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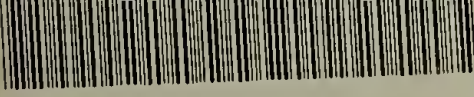
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RHEOLOGICAL PROPERTIES OF LIQUID-CRYSTALLINE
STAR-BLOCK COPOLYMERS

A Dissertation Presented

by

MATTHEW CAMPBELL MUIR

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

DOCTOR OF PHILOSOPHY

May 1989

Polymer Science and Engineering

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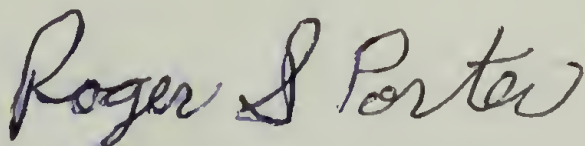
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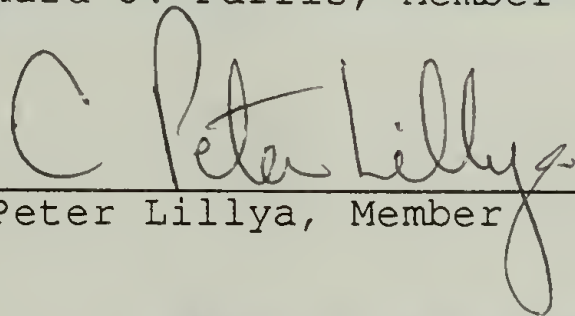
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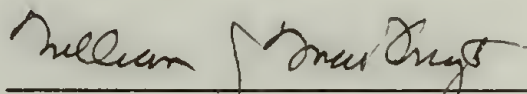
Roger S. Porter, Chairperson of Committee



Richard J. Farris, Member



C. Peter Lillya, Member



William J. MacKnight, Department Head
Polymer Science and Engineering

DEDICATION

To my parents, who constantly
impressed upon me the paramount
importance of education.

ACKNOWLEDGEMENTS

As one reaches the end of a Ph.D. program, he is remiss if he does not notice that any such degree is not wholly an individual effort. Indeed, science itself cannot be seriously attempted by anyone without enlisting the help of several people. This section of the dissertation is intended to thank friends, colleagues, and those who provided guidance to me as I needed it.

I would like to express my sincere appreciation to my advisor, Professor R.S. Porter. His scientific insight regarding my project was invaluable, and his encouragement during lean times of my work made me feel lucky to be working for a man who so well understood both science and people.

I also wish to thank the members of my committee, Professors C.P. Lillya and R.J. Farris, whose many suggestions, comments, and criticisms were an essential component of my understanding of the project.

I would particularly like to thank Bill Dickstein, the highly creative initiator of this project, who synthesized the star-block copolymers and interested me in the project. His enthusiasm for and ideas about the project taught me much.

Jerry Parmer, Youngchul Lee, Kevin Schell, and Eric Beckman, with whom I entered Dr. Porter's research group and sweated out the cures, deserve special mention for their friendship and diverse interests. Over the years, I have learned greatly from and been broadened by each of them.

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I hope I can be forgiven for not mentioning the names of everyone outside of Dr. Porter's group, but some who come to mind immediately are: Scott Starry, never too busy to be an unpaid consultant on X-Ray and computers, and Margaret Rakas, who helped me understand X-Ray and fibers.

Lastly, I am most grateful to my wife, Eva. I will never forget nor cease to appreciate her constant love and support during this long, arduous sojourn.

ABSTRACT

RHEOLOGICAL PROPERTIES OF LIQUID-CRYSTALLINE
STAR-BLOCK COPOLYMERS

MAY, 1989

MATTHEW C. MUIR, B.S., UNIVERSITY OF MASSACHUSETTS

Ph.D., UNIVERSITY OF MASSACHUSETTS

Directed by: Professor Roger S. Porter

This dissertation details the study of the properties of some unique radial, or 'star', liquid-crystalline polymers: block copolymers with poly(dimethyl siloxane) (at the arm centers) (PDMS) and poly(p-benzamide) (at the ends) (PBA). They were studied in the solid state and in solutions with dimethylacetamide/ lithium chloride. The critical variable was the molecular weight of the siloxane, which was varied from 650/arm to 4250/arm. The molecular weight of the PBA was held constant, at an $M_n = 7000/\text{arm}$, for all the star-block copolymers. In total, there were four such radial copolymers for study, as well as one linear block copolymer, used as a standard for comparison.

Characterization of the solid copolymers was performed using Thermogravimetric Analysis (TGA) and X-Ray Scattering. The copolymers are soluble with difficulty. The solutions obtained were characterized in the quiescent state by polarized-light microscopy (PLM), and by Wide- and Small-Angle X-Ray Scattering (WAXS, SAXS). It was found by PLM

that the PDMS spacer length greatly influenced the ability of the polymers to form a liquid-crystalline solution. The block copolymers of highest PDMS molecular weight (largest flexible spacer), above 1500/arm, formed anisotropic solutions. Below this molecular weight, the solutions were isotropic at concentrations up to saturation.

Rheological characterization was performed by steady-shear solution rheology in both the cone-plate and parallel-disk modes. The viscosity and normal-stress behavior of the solutions were evaluated with respect to concentration and liquid-crystallinity. It was found that both the isotropic and mesophasic solutions were sharply shear-thinning, with no low-shear Newtonian plateau. The liquid-crystalline polymers were found to exhibit a "rheological phase diagram", a peak in viscosity vs. concentration, confirming the phase behavior observed by polarized-light microscopy. The solutions showed a positive primary normal-stress coefficient which decreased with increasing shear rate, and which also was dependent on the presence or absence of liquid-crystallinity in the solutions.

To understand further the deformation behavior of the solutions, fibers were spun from the solutions and the results characterized by X-Ray Scattering. It was found that the fibers spun from anisotropic solutions showed a greater degree of crystalline orientation.

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CHAPTER 1

INTRODUCTION

1.1 Definition of The Project

The intense interest of recent years in liquid-crystalline polymers (LCPs) has recently been merged with that of another compositional aspect of polymer science: that of 'star', i.e., polymers of radial geometry. The former have found broad applications as high-strength, high-modulus fibers; the latter have been of interest as theoretical tests of theories of polymer viscoelasticity and as polymers with specialized uses such as viscosity modification or functionalization of endgroups.

The synthesis of a set of star LCPs by Dickstein¹ opened interesting technical questions. As a new class of LCPs, the rheological and morphological properties of any such copolymers would be of interest. In addition, the copolymers may have the potential for improving the transverse properties of fibers and films formed from LCP solutions and melts.

The copolymers synthesized, star-block copolymers of poly(dimethyl siloxane) (PDMS) and poly(p-benzamide) (PBA), are of interest not only for their star morphology and their liquid-crystallinity. These polymers are also of interest for the fact that they are copolymers of an extremely rigid polymer backbone with one of the most flexible. In addition,

the compatibility of the two is of interest: PDMS and PBA are at opposite ends of the solubility-parameter chart.

The work of Dickstein identified which of the star copolymers were in fact LCPs in solution, but did not identify the concentrations of the isotropic-liquid crystalline transition. Nor was there insight into the morphological and rheological properties. The purpose of this dissertation has been to investigate some of these questions, focusing primarily on the steady shear rheology of the solutions.

This dissertation is composed of five main chapters. The first contains the rationale for the investigation, and literature reviews of the rheology of LCPs and star polymers. The second details the characterization work, focusing on polarized-light microscopy, thermogravimetric analysis, and x-ray scattering. The third describes the rheological investigation, in which the steady-shear behavior of the polymers in solution was studied. Chapter 4 describes morphological work performed on the solutions, solid polymers, and fibers spun from solutions. The final chapter includes suggestions for future investigations in the general field of star LCPs.

1.2 Literature Review: Processing Rheology of Liquid-Crystalline Polymers

1.2.1 Introduction

The success realized by duPont with Kevlar^R and similar lyotropic polyaramides has led to considerable interest in the processing and properties of liquid-crystalline polymers (LCPs). The attractiveness of lyotropic LCPs lies, for the most part, in their ease in attaining high uniaxial orientation. As a consequence, the fibers formed show excellent tensile modulus and tensile strength.

The rheology of LCPs has been reviewed by Porter and Johnson², Baird³, and Wissbrun⁴. The formation of fibers and other properties of LCPs have been reviewed by Black⁵, Chandrasekhar⁶, by Dobb and McIntyre⁷, and by White⁸. In addition, the book by Ciferri, Krigbaum, and Meyer⁹ contains several useful reviews. The reader may also wish to refer to the bibliography recently compiled by Hinov¹⁰ for a list of recent thermotropic references. This review shall focus on recent developments concerning the effect of main-chain LCP rheology on processing variables and ultimate properties.

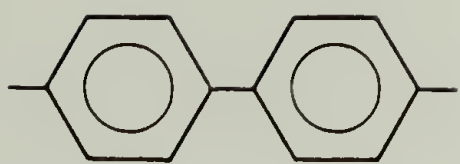
The aggressive solvents required to process lyotropic LCPs suggest the alternative of thermotropic polymers (TLCPs) to achieve similar results, while avoiding the costly and difficult processing schemes inherent in lyotropic LCPs. The advantages of TLCPs also include the fact that conventional

processing equipment can be employed, and that complicated parts can be manufactured.

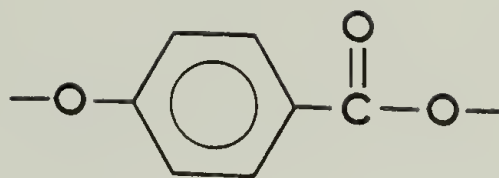
The field of TLCPs was pioneered by such industrial workers as Economy¹¹, who made wholly aromatic copolyesters of p-hydroxybenzoic acid (HBA) and terephthalic acid (TA), and copolyesters of hydroquinone (HQ), and HBA, TA, and 4,4'-biphenyl (BP); Jackson and Kuhfuss¹², who synthesized a copolyester of poly(ethylene terephthalate) and HBA; Morgan¹³, who spun fibers from aromatic polyazomethines. A number of fully aromatic TLCPs, including copolyester combinations of HBA, hydroxynaphthoic acid (HNA), and hydroquinone (HQ), have been made by Calundann and coworkers at Celanese¹⁴. Figure 1.1 summarizes the structures of some typical TLCPs.

1.2.2 Control of Processing Temperature

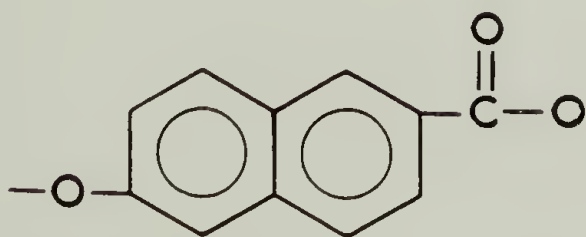
The classic problem with TLCPs has been that of compromise: in order to obtain a processible system, it has been commonly deemed necessary to incorporate chain units to disrupt the otherwise rigid, linear aromatic chain. These disrupting units may take the form of random copolymerization, bent or "swivel" components. The common theme in each of these approaches is that they disrupt the crystalline structure and thus lower the crystal-nematic transition temperature, T_{kn} . While these randomizing and kinking components serve the recognized function of



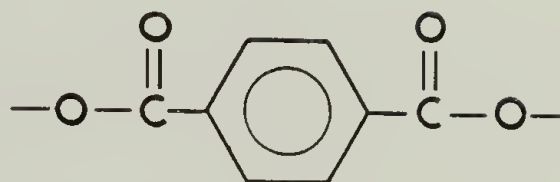
Biphenyl (BP)



p-Hydroxybenzoic Acid (HBA)



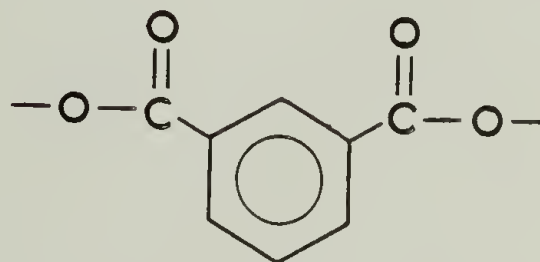
Hydroxynaphthoic Acid (HNA)



Terephthalic Acid (TA)



Hydroquinone (HQ)



Isophthalic Acid (IA)

Figure 1.1. Typical structural components of thermotropic polymers.

tractabilizing the polymers, they also limit the attainable modulus through imposing limitations on attainable crystallinity and on chain orientation. One scheme to resolve this dilemma is that of George and Porter¹⁵, who mixed a low-molecular weight thermotropic liquid-crystalline species (LMLC) with a polymeric TLCP. In principle, by proper choice of LMLC and TLCP, the desired depression in T_{kn}^{16} can be achieved for ease of processing; once the blend is formed into a fiber or shaped part, a solid-state transesterification can be induced by heat, resulting in a fully rigid, high-strength solid. Model experiments confirmed the premise of this scheme, including a lower melt viscosity of the blend and a higher thermal stability of the finished, heat-treated product; however, aided processing of a TLCP has not yet been further demonstrated.

1.2.3 Three-Region Flow Curve

One method for categorizing the rheology of LCPs is the three- region flow curve proposed by Onogi and Asada¹⁷. Briefly, they describe a phenomenon, seen with some LCPs, where the η - $\dot{\gamma}$ curve can be divided into three sections: Region I, II, and III. As Figure 1.2 shows, Regions I and III are shear-thinning; Region II shows slight or zero variation of log viscosity with log shear rate. This behavior contrasts with that observed for isotropic polymer melts and solutions, as Figure 1.2 also shows.

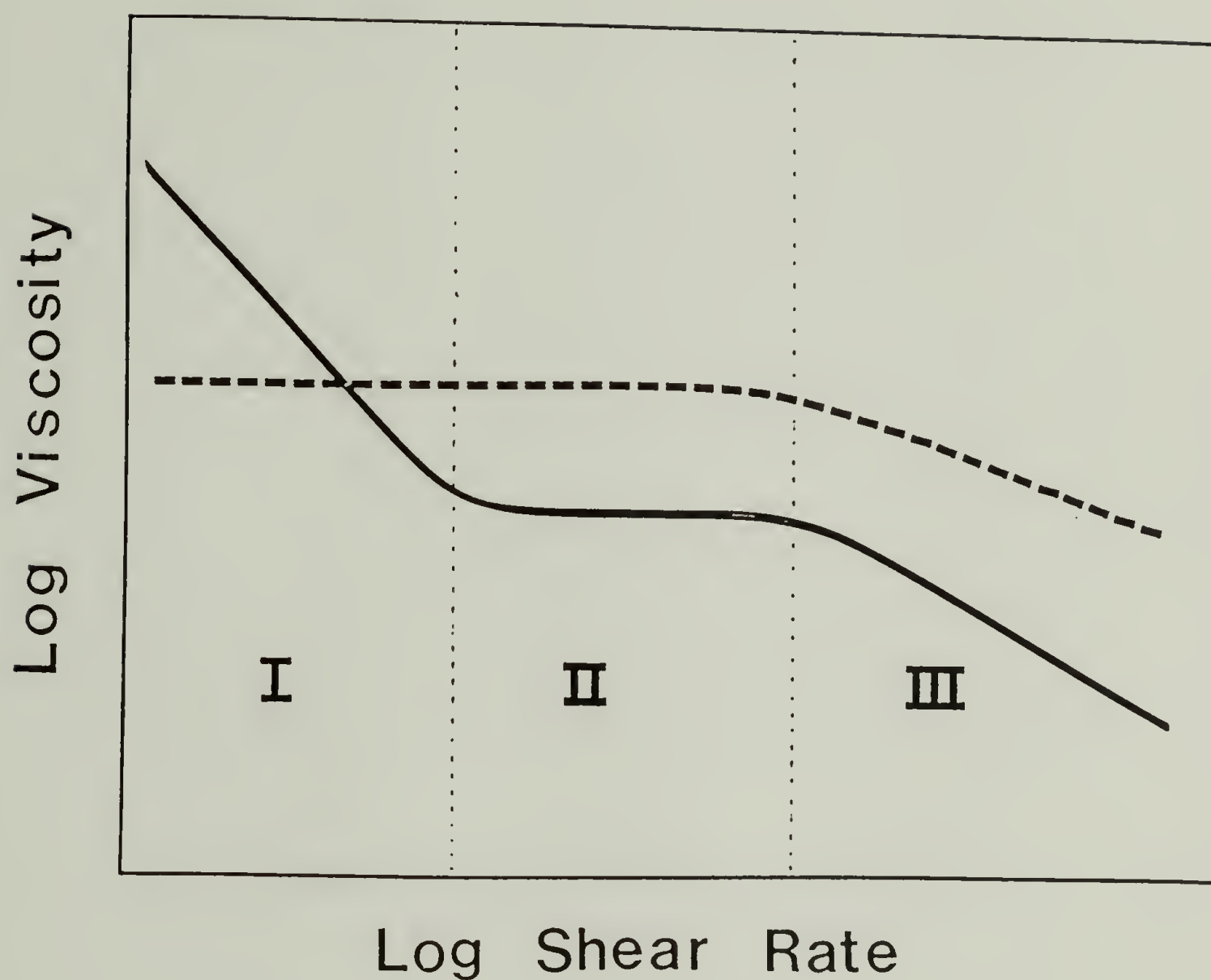


Figure 1.2. The Asada Three-Region Flow Curve. The solid line represents the proposed general curve for LCPs; the dotted line, the general curve for conventional polymer solutions and melts.

Generally, many LCPs show at least shear thinning at low shear rates (Region I). This has been described as yield, but this term is probably inexact for most LCP behavior. Metzner and Prilutski¹⁸ observed, with lyotropic HPC solutions, that small bubbles rose out of the quiescent fluids, indicative of a finite zero-shear viscosity. In addition, the slope of the $\log \eta$ vs. $\log \dot{\gamma}$ curve is not -1, which would be expected for systems showing a yield stress.

Rheo-optical observations suggest that flow in Region I occurs by motion of "domains", which become smaller in size and more oriented with increasing shear rate¹⁹.

Many theoretical treatments have been advanced to describe Region I behavior. Marrucci²⁰ applied Asada's observations to a model which predicts Regions I and II. The model involves the concept that a "domain" is a set of disclinations in a director field such that there is no net orientation over the entire domain (Figure 1.3). This model, however, predicts an increase in net orientation of the domains with shear rate, and that the number of domains remains constant as they decrease in size.

A revision of the Marrucci model was made by Wissbrun²¹, including the same definition of a domain, but rejecting the assumption of flow-induced orientation, and allowing the number of domains to increase commensurate with their decrease in size. His calculations, with the aid of non-equilibrium molecular dynamics, result in a slope of the \log

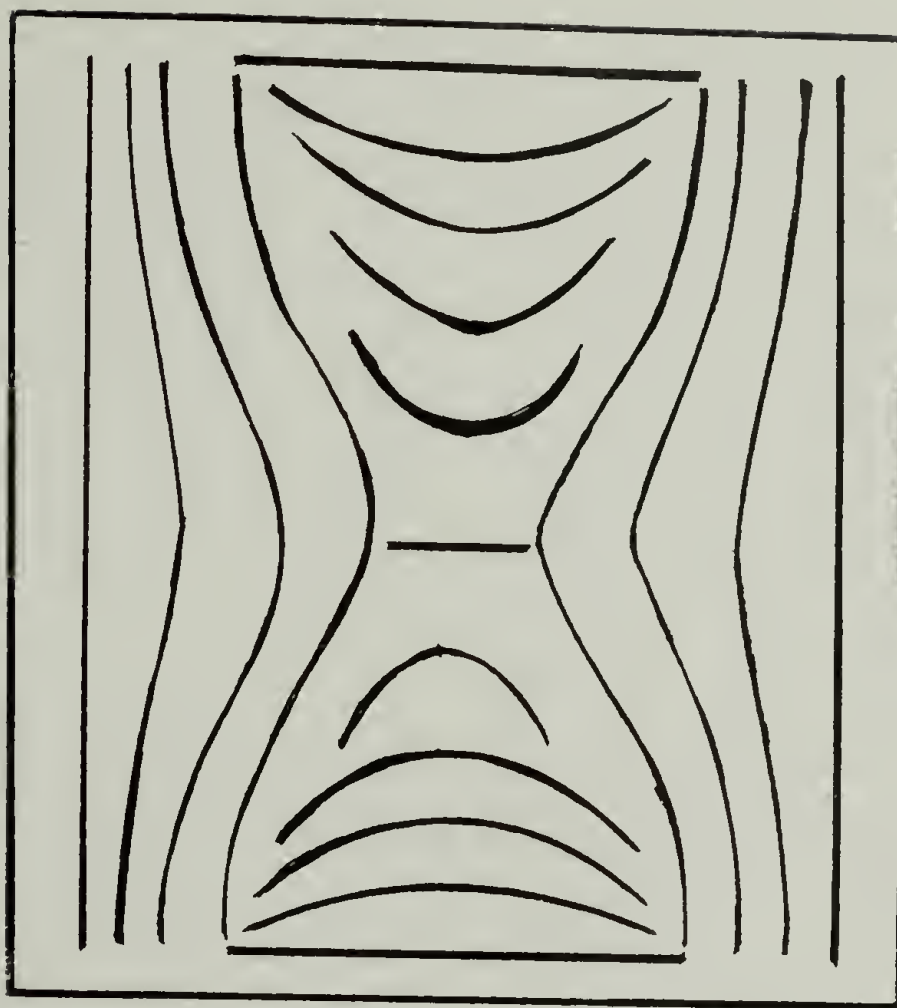


Figure 1.3. Marrucci's description of a "domain", a collection of liquid-crystalline moities exhibiting disclinations and no net orientation.

viscosity-log shear rate curve which varies from $-1/3$ to -1 , and no prediction of a Region II.

Asada et. al. hypothesize that the 3-region curve is characteristic of all LCPs, lyotropic and thermotropic, to the extent of suggesting that this behavior be recognized as a criterion of liquid-crystallinity in polymers²². However, this behavior may not be so general. In particular, many TLCPs show only region I or III²³. Yanase and Asada claim to see I, II, and III with a PHB/PET thermotropic copolyester, 'UT-4', but his data are not conclusive. For example, in their Figure 4, the existence of Region I is claimed on the basis of only one datum.

Even lyotropic LCPs do not comply uniformly with this "rule". Regions I, II, and III are seen by Yanase and Asada²⁴, but not by Moldenaers and Mewis²⁵ with nematic solutions of PBG. The data were obtained for similar molecular weights, and over a similar range of shear rates, but Yanase's solutions were more concentrated. Einaga et. al.²⁶ observed all three regions with nematic solutions of PBT, extending to shear rates as low as 10^{-4} s^{-1} . The importance of this last work must be emphasized, as many of the observations, i.e., the lack of all three regions can be the studies have been limited to shear rates in the range of 10 to 10 s^{-1} . This can be seen as a limitation of many of attributed to insufficient data at low or high shear.

In fact, extending the shear range would be desirable. If orientation of molecules or breaking of a domain structure is to be accepted as the mechanism for the shear-thinning behavior, then "Newtonian" regions must be observable at sufficiently high and low shear rates. A dimensional analysis model by Chaffey and Porter²⁷ describes regions II and III, as well as a high-shear plateau viscosity η .

Incidentally, much of the data obtained has been based on oscillatory shear. This has some analogy to processing conditions, particularly when the "Cox-Merz" rule, indicating a direct equivalence between dynamic and steady shear, applies²⁸. However, one must be cautious in drawing such analogies, because some LCPs show behavior that violates this rule²⁹.

1.2.4 Thermal and Shear Dependence of Viscosity

LCPs are unique in the richness of variations in their behavior with respect to thermal and shear history. Variables which may often increase the viscosity of conventional polymers can have the reverse effect with LCPs, a phenomenon which has exciting implications for processing. One point of interest with TLCPs has been the anomalous temperature behavior of bulk viscosity η , as seen, for instance, in the work of Kiss³⁰, with a HBA/HNA/HQ copolyester (Figure 1.4); Acierno, et. al.³¹, with a series of PET/HBA polymers; Simoff³², with a bisphenol E/isophthalate-naphthalate terpolymer; and Tuttle et. al.³³,

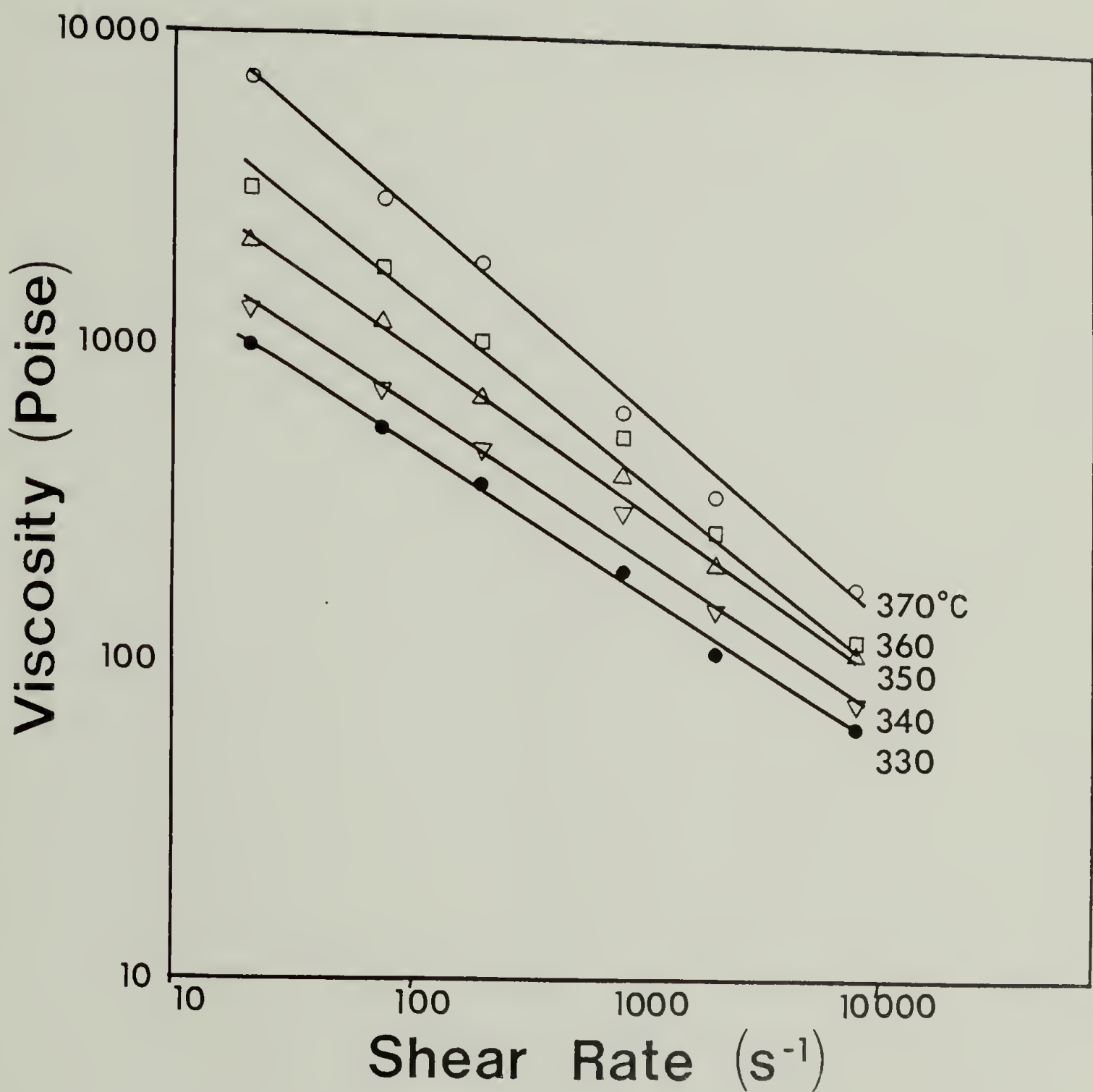


Figure 1.4. Viscosity vs. shear rate at several temperatures for a HBA/IA/HQ copolyester TLCP, showing anomalous behavior (from Kiss³⁴).

with an aromatic/aliphatic polyester. With these TLCPs, a lowering in viscosity with decreasing temperature has been observed. The lower energy requirements inherent in processing lower-viscosity materials may represent a significant advantage. This behavior was predicted as an analog to the behavior of viscosity with concentration in lyotropic polymers³⁵, the proposed explanation lying in the ease of orientation of the liquid-crystalline domains. This would reduce the effective hydrodynamic volume of the system, and thus lower the viscosity³⁶. This explanation conforms to the observation of a subsequent increase in viscosity with further increasing temperature, as the ease of orientation of domains is reduced.

Kiss explained his observations with the existence of a biphasic state: an "isotropic-anisotropic melt", produced in part by a variation in composition, and thus in chain stiffness, of the random copolymer. The competition between these phases is said to be influenced by composition, temperature, and shear, although no direct evidence to support his assertion of the existence of a biphasic melt is reported.

It must be emphasized that this phenomenon- increasing η with temperature- is not general for all TLCPs. For example, Bickel et.al.³⁷ observed, for a modified PET-HBA-like polyester, a nearly monotonic decrease in η with T , with a shoulder seen in the curve in the vicinity of T_{ni} .

Complicating these phenomena is the observation of time- and shear-dependent rheology in TLCPs. Gochanour and Weinburg³⁸ observed, after shearing, increases in the dynamic viscosity η^* , in the non-Newtonian character, and in the elasticity of the melt. The explanation they advanced is that the content of a crystalline phase is continually increasing with time at elevated temperature. They offer support in the form of DSC studies of annealing.

Wissbrun and Griffin³⁹ observed interesting phenomena with an aromatic thermotropic polyester. In the isotropic phase, no history-dependence was observed, but the dynamic loss modulus and viscosity in the nematic state decreased markedly after being subjected to steady shear. This behavior was erased after reheating to the isotropic phase. No explanation was offered, but this behavior may be due to thermally-reversible orientation of domains in the nematic state.

Similar observations have been reported with another TLCP by Cogswell⁴⁰, who observed a lowering in the viscosity after pre-shearing. This observation is consistent with the work of Krigbaum and Salaris⁴¹, by whose DSC studies they showed a dependence of phase behavior on thermal history for the same copolyester (Figure 1.5). The explanation advanced by Cogswell is that of a heterogeneous "melt", similar to Kiss' suggestion.

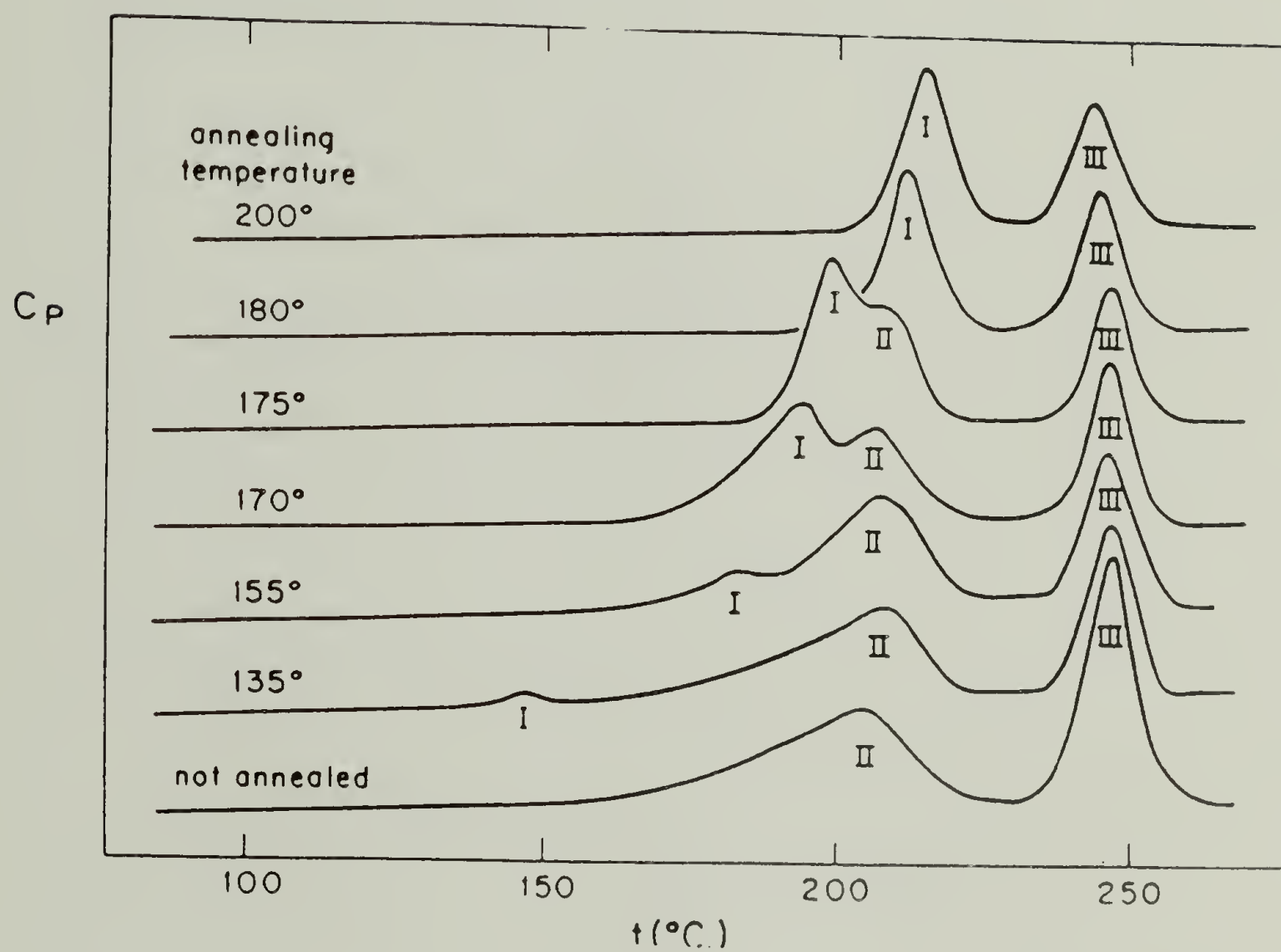


Figure 1.5. DSC scans for a PET/HBA TLCP, showing the influence of thermal history on the phase behavior⁴².

1.2.5 Mechanism of High Orientation

A problem of considerable interest, from both the academic and industrial points of view, is the mechanism for the high orientation obtainable in LCPs. In fact, the initial rationale for synthesizing TLCPs, production of inexpensive high-strength fibers and films, has met with disappointment. Table 1.1 compares the fiber properties of several LCPs with those of other materials. It is seen that the tensile moduli of TLCPs do not compare favorably with those of lyotropic LCPs or many other materials. The reason for interest in orientation behavior is then clear: an understanding of the orientation mechanism would contribute to improved properties of fibers, as well as allowing orientation to be inhibited when that is desirable.

Significant strides have been made in this area lately. The classical theory of Ericksen⁴³, Leslie⁴⁴ and Parodi⁴⁵ describes the flow of a low-molecular-weight liquid crystal (LMLC) in terms of ordering of the director in shear. Many of the qualitative predictions of this theory have been borne out with LCPs. A difficulty with this model is that it describes the base fluid as Newtonian, a questionable assumption with LCPs. Akay and Leslie⁴⁶ address this shortcoming with a model which describes well the orientation of LCPs and fiber-reinforced thermoplastics in converging and diverging flow. More recently it has been found experimentally that, especially with TLCPs, a shearing flow

Table 1.1. Properties of high-strength, high-modulus fibers.

<u>Material</u>	<u>Strength</u>		<u>Modulus</u>		<u>Elongation</u>
	<u>GPa</u>	<u>g/d</u>	<u>GPa</u>	<u>g/d</u>	<u>to Break, %</u>
<u>Lyotropics</u>					
Polyazomethines ⁴⁷		38		1012	4.4
PBT ⁴⁸	2.4	20	250	2000	
Aramid fiber	2.8	22	124	970	2.8
PPT, PBA Dry-spun	1.1		65		3.1
Annealed	2.2		137		1.9
PPT/PPA As-spun	2.2	17	76	570	4.5
Heat-treated	2.5	19	265	2000	1.0
Kevlar ^R 29 Wet-spun ⁴⁹	2.6	21	59	460	4.0
49	2.6	21	128	1000	2.4
<u>Thermotropics</u>					
HBA/HNA As-spun	1.2	10	74	600	
Heat-treated ⁵⁰	2.4	20	124	1000	
PET/HBA	1.7	14	40	320	
<u>Other Thermoplastics</u>					
Nylon Yarn	1.0	9.8	6	55	18
Polyester Yarn	1.1	9.2	14	110	15
Polyethylene (Gel-spun) ⁵¹	3.9	44	124	1400	
Nomex	0.7	5.7	17	140	22
<u>Other Materials</u>					
E-HTS Glass	2.4	11	69	310	3-4
S-Glass	3.3	14.5	88	390	3-4
Steel Wire	3.1	4.5	210	300	2-3
Carbon I	2.0	11.6	40	2300	0.5
II	2.6	16.8	260	1700	1.0

field alone is not sufficient to form a highly oriented system. In particular, the work of Viola and Baird⁵² has shown that, not only does shear flow not always generate exceptional orientation, but the orientation induced, even by extensional flow, can relax at a high rate. Their amendment to the commonly accepted model suggests that the behavior seen with LCPs is due to a disruption of a domain structure, rather than the alignment of rod-like molecules in a domain. This model, and Viola and Baird's observations of a lack of orientation, is consistent with the wide observation of a "skin-core" morphology (Figure 1.6) in fibers spun and parts molded from thermotropic polymers⁵³. Although the difficulty in attaining and holding high degrees of orientation in shear flow is not unique to TLCPs, This problem is perhaps particularly acute with TLCPs, since the low degree of crystallinity which they often possess⁵⁴ results in a strict requirement of orientation development for exceptional properties. Acierno et. al.⁵⁵ note that, in some cases, the nematic phase constitutes little advantage in fiber formation. With the HBA/PET samples which they spun into fibers, they found that those spun from an isotropic melt showed a higher modulus than fibers spun from the nematic state. This was explained by chain entanglements in the melt; especially with polymers of lower molecular weight than that required for facile entanglements, the desired

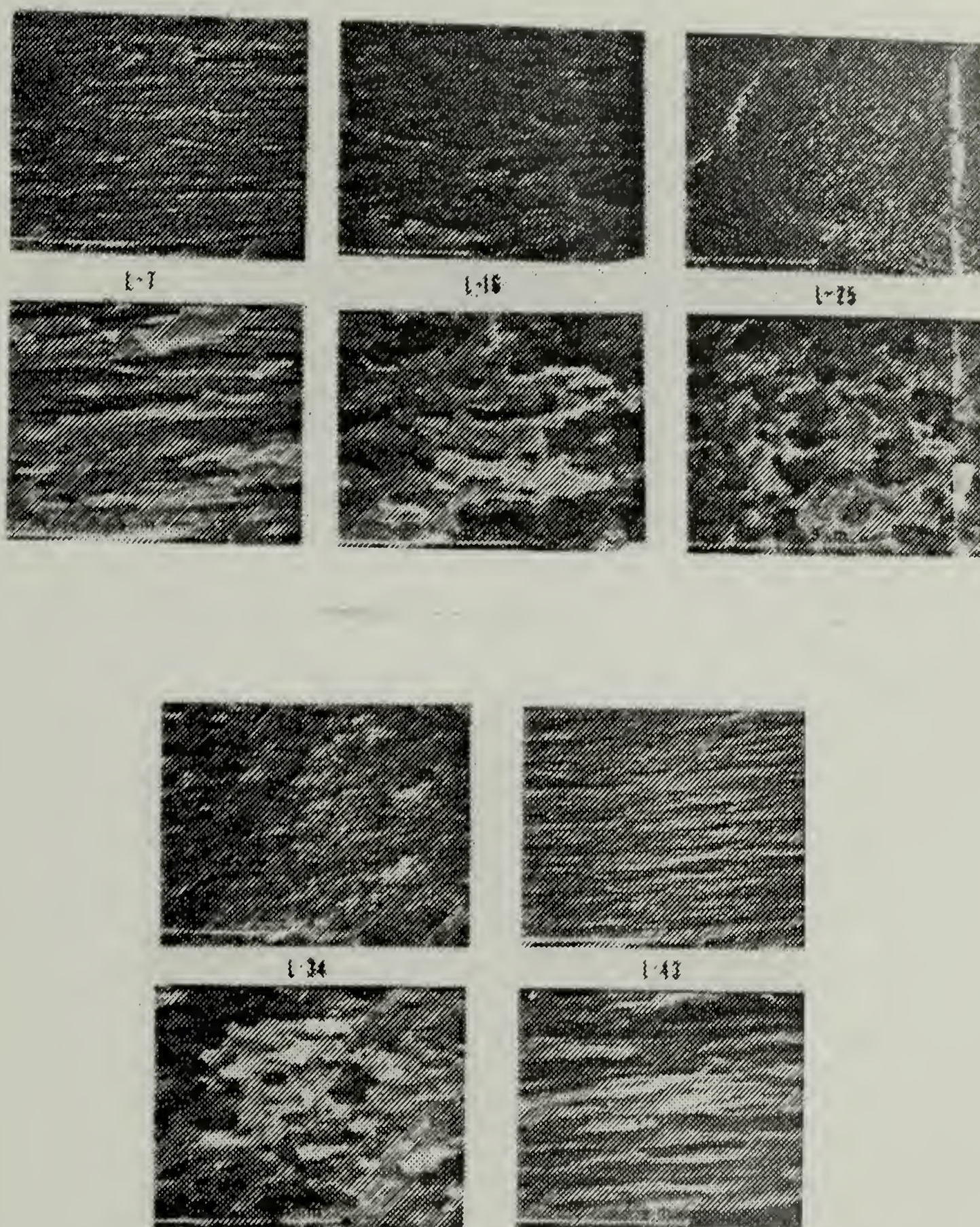


Figure 1.6. Photomicrographs of an extruded HBA/PET TLCP, showing skin-core morphology⁵⁶.

orientation may in fact reduce entanglement density, lowering the attainable modulus.

1.2.6 Transverse Properties

Highly oriented LCP fibers necessarily means that secondary forces (e.g., hydrogen bonding) are responsible for all strength in directions perpendicular to the fiber axis⁵⁷. This leads to weakness in any loading other than tensile. Thus, compressive, transverse, or cyclic loading can result in fibrillation in fibers and delamination in films. One approach to minimizing this weakness is the synthesis of block copolymers. Takayanagi and coworkers have synthesized block copolymers of nylon and Kevlar⁵⁸; Dickstein and Lillya⁵⁹ have synthesized unique lyotropic and thermotropic radial block LCPs. Hwang, et. al.⁶⁰ formed triblocks of poly(p-phenylene benzobisthiazole) with aromatic thermoplastics. The rationale for each of these syntheses is that the amorphous components can form interlamellar tie chains, hopefully resulting in improved strength in the transverse direction, perhaps with some loss of properties in tension. Although each of these techniques can result in a molecular composite, ultimate properties have not thus far been tested.

1.2.7 Blends With Isotropic Polymers

Another interesting idea utilizing TLCPs is that of forming blends with isotropic polymers, both crystalline and

amorphous. Blends prepared by Kiss⁶¹, a series of blends of poly(ether sulfone) (PES) and naphthalene-containing polyesters; Cogswell et. al.⁶², of several thermoplastics and TLCPs; and Apicella, et. al.⁶³, of polystyrene with a copolyester, have shown several advantages: improvement in mechanical properties (i.e., an in situ composite), lowering of viscosity of the melt, lowering of processing temperature, and avoidance of wear on processing equipment. All of these studies differ from that of Huh et. al.⁶⁴, who blended LMLCs with polystyrene, with the intent of having the low-viscosity LMLC phase-separate and lubricate the isotropic polymer in processing.

1.2.8 Normal Stresses and Die Swell

Another observation of great practical interest had its roots in the observation of a negative first normal stress difference in some lyotropic systems⁶⁵. It was postulated that this would lead to negative "extrudate swell". While the origin of this unusual normal stress behavior is poorly understood, the effect- negative extrudate swell- has been observed for some systems⁶⁶, while very low extrudate swell has commonly been seen with TLCPs. This feature is clearly very attractive to those interested in the design of dies and injection cavities for TLCP processing, particularly for thin sections.

The mechanism for this behavior is not well understood. A dimensional analysis by Chaffey and Porter⁶⁷ describes the

phenomenon in terms of a dumbbell model and a compressive force along the streamlines. The magnitude of the predicted negative normal stress and the shear-rate range over which it occurs are underestimated, perhaps due to their assumptions in the intermolecular interaction potential.

1.2.9 Summary

The processing rheology of TLCPs is complex. There are several issues in need of solution. Perhaps the greatest of these lies in the measure and control of orientation. While TLCPs have found some applications as moderately high-strength, low-weight, high-temperature materials, they lag the lyotropics. More work needs to be done in terms of a complete characterization of orientation in extensional and biaxial flow fields. More data are required in steady shear flow, also, for careful application of rheological data to processing conditions. Regarding the three-region flow curve, it appears that this is a characteristic of several, but not all, lyotropic systems and few or no thermotropic systems. In pursuit of an explanation of the curve, extension of the data on several systems to low shear rates would be highly enlightening to see if indeed there is a low-shear limit justifying the liquid aspect of thermotropic polymer liquid crystals.

1.3 Literature Review: Star Polymers and Star-Block Copolymers

As described in section 1.1, star polymers serve as a testing device for rheological theories. In particular, the morphology of branched and star polymers lends itself to facile manipulation of the elements of the Doi-Edwards "reptation" theory⁶⁸ of polymer viscoelasticity.

In addition, as noted previously, star-block copolymers have proved valuable in the interesting phase and morphological behavior which they display, in part due to their blocky nature.

1.3.1 Rheological Studies

The rheology of star polymers has been studied by Pearson and Helfand⁶⁹, whose model focused on an arm of a star, which would have to retract into a "tube" coincident with that surrounding other arms. This "reptation" formulation of the problem was first studied by Doi and Kuzuu⁷⁰. The resulting lower net rate of diffusion results in a viscosity much higher than that of the corresponding linear polymer. In comparison to linear polymers, the self-diffusion rate would be lowered further by higher hydrodynamic volume: because of excluded volume interactions at the center of the star, Vlahos and Kosmas⁷¹ found that the arms of stars would have a greater mean square radius of gyration than linear polymers of equivalent molecular weight. This effect was found to be greater with lower molecular

weight and with a greater number of arms; both variables are related to the relative effect of the excluded volume interactions at the center. Miyake and Freed⁷² determined that, while the star centers show an extended conformation, the ends have a conformation that is nearly a random walk, i.e., the excluded volume interactions are of less consequence as the length of the arms increases. These theoretical predictions were experimentally verified by Roovers et. al., utilizing ultracentrifugation, gel permeation chromatography, and small-angle light scattering⁷³ for dilute solutions of 12- and 18-arm polystyrenes. By sedimentation velocity and intrinsic viscosity, they found that the polymers in dilute solution had nearly the hydrodynamic characteristics of hard spheres.

Masuda et. al.⁷⁴ studied a series of star polystyrenes with branch molecular weights varying from 13 000 to 200 000 and with number of arms varying from 7 to 39. They found that stars with many arms (≥ 15) displayed two sets of relaxation times, which were attributed to the normal relaxation time spectrum of the parent polymer, in addition to a spectrum resulting from the branching.

For 12-armed polystyrenes in ternary solutions with poly(vinyl methyl ether), Lodge and Markland⁷⁵ found that the star topology was not important in determining the translational diffusion of the PS; nor was reptation a significant mechanism for the flow behavior. These results,

obtained from dynamic light scattering, were interpreted as showing higher mobility of PVME than of the PS stars.

1.3.2 Phase Behavior of Star-Block Copolymers

The fact that many star polymers are also block copolymers has led to interesting phase behavior. The morphology of block copolymers is well known. Possible morphologies of AB and ABA block copolymers include spheres, cylinders, and lamellae of the dispersed medium in the continuous component. For star-block copolymers, however, an ordered bicontinuous double diamond (OBDD) structure was observed by Alward et. al.⁷⁶, Kinning et. al.⁷⁷, Thomas et. al.⁷⁸, and Herman, et. al.⁷⁹. The characteristic of this structure, seen by transmission electron microscopy, is a set of two three-dimensional networks, mutually interwoven but unconnected, of tetrahedrally arranged polystyrene embedded in a polyisoprene matrix.

The OBDD structure, seen at concentrations intermediate between those of PS/PI lamellae and those of PS cylinders in a PI matrix, is described as occurring as a result of slight curvature of the PS/PI interface.

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CHAPTER 2

GENERAL CHARACTERIZATION OF THE SYSTEMS

2.1 Introduction

Samples of the five star-block copolymers, listed in Table 2.1, were obtained as synthesized by Dickstein⁸⁰. Each radial polymer was a four-armed, star-block copolymer of poly(p-benzamide) (PBA) and poly(dimethylsiloxane) (PDMS), with the siloxane block attaching the PBA block to the center of each arm (Figure 2.1). For comparison, a linear PBA-PDMS-PBA tri-block copolymer was obtained, approximating the characteristics of the radial copolymer of lowest molecular weight. The M_n /arm of the siloxane centers ranged from 650 (ST-1) to 4250 (ST-4), with corresponding compositions of 9.8 to 35.3 wt. % PDMS (Table 2.1). The PDMS was synthesized anionically, with polydispersity of ~1.3. The PBA was synthesized by the "Yamazaki" condensation reaction⁸¹.

There are two known solvents for PBA: Dimethylacetamide (DMAc)/Lithium Chloride (LiCl) and Sulfuric Acid⁸². The latter is incompatible with PDMS; thus the former was chosen as the solvent. All copolymers were dissolved in an anhydrous solution of 3.0 wt. % LiCl in DMAc. The lithium salt is thought to complex with the PBA, thus solubilizing the polymer in DMAc⁸³. To conserve copolymer while studying a range of concentrations, solutions were successively diluted, in order to avoid complications of increased LiCl concentration upon volatilizing the DMAc.

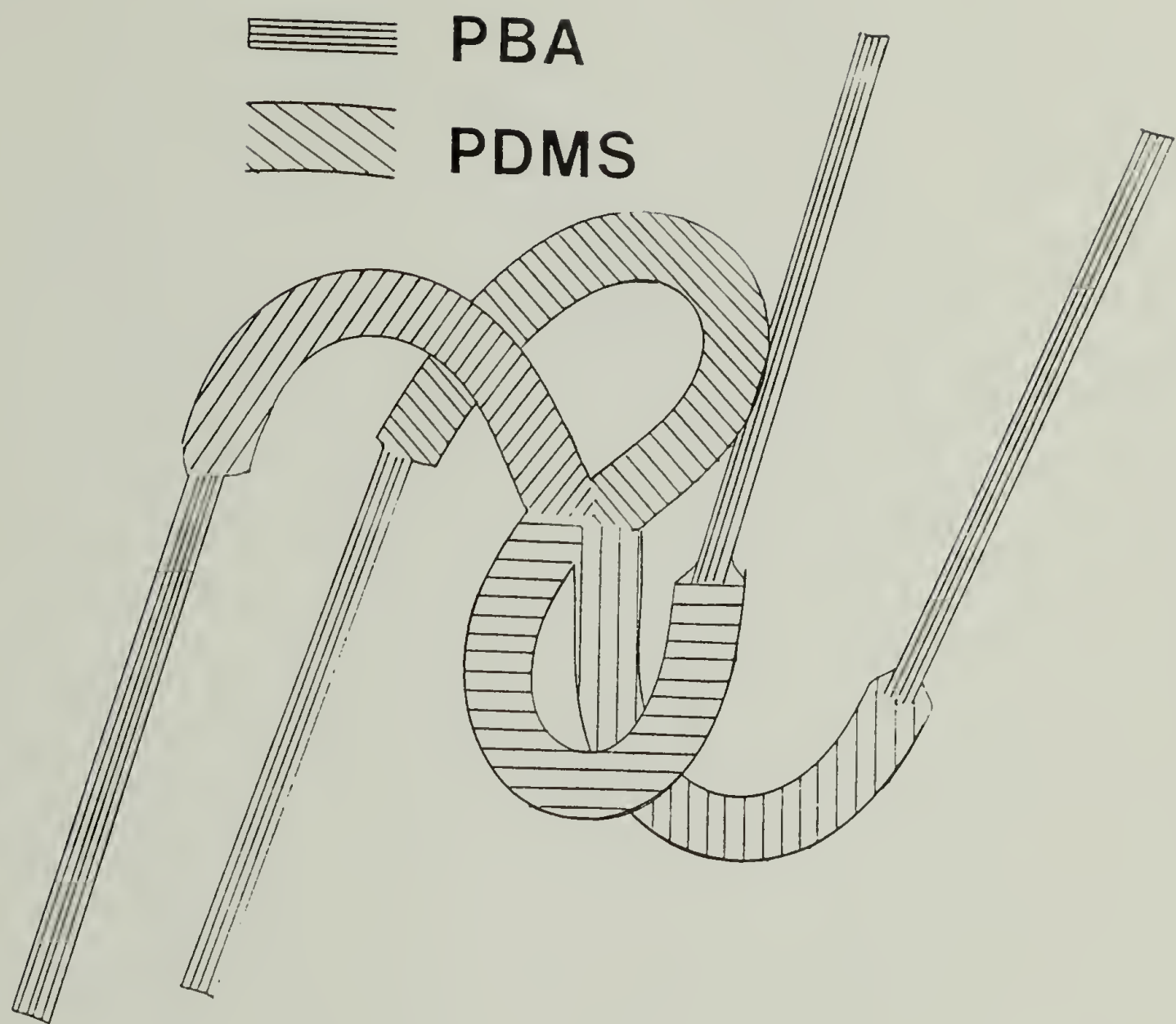


Figure 2.1. Representation of Star-Block Copolymers, showing potential liquid-crystalline alignment (Adapted from Dickstein¹.)

Table 2.1. Polymers Used in This Study. "ST" refers to star-block copolymers, "LB" to the linear analog (Figure 1). The M_n of the PBA end-group is 7000. Intrinsic Viscosity in DMAc/LiCl at 25°C (Adapted From Dickstein.)

<u>Polymer</u>	<u>PDMS</u>	<u>PDMS</u>	<u>Wt. % PDMS</u>	<u>$[\eta]$</u>
	<u>M_w/Arm</u>	<u>M_w/M_n</u>	<u>in polymer</u>	<u>(dl/g)</u>
ST-1	650	1.32	9.8	2.64
ST-2	975	1.20	15.5	2.87
ST-3	1550	1.31	24.8	2.55
ST-4	4250	1.32	35.3	2.34
LB-1	1050	1.13	9.6	2.26

These star-block copolymers were available in limited quantities (approximately 1-2 grams each) and soluble with difficulty. The characterization methods which could be employed were thus limited, and care had to be taken in the choice of characterization techniques.

It was of primary interest to gain an understanding of the copolymers in solution and in the solid state. To help identify the mesophasic character of each copolymer with respect to solution concentration, polarized-light microscopy (PLM) was utilized. To compare the thermal stability of the copolymers with their precursors, thermogravimetric analysis (TGA) was used. Finally, to gain an insight into the crystalline structure of the block copolymers, Wide-Angle X-Ray Scattering (WAXS) was utilized.

2.2 Polarized-Light Microscopy

Photos were taken with a Zeiss microscope of samples between glass plate and cover slip and with crossed polarizers. The magnification ranged from 200 to 400. All observations were made at room temperature. The results may be summarized as follows: the low-molecular-weight star polymers, ST-1 and ST-2, did not form birefringent solutions at concentrations up to c_m , that of maximum solubility, nor was there any evidence of shear-induced birefringence. At concentrations between 6.0 % and c_m of 7.6 %, the copolymer ST-3 formed birefringent solutions. When left quiescent for several days, these solutions phase-separated into two

solutions, one of which was pearlescent and the other clear. The pearlescent portion was birefringent when viewed under crossed polars. This birefringence was not indicative of residual crystals in the solution; the 'domains' flowed as a fluid when the solution was stressed. Below $c = 6.0$ wt. % copolymer, only a clear solution, exhibiting no birefringence, was obtained. Thus, ST-1, and ST-2 do not form liquidcrystalline solutions. ST-3 forms a LC-isotropic biphasic.

The linear block copolymer LB-1 and the high- M_w radial block copolymer ST-4 can form LC-isotropic biphases and LC monophases, as evidenced by stir-opalescence and polarized-light microscopy. Microscopy shows LB-1 have a LC monophase from 7.6 wt. % copolymer to c_m at 12.4 %. ST-4 is liquid-crystalline from 6.4 % to c_m of 12.0 %. Figure 2.2 shows a micrograph of ST-4, displaying the birefringence characteristic of a mesophasic solution. These results are summarized in Table 2.2.

A distinction was noticed between the ST-4 and the LB-1 solutions. The ST-4 solutions generally had large black regions (Fig. 2.2), which were too large ($= 10 \mu\text{m}$) to be attributed to phase-separated regions of the PDMS. These black regions exhibited "flash birefringence" when stressed, either by shearing the sample between glass and cover slip, or by pressing on the cover slip. This birefringence was quickly reversible, relaxing to extinction within 1 s. This

behavior contrasts with that of the LB-1 solutions, which also showed extinction regions, but which could readily be sheared into a near monodomain, a texture of uniform orientation which would persist for a minimum of two hours (Figs. 2.3, 2.4).

The difference in behavior of the two polymers is likely attributable to the star morphology and/or the high siloxane content of the ST-4 polymer. This would tend to promote homeotropic orientation, i.e., orientation of the rigid rods perpendicular to the surface, as the PDMS would preferentially wet the glass slide.

As yet there are no theories directed at predicting the concentration, c^* , of the isotropic-mesophase transition in radial polymers. These experimental results can be nonetheless compared with those of PBA homopolymers with molecular weights equivalent to the PBA M_w /arm. Papkov's modification of the Flory equation⁸⁴, specific for PBA,

$$c^* = (990/M_w) (1 - 248/M_w), \quad (2.1)$$

has been derived directly from Flory⁸⁵, with the substitution of an approximation for the axial ratio p for PBA,

$$p = .96M_w/120. \quad (2.2)$$

where M_w is the molecular weight of the rigid polymer.

As the Papkov equation is specific for PBA, the inclusion of the siloxane blocks in the copolymers must be taken into account. Inserting c_p , the wt. % of the PBA in

Table 2.2. Phase behavior of star-block and linear block copolymers, from PLM and stir-opalescence. c^* , c^* , and c_m refer, respectively, to the theoretical isotropic-mesophase transition (by equation 2.3), the experimentally determined isotropic-mesophase transition, and the maximum solubility of the block copolymers in DMAc/LiCl solution at room temperature.

<u>Polymer</u>	<u>c^*</u> <u>(wt. %)</u>	<u>c^* (biphase)</u> <u>(wt. %)</u>	<u>c^* (monophase)</u> <u>(wt. %)</u>	<u>c_m</u> <u>(wt. %)</u>
ST-1	7.8	none	none	6.4
ST-2	8.3	none	none	6.6
ST-3	9.4	6.0	none	7.4
ST-4	10.9	6.4	7.1	12.0
LB-1	7.8	6.6	7.6	12.4

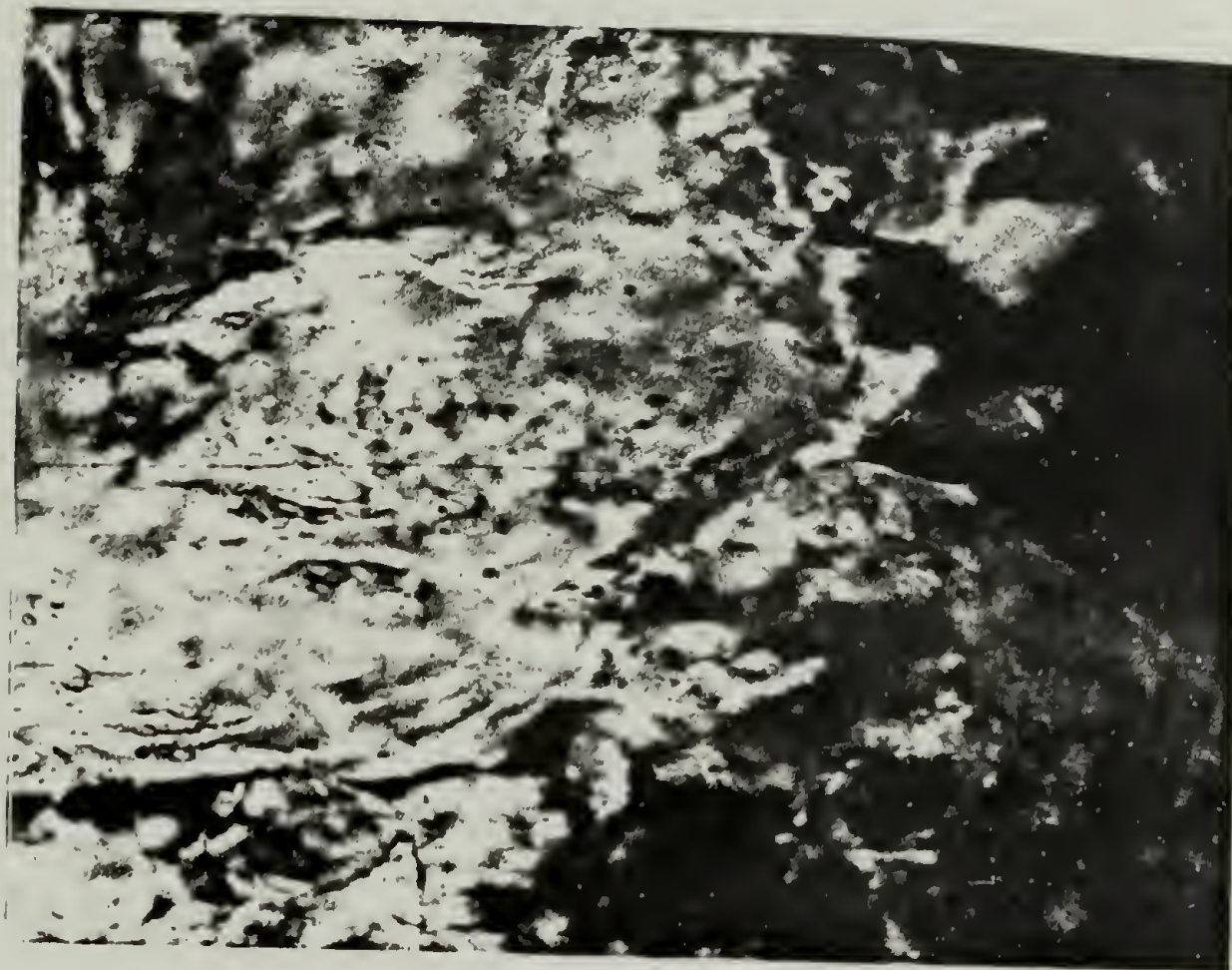


Figure 2.2. Polarized Light Micrograph of 10.7 % ST-4
Solution in DMAc/LiCl.



Figure 2.3. Polarized Light Micrograph of Quiescent 10.7%
LB-1 Solution in DMAc/LiCl.



Figure 2.4. Polarized Light Micrograph of Sheared 10.7% LB-1 Solution in DMAc/LiCl.

the copolymer, gives

$$c^* = (990 / [M_w * c_p]) (1 - 248 / M_w), \quad (2.3)$$

to yield the copolymer concentration which would be expected to induce a nematic mesophase.

Table 2.3 shows that the solutions are mesomorphic at polymer concentrations lower than those predicted by the Papkov equation. A possible explanation for this is that the individual PBA rods, held in close proximity by the siloxane core, exist in a locally increased mesogenic concentration. Alternatively, this constraint on the PBA chains may be considered to lower the entropy of transition from the anisotropic to the isotropic phase, thus shifting the equilibrium to the mesophase.

The role of the PDMS blocks in determining the mesophase character of the star-block copolymers is then twofold: for those polymers with low siloxane molecular weight (small flexible spacer), the PDMS inhibits liquid-crystallinity by steric hindrance, in analogy to side-chain LCPs. As the siloxane block molecular weight is increased, however, the liquid-crystallinity is enhanced, presumably by increasing the local concentration of the rigid unit..

Ternary systems of rodlike and coil-like polymers with a solvent were considered by Flory⁸⁶. His calculations find that the differing solubility of the rod and the coil will induce a phase separation, resulting in a larger biphasic

region than that seen with conventional rod/solvent systems. A numerical analysis of the Flory calculations yields the phase diagrams given in Fig. 2.5, for the systems considered as unconnected PBA and PDMS solutes in DMAc. Coincidentally, the isotropic-anisotropic binodal would be expected at 15 vol. % polymer for each of the systems considered. This concentration is far above that required for the ST-4 and LB-1 LC systems, and is beyond the limit of solubility of the others. This model does not fit as a quantitative model for the star polymers studied here, presumably on account of the connectivity, and thus the enforced proximity, of the PDMS and PBA; nonetheless, this supports the finding of a significant biphasic region in many of the star polymers.

2.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was employed in order to determine the thermal stability of the star-block copolymers.

Data were collected on a Perkin-Elmer TGS-2, interfaced with a TADS data station and a System 4 microprocessor controller. The scanning rate was 20°C/min. All temperature scans were carried out under a helium atmosphere.

In addition to the TGA performed on the lyotropic LCPs, the thermal degradation of some similar thermotropic LCPs, also synthesized by W.H. Dickstein, was studied. These thermotropic polyesters consisted of the same PDMS star

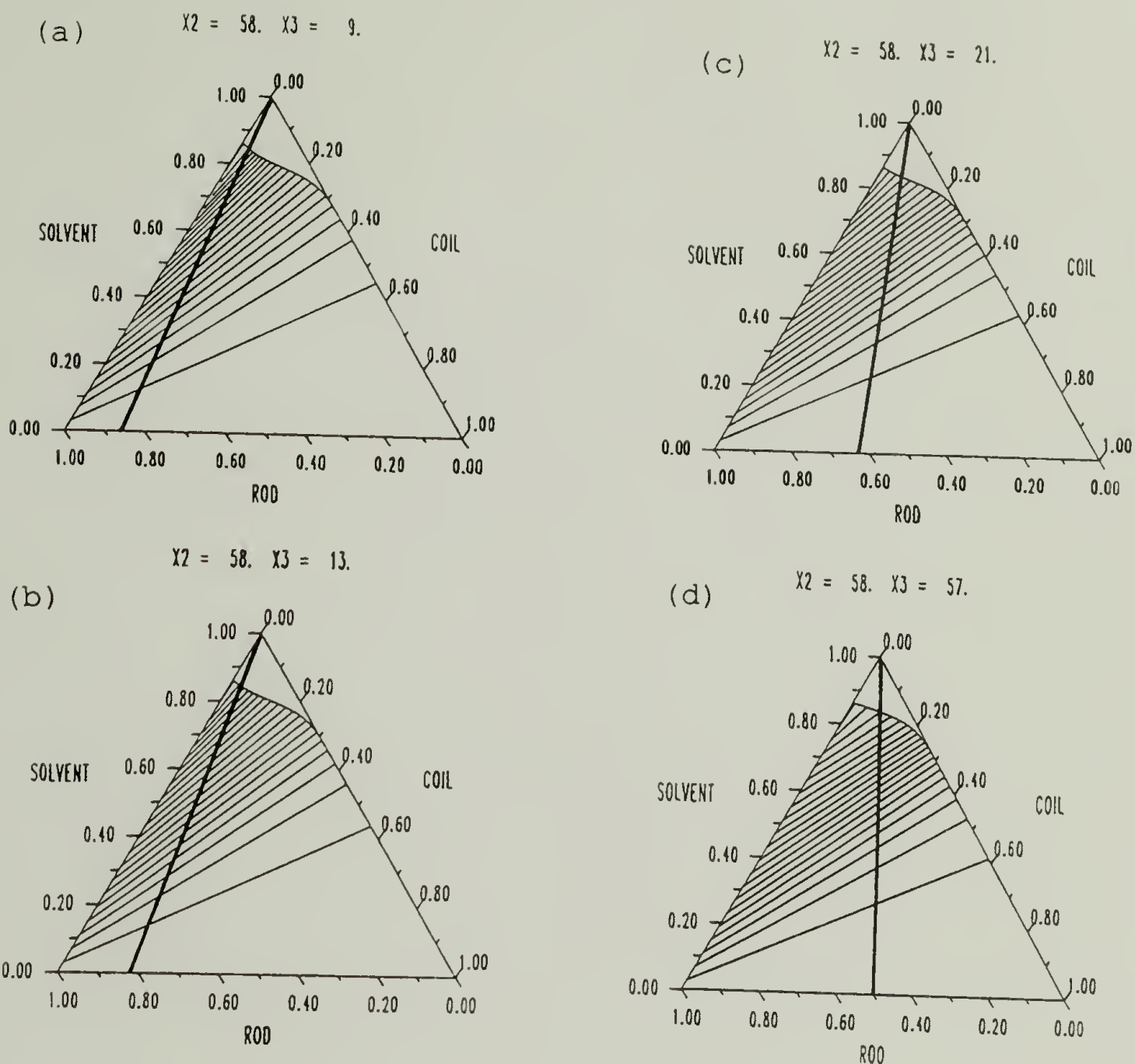


Figure 2.5. Three-component phase diagrams, predicted by the Flory theory. X_2 refers to the degree of polymerization of PBA; X_3 , PDMS. The heavy line depicts concentrations allowed by the PBA/PDMS proportion in each polymer. (Concentrations are volume fraction.) (a) ST-1, LB-1; (b) ST-2; (c) ST-3; (d) ST-4. (Program courtesy of M. Magliochetti.)

Table 2.3. Effective Molecular Weights M_{eff} , calculated from Equation 2.3, for block copolymers forming anisotropic solutions. c^* as in Table 2.1.

<u>Polymer</u>	<u>c^* (PDMS+PBA)</u>	<u>c^* (PBA only)</u>	<u>M_{eff}</u>
LB-1	6.0	5.9	17 000
ST-3	6.4	4.8	20 000
ST-4	6.6	4.3	22 000

center, but they differed from the lyotropic copolymers in the mesogenic block: in this case, a hydroxybenzoic acid polymer. Representative results of the TGA studies are shown in Figs. 2.6-2.8, and all results are summarized in Table 2.4. These experiments are summarized in Dickstein's thesis, but are also included here as they are an important aspect of the characterization of the polymers and because the work was that of the present author.

One remarkable result of the TGA is that the block copolymers were, in many cases, more thermally stable than the precursor homopolymers, PDMS and PBA (Figure 2.8). For instance, LB-1, ST-1, and ST-2 are more stable by 20°C, when measured by 5 % wt. loss, and by 40°C, when measured by the point of maximum slope of weight loss T_m , than the PBA synthesized under the same conditions. The data for ST-3 and ST-4 are more ambiguous: when measured by 5 % weight loss, they are less stable than the PBA; by T_m , they are considerably more stable. Similarly, all of the lyotropic block copolymers, with the exception of ST-5, are more stable than the PDMS precursor. Oxidizing conditions were not tested.

The cause of the exceptional thermal stability is not well understood. The higher molecular weight of the block copolymers could conceivably contribute to greater thermal stability, but since the PBA was synthesized by a condensation reaction, any type of "unzipping" degradation

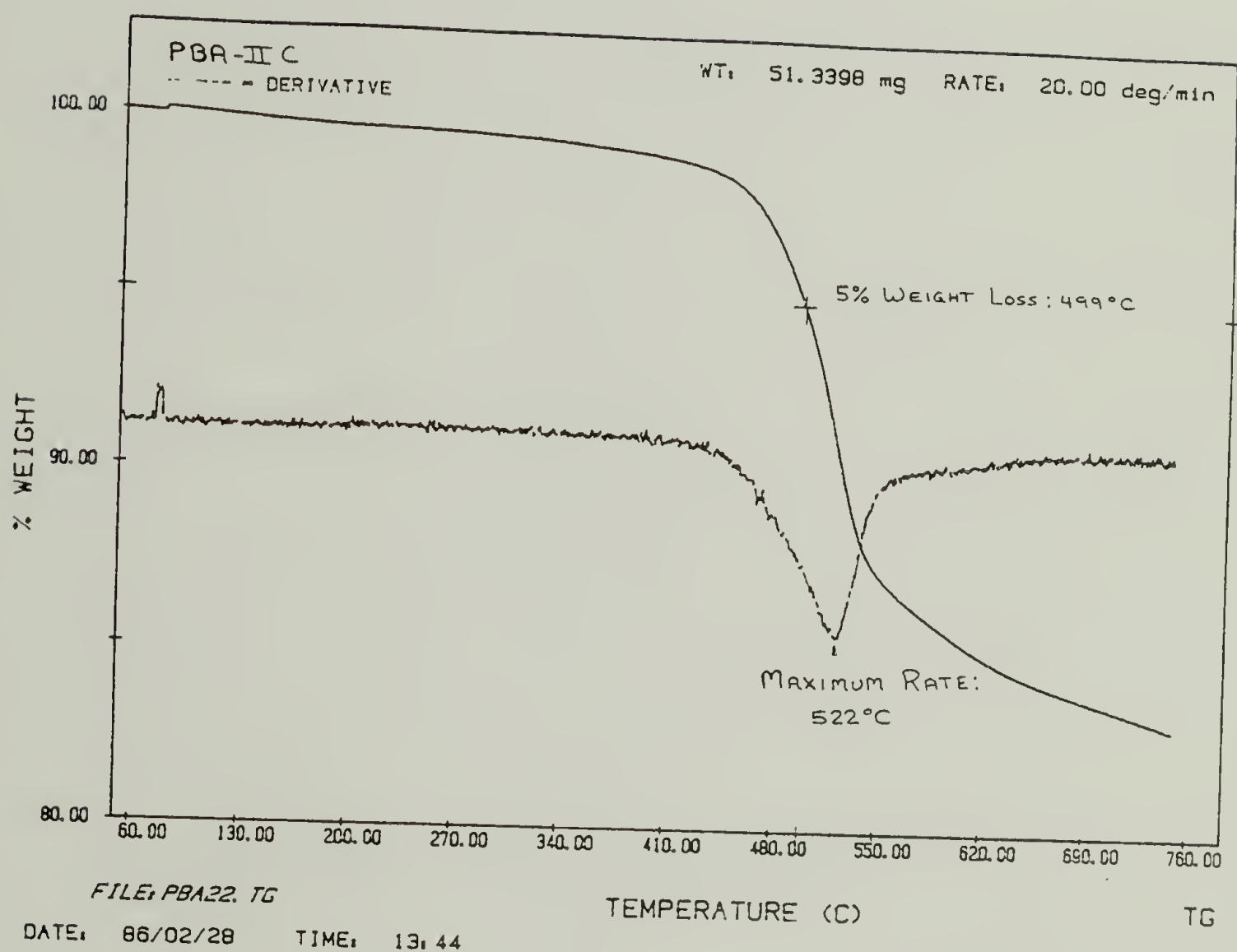


Figure 2.6. TGA of Solid Poly (p-benzamide). The solid line represents the weight of the polymer sample; the dotted line, the derivative of the weight with respect to temperature.

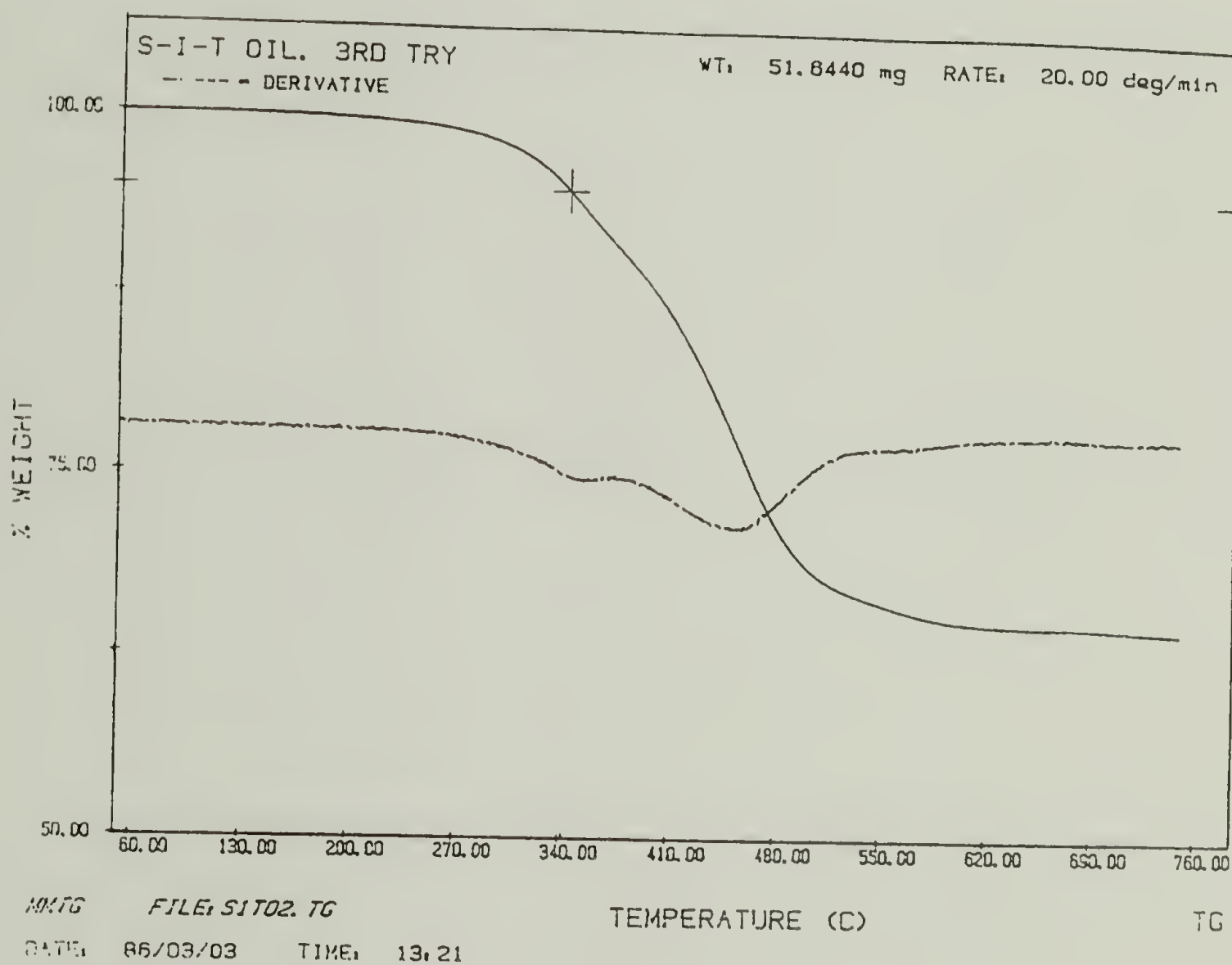


Figure 2.7. TGA of ST-1T Oil (Star Siloxane Precursor.)

The solid and dotted lines are as in Figure 2.5.

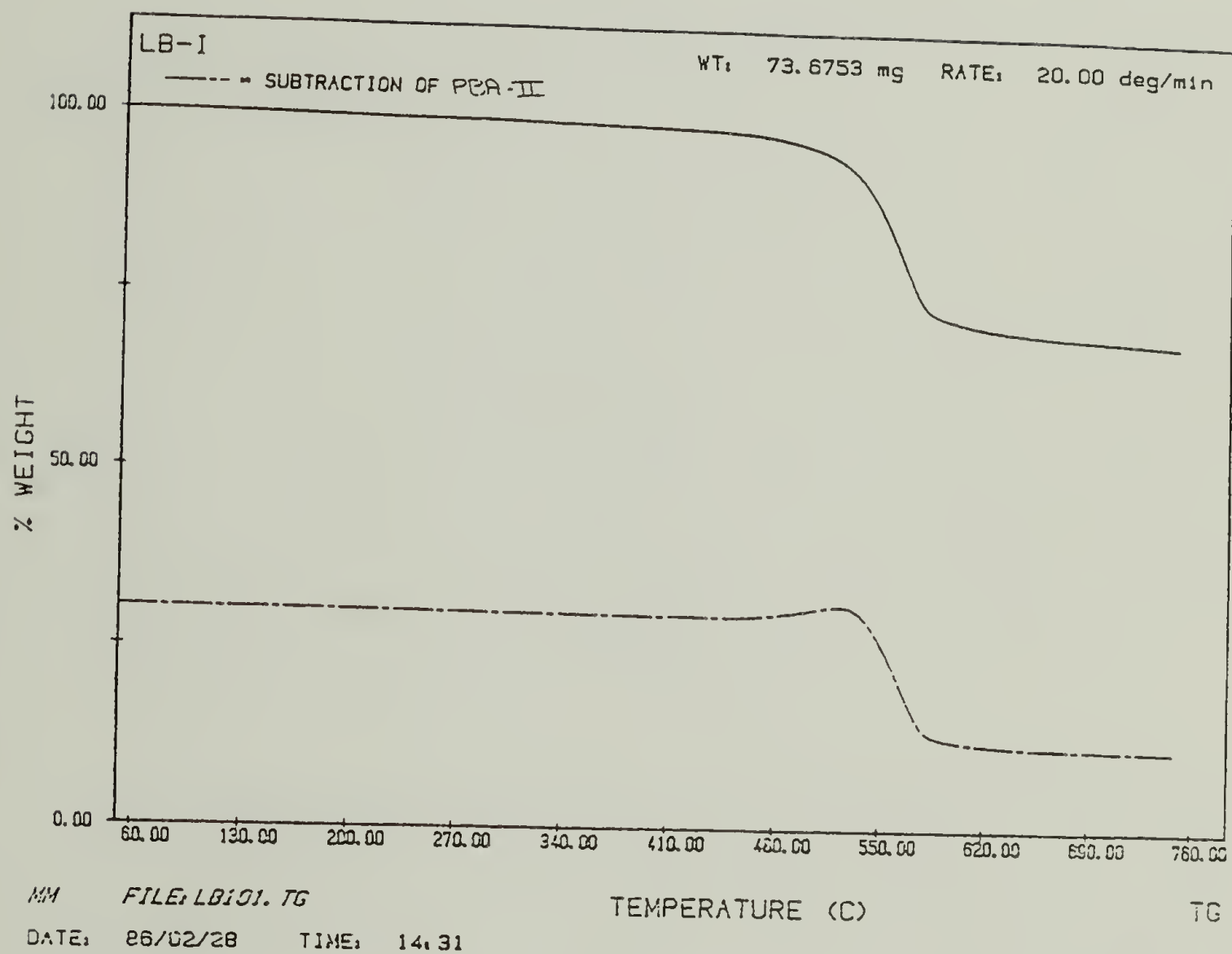


Figure 2.8. TGA of Solid LB-1. The solid line represents the weight of the polymer sample; the dotted line, the result of subtracting the PBA results. The peak at 530°C shows the high thermal stability of the copolymer relative to the PBA.

Table 2.4. Results of Thermogravimetric Analysis on
Lyotropic and Thermotropic Star and Linear Block
Copolymers.

<u>Polymer</u>	<u>5 % wt. Loss</u> <u>(°C)</u>	<u>Maximum</u> <u>Degradation (°C)</u>
<u>Lyotropics</u>		
PBA-2	499	523
LB-1	522	564±2
ST-1	523	563±2
ST-2	522	559±3
ST-3	474	565±2
ST-4	479	563
ST-5	150	498±3
<u>Thermotropics</u>		
ST-1T	341±2	452
ST-2T	451	457
ST-3T (Powder)	482	486
(Oil)	422	462
ST-4T	489	508
ST-5T	477	506

reaction is unlikely. Moreover, no significant weight losses are expected on the basis of vapor pressure of the PDMS or PBA or their respective solvents.

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CHAPTER 3

RHEOLOGICAL PROPERTIES

3.1 Steady-Shear Viscosity

3.1.1 Introduction

Although there have been several reported studies on the rheology of liquid-crystalline polymers (LCPs)⁸⁷ and of "star", or radial polymers⁸⁸, no work has yet been reported concerning the rheological properties of star LCPs. The objective of this chapter was to determine the influence on the rheological properties of the star morphology and of the liquid-crystalline character of the solutions.

3.1.2 Experimental

As mentioned in Chapter 2, solutions of the block copolymers were successively diluted from the maximum solubility c_m , in order to prevent spurious effects of increased concentration of LiCl in the solutions, which could result from cycles of heating and dissolution of polymer in the mixed solvent.

As a model experiment to assess the solubility of the PDMS in DMAc/LiCl, the dissolution of silicone oils, of molecular weights of 1000, 1500, and 2000, comparable to the range encountered for the PDMS blocks, in the same solvent system was attempted. Although LiCl/DMAc is a solvent for PBA, it is confirmed not to be a solvent for PDMS, since in all cases, a two-phase system persisted. This observation leads to the conclusion that these "solutions" likely show

microphase separation between the PBA and the PDMS blocks. In addition, this property is shown to limit the solubility of each copolymer in the solvent.

The viscosity of the DMAc/LiCl solvent system was tested by capillary at 25°C, and found to be 1.8 ± 0.1 cp = 1.8×10^{-3} Pa*s.

Rheological measurements were made on a Rheometrics Mechanical Spectrometer, Model RMS-7200 (RMS), with a cone and plate in the steady-shear mode. Data were collected on a Bascom-Turner digital plotter. A low cone angle of .01 radian, which conserves sample, was utilized for all solutions. On selected solutions, supplementary tests were made with a cone angle of .04 Radians. The diameter of each was 50 mm. The data from the two cone-plate geometries coincided within 20%. Care was taken to preserve the anhydrous nature of the solvent by coating the solution exposed at the gap with low-viscosity silicone oil.

In order to compare data from different instruments, data were also collected on a Rheometrics Constant Stress Rheometer, Model CSR, in the cone-plate mode. For these tests, the cone angle was .040 Radians and the diameter, 25 mm. In order to investigate whether the data were independent of geometry, measurements were made on the RMS in the parallel-disk mode with a diameter of 50 mm. The gap was sequentially reduced from .200 mm to .010 mm to obtain a range of shear rates and to ascertain any dependence of the measured viscosity on the gap. All parallel-disk data were

corrected for non-Newtonian behavior with the Rabinowitsch-like equation⁸⁹

$$(\eta_R) = \{[T/(2R^3)]/\eta_R\} \{3 + d\ln[T/(2\pi R^3)]/d\ln\gamma_R\}. \quad (3.1)$$

In this equation, γ_R refers to the shear rate at R , the radius of the disk, and T refers to the torque measured.

3.1.3 Results and Discussion

Figures 3.1 through 3.5 are plots of viscosity vs. concentration at constant shear rate for the four star-block copolymers and for the linear block copolymer LB-1. Figures 3.1, 3.2, and 3.3, for polymers ST-4, ST-3, and LB1, show a peak in viscosity near the experimentally determined c^* . In each case, the peak is less pronounced at ever higher shear rates, consistent with prior findings. Within experimental error, c^* is independent of shear rate.

Figures 3.4 and 3.5 show a monotonically increasing η vs. c for ST-1 and ST-2. The pronounced slope at concentrations approaching c_m suggests that these copolymers would show a c^* if soluble to a concentration slightly above c_m . The marked increase in viscosity near c_m suggests some ordering of the rigid segments at these concentrations. It must be emphasized, however, that neither ST-1 nor ST-2 shows birefringence when sheared under crossed polarizers. The scale of any shear-induced order must therefore be smaller than the wavelength of visible light.

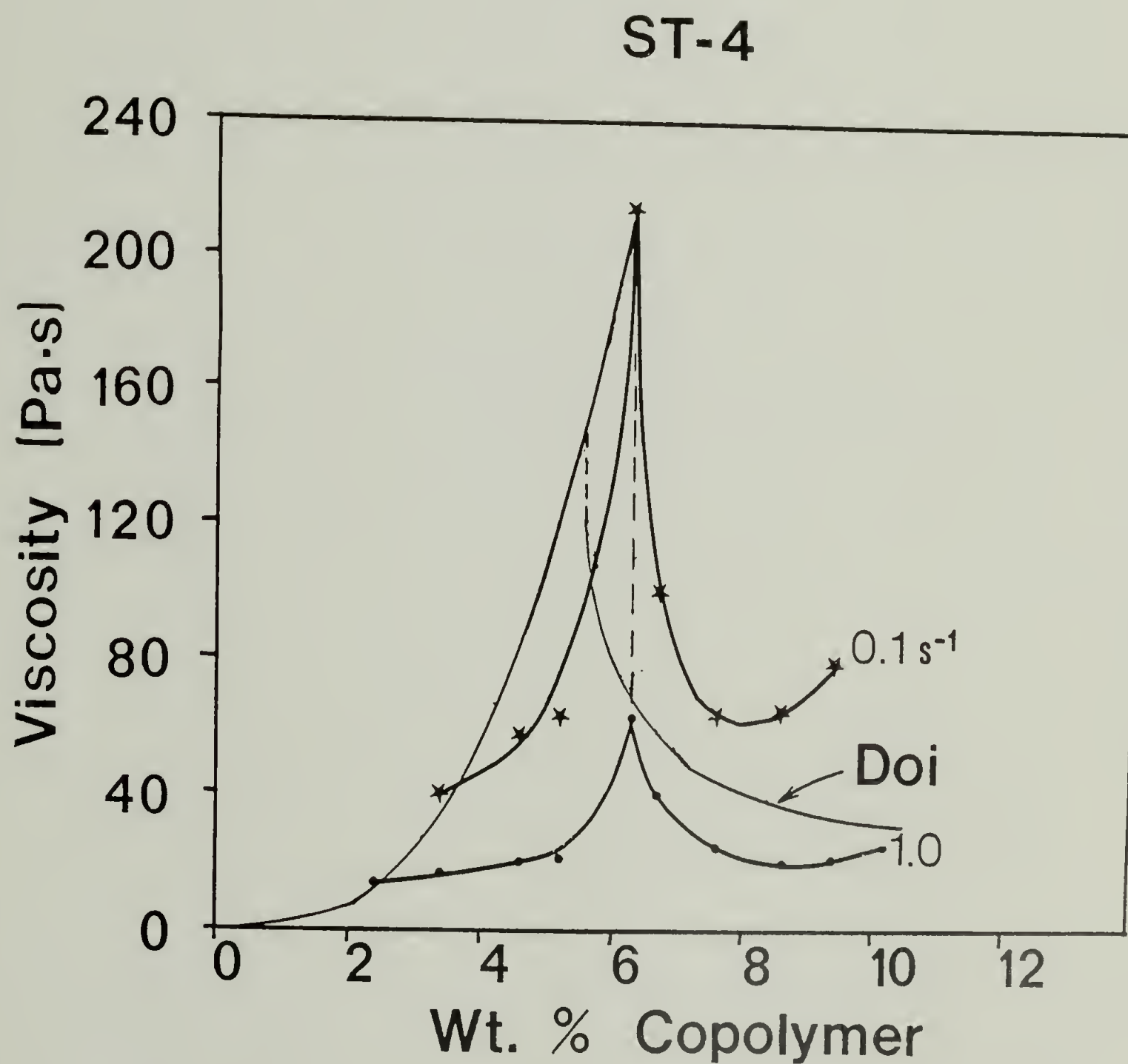


Figure 3.1. Rheological Phase Diagram of ST-4.

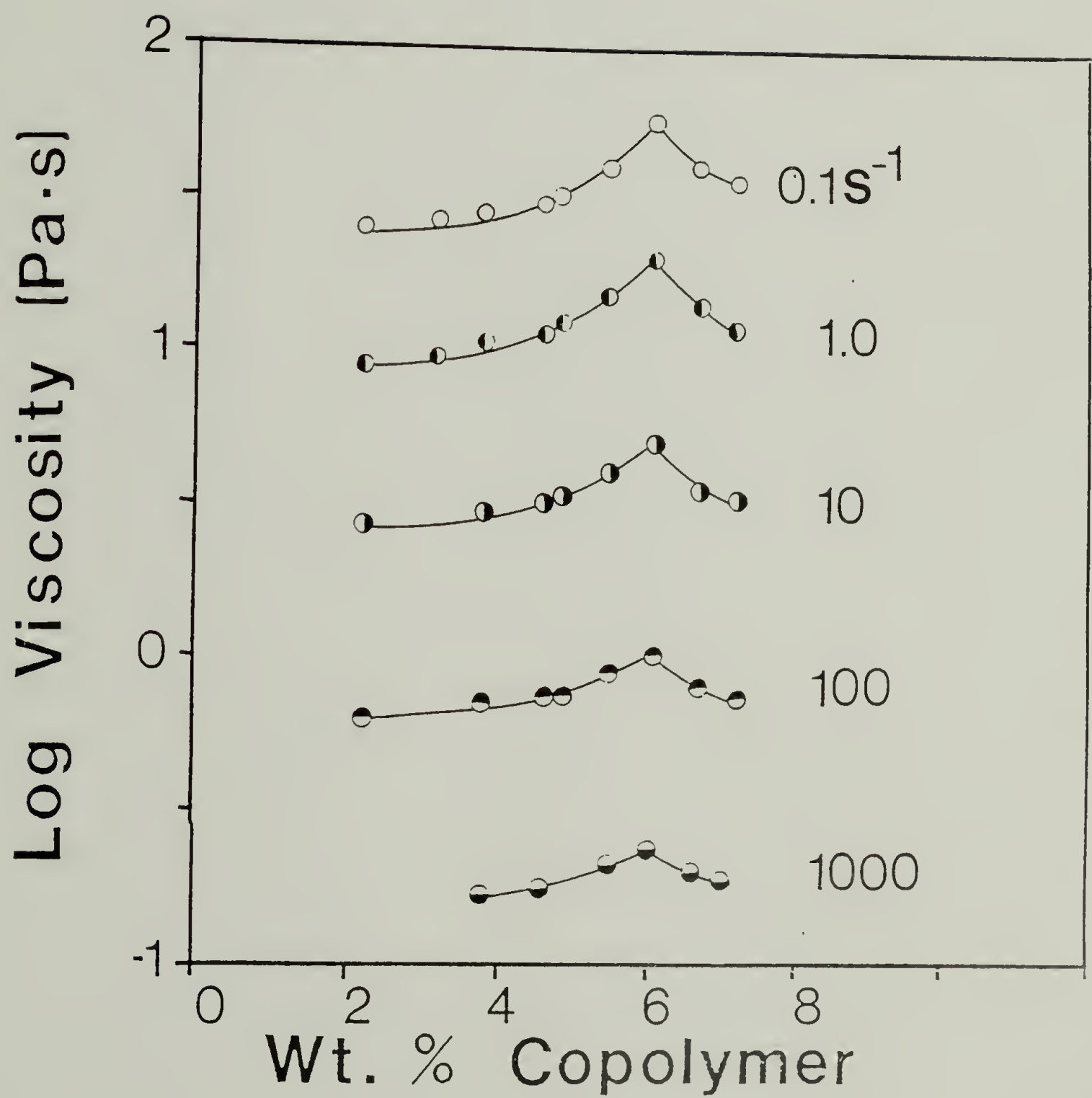


Figure 3.2. Rheological Phase Diagram of ST-3.

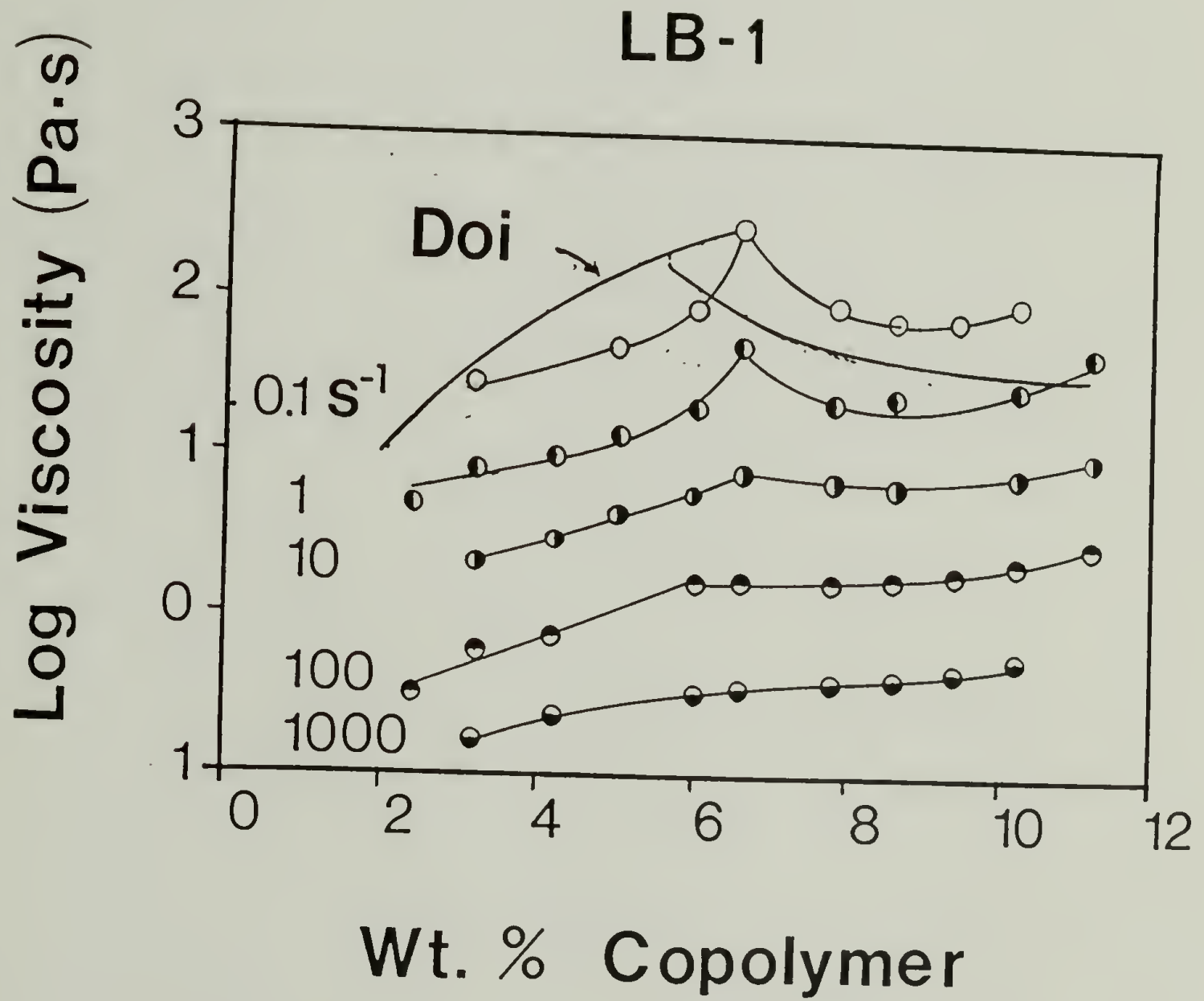


Figure 3.3. Rheological Phase Diagram of LB-1.

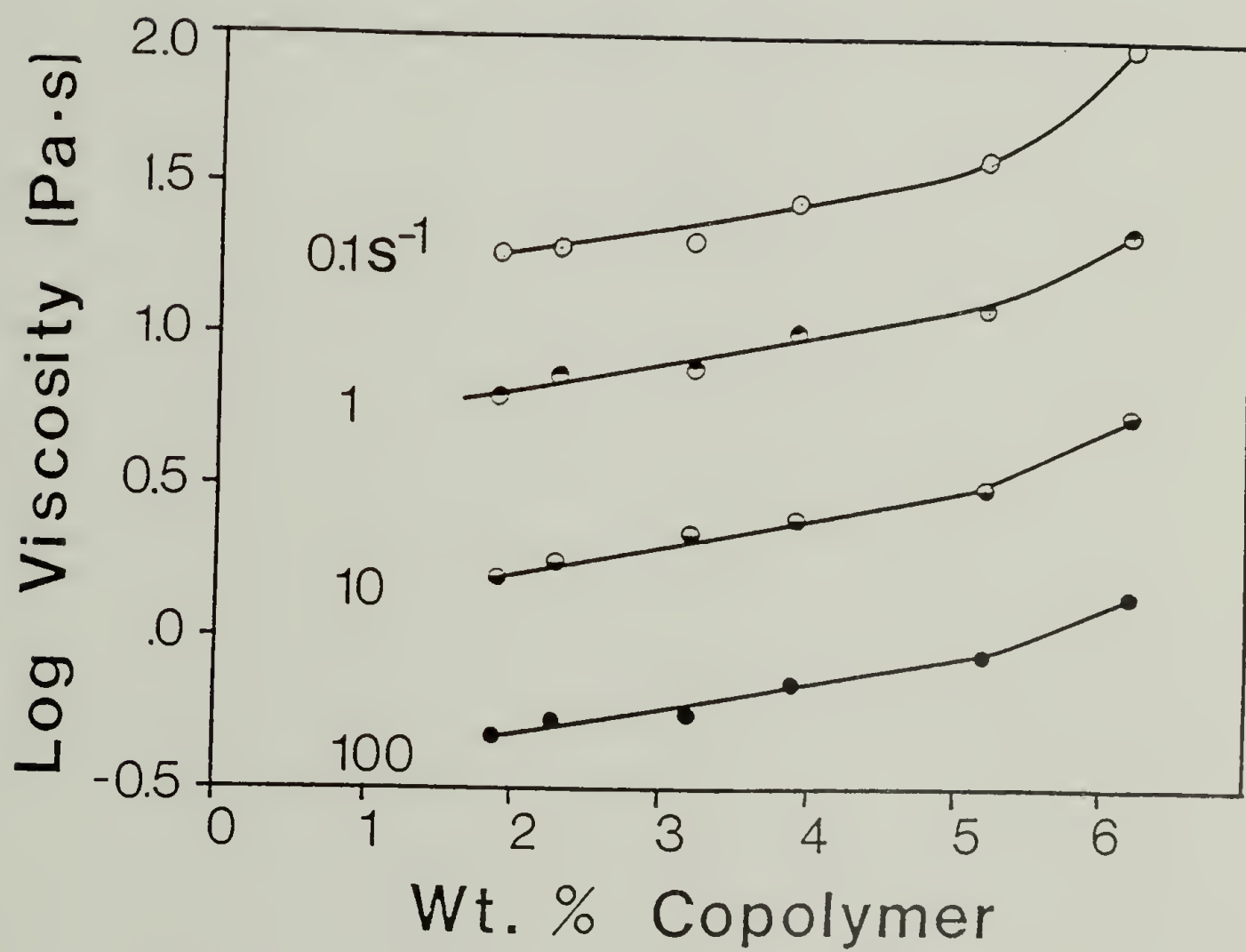


Figure 3.4. Rheological Phase Diagram of ST-1.

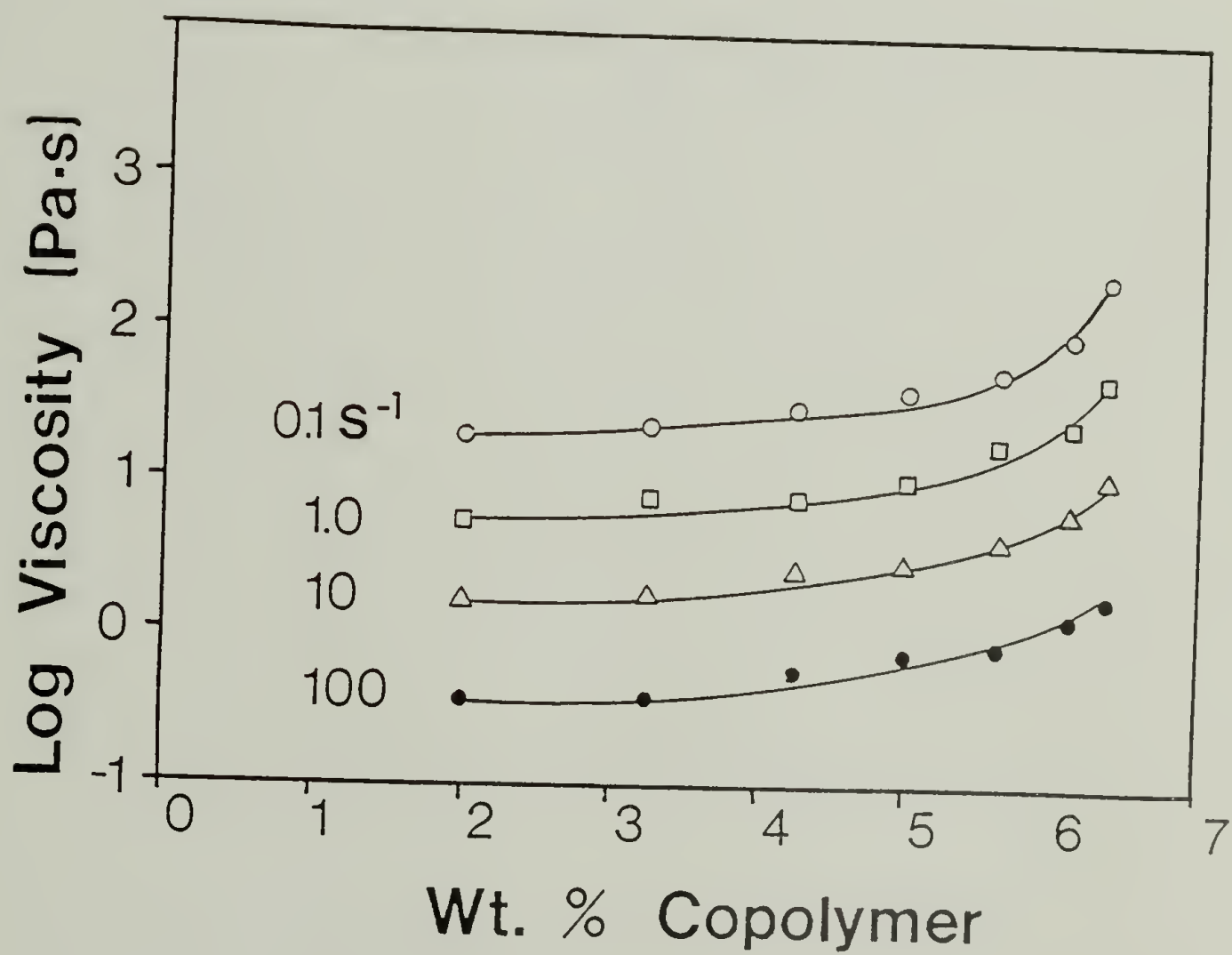


Figure 3.5. Rheological Phase Diagram of ST-2.

One distinction seen between the behavior of the star-block copolymers and that of PBA homopolymer lies in the shape of the rheological phase diagram. At low concentrations ($\leq 2-5$ wt. %, depending on M_n), the viscosity of PBA solutions falls nearly to zero⁹⁰. For the solutions studied here, the peak is not so dramatic. Clearly, although the liquid-crystallinity is an important determining factor in the rheology of the solutions, the role of the siloxane blocks is also critical.

Figure 3.6 shows curves of the viscosity of solutions of ST-4, some of which are isotropic at rest and some are anisotropic. Similar behavior is seen in all plots. The most striking aspect of the behavior shown is the sharply shear-thinning nature of the solutions, showing no Newtonian limits. Results are independent of shear history. Two possible spurious causes of a lowered viscosity during a scan of increasing shear rates are stress-induced degradation and viscous heating. These were simultaneously investigated by reducing the shear rate and comparing the torque to that seen for earlier runs at the same shear rate. The equivalence of the values thus obtained showed that any viscous heating or shear-induced degradation was minimal, and that the solutions are fluids (no viscosity hysteresis).

A model for LCP rheology was presented by Doi⁹¹. This model describes the order parameter, S , as

$$S = \begin{cases} 0 & \phi < \phi^* \\ 1/4 + 3/4(1-8\phi/9\phi^*)^{1/2} & \phi > 8/9 \phi^* \end{cases}, \quad (3.2)$$

where ϕ/ϕ^* is the reduced volume fraction of rigid segments.

The zero-shear viscosity is related to ϕ , S , and the molecular weight M by

$$\eta \propto \phi^3 M^6 (1-S)^4 (1+S)^2 (1+2S) (1+3S/2) (1+S/2)^{-2}. \quad (3.3)$$

Figures 3.1 and 3.3 compare the Doi theory with the data for ST-4 and LB-1 at the lowest attainable shear rate. In both cases, the data show a sharper peak than is predicted by the theory. More striking is the upturn seen in viscosity with increasing concentration above c^* . This phenomenon is not predicted by the Doi model. Although some of the differences may be attributed to the block copolymeric nature of the polymers, the upturn in viscosity above c^* is also seen with LC homopolymers^{92,93}.

The observed power law behavior is described by the equation

$$(\eta) = \eta_0 (\gamma/\gamma_0)^{(n-1)}, \quad (3.4)$$

where γ_0 is an arbitrarily-defined low shear rate, η_0 is the viscosity at γ_0 , and n is the power-law index. In this case, n varies from 0.4 to 0.5. This behavior is often seen with phase-separated systems⁹⁴. The effect may be considered a quasi-yielding phenomenon; true yield would be indicated by a power-law index of 0, and by a stress which does not relax to zero on removal of the imposed strain. Within sensitivity limits, the latter effect is not seen here. Nor is rigidity seen at quiescent conditions, i.e., bubbles inserted into the

solutions were observed to rise. However, the absence of a low-shear Newtonian limit might imply the presence of structure, reversibly upset by shear.

The variance of the power-law index with concentration is of interest. In Figure 3.6, it is seen that n varies from 0.4 to 0.5, with the minimum (most shear-thinning) occurring near the point of the viscosity maximum. This is manifested in Figures 3.1 to 3.5, for ST-4 as well as the other block copolymers, by the diminished peak with increasing shear rate, which indicates that shear ordering effect diminishes the differences in liquid-crystallinity of the different concentrations.

The empirical Casson Equation,

$$\sigma^{1/2} = k_0 + k_1 \gamma^{1/2}, \quad (3.5)$$

where σ is the shear stress, γ the shear rate, and k_0 and k_1 are constants, is often used to describe yield in particulate systems and suspensions. A linear plot of $\sigma^{1/2}$ vs. $\gamma^{1/2}$ would give the yield stress as the square of the intercept. Fig. 3.7 shows a representative curve for a solution of one of the block copolymers. The curve is not linear, nor does it extrapolate to a perceptible yield stress.

The similar behavior which is shown by liquid-crystalline solutions and solutions which are isotropic at rest indicates that any structure must be independent of the domain structure postulated for anisotropic solutions.

ST-4

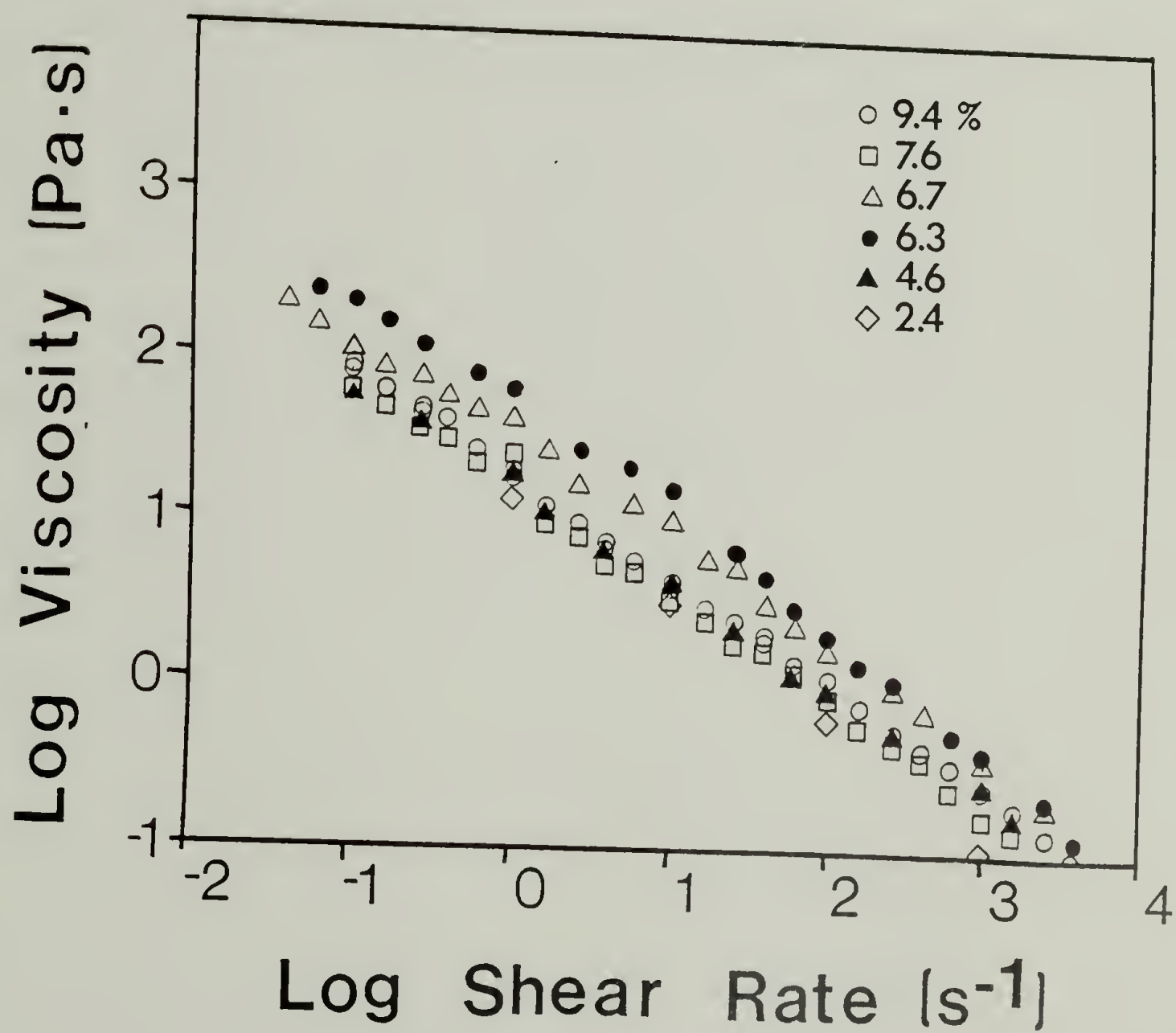


Figure 3.6. Steady Shear of ST-4 Solutions in Cone-Plate Mode.

The comparisons of different viscosity measurements are outlined in Figures 3.8 and 3.9. Figure 3.8 compares viscosity, as a function of shear rate, determined from the RMS, CSR, and capillary-flow data. Within experimental error, the viscosity arrived at is not a function of the instrument at use.

Figure 3.9 compares representative curves from the cone-plate and parallel-disk geometries. It is seen that, although the two are not coincident, the slope and general behavior of the viscosity-shear rate curves are similar. This indicates that the results shown are geometry-independent.

It is also noted, in Figure 3.9, that the steady flow behavior is independent of gap width within the range studied. This indicates that the structure present in the solutions must have a characteristic size less than the smallest gap, 10 μm , and that there is no immobilized surface layer.

3.2 Normal Stress Behavior

This section is concerned with the primary normal stress difference N_1 of the star-block copolymers and the corresponding linear block copolymer in steady shear flow. N_1 is defined by the tensor equation

$$N_1(\gamma) = \sigma_{22} - \sigma_{11}, \quad (3.6)$$

where $\underline{\sigma}$ is the stress tensor. For shorthand, we shall refer to N_1 as the normal stress. The primary normal stress

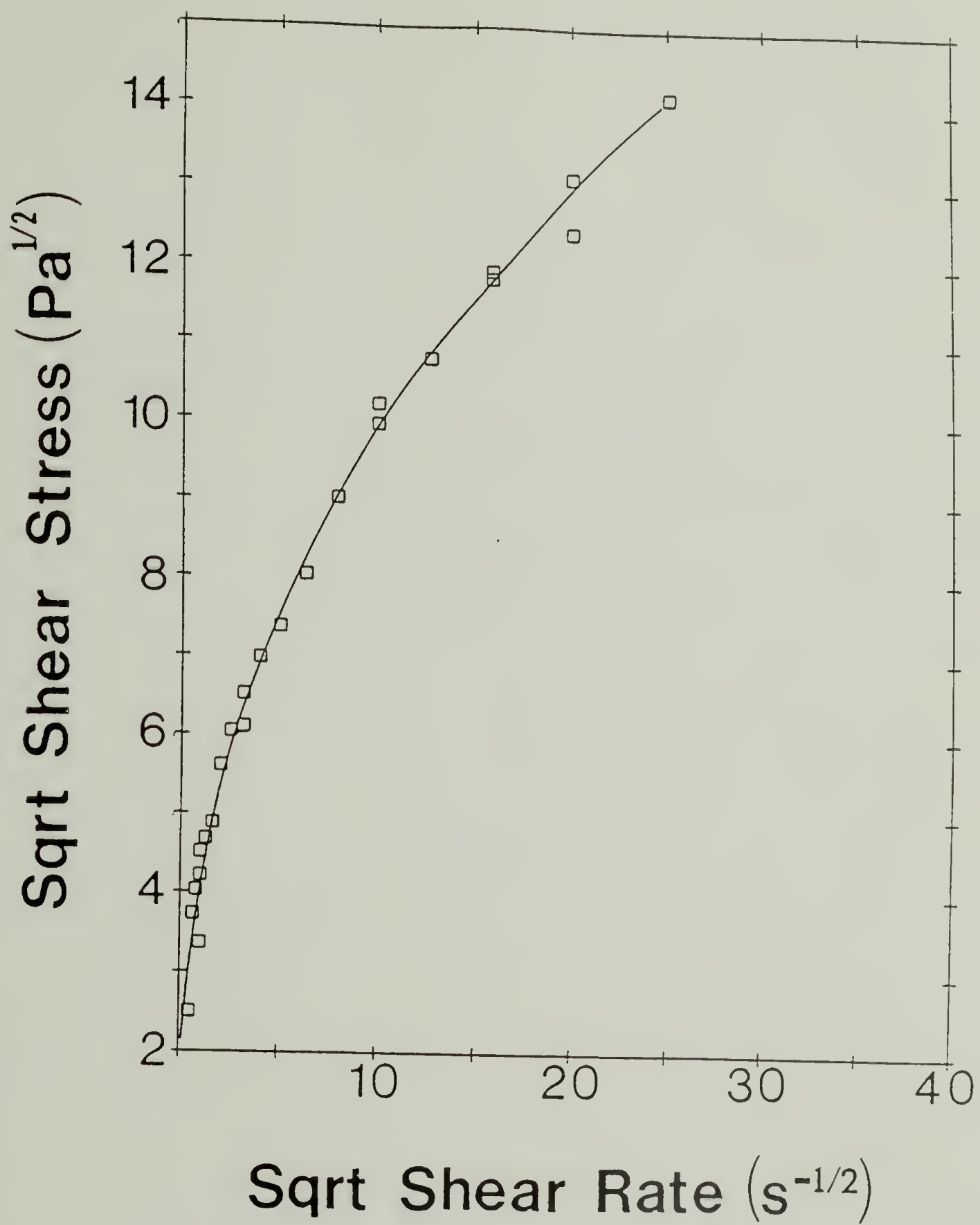


Figure 3.7. Casson Plot of Isotropic 3.66 Wt. % ST-2 Solution in Cone-Plate Mode.

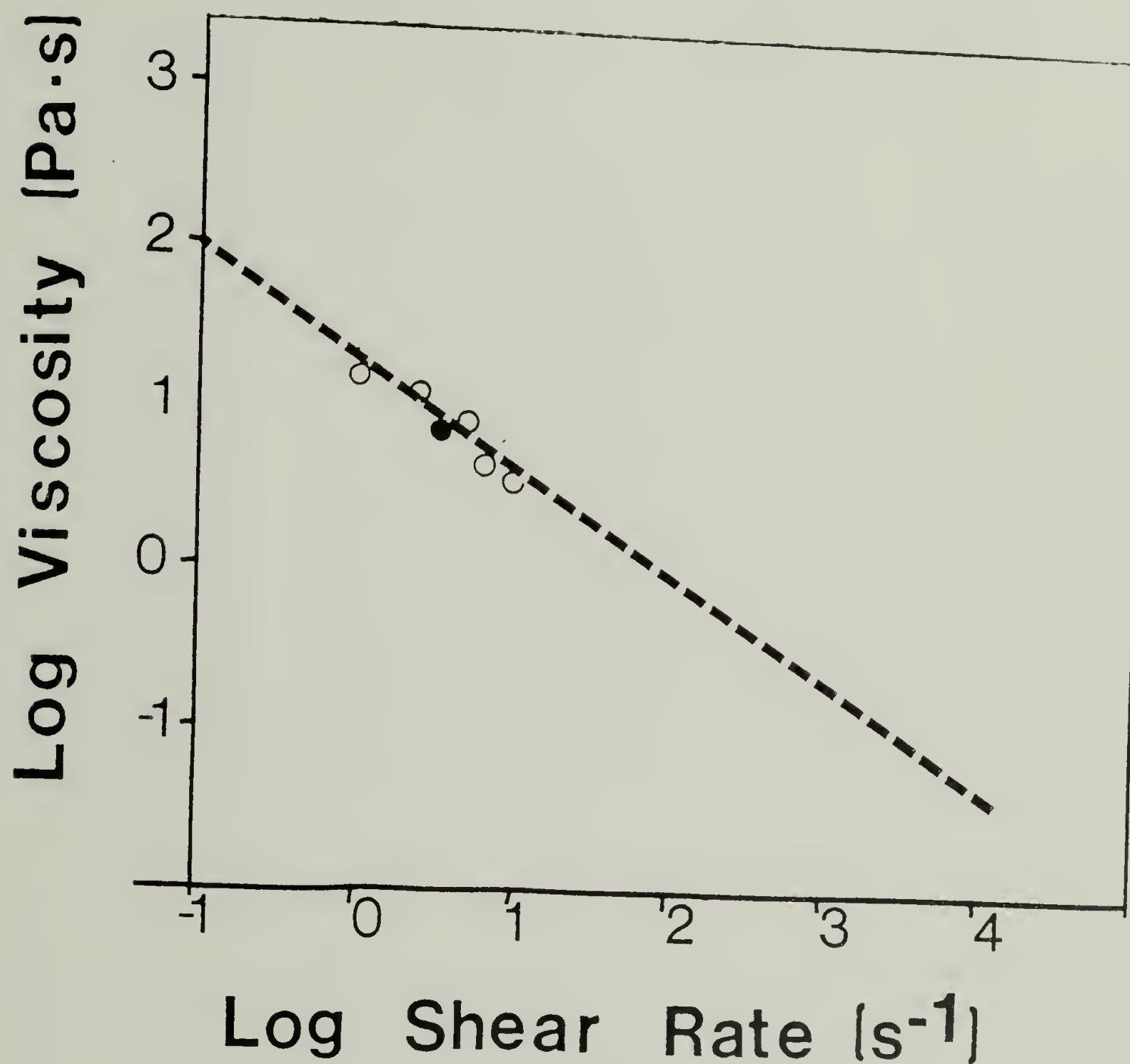


Figure 3.8. Comparison of Viscosities From RMS and CSR, both cone-plate geometry, and capillary. Dotted line represents RMS (individual data points omitted for clarity.) Other points as shown.

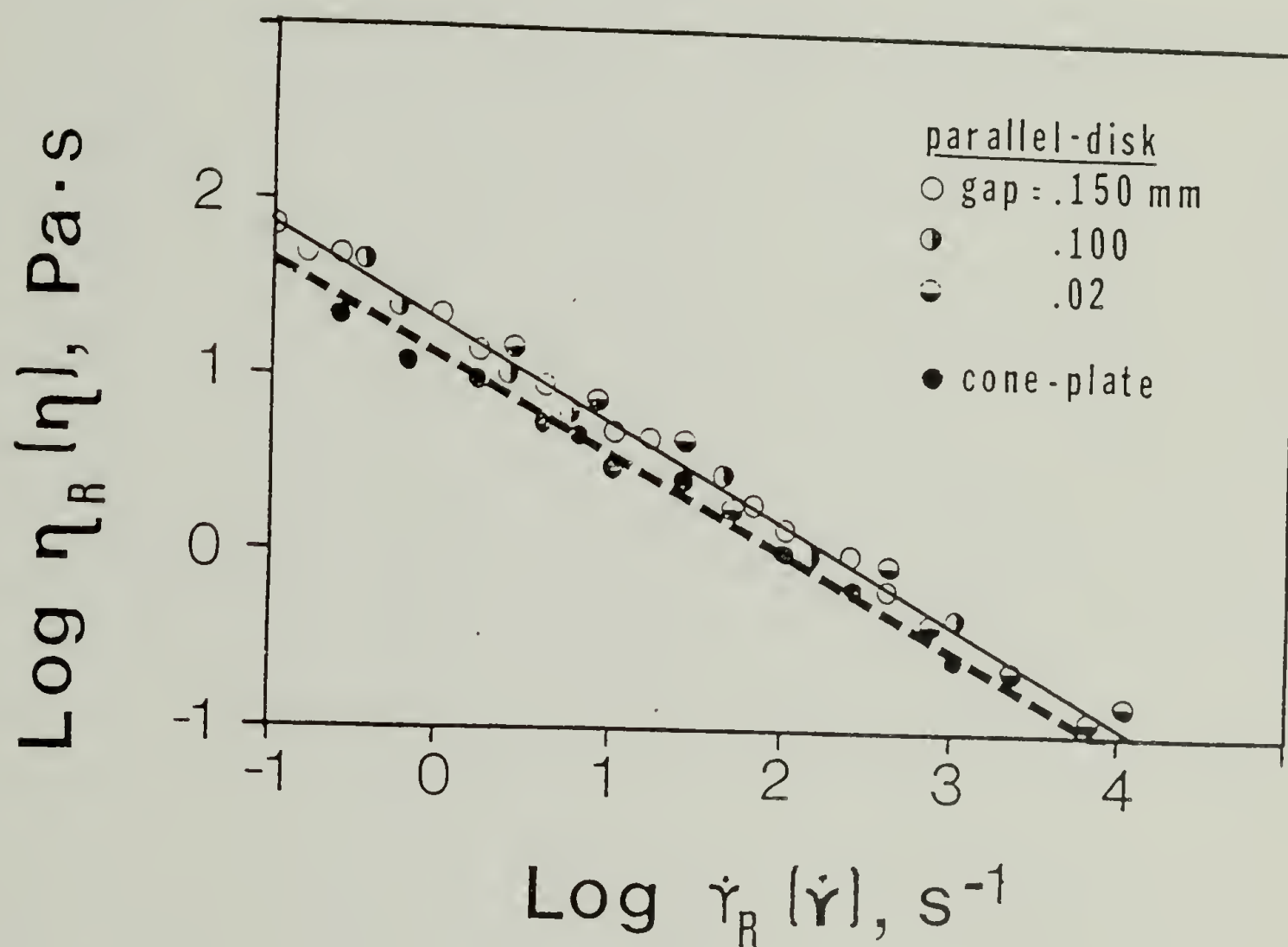


Figure 3.9. Comparison of Viscosities From Cone-Plate and Parallel-Disk Geometries for ST-4. The dotted line represents cone-plate results; the solid line, parallel-disk.

coefficient Ψ is defined by

$$(\Psi) = N_1(\gamma) / \gamma^2. \quad (3.7)$$

As discussed in Section 1.2.8, the normal-stress properties of LCPs are unique. The discoveries of negative normal stresses⁹⁵, and of a rheological phase diagram similar to that seen with viscosity⁹⁶, seem to be unique to LCPs, although neither is fully characteristic of LCPs. The interest in studying normal stresses was to compare the normal-stress behavior seen for these polymers with their viscosity behavior and with other workers' observations of normal stresses in LCPs and in flexible polymers.

3.2.1 Experimental

Data were collected on the RMS simultaneously with the viscosity data (Section 3.1). In cone-plate geometry, the value for N_1 as a function of shear rate is⁹⁷

$$N_1 = 2F / (2\pi R^3), \quad (3.8)$$

where F is the force required to keep the tip of the cone in contact with the plate. In the parallel-disk geometry, the non-homogeneous shear field complicates the equation, which becomes

$$N_1(\gamma_R) = (F/\pi R^3) [3 + d\ln(F/\pi R^3)/d\ln \gamma_R], \quad (3.9)$$

where F is now defined as the force required to keep the distance between the two plates constant (compare Equation 2.1).

3.2.2 Results and Discussion

For all of the copolymer solutions the steady-shear normal stress was positive. Figure 3.10 shows N_1 vs. $\dot{\gamma}$ for several concentrations of ST-4. In contrast to the behavior seen by Baird, no peak is seen in N_1 with concentration. Near the isotropic-mesophase transition concentration for the liquid-crystalline polymers, the log-log slope of N_1 vs. shear rate does increase, from an average of 0.25 to 0.5. Both slopes are low when compared to flexible polymer systems, which can show N_1 - $\dot{\gamma}$ slopes ranging from 1 to 2. A similar phenomenon was seen near the cm for the non-liquid-crystalline copolymers. The slope, however, is similar to that seen by Baird⁹⁸ with LC solutions of Kevlar^R in sulfuric acid. The slope of the normal-stress coefficient with respect to shear rate thus ranged from 1.7 to 1.5. The slopes of the Ψ - $\dot{\gamma}$ curves are plotted vs. concentration in Figure 3.15. There is a resemblance between this figure and Figures 3.1 to 3.5, the rheological phase diagrams. The slopes, generated by a least-square linear-regression analysis, are shown numerically in Table 3.1, with the corresponding correlation coefficients. The random experimental error ranges from less than 5% at 10^4 s^{-1} to 20% at 1.0 s^{-1} . Although this uncertainty is high, the high correlation coefficients generated justify confidence in the slopes reported.

The magnitude of N_1 for our solutions is similar to that seen for some of the less-concentrated solutions which Baird

studied. One effect which Baird observed, not seen in the current work, is that of a low-shear plateau in Ψ .

The magnitude of the normal stresses show much less variation for our solutions than those seen in the systems studied by Kiss and Porter⁹⁹. In the latter studies, N_1 varied from $(\pm)10^0$ to $(\pm)10^4$ Pa*s, while for the solutions viewed here, N_1 varied from $(+)10^2$ to 10^4 Pa*s. This may be indicative of a more elastic solution, with less shear-induced orientation.

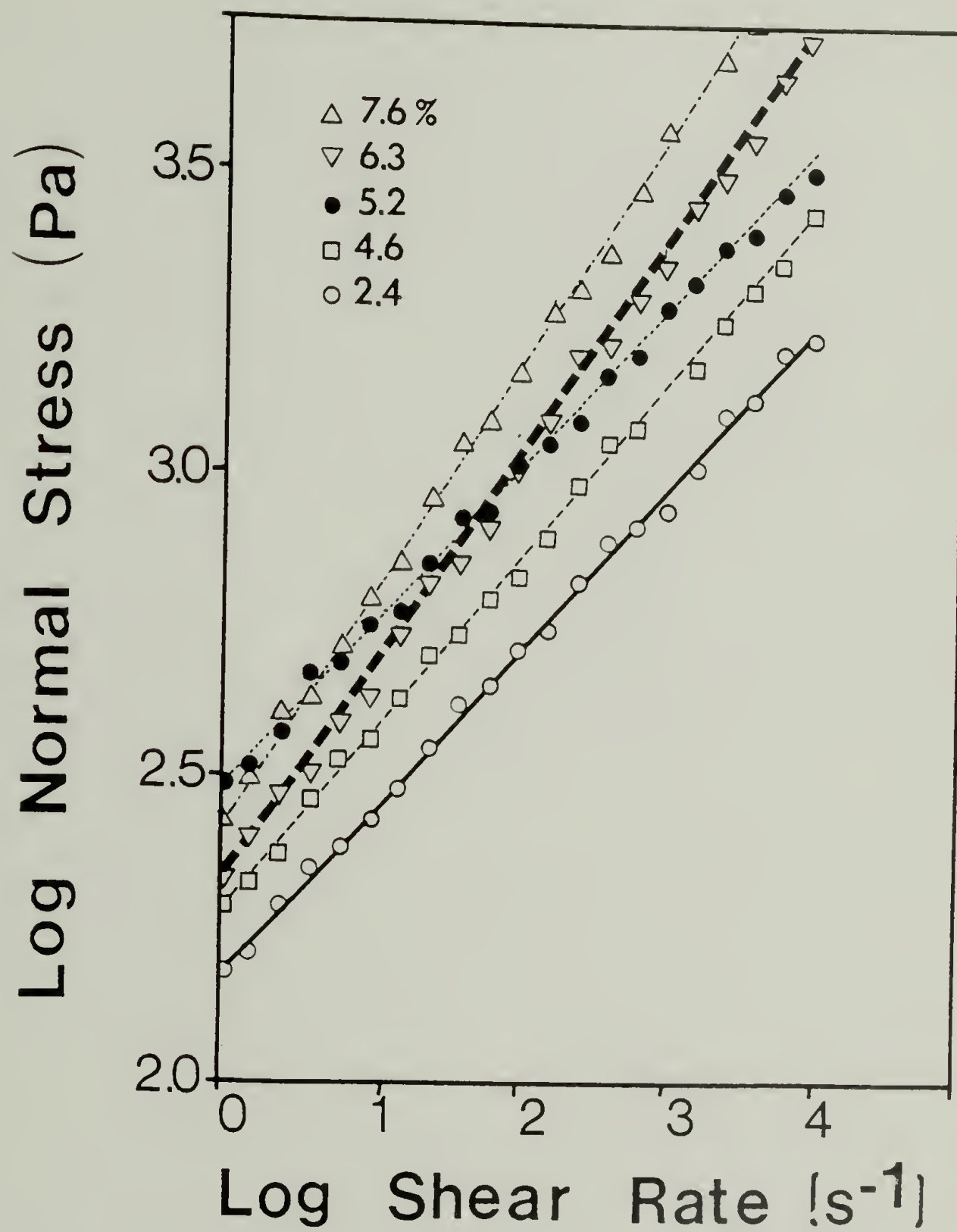


Figure 3.10. Normal stress vs. shear rate for ST-4.

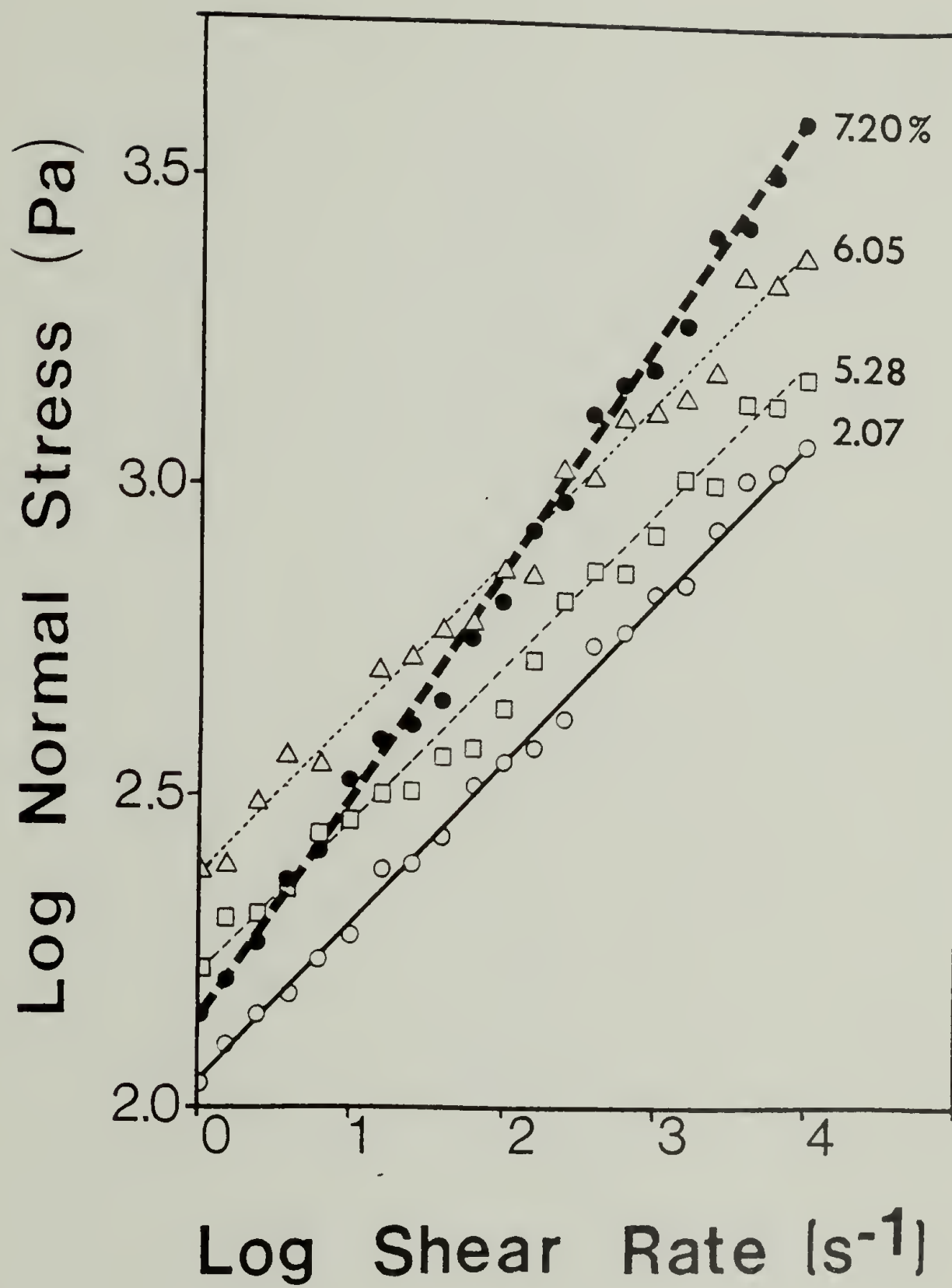


Figure 3.11. Normal stress vs. shear rate for ST-3.

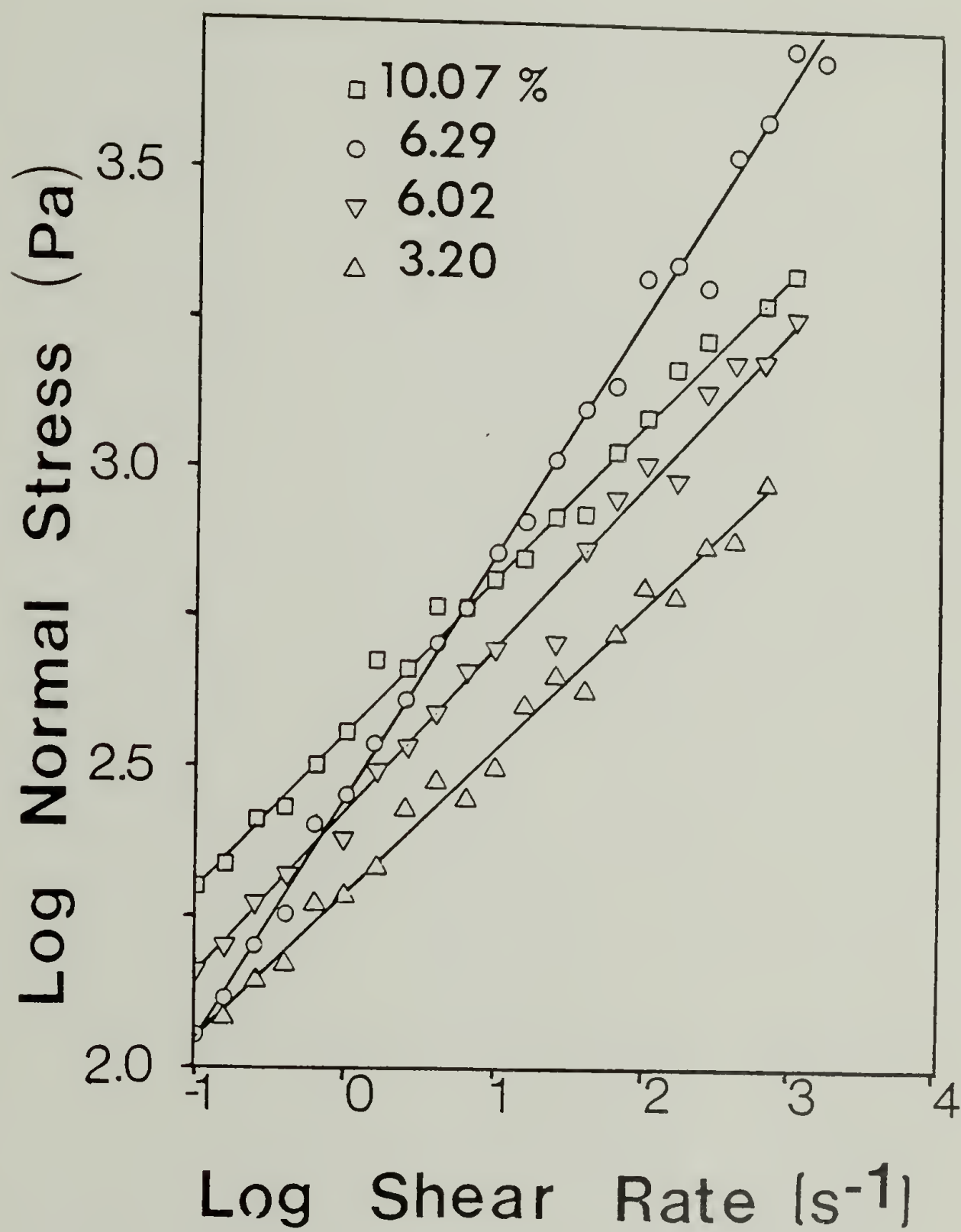


Figure 3.12. Normal stress vs. shear rate for LB-1.

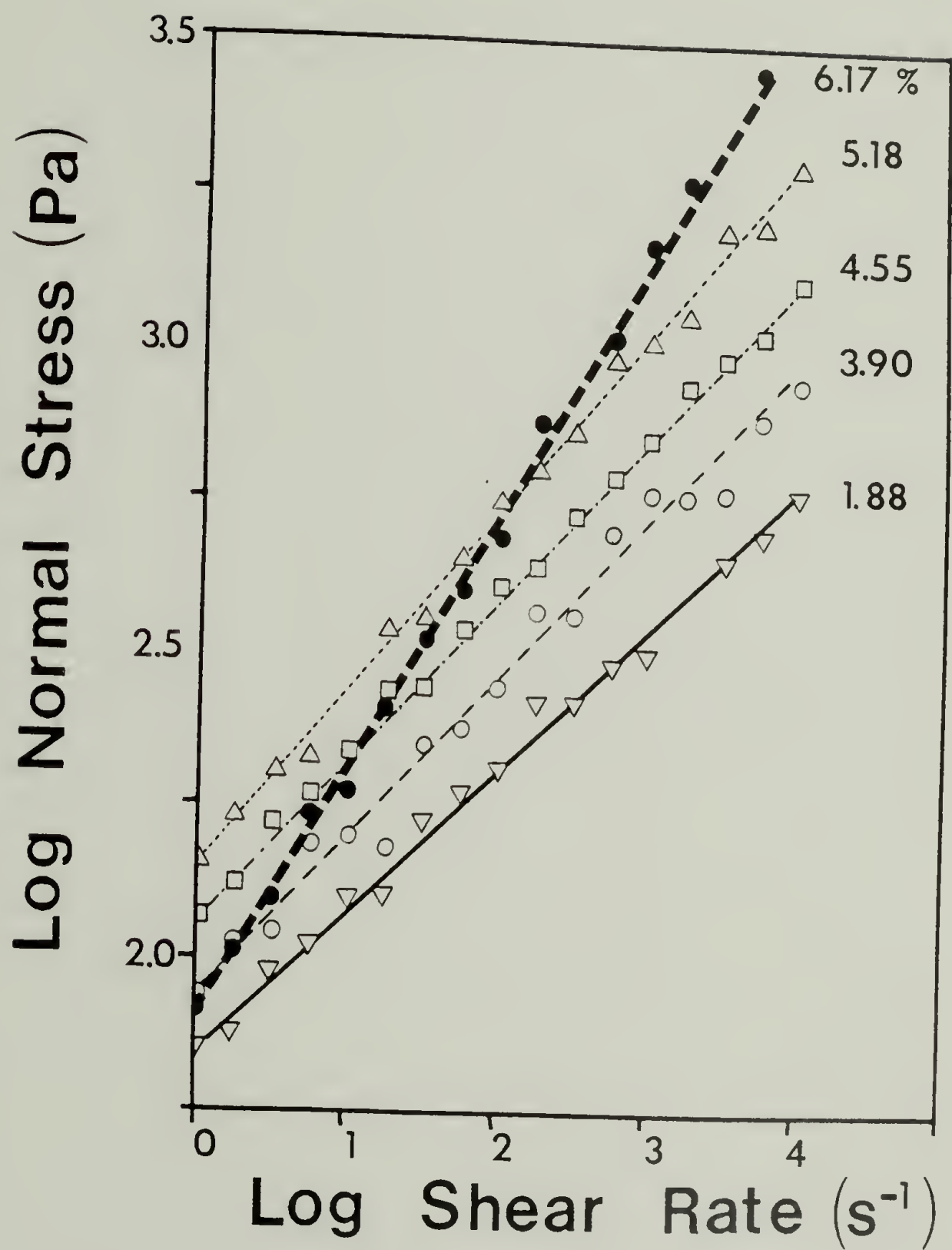


Figure 3.13. Normal stress vs. shear rate for ST-1.

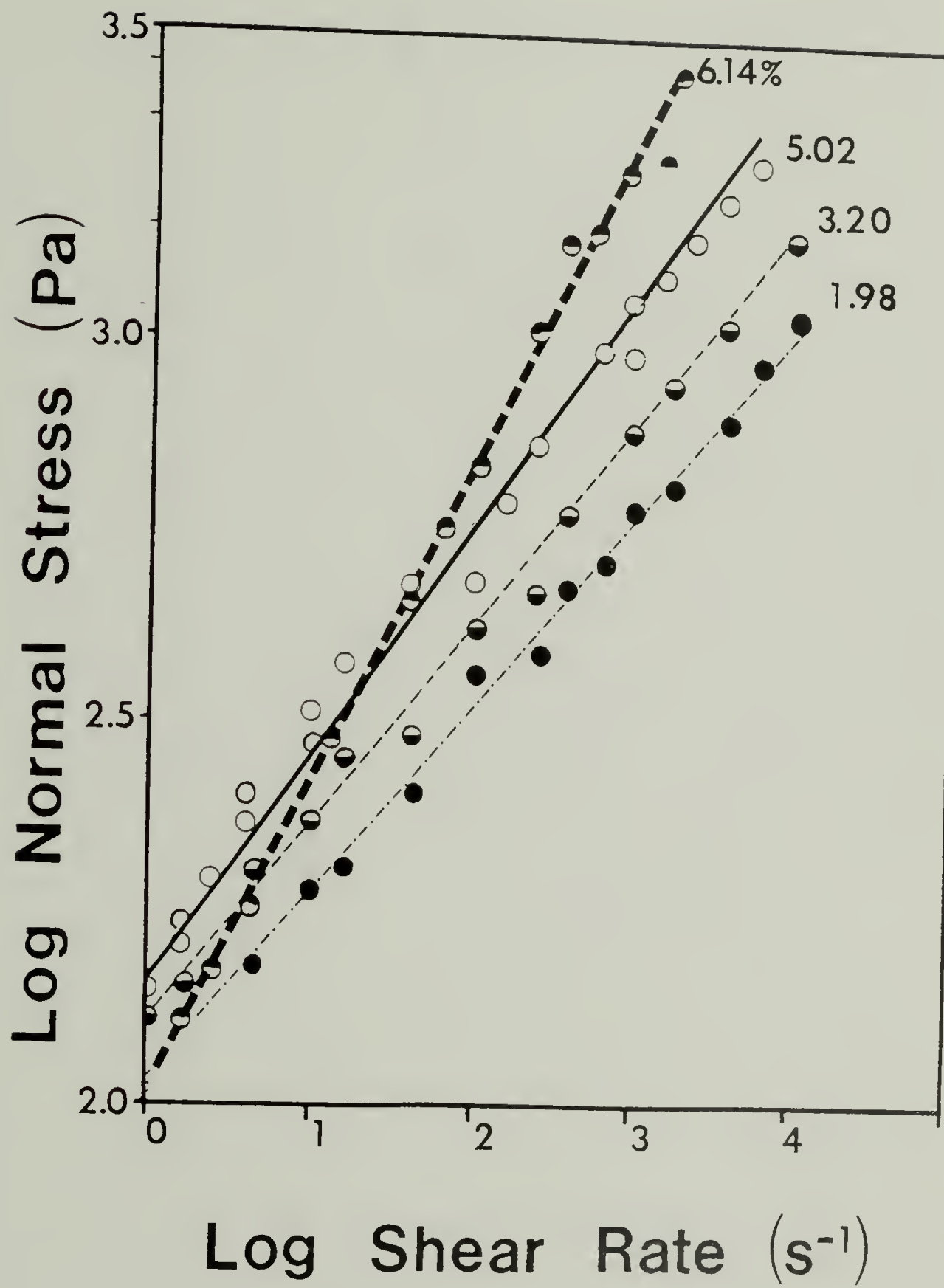


Figure 3.14. Normal stress vs. shear rate for ST-2.

Table 3.1. Slopes of Normal Stress-Shear Rate curves for Star-Block Copolymers.

<u>Polymer</u>	<u>Concentration</u> <u>(Wt. % Copolymer)</u>	<u>$d(\log N_1)/d(\log \dot{\gamma})$</u>	<u>corr.</u> <u>coef.</u>
ST-1	1.88	0.27	0.988
	3.90	0.25	0.994
	4.55	0.27	0.991
	5.18	0.29	0.978
	6.17	0.39	0.990
ST-2	1.98	0.28	0.998
	3.20	0.29	0.991
	5.02	0.33	0.986
	6.14	0.47	0.993
ST-3	2.07	0.26	0.985
	5.28	0.24	0.994
	6.05	0.25	0.996
	7.20	0.36	0.978
ST-4	2.38	0.26	0.990
	4.63	0.29	0.993
	5.16	0.28	0.982
	6.3	0.34	0.988
	7.6	0.28	0.997

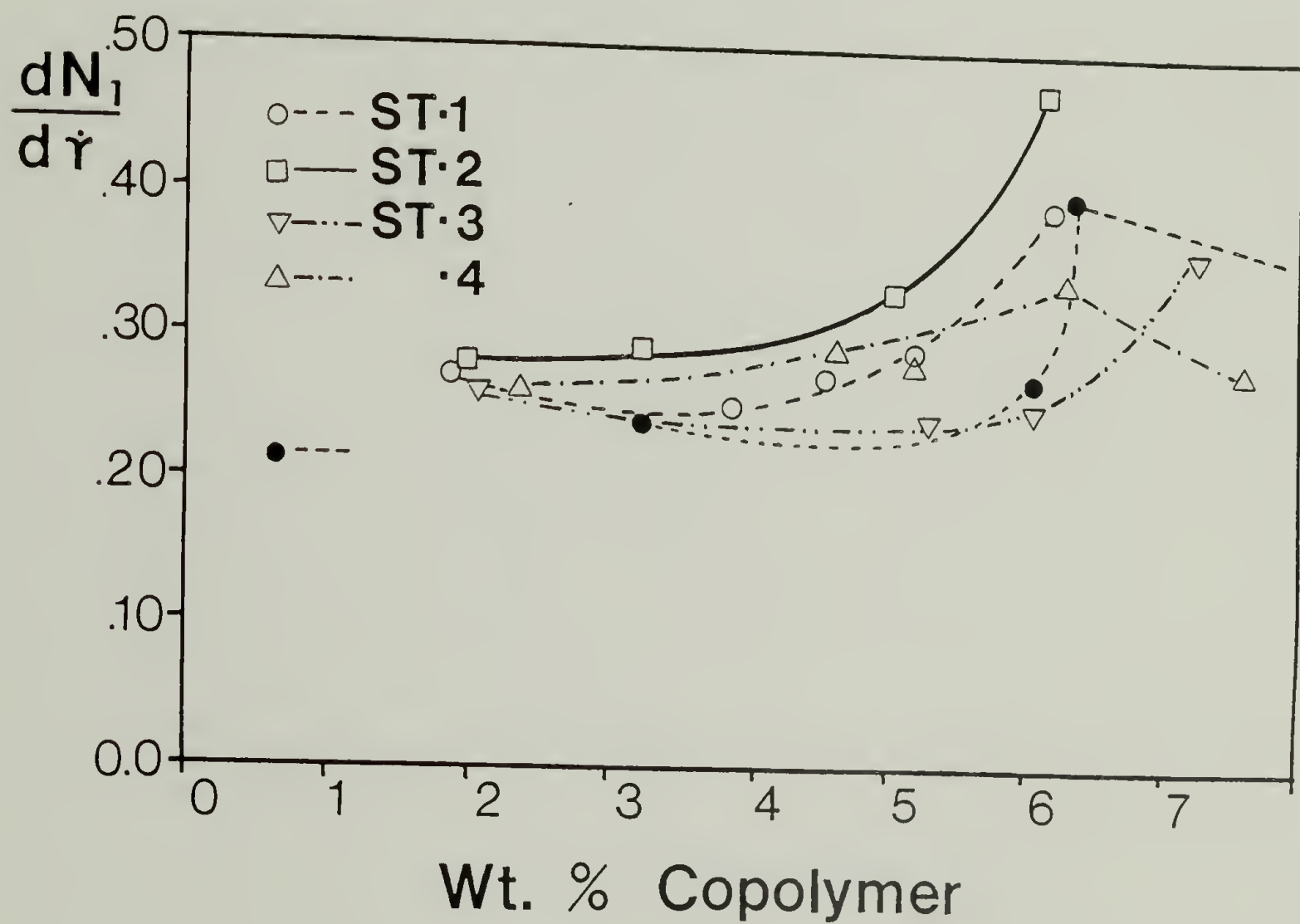


Figure 3.15. The slopes of the Normal Stress-Shear Rate curves for the block copolymers.

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CHAPTER 4

FIBER PROPERTIES AND MORPHOLOGY

4.1 Fiber Spinning

4.1.1 Experimental

As part of the morphological investigation of these copolymers and to determine the effect of the mesophase on ultimate properties, fibers were dry-jet, wet-spun from solutions into a water coagulant bath. Some, noted in Table 4.1, were spun by Carmen Gabriel. On these fibers, Carmen Gabriel also measured tensile properties, which were subsequently confirmed by the author. In general, no heat-treatment was performed.

4.1.2 Results and Discussion

A nonuniform cross-section rendered quantitative determination of the strengths and moduli impossible, but the trend was that the fibers spun from anisotropic solutions were stronger and stiffer than those spun from isotropic solutions, as Table 4.1 shows. In addition, the tensile properties of fibers spun from the anisotropic PBA solution were greater than those spun from solutions of the block copolymers. This is presumably due to the weakening effect of the coil-like PDMS. The tensile strengths and moduli of each of the fibers spun from the block copolymer solutions, except the anisotropic LB-1 solution, could be approximated by the respective property of neat PBA, divided by the percentage of PBA in the polymer. This may be coincidental.

Moreover, comparison with the literature values (Table 1.1) for the tensile properties of PBA reveals that our fibers fall short of the optimum achievable. This may be due to the affinity of the DMAc for water, which can lead to nonuniform coagulation, and hence defects, of the fiber. It may be emphasized, however, that this experiment was less an exercise in optimization than a comparison of similar species under equivalent conditions. Because compressive strength is much more sensitive to defects in the fiber than is tensile strength, the compressive strength of the fibers could not be estimated or compared.

4.2 X-Ray Scattering Studies

Once a difference was noted in tensile properties between fibers spun from isotropic solutions and those spun from anisotropic solutions, a comparison in microstructural perfection was indicated.

4.2.1 Experimental

X-Ray Scattering was performed in a Statton camera at ambient temperature. The d-spacings were calculated by the Bragg equation,

$$d = \lambda / \{2 \sin[\tan^{-1}(D/2L)]\}, \quad (4.1)$$

Where L is the distance from the center of the film to the reflection, D is the distance from sample to detector, and λ is the wavelength of the radiation. For these tests, the sample-to-film distance was 53.1 mm; λ for the radiation utilized, $\text{CuK}\alpha$, was $1.54178 \text{ \AA}^{100}$.

4.2.2 Results and Discussion

Table 4.2 summarizes the calculated d-spacings. It is noted that there is little difference in crystalline microstructure between those fibers spun from anisotropic solutions and those spun from isotropic solutions. Consideration of the actual films, however, shows differences in orientation. It is seen that the reflections are sharper for the LB-1A and ST-4 fibers than for the ST-1 and LB-1I fibers.

The d-spacings calculated for these fibers are nearly identical to those calculated for PBA fibers¹⁰¹. From this, we may conclude that the PDMS is non-crystalline and unoriented, even in the fiber.

Table 4.1. Fibers spun and tensile properties.

<u>Polymer</u>	<u>Conc.</u> <u>(wt. %)</u>	<u>Strength</u>		<u>Modulus</u>		<u>Elongation</u> <u>to Break (%)</u>
		<u>(MPa)</u>	<u>(MPa/ϕ)</u>	<u>(GPa)</u>	<u>(GPa/ϕ)</u>	
LB-1A [*]	10.4	121.2	1320	7.76	84.3	7.0
LB-1I [*]	4.0	52.3	570	2.33	25.3	29.1
ST-1 [*]	4.0	49.1	530	2.23	24.2	28.3
ST-4A	10.1	105.9	300	6.88	19.5	7.2
PBA	9.7	525	525	20.5	20.5	2.5

* Denotes fibers spun by C. Gabriel.

"I" denotes LB-1 fibers spun from isotropic solution;

"A", those spun from anisotropic solution.

"MPa/ ϕ " and "GPa/ ϕ " denote the respective property, divided by the weight percent PBA in the block copolymer.

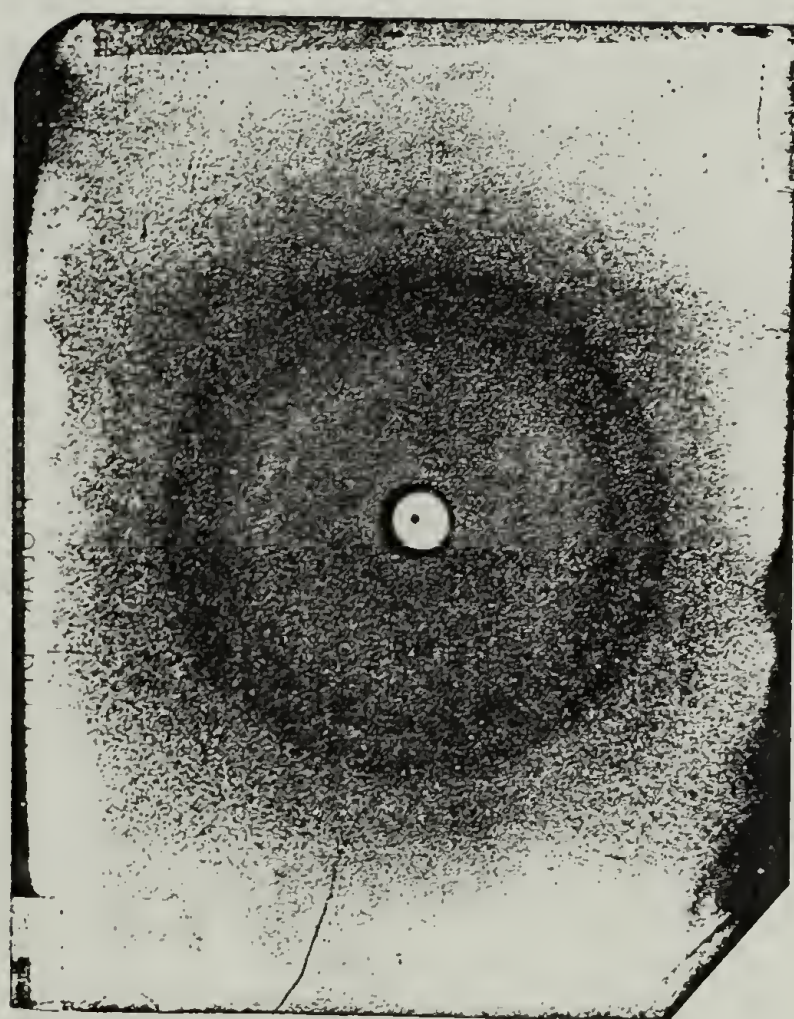


Figure 4.1. WAXS Pattern of ST-1 Fiber (spun from isotropic solution).



Figure 4.2. WAXS Pattern of ST-4 Fiber (spun from anisotropic solution).

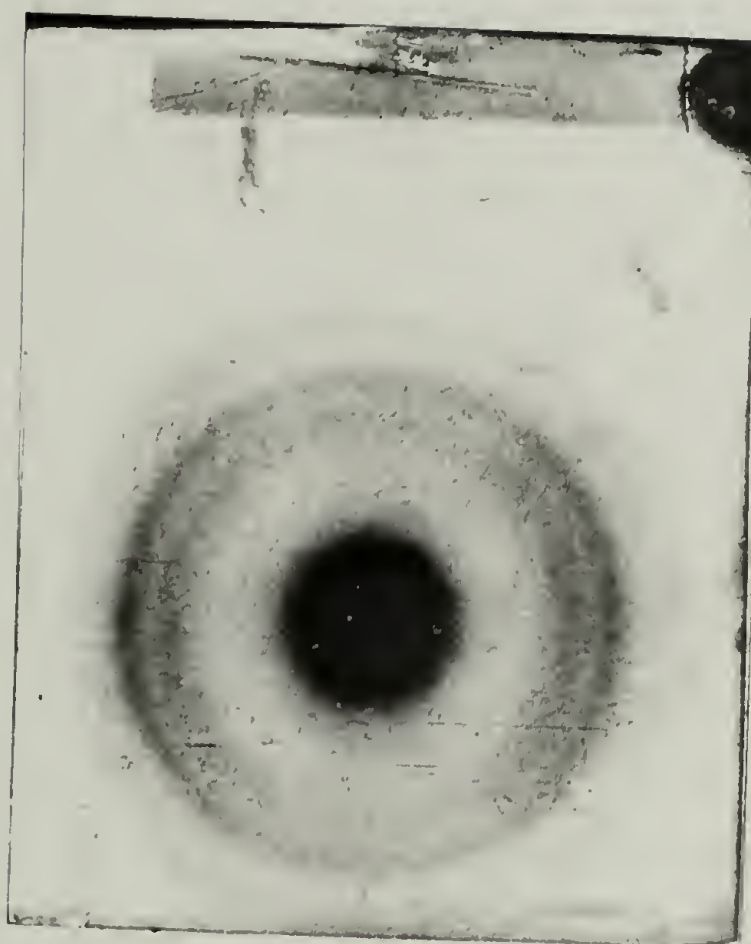


Figure 4.3. WAXS Pattern of LB-1 Fiber (spun from isotropic solution).

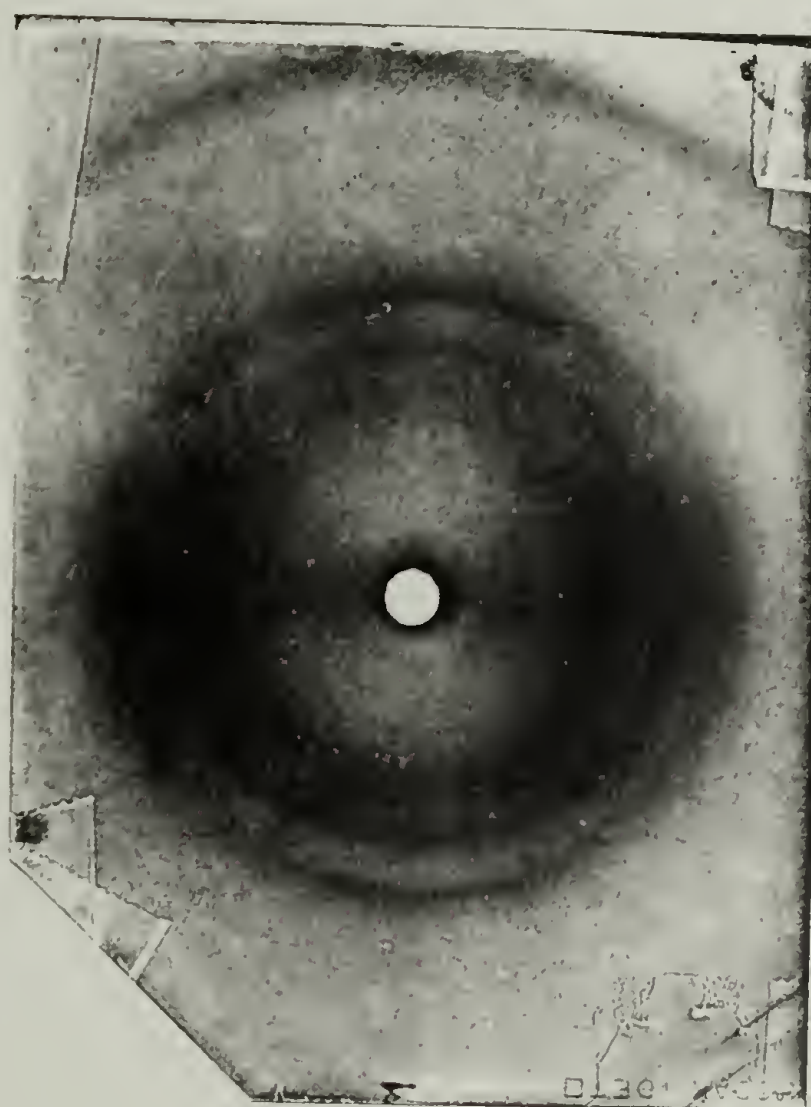


Figure 4.4. WAXS Pattern of LB-1 Fiber (spun from anisotropic solution).



Figure 4.5. WAXS Pattern of PBA Fiber (spun from anisotropic solution).

Table 4.2. Results of X-Ray analysis on fibers.

<u>Fiber</u>	<u>d(A)</u>
ST-1 [*]	2.99, 3.12, 3.73, 4.30
LB-1A [*]	e: 2.97, 3.73, 4.30 m: 3.11
LB-1I [*]	e: 3.76, 4.40 m: 3.15
ST-4	e: 3.01, 3.75, 4.40 m: 3.10
PBA	e: 3.00, 3.70, 4.29 m: 3.13

* Denotes fibers spun by C. Gabriel.

"I" denotes LB-1 fibers spun from isotropic solution;

"A", those spun from anisotropic solution.

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CHAPTER 5

SUGGESTIONS FOR FUTURE WORK

Further Work With Star LCPs

At this point, with these unique compositions synthesized and their rheology characterized, there are several interesting experiments which suggest themselves. Many of these relate to one of the original goals of the star LCP synthesis, that of forming fibers and films with improved transverse properties. Others relate to problems of purely scientific interest.

Firstly, a fundamental limitation on the attainable strengths and moduli of fibers and films is the PDMS component of the star polymers. The synthesis and characterization of star polymers incorporating flexible polymers of higher moduli and strengths, such as polystyrene, polycarbonate, or aliphatic polyamides, would be likely candidates.

Secondly, another approach would be to form fibers and films from some of the thermotropic stars synthesized by Dickstein or their analogues. This would of course necessitate synthesis in much greater quantities than those currently available. Additionally, blends of these polymers with their linear analogues would be interesting and potentially profitable.

In a similar vein, studies of co-solutions of these star polymers with PBA homopolymers would be interesting.

Solution properties such as phase diagrams, rheology, and processing could be essayed.

With the systems studied in this dissertation, significant distinctions were found between the linear copolymer LB-1 and the star ST-1. The sole difference between the two was the number of arms. Synthesizing and studying polymers which differ only in the number of arms could yield important insights. It is likely that increasing the number of arms would inhibit liquid-crystallinity, but this remains to be verified.

As noted in Chapter 2, the PDMS flexible block had both an enhancing and inhibiting effect on the liquid-crystallinity of the star-block copolymers. This leads to several questions, including: At what flexible spacer length does the behavior of the PDMS invert? This work identified the answer as lying between 950 and 1550, but further precision, accessible only with more synthesis, would be interesting. In addition, one may expect that similar behavior would be observed with other star-block LC polymers, but this has not been demonstrated. Finally, the question of how the mesophasic character depends on PBA block molecular weight has yet to be addressed.

With the strongly shear-thinning character of all of the solutions studied, and with the sharply increasing viscosity with concentration for ST-1 and ST-2, one may expect interesting effects of shear or elongation on the birefringence of several of the solutions, even those

isotropic at rest. The available apparatus and limitations on sample quantities precluded such studies for this dissertation, but a logical extension of this work would be to study rheo-optics of these solutions in the manner of Asada¹⁰² or Kiss¹⁰³. Studies of effects of start-up and cessation of shear, as well as light scattering of the solutions in flow, would be highly illuminating.

The phase-separated nature of the distinct blocks in the copolymers is an inescapable fact of the systems, according to current knowledge. However, if a cosolvent system could be developed, either by finding another solvent for PBA which is also a solvent for PDMS, or by synthesizing lyotropic polymers with more compatible blocks, the liquid-crystallinity could be enhanced.

5.2 References

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