Structure and Thermal Expansion of Some Polymers with Mesomorphic Ordering

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ABSTRACT: The mesomorphic organization of polymers obtained by polymerization of difunctional monomers from liquid crystalline states is not necessarily that of the monomer. A nematic monomer can yield a polymer with smectic ordering. Well-oriented side chains (orientation function of 0.7) resulted from polymerization from the nematic state in a 4.5 kG magnetic field. The anisotropy of thermal expansion of this oriented polymer is reported. The values for the average distance between side groups are in agreement with values anticipated based on intermolecular distance of low molecular weight compounds in the corresponding mesomorphic states.

Mesomorphic order in polymers may be displayed by two types of polymers: those with rodlike conformation[1,2] and polymers with mesomorphic or potentially mesomorphic side groups.[3] We have been working with the latter category. This field has been reviewed recently.[4] In this paper we will present data concerning the molecular structure and bulk properties of polymers with mesomorphic Schiff-base side groups.

Mesomorphic Schiff-base monomers have been recently polymerized by several authors.[3,5–8] Labes et al.[5,6] reported the preparation and polymerization of several *N*-(*p*-alkoxybenzylidene)-*p*-aminostyrenes, emphasizing the kinetic aspects. Perplies et al.[7] polymerized a number of Schiff bases, and reported the formation in some cases of long range smectic order in the polymer. The influence of a 70 kG magnetic field on the polymerization kinetics and the orientation of the resulting structure was briefly described.[8]

Liebert and Strzelecki[9–11] have studied by polarizing microscopy a number of Schiff-base compounds polymerized under various conditions, including orientation by a magnetic field. They concluded that the molecular order of the mesomorphic phase of the monomer could be retained through polymerization, provided a high concentration of divinyl molecules are present. The resulting three-dimensionally cross-linked polymeric networks were strongly optically anisotropic and kept the molecular order of the monomeric mesophase up to the decomposition temperature of the polymer.

However, Blumstein et al.[3] showed that neither monomer mesomorphism, nor the presence of a cross-linking agent, is necessary for the development of mesomorphic order in polymers. In addition, Newman et al.[12] obtained smectic ordering in a polymer prepared from a monomer which does not display mesomorphism.

In all these studies the structure and anisotropic properties of the mesomorphic polymers were primarily given qualitative description. In the present study a more quantitative approach was adopted to determine some structural parameters and anisotropic properties. A number of Schiff-base monomers were polymerized under different conditions, including orientation by a field of 4.5 kG, with subsequent examination of the structure by x-ray diffraction. The discussion focuses on two structural parameters: the distance between planes for polymers with smectic organization, and the average distance *D* between side groups. The latter values are compared to the corresponding values for low molecular weight compounds in mesomorphic states.[13] In addition, the orientation function is calculated for the sample polymerized in the magnetic field. The anisotropy of thermal expansion is also described for a well oriented mesomorphic polymer.

Experimental Section

Mesomorphic Compounds. The compounds given in Table I were synthesized according to a procedure previously described.[14]

Polymerization. Bulk polymerizations of various monomers were conducted above the respective crystal melting temperatures without addition of initiator. The powdered monomer was pressed into a pellet of ½ in. diameter which was then placed into a cell made from aluminum or Teflon and rapidly heated to the desired temperature. Placing the cell between the poles of an electromagnet allowed the monomer to polymerize in a 4.5-kG field. Polymerization was also carried out directly on glass slides placed on a Mettler FP hot stage mounted on a Leitz Ortholux polarizing microscope.

X-ray diffraction photographs were made with a Warhus camera, provided with a sample heater, mounted on a Norelco generator (Ni filtered Cu radiation). The sample to film distance for the wide angle cassette position was determined by diffraction from aluminum foil. Further photographic studies were performed on a Rigaku small angle camera-goniometer mounted on a Rigaku generator (Ni filtered Cu radiation). Solid samples were clamped in a Rigaku heater (for fiber specimen) for the high-temperature studies. Wide angle diffraction traces were made with a Rigaku SG-7B goniometer with Ni filtered Cu radiation or with unfiltered Mo radiation. The orientation function data were obtained with the small-angle goniometer.

The thermal expansion of bulk samples was determined with a Perkin-Elmer thermomechanical analyzer, TMS-1, calibrated with a small aluminum block.

Results and Discussion

Table I gives the phase transition temperatures of the compounds used in this work.

(1) diABAB and diABAB–ABBA Mixtures. Monomer 1 was polymerized in bulk, or in a 50:50 mixture (by weight) with monomer 2 in order to achieve a lower smectic–nematic transition temperature. The lower concentration of double bonds and lower temperature allowed for better control of polymerization.

Polymerization of monomer 1 for 75 min in the aluminum cell from the smectic state at 194 °C (±2 °C) gave a solid specimen (run A); also see ref 5. X-ray diffraction data are given in Figure 1 and Table II. Another specimen with a shorter polymerization time (40 min) showed lines 1 and 2 to be of about equal intensity. Upon reheating this latter sample to 195° for 3 h, line 1 became very weak. After polymerization of another sample for 2 h at 200 °C (run B) in the DSC, line 1 was barely detectable while line 2 was intense. Line 3 also became weaker as polymerization time increased, and was not detected after run B. Polymerization in run C at 250 °C for sufficient time (10 min) led to a polymer displaying the same x-ray pattern as that prepared at 200 °C for 2 h as shown in Table II. As the polymerization time increases, again the intensity of line 1 decreases while line 2 becomes more intense.

At 250 °C the monomer is in the nematic state, based on

Table I
Monomer Structure and Transition Temperatures[14]

No.	Abbreviation	Name and structure	Transitions, °C
1	diABAB	Di(*N*-*p*-acryloyloxybenzylidene)-*p*-diaminobenzene $\mathrm{CH_2{=}CH{-}CO_2{-}Ph{-}CH{=}N{-}Ph{-}N{=}CH{-}Ph{-}CO_2{-}CH{=}CH_2}$	$\mathrm{K} \xrightarrow{180} \mathrm{S} \xrightarrow{a} \mathrm{Polym}^{b}$
2	ABBA	*N*-(*p*-Acryloyloxybenzylidene)-*p*-*n*-butylaniline $\mathrm{CH_2{=}CH{-}CO_2{-}Ph{-}CH{=}N{-}Ph{-}C_4H_9}$	$\mathrm{K} \xrightarrow{48.5} \mathrm{N} \xrightarrow{56.6} \mathrm{I}$
3	diABH	Di(*N*-*p*-acryloyloxybenzylidene)hydrazine $\mathrm{CH_2{=}CH{-}CO_2{-}Ph{-}CH{=}N{-}N{=}CH{-}Ph{-}CO_2{-}CH{=}CH_2}$	$\mathrm{K} \xrightarrow{138} \mathrm{N} \rightarrow \mathrm{Polym}^{b}$
4	PMAS	*p*-Phenylenebis(*N*-methylene-*p*-aminostyrene) $\mathrm{CH_2{=}CH{-}Ph{-}N{=}CH{-}Ph{-}CH{=}N{-}Ph{-}CH{=}CH_2}$	$\mathrm{K} \overset{\sim 180}{\rightarrow} \mathrm{N} \rightarrow \mathrm{Polym}^{b}$

[a] There exists indirect evidence for a nematic state. See text. [b] Polymerization commences immediately after crystal melting.

Table II
X-Ray Diffraction Results, Poly(diABAB)

Polymerization temp	Monomer phase–polymer organization	Line No.	*d*, Å
194 °C (run A, 75 min, partial polymerization)[a]	Smectic–smectic	1	43.3 ± 0.4 med
		2	22.2 ± 0.2 strong
		3	4.88 ± 0.02 med
			Halo, ca. 4.4
200 °C (run B, 2 h, nearly complete polymerization)	Smectic–smectic	1	43 v weak
		2	22 strong
			Halo, ca. 4.4
250 °C (run C)	Nematic–smectic	1	43.5 v weak
		2	22.2 strong
			Halo, ca. 4.4

[a] Higher orders also observed on long exposure.

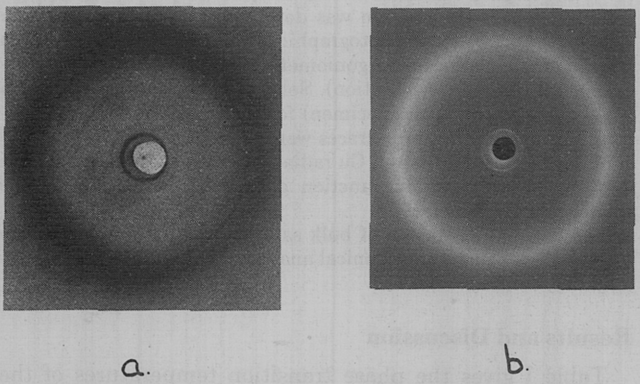

Figure 1. *X-ray diffraction photograph after bulk polymerization* of monomer 1 at 194 °C: (a) partial polymerization (line 1 is behind beam stop); (b) complete polymerization.

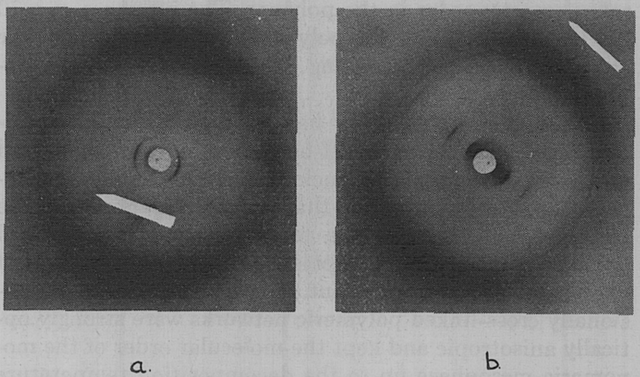

Figure 2. X-ray diffraction photographs after bulk polymerization at 195 °C in a magnetic field: (a) monomer 1; (b) monomer 1–monomer 2 mixture. Arrows show field direction.

observations under the polarizing microscope. Crystals were placed on a slide preheated to 250°, and developed on melting the characteristic nematic Schlieren patterns. The nematic texture lasted only 1–2 s, due to the rapid polymerization. The polymer displayed a smectic texture. Furthermore, the saturated analogue of monomer 1 (di(*N*-*p*-propionoyloxybenzylidene)-*p*-diaminobenzene) synthesized in this laboratory[14] displayed a smectic and nematic phase. However, due to rapid polymerization, the smectic–nematic transition of monomer 1 was not observable by differential scanning calorimetry, even at a heating rate of 80 °C/min.

The nematic nature of monomer 1 at 250 °C is confirmed by the fact that it orients in a magnetic field. The x-ray pattern is shown in Figure 2a. The oriented nematic monomer gave a smectic polymer with side chains preferentially aligned with the field, and the polymer backbone chains confined to strata perpendicular (or nearly so) to the side groups.

Thus for this divinyl monomer, polymerization from the nematic state can lead to a network displaying smectic organization. This is in contrast to the statement by Liebert and Strzelecki[9] that polymerization of such difunctional monomers preserves their state of organization. Perplies et al.[7,8] have shown that monofunctional monomers polymerized from the nematic and from the isotropic states can yield polymers with smectic organization, and we have also shown[3] that potentially mesomorphic monomers polymerized in the isotropic state can give polymers with smectic organization.

Since polymerization occurs rapidly at 250°, it was believed that the monomer molecules in the nematic state might not achieve their highest possible orientation. In order to slow down the polymerization and thereby reduce the viscosity of the polymerizing system, a 50:50 mixture of monomers 1 and 2 was polymerized in the magnetic field at 195 °C. It is apparent from Figure 2b that high side chain orientation is achieved indicating that the mixture is nematic at 195 °C. The orientation function for the sample shown in Figure 2b was calculated to be $f = \frac{1}{2}(3 \cos^2 \theta - 1)$

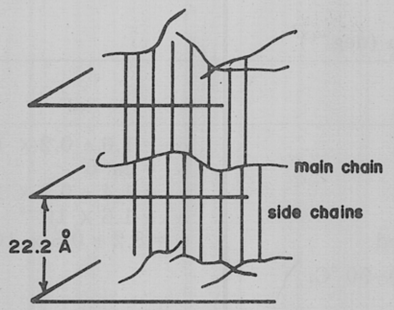

Figure 3. Model for the polymer prepared from monomer 1. The main chains lie in planes.

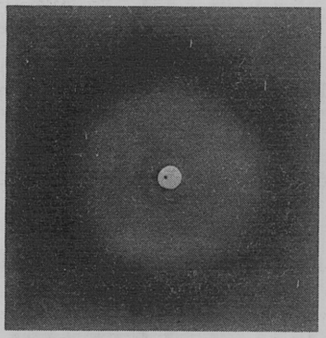

Figure 4. X-ray diffraction photograph for poly(diABAB) polymerized in solution.

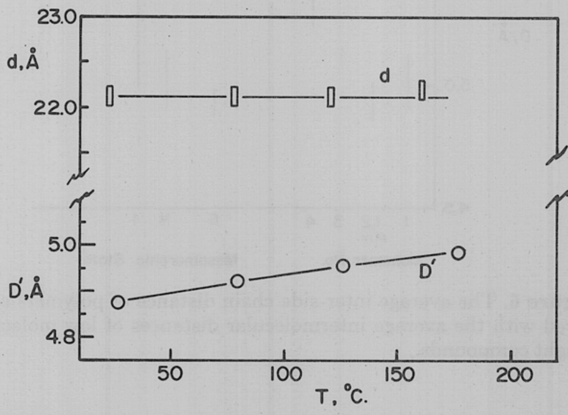

Figure 5. Thermal expansion by x-ray diffraction of poly(diABAB).

= 0.70 using x-ray line 1, assuming cylindrical symmetry, and keeping the orientation axis perpendicular to the x-ray beam. Line 1 remains the most intense line for the solid polymer prepared from this mixture. The orientation appears to be higher than that reported by Perplies, et al.,[8] using a 70-kG field. Thus with the proper monomer system and temperature giving a suitable relationship between monomer relaxation time and polymerization rate, high orientation can be obtained and fixed by polymerization.

As polymerization of monomer 1 nears completion, line 2 becomes the dominant low angle peak (inner ring) whereas line 1 approaches zero intensity. Also, line 3 decreases in intensity and disappears. In order to explain these results, we propose the following model. The main chains are contained within lamellar strata with the side groups nearly perpendicular to these planes as shown in Figure 3. This model is similar to that of Liebert and Strzelecki[9] with the exception that the side chains tilt at the most a few degrees from the normal to the planes. In Figure 2b the noncrystalline scattering (halo) around 4.4 Å due to packing of side chains is nearly perpendicular to the sharp multiple arcs due to the smectic strata containing the main chains.

The polymeric network develops at the start of polymerization from only one double bond in the difunctional molecules, that is, in one of the layers. Thus in the beginning, the predominant spacing will be approximately double the length of the side chain, or about 44 Å. As polymerization proceeds, an increasing number of double bonds attached to the already formed polymeric chain react, so that as polymerization nears completion, essentially equivalent layers of side chains separate the main chains at 22 Å. This model explains the originally intense 44 Å reflection becoming progressively replaced by the 22 Å line. In the 50:50 mixture of monomers, line 1 remains the most intense since over half of the monomer molecules can react at only one end, giving a majority of side chains bonded to the main chain at a single point.

The sharp line at 4.88 Å prior to completion of polymerization shows that chains attached by one end can pack in a regular fashion. X-ray diffraction from the monomer shows that this reflection is not due to any remaining monomer crystals. The spacing is nearly the same as that between the long side chains of poly(alkyl acrylates) with hexagonal packing (twice d_{110}) reported by Platé and Shibaev.[15] There is no evidence in the present case, however, to suggest hexagonal packing. After complete polymerization of monomer 1, the orderly packing of side groups disappears and the one sharp inner ring and outer halo show the organization to be of the smectic A or C type, Figure 1b. The presence of an intense 4.88 Å line in all cases of polymerized monomer 1–monomer 2 mixture supports this interpretation of the reflection being due to packing of side chains bonded at one end only. The lack of orientation of this line in Figure 2b suggests that part of the polymer formed in the smectic state, during the heating, before the nematic state was achieved. Side groups attached to the polymer chain would not orient appreciably in the magnetic field due to the low segmental mobility of the polymer.

Polymerization of the diABAB–ABBA mixture in a dimethylformamide (DMF) solution at 120 °C yielded a product which gave the diffuse small angle x-ray peak shown in Figure 4. During precipitation and subsequent drying the organization which developed appears to be a poorly developed smectic type.

(2) Anistropy of Expansion of Polymeric Networks. The anisotropy of thermal expansion for poly(diABAB) prepared at 194 °C is shown in Figure 5. D' refers to the interside chain distance calculated from the sharp peak near 4.9 Å. The coefficient of linear expansion calculated from the slope is 1.6×10^{-4} deg^{-1}. See Table III. The expansion in the direction normal to the smectic layers is zero within the experimental error.

Thermomechanical analysis data on the highly oriented polymer prepared from the mixture of monomers 1 and 2 gave the results in Table III. The $\alpha_{\parallel}$ value of 1.4×10^{-4} deg^{-1} (expansion parallel to the smectic layers) agrees well with that obtained from poly(diABAB) by x-ray diffraction. The $\alpha_{\perp}$ value of 1.6×10^{-5} deg^{-1} was obtained from the first run; subsequent runs gave values greater by a factor of 2–3. The expansion coefficient for unoriented polymer prepared outside the magnetic field was found to be 8.2×10^{-5} deg^{-1}.

The values of lateral expansion coefficients of the side groups are slightly smaller than the values of expansion for low molecular weight smectics reported by deVries.[13,16] The present specimen are solid, glassy materials, however, and one would expect lower values of α than for mesomorphic fluids. In addition, we found that the expansion coeffi-

Table III
Coefficients of Linear Expansion α ($\deg^{-1}$)

Monomer	Polymerization temp, °C	Method	α^a
1	194	X ray	$\alpha_{\parallel} = 1.6 \pm 0.2 \times 10^{-4}$ $\alpha_{\perp}$ = ca. 0
1:2, 50:50 mixture	195	TMA^b	$\alpha_{\parallel} = 1.4 \pm 0.3 \times 10^{-4}$ $\alpha_{\perp} = 1.6 \times 10^{-5}$
		Unoriented	$\alpha = 8.2 \pm 0.5 \times 10^{-5}$

[a] $\parallel$ refers to expansion parallel to smectic layers. [b] Temperature range: 30–90 °C.

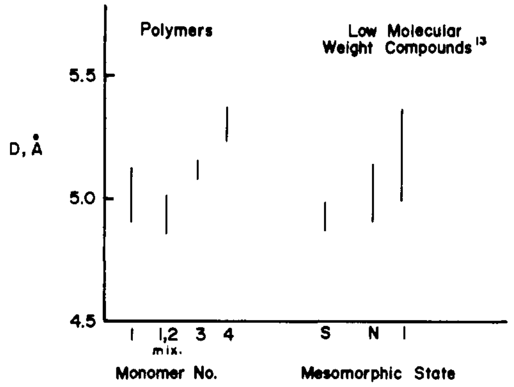

Figure 6. The average inter-side chain distance of polymers compared with the average intermolecular distances of low molecular weight compounds.

cient α for unoriented polymer was in agreement with values given by literature[17] for glassy polymers.

The lack of expansion perpendicular to the smectic planes observed by x-ray diffraction has been generally observed for smectic liquid crystals.[16,18] The nonzero value of $\alpha_{\perp}$ measured by TMA can be explained as due to the randomly oriented smectic regions of the sample. These regions could have been produced in the short time before a nematic oriented state was achieved, and are responsible for the sharp continuous x-ray ring in Figure 2b.

(3) (Monomers 3 and 4). Neither of these monomers, when polymerized from the nematic state, gave a polymer with smectic organization (no sharp inner ring on x-ray diffraction photographs). The polymers show birefringence when viewed under the polarizing microscope and appear to have a nematic organization. The diffuse ring expected of nematics[13] has not been detected, however. This may be due to the homogeneity of electron density in these polymers prepared from difunctional monomers. The lack of chain ends and the random disposition of main chain–side chain bonds results in an essentially even distribution of electron density. Monofunctional monomers polymerized in the nematic state give rise to an inner x-ray diffraction ring.[3,19] Further studies will show whether very weak scattering may be observed at low angles from these samples.

(4) Distance between Side Groups. The average intermolecular distance D in mesomorphic low molecular weight compounds was reported by deVries.[13] The following ranges were found from the peak of the x-ray diffraction diffuse outer rings (halos) for the different phases: smectic, 4.85–4.97 Å; nematic, 4.85–5.13 Å; isotropic, 4.96–5.46 Å.

Values of D, using the equation[20] $2D \sin \theta = 1.117\lambda$, were obtained from the polymer samples studied in this work. The angle 2θ was obtained in each case by extrapolating to intersection the diffractometer traces on each side of the diffuse peak. Since differences on the order of a few tenths of an ångström unit are discussed, an aluminum foil sample was run as a calibration check immediately before or after each polymer specimen. The results are shown in Figure 6, the bars representing a range of values from several runs.[21]

The diABAB sample with smectic organization gave D values slightly greater than, or at the upper end of, the smectic range for low molecular weight compounds. Moreover, measurements in this work were performed at room temperature, while the literature values were made at the higher temperatures of the smectic range. The higher value for the polymer may result from increased randomness caused by the junction of the side groups with the backbone. The lower value of D for the 50:50 mixture, which is in the range for smectics,[13] is consistent with this explanation. The shorter monomer 2 molecule joined to the polymer backbone at one end only would provide fewer junction points and hence less disruption of side chain alignment.

Results from the nematic polymer from difunctional PMAS were at the upper end of the nematic range for low molecular weight compounds. This is in agreement with the discussion in the previous paragraph. However, the nematic diABH polymer gave values in the range D = 5.24–5.36 Å, much higher than expected for nematic organization. The reason for this is unclear at the present time, but may be due to the increased average cross-sectional area of the side groups due to the hydrazine moiety. No hydrazine derivatives were among those compounds listed by deVries.[13]

Conclusions

Polymerization of difunctional monomers in their mesomorphic state does not lead exclusively to the "freezing" of molecular organization prevalent at the start of polymerization, but in some cases produces a more ordered polymer. This phenomenon seems to be dependent on the ability of interacting side groups to pack into an orderly, layered arrangement without disturbing the regular disposition of the polymeric backbone. The polymer of diABAB and the 1:1 copolymer of diABAB and ABBA provide an example of a monomer which polymerized in its nematic state gives a polymer with a smectic organization. High degrees of side chain orientation (f = 0.7) have been achieved in a magnetic field. Thermal expansion of this polymer showed a large anisotropy. It is anticipated that other physical properties will also be anisotropic.

Polymerization of diABH and PMAS (monomers 3 and 4) in the nematic state leads to polymers with nematic order. The values for the average distance between side groups are in agreement with the values anticipated based on the corresponding low molecular weight mesomorphic fluids.

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Rheological Properties of Linear and Branched Polyisoprene

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ABSTRACT: Viscosity η and first normal stress N_1 have been measured as functions of shear rate $\dot{\gamma}$ for solutions of linear, four-arm star, and six-arm star polyisoprenes, all with narrow molecular weight distributions. Concentrations in tetradecane ranged from 0.02 g/ml to 0.33 g/ml; molecular weights ranged from 35 000 to 2 000 000. All measurements were made at 25 °C in a Weissenberg Rheogoniometer. The effects of branching on zero shear viscosity η_0, steady state compliance $J_e{}^0$, the characteristic shear rate (marking the onset of shear rate dependence in η) $\dot{\gamma}_0$, and the shape of the η vs. $\dot{\gamma}$ master curve were determined. At low concentrations and molecular weights the values of η_0 and $J_e{}^0$ were lower for the branched samples, while at high concentrations and molecular weights the reverse became true and substantial enhancements in η_0 and $J_e{}^0$ were found. On the other hand, the product $\eta_0 J_e{}^0 \dot{\gamma}_0$ was essentially the same for all samples irrespective of concentration, molecular weight, or branching, and the form of the master curve appeared to be independent of branching. Enhancement factors were determined and compared with results reported by Kraus and Gruver on star-branched polybutadienes. Data on viscosity enhancement for the two polymers reduced to essentially the same curve when correlated in terms of $\Phi^{5/6}(\Phi M_b/M_c)$, Φ being the volume fraction of polymer, M_b the molecular weight of the branches, and M_c the characteristic molecular weight for entanglement in the respective undiluted linear polymers. The form of this correlating parameter was arrived at by considerations on the effect of long branches on macromolecular mobility in entangling systems. The interpretation of enhancement in η_0 and $J_e{}^0$ in relation to the spectrum of relaxation times and their practical effects on η vs. $\dot{\gamma}$ behavior are discussed.

I. Introduction

The flow properties of polymers are altered by branching in important and unexpected ways.[2-8] Quantitative information on the relationship between branch structure and behavior is still scanty, however, and molecular explanations for the observations are almost totally lacking. This paper presents some results obtained in steady shearing flow on star-branched polyisoprenes, all of narrow molecular weight distribution and all well characterized by dilution solution methods.[9] It also contains some preliminary attempts to unify the observations with those published for other branched polymers.

Three series of polyisoprene samples were studied: linear molecules, star molecules with four equal arms, and stars with six equal arms. Solutions in tetradecane encompassing a range of polymer concentration c and molecular weight M were prepared with each series. Shear stress σ and first normal stress difference N_1 were measured at 25.5 °C as functions of shear rate $\dot{\gamma}$ in a plate-cone rheometer. Values of the viscosity at zero shear rate η_0, the steady state recoverable compliance $J_e{}^0$ (estimated from N_1 at low shear rates), and the characteristic shear rate $\dot{\gamma}_0$ (locating the onset of shear rate dependence in the viscosity) were determined and correlated with structure.

II. Theoretical Background

A. Zero Shear Viscosity. The effects of branching are best established for the case of the zero shear viscosity η_0. When the branches are not too long or when the polymer concentration is sufficiently low, η_0 is less than that for linear chains of the same total molecular weight, presumably due to the smaller mean radius of gyration S of branched molecules. On the other hand, for long branches at high polymer concentrations the viscosity becomes larger in branched systems.

Berry and Fox[2a] discuss the viscosity behavior relative to linear systems in terms of two factors. One governs the reduction, which is assumed to depend only on the ratio of radii and to operate at all concentrations and branch lengths. The other governs enhancement and becomes important, then dominating, at high concentrations and branch lengths. They note that, when the reduction factor alone is acting, the viscosity of branched polymers is approximately the same as for linear polymers of the same ra-