

AD-A205 921

2

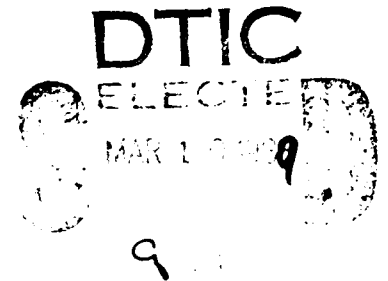
AFOSR-TR- 89-0288

CPS.GCB 2/8/89

COMPLETED PROJECT SUMMARY

TITLE: Physical-Chemical Studies of Solutions Processing of Nematic Polymers

PRINCIPAL INVESTIGATOR: Professor Guy C. Berry
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213



INCLUSIVE DATES: 1 September 1985 → 31 August 1988

COSTS AND FY SOURCE: \$163,327 FY 86
\$150,255 FY 87
\$159,978 FY 88

SENIOR RESEARCH PERSONNEL:	Dr. K. Se	Dr. G. B. Sohoni
	Dr. K. Suresh	Mr. L. Du

JUNIOR RESEARCH PERSONNEL:	C. Wei-Berk	C. P. Spencer
	C. S. Kim	M. Srinivasarao

PUBLICATIONS:

"Studies on Dilute Solutions of Rodlike Macroions. III. Integrated Intensity and Photon Correlation Light Scattering Investigation of Association", Y. Einaga and G. C. Berry, in *Micordomains in Polymer Solutions*, Ed. by P. Dubin, Plenum Publishing Co. New York 1985, Chapter 11.

"Rheological Properties of Rodlike Polymers in Solution. 2. Linear and Nonlinear Transient Behavior", S. Venkatraman, G. C. Berry and Y. Einaga, *J. Polym. Sci., Polym. Phys. Ed.* 23, 1275-1295 (1985).

"Rheological Properties of Rodlike Polymers in Solution. 3. Transient and Steady-State Studies on Nematic Solutions", Y. Einaga, G. C. Berry, and S.-G. Chu, *Polym. J.*, 17, 239 (1985).

"Rheological and Rheo-optical Studies of a Constitutive Equation for Nematogenic Solutions of Rodlike Polymers", G. C. Berry, *Disc. Faraday Soc.* No., 79, 141-148 (1985).

"Studies on Dilute Solutions of Rodlike Macroions. 4. Aggregation with Enhanced Orientational Correlation", R. Furukawa and G. C. Berry, *Pure Appl. Chem.*, 57, 913-920 (1985).

"Rheological and Rheo-Optical Properties of Solutions of Rodlike Polymers", G. C. Berry, *Polym. Mater. Sci. Eng.*, 52, 82 (1985).

89 0 00 000

"Light Scattering Studies of Orientational Order in Supramolecular Aggregates of Rodlike and Multipli-Broken Rodlike Molecules", G. C. Berry, C. C. Wei and R. Furukawa, *Polym. Preprints, Am. Chem. Soc.*, **27** (1), 228 (1986).

"Rheological and Rheo-Optical Studies with Nematogenic Solutions of a Rodlike Polymer: A Review of Data on Poly(phenylene benzobisthiazole)", G. C. Berry, in *Institute for Mathematics and its Applications, Vol. 5, Theory & Applications of Liquid Crystals*, Ed. By J. L. Ericksen and D. Kinderlehrer, Springer-Verlag, New York (1987), p. 1.

"Nematic Solutions of Rodlike Polymers. 1. Light Scattering from Nematic Solutions with Complex Texture; and Phase Separation in Poor Solvents", Kazunori Se and G. C. Berry, in *Reversible Polymer Gels and Related Systems*, Ed. by P. S. Russo, *Am. Chem. Soc. Symposium Series* (1987), p. 129.

"Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solution of a Rodlike Polymer", Kazunori Se and G. C. Berry, *Mol. Cryst. Liq. Crystal* **153**, 133 (1987)

"Rheological, Rheo-optical and Light Scattering Studies on Nematic Solutions of Poly(1,4-phenylene-2,6-benzobisthiazole)", G. C. Berry, Kazunori Se, and Mohan Srinivasaro, in *High Modulus Polymers*, Ed. by A. E. Zachariades and R. S. Porter, Marcel Dekker, New York (1988), p. 195.

"Rheological Studies on Blends of Rodlike and Flexible Chain Polymers", C. S. Kim, V. S. Sullivan, and G. C. Berry, *Confr. Proceed, 46th. Tech. Confr., Soc. Plastics Engineers* **34**, 990 (1988).

"Rheological Properties of Nematic Solutions of Rodlike Polymers", G. C. Berry, *Mol. Cryst. Liq. Cryst.*, **165**, 273 (1988).

"Studies on Aligned Nematic Solutions of a Rodlike Polymer", G. C. Berry and M. Srinivasarao, *Abstracts, Int'l. Symp. on Dynamics of Macromolecules by Electric and Optical Methods, Tokyo* (8-10 August, 1988).

"Properties of Solutions of Rodlike Chains From Dilute Solutions to the Nematic State", G. C. Berry, *Proceedings, Materials Research Society, Boston, November 1988*.

"Molecular Composites Formed by Solutions of a Rodlike Polymer (PBT) in Polyphosphonic Acid", A. F. Charlet and G. C. Berry, *Polymer*, in press.

"Studies on Dilute Solutions of Rodlike Macroions. 5. Electrostatic Effect on Intermolecular Association", C. Wei-Berk and G. C. Berry, to be submitted.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Investigations have involved solutions of the rodlike chain poly(1,4-phenylene-2,6-benzobisthiazole), PBT, and related copolymers containing a small fraction of the phenylene replaced by bipyridyl ether. Studies include: 1) The kinetics of polymerization of PBT in the nematic phase; 2) The supramolecular structure of PBT in solution; 3) The phase equilibria of blends of PBT and nylon in solution; 4) The rheological properties of blends of PBT and nylon in solution; and 5) The properties of fully aligned monodomains in nematic solutions of PBT.

The polymerization kinetics of PBT did not show any change in rate at the isotropic to an anisotropic phase transition for the solutions studied. At higher conversions (above 90%), the polymerization rate constant decreases markedly. This is attributed to effects on the diffusion of the chains along their axes, and comparisons are made to available theoretical models.

Static and dynamic light scattering and viscometric studies on solutions of a PBT copolymer show that its conformation is controlled by intramolecular electrostatic interactions. These cause the chain to expand with decreasing ionic strength of the solvent, but do not lead to a rodlike conformation for the PBT copolymer, even at the lowest ionic strength encountered (10^{-3} mol/l) in this work. In some solvents PBT or its copolymer tend to aggregate. This can lead to a thermochromic effect accompanied by enhanced intermolecular order if the solvent becomes thermodynamically poorer with change in temperature. Such behavior, which can be understood on the basis of theoretical work by Flory and coworkers, could have undesirable effects in solution processing.

The rheological properties of isotropic blends of rodlike PBT and flexible chain nylon show some dramatic effects, including a higher viscosity for the blend than is observed for either component. This behavior is understood in terms of constraints on the diffusion of the rodlike chains caused by the flexible chains. The effect occurs only if the reptational diffusion of the latter is slow enough to make its time constant at least as long as that for diffusion of the rod along its contour. Otherwise, the presence of the flexible chains merely alters the local mobility, such that the viscosity for the blend may be represented by the expression for the viscosity of an isotropic rodlike solution, with the solvent viscosity in the latter replaced by the viscosity of the flexible chain solution.

Fully aligned (monodomains) samples of nematic PBT solutions have been prepared and used in static and dynamic light scattering experiments to study the Frank elastic constants and the Leslie-Ericksen viscosities of nematic PBT solutions. The effects of magnetic fields and shear deformations on the director alignment has also been studied with the monodomain samples. It has been found that shear flow is stable only if initiated from an aligned state with the director in the flow direction. Flow instabilities develop otherwise, explaining some of the features previously observed in the shear flow of nematic solutions of PBT.

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; Distribution unlimited		
2b DECLASSIFICATION DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 89-0288		
6a NAME OF PERFORMING ORGANIZATION Carnegie-Mellon University		6b OFFICE SYMBOL (If applicable)		7a NAME OF MONITORING ORGANIZATION AFOSR/NC	
6c ADDRESS (City, State, and ZIP Code) 4400 Fifth Avenue Pgh., PA 15213				7b ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	
8a NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR		8b OFFICE SYMBOL (If applicable) NC		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-85-C-0140 F49620-85-C-1040	
8c ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO 61102F		PROJECT NO 2303	
				TASK NO A3	
				WORK UNIT ACCESSION NO	
11 TITLE (Include Security Classification) Physical-Chemical Studies of Solution Processing of Nematic Polymers					
12 PERSONAL AUTHOR(S) Guy C. Berry					
13a. TYPE OF REPORT Final Report		13b. TIME COVERED FROM 1/9/85 TO 31/8/88		14. DATE OF REPORT (Year, Month, Day) 1989 February 8	
15. PAGE COUNT 32					
16. SUPPLEMENTARY NOTATION					
17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			Rheology, Rodlike Polymer, Blend, Molecular Composites, Kinetics		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Investigations have involved solutions of the rodlike chain poly(1,4-phenylene-2,6-benzobisthiazole), PBT, and related copolymers containing a small fraction of the phenylene replaced by bipyridyl ether. Studies include: 1) The kinetics of polymerization of PBT in the nematic phase; 2) The supramolecular structure of PBT in solution; 3) The phase equilibria of blends of PBT and nylon in solution; 4) The rheological properties of blends of PBT and nylon in solution; and 5) The properties of fully aligned monodomains in nematic solutions of PBT. The polymerization kinetics of PBT are related to the translational diffusion in the nematic phase at high conversions. It is shown that the supramolecular structure can lead to enhanced order and a thermochromic effect under certain conditions. The rheology of blends of PBT and nylon is found to be controlled by the time constants for diffusion of the rodlike and flexible chains along their contours. Under certain conditions the viscosity of the blend may be much larger than that of either component. Studies on fully aligned nematic solutions of PBT provide insight to flow instabilities relevant to solutions processing in shearing deformations.					
20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Lt Col Larry P. Davis			22b. TELEPHONE (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL NC

TABLE OF CONTENTS

	PAGE
1. INTRODUCTION	1
2. DESCRIPTION OF RESEARCH RESULTS	1
2.1 KINETICS OF PBT POLYMERIZATION	1
2.2 STUDIES OF SUPRAMOLECULAR STRUCTURE IN PBT SOLUTIONS	2
2.3 PHASE EQUILIBRIA OF BLENDS	5
2.4 RHEOLOGY OF PBT-NYLON BLENDS	6
2.5 MONODOMAINS OF NEMATIC SOLUTIONS OF PBT	10
3. PUBLICATIONS	11
3.1 THESES	11
3.2 PUBLICATIONS	11
4. OTHER ACTIVITIES	13
5. REFERENCES CITED	17

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	☐

8718LCOM.GCB 2/8/89



A-1

Approved for public release;
distribution unlimited.

1. INTRODUCTION

Work supported by contract F49620-85-C-1040 for the period 1 September 1985 to 31 August 1988 has been in several areas:

1. Kinetics of polymerization of PBT in the nematic phase
2. Studies of supramolecular structure in PBT solutions
3. Phase equilibria of blends of PBT and nylon in solution
4. Rheological studies on blends of PBT in nylon
5. Studies on monodomains of nematic solutions PBT

Here PBT refers to poly(1,4-phenylene-2,6-benzobisthiazole), trans isomer. These areas are discussed in turn in the following.

2. DESCRIPTION OF RESEARCH RESULTS

2.1 KINETICS OF PBT POLYMERIZATION

The Ph.D. thesis of Cynthia Spencer on the polymerization of PBT in the nematic phase was completed and accepted in October 1987. (See Section 3.1) This work has been presented at a meeting of the American Chemical Society (See Section 4), but not yet submitted for journal publication. In this study the change of the intrinsic viscosity and the molecular weight averages (M_w and M_n) were followed as functions of the polymerization time for a solution in the nematic phase. Molecular weights were determined by size exclusion chromatography (SEC). Typical results are displayed in Fig. 1. The polymerization followed second-order kinetics for conversions up to about 97%. The transition from the isotropic to the nematic phase was not marked by any change in the rate constant, showing that the reactions studied were not diffusion controlled at that stage. The results for one polymerization are

shown in Fig. 2. By contrast, with monomer concentration low enough that the solution does not become nematic, the reaction becomes diffusion limited owing to the reduction in the rotational diffusion constant D_R and the nearly random orientation of the rods. [1] With increased monomer concentration, D_R is still relatively high when the solution forms a nematic phase, preventing diffusion control of the reaction. The alignment in the nematic phase makes further reactions dependent on the translational diffusion along the rod axis (diffusion constant $D_{T,||}$). Since $D_{T,||}$ does not decrease as rapidly as D_R with increasing chain length, the reaction remains free of diffusion limitations, at least until the conversion is high. The decrease in the rate constant for conversions in excess of 97% may reflect the effects of phase separation or intermolecular association.

2.2 STUDIES OF SUPRAMOLECULAR STRUCTURE IN PBT SOLUTIONS

The Ph.D. Thesis of Carolyn Wei on light scattering studies on rodlike and multipli-broken rodlike PBT polymers was completed and accepted in November 1986. (See Section 3.1) The work encompasses investigations on solutions in methane sulfonic acid (MSA), chlorosulfonic acid (CSA), and phosphoric acids. The results in the former two are discussed in terms of the effects of electrostatic interactions on chain dimensions, with these effects being particularly noted for solution in CSA owing to the low ionic strength of the latter. One part of this study has been prepared for journal publication, and will be submitted shortly. Studies on dilute solutions in phosphoric acids revealed that under suitable conditions these solutions exhibit enhanced orientational interchain order.

The data obtained on dilute solutions of a multipli-broken rodlike PBT copolymer included data on the intrinsic viscosity $[\eta]$, the light scattering

averaged second virial coefficient, $A_{2,LS}$, hydrodynamic radius $R_{H,LS}$, and mean square radius of gyration $R_{G,LS}^2$ and the ratio of the depolarized and polarized Rayleigh ratios, R_{HV}/R_{VV} . The latter proved to be negligibly small in solutions in CSA, MSA and 100% H_3PO_4 , showing that the copolymer did not adopt a rodlike conformation in dilute solution in these solvents. However, values of the molecular parameters varied among the solvents, and varied with concentration for solutions in CSA and MSA. Using relations summarized in the Appendix, these results are interpreted in terms of the electrostatic interactions among the charged copolymers causing contributions to the persistence length ρ and the excluded volume parameter B that increase with decreasing ionic strength of the solution. These effects are suppressed for solutions in 100% H_3PO_4 owing to the high ionic strength of the latter. Unfortunately, intermolecular association occurs in the latter system except for very low polymer concentration. The results explain some of the heretofore puzzling observations made on dilute solutions of PBT or similar polymers.

Rather different behavior was observed with solutions of the copolymer in 87% H_3PO_4 . In particular, a thermochronic effect was observed with increasing temperature, along with a simultaneous increase in R_{HV} , R_{VV} and the ratio R_{HV}/R_{VV} at all scattering angles, see Figures 2 and 3. The effects culminate in physical phase separation if the polymer if the temperature is high enough. By contrast, $R_{H,LS}$ is observed to decrease slightly with increasing T . The results also reveal molecular association in 87% H_3PO_4 , even at low concentrations. The observed behavior is rationalized on the basis of theoretical treatments given by Flory and coworkers [2]. In these theories a wide biphasic gap can develop under poor solvent conditions, with an ordered concentrated phase in equilibrium with a disordered, dilute phase. The disordered supramolecular aggregates represent microdomains high enough in

polymer concentration to form such an ordered phase under poor solvent conditions ($A_2 \approx 0$). For example, with solutions in 87% H_3PO_4 , A_2 is small at 25°C, and the ordered phase may be reversibly formed by increased temperature and destroyed by decreased temperature [2]. The ordered phase may also be formed by the addition of salt [4] or water [3] to solutions in other protic acid solvents. Effects of this kind may have profound effects on the processing of concentrated solutions of rodlike chains or their copolymers.

The slow addition of water to a nematic phase of PBT in solution in methane sulfonic acid has also been observed to cause effects similarly related to the thermodynamic behavior predicted by Flory and coworkers [2]. With very slow water uptake (from the vapor), a nematic phase was observed to become isotropic [5]. Depolarized light scattering studies revealed supramolecular structures, with the rodlike molecules aggregated with their axes nearly parallel. The effect of such aggregation was to reduce the number of independent rodlike entities below the level required to sustain an ordered state, with consequent transition to a disordered phase. With increased water uptake the thermodynamic condition became poor enough to force the system into the wide-biphasic gap described above, such that a very turbid nematic phase was formed. This could be reversibly transformed to an isotropic phase by increased temperature. We postulate that aspects of this sort of phase transformation are important in the coagulation step in the solution processing of PBT solutions. The turbidity mentioned above reflects the formation of an ordered, concentrated phase, perhaps by a spinodal decomposition. Such a tendency in the coagulation step would lead to a fibrillar structure early in the coagulation. The much reduced mobility of the rods in such a state would promote retention of such a structure in the final

form, giving a multitude of structural defects and a fibrillar microstructure in the solid state, as has been repeatedly observed.

2.3 PHASE EQUILIBRIA OF BLENDS

Blends of PBT and nylon in solution in methane sulfonic acid (MSA) were selected as a model system for solutions to be used in the preparation of molecular composites. The system has been studied previously, principally with respect to its use in the formation of films [6]. A single phase of the three component solutions is an essential requirement in the preparation of a molecular composite. Accordingly, ternary phase diagrams were examined for mixtures of a nylon and different PBT samples. The observations made for one of these is shown in Fig. 5. The solid lines in Fig. 5 were constructed with a theory of Flory and coworkers [4]. The chain length x_R of the rods was chosen to force agreement with the equilibria observed for the PBT-MSA solutions, and that x_F of the flexible chain was selected to mimic the onset of nematic phase formation in the ternary mixtures. One substantial surprise refers to compositions 630 and 720, both of which were observed to be isotropic in a range of compositions where a nematic phase was expected. This behavior is believed to reflect the formation of molecular aggregates of PBT, with the chain axes in parallel array. The formation of such aggregates reduces the number of effective (independent) particles, and can cause a nematic to isotropic phase transition as discussed in the preceding section [5]. Such aggregation could have a deleterious effect on the mechanical properties a molecular composite processed from the solution. This deterioration in properties is attributed to a suppressed number density of independent particles, as well as possible decrease in the length to diameter ratio of the existing particles (see below).

Measurements of the depolarized Rayleigh ratio $R_{HV}(q)$ on several compositions well into the isotropic phase regime give $R_{HV}(q)/c$ (for $q = 0.005 \text{ nm}^{-1}$) that is similar to $R_{HV}(0)/c$ for the isotropic solutions, suggesting the absence of significant aggregation in such cases.

The work described above comprises part of the Ph.D. research of C. Kim accepted for publication in August, 1988.

2.4 RHEOLOGY OF PBT/NYLON BLENDS

Rheological data have been obtained on compositions in the single phase region of the phase diagram. These measurements include the linear creep compliance $J_0(t)$, the linear recoverable compliance $R_0(t)$, and the viscosity η_κ , recoverable compliance R_κ and flow birefringence following steady-state flow. The limiting values of η_κ and R_κ at small κ are the linear viscosity η_0 and recoverable compliance R_0 , respectively. In all cases $R_0(t)$ is used to compute the retardation times λ_i and weights r_i defined by the expression [7]

$$R_0(t) = R_0 - (R_0 - R_g) \sum r_i \exp(-t/\lambda_i) \quad (1)$$

where R_g is the "instantaneous" value of $R_0(t)$. To first order, the distribution of the normalized retardation times λ_i/τ_c are those of the PBT solution without nylon, where $\tau_c = \eta_0 R_0$. (Of course, as discussed below, η_0 depends markedly on the composition, so the unnormalized λ_i do depend markedly on the composition). The relative invariance of the λ_i/τ_c distribution with composition for a given PBT sample is attributed to the enormous separation of the λ_i for PBT solutions as compared with the much smaller λ_i for the nylon solutions used. With use of the convolution integral [7]

$$\int_0^t ds G_0(s) J_0(t-s) = t, \quad (2)$$

the r_i, λ_i distributions have been converted by means given elsewhere [3] to distributions of relaxation times τ_i obtaining in the linear shear modulus $G_0(t)$:

$$G_0(t) = G_0 \sum g_i \exp(-t/\tau_i) \quad (3)$$

It is found that the data on η_K and R_K may be represented by use of a single-integral constitutive equation used previously to represent the behavior of PBT solutions [9,10].

$$\sigma_m(t) = G_0 \sum g_i \tau_i \int_0^t ds [\Delta\gamma(t,s)]^m F[\Delta\gamma(t,s)] \exp(-s/\tau_i) \quad (4)$$

where $\Delta\gamma(t,s) = \gamma(t) - \gamma(t-s)$ with γ the strain, and $F(\Delta\gamma)$ is a (nearly) universal function of the relative strain; $m = 1$ for the shear stress and $m = 2$ for the normal stress. The nonlinear behavior rests in the function $F(\Delta\gamma)$. Although small differences in the r_i, λ_i (or g_i, τ_i) distributions for different compositions show up in the dependence of η_K/η_0 and R_K/R_0 on shear rate for $\eta_0 R_0 \dot{\epsilon} > 50$, see Figs. 6 and 7, the dependence of η_K/η_0 and R_K/R_0 on $\eta_0 R_0 \dot{\epsilon}$ is similar enough that the behavior of the isotropic ternary compositions can be taken as that of the nylon free PBT solution if η_0 and R_0 are known for the ternary system.

For solutions of PBT, η_0 is well fitted [10] by the theoretical relation [11]

$$\eta_0 = \eta_s K N_A^2 M^{1/2} (\eta_{sp}/c) f(c) \quad (5a)$$

$$f(c) = [1 - Bc/c_{NL}]^{-4} \quad (5b)$$

where c is the polymer concentration, $M_L = M/L$, η_s is the solvent viscosity, K and B are constants nearly equal to unity, and c_{NI} is the concentration required to form a nematic phase with a chain of length L . For most of the compositions studied here, the concentration c_R of the PBT is small enough that in the absence of the nylon, η_0 is given by Eqn. (5a) with $f(c) \approx 1$, i.e., $\eta_0 = M[\eta](cL)^3$. In all cases, the viscosity η_F of the PBT-free nylon solution at the concentration c_F used in the ternary mixtures is much smaller than viscosity of the nylon-free PBT solution of concentration c_R used -- for the range of c_F studied, $\eta_F \ll c_F$ for the nylon solutions. Consequently, one might expect to find η_0 for the mixture given by Eqn. 5 with η_s replaced by the viscosity η_F of the nylon solution with concentration c_F . Such an approximation does not fit η_0 observed for ternary blends of PBT and nylon used to obtain the data in Fig. 8. As shown in Fig. 8, η_0 for the blend may exceed η_0 for the nylon-free solution at the same c_R by a large factor. Although no theoretical treatment is available, we postulate that the effect on η_0 is related to the function $f(c)$ in Eqn. 5. This function takes account of the restriction to translation of the rod parallel to its long axis caused by collisions with other rods. This provides a constraint release mechanism that becomes increasing important as c approaches c_{NI} [11]. In a blend, collisions with the flexible chains may play a similar role. If the translation of a flexible chain orthogonal to its curvilinear contour is slow enough in the ternary blend, η_0 might be given by Eqn. 5 calculated with $c = c_R$ and $f(c)$ calculated from Eqn. 5b using the total polymer concentration $c_R + c_F$ for c . The relevant parameters would be the time constants τ_R and τ_F for diffusion of the rod and flexible chains along their contours, respectively. As seen in Table 1, the calculated ratio τ_R/τ_F is not much larger than unity for samples P-53/Z-42 used to obtain the data in Figs. 6-8. Here,

$$\tau_R = \tau_R^0 [1 - (E/C_R)(C_R^*)^{3/2}]^{-1}$$

$$\tau_R^0 = 2\pi\eta_s L_R^3 / kT \ln(L_R/d)$$

$$\tau_F = 40\eta_s R_G^3 / (\pi^2 kT) [L_F C_F / (a \rho_F)]^{2/3}$$

with C_R^*/E equal to the concentration for which the rotational diffusion becomes vanishingly small, L_R and L_F the contour lengths of the rodlike and flexible chains, respectively, R_G the root-mean square radius of gyration of the flexible chain, ρ_F the density of the latter, and a the contour length of the flexible chain between its entanglement constraints (including those imposed by the rodlike chains).

In some cases studied, it appears that the viscosity is given by Eqn. 5 with $f(c)$ closer to unity than for the examples shown in Fig. 8, even though the composition is similar to those shown in Fig. 8. As seen in Table 1 for sample P-28/Z-42, this behavior corresponds to cases with much larger τ_R/τ_F . In such cases, the simple approximation mentioned above, with η_s merely replaced by the viscosity of the flexible chain solution provides a good representation of η_0 . In these cases, the flexible chain moves rapidly enough that it does not provide a geometric constraint to the diffusion of the rodlike chains. Rather, the presence of the flexible chains merely alters the local mobility. Depolarized light scattering studies are in progress to assess this postulate.

The rheological studies described in the preceding comprises part of the Ph.D. research of C. Kim, accepted in August 1988.

2.5 MONODOMAINS OF NEMATIC SOLUTIONS OF PBT

As discussed in references 5 and 12, methods have been developed to prepare monodomains of nematic PBT solutions. Elastic and quasielastic light scattering have been used to evaluate the Frank elastic constants and the viscosities for splay, bend and twist distortions of the director field [12]. In this work we have examined the effects of magnetic fields on the director field using monodomains of nematic PBT or isotropic PBT solutions with c near c_{NI} . [13] In principle, as discussed below orientation in a magnetic field might find use in the preparation of certain molecular composites. Molecular orientation is observed with isotropic solutions of PBT, with the behavior giving a positive diamagnetic susceptibility anisotropy $\Delta\chi$, where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ with $\chi_{\parallel}$ and $\chi_{\perp}$ the susceptibility parallel and perpendicular to the chain axis, respectively. With nematic solutions, the elastic constraints (i.e., as reflected in the Frank elastic constants) imposed by the nematic organization, including the effects of any adsorbed layer, may result in a complex director field $n(r)$ as the rodlike chains adjust in the external field -- such flow behavior has been observed with nematic solutions of PBT [13]. Nevertheless, it has been possible to achieve uniform, essentially defect free alignment in an external magnetic field. Most of this work has been carried out with a field strength of 4.7T, although a 14.7T field is available and has been used in some cases.

The ability to obtain aligned samples has provided the opportunity to examine flow behavior as a function of the orientation of the rodlike chains. Results to date show that slow flow is stable provided the axes of rodlike chains are initially aligned parallel to the flow directions. With other initial alignments (including that with the chains orthogonal to the flow direction and parallel to the shearing surface) instabilities develop at small strain, leading to a turbid solution in "steady-state" flow. This behavior explains the origin

of the results observed previously on flow if unaligned nematic solutions of PBT. It suggests that it may be difficult or impossible to obtain well oriented films by processing such solutions in simple shear.

3. PUBLICATIONS

A list of publications based on work sponsored in full or in part the AFOSR from 1985 to the present is given below. In addition, Ph.D. theses completed and accepted based on work sponsored in full or in part by AFOSR are listed.

3.1 THESES

1. Ruth Furukawa - Dilute Solution Characterization of Rodlike Poly [1,4-Phenylene Benzobisthiazole] (PBT) and Articulated Copolymers of PBT and Poly-1,4-Phenylene Benzobisoxazole] (PBO) (1985).
2. Caroline C-H. Wei - Study of Dilute Solution Properties of Rod and Rodlike Polymers (1986).
3. Cynthia Spencer - Anisotropic Phase Polymerization Kinetics of Rodlike Polymer Poly[(benzo(1,2,-3:4,5-d') bisthiazole-2,6-diyl)-1,4-phenylene] (1987).
4. C. S. Kim - Rheological Behavior of Blends of Rodlike and Flexible Chain Polymers in Isotropic Solutions (1988).

3.2 PUBLICATIONS

1. Studies on Dilute Solutions of Rodlike Macroions. III. Integrated Intensity and Photon Correlation Light Scattering Investigation of Association, Y. Einaga and G. C. Berry, in *Micordomains in Polymer Solutions*, Ed. by P. Dubin, Plenum Publishing Co. New York 1985, Chapter 11.
2. Rheological Properties of Rodlike Polymers in Solution. 2. Linear and Nonlinear Transient Behavior, S. Venkatraman, G. C. Berry and Y. Einaga, *J. Polym. Sci., Polym. Phys. Ed.* **23**, 1275-1295 (1985).
3. Rheological Properties of Rodlike Polymers in Solution. 3. Transient and Steady-State Studies on Nematic Solutions, Y. Einaga, G. C. Berry, and S.-G. Chu, *Polym. J.*, **17**, 239 (1985).

4. Rheological and Rheo-optical Studies of a Constitutive Equation for Nematogenic Solutions of Rodlike Polymers, G. C. Berry, *Disc. Faraday Soc. No.*, **79**, 141-148 (1985).
5. Studies on Dilute Solutions of Rodlike Macroions. 4. Aggregation with Enhanced Orientational Correlation, R. Furukawa and G. C. Berry, *Pure Appl. Chem.*, **57**, 913-920 (1985).
6. Rheological and Rheo-Optical Properties of Solutions of Rodlike Polymers. G. C. Berry, *Polym. Mater. Sci. Eng.*, **52**, 82 (1985).
7. Light Scattering Studies of Orientational Order in Supramolecular Aggregates of Rodlike and Multipli-Broken Rodlike Molecules, G. C. Berry, C. C. Wei and R. Furukawa, *Polym. Preprints, Am. Chem. Soc.*, **27** (1), 228 (1986).
8. Rheological and Rheo-Optical Studies with Nematogenic Solutions of a Rodlike Polymer: A Review of Data on Poly(phenylene benzobisthiazole), G. C. Berry, in *Institute for Mathematics and its Applications, Vol. 5, Theory & Applications of Liquid Crystals*, Ed. By J. L. Ericksen and D. Kinderlehrer, Springer-Verlag, New York (1987), p. 1.
9. Nematic Solutions of Rodlike Polymers. 1. Light Scattering from Nematic Solutions with Complex Texture; and Phase Separation in Poor Solvents. Kazunori Se and G. C. Berry, in *Reversible Polymer Gels and Related Systems*, Ed. by P. S. Russo, Am. Chem. Soc. Symposium Series (1987), p. 129.
10. Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solution of a Rodlike Polymer, Kazunori Se and G. C. Berry, *Mol. Cryst. Liq. Crystal* **153**, 133 (1987).
11. Rheological, Rheo-optical and Light Scattering Studies on Nematic Solutions of Poly(1,4-phenylene-2,6-benzobisthiazole), G. C. Berry, Kazunori Se, and Mohan Srinivasaro, in *High Modulus Polymers*, Ed. by A. E. Zachariades and R. S. Porter, Marcel Dekker, New York (1988), p. 195.
12. Rheological Studies on Blends of Rodlike and Flexible Chain Polymers, C. S. Kim, V. S. Sullivan, and G. C. Berry, *Confr. Proceed*, 46th. Tech. Confr., Soc. Plastics Engineers **34**, 990 (1988).
13. Rheological Properties of Nematic Solutions of Rodlike Polymers, G. C. Berry, *Mol. Cryst. Liq. Cryst.*, **165**, 273 (1988).
14. Studies on Aligned Nematic Solutions of a Rodlike Polymer, G. C. Berry and M. Srinivasarao, Abstracts, Int'l. Symp. on Dynamics of Macromolecules by Electric and Optical Methods, Tokyo (8-10 August, 1988).
15. Properties of Solutions of Rodlike Chains From Dilute Solutions to the Nematic State, G. C. Berry, *Proceedings, Materials Research Society, Boston*, November 1988.

16. Molecular Composites Formed by Solutions of a Rodlike Polymer (PBT) in Polyphosphonic Acid, A. F. Charlet and G. C. Berry, *Polymer*, in press.
17. Studies on Dilute Solutions of Rodlike Macroions. 5. Electrostatic Effect on Intermolecular Association, C. Wei-Berk and G. C. Berry, to be submitted.

4. OTHER ACTIVITIES

The P. I. has served as a consultant to Foster-Miller, Inc., in their programs related to molecular composites based on PBX polymers (seven visits). Lectures based on research sponsored in full or in part by AFOSR include:

1. "Rheological Studies on Mixtures of Rodlike and Flexible Chain Polymers in isotropic Solutions", Soc. Rheology Symp. on Viscoelasticity, Gainesville, FL, 12-16 February 1989.
2. "Studies on Aligned Nematic Solutions of a Rodlike Polymer", Lecture, University of Pittsburgh, Department of Physics, 26 January 1989.
3. "Physical Chemical Studies on Solutions of Rodlike Polymers", Lecture, University of Rochester, Department of Chemical Engineering, 10 November 1988.
4. "Properties of Rodlike Chains from Dilute Solutions to the Nematic State" (Invited Lecture), Symp. on the Materials Science and Engineering of Rigid-Rod Polymers, Am. Chem. Soc., Boston, MA, 28-30 November 1988.
5. "Viscoelastic Studies on Monodomain Nematic Solutions of Rodlike Polymers", Polymer Science and Engineering Colloquium, Univ. of Massachusetts, 4 November 1988.
6. "Kinetics of Polymerization of a Rodlike Polymer (PBT) in Nematic and Isotropic Solutions", Symp. on Recent Advances in Polymer Synthesis, Characterization and Properties, Am. Chem. Soc., North Carolina State University, 8-9 September 1988.
7. "Studies on Aligned Nematic Solutions of a Rodlike Polymer", Int'l. Symp. on Dynamics of Macromolecules by Electric and Optical Methods, Tokyo, 8-10 August 1988.
8. "Blends of Rodlike and Flexible Chains: Phase Equilibria and Rheology of Isotropic Compositions", Gordon Conference on Polymer Physics, 18-22 July 1988, Andover, NH.

9. "Flow of Aligned Nematic Polymer Solutions", Gordon Conference on Liquid Crystalline Polymers, 11-15 July 1988, New London, NH.
10. "Rheology of Flexible-Coil and Rodlike Polymer Chains", Invited Speaker, First International Symposium on Polymer Analysis and Characterization, 2-3 June 1988, Toronto, Canada.
11. "Rheological Studies on Blends of Rodlike and Flexible Chain Polymers", Annual Technical Conference Society of Plastics Engineers, 18-21 April 1988, Atlanta, GA.
12. "Rheological Properties of Nematic Solutions of Rodlike Polymers", University of Osaka, June 1987.
13. "Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solutions of a Rodlike Polymer", Kyoto University, June 1987.
14. "Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solutions of a Rodlike Polymer, Int'l. Conf. on Liquid Crystal Polymers, June 1987, Bordeaux, France.
15. "Rheological Aspects of Nematic Polymer Solutions", IBM Polymer Colloquium '87 on Contemporary Topics of Polymer Science, June 1987, Fuji, Japan.
16. "Rheological Aspects of the Processing of Nematic Polymer Solutions", Int'l. Symp. on Approaches to Property Limits in Polymers, Am. Chem. Soc., Princeton, NJ, 10-13 August 1986.
17. "Physical Chemistry and Processing of Liquid Crystalline Polymer Solutions", Sigma Xi Lecture, Olin Chapter, Cheshire, CT, 8 May 1986.
18. "Supramolecular Aggregates of Rodlike and Multipli-Broken Rodlike Molecules", Am. Chem. Soc. Meeting, New York, 16 April 1986.
19. "Rheological and Rheo-Optical Studies of a Nematic Polymer Solution", Workshop on Liquid Crystals, Am. Chem. Soc., Montreal, 7 April 1986.
20. "Studies of the Phase Equilibria and Rheological Properties of Mixtures of Rodlike and Flexible-coil Polymers in Solution", Am. Phys. Soc. Meeting), Las Vegas, 1 April 1986.
21. "Physical Chemical Studies on Solutions of Rodlike Polymers", Materials Engineering Program, University of California, Santa Barbara, 8 January 1986.

APPENDIX

The following is a summary of the relations used to analyze dilute solution parameters using the charged wormlike chain model for a polyelectrolyte [14-19]. In general, the parameters of interest may be expressed in the form [20-22]

$$[\eta] = \sum w_\nu [\eta]_\nu = \pi N_A \sum w_\nu K_\nu R_{G,\nu}^2 R_{H,\nu} M_\nu \quad (15)$$

$$R_{H,LS} = M_W \sum w_\nu M_\nu R_{H,\nu}^{-1} \quad (16)$$

$$R_{G,LS}^2 = M_W^{-1} \sum w_\nu M_\nu R_{G,\nu}^2 \quad (17)$$

where w_ν is the weight fraction of species having molecular weight M_ν . Expressions used for $R_{G,\nu}$, $R_{H,\nu}$ and K_ν for a wormlike chain in the absence of excluded volume (i.e., $A_2 = 0$) are given in the form [17]

$$R_{G,\nu}^2 = (L_\nu \rho / 3) S(L_\nu / \rho) \quad (18)$$

$$R_{H,\nu} = (L_\nu / 2) H(L_\nu / \rho, d / \rho) \quad (19)$$

$$K_\nu = K(L_\nu / \rho, d / \rho) \quad (20)$$

where $L_\nu = M_\nu / M_L$, with M_L the mass per unit length. Approximate expressions for S and K are given elsewhere [4]:

$$S(y) = (1 - 4y)^{-1} \quad (21)$$

$$H(y, x) = (27y/16 + \ln^2 3x/2)^{-1/2} \quad (22)$$

$$K(y, x) = 1 + (7/6)(1 + \tanh [0.25 \ln y \sigma(x)/340]) \quad (23)$$

Here, $\sigma(x) \approx \exp(5.92 \sqrt{x})$, and the expression for K is limited to $L/\rho \gg 1$.

To account for excluded volume effects, S and the term $27y/16$ are multiplied and divided by $\alpha_{L,v}^2$, respectively, where $\alpha_{L,v}$ is the expansion factor for the chain dimension, given for small A_2 by [19]

$$\alpha_{L,v}^2 = 1 + \frac{1}{3} \hat{z}_v + \dots \quad (24)$$

Here, $\hat{z}_v = A(\rho/L_v)z_v$, with

$$z_v = (B/2\rho)(L_v/2\rho)^{1/2} \quad (25)$$

and A a function that is zero for small L_v/ρ (rodlike limit) and unity for large L_v/ρ (coil-like limit). To a reasonable approximation, $A(2x) \approx (1 + x^{1/2})(1 + x^{1/2})^{-1} \exp(-3.46x^2)$ [23]. Since Eqn. (24) is limited to small $\hat{z}_v$, but has the same form as the expansion for α_L in z for a flexible coil, closed forms for the latter are used to estimate α_L for $\hat{z}_v$ too large to use the linear expansion. In calculations reported here, the relation [24]

$$\alpha_{L,v}^2 = [1 + 7.524\hat{z}_v + 11.06\hat{z}_v^2]^{0.1772} \quad (26)$$

was used. As discussed in the text, ρ and B were taken as the sums $\rho_N + \rho_e$ and $B_N + B_e$, respectively. In the range of ionic strengths of interest $B \approx B_e$. Relations to estimate B_e and ρ_e are discussed in the text. For the calculations discussed in the text, a Zimm-Shultz distribution of chain lengths is assumed, so that (e.g., see reference [21])

5. REFERENCES CITED

1. D. B. Cotts and G. C. Berry, *Macromol.* **14**, 930 (1981).
2. P. J. Flory, *Adv. Polym. Sci.* **59**, 1 (1984).
3. G. C. Berry, C. C. Wei and R. Furukawa, *Polym. Prepr. Am. Chem. Soc.* **27**(1), 228 (1986).
4. R. Furukawa and G. C. Berry, *Pure Appl. Chem.* **57**, 913 (1985).
5. R. Furukawa and G. C. Berry, *Pure Appl. Chem.* **57**, 913 (1985).
6. Kazunori Se and G. C. Berry, in Reversible Polymer Gels and Related Systems, Ed. by P. S. Russo, *Am. Chem. Soc. Symp. Series*, 1987.
7. W. F. Hwang, D. R. Wiff and C. L. Benner, *J. Macromol. Sci. Phys. B* **22**, 231 (1983).
8. G. C. Berry and D. J. Plazek, in Glass Science and Technology, Vol. 3 Ed. by D. R. Uhlmann and N. J. Kreidl, Academic Press, New York, 1986, Chapter 6.
9. K. Nakamura, C.-P. Wong and G. C. Berry, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 1119 (1984).
10. G. C. Berry, *Disc. Faraday Soc.*, No. **79**, 141 (1985).
11. G. C. Berry, in "Theory and Applications of Liquid Crystals", Ed. by J. L. Ericksen and D. Kinderlehrer, Springer-Verlag, New York, 1987, p. 1.
12. M. Doi and S. F. Edwards, "The Theory of Polymer Dynamic", Oxford University Press, Oxford, 1986.
13. Kazunori Se and G. C. Berry, *Mol. Cryst. Liq. Cryst.*, **153**, 133 (1987).
14. M. Srinivasarao and G. C. Berry, Studies on Aligned Nematic Solutions of a Rodlike Polymer, Abstracts, Int'l. Symp. on Dynamics of Macromolecules by Electric and Optical Methods, Tokyo (8-10 August, 1988).

15. R. M. Davis and W. B. Russel, *J. Polym. Sci., Pt. B: Polym. Phys.*, **24**, 511 (1986).
16. M. Fixman and J. Skolnick, *Macromol.* **11**, 863 (1978).
17. H. Yamakawa, Modern Theory of Polymer Solutions, Harper & Row, New York (1971): a. p. 80, b. p. 330, c. p. 300, 310, d. p. 180, e. p. 165.
18. G. Manning, *J. Chem. Phys.*, **51**, 924 (1964).
19. H. Yamakawa and W. H. Stockmayer, *J. Chem. Phys.* **57**, 2843 (1972).
20. G. C. Berry, in *Encyclopedia of Polymer Science and Engineering*, Vol. 8, H. Mark *et al*, Ed. John Wiley & Sons, New York (1987), p. 721.
21. G. C. Berry, in *Encyclopedia of Materials Science and Engineering*, M. B. Bever, Ed. Pergamon Press, Oxford 1986, p. 3759.
22. G. C. Berry, *J. Polym. Sci., Part B* **26**, 1137 (1988).
23. C. Wei-Berk and G. C. Berry, to be published.
24. M. Muthukumar and B. G. Nickel, *J. Chem. Phys.*, **86**, 460 (1987).

TABLE 1 Values of $10^4 \eta_R L_R^2$ (nm²/a) and estimated reptation times for each component to move along its own contour length.

SYSTEM	SOL. #	$10^4 \eta_R L_R^2$ nm ² /a	τ_F sec	τ_R sec	τ_R^0 sec	τ_R / τ_F
P-28/Z-42	80/20	0.6	0.0010	0.5	0.02	500
	70/30	0.7	0.0017	0.1		59
	60/40	0.9	0.0018	0.06		33
	40/60	1.1	0.0027	0.04		15
	50/50	1.1	0.0015	0.04		27
	30/70	1.5	0.0022	0.03		14
	20/80	2.3	0.0014	0.03		21
P-53/Z-42	320	1.6	0.00023	0.007	0.005	30
	330		0.00041			17
	340		0.00062			11
	350		0.00085			8
	360		0.0011			6
	370		0.0015			5

$$\tau_F = \frac{40}{\pi^2} \left[\eta_s R_G^2 / a \right] (L_F / a)^3 (c_F / \rho_F)^{1/2} k_B T.$$

$$\tau_R^0 = 2\pi \eta_s L_R^3 / k_B T \ln(L_R / d).$$

$$\tau_R = \tau_R^0 [1 - B(c_R / c_R^{*1/2})^{-1}].$$

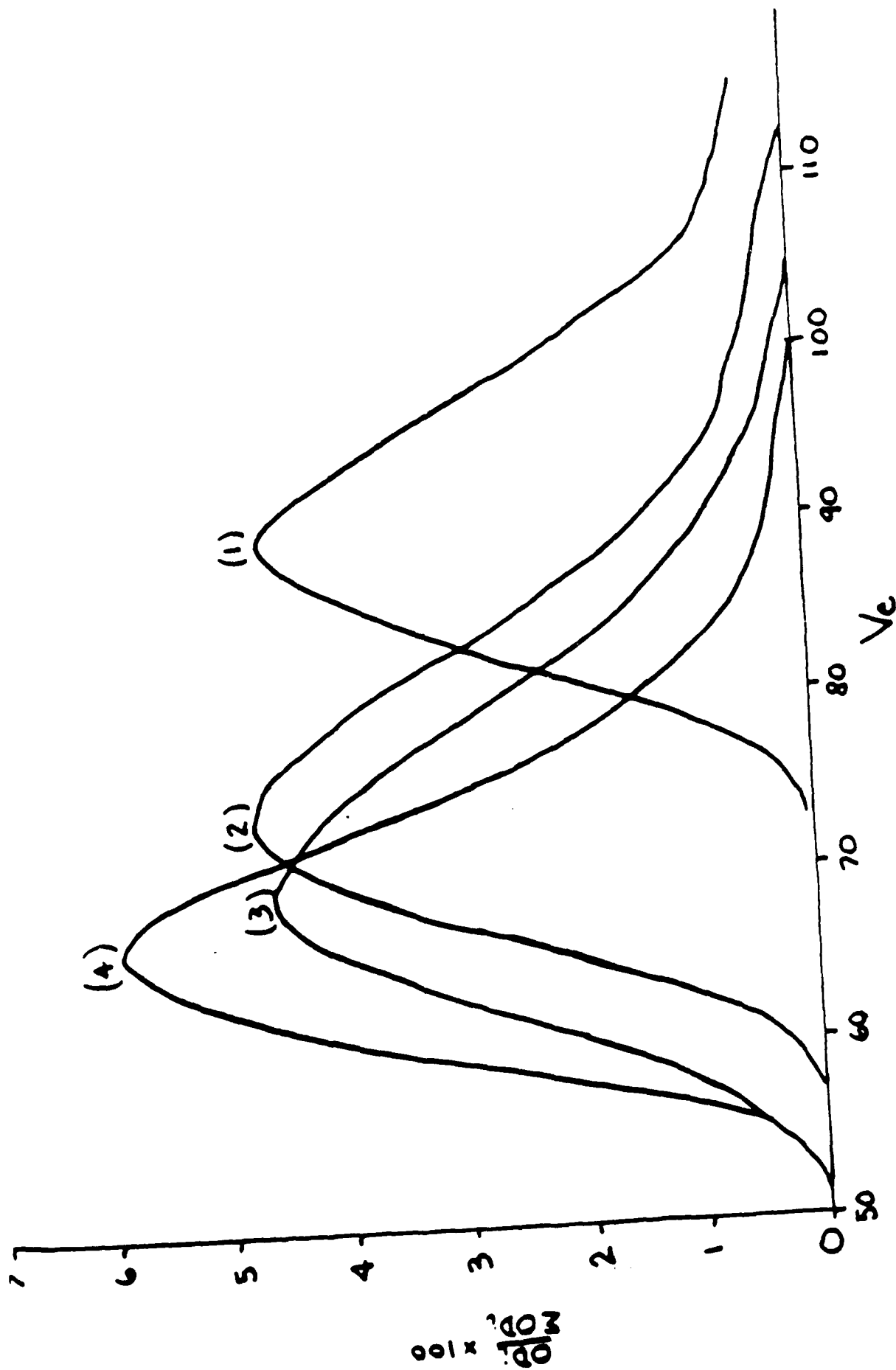


Figure 1 SEC chromatograms for the polymerization of PBT in ampoules.
 (1) precursor, SAI 0 (2) 1/2 hour (3) 2 hours (4) 10 hours.
 Note exclusion limit at $V_e = 55$.

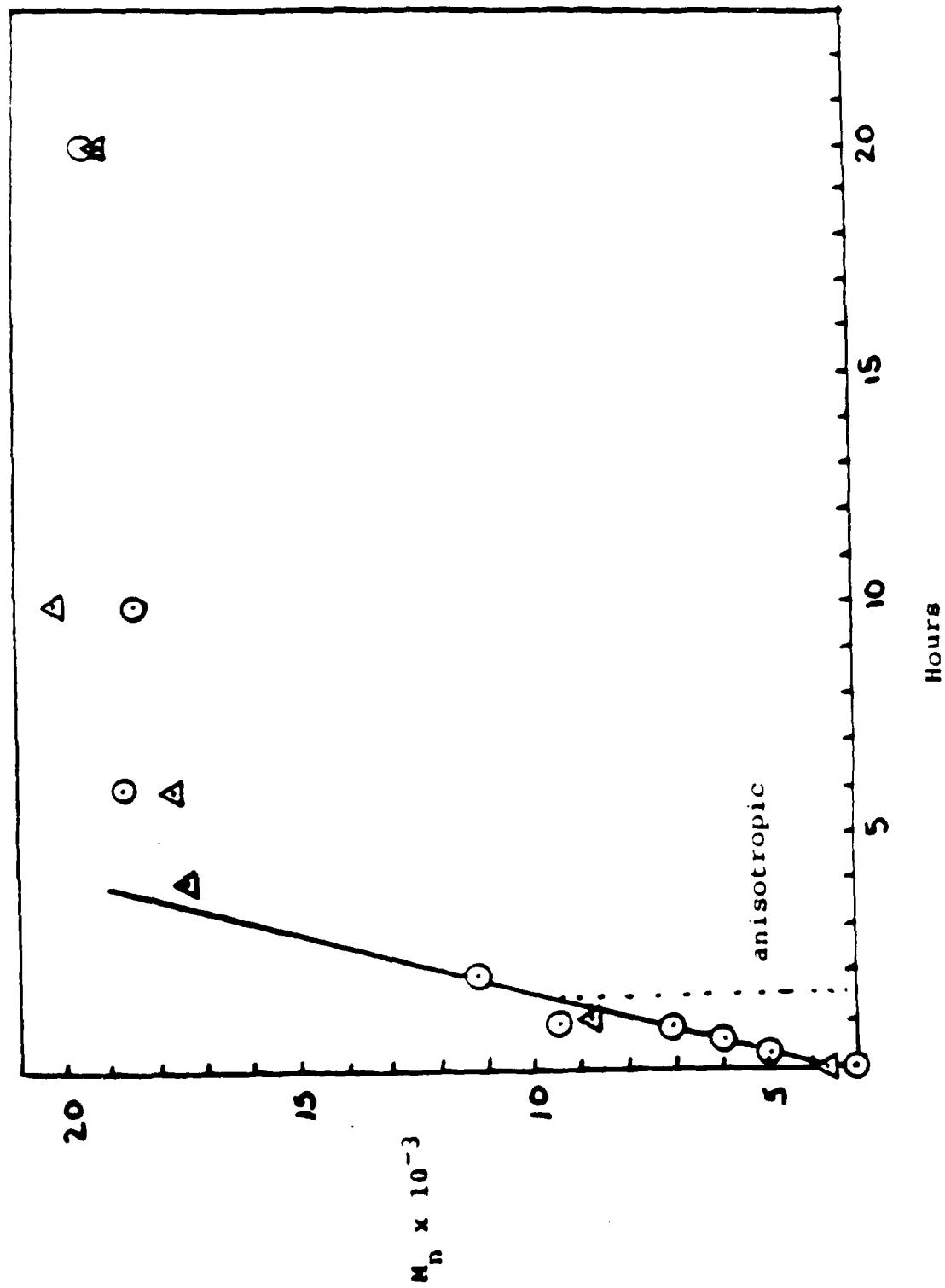


Figure 2 M_n as a function of hours reacted for the polymerization of PBT in ampoules. Δ $[\eta]$ measurement $\circ$ - SEC measurement.

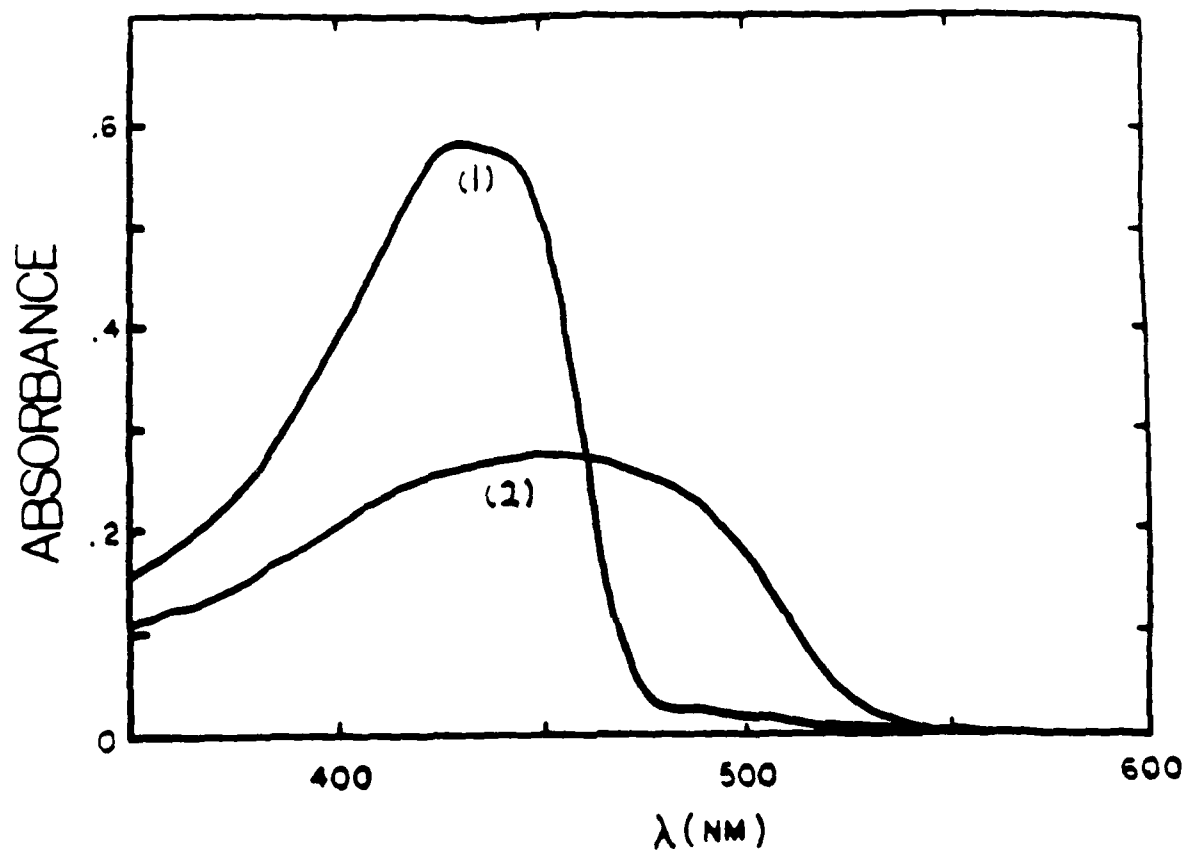


Figure 3 The electronic absorption spectra of SPBT410-30/PPA in 87% H_3PO_4 as function of temperature, $C = 0.0425$ g/dl. Curve 1 is at $25^\circ C$ and curve 2 is at $60^\circ C$ for ~120 hours.

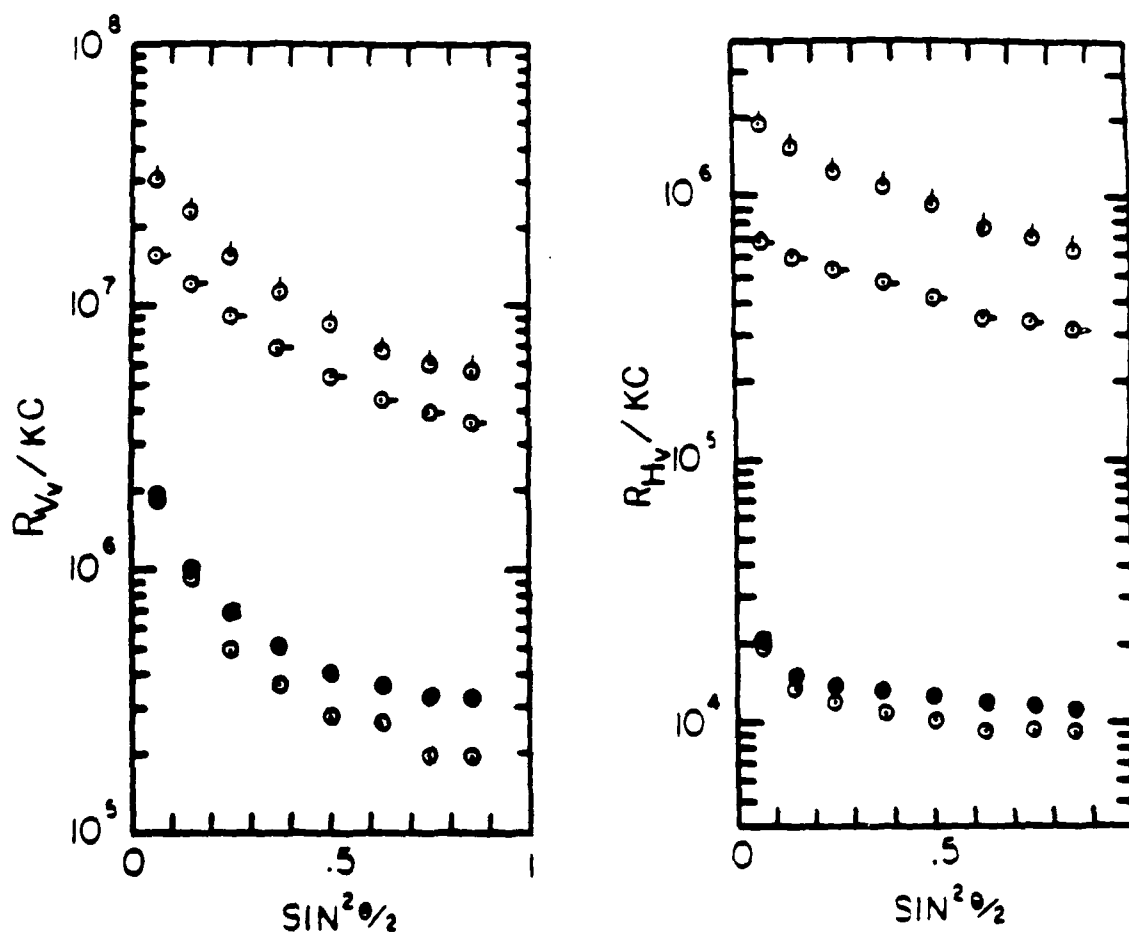


Figure 4

$R_{VV}(\theta)/Kc$ and $R_{HV}(\theta)/Kc$ of SPBT 410-30/PPA in 87% H_3PO_4 at 647nm, $C = 0.0424$ g/dl. $\circ$ 25°C, $\circ$ 60°C for ~ 40 hours, $\bullet$ 60°C for ~ 120 hours, $\bullet$ return to 25°C.

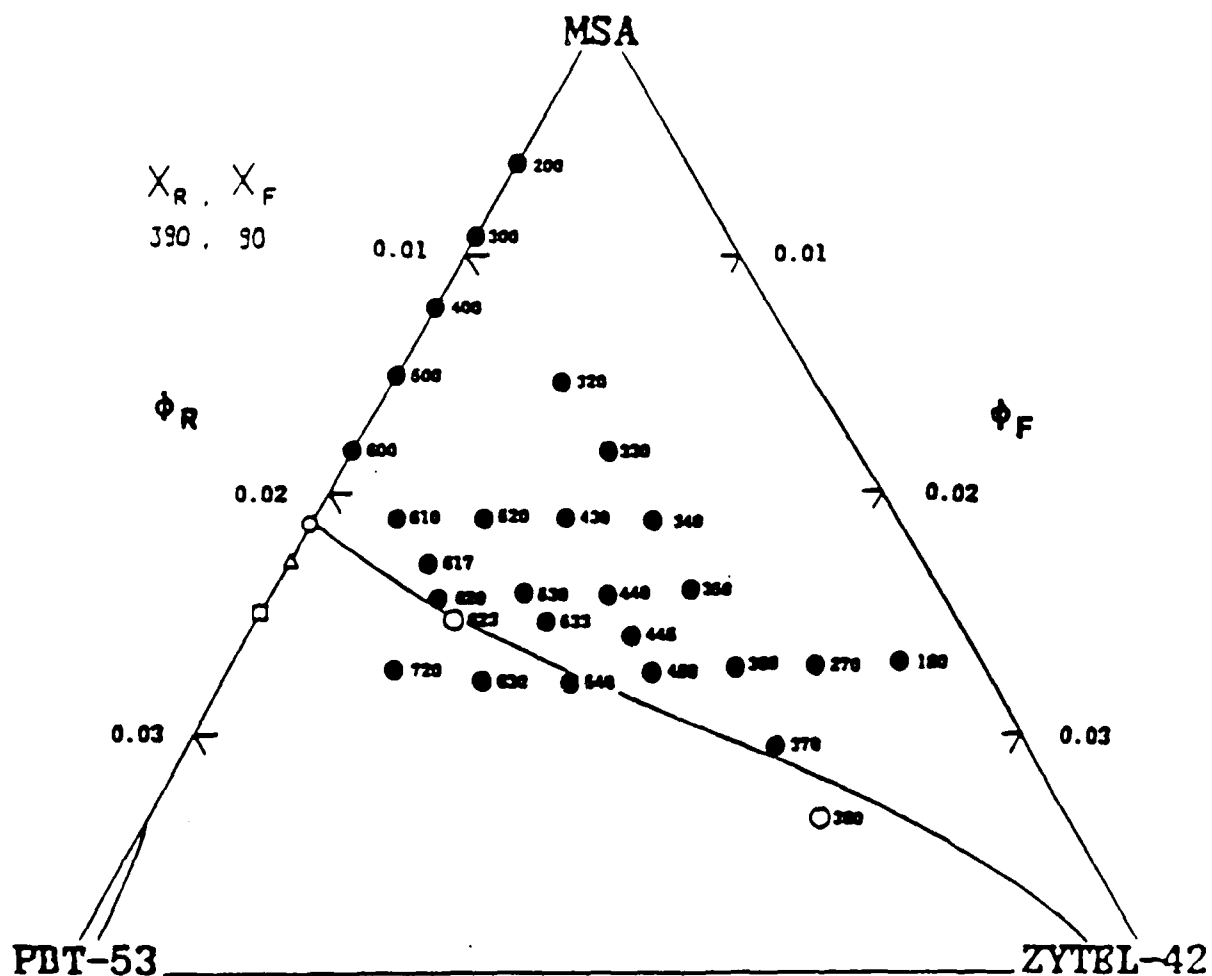


Figure 5 Phase equilibria for solutions of PBT and nylon in methane sulfonic acid. The filled and unfilled circles represent isotropic and nematic compositions, respectively. The curves are theoretical predictions [2] for a mixture of a rod with 390 segments and a coil with 90 segments.

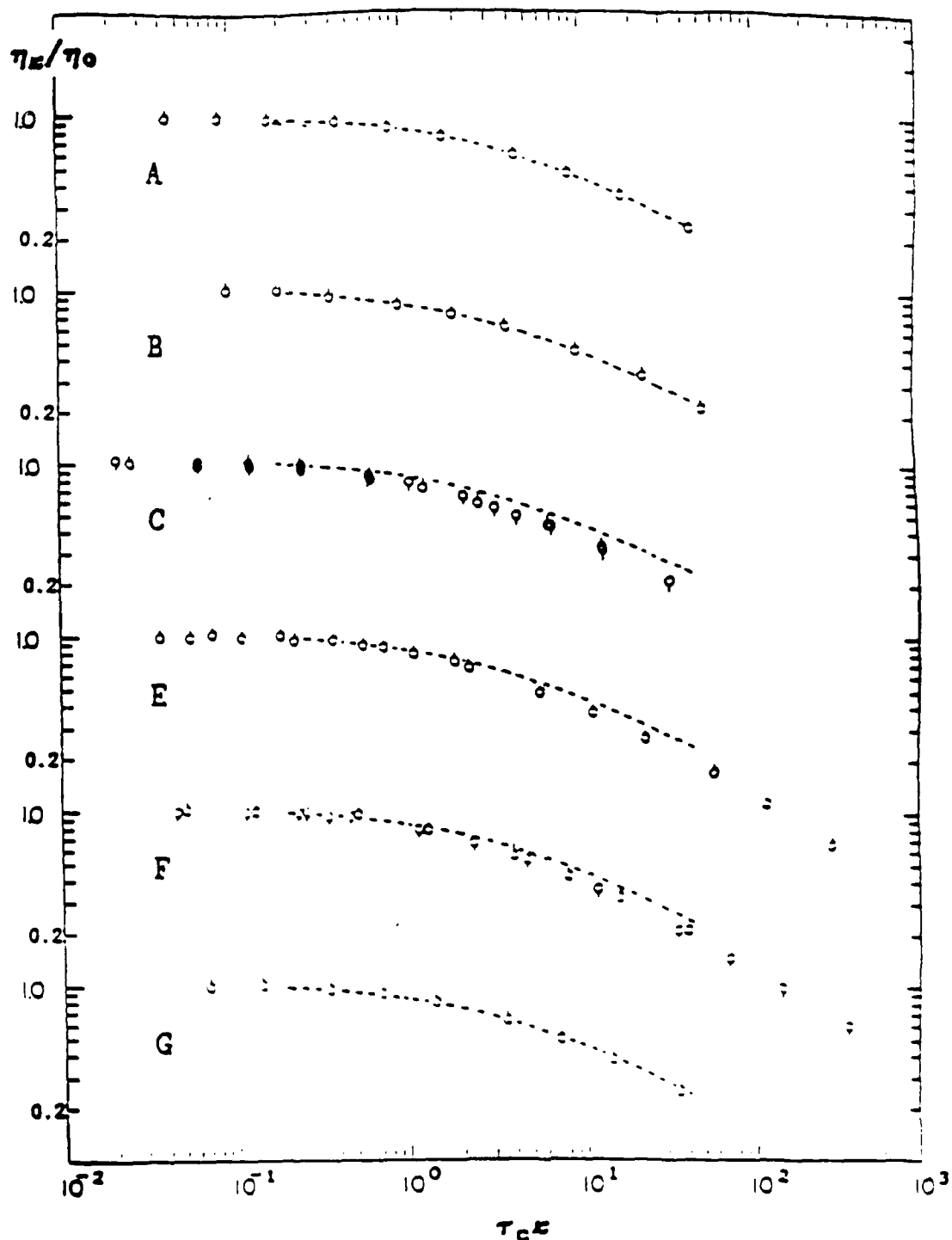


Figure 6

Typical flow curves for isotropic PBT-nylon mixtures in methanesulfonic acid; 0.0175 weight fraction PBT in all cases. Curve A, no nylon; curves B to G, nylon increasing to 0.017 weight fraction. Curve — represent curve A in all cases; $\circ$ and $\square$ denote 347 and 301° K, respectively

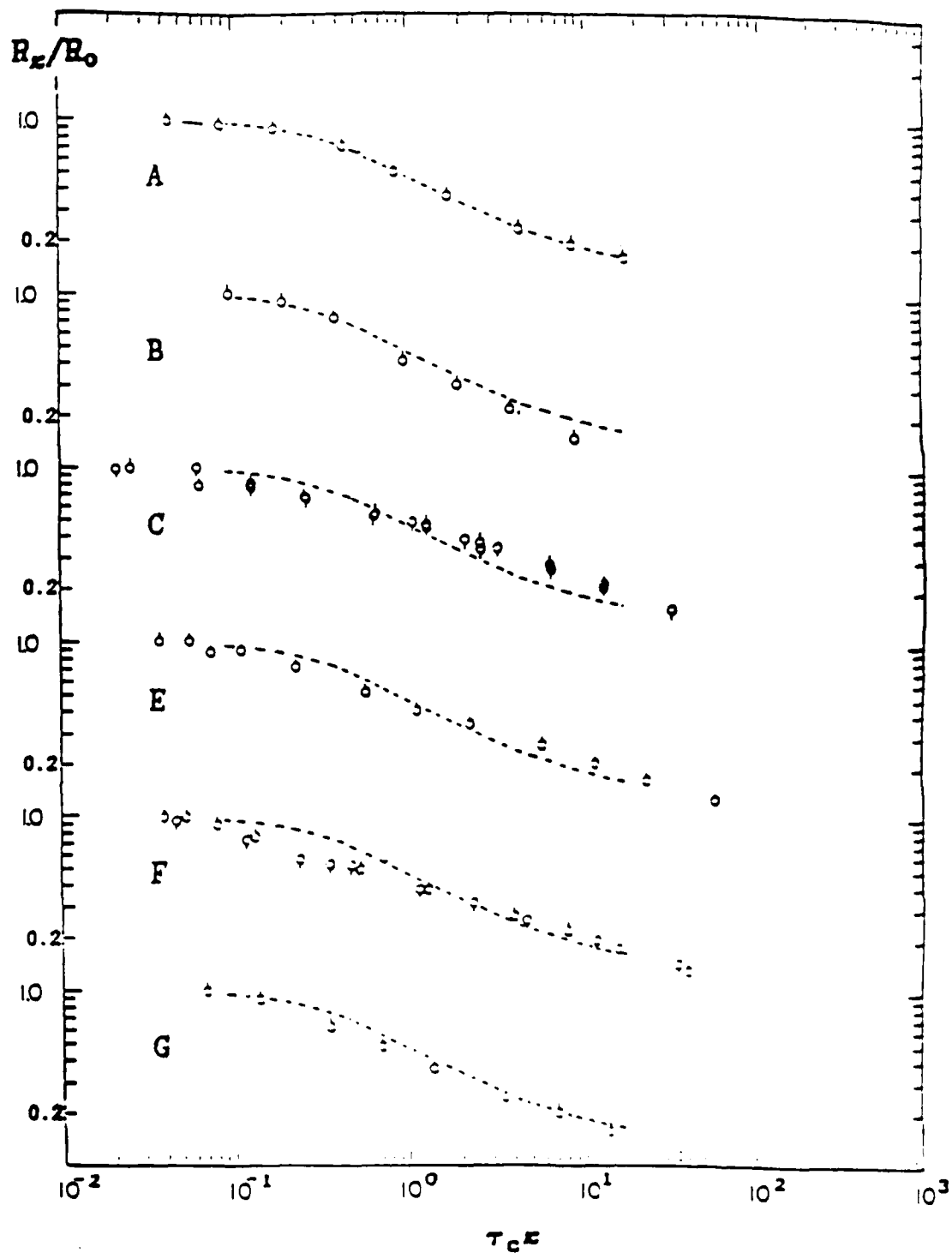


Figure 7

Typical steady state recoverable compliance versus reduced shear rate for solutions described in Fig. 2.

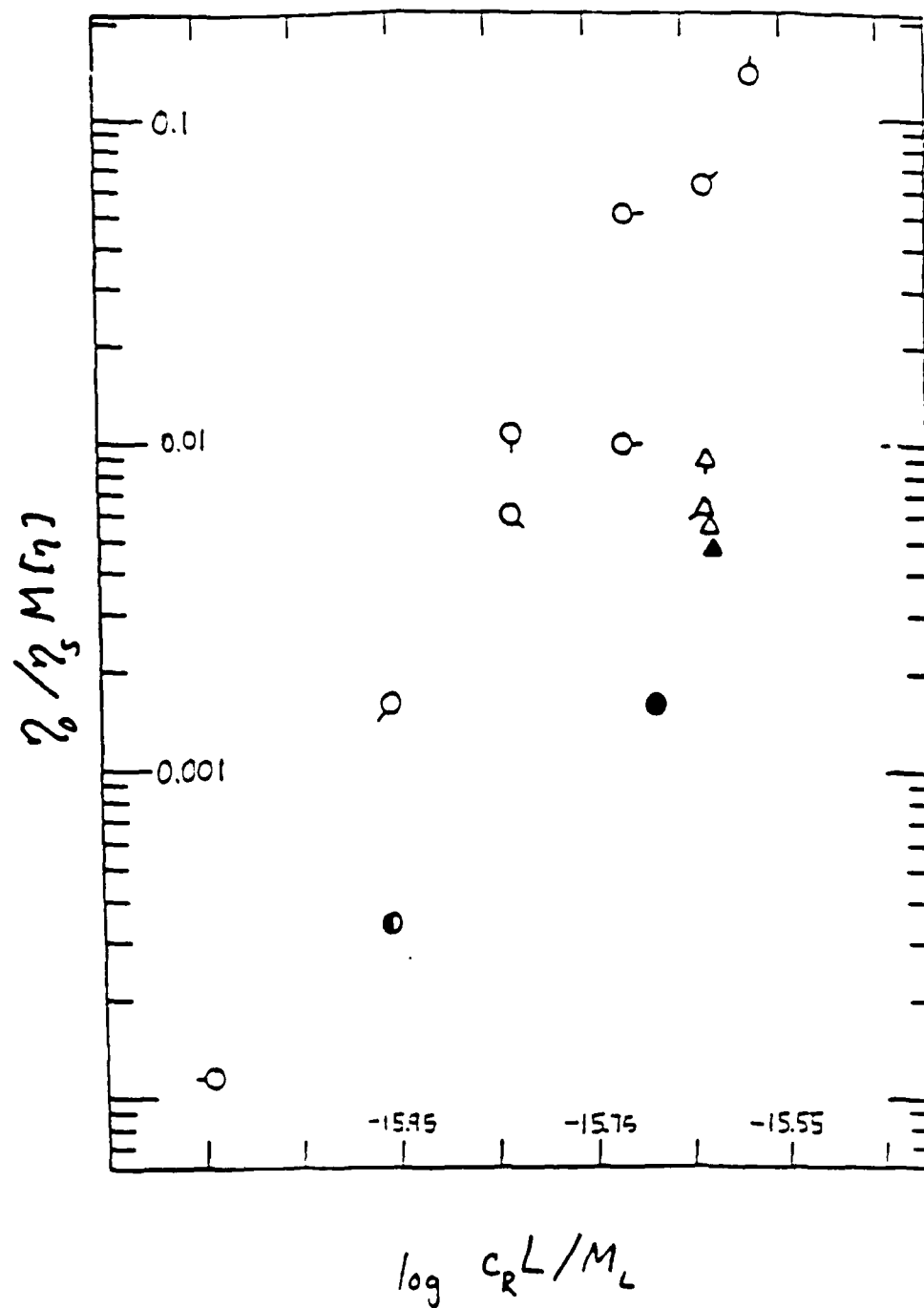


Figure 8

Viscosity data for blends of PBT and nylon ($T = 297^\circ\text{K}$). Filled or partly filled symbols are for nylon free PBT solutions; c_R is the rodlike chain concentration in blends.