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Temperature Dependence of the Dynamic Viscoelastic Response of Amorphous Poly(Diethylene Glycol Terephthalate) Chains

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Summary

Experimental values of the storage $G'(\omega)$ and loss $G''(\omega)$ moduli were obtained at different temperatures for several fractions of poly(diethylene glycol terephthalate). By assuming that all the relaxation mechanisms have the same temperature dependence, free volume parameters were obtained. The qualitative analysis of the molecular weight dependence of the viscosity at zero shear rate suggests that well developed entanglements are present in the relatively low molecular weight fractions investigated.

Introduction

Conformational studies carried out on poly(diethylene glycol terephthalate) (PDET) chains suggest that gauche states about CH_2–CH_2 bonds of the repeat unit have an energy ca. 0.8 Kcal mol^{-1} lower than the alternative trans states (RIANDE et al. 1982, SAN ROMAN et al. 1982). As consequence, a high fraction of the chains probably fold back in themselves and the elastic properties of networks prepared from this polymer are enhanced. PDET networks exhibit an equilibrium elastic modulus significantly higher than it would be expected on theoretical grounds (LLORENTE et al. submitted). The chemical crosslinks are not enough to account for the modulus observed, so that the unusually high value of this quantity should be attributed either to reinforcing effects from network crystallization or to contributions from topological entanglements. Since birefringence-strain experiments did not detect crystallinity vestiges in the stretched networts (RIANDE et al.submitted), it was concluded that topological entanglements play a major role in the elastic behavior of these networks.

The absence of crystallinity in stretched PDET networks, even at elongation ratios larger than 6, prompted this investigation in which the linear viscoelastic behavior of uncrosslinked amorphous PDET is examined at several temperatures. Studies of this kind on aromatic polyesters are scarce owing to the physical characterictics of the polymers. Most of the aromatic polyesters are crystalline and melt well above room temperature, so that the study of the viscoelastic behavior of amorphous polyesters, at temperatures relatively near to the glass transition temperature , are precluded. In this investigation, the temperature dependence of the relaxation viscoelastic mechanisms of PDET chains in the plateau and terminal regions, is analyzed.

Experimental

Poly(diethylene glycol terephthalate) was prepared by the standard melt phase method using tetraisopropyl titanate as catalyst (DE LA CAMPA 1981). Fractions of number average molecular weight 4600, 8000, 11700 and 24700 were obtained at 30°C from the unfractionated polymer, by using chloroform-methanol as solvent/nonsolvent system. The glass transition temperatures of the fractions, determined by DSC calorimetry, are shown in Table I. The dynamic storage and loss moduli G′and G′′were measured with a Rheometrics Dynamic Spectrometer at temperatures lying in the range 40-90 °C (in the highest molecular weight fraction the moduli were also determined at 110 °C). The values of the frequency ranged from 10^{-1} to 500 rad/sec.

TABLE I

Mn	T_g, °C	T_∞, °C	Φ_g/B	log η_0(90°C)	log η_0($T-T_g$=70°C)
4600	12	-40	0.033	3.10	3.36
8000	16	-32	0.037	4.03	4.18
11700	18	-30	0.040	4.76	4.79
24700	20	-30	0.040	5.47	5.47

η_0 is given in poises.

Results and Discussion

The double logarithmic plot of the experimental values of the storage G′ and loss G′′ moduli against frequency, at different temperatures, could superpose to a common reference temperature T_0 (90°C) by horizontal shift along the frequency axis, reflecting the fact that the chief effect of temperature changes is to multiply all the relaxation times, τ_i, by a common factor such that at any temperature T (FERRY 1981)

$$\tau_i\,(T) = a_T\ \tau_i(T_0) \qquad (1)$$

As can be observed in the G′ and G′′ master curves of Figure 1, relatively good superposition is achieved without multiplying the experimental data by the factor $\rho_0 T_0/\rho T$, where ρ and ρ_0 are the densities of the polymer at T and T_0 respectively, which accounts for the entropic correction. The general features of the plateau zone of linear viscoelastic behavior is apparent in the figure. In the set of fractions investigated it was found that the length of the plateau increases as the molecular weight increases, as expected.

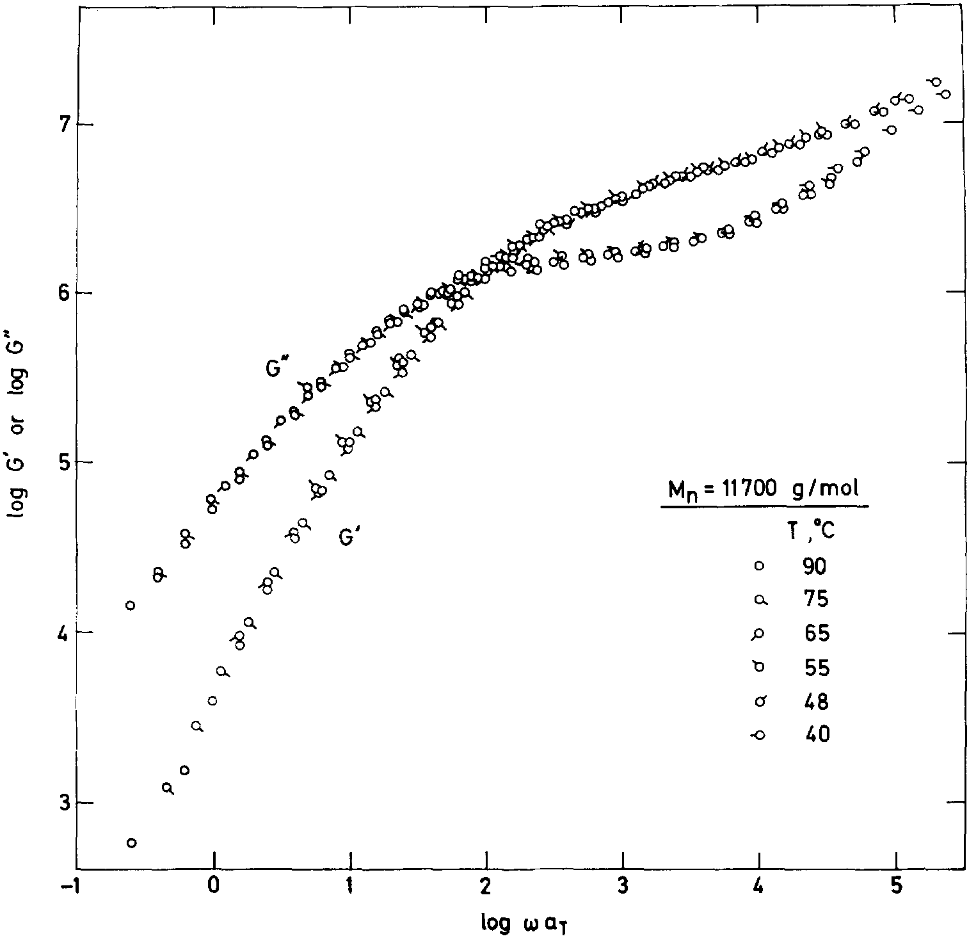

Figure 1

Composite curves for the storage and loss moduli corresponding to the fraction of molecular weight 11700 g./mol, at 90°C. The moduli are given in dynes/cm^2.

The variation of the shift factor, log a_T, with temperature for all of the samples investigated is shown in Figure 2. It should be stressed that almost the same values of a_T superpose the two viscoelastic functions G′ and G″. The analysis of a_T was carried out by making explicit the indirect effect of temperature on τ_i, which is a function of free volume. Assuming that the volume is a linear function of temperature, the Doolittle free volume equation (DOOLITTLE 1951, PLAZEK and O′ROURKE 1971)

$$\tau_i = A \exp(B/\Phi) \qquad (2)$$

$$\log a_T = A' + (C/2.303)/(T-T_\infty) \qquad (5)$$

The relation between the Vogel parameters C and T_∞ and the Doolittle free volume Φ and B are given by

$$C = (B/\Phi)(T-T_\infty) = (B/\Phi_g)(T-T_g) \qquad (6)$$

where Φ_g is the relative free volume at the glass transition temperature. Fitting of the experimental data to equation 5 requires a choice of T_∞ ; trials were made with different values of T_∞ until curvature was eliminated, using the rule of thumb that T_∞ is usually about 50°C below the glass transition temperature (FERRY 1981). The values obtained for T_∞ are given in the third column of Table I. The time scale shift factors for the fractions studied can be described, within experimental error, as linear functions of $1/(T-T_\infty)$, as can be seen in Figure 3, where one of these plots is shown. The analysis of the free volume parameters obtained from individual samples indicates that the average value of Φ_g/B (see the fourth column of Table I) is 0.038 ±0.003. This value is somewhat higher than the average value of 0.025 obtained for most polymers, but it is similar to that found for other rubberlike materials such as polybutadienes(FERRY 1981) with different cis-trans content, where Φ_g/B is about 0.039.

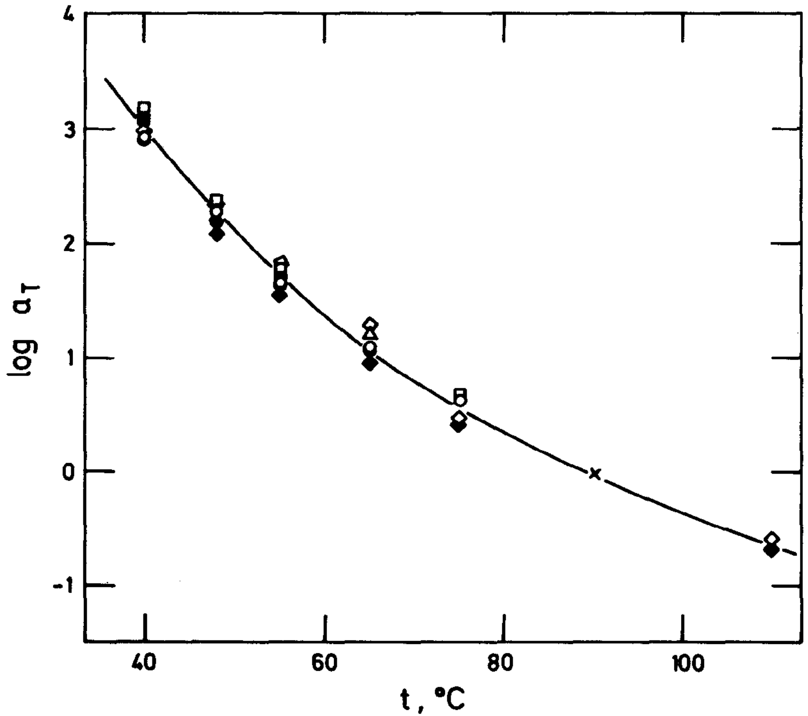

Figure 2

Temperature dependence of the shift factors a_T. Open symbols refer to values of a_T obtained from the storage modulus for different fractions: (○) Mn = 4600 ; (△) Mn = 8000 ; (□) Mn = 11700 ; (◇) Mn = 24700. Filled symbols represent the values of a_T obtained from the loss modulus.

A few comments should be made concerning the influence of the molecular weight on the viscosity of PDET chains. At high temperatures and low frequencies the double logarithm plot of the loss modulus against frequency is a straight line with slope unity, in agreement with the predictions of linear viscoelasticity. The viscosity at zero shear rate can be obtained converts into the Vogel equation (VOGEL 1921)

$$\tau_i = B'\exp(C/T-T_\infty) \qquad (3)$$

A, B and C are characterizing constants and Φ is the relative free volume

$$\Phi = (v-v_o)/\ v_o \qquad (4)$$

where v_o may be considered to be that volume which is unavailable to the molecular process of interest and T_∞ is the temperature at which the free volume $(v-v_o)$ would disappear were it not for the intervention of glass formation. Since $a_T = \tau_i / \tau_{i,o}$ where $\tau_{i,o}$ is the value of the relaxation mechanism of interest at the chosen reference temperature (PLAZEK and O'ROURKE 1971)

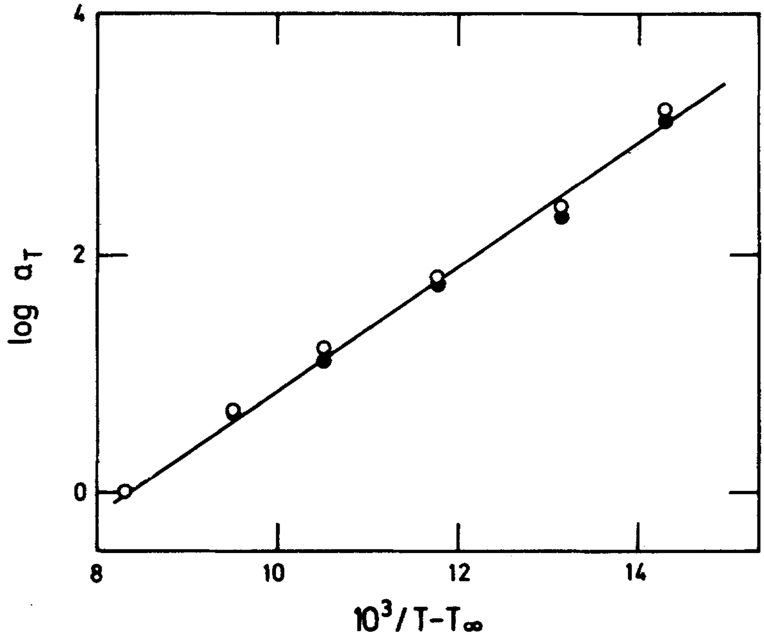

Figure 3

Values of log a_T against $1/(T-T_\infty)$ for the fraction of molecular weight 11700 g./mol. Open and filled symbols refer to values of a_T obtained from G′ and G′′, respectively.

from G´´ by the equation (FERRY 1981, GRAESSLEY 1974)

$$\eta_o = \lim_{\omega \to 0} G''(\omega)/\omega \qquad (7)$$

Values of η_o at 90°C for the PDET fractions used in this work are given in the fifth column of Table I. The effect of molecular weight distribution on η_o can be described simply by the well-known relation that η_o is determined by weight average molecular weight M_w. However, the value of this latter quantity was not available in the present study and, therefore, no reliable relationship could be established between the molecular weight and the viscosity. By assuming, however, that the molecular weight distribution of each fraction obeys the most probable distribution (WALLACH 1967), and using the values of η_o at temperatures at which $T-T_g = 70°C$, one finds that the viscosity is proportional to M^a, the value of a being about 3. Although these results are qualitative in nature, the strong dependence of η_o on M suggests that well developed entanglements are actually present in relatively low molecular weight chains, confirming earlier results obtained from the study of the molecular aspects of rubber elasticity of PDET networks according to which the molecular weight between entanglements should lie in the vicinity of 2000 g./mol.

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