(6) Phase II crystals with molecular chains perpendicular to the film transform to an all-parallel phase II or phase IV structure.

In future studies, these conclusions will be examined using complete pole figure analysis. However, these preliminary studies were necessary since pole figure analysis cannot be carried out in an unambiguous way for samples containing different crystal structures with many reflections in common. We are also poling films with special orientations, for example, with molecular chains perpendicular to the plane of the film, to provide cases where a unique polarization mechanism can be isolated.

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Light Beating Spectroscopy of Branched Poly(propylene glycol)

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ABSTRACT: Linear and trifunctional star polymers of propylene glycol with about the same molecular weight ($\simeq$3000) were studied by the laser light beating spectroscopic technique. Macroscopic shear viscosity measurements were also carried out. The time correlation functions for the density fluctuation were determined for both the linear and the branched polymers. The time correlation functions display a nonexponential shape. The results show that although the two polymers have about the same viscosity over the temperature range between −30 and +25 °C, the relaxation time for branched poly(propylene glycol) is several times longer than that of linear poly(propylene glycol), in contrast to dielectric relaxation data, which show that linear and branched polymers have nearly identical dielectric behavior.

Introduction

Studies of the dynamics of segmental motion of a bulk polymer liquid by the laser light beating spectroscopic technique are of considerable current research interest. The dynamic light scattering data have provided very useful insight into the physical processes associated with the glass transition processes.

In a recent article, we reported the results of a comprehensive laser light beating spectroscopic study of linear poly(propylene glycol) (PPG).[1] The study deals with the measurements of the homodyne intensity time correlations of the scattered field as a function of temperature for linear PPG of different molecular weights. The time correlation functions for the fluctuations of the polarizability density which give rise to light scattering were extracted from the measured homodyne intensity time correlation function. The important results found are as follows: (1) Over the time scale from 1 to 10^{-6} s, the time correlation functions from both VV and VH scattering geometries are independent of the scattering angle. The mean relaxation times derived from the VV and VH time correlation functions are, however, nearly equal. (2) The temperature dependence of the mean relaxation times follows the Vogel–WLF equation but not the Arrhenius equation. (3) The mean relaxation times for all polymers depend only on temperature and not on the macroscopic shear viscosity associated with the difference in the molecular weight for different polymers. When the mean relaxation time is scaled according to the "segment viscosity", all temperature-dependent data from polymers of different molecular weights fall on a master curve. This result suggests that the localized side-group orientation and the backbone motion associated with the conformational flip are the mechanisms responsible for the dynamic light scattering in PPG.

In this paper, we report the result of the effects due to branching on the homodyne time correlation function, keeping the molecular weight of PPG fixed. This complements the result of a similar study using the dielectric relaxation technique by Stockmayer and Burke.[2] These

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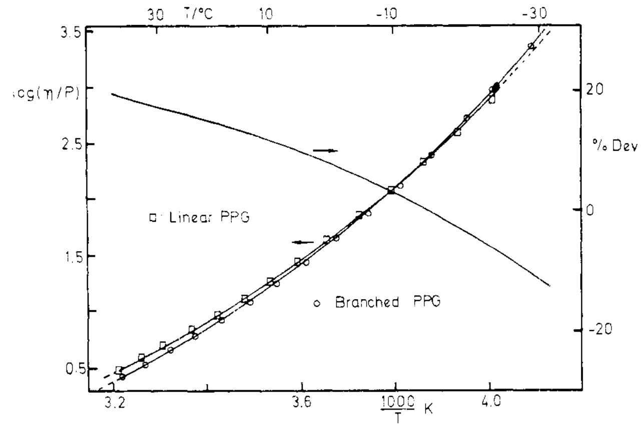


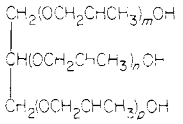
Figure 1. Viscosity data of linear and branched poly(propylene glycols) plotted as a function of temperature. The curves were calculated according to the Vogel–WLF equation (eq 1) using the parameters given in the text.

authors found that branching has a negligible effect on the main dielectric loss mechanism. However, the present work shows that branching gives rise to a pronounced effect on the mean relaxation time, despite the fact that it only influences the macroscopic shear viscosity of the polymer negligibly.

Experimental Procedure and Results

The homodyne single-clipped photon correlation functions of the linear and branched poly(propylene glycol) were measured at temperatures between −49 and −66 °C at a 90° scattering angle using a 96-channel Malvern correlator. The excitation light source was an argon ion laser (Spectra-Physics 165) operating at 5145 Å with about 800-mW power. The time correlation functions cover more than 4 decades in the time scale. In order to cover such a wide dynamic range, overlapping data at each temperature from different runs using several increment sample times differing by a factor of 4–5 were first obtained and then joined together to construct a composite time correlation function. The method of matching the data obtained using different increment sample times was described in ref 1.

The two samples used in the investigation (kindly provided by Dr. H. Hespe of Bayer AG Leverkusen, West Germany) were (a) linear atactic hydroxyl-terminated poly(propylene glycol) (PPG) having a number-average molecular weight of 3100 and (b) trifunctional star atactic PPG with three hydroxyl end groups having the structure



$$\begin{array}{l} CH_2(OCH_2CHCH_3)_mOH \\ | \\ CH(OCH_2CHCH_3)_nOH \\ | \\ CH_2(OCH_2CHCH_3)_pOH \end{array}$$

where $m \simeq n \simeq p \simeq 15$, but the precise m, n, and p values are, of course, statistically distributed. The average molecular weight is about 3000 in the branched polymer.

A Lauda temperature bath was used to control the sample cell temperatures to ±0.5 K by circulating liquid CH_3OH around a copper holder containing the scattering cell. Because of the large change of the relaxation time with temperature, great care was taken to ensure the stability of the sample temperature when the photon correlation data were taken. The viscosity of each sample was measured from −40 to +30 °C with a Höppler (falling ball) viscometer. The overall experimental setup employed in the present work is identical with that described in ref 1. The viscosities of the linear and branched PPG were plotted as a function of temperature in Figure 1. Although the viscosity values of the two polymers are nearly the same, there is a slight noticeable difference as shown by the percent deviation plot, also given in Figure 1. Furthermore, one notes that over the temperature range studied, the viscosity of each sample displays a non-Arrhenius temperature dependence. However, it is possible to fit the viscosity data to the Vogel–WLF equation of the form

$$\ln \eta_s = \ln \eta_0 + B(T - T_0)^{-1} \qquad (1)$$

The fit gives the parameters η_0, B, and T_0 equal to 2.31 (±0.50) × 10^{-3} P, 1009 (±41) K, and 170.6 (±2.0) K, respectively, for linear PPG, and 1.66 (±0.20) × 10^{-3} P, 1019 (±23) K, and 172.1 (±2.0) K, respectively, for branched PPG. These parameters are rather similar to those obtained for linear PPG at different molecular weights reported in ref 1.

One notes that the η_0 value for branched PPG is smaller than that for linear PPG; this supports the observation for Stockmayer and Burke,[2] who have shown that at high temperature, the difference in viscosity between the linear and star samples is very close to $^7/_9 = 0.778$ if the molecular weights for the two are identical and the free-draining assumption (Rouse model) is applicable. Indeed, the fitted η_0 values are in the ratio of 0.72. However, the parameters of the branched polymer differ somewhat from the values of Stockmayer and Burke ($\eta_0 = 5.9 \times 10^{-3}$ P, B = 824 – 838 K, and T_0 = 180 K). This is probably due to the fact that they extracted the parameters using the data obtained over a narrower temperature range (5–25 °C). Below −10 °C, the viscosity of branched PPG is larger than that of linear PPG; this is reflected in the slightly larger values of B and T_0 parameters for the branched polymer. The crossover in viscosity occurring at lower temperature is probably due to the fact that the star sample has 50% more OH end groups and thus has more hydrogen-bonding possibilities at low temperature. Hydrogen bonding in the star polymer at low temperature is expected to play a role in light scattering.

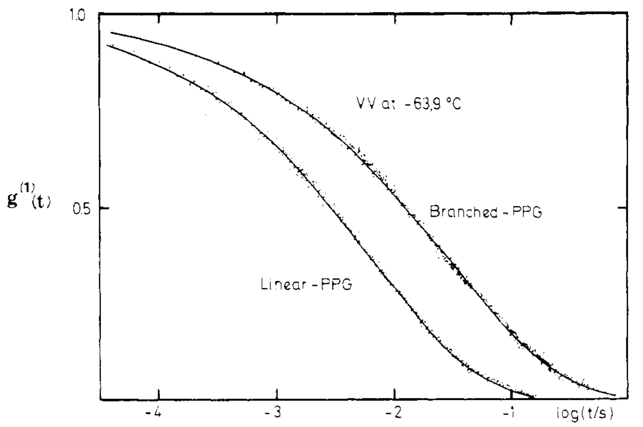


Figure 2. Normalized time correlation functions of the scattered field $g^{(1)}(t)$ extracted from the measured homodyne autocorrelation functions plotted as a function of log t for linear and branched poly(propylene glycols) at T = −63.9 °C. The curves are calculated according to the William–Watts function using the parameters $\beta = 0.43$ and $\tau_0 = 2.14 \times 10^{-2}$ s for linear PPG and $\tau_0 = 1.24 \times 10^{-1}$ s for branched PPG.

The normalized time correlation functions of the scattered field $g^{(1)}(t)$ obtained using the VV scattering configuration for linear and branched PPG at −63.9 °C are shown in Figure 2. The time correlation functions $g^{(1)}(t)$ were calculated from the directly measured homodyne single-clipped correlation function $G_{\text{obsd}}^{(2)}(t)$ using the previously described procedure. One notes that the cor-

Table I
Mean Relaxation Times Obtained from the VV Spectrum for Linear and Branched PPG at Various Temperatures

linear PPG		branched PPG	
T/°C	$\bar{\tau}$/s	T/°C	$\bar{\tau}$/s
−49.3	1.02×10^{-4}	−49.3	3.16×10^{-4}
−50.9	1.51×10^{-4}	−50.1	3.09×10^{-4}
−52.5	2.00×10^{-4}	−52.5	8.71×10^{-4}
−55.2	5.89×10^{-4}	−54.1	1.38×10^{-3}
−58.3	2.69×10^{-3}	−55.2	2.57×10^{-3}
−60.7	1.00×10^{-2}	−57.3	6.76×10^{-3}
−61.2	1.14×10^{-2}	−58.4	1.17×10^{-2}
−63.9	5.89×10^{-2}	−60.8	6.31×10^{-2}
−64.1	8.12×10^{-2}	−61.3	7.76×10^{-2}
−65.7	3.09×10^{-1}	−63.9	3.39×10^{-1}
−66.7	5.37×10^{-1}	−64.8	1.00

relation functions cannot be represented by a single-exponential function but it is well fitted by a single William–Watts function given by

$$g^{(1)}(t) = \exp(-t/\tau_0)^{\beta} \qquad (2)$$

with $\beta = 0.43$ for both polymers. However, there is a large difference in the τ_0 values for the two types of PPG ($\tau_0 = 2.14 \times 10^{-2}$ s for linear PPG and $\tau_0 = 1.24 \times 10^{-1}$ s for branched PPG). The parameter β is a measure of the width of the distribution of the relaxation times and this β value indicates that there is a fairly wide relaxation time distribution.

The mean relaxation time $\bar{\tau}$ is obtained from eq 3 according to

$$\bar{\tau} = \int_0^{\infty} \mathrm{d}t \, \exp(-t/\tau_0)^{\beta} = \frac{\tau_0}{\beta}\Gamma(\beta^{-1}) \qquad (3)$$

where $\Gamma(\beta^{-1})$ is the gamma function. Shown in Table I are the values of $\bar{\tau}$ calculated using eq 3 at various temperatures for linear and branched PPG. The parameter β is found to increase slightly with decreasing temperature, increasing from 0.40 at −49.3 °C to 0.43 at −63.9 °C. This behavior is similar to that found previously for other linear PPG with molecular weights equal to 400, 1025, 2000, and 4000.

The $\bar{\tau}$ values obtained for both polymers are plotted as a function of temperature in Figure 3. Over the −49.3 to −66.4 °C temperature range, the variation of $\bar{\tau}$ does not follow the Arrhenius equation with a constant energy. A calculation of $\bar{\tau}$ according to the Vogel–WLF equation

$$\ln \bar{\tau} = \ln A + B/(T - T_0) \qquad (4)$$

using the B and T_0 values derived from the viscosity measurements fit the $\bar{\tau}$ data well. The fits give $A = 9.6$ (±3.5) $\times 10^{-13}$ s for linear PPG and $A = 7.1$ (±2.6) $\times 10^{-13}$ s for branched PPG. Although the uncertainty in the parameter A is quite large, the value of A given for the branched polymer is smaller than that for the linear polymer. The fact that over the observable range, the branched polymer always has the longer relaxation time $\bar{\tau}$ indicates that the mechanisms that determine the parameters B and T_0 are responsible for the inversion of the relaxation time $\bar{\tau}$. However, since the temperature range of the light scattering work does not overlap the range of the viscosity measurements, there exists a possibility that the parameters B and T_0 obtained from the viscosity data may not be appropriate for the $\bar{\tau}$ data. For this reason, we have fitted the relaxation time data according to

$$\ln \bar{\tau} = \ln A' + B'/(T - T_0') \qquad (5)$$

without using the parameters B and T_0 obtained from the viscosity results. In this fit, the quantities A', B', and T_0 are treated as free parameters. This fit gives $A' = 5.7$ (±4.5) $\times 10^{-10}$ s, $B' = 488$ (±96) K, and $T_0' = 183$ (±5) K for linear PPG and $A' = 1.1$ (±1) $\times 10^{-10}$ s, $B' = 636$ (±193) K, and $T_0' = 180$ (±5) K for branched PPG. While the results obtained for A', B', and T_0' are considerably different from those obtained using eq 4, the trend in the parameters is quite similar to that derived from eq 4; i.e., for the branched polymer A' and T_0' are smaller and B' is larger. However, the fact that the fits do not give a unique set of parameters for A, B, and T_0 warns against giving too much quantitative significance to the interpretation of these fitting parameters introduced in the Vogel–WLF equation.

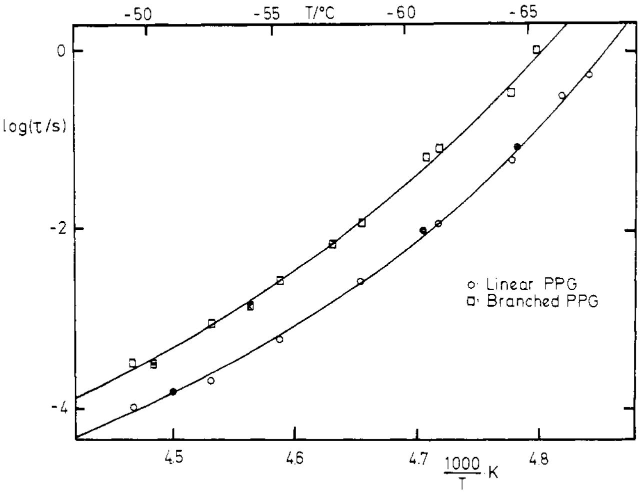


Figure 3. Semilog plot of the mean correlation times $\bar{\tau}$ associated with $g^{(1)}(t)$ for linear and branched poly(propylene glycols) vs. $1/T$. The curves are calculated using eq 4.

Over the entire temperature range studied, $\bar{\tau}$ for branched PPG is several times larger than $\bar{\tau}$ for linear PPG. For example, at −50 °C, the $\bar{\tau}$(branch)/$\bar{\tau}$(linear) ratio is 3.1; the ratio becomes 6.9 at −65 °C. Since the VV scattering intensity in PPG mainly reflects the density fluctuation (the depolarization ratio being quite small, less than 0.15), the significant differences reflected in the time correlation functions and in $\bar{\tau}$ indicate that the dynamics of density fluctuations is sensitive to the effect of branching. This is in contrast to the result of dielectric relaxation studies, in which the values of the dielectric relaxation times found for linear and branched PPG are quite close to each other.

In the previous paper,[1] suggestions were made that local motion involving the conformational transitions via the gauche migration and the gauche production steps are possible mechanisms responsible for VV and VH scattering.[3] These types of motion are effective in causing the density fluctuations, as well as inducing the coupling of the segment center-of-mass motion to the reorientation of the chemical units.

Our DTA data obtained by cooling the present linear and branched PPG samples at a rate of 10 °C/min have shown a slight difference in the glass transition temperature ((T_g(branched) = −61.5 °C) − (T_g(linear) = −64 °C) = 2.5 (±0.5) °C). This is about equal to the different of the T_0 values found for the two polymers from fitting the viscosity data to either eq 1 or eq 5 and suggests that the larger $\bar{\tau}$ values found in the branched PPG are closely related to the mechanism that leads to a higher glass transition temperature (or T_0 in the Vogel–WLF equation). Using a simple three-state rotational isomer model, Miller has related the parameter B in the Vogel–WLF equation to the barrier of rotation about the main-chain bonds and related T_0 to the conformational entropy.[4] A higher B value corresponds to higher steric hindrance and a higher T_0 value, to greater configurational entropy. It should be pointed out that the effect on the glass transition temperature due to branching in PPG is quite similar to that found in poly(ethyl acrylate), in which the methyl substitution causes T_g to shift higher by 80 °C. The $\bar{\tau}$ value found for poly(ethyl methacrylate) is also greater than that found in the acrylate polymer.[5]

In conclusion, we have shown that branching of the side group in PPG has a pronounced effect on the dynamics of the density fluctuations. The density–density correlation function relaxes slower in the branched than in the linear PPG.

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Light Spectroscopy in Polymer Solutions at Θ Conditions in the Crossover Concentration Domain between the Dilute and Semidilute Regimes

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ABSTRACT: The concentration dependence of the diffusion constant has been measured by light spectroscopy for solutions of polystyrenes of molecular weight ranging from 20 000 to 2 × 10^6 at Θ conditions. In the concentration domain extending from the very dilute limit to slightly beyond the crossover concentration c^* between the dilute and semidilute regimes, the data can be represented in the form of a universal normalized hydrodynamic plot. The temperature dependence of the diffusion constant has been investigated in the vicinity of the critical point and compared to the predictions of the critical phenomena theory.

Introduction

The functional dependence upon temperature and monomer concentration of the microscopic and thermodynamic parameters describing solutions of flexible polymers has been derived by Daoud and Jannink[1] on the basis of the analogy between the Θ point in polymer solutions and the tricritical point.[2] This dependence was represented in the form of a molecular weight independent diagram of $\tau M^{1/2}$ vs. $cM^{1/2}$, where c is the polymer concentration (expressed in g cm^{-3}), M the molecular weight of the polymer, and τ the reduced temperature: $\tau = (T - \Theta)/\Theta$ (T, absolute temperature; Θ, theta temperature). Experimental verification of such a diagram was provided by both small-angle neutron scattering experiments[3] and precipitation curves obtained earlier by Schultz and Flory.[4]

Also, scaling approaches have been used to predict dynamic properties of polymer solutions at temperatures equal to the Θ temperature.[5] However, the experimental studies did not provide clear evidence of the theoretically predicted behavior.[6–13] For instance, the concentration dependence of the cooperative diffusion constant in the semidilute regime could not be verified from light spectroscopy experiments because of complications arising from the superposition of several modes in the spectrum of scattered light.[6,7] On the other hand, sedimentation[8–11] and concentration gradient diffusion (CGD)[12] experiments performed over a rather limited range of concentrations provided results in good agreement with the scaling predictions. Also, the sedimentation behavior in the dilute range at the Θ temperature could be approximately represented on a "hydrodynamic normalized plot" by a single curve in the molecular weight range 110 000–950 000.[11] In order to examine whether a similar behavior is observed for the diffusion constant, we have investigated by light spectroscopy solutions of polystyrene of weight-average molecular weights ranging from $\bar{M}_w$ = 20 000 to $\bar{M}_w$ = 2 × 10^6 in two Θ solvents (cyclohexane at 34.5 °C and cyclopentane at 20.4 °C) and at concentrations extending from the very dilute limit to slightly beyond the crossover concentration c^* between the dilute and semidilute regimes. We have also measured the diffusion constants of a cross-linked polystyrene network swollen at equilibrium either in cyclohexane at 34.5 °C or in cyclopentane at 20.4 °C, in order to compare the behavior of linear and cross-linked polymeric systems at the Θ conditions. Finally, we present some measurements of the temperature dependence of the diffusion constant of Θ solutions in the crossover concentration domain. The results are compared with the theoretical predictions for the critical phase separation of binary mixtures.

Experimental Section

A. Samples. Linear polystyrenes of low polydispersity ($\bar{M}_w/\bar{M}_n$ < 1.15) were prepared under an inert atmosphere by anionic polymerization in an aprotic solvent (THF) with an efficient initiator such as α-methylstyrene tetramer or potassium naphthalenide. The polydispersity of the samples was checked by GPC and the molecular weights were determined by light scattering measurements in THF. The obtained values of $\bar{M}_w$ are 20 000, 130 000, 570 000, and 10^6. The sample with $\bar{M}_w$ = 2 × 10^6

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