Temperature Dependence of Relaxation in Polypropylene and Poly(ethylene-*co*-propylene)

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Introduction

Thermorheological Complexity. It is well-established[1] that many neat polymers exhibit thermorheological complexity in their viscoelastic spectra, usually evidenced by a different temperature dependence for the softening and terminal dispersions. Examples of this breakdown of the time−temperature superposition principle include polystyrene,[2] poly(vinyl acetate),[3] poly(propylene glycol),[4] poly(phenylmethylsiloxane),[5] polyisoprene,[6] and polyisobutylene.[7] A similar result has been reported for atactic polypropylene (a-PP).[8] However, in this case the conclusion was based on nonoverlapping data. The segmental and the terminal modes, while apparently described by different time−temperature shift factors, could not be measured at the same temperature. In fact, the compliance curves measured at different temperatures were successfully superpositioned to yield a master curve, notwithstanding the authors' averment of thermorheological complexity.[8]

Subsequently, dynamic light scattering (DLS) experiments were carried out[9] on the same a-PP sample used for the creep study. Photon correlation functions for the local segmental motion were obtained over a temperature range corresponding to that of the terminal creep data. The results indicated that the respective temperature dependences of the softening and terminal dispersions were indeed different. However, since there is no overlapping of the segmental relaxation data for the two experimental techniques, the results could not unambiguously establish that amorphous polypropylene is thermorheological complex. The different temperature dependences might simply be the result of a differing probe dependence of the measured relaxation behavior. Such effects are known; for example, in both poly(vinyl acetate) and poly(propylene glycol), DLS shift factors exhibit a stronger temperature dependence than the shift factors determined for the same modes using dielectric spectroscopy.[10] This is not an indication of thermorheological complexity but rather demonstrates that correlation times measured by the two spectroscopies do not necessarily bear a relationship to one another. In this note we describe dynamic mechanical measurements in the glass transition zone of atactic polypropylene. By employing the same sample used in the earlier studies,[8,9] our purpose was to verify that a-PP is thermorheologically complex.

Correlation of Time and Temperature Dependences. Another noteworthy aspect of polymer dynamics is the correlation between the shape of the relaxation function and the fragility.[11−17] The term fragility refers to the temperature dependence of glass-forming liquids near T_g, as represented by semilogarithmic plots of the relaxation time versus T_g/T. T_g here is an operationally defined reference temperature at which the relaxation time assumes an arbitrary value. More fragile glass formers are those whose relaxation times change more with change in T_g-normalized temperature, i.e., have larger apparent activation energies. This terminology originates from the (now passé) idea that property changes near T_g reflect the rapidity with which a liquid's "structure" is modified or degraded as the temperature is increased through the glass transition region.[18,19] We have carried out dynamic mechanical measurements on a random copolymer of ethylene and propylene in order to compare its segmental relaxation behavior to that of the homopolymer a-PP. The differences should be interpretable in terms of the chemical structure of the two materials.

Experimental Section

The polypropylene (obtained from D. J. Plazek) was 97% atactic and completely amorphous. It is the identical material used in earlier creep[8] and dynamic light scattering studies.[9] The ethylene−propylene copolymer, Vistalon 404 from Exxon Chemical Co., has an equimolar amount of the two monomers, which corresponds to 60% by weight of propylene units. Dynamic mechanical data near the glass transition temperature were obtained on films (7 × 19 × 2 mm) in tension, using an Imass Corp. Dynastat instrument. Isothermal measurements were obtained from 0.01 to 100 Hz, with temperature control better than ±0.1 °C. The small contribution to the data from instrumental compliance was corrected for using standard procedures.[20] Any creep of the samples during the measurements was monitored and corrected.

Results and Discussion

Atactic Polypropylene. Dynamic mechanical measurements were carried out at temperatures overlapping the earlier creep and DLS experiments. From the mechanical data, segmental relaxation times can be defined as $\tau = 1/2\pi f_{\text{peak}}$, where f_{peak} is the frequency of the maximum in the loss modulus dispersion in the glass transition zone. The τ's obtained for various temperatures are shown in Figure 1, along with the previous creep and DLS results.

The DLS experiments yield average retardation times defined as the first moment of the spectral distribution obtained by Fourier transformation of the experimental DLS correlation function.[9,21] Such retardation times are proportional, but not equal, to relaxation times, the former invariably being larger.[22] Accordingly, in Figure 1 we have multiplied the DLS retardation times by an empirical factor of 0.435 to bring them into coincidence with the dynamic mechanical relaxation times.

Since creep experiments only yield shift factors, vertical scaling of the creep data in Figure 1 is arbitrary. We have multiplied the shift factors reported in ref 8 by a factor of 4.65×10^{-5}, which superposes the lower temperature creep data, representing local segmental dynamics, and the dynamic mechanical data. The creep data for higher temperatures reflects the terminal dispersion (i.e., the chain modes), which clearly depart from the curve for the DLS and dynamic mechanical times determined at lower temperatures. In light of this, we fit separately the high-temperature creep data and the mechanical, DLS, and low-temperature creep results to the Vogel−Fulcher equation[23]

$$\tau = A \exp\left(\frac{B}{T - T_\infty}\right) \qquad (1)$$

The obtained parameters are given in Table 1.

The most important result of Figure 1 is the direct substantiation that the terminal and segmental dynamics in amorphous polypropylene have a different tem-

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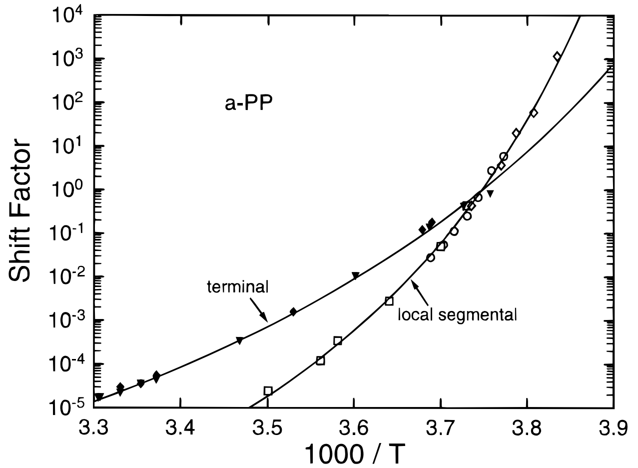

Figure 1. Relaxation times for atactic polypropylene obtained from dynamic mechanical (○), dynamic light scattering[9] (□), and creep[8] compliance (◇,◆) and viscosity (▼). The hollow symbols represent local segmental modes, while filled symbols refer to the terminal relaxation. The DLS and creep data have been vertically shifted as described in the text.

Table 1. Vogel–Fulcher Parameters

	mode	A	B	T_0 (K)	$T_g{}^a$ (K)
a-PP	terminal	8.49×10^{-13}	1492	213.2	266.8
a-PP	segmental	6.77×10^{-14}	1021	233.2	266.8
EP	segmental	8.01×10^{-9}	346.2	191.0	209.6

[a] Temperature at which mechanical relaxation time equaled 1 s.

perature dependence, a consequence of which is thermorheological complexity in the glass transition region of the viscoelastic spectrum. Previously available data did not overlap in temperature and thus thermorheological complexity could only be inferred from an apparent change in shape of the Arrhenius curve.[8] It is worth noting that, similarly to other polymers,[1] the segmental modes in a-PP display a greater sensitivity to temperature than do the terminal modes or the viscosity. Such behavior is predicted by the coupling model of relaxation.[24]

Poly(ethylene-*co*-propylene). There exist many studies of the effect of chemical structure on the segmental relaxation behavior of polymers.[25–38] It has been demonstrated for a wide range of polymers and small molecular glass formers that both the time and temperature dependence of the softening dispersion are related to the degree to which to which local structure engenders steric constraints on the relaxation from neighboring nonbonded segments.[12,35–37] Specifically, polymers with smooth, compact, symmetrical chain backbones generally have narrow segmental relaxation functions and segmental relaxation times with weaker T_g-normalized temperature dependencies. Conversely, less flexible polymers and those having sterically hindering pendant groups exhibit broad segmental dispersions and more "fragile" temperature dependencies; these characteristics reflect segmental relaxation that is strongly intermolecularly cooperative. The fact that chemical structure governs the strength of the intermolecular interactions enables predictions concerning the effect of structural modifications on the time and temperature dependence of segmental relaxation.

The random copolymer of ethylene and propylene is expected to experience weaker intermolecular constraints from neighboring chains, due to the dilution of the pendant group and to the reduction in the symmetry of the chain structure. A consequence of less intermolecularly cooperative relaxation will be segmental relaxation times which are less sensitive to temperature changes (less fragile).[12] The predicted effect on the relaxation function itself is problematic. While reduced intermolecular cooperativity *per se* narrows the dispersion, the presence of two chemically distinct repeat units in the backbone can give rise to inhomogeneous broadening of the relaxation spectrum, that is, a distribution of relaxation behaviors, each potentially associated with different relaxation times and/or correlation functions. This would correspond to different conformational transition rates in the Hall–Helfand model[34] or to different primitive relaxation times in the coupling model.[1,12] Such inhomogeneous broadening has previously been reported in copolymers of 2-methyl-1,2-epoxy-1,4-butanediyl and 2-methyl-1-butenylene (epoxidized natural rubber)[36] and in cross-linked elastomers,[37] in which the cross-link junctions function as the second repeat unit. Inhomogeneous broadening is the only known source of a breakdown of the correlation between the time and temperature dependencies of segmental relaxation in neat polymers.

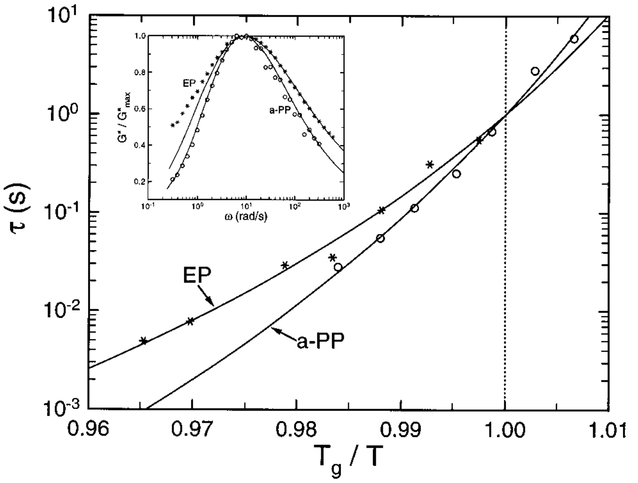

Figure 2. Segmental relaxation times for polypropylene (○) and ethylene–propylene copolymer (*), with abscissa values normalized by the temperature at which the respective polymer's relaxation time equals 1 s. The inset shows the softening dispersion in the loss modulus of atactic polypropylene (○) and ethylene–propylene copolymer (*), along with the best fit of eq 2. Note that because of inhomogeneous broadening of the relaxation, the data for the copolymer do not conform well to the KWW function.

Segmental relaxation times were determined for the EP copolymer at a series of temperatures, again using $\tau = 1/2\pi f_{\text{peak}}$ from the peak in the dynamic mechanical loss modulus. The results were fitted to eq 1, with the Vogel–Fulcher parameters listed in Table 1. In the usual fashion,[1,12,17] we define a glass transition temperature, in a manner appropriate for dynamics, as the temperature at which the segmental relaxation time equals 1 s. T_g-normalized Arrhenius plots are then constructed from the data for both a-PP (from Figure 1) and EP. As clearly seen in Figure 2, the copolymer, associated with weaker intermolecular constraints on its relaxation, exhibits a weaker normalized temperature dependence.

Representative dispersions for the two polymers, shown in the inset to Figure 2, reveal that the segmental relaxation function is broader for the copolymer than for homopolymer a-PP. This is because of inhomogeneous broadening; for the copolymer, the segmental relaxation mechanism has two origins, corresponding to different conformation transition rates for the two backbone units. The data were fitted to the Kohlrausch−Williams−Watts function

$$E(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{2}$$

using

$$E''(\omega) = \omega\int_0^{\infty} E(t)\cos(\omega t)\,\mathrm{d}t \tag{3}$$

Of course, the actual data do not decay to zero as suggested by eq 2, but the point is moot when a linear ordinate scale is employed. Two features in the $E''(\omega)$ data of Figure 2 are of interest: (i) eq 2 gives a poor fit to the copolymer dispersion, unlike the fitting of the homopolymer loss peak, and (ii) the best-fit stretch exponent for EP, $\beta = 0.4$, is significantly less than for a-PP, $\beta = 0.49$. Both are a consequence of an inhomogeneous relaxation in the EP copolymer.[37,38] Finally, we point out that the stretch exponent obtained herein for a-PP is larger than the previously reported value.[9] The latter determination was based on light scattering data. Different experimental techniques can have different correlators, in which case differences between the obtained β values are real. Also, different analyses can yield different results if the fitting function does not exactly describe the data. Fitting in the frequency domain, as done herein, weights the tails of the dispersion, whereas fitting time-domain light scattering data may emphasize more the wings of the peak. We can only remark that, at present, the origin of the difference between the β from mechanical spectroscopy and that from light scattering is an open question.

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