tographic behavior is obtained and the retention time and volume will decrease with increasing temperature. From the slope of this upper part of the curve one can estimate the heat of mixing of the solute in the polymer phase. One may also of course estimate other thermodynamic quantities from this portion of the curves as was done by Smidsrød and Guillet for polyisopropyl acrylamide with various solutes. However, there is still some question about the thermodynamic interpretation of these data and hence we have not reported them in this communication. The positive heat of mixing obtained in these experiments is approximately 3 kcal/mol and is of the order of magnitude which might be expected for systems of this type.

Since the phenomenon appears to be quite general, we suggest that this method may well prove to be a reliable procedure for estimating glass transition temperatures in polymers either to supplement or to replace thermal measurements. Since one can quite easily vary the size of the penetrating solute molecule, the possibility exists that one may obtain a measure of the free volume available in the polymer at temperatures above T_g or from the value of T_g itself as it may vary with the size of the penetrating molecule. Further applications of the technique will be discussed in a later communication.

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Dielectric Properties of Polypropylene Oxide as a Function of Concentration

In a recent publication Baur and Stockmayer[1] discussed the dielectric properties of polypropylene oxide of molecular weight 2025. In particular they identified a very strong dispersion region associated with a dipole moment perpendicular to the chain contour and whose frequency ν_m at which maximum loss occurred was independent of molecular weight. At −35° ν_m for this dispersion was 2×10^5 cps.

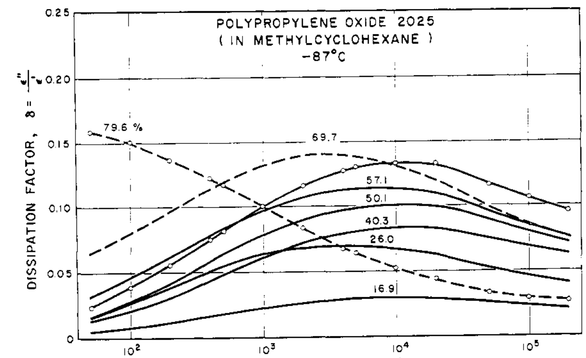

Figure1.

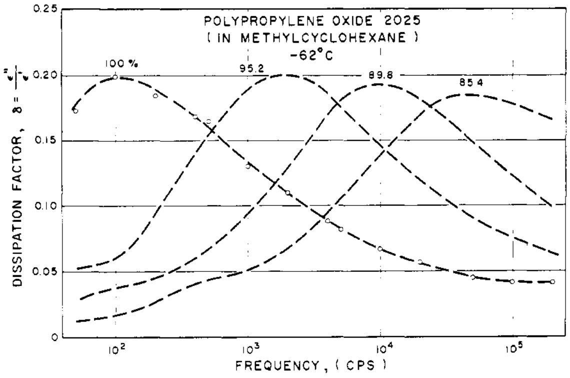

Figure 2.

We thought that it would be interesting to study ν_m as a function of polymer concentration in a nonpolar solvent, methylcyclohexane.

We found an interesting result: ν_m was dependent on polymer concentration between 65 and 100 wt % of polymer. At concentrations below 65 wt % of polymer, ν_m was nearly independent of polymer concentration.

We used a similar bridge as in ref 1. Measurements could be made between 50 and 2×10^5 cps. In order to broaden the frequency scale we made measurements at different temperatures and used the time–temperature superposition principle in the same manner as in ref 1. Measurements were made at −89, −78, −62, −33, and 25°.

Some of the results are presented in Tables I and II and in Figures 1–3. Figure 1 shows experimental data at −87°, Figure 2 shows experimental data at −62°, and Figure 3 shows temperature–frequency superposed data (from numerous temperatures) reduced to −33°. The figures show the dissipation factor $\delta = \epsilon''/\epsilon'$ plotted against log ν. The tables show ν_m, δ_m (measured at ν_m), the logarithmic half width of the dispersion region, and the viscosity η of the solutions, all data reduced to −33°.

If the damping were related to solution viscosity, the

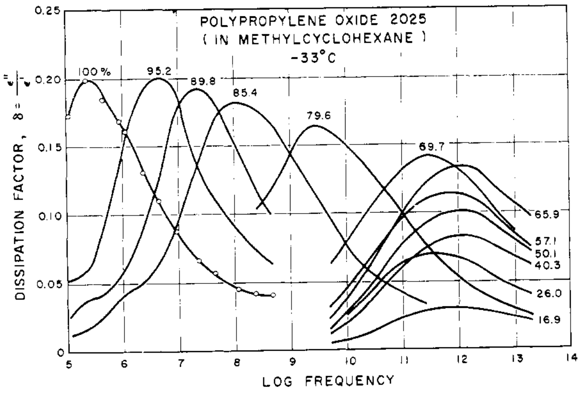

Figure 3.

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[1] M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, 43, 4319 (1965).

TABLE I
PPO-2025 (Reduced to −33°)

Polymer concn, wt %	ν_m (max loss)	Half-width	η, P	$\nu_m\eta$	δ_m
16.9	1.0×10^{12}	3.6	4.44×10^{-2}	4.4×10^{10}	0.03
26.0?	4.0×10^{11}	3.6	8.34×10^{-2}	3.3×10^{10}	0.07
40.3	1.0×10^{12}	3.6	2.40×10^{-1}	2.4×10^{11}	0.08
50.1	1.3×10^{12}	3.6	5.70×10^{-1}	7.4×10^{11}	0.10
57.1	8.0×10^{11}	3.6	1.02	8.2×10^{11}	0.11
65.9	1.3×10^{12}	3.6	2.61	3.4×10^{12}	0.13
69.7	3.2×10^{11}	3.6	4.53	1.4×10^{12}	0.14
79.6	3.0×10^{9}	3.2	9.33	2.8×10^{10}	0.16
85.4	1.3×10^{8}	2.8	2.27×10^{1}	2.9×10^{9}	0.18
89.8	2.0×10^{7}	2.2	3.97×10^{1}	7.9×10^{8}	0.19
95.2	4.0×10^{6}	2.2	1.98×10^{2}	7.9×10^{8}	0.20
100.0	2.0×10^{5}	1.8	6.56×10^{2}	1.3×10^{8}	0.20

TABLE II
PPO-2025

Polymer concn, wt %	T, °C	ν_m (exptl), cps
16.9	−87	1.0×10^{4}
26.0	−87	5.0×10^{3}
40.3	−87	1.4×10^{4}
50.1	−87	1.4×10^{4}
57.1	−87	1.0×10^{4}
65.9	−87	1.4×10^{4}
69.7	−87	2.8×10^{3}
79.6	−87	$\ll 5.0 \times 10^{1}$
85.4	−62	5.0×10^{4}
89.8	−62	1.0×10^{4}
95.2	−62	2.0×10^{3}
100.0	−62	1.0×10^{2}

product $\eta\nu_m$ should be independent of concentration. In fact this product seems to reach a cusplike maximum at 65 wt % concentration of polymer.

The fact that ν_m becomes independent of polymer concentration and solution viscosity below 65 wt % of polymer suggests that the damping in this concentration region is independent of intermolecular environment and may be intramolecular in origin.

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