Temperature Dependence of Segmental and Terminal Relaxation in Atactic Polypropylene Melts

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It has been established for more than 35 years that homopolymer melts can exhibit thermorheological complexity, i.e., different relaxation processes which contribute to viscoelasticity have different temperature dependences.[1,2] In particular, segmental and terminal relaxation processes are known to have different temperature dependences for polystyrene,[3] poly(vinyl acetate),[4] polypropylene glycol,[5,6] poly(phenylmethylsiloxane),[7] polyisoprene,[8,9] and polyisobutylene.[10,11] Atactic polypropylene (aPP) is an interesting model polymer for understanding melt dynamics, being the simplest vinyl polymer which is completely amorphous. The purpose of this communication is to show the relationship between recent NMR and dielectric relaxation results on aPP with earlier light scattering, creep, and dynamic mechanical measurements. The combined data set covers 15 decades of segmental relaxation times and 10 orders of magnitude in terminal relaxation shift factors. While the earlier work established different temperature dependences for segmental and terminal relaxation near T_g, the new results indicate that they have essentially the same temperature dependences at high temperature.

Figure 1 shows shift factors for terminal relaxation in aPP melts. Plazek and Plazek[12] determined shift factors for the terminal mode from both viscosity and creep recovery measurements over the range from −7 to +70 °C. Subsequently, Pearson et al.[13] reported shift factors for the terminal viscosity of aPP at temperatures between 24 and 190 °C. Despite the use of different aPP samples, the data from the two laboratories agree as evidenced by the fit to a single Vogel–Fulcher–Tamman–Hesse equation in Figure 1. More recent viscosity data due to Plazek[14] are also included in the figure.

Also shown in Figure 1 are segmental relaxation times for aPP melts as determined by a number of different techniques. Plazek and Plazek determined shift factors (but not absolute relaxation times) from creep data for the softening (segmental) mode.[12] Segmental relaxation times for the same sample used by Plazek and Plazek[12] were measured by photon correlation[15] and dynamic mechanical[16] spectroscopies. These results cover the temperature range from −8 to +12 °C. From 0 to 26 °C, dielectric results from Pakula are shown.[17] From 42 to 225 °C, segmental relaxation times determined by fitting ¹³C NMR data are shown, as reported by Ediger and co-workers.[18,19] These dielectric
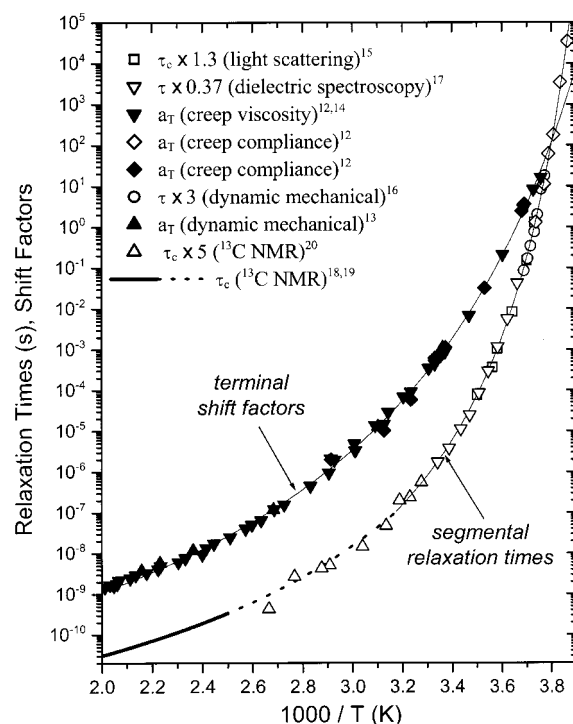
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Figure 1. Atactic polypropylene segmental relaxation times obtained from dynamic mechanical spectroscopy (○),[16] dynamic light scattering (□),[15] dielectric relaxation (▽),[17] and ¹³C NMR (− - -)[18,19] (△),[20] along with terminal time–temperature shift factors for aPP from dynamic mechanical spectroscopy (▲),[13] creep compliance (◇, ◆),[12] and viscosity (▼).[12,14] The hollow symbols represent local segmental modes, while filled symbols refer to the terminal relaxation. The legend indicates vertical shifts applied to the relaxation time data. The symbol τ_c indicates the time integral of the segmental portion of the relevant time correlation function, while for the frequency domain techniques the symbol τ indicates $(2\pi f_{max})^{-1}$. All other data are shift factors, vertically scaled for superpositioning. The thin, solid curves are best fits to the VFTH equation.

and NMR results were obtained on an aPP sample prepared in the same way as the one used by Pearson et al. and thus can be fairly compared with the other data sets. Finally, from 33 to 100 °C, segmental relaxation times from ¹³C NMR data due to Dekmezian et al.[20] are shown. These experiments were performed on a different aPP sample, with a T_g which is 17 K lower than the sample used in ref 18.

The construction of Figure 1 requires a few comments. All the terminal relaxation data represent temperature shift factors, which have been vertically shifted to coincide. The absolute vertical placements of these data points in the figure are thus arbitrary. For the segmental relaxation, the creep data have been vertically shifted to overlap the other measurements. All other segmental relaxation results in Figure 1 are absolute relaxation times. With the exception of the ¹³C NMR results of Dekmezian et al., the segmental relaxation times have been vertically shifted by small factors (3 or less) in order to provide good superposition with the results of ref 18. Shifts of this magnitude are reasonable given that different experimental observables are involved. For example, the NMR relaxation time for the rotation of a sphere in a viscous continuum is three times shorter than the corresponding dielectric relax-

ation time. The ^{13}C NMR results of Dekmezian et al. have been shifted by a factor of 5 in order to overlap with the results of ref 18. The justification for this shift lies in the different T_g values of the samples, as described in ref 18. Finally, we note that the data from ref 18 are presented as a curve since NMR results from across this temperature range were fit collectively, to produce the segmental relaxation times shown; the dashed section of the curve indicates a range of increased uncertainty in the reported segmental relaxation times.

The combined data sets in Figure 1 provide a comprehensive view of the segmental and terminal relaxation processes in aPP melts. Quite different temperature dependences are apparent at low temperatures while, at high temperatures, the two processes have the same temperature dependence within experimental error. Footnote 24 of ref 18 indicated that certain aspects of the data in Figure 1 could not be reconciled. This publication corrects that error.

References and Notes

(1) Plazek, D. J. *J. Phys. Chem.* **1965**, *6*, 612.

(2) Ngai, K. L.; Plazek, J. J. *Rubber Chem. Technol. Rubber Rev.* **1995**, *68*, 376.

(3) Ngai, K. L.; Plazek, D. J., *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1986**, *24*, 619.

(4) Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 729.

(5) Ngai, K. L.; Schonhals, A.; Schlosser, E. *Macromolecules* **1992**, *25*, 4915.

(6) Nicolai, T.; Floudas, G. *Macromolecules* **1998**, *31*, 2578.

(7) Plazek, D. J.; Bero, C.; Neumeister, S.; Floudas, G.; Fytas, G.; Ngai, K. L. *Colloid. Polym. Sci.* **1994**, *272*, 1530.

(8) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 3715.

(9) Adachi, K.; Hirano, H. *Macromolecules* **1998**, *31*, 3958.

(10) Plazek, D. J.; Chay, I.-C.; Ngai, K. L.; Roland, C. M. Macromolecules **1995**, *28*, 6432.

(11) Ngai, K. L.; Plazek, D. J.; Rizos, A. K. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 599.

(12) Plazek, D. L.; Plazek, D. J. *Macromolecules* **1983**, *16*, 1569.

(13) Pearson, D. S.; Fetters, L. J.; Younghouse, L. B.; Mays, J. W. *Macromolecules* **1988**, *21*, 478.

(14) Plazek, D. J. Unpublished data.

(15) Fytas, G.; Ngai, K. L. *Macromolecules* **1988**, *21*, 804.

(16) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1996**, *29*, 3651.

(17) Pakula, T.; Paluch, M. To be published.

(18) Moe, N. E.; Qiu, XH.; Ediger, M. D. *Macromolecules* **2000**, *33*, 2145

(19) Qiu, XH.; Moe, N. E.; Ediger, M. D. *J. Chem. Phys.* **2000**, *113*, 2918.

(20) Dekmezian, A.; Axelson, D. E.; Dechter, J. J.; Borah, B.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 367.

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