C)
#ST-I-oil	343	455
#ST-IV-oil	421	462
~L-I	350	433
~ST-I	318	414
ST-T-II	451	456
ST-T-III	482	486
ST-T-IV	489	510
ST-T-V	477	505

---

* All runs performed on a Perkin-Elmer TGS-2 at a heating rate of 20°C/min in a Helium atmosphere.

\+ Max. Degrad. is that temperature at which maximum degradation is observed from the derivative of the weight loss curve.

These polymers are telechelic siloxanes, not thermotropic copolymers.

~ Performed at 10°C/min.

> The S and L designation for the copolymer samples indicates a star and linear shape respectively.

into a nematic liquid crystalline phase upon heating above its 213°C melting point. Figure 5.9 shows a photomicrograph of the mesophase of this ester/amide heated between cross polars; the mesophase persisted until degradation.

Figure 5.10 shows a sample DSC scan and Table 5.6 tabulates the results of the high temperature DSC studies of the six copolymers. A transition closely resembling a glass transition was apparent in all six of the copolymers prior to their melting endotherms. DSC experiments indicated that this apparent glass transition persisted on successive heatings as well as on successive heatings following quick coolings from the melt. However, there remains some question as to whether this change in slope is truly a glass transition. Further study will be necessary to establish this point definitively.

Figure 5.11 shows a graph of the temperature of the maximum of the melting endotherm versus the poly(dimethylsiloxane) arm length for the melting of the rigid unit of the star-block copolymers. Clearly, as the arm length of the siloxane increases, the melting temperature of the mesogenic unit asymptotically approaches that of the ester/amide model compound. As do the data on the melting of the siloxane units of the

Figure 5.9

A photomicrograph of the nematic mesophase between crossed polarizers of the model compound, 4-(4'-methoxybenzoyloxy)-4-_n_-butylbenzamide. The liquid crystalline phase persists to the onset of degradation.

MODEL COMPOUND at 220°C

Figure 5.10

A DSC thermogram of a thermotropic block copolymer. Note the very low enthalpy of the melting transition for this copolymer. Although not prominent on this scan, all of the copolymers do show an apparent glass transition below their melting endotherms.

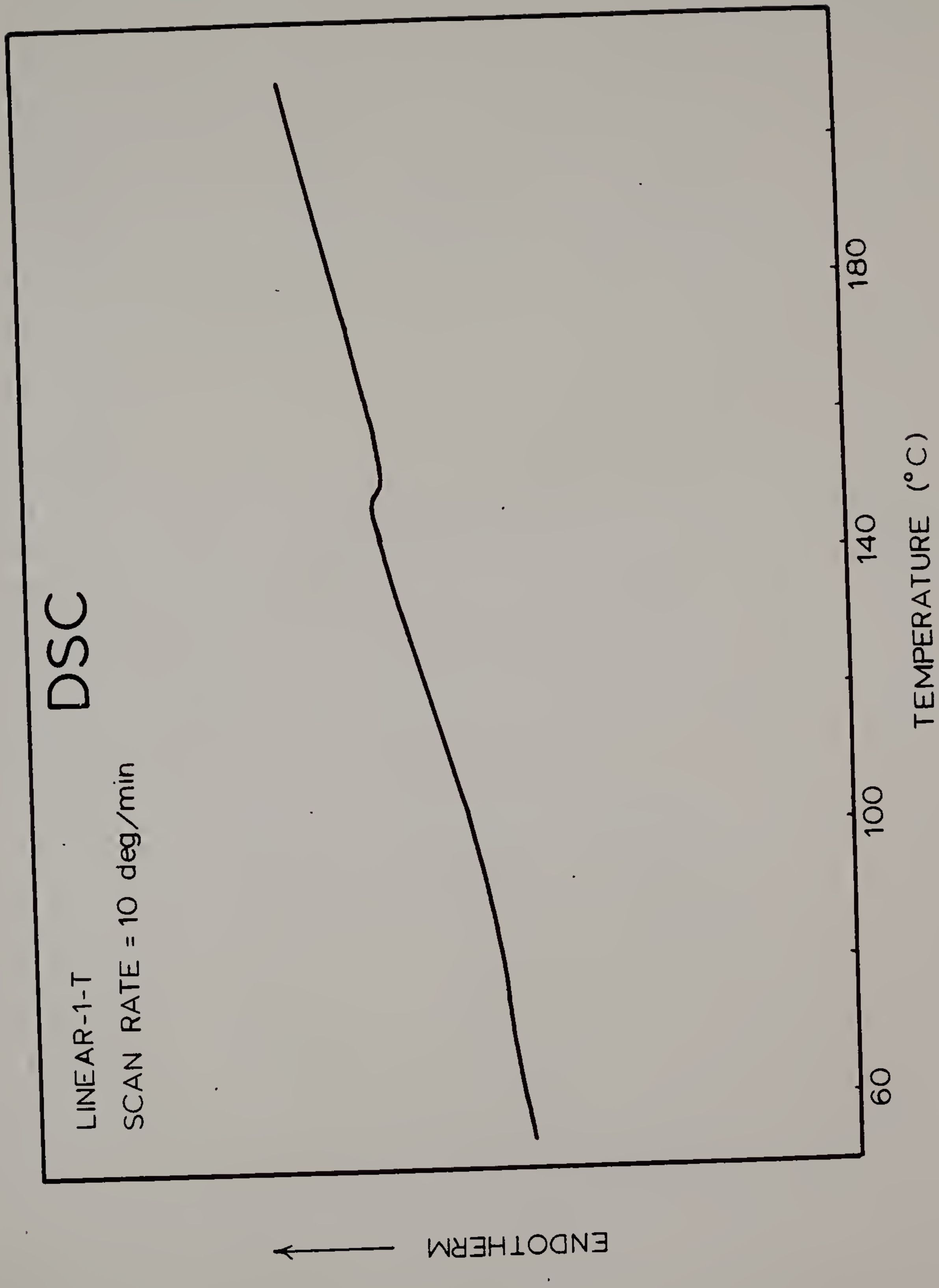

DSC
LINEAR-1-T
SCAN RATE = 10 deg/min
60
100
140
180
TEMPERATURE (°C)
ENDOTHERM

Table 5.6

High temperature DSC results from the studies of the block copolymers in this work. All of these copolymers exhibited a wide liquid crystalline mesophase above their respective melting points. The enthalpies of melting reported in this table are on a per gram polymer basis. These low enthalpy values contain considerable error, and should be viewed only in a very relative sense.

GLASS TRANSITION TEMPERATURES, MAXIMUM MELTING TEMPERATURES, AND ENTHALPY OF MELTING TRANSITIONS OF RIGID SEGMENT OF COPOLYMERS#

Polymers	Mn/arm	%Cryst*	Tg	Tmax	Enthalpy<
L-T-I	800	33	77.5	143.5	1.00
ST-T-I	650	38	68.3	123.9	0.52
ST-T-II	975	29	54.1	166.7>	0.85>
ST-T-III	1550	21	91.0>	178.6>	0.23>
ST-T-IV	4250	9	88.9>	200.0>	0.05>
ST-T-V	6000	6	82.0>	201.0>	0.06>

#Measurements made at a heating rate of 10°C/min after a first heating to 210°C at 20°C/min followed by a 20°C/min cooling to 50°C.

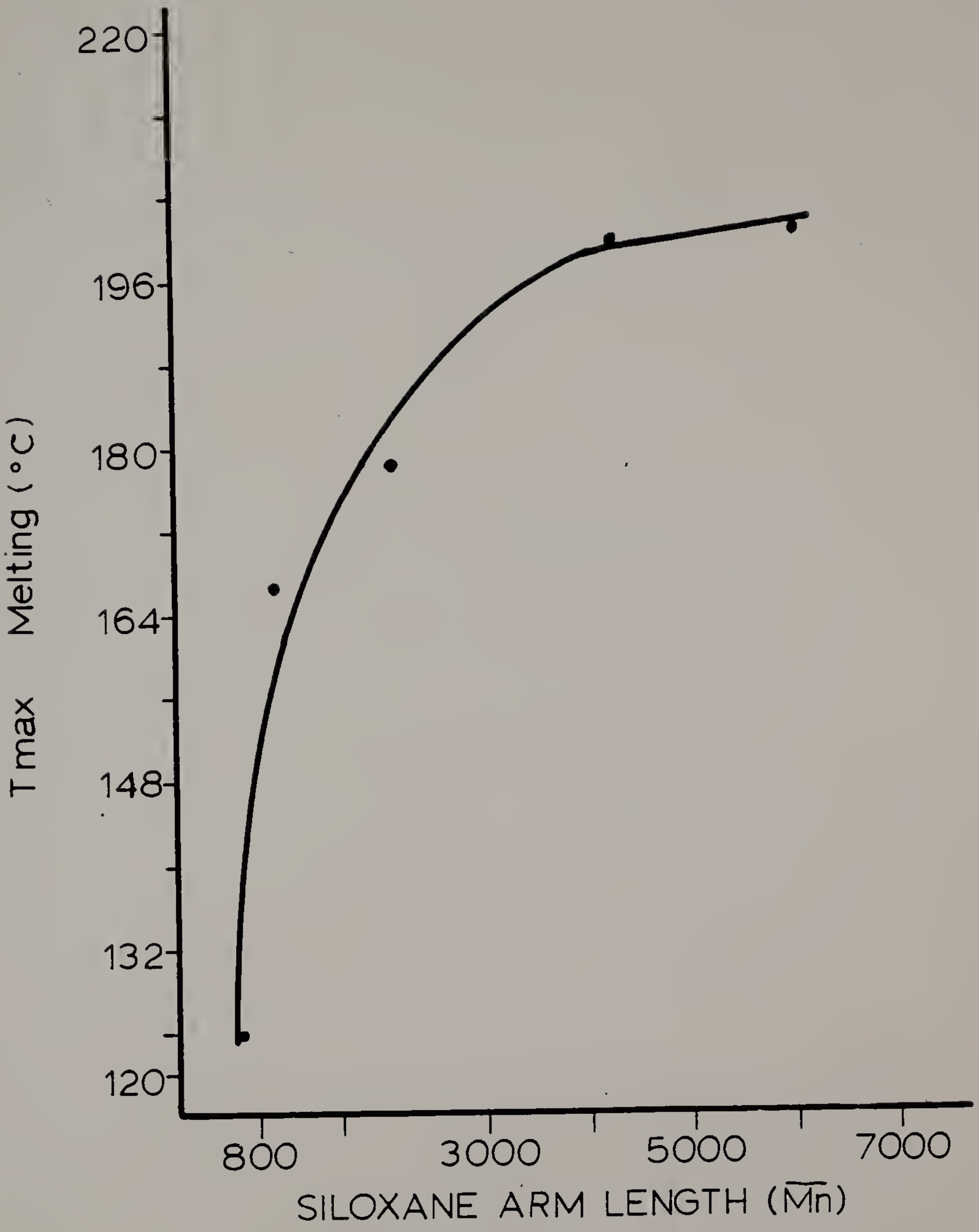
* This value represents the fraction by weight of rigid, crystallizable segment in the copolymers

< All enthalpy of melting values in cal/gram

> These values are reported for a first heating at 20 °C/min.

Figure 5.11

A graph of the temperature of the maximum of the melting endotherm versus the flexible arm length for the rigid, mesogenic segment of the star-block copolymers. With increasing length of the flexible arm, the temperature of melting asymptotically approaches that of the ester/amide model compound.


220
196
180
164
148
132
120
Tmax Melting (°C)
800
3000
5000
7000
SILOXANE ARM LENGTH ($\overline{Mn}$)

star-block copolymers, these data also indicates a high degree of phase separation, and also suggests a greater degree of perfection of the crystalline phase of the mesogenic unit with increasing arm length of the flexible siloxane. However, as can be seen both in Figure 5.10 and Table 5.6, the melting enthalpies for the mesogenic segment of the copolymers were extremely low. These small enthalpies of melting for the rigid segments are due in part to the low amount of rigid segment present in these copolymers. Additionally, these low melting enthalpies could be due to other factors such as the degree of order in the liquid crystalline mesophase which was observed by optical microscopy and is discussed in the next paragraph.

Hot stage optical microscopy between crossed polarizers clearly showed that all six of the copolymers showed a liquid crystalline phase above their respective melting temperatures. Figure 5.12 shows photomicrographs of the liquid crystalline phases of the linear and lowest molecular weight star-block copolymers. All of the copolymers showed an initial homeotropic phase which in the case of the linear and lowest molecular weight star-block copolymers gave way to the stable, nonhomeotropic mesophases shown in Figure 5.12. The mesophases of all of the copolymers persisted to at least 300°C, at which

Figure 5.12

Photomicrographs of the stable nonhomeotropic liquid crystalline mesophases between crossed polarizers of the linear and lowest molecular weight star- block copolymers. These mesophases persist to at least 300°C, at which point the optical microscopy study was terminated.

L-T-I @175°C

ST-T-I @200°C

point optical microscopy was terminated.

The breadth of these mesophases are similar to the wide mesophases reported for some side chain thermotropic liquid crystalline polymers with siloxane backbones (12, 20). Particularly the side chain systems prepared by Jones (21) showed mesophases persisting above 300°C as exhibited in the copolymers prepared in the present work. Certainly in the present work, and perhaps in the work of others in side chain systems, the stability of the mesophases can be explained by the degree of phase separation of the mesogenic unit from the supporting phase--be that a star core or a linear backbone support. As the degree of phase separation becomes more distinct, the mesogenic unit will be surrounded more completely by its own rigid phase which should lead to more enthalpic driving force for a stable mesophase. Other workers have also suggested that side chain liquid crystalline polymers containing phenyl benzoate mesogens are microheterogeneously phase separated if the flexible chain end on the phenyl benzoate is sufficiently long (21, 22).

Recently, the preparation of linear, segmented block copolymers where mesogenic units are linked by flexible polyether chains has been reported (23). Like the systems in the present work, these segmented block copolymers were reported to be phase separated and to also display a liquid crystalline phase. The role of phase separation in the formation and stability of liquid crystalline mesophases appears to be a subject worthy of further investigation.

The general synthetic procedure for the preparation of these thermotropic rigid rod star-block copolymers suggests the preparation of a large number of new copolymers. The star core could be prepared from a number of different monomers to desired lengths as well as any number of arms up to eighteen using known literature techniques. Further, various types of mesogenic units could be attached at the extremities of the arms including cholesteric, smectic, and discotic low molecular weight mesogens. Thermotropic and lyotropic main chain liquid crystalline polymers could also be attached at the ends of the flexible star cores. The next chapter will describe the preparation of a lyotropic rigid rod star-block copolymer which contains rigid poly(p-benzamide) blocks at the extremities of poly(dimethylsiloxane) star cores. Hypothetically, these new copolymers, once properly processed, could result in the preparation of materials with high multi-dimensional strength and low weight.

REFERENCES

1. A. Roviello and A. Sirigu, J. Polym. Sci., Letters Ed., 13, 455 (1975).

2. J.I. Jin, S. Antoun, C. Ober, and R.W. Lenz, Liquid Crystal Polymer Symposium, 16-17 July (1980).

3. S. Antoun, R. W. Lenz, and J.I. Jin, J. Polym. Sci., Chem. Ed., 19, 1901 (1981).

4. A.C. Griffen and S.J. Havens, J. Polym. Sci., Phys. Ed., 19, 951 (1981).

5. A. Blumstein, S. Vilasager, S. Ponrathnam, S.B. Clough, and R.B. Blumstein, J. Polym. Sci., Phys. Ed., 20, 877 (1982).

6. W.J. Jackson and H.F. Kuhfuss, J. Polym. Sci., Chem. Ed., 14, 2043 (1976).

7. L. Strzelecki, Bull. Soc. Shim. Fr., 597 (1973).

8. V.P. Shibaev, V.M. Moiseenko, T.S. Friedzon, and N.A. Plate, Eur. Polym. J., 16, 277 (1980).

9. V.P. Shibaev, N.A. Plate, and Y.S. Friedzon, J. Polym. Sci., Chem. Ed., 17, 1655 (1979).

10. H. Finkelmann and G. Rehage, Makrom. Chem., Rapid Commun., 1, 31 (1980).

11. W. Kreuder and H. Ringsdorf, Makrom. Chem., Rapid Commun., 4, 807 (1983).

12. H. Ringsdorf and A. Schneller, Makrom. Chem., Rapid Commun., 3, 557 (1982).

13. B. Reck and H. Ringsdorf, Makrom. Chem., Rapid Commun., 6(4), 291 (1985).

14. H. Hoshino, J.I. Jin, and R.W. Lenz, J. Appl. Poly. Sci., 29, 547 (1984).

15. Chapter Four of this Thesis

16. Chapter Three of this Thesis

17. W.R. Young, I. Haller, and D.C. Green, J. Org. Chem., 37(23), 3707 (1972).

18. Vorlander, Z. Phys. Chem., 105, 211 (1923).

19. R.E. Rondeau, M.A. Berwich, R.N. Steppel, and M.P. Serve, J. Amer. Chem. Soc., 94(4), 1096 (1972).

20. B.A. Jones, J.S. Bradshaw, M. Nishioka, and M.L. Lee, J. Org. Chem., 49, 4947 (1984).

21. T.S. Lipatov, V.V. Tsukruk, and V.V. Shilov, Polym. Comm., 24, 75 (1983).

22. V.V. Shilov, V.V. Tsukruk, V.N. Bliznyak, and T.S Lipatov, Polymer, 23(4), 484 (1982).

23. J.D. Shaffer and V. Percek, ABS PAP ACS, 190(Sept.), 104 (1985).

CHAPTER SIX

SYNTHESIS AND CHARACTERIZATION OF LYOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

I. INTRODUCTION

The field of lyotropic liquid crystalline polymers has generally divided itself into the two primary areas of rigid, extended chain (1-5) and rigid, helical linear polymers (6, 7). Whether helical or extended chain, lyotropic liquid crystalline polymers form an anisotropic phase in solution above a critical polymer concentration. In addition to theoretical interest, these polymers have generated considerable technological applications in the area of high strength/low weight fibers (8).

Fibers spun from nematic solutions of extended chain, linear liquid crystalline polymers exhibit high modulus and strength in the direction of the fiber axis, however, perpendicular to the fiber axis the modulus and strength are poor. This situation has been discussed theoretically by Halliday and White (7). They state that the modulus perpendicular to the chain axis is roughly proportional to the cohesive energy density of the chosen polymer. This dependence on secondary forces for lateral strength has led to poor compressive strength in fibers, and similarly has led to delamination problems in films formed by biaxially orienting nematic liquid crystalline polymer solutions.

Hypothetically, the use of block copolymer systems to form molecular composites could overcome some of these directional strength problems (10-12). Takayanagi has prepared block copolymers where flexible polyamide blocks link liquid crystalline polyamide blocks and suggested that the flexible segments could act as tie molecules to provide for improved multi-dimensional strength (11). Additionally, the phase separated nature of these materials could give additional strength via inhibition of crack propagation, a primary mode of polymer mechanical failure (11). Others have suggested that cholesteric liquid crystalline polymers could be useful in the preparation of high strength bonded laminates (13-15).

This chapter will discuss the synthesis and characterization of lyotropic rigid rod star-block copolymers. As depicted in Figures 6.1 and 6.2, these novel copolymers once properly processed into extended chain fibers and films, could achieve improved multi-dimensional properties. It is envisioned that the flexible segments of these copolymers could act like tie

Figure 6.1

A schematic of a lyotropic rigid rod star-block copolymer. These novel liquid crystalline polymers are comprised of a flexible star-core at the extremities of which are attached the lyotropic mesogenic blocks.

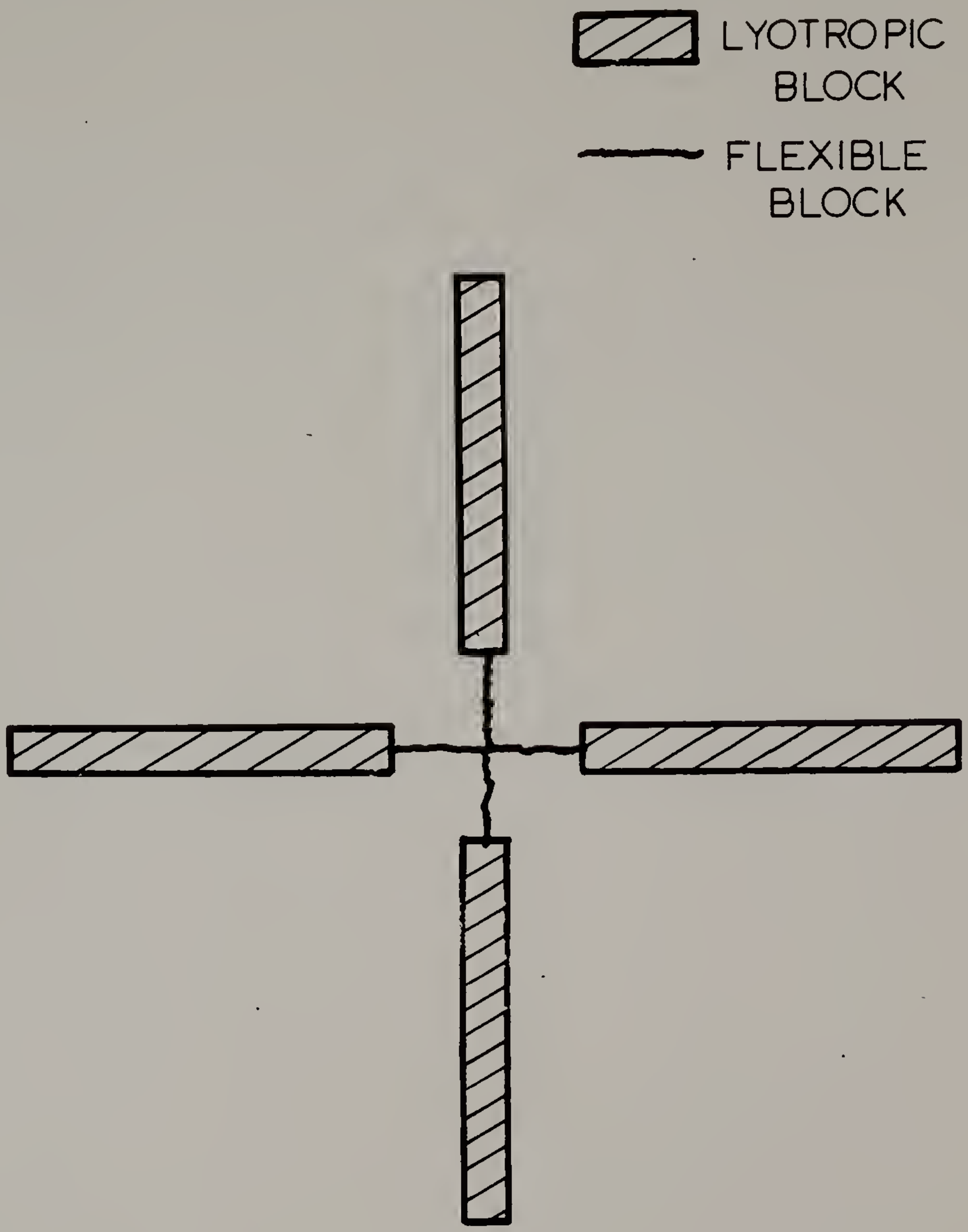
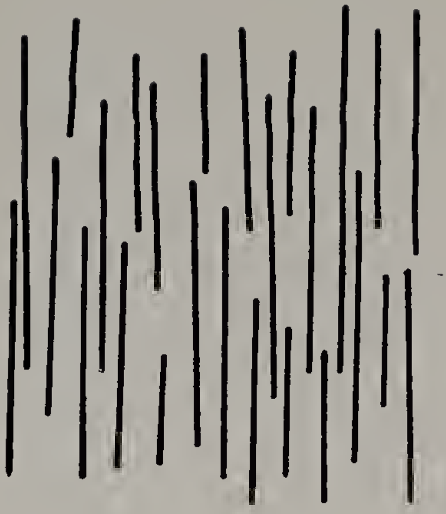

LYOTROPIC BLOCK
FLEXIBLE BLOCK

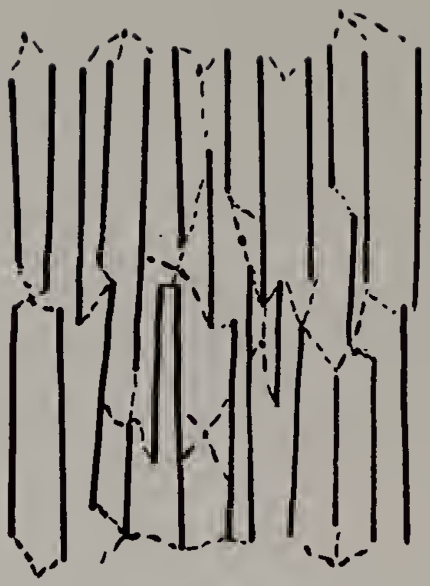
Figure 6.2

This figure depicts the rationale for making rigid rod star-block copolymers. The flexible spacers, depicted by dashed lines in this figure, hypothetically act as tie molecules in semicrystalline polymers. These tie molecules result in real strength in directions other than that of the chain extension.

FIBERS

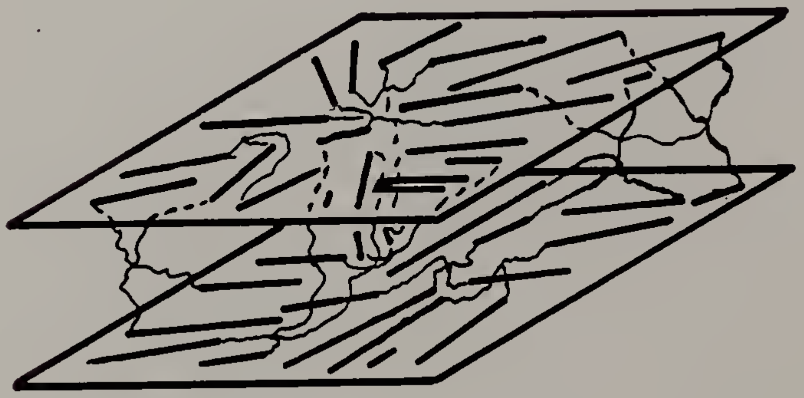


IDEALIZED NEMATIC
LINEAR FIBER



RIGID ROD STAR-
BLOCK COPOLYMER

2-D APPLICATIONS



TWO DIMENSIONAL APPLICATION
OF RIGID ROD STAR-BLOCK COPOLYMERS

molecules in semi-crystalline polymers to provide for enhanced strength in directions other than that of the chain extension.

II. EXPERIMENTAL SECTION

Materials: The previously prepared telechelic poly(dimethylsiloxane) intermediates are described in Table 6.1 (16). p-Aminobenzoic acid was obtained from Aldrich Chemical Co., recrystallized twice from an ethanol/water mixture, dried for twenty hours at 65°C under vacuum ($\leq$ 0.05 mm Hg), and stored away from light under argon prior to use. p-N-Butylphenyl-4'-anisamide was prepared as previously described (17). 1-Methyl-2-pyrrolidinone was obtained from Aldrich Chemical Co., stirred over calcium hydride under argon for several hours, vacuum distilled into activated three angstrom Molecular Sieves, and stored under argon prior to use. Pyridine was obtained from Fisher Scientific, refluxed under argon and over calcium hydride for three hours, fractionally distilled under argon into activated three angstrom Molecular Sieves, and stored under argon prior to use. Benzene was purified as previously described (18). Triphenyl phosphite was obtained from Aldrich Chemical Co., vacuum distilled, and stored under argon

Table 6.1

The pertinent data for the previously prepared telechelic poly(dimethylsiloxane) intermediates (18). The copolymers were prepared by growing poly(p-benzamide) from the aromatic amine end-groups of these intermediates.

SUMMARY OF TELECHELIC SILOXANES

Polymer	Mn (theo)*	Mn (found)#	Functionality+	Mw/Mn>
L-I	1700	2100 ± 100	2.0 ± 0.2	1.13
ST-I	3200	2600 ± 200	4.1 ± 0.3	1.32
ST-II	5100	3900 ± 500	3.7 ± 0.4	1.20
ST-III	9000	6190 ± 1100	3.7 ± 0.5	1.31
ST-IV	16,000	17,000 ± 2000	4.1 ± 0.4	1.32
ST-V	24,000	24,000 ± 2000	4.3 ± 0.5	1.27

---

* Theoretical Mn based on [(Monomer/(Initiator)]x(Monomer MW).

#Mn found via vapor phase osmommetry, chloroform @ 37°C. Polymers ST-IV and ST-V Mn based on GPC extrapolation.

+Functionality found via infrared spectroscopy of 1600 wavenumbers phenyl ring vibration combined with Mn data.

>Mw/Mn based on polystyrene calibrated GPC in THF with no correction for broadening.

prior to use. Lithium chloride (99+%) was obtained from Baker Chemical Co., dried under vacuum ($\leq$ 0.05 mm Hg) at 150°C for forty-eight hours, and stored under argon prior to use. Chloroform was obtained from Fisher Scientific (spectroscopic grade) and used as received. N,N-Dimethylacetamide was obtained from Aldrich Chemical Co. and used as received.

Preparation of poly(p-benzamide): Poly(p-benzamide) was prepared as follows by the method of Yamazaki (19). Into a clean, dry, argon filled, three-neck 1000-mL round bottom flask was added 4.11g (0.0300 mol) of p-aminobenzoic acid and 3.10g of lithium chloride. After fitting the flask with a water condenser, under argon was added 48 mL of 1-methyl-2-pyrrolidinone and 25 mL of pyridine. The flask was then immersed in a 90°C oil bath and with stirring a clear solution formed. Twenty minutes after immersion into the oil bath, 7.9 mL (0.0302 mol) of triphenyl phosphite was added to the stirring solution. The reaction proceeded under argon for 16 hours at 91°C yielding a gelled, slightly cloudy product. After cooling to room temperature, 20 mL of methanol was added to the reaction flask, the solid polymer was collected over a Buchner funnel, extracted with methanol for 25 hours in a Soxhlet extractor, and finally collected and dried under vacuum ($\leq$ 0.05 mm Hg) for 25 hours at 75°C. A quantitative yield of 3.57g of polymer was collected with an inherent viscosity in sulfuric acid of 1.72 dL/g.

Preparation of a Lyotropic Rigid Rod Star-Block Copolymer (ST-L-2): Into a clean, dry, argon filled, three-neck 1000-mL round-bottom flask was added 2.75g (0.0020 mol) of p-aminobenzoic acid and 2.03g of lithium chloride. After fitting the flask with a condenser, under argon was added 35 mL of 1-methyl-2-pyrrolidinone, 15 mL of pyridine, and 3.5 mL of a benzene solution containing 0.43g of poly(dimethylsiloxane) telechelic star intermediate ST-II. After immersing the flask in a 90°C oil bath for 15 minutes, with vigorous stirring was added 5.52 mL (0.020 mol) of triphenyl phosphite. The reaction proceeded for 20 hours at 88°C under argon at which time the contents of the flask had gelled into a lightly colored, homogeneous mass. After addition of 200 mL of ethanol to the flask, the product was collected by filtration, washed successively with water, methanol, and hexane, extracted with methanol in a Soxhlet extractor for 48 hours, and finally collected and dried for 26 hours under vacuum ($\leq$ 0.05 mm Hg) at 65°C. A total of 2.75 g (97.5% yield) of product was collected with an inherent viscosity in N,N-dimethylacetamide (w/2.85 % LiCl) of 2.87 dL/g.

A model reaction of a telechelic poly(dimethylsiloxane) with anisic acid under "Yamazaki" conditions: This reaction was performed to quantitatively investigate the reaction of a telechelic poly(dimethylsiloxane) with an aromatic acid under Yamazaki conditions similar to that used in the preparation of the block copolymers. To a clean, dry, argon filled 100-mL round-bottom flask was added 0.34g (0.00223 mol) of anisic acid, 0.78g of lithium chloride, 14 mL of 1-methyl-2-pyrrolidinone, 6 mL of pyridine, and 8.2 mL of a benzene solution containing 0.9g of a telechelic poly(dimethylsiloxane) which contained 0.0010 moles of aromatic amine per gram of total polymer. After immersing the reaction flask in a 90°C oil bath for five minutes, 0.54 mL (0.00212 mol) of triphenyl phosphite was added, and the reaction was allowed to proceed under argon for twenty hours at 90°C. After adding 40 mL of distilled water, the reaction mixture was washed several times with water in a separatory funnel, and the oily layer containing the product was collected and condensed via rotary evaporation. The product was then dissolved and reprecipitated three times, condensed via rotary evaporation, and dried under vacuum ($\leq$ 0.05 mm Hg) at 63 °C for 17 hours. Quantitative infrared spectroscopy indicated that the final oily product contained 0.00080 moles of amide per gram of total polymer which converted into an extent of amidation of 93±5%. Gel permeation chromatography was also performed to insure that the Yamazaki conditions did not degrade the substrate polysiloxane. No degradation was observed.

Measurements: Qualitative and quantitative infrared spectroscopy were performed as previously described (17). Gel permeation chromatography was performed with a Waters chromatograph with tetrahydrofuran as solvent and calibration with polystyrene standards. Optical microscopy was performed by placing appropriate solutions of the polymers between cover slips and then placing this assembly between crossed polarizers. Inherent viscosity of poly(p-benzamide) was performed at a concentration of 0.5 g/dL in both reagent grade sulfuric acid and N,N-dimethylacetamide containing 2.85% lithium chloride. Inherent viscosities of the copolymers were performed exclusively in N,N-dimethylacetamide containing 2.85% lithium chloride at a copolymer concentration of 0.5 g/dL. Low temperature differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-II and higher temperature DSC was performed on a Perkin-Elmer DSC-IV. Thermal gravimetric analysis was done on a Perkin-Elmer TGS-II.

Solutions of the poly(p-benzamide) and the copolymers were prepared by increasing the concentration of polymer sample in N,N-dimethylacetamide containing 2.85% lithium chloride until no more polymer could be dissolved. Observations on these solutions were made during their preparation to determine at what point a lyotropic liquid crystalline phase occurred and at what point no more material could be dissolved into solution.

III. RESULTS AND DISCUSSION

The poly(p-benzamide) and block copolymers prepared in this work were all synthesized via the "Yamazaki" reaction (19). This reaction has been shown to be very effective in the preparation of polyamides from aromatic and aliphatic carboxylic acids and aromatic amines (19). The Yamazaki reaction has been utilized by several workers to synthesize poly(p-benzamide) and similar polymers and copolymers with consistent results (11, 19, 20, 23). In this work, poly(p-benzamide) was prepared twice with inherent viscosities at 30°C in sulfuric acid of 1.71 and 1.72 dL/g respectively. Relying on the work of Papkov, the $\overline{Mn}$ of these homopolymers can be calculated to be approximately 13,000 (22).

In the synthesis of the block copolymers, the ratio of moles of p-aminobenzoic acid to the moles of aromatic amine end-groups on the siloxane polymers was kept constant at approximately sixty. Assuming a complete reaction without the formation of poly(p-benzamide) homopolymer, an assumption which is far from assured, each of the arms of the copolymers would contain a rigid, poly(p-benzamide) block averaging 7000 $\overline{Mn}$ at their extremities. This 7000 Mn value is only slightly greater than one half the value for the poly(p-benzamide) homopolymers. The low ratio of p-aminobenzoic acid to aromatic amine end-group on the siloxanes was chosen to discourage homopolymer formation.

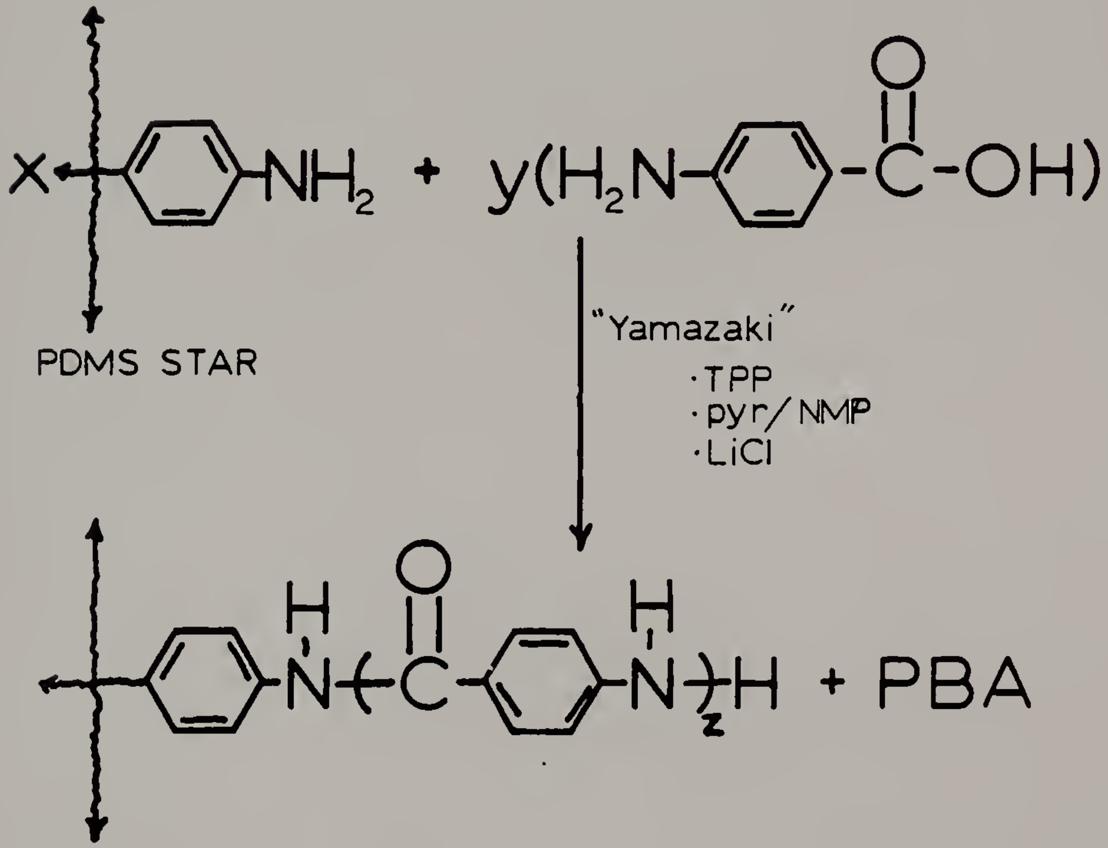
Figure 6.3 shows the reaction scheme for the preparation of the lyotropic rigid rod star-block copolymers described in this work. As the reactions proceeded, three distinct visual phases were generally observed. On initial addition of the triphenyl phosphite the reaction mixture was fully fluid, homogeneous, and slightly cloudy. After the reaction had proceeded for approximately 15 minutes to one hour, polymer would start to precipitate and cling to the stirring bar. This precipitate was presumably mostly siloxane polymer that

Figure 6.3

The synthetic scheme for the preparation of lyotropic rigid rod star-block copolymers. The poly(p-benzamide) is grown from the reactive aromatic amine end-groups of the siloxane intermediates. It is also hypothetically possible that some homo-poly(p-benzamide) is also synthesized during the reaction.

LYOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

Synthesis



had a small amount of poly(p-benzamide) growing at its extremities. Hypothetically, the copolymer at this point had enough polyamide growing from it to no longer be an oily material, yet not enough polyamide to make it fully soluble in the amide solvents. In the third stage, the product would start to go back into solution, hypothetically due to the presence of enough polyamide in the copolymer to render it soluble in amide solvents, and the reaction mixture would be a homogeneous, slightly cloudy gel at the termination of the reaction.

These general observations occurred during synthesis of the copolymers prepared and summarized in Table 6.2 except for ST-L-V. The preparation of ST-L-V involved the use of a poly(dimethylsiloxane) intermediate of 24,000 $\overline{Mn}$, and this highest molecular weight siloxane did not mix well into the initial reaction solution. Similarly, as the reaction proceeded, the resulting copolymer failed to redissolve in the reaction solvents. In all of the other copolymerizations shown in Table 6.2, the growing copolymer redissolved at a rate that decreased as the molecular weight of the siloxane increased. Clearly, a different solvent system, mixing procedure, or both would be required to prepare the described copolymers with poly(dimethylsiloxane) intermediates of over approximately 20,000 $\overline{Mn}$.

Table 6.2

A summary of the results of the lyotropic rigid rod block copolymers prepared in this work. Included is yield, inherent viscosity, siloxane content, and solution property data. The lengths of the siloxane flexible spacers for the respective copolymers can be found in Table 6.1.

SUMMARY OF RESULTS OF LYOTROPIC RIGID -ROD STAR-BLOCK COPOLYMERS

Polymer >	Yield	Inh. Vis. +	Wt. % Silox. *	Properties #
L-L-I	99+%	2.26	9.6%	LCM
ST-L-I	99+%	2.64	9.8%	NLC
ST-L-II	97.5%	2.87	15.5%	NLC
ST-L-III	98.5%	2.55	24.8%	LCB
ST-L-IV	98%	2.34	35.3%	LCM
ST-L-V	93.5%	1.74	46.5%	LCM
PBA-I	95%	2.32(1.71)	----	LCM
PBA-II	99+%	(1.72)	----	LCM

> L-L-I is a linear block copolymer, All ST polymers are four armed stars, and PBA polymers are poly(p-benzamide).

+Inherent viscosities performed at 30°C in N,N,-Dimethylacetamide with 2.85%(w/w) LiCl. All values in parentheses performed in sulfuric acid. All performed @0.5% grams/ml and reported in dL/g.

*Weight percentage siloxane in the feed, the ratio of p-aminobenzoic acid monomer to aromatic amine endgroups on the telechelic siloxanes held constant.

LCM stands for capabilility to form a liquid crystalline monophase; NLC stands for no ability to form a liquid crystalline phase; LCB stands for the ability to form a liquid crystalline biphase but no liquid crystalline monophase.

Table 6.2 summarizes the syntheses and solution properties for the polymers and copolymers prepared in this work. The reported yields for all of the copolymers are essentially quantitative, except for ST-L-V discussed above, yet this does not necessarily indicate that all of the arms of the copolymers contain poly(p-benzamide) blocks at their extremities. Although it is unlikely to occur considering the kinetics of condensation polymerization, the attachment of a long poly(p-benzamide) segment to only one of the four arms of the siloxane substrate could result in a quantitative yield as well as solubility in amide solvents. Figures 6.4 and 6.5 show typical infrared spectra for a telechelic siloxane substrate and a final lyotropic rigid rod star-block copolymer product. The expected absorptions for both the siloxane segment and the polyamide segment are clearly observed in the infrared spectrum of the copolymers. However, as with the reported quantitative yield data, the infrared spectral data supports but does not establish that polyamide segments reside at the extremities of all of the arms of the copolymers.

To gain insight into this matter, a model reaction between a telechelic poly(dimethylsiloxane) and an aromatic carboxylic acid, anisic acid, was performed under the same Yamazaki conditions used in the

Figure 6.4

The infrared spectrum of a telechelic poly(dimethylsiloxane) intermediate. The bands typical of siloxanes can be seen in addition to the phenyl and primary amine absorptions due to the attached aromatic amine function at the siloxane's extremities.

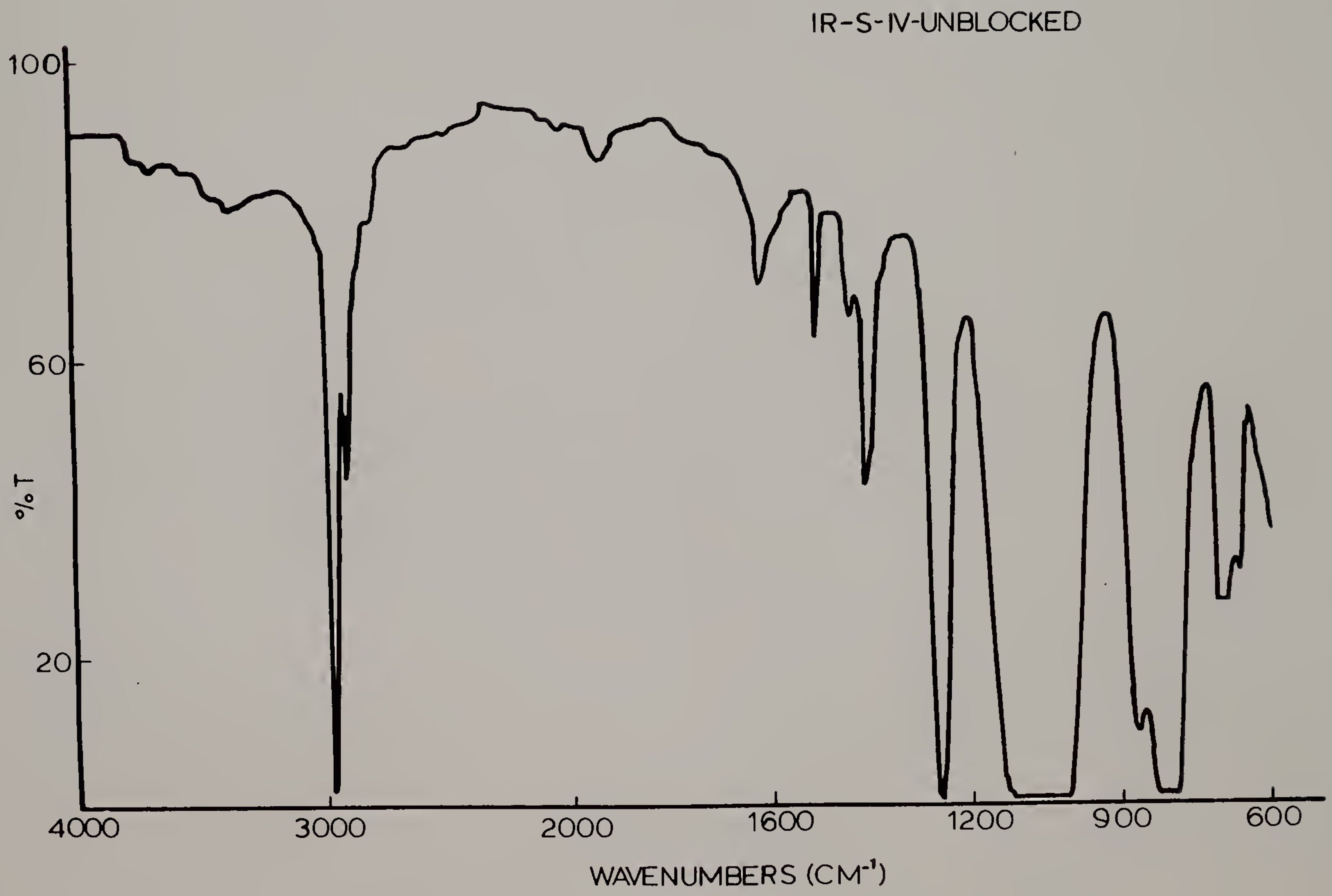
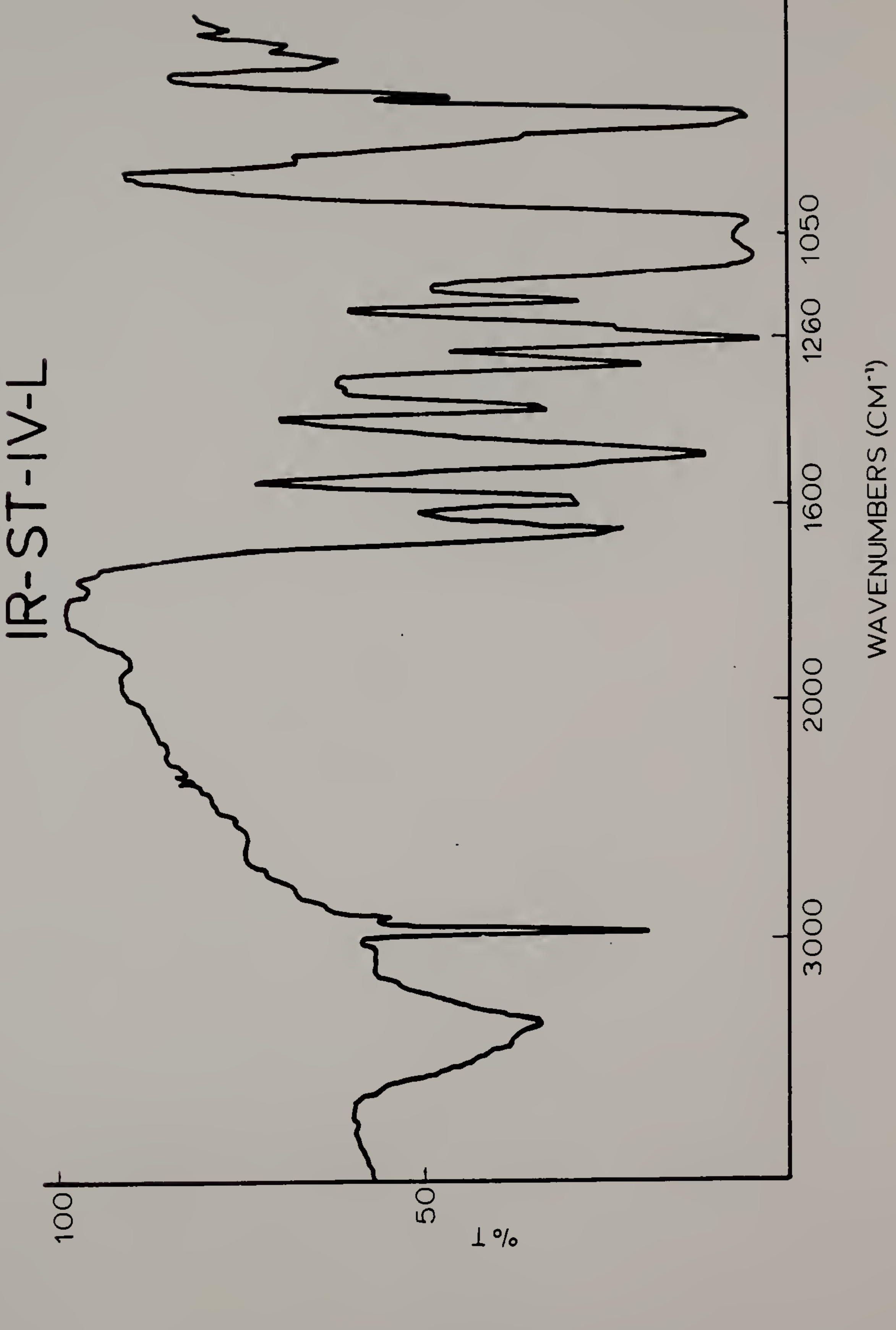

IR-S-IV-UNBLOCKED
100
60
20
%T
4000
3000
2000
1600
1200
900
600
WAVENUMBERS (CM^{-1})

Figure 6.5

Infrared spectrum of a lyotropic rigid rod star-block copolymer. In addition to the bands typical of the siloxane segment, the absorption bands typical of poly(p-benzamide) can clearly be seen.


IR-ST-IV-L
100
50
% T
3000
2000
1600
1260
1050
WAVENUMBERS (CM⁻¹)

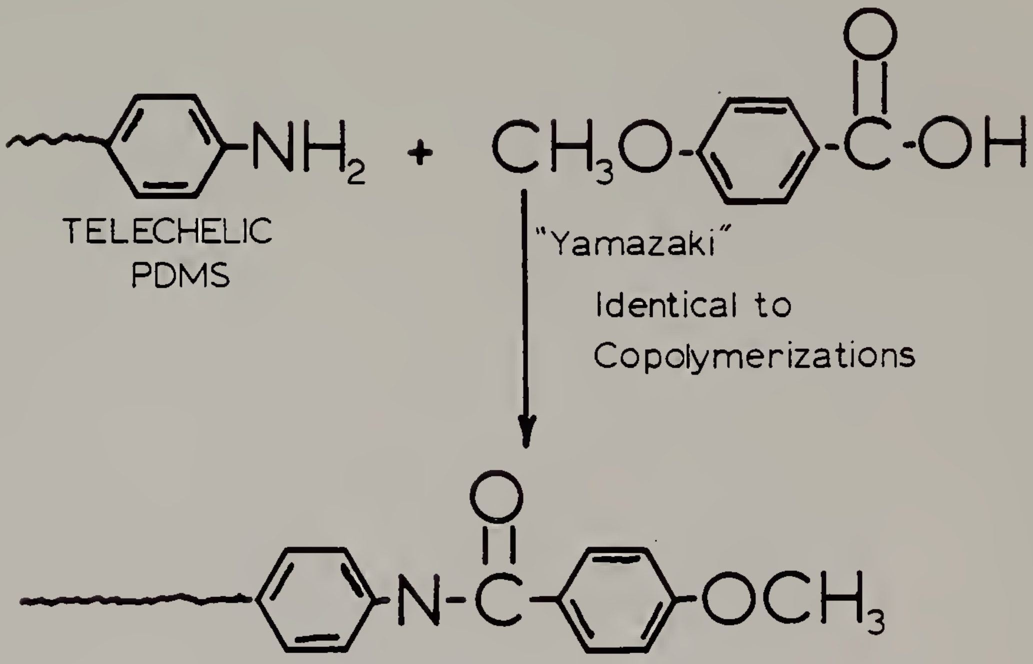
copolymerizations. It is asserted that if the aromatic carboxylic acid reacted in high yields with the aromatic amine end-groups of the siloxane under Yamazaki conditions, that taking into account the yields, infrared spectra, and the nature of the kinetics of condensation polymerization, that one could comfortably assert that all or most of the arms of the siloxane substrate had poly(p-benzamide) at its extremities. Additionally, gel permeation chromatography could be performed on the product of this model reaction to ascertain if the Yamazaki reaction conditions in any way degraded the siloxane substrate.

Figure 6.6 shows the model reaction scheme and Figure 6.7 presents the gel permeation chromatography results of this study. The oily product was found to have an extent of amidation of 93 ± 5% by quantitative infrared spectroscopy with p-N-butylphenyl-4'-anisamide as the model compound for infrared analysis. The gel permeation chromatography results showed no degradation of the siloxane substrate and the expected shifting of the product to slightly decreased elution volume. This model reaction, when combined with the favorable data shown in Table 6.2, the infrared spectral data, and taking into consideration the nature of condensation kinetics, clearly supports the assertion that the

Figure 6.6

The schematic of the model reaction of a telechelic poly(dimethylsiloxane) with anisic acid. The extent of amidation was found to be 93±5% and gel permeation chromatography showed that the Yamazaki reaction conditions did not degrade the siloxane substrate. These results strongly support the assertion that all or most of the copolymers have the rigid, poly(p-benzamide) block at the extremity of each arm.

MODEL REACTION: Extent of Reaction of Telechelic Siloxanes.



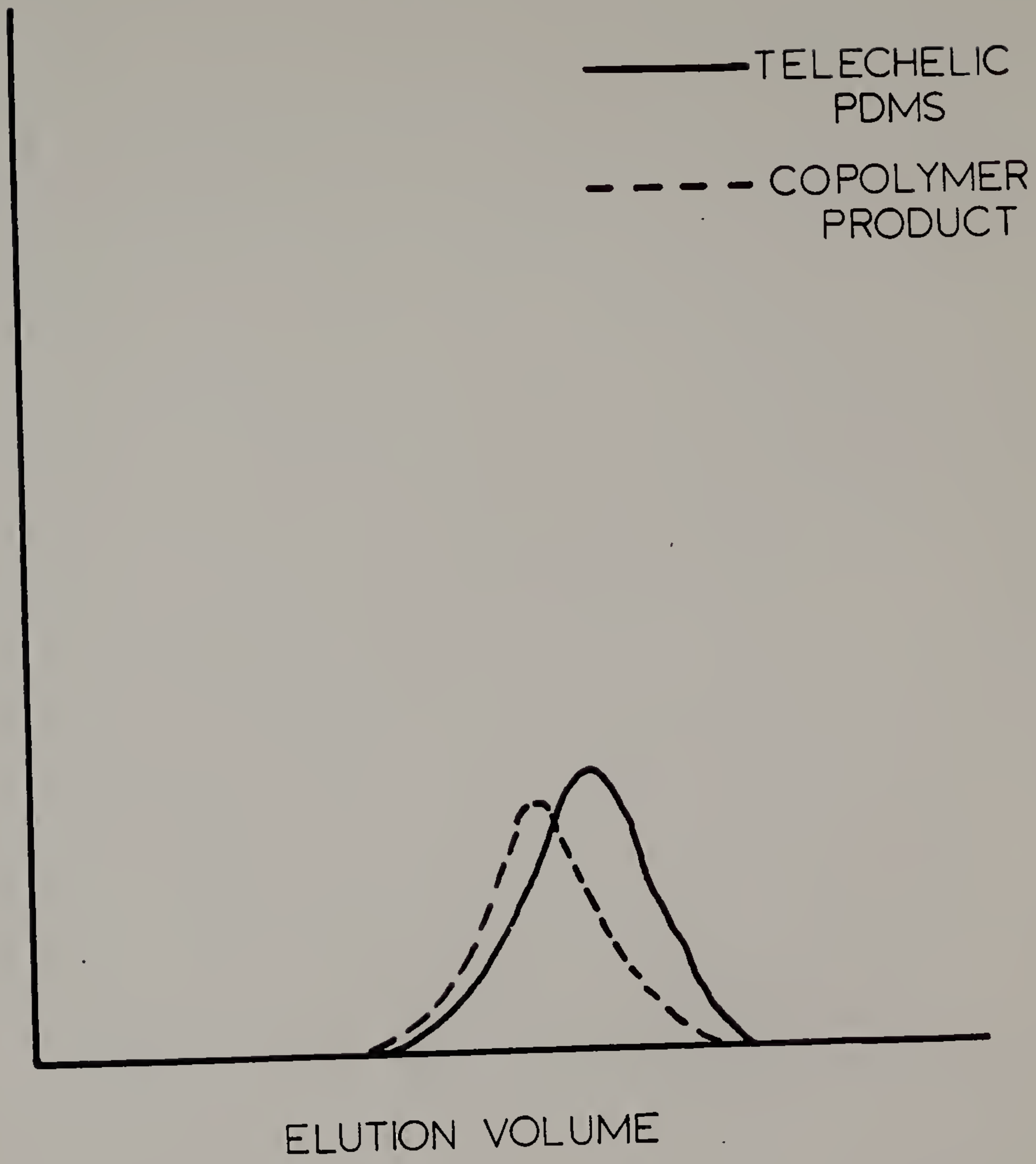
Quantitative Results:

1. Extent of Amidation is 93 ± 5% by quantitative infrared spectroscopy.
2. There is no degradation of the telechelic poly(dimethylsiloxane) under these reaction conditions. GPC shows no sign of degradation or change in polydispersity.
3. The final material is an oil, not a solid.

Figure 6.7

Gel permeation chromatography results of the model reaction of a telechelic siloxane substrate with anisic acid under Yamazaki conditions. These traces show no sign of degradation of the siloxane substrate and, as expected, the product is shifted to a slightly lower elution volume.

GPC - MODEL REACTION



copolymers prepared in this work do have poly(p-benzamide) segments at the extremities of all or most of the siloxane arms. The solution properties, to be discussed later, also support this assertion as the solution properties can best be explained by the presumed radial nature of the block copolymers.

All of the copolymers were investigated as to their thermal properties with DSC and thermal gravimetric analysis. Figure 6.8 shows a sample trace of a low-temperature DSC of a star-block copolymer. As with the thermotropic rigid rod star-block copolymers (17), these copolymers did show a clear glass transition typical of homo-poly(dimethylsiloxane) at approximately -120°C. The glass transition temperatures of the siloxane segment of the copolymers are tabulated in Table 6.3, and these data suggest a high degree of phase separation between the flexible and rigid segments of the block copolymers. Table 6.4 summarizes the crystallinity results for the siloxane segments of the block copolymers. Only ST-L-IV and ST-L-V, the block copolymers with the two longest siloxane segments, show any crystallinity of the siloxane segment under the conditions used in this DSC experiment. The small enthalpy of melting reported for ST-L-V is probably due to the synthetic difficulties mentioned previously, however, the higher temperature of melting

Figure 6.8

The low temperature DSC thermogram of a lyotropic rigid rod star-block copolymer. This copolymer, ST-L-IV, shows a low temperature glass transition typical for siloxanes as well as both cold crystallization and melting of the siloxane segment of the copolymer.

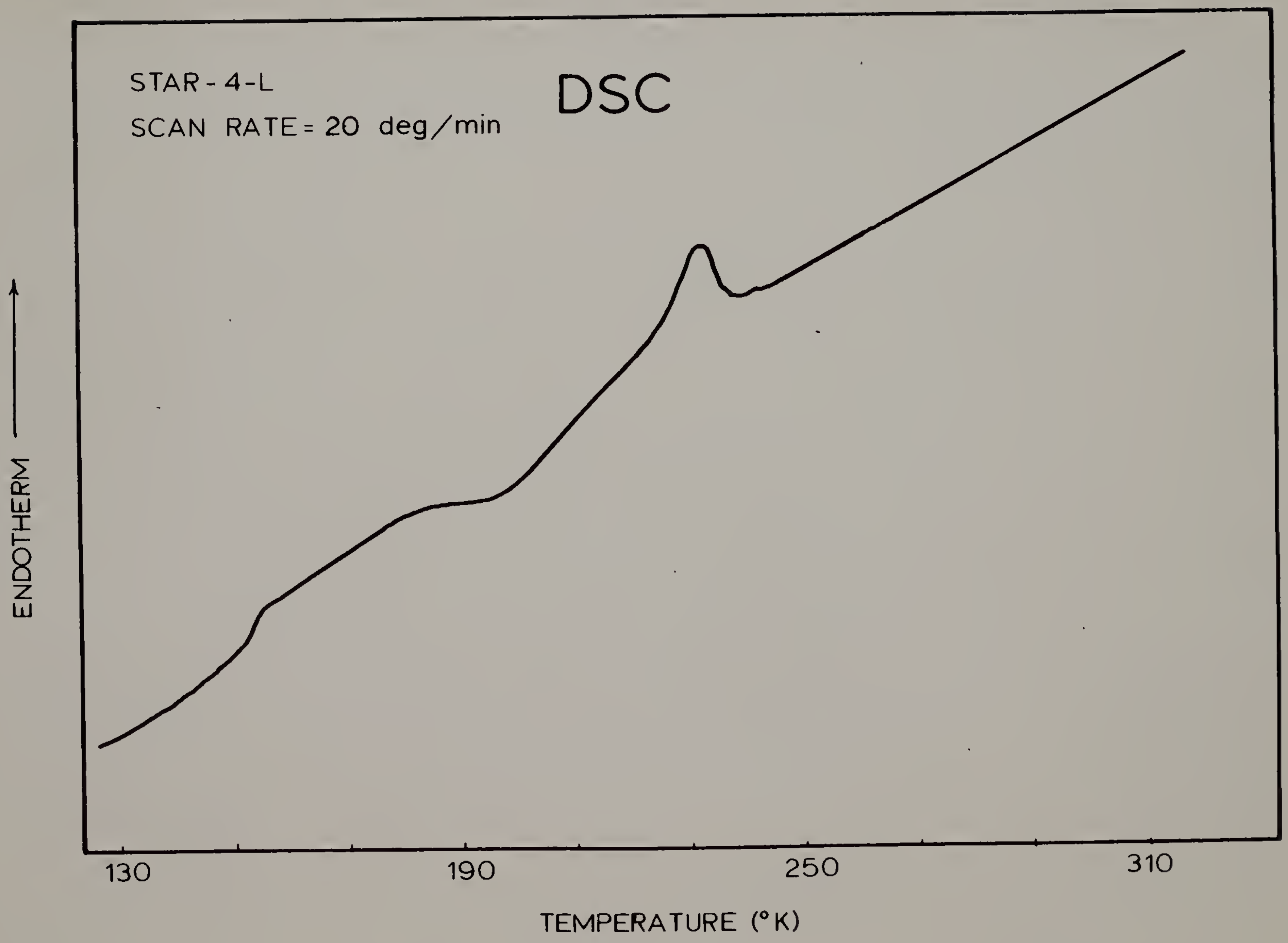

STAR - 4 - L
SCAN RATE = 20 deg/min
DSC
ENDOTHERM
130
190
250
310
TEMPERATURE (°K)

Table 6.3

The low temperature glass transition temperatures of the siloxane segment of the copolymers. These values were found using DSC analysis. The DSC run was done at a heating rate of 20°C/minute after the sample was quickly cooled from 50°C.

GLASS TRANSITION TEMPERATURES OF SILOXANE SEGMENT OF COPOLYMERS

POLYMER	Mn/arm	Tg (°C)
L-L-I	1050	-120.8
ST-L-I	650	-122.6
ST-L-II	975	-121.3
ST-L-III	1550	-120.1
ST-L-IV	4250	-120.3
ST-L-V	6000	-122.4
ST-I*	650	-115.2
ST-IV*	4250	-119.3

---

* Signifies that these polymer samples are unreacted telechelic siloxane oils, not copolymers with PBA.

Table 6.4

The temperature of melting and the respective enthalpies of melting of the siloxane segments of the copolymers. Under the conditions of this DSC experiment, only ST-L-IV and ST-L-V showed any crystallinity of the siloxane segment.

TEMPERATURES OF MELTING AND ENTHALPIES OF SILOXANE SEGMENT OF COPOLYMERS

Polymer	Mn/arm	Tmax(°C)*	Enthalpy (cal/g)
L-L-1	1050	none	----
ST-L-I	650	none	----
ST-L-II	975	none	----
ST-L-III	1550	none	----
ST-L-IV	4250	-41.4	1.94
ST-L-V	6000	-38.8	0.86+
ST-I#	650	none	----
ST-IV#	4250	-38.3	6.67

---

* All runs performed at a heating rate of 20°C/min on samples quenched to -150°C from 50°C at a cooling rate of 320 C/min.

These polymers are telechelic amine siloxanes; they are not copolyners with PBA.

+ This low value is indicative of the mentioned synthetic problems due to the high amount and molecular weight of the siloxane segment.

reported for the siloxane segment of this copolymer suggests that the siloxane segments that do exist have a more ordered crystal structure. Higher temperature DSC was performed on all of the copolymers. A change in the slope of the DSC thermogram was evident in all of the six copolymers at about 260-300°C, but it cannot be definitively shown to be a glass transition without further study. No higher temperature endotherms were observed. This behavior is expected, since the poly(p-benzamide) segments should degrade prior to melting.

Figure 6.9 shows a thermal gravimetric analysis scan typical of the block copolymers. Table 6.5 summarizes these results. It is surprising to observe the exceptional thermal stability of these block copolymers. As seen in Table 6.5, the thermal stability by sweeping thermal gravimetry of the block copolymers exceeds the stability of both the siloxane and poly(p-benzamide) homopolymers. Past work has showed that poly(p-benzamide) shows no loss of volatile material below 480°C (23). This is supported by the thermal studies of this work. However, the reason for the superior thermal stability of the block copolymers is unclear. Nonetheless, the block copolymers show a thermal stability roughly 50°C higher than the poly(p-benzamide) homopolymer.

Figure 6.9

Thermal gravimetric analysis scan of a lyotropic rigid rod star-block copolymer. The scan was taken at a rate of 20°C/minute in a helium atmosphere. The copolymers show superior thermal stability when compared to either siloxane or poly(p-benzamide) homopolymers.

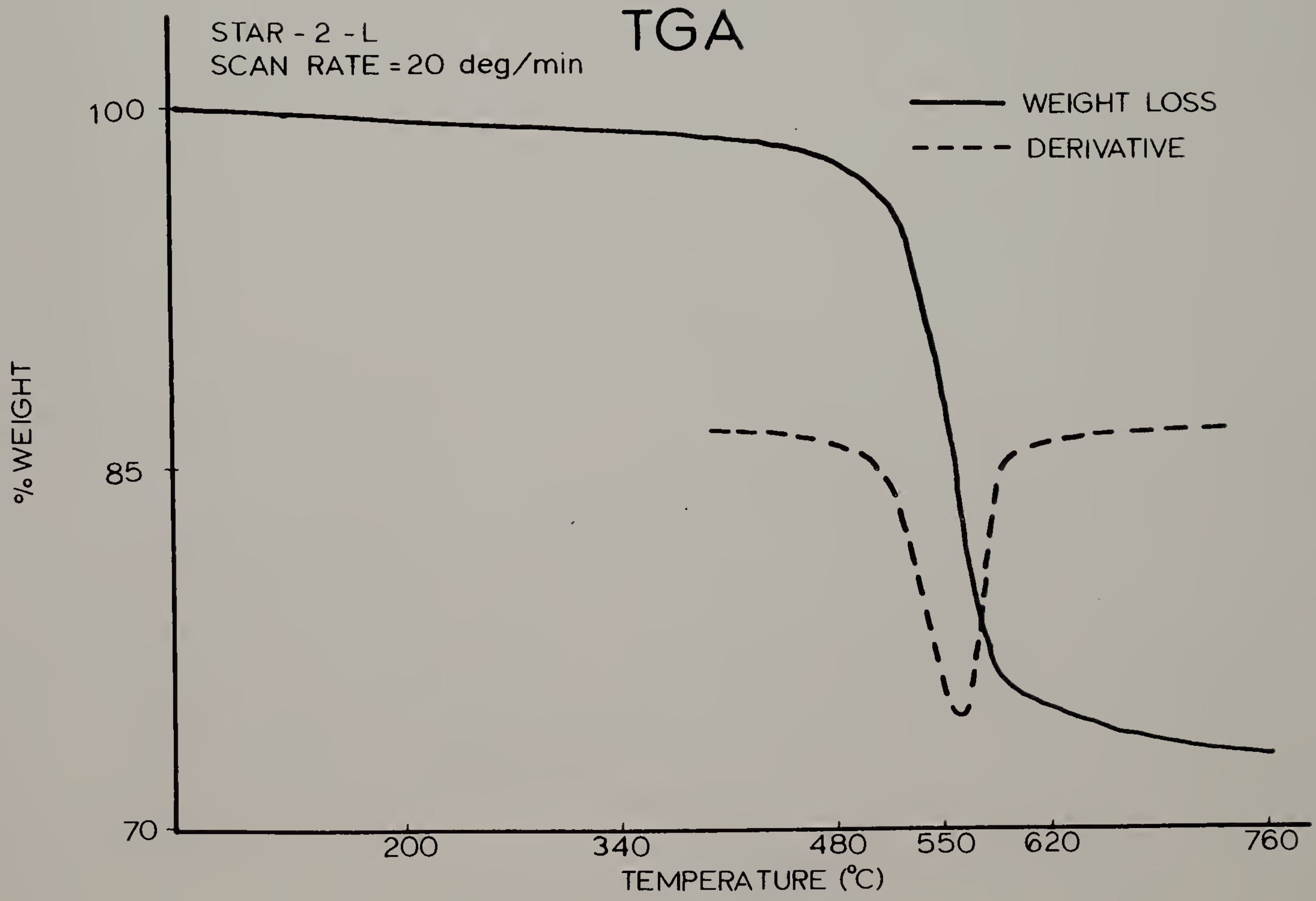

STAR - 2 - L
SCAN RATE = 20 deg/min
TGA
WEIGHT LOSS
DERIVATIVE
% WEIGHT
100
85
70
200
340
480
550
620
760
TEMPERATURE (°C)

Table 6.5

A summary of the thermal gravimetric analysis of the materials reported in this work. On scanning, the block copolymers show remarkable thermal stability compared to either the siloxane or poly(benzamide) homopolymers.

SUMMARY OF THERMAL GRAVIMETRIC ANALYSIS OF THE LYOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS.

Polymer	5% wt. loss(°C)	Max. Degrad.+(°C)
#ST-I	343	455
#ST-IV	421	462
PBA	470	518
L-L-1	522	563
ST-L-I	523	561
ST-L-II	522	560
ST-L-III	483	563
ST-L-IV	479	562
ST-L-V	---	505

---

* All runs performed on a Perkin-Elmer TGS-2 at a heating rate of 20° C/min in a Helium atmosphere.

+ Max. Degrad. is that temperature at which maximum degradation is observed from the derivative of the weight loss curve.

These polymers are telechelic siloxanes, not lyotropic copolymers.

The liquid crystalline properties of the block copolymers were observed with optical microscopy on solutions of the materials in N,N-dimethylacetamide containing 2.85% lithium chloride. Several solvents were used in an attempt to dissolve the copolymers prepared in this work. Only N,N-dimethylacetamide containing a moderate amount of lithium chloride successfully dissolved these copolymers. It is well known that above a critical concentration, lyotropic liquid crystalline polymers exhibit an anisotropic phase that can be readily observed by optical microscopy (4, 24). These solution studies were performed by adding polymer to the solvent until no more polymer would dissolve; the presence or lack of liquid crystallinity was noted during this process. Table 6.2 summarizes these results. Looking at just the results for the star-block copolymers, the two copolymers of shortest siloxane flexible spacer length failed to show any liquid crystallinity and formed completely clear, gelled phases at less than 6.0% polymer concentrations. ST-L-III formed a biphase solution at near 7.0% polymer concentration by weight, where liquid crystalline and isotropic phases coexisted in equilibrium. ST-III-L could be dissolved into the solvent up to around 7.5% by weight. The two star-block copolymers of longest siloxane spacer lengths showed the formation of entirely anisotropic, liquid crystalline phases, and could be made up into solutions at well above 10% by weight. This clearly suggests that the radial nature of these copolymers inhibits the formation of a liquid crystalline phase below a certain flexible spacer length. To further substantiate this assertion, the linear block copolymer L-L-I was prepared with a flexible siloxane spacer length between that of ST-L-I and ST-L-II. As expected, this linear block copolymer showed the formation of an entirely liquid crystalline phase, thus supporting the explanation for the solution behavior for the star-block copolymers.

Ongoing work on these copolymers includes the use of optical microscopy and rheological investigations to construct phase diagrams as well as to better understand the solution properties of these novel copolymers. Additional work will also concentrate on the fiber and film properties of these copolymers.

As briefly mentioned in the introduction to this chapter, the rationale for the synthesis of these star-block copolymers was to prepare materials that might show ultimate multidimensional strength and modulus, yet have the low density typical of organic systems. It is envisioned that the flexible segments would act as tie molecules in semicrystalline polymers and provide for real strength in directions other than that of the chain extension. Superior properties could probably best be achieved by blending these star-block copolymers with high molecular weight poly(*p*-benzamide) or poly(*p*-phenyleneterapthalamide). The appropriate arm lengths and arm numbers to achieve ultimate properties would have to be experimentally discovered. However, the synthetic procedure as outlined in this thesis, is sufficiently general so that the flexible arm length and arm number could be readily manipulated as desired. The final chapter of this thesis will discuss ongoing, future, and suggested work regarding these novel star-block copolymers.

REFERENCES

1. R.C. Evers, F.E. Arnold, and T.E. Helminiak, Macro., 14, 925 (1981).

2. M.B. Polk, K.B. Bota, M. Nandu, M. Phingbodhlipakkiya, and C. Edeogu, Macro., 17, 129 (1984).

3. P.W. Morgan, Macro., 10(6), 1381 (1977).

4. S.L. Kwolek, P.W. Morgan, J.R. Schaefgen, and L.W. Gulrich, Macro., 10(6), 1390 (1977).

5. R.W. Lenz, Organic Chemistry of Synthetic High Polymers, N.Y., Interscience Publ., p. 467 (1967).

6. A. Elliott and E.J. Ambrose, Discuss. Faraday Soc., 9, 246 (1950).

7. C. Robinson, J.C. Ward, and R.B. Beevers, Discuss. Faraday Soc., 25, 29 (1957).

8. A. Ciferri, Polym. Engin. and Sci., 15, 191 (1975).

9. L. Halliday and J.W. White, Pure Applied Chem., 26, 545 (1971).

10. S.M. Aharoni, J. Polym. Sci., Phys Ed., 19, 281 (1981).

11. M. Takayanagi, T. Ogata, M. Morikawa, and T. Kai, J. Macromol. Sci., Phys., B17(4), 591 (1980).

12. J.C. Halpin, Polym. Engin. and Sci., 15, 132 (1975).

13. W.R. Krigbaum, A. Ciferri, and J. Asrar, Mol. Cryst. Liq. Cryst., 76, 79 (1981).

14. W.R. Krigbaum, F. Salaris, and A. Ciferri, J. Polym. Sci., Letters Ed., 17, 601 (1979).

15. E. Chiellini, G. Galli, C. Malanga, and N. Spassky, Poly. Bull., 9, 336 (1983).

16. Chapter IV of this thesis.

17. Chapter V of this thesis.

18. Chapter III of this thesis.

19. N. Yamazaki, M. Matsumoto, and F. Higashi, J. Polym. Sci., Chem. Ed., 13, 1373 (1975).

20. Y. Imai, M. Kajiyama, S. Ogata, and M. Kakimoto, Poly. J., 16, 269 (1984).

21. J. Asrar, J. Preston, and W.R. Krigbaum, J. Polym. Sci., Chem. Ed., 20, 79 (1982).

22. S.P. Papkov, J. Polym. Sci., Phys. Ed., 12, 1753 (1974).

23. A.T. Kalashnik, N.P. Panikova, E.V. Povbii, G.V. Kozhina, V.D. Kalmykova, and S.P. Papkov, Vysokomol. Soedin, Ser. A, 19(12), 2747 (1977).

24. C.Balbi, E. Bianchi, A. Ciferri, and A. Tealdi, J. Polym. Sci., Phys. Ed., 18, 2037 (1980).

CHAPTER SEVEN

ONGOING, FUTURE, AND SUGGESTED WORK BASED ON THIS THESIS

I. INTRODUCTION

This thesis has described the synthesis and characterization of rigid rod star-block copolymers. In addition to these novel star-block copolymers, several new intermediates have been prepared for use in this work. This final chapter will describe the ongoing, future, and suggested work with respect to all of the new materials and procedures outlined in this thesis.

The novel materials prepared in this thesis have been the blocked amine functional anionic initiator, the telechelic linear and star shaped poly(dimethysiloxane)s, and the thermotropic and lyotropic rigid rod star-block copolymers. Many variations and new courses could be launched based on both the novel intermediates and the new star-block copolymers. Below, each of the four areas will be delved into furthur, with an eye towards exploitation of the new possibilities brought about by them.

II. THE BLOCKED AMINE FUNCTIONAL ANIONIC INITIATOR

As described in Chapter Three of this thesis, the new blocked amine functional anionic initiator opens up new possibilities for the synthetic polymer chemist. The key property of this new initiator is its solubility in nonpolar solvents. This allows for the preparation of new end-reactive materials by living anionic polymerization. In addition to the preparation of novel telechelic poly(dimethylsiloxane)s, this new initiator should be of particular utility in the preparation of high cis-1-4 telechelic dienes (1). The extensive use of diene polymers should make this new possibility an important one.

This new initiator was prepared by the quantitative reaction of sec-butyllithium with a styrene derivative. It is reasonable that other initiators could be prepared from suitably blocked functional styrene derivatives. A blocked p-hydroxystyrene monomer has been prepared and used to synthesize well-defined poly(p-hydroxystyrene) (2). This could lead to a new blocked hydroxyl functional anionic initiator with good nonpolar solubility.

III. NEW TELECHELIC POLYMERS

The successful preparation of the new blocked amine functional anionic initiator led directly to the preparation of the novel amine telechelic star polymers described in Chapter Four of this thesis. Although the telechelic poly(dimethylsiloxane)s were used as mere intermediates in the bulk of the thesis work, they could have several new and interesting scientific and technological applications.

Since the new blocked functional initiator is soluble in nonpolar solvents and should have the initiating power of a styrl anion, a great number of new amine telechelic linear and star polymers could be prepared using the methods outlined in this thesis. In addition to preparing new poly(dimethylsiloxane) telechelic star polymers of various arm numbers as described by Fetters (3), it should also possible to synthesize unique amine telechelic star polymers with other monomers such as styrene, diene monomers, ethylene oxide, or any other monomer capable of being used in living anionic polymerizations (4).

The siloxane telechelic stars prepared in this work showed some very interesting crystallinity properties that suggest future study. Most previously reported star polymers have been prepared from styrene and diene monomers to result in primarily amorphous materials (5). A study of the effect of arm number, arm length, and crystallization conditions on the crystallinity and morphology of the siloxane star polymers could prove quite interesting.

The preparation of well-defined, telechelic star polymers could lead to the synthesis of additional novel block copolymers. The work of this thesis concentrated on the attachment of rigid, mesogenic units onto the extremities of the flexible, star cores, however, any number of rigid and/or flexible segments could be attached via the amine function of these star polymers. It might be particularly interesting to design star-block copolymers where the degree of compatibility of the two blocks is varied over a wide range. This could lead to an interesting study on the effect of phase separation on the properties of well-defined star-block copolymers

These new telechelic star polymers could also be used in the preparation of ideal networks. Ongoing work in the research group is designed towards that end. The unique nature of such star polymers offers the opportunity to study well-defined networks.

IV. THE THERMOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

There are practically an infinite number of new possibilities regarding the development of thermotropic rigid rod star-block copolymers. However, it would be first useful to further characterize the novel thermotropic copolymers prepared in this thesis. Then any number of new thermotropic rigid rod star-block copolymers could be prepared.

Further study of the thermotropic rigid rod star-block copolymers prepared in this thesis should concentrate on the general morphology of the copolymers in the solid and mesophase state. It is likely that x-ray studies on these materials, both wide and small angle, could give interesting results. The key questions to be answered center around the morphology in the mesophase of these copolymers and the domain sizes of the rigid and flexible phases both in the mesophase and in the solid polymer states.

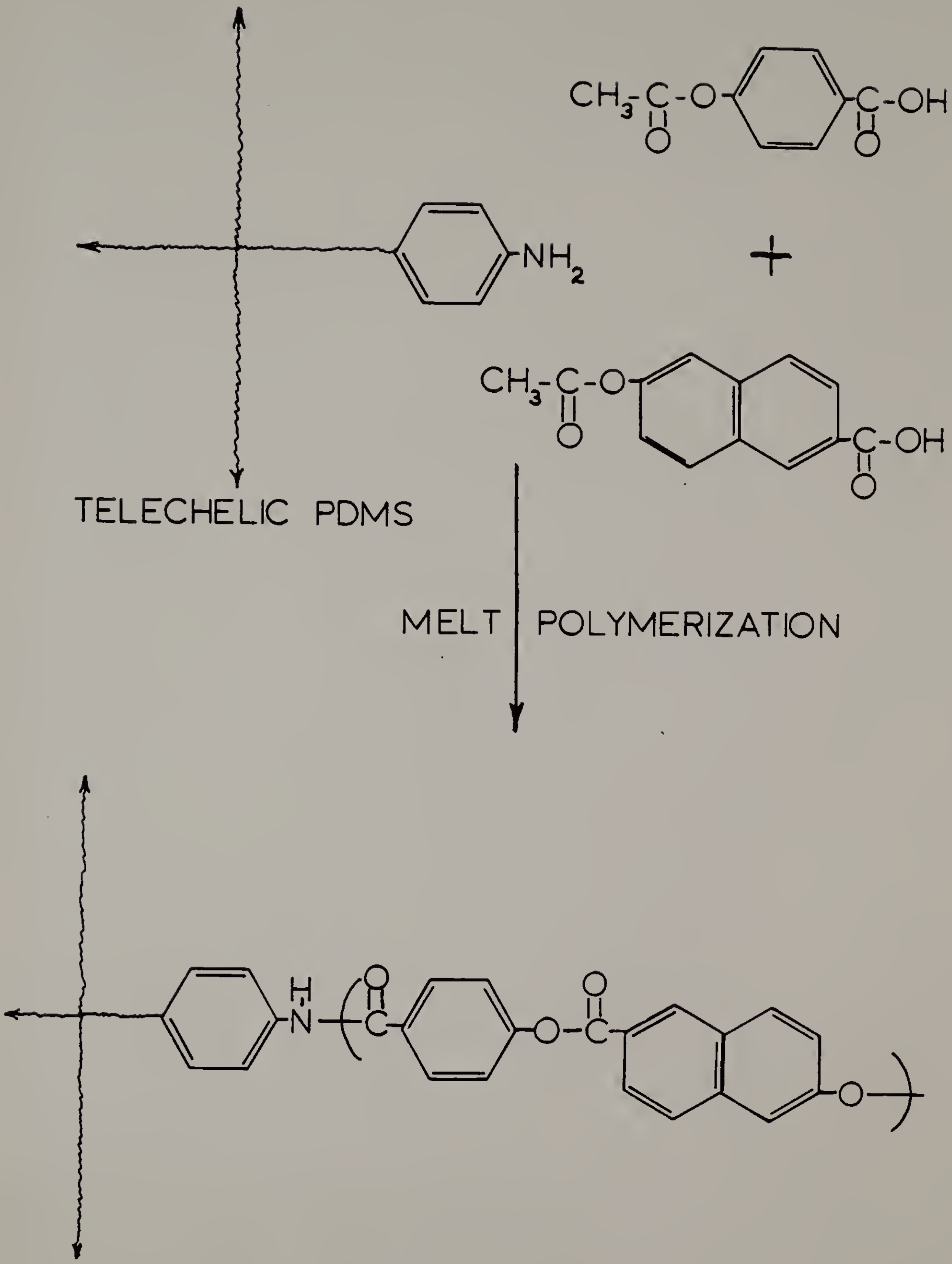
It would be interesting to attach other types of low molecular weight mesogens to the ends of the siloxane star cores. The attachment of various smectic, cholesteric, and especially discotic low molecular weight mesogens to the ends of the flexible star polymers should be straight forward due to the favorable reactivity of the aromatic amine end groups on the star siloxanes. Combined with scattering studies to understand the morphology of these materials, one could discover whether the star topology results in peculiar properties.

The preparation of thermotropic rigid rod star-block copolymers where the rigid unit is a high polymer would be particularly valuable work. It would be most reasonable to perform the synthesis described in Figure 7.1. This would result in the attachment of the recently commercialized Celanase thermotropic liquid crystalline polymer onto the ends of the siloxane star cores (6). This could lead to a study of the hypothesis regarding multi-dimensional strength outlined in Chapter One of this thesis with a thermotropic liquid crystalline polymer.

Finkelmann has described the preparation of unique liquid crystalline networks based on his side chain siloxane liquid crystalline polymers (7). The polymers which he has prepared have shown interesting liquid crystalline properties, however, they suffer due to their lack of a well-defined structure. The use of the methods outlined in this thesis could result in the preparation of well-defined liquid crystalline polymer networks.

Figure 7.1

A suggested reaction scheme for the preparation of a thermotropic rigid rod star-block copolymer with a high polymer block at its extremities. The resulting polymer would most probably be a melt processable thermotropic liquid crystalline copolymer. It would be best to perform a melt polymerization with the ester/acids shown.


CH3-C-O
C-OH
NH2
+
TELECHELIC PDMS
MELT
POLYMERIZATION
H
N
O
C

V. LYOTROPIC RIGID ROD STAR-BLOCK COPOLYMERS

There is a considerable amount of ongoing and future work planned or reasonable to perform regarding the lyotropic rigid rod star-block copolymers outlined in this thesis. After briefly discussing the ongoing work, some potentially interesting future and suggested work will be discussed in this section.

The ongoing work based on the lyotropic copolymers is in the areas of phase diagrams, rheology, optical microscopy, and fiber and film preparation. A complete rheological study of the lyotropic block copolymers has been progressing by Matt Muir under the supervision of Professor R.S. Porter. This work is designed to study many rheological properties including the effect of polymer concentration, effect of shear rate, and resulting normal force data on these novel block copolymers. Combined with optical microscopy, this work should lead to phase diagrams for the six block copolymers prepared in this thesis.

Studies are presently commencing with Professor R. Farris to study the fiber and film properties of the lyotropic copolymers. Used as homopolymers, or blended with suitable liquid crystalline polymers such as poly(_p_-benzamide) of poly(_p_-phenyleneterepthalamide), the block copolymers described in this thesis will be solution spun into fibers and films. This work will hopefully lead to a test of the hypothesis of multi-dimensional strength discussed in Chapter One of this thesis. Presumably, many new lyotropic rigid rod star-block copolymers will have to be prepared with varying flexible arm lengths and arm numbers as well as varied lengths of the rigid poly(p-benzamide) block to fully investigate this multi-dimensional strength hypothesis. In addition to the tie-molecule hypothesis, the effect of phase separation on crack propagation could prove to be interesting.

Other lyotropic rigid rod star-block copolymers could be prepared using the methods outlined in this thesis. Of particular interest, would be the preparation of copolymers with rigid poly (γ-benzyl-L-glutamate) (PBLG) blocks at the extremities of the star cores (8, 9). Hypothetically, this could lead to the preparation of star-block copolymers with well-defined rigid units as PBLG has been reported to be prepared by living anionic polymerization techniques (4).

In conclusion, the work described in this thesis can lead to the preparation and study of many new and interesting materials. These studies cover the fields of anionic polymerization, telechelic polymers, star polymers, block copolymers, and the general field of liquid crystalline polymers, fibers, films and networks.

REFERENCES

1. D.N. Schulz, J.C. Sanda, and B.G. Willoughby, *ACS Sym. Ser.*, *166*, 427 (1981).

2. A. Hirao, K. Takenaka, S. Packirisamy, K. Yamaguchi, and S. Nakahama, *Makromol. Chem.*, *186*, 1157 (1985).

3. N. Hadjichristidis and L.J. Fetters, *Macro.*, 13(1), 191 (1980).

4. R.W. Lenz, *Organic Chemistry of Synthetic High Polymers*, N.Y., Interscience Publ., (1967).

5. G. Odian, *Principles of Polymerization*, N.Y., Interscience Publ., (1981).

6. G.W. Calundann, U.S. Patent 4,161,470 (July 17, 1979).

7. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, *2*, 317 (1981).

8. A. Elliott and E.J. Ambrose, *Discuss. Faraday Soc.*, *9*, 246 (1950).

9. C. Robinson, J.C. Ward, and R.B. Beevers, *Discuss. Faraday Soc.*, *25*, 29 (1957).