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Effects of Aggregation and Solvent Quality on the Viscosity of Semidilute Poly(vinylbutyral) Solutions

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ABSTRACT: The relative viscosities at 25 °C of solutions containing 12% (w/v) poly(vinylbutyral) in pure methanol (MeOH), 1:1 methyl isobutyl ketone (MIBK)/MeOH by volume, and 9:1 MIBK/MeOH were in the ratio 1.0:0.9:4.3, respectively. The apparent activation energy for flow was 20 kcal/mol in the latter solution and only 8 kcal/mol in the former two. The dramatic influence of the solvent on the solution viscosity is attributed to the separate effects of solvent quality and polymer aggregation. Better solvents tend to reduce the viscosity while polymer aggregation tends to increase it. Aggregation is controlled not by solvent quality but by solvent polarity and manifests itself as a hysteresis in plots of viscosity vs. $1/T$. Aggregates disperse and re-form slowly—weeks may be required to reach equilibrium at room temperature. The thermodynamic quality of various solvents and solvent mixtures was determined by light scattering and intrinsic viscosity measurements. These data demonstrated that most mixtures of MIBK and MeOH are better solvents for PVB than either individual solvent.

Introduction

Most investigations of the viscosity of semidilute polymer solutions have focused on the dependences on molecular weight, concentration, and temperature; fewer have studied the effects of the solvent.[1-11] The increase in intrinsic viscosity of a given flexible polymer in better solvents may be attributed to excluded volume effects, but these are expected to be minimal at higher concentrations. It has been reported that in the semidilute concentration range the relative viscosity of a polymer solution increases more rapidly with concentration with poor solvents[3] and that at sufficiently high concentrations the relative viscosity has been observed to be greater with poor solvents than with good ones, by up to more than an order of magnitude.[5] This phenomenon has been observed with polar polymers such as poly(methyl methacrylate),[5] ethylcellulose,[6] and poly(vinyl chloride–acetate) copolymers[7] as well as with poly(styrene)[5,10] and poly(α-methylstyrene),[11] nonpolar polymers. In some cases, enhanced viscosity in poor solvents has been attributed to clustering or aggregation of polymer segments, which reduces the molecular mobility.[4,5] Other studies[8,9] have found that the relative viscosity remains higher in the better solvent until relatively high concentrations ($c \sim 25\%$), where excluded volume effects are minimal and η becomes independent of solvent quality. An increased η at a given concentration in the semidilute region for a poor solvent[9] was attributed to a larger concentration dependence of the friction coefficient for the poor solvent.

This study addresses two questions: (1) Is polymer aggregation in solutions directly related to solvent quality? (2) If not, does solvent quality exert an effect on the viscosity of semidilute solutions separate from the effect of aggregation? The copolymer poly(vinylbutyral) (PVB) was chosen for this investigation. PVB is known to aggregate in several solvents.[12] Light scattering and intrinsic viscosity measurements were used to assess solvent quality. Viscosities were measured at one concentration in three solvents and temperatures from 25 to 55 °C.

Equipment and Procedures

The solvents were MCB reagent-grade methyl isobutyl ketone (MIBK) and glacial acetic acid, EM Science glass-distilled methanol (MeOH), and MCB Omni Solv glass-distilled tetrahydrofuran (THF) with 250 ppm BHT as a stabilizer. Poly(vinylbutyral) was purchased from Monsanto. It has the structure shown in Figure 1. This copolymer consists of 79.5 wt. % acetal, 19% alcohol, and 1.5% acetate units.[13] The sample is polydisperse with $M_w/M_n \cong 2.9$ (by gel permeation chromatography) but uniform in functional group composition.[12] Prior to use, the polymer was dried in a vacuum oven at 50 °C for several days and stored in a desiccator.

A. Light Scattering. PVB was dissolved at room temperature with the aid of a small magnetic stirring bar; this usually required at least 4 h. The Rayleigh factor, R_θ, was measured with a Chromatix KMX-6 low-angle light scattering photometer. With this instrument, R_θ is measured directly—without reference to any standards. Solutions were filtered directly into the light scattering cell through two 0.2-μm Fluoropore filters (Millipore Co.). Measurements at room temperature were made while the solution flowed slowly through the scattering cell under the action of a syringe pump. In this way, dust, which appears as spikes in scattering intensity from the small ($\sim$5 μL) scattering volume, was easily detected and ignored and an accurate base line of scattering intensity determined. Measurements were made at higher temperatures with a cell that contains copper coils imbedded in the Teflon around the sample volume. Heated water flows through these coils, and the temperature is measured with a thermocouple. At higher temperatures, sample solutions were pumped through the cell until the scattering intensity appeared dust free. Flow was then stopped while the solution temperature reached that of the sample cell. For measurements in MIBK, in which the polymer is not soluble at room temperature, it was necessary to preheat the syringe and heat the filter housing to prevent precipitation.

The scattering equation for dilute polymer solutions is

$$Kc/R_\theta = \frac{1}{P(\theta)M_w}(1 + 2A_2M_wc + ...) \tag{1a}$$

where K is the optical constant, c is the polymer concentration in g/mL, M_w is the polymer weight-average molecular weight, $P^{-1}(\theta)$ is the particle scattering function, and A_2 is the second virial coefficient. Because of the angle employed in the Chromatix KMX-6 is typically only $\sim$4° and light scattering measurements with Brookhaven light scattering goniometer for $30° < \theta < 135°$ demonstrated that $P^{-1}(\theta)$ is unity at θ of 4° within the limits of experimental determination, eq 1a reduces to

$$\lim_{\theta\to0} Kc/R_\theta = 1/M_w + 2A_2c \tag{1b}$$

The optical constant, K, is given by (for vertically polarized light or at low angles)

$$K = 4\pi^2n^2(\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda_0^4 \tag{2}$$

when n is the refractive index of the solvent, N_A is Avogadro's number, $\mathrm{d}n/\mathrm{d}c$ is the specific refractive index increment, and λ_0 is the wavelength of the incident light in a vacuum (632.8 nm). Once K is evaluated for a given system, a plot of Kc/R_θ vs. c yields $1/M_w$ from its $c = 0$ intercept and A_2 from its initial slope.

Evaluation of the optical constant, K, requires values of n and $\mathrm{d}n/\mathrm{d}c$. For $n_{632.8\mathrm{nm}}$ literature values of $n_D \cong n_{632.8\mathrm{nm}}$ were used.[14] With solvent mixtures, we used volume-fraction-average values of $n_{632.8\mathrm{nm}}$. Measurements of $\mathrm{d}n/\mathrm{d}c$ were made with a Chromatix KMX-16 laser differential refractometer. This instrument operates at the same wavelength as the KMX-6. In MIBK $\mathrm{d}n/\mathrm{d}c$

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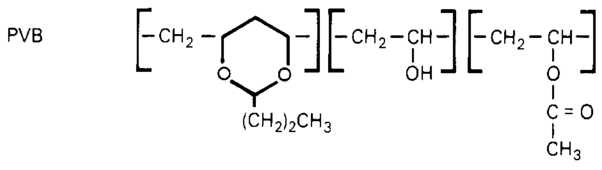

	Acetal	Alcohol	Acetate
mole%	55	43	2
wt%	79½	19	1½

Figure 1. Structure of poly(vinylbutyral) (PVB).

Table I
d*n*/d*c* vs. Solvent and Temperature

solvent	temp, °C	d*n*/d*c*
3:1 MIBK/MeOH	25	0.1145
(by volume)		(0.112)[a]
MeOH	25	0.1562
	50	(0.1676)[b]
MIBK	44	(0.1015)[b]
acetic acid	25	0.1173
	80	0.1302

[a] Estimated from eq 3. [b] Estimated from eq 3 and 4.

was not directly determined but estimated from the following approximation of the Gladstone–Dale relationship:

$$\nu \equiv dn/dc = (1/\rho_2)(n_2 - n_1) \quad (3)$$

where ρ_2 is the effective density of the polymer in solution and n_2 and n_1 are the polymer and solvent refractive indices, respectively. From data in 10 solvents, Cotts and Ouano[12] determined ρ_2 (25 °C) = 1.052 g/mL and n_2 (25 °C) = 1.495 for PVB containing ~20% by weight alcohol units. They also found that d*n*/d*c* was only very weakly affected by the alcohol content. The temperature dependence of ν is weak but not insignificant. It can be estimated from density data at different temperatures with (see derivation in the Appendix)

$$\frac{\delta\nu}{\delta T} \cong \left(\frac{n_1 - 1}{\rho_1}\right)\left[\frac{1}{\rho_1}\left(\frac{\delta\rho_2}{\delta T} - \frac{\delta\rho_1}{\delta T}\right) - \frac{(\rho_2 - \rho_1)}{\rho_1^2}\left(\frac{\delta\rho_1}{\delta T}\right)\right] \quad (4)$$

where ρ_1 is the density of the solvent. The value of $\delta\rho_2/\delta T$ was estimated to be 5×10^{-4} g/mL K based on the measured temperature dependence of ν in acetic acid. From $\delta\rho_2/\delta T$ and ρ_2 (25 °C), ρ_2 at other temperatures was estimated for use in eq 4. All measured and estimated values of d*n*/d*c* are listed in Table I.

B. Viscometry. 1. Intrinsic Viscosity. Kinematic viscosities ($\nu \equiv \eta/\rho$, where η is the viscosity) were measured in a Cannon–Ubbelohde capillary viscometer employing a Wescan automatic viscosity timer. Flow times were well over 100 s, and thus kinetic energy losses were considered negligible. At least four concentrations, covering the relative viscosity range ($\eta_r \equiv \nu/\nu_s$, where the subscript s denotes the solvent) from about 1.8 to 1.2 were used to construct Schulz–Blaschke plots. These plots of η_{sp}/c vs. η_{sp}, where $\eta_{sp} \equiv \nu/\nu_s - 1$, yield a slope of $k_{SB}[\eta]$ and an intercept of $[\eta]$ according to the Schulz–Blaschke equation[15]

$$\eta_{sp}/c = [\eta] + k_{SB}[\eta]\eta_{sp} + ... \quad (5)$$

This equation was used rather than the more traditional Huggins and Martin equations because of its stronger theoretical foundation. However, all three plots yielded nearly identical values of $[\eta]$.

PVB was dissolved at room temperature with the aid of a small magnetic stirring bar. Solutions were then filtered through 0.5-μm disposable PTFE filters (Millipore Company) into dust-free bottles. (Dust was eliminated from these bottles by placing them upside down in a container of refluxing 2-propanol.) The filtered solutions were then pipetted into the viscometer. Solvent loss during measurements was avoided by attaching a simple apparatus, consisting of tubing and stopcocks, which forces all air entering the viscometer to first bubble through a reservoir of solvent immersed in the same temperature bath as the viscometer. For determining solution concentrations, solvent densities were measured with a pycnometer. Solvent mixtures of MeOH and MIBK exhibited a slight (<0.5%) negative excess volume of mixing.

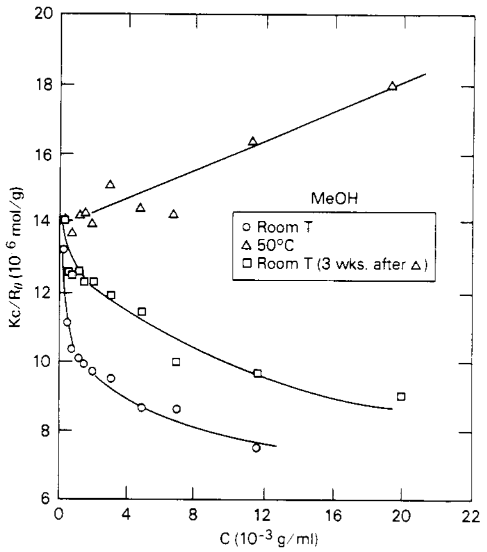

Figure 2. Light scattering plots for PVB in MeOH.

2. Viscosity of 12% PVB Solutions. Solutions were prepared with 0.1185 < *c* < 0.1188 g/mL at 25 °C. Dissolution was accomplished by first sonicating each sample for 20 min to remove air bubbles, heating at 55 °C for 4 h, and finally stirring it with a magnetic stir bar until homogeneous. Kinematic viscosities were measured in a size 400 Cannon–Zhukov viscometer. After adding a solution to the viscometer it was degassed twice, using the freeze–evacuate–thaw procedure, and the viscometer was sealed with a torch. Sealing the viscometer eliminated the possibility of solvent loss during measurements. To avoid the possibility of solvent reflux within the viscometer, it was completely submerged in a temperature bath. The upper bulb was filled by tilting the viscometer while still submerged. Flow times were converted to kinematic viscosities with the calibration constant determined by the manufacturer. The viscosity was then calculated by multiplying the kinematic viscosity by the solution density. Densities at room temperature were determined with a pycnometer. At higher temperatures, densities were estimated based on a thermal expansion coefficient for PVB of 5×10^{-4} g/mL K (estimated as previously described), and the expansion coefficient, which applies to both MeOH and MIBK, was estimated at 10×10^{-4} g/mL K.[16]

The shear stress at the wall, τ_w, in this viscometer is ~50 dyn/cm^2 for the solution densities covered in this study. Consequently, the apparent shear rate at the wall, $\dot{\gamma}_w \equiv \tau_w/\eta$, ranged from 2.5 to 40 s^{-1}. It is possible that non-Newtonian effects were present even at these low shear rates. However, such effects would only alter the data quantitatively—not qualitatively—and the qualitative features of the data are the focus of this investigation.

Results

A. Light Scattering. Light scattering data were taken with the aim of ranking by quality the various solvents for PVB with the measured second virial coefficients, A_2. Scattering plots from PVB in MeOH are shown in Figure 2. According to eq 1b, the $c = 0$ intercept of these plots should yield $1/M_w$, while the slope in this limit is $2A_2$. With the measurements obtained at ~24 °C (○ and □), neither of these quantities could be accurately determined due to the strong curvature as $c \rightarrow 0$. Such curvature is symptomatic of polymer aggregation in a poor solvent.[17] Aggregation enhances the scattering (R_θ), thus reducing Kc/R_θ. PVB is known to aggregate in both poor solvents, such as MeOH and EtOH, as well as in THF, a fairly good solvent.[12] The measurements at 50 °C shown in Figure 2 (△) form a linear plot and allow a more accurate determination of the intercept, $1/M_w$. Apparently, heating these samples to 50 °C removed some of this aggregation

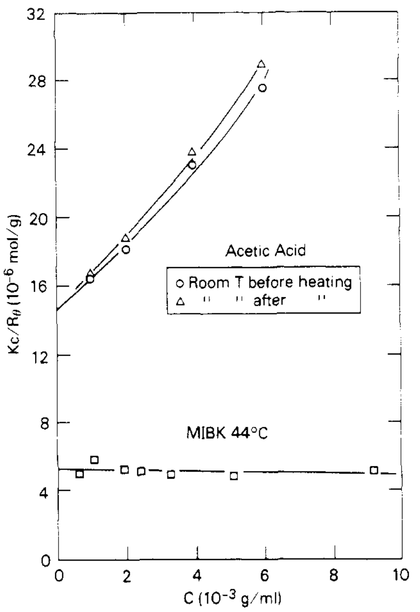

Figure 3. Light scattering plots for PVB in acetic acid and MIBK. Heating of the acetic acid solutions was for 2 h at 80 °C.

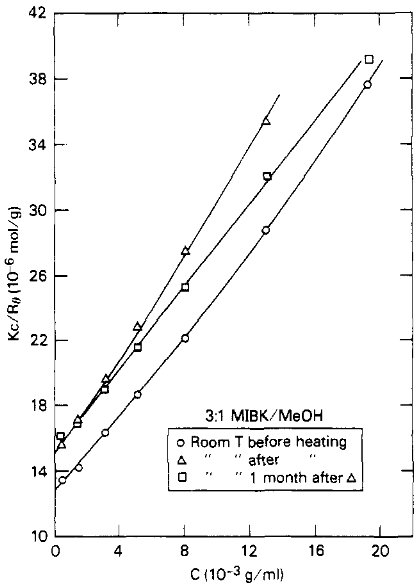

Figure 4. Light scattering plots for PVB in 3:1 MIBK/MeOH. Heating was for 4 h at 55 °C.

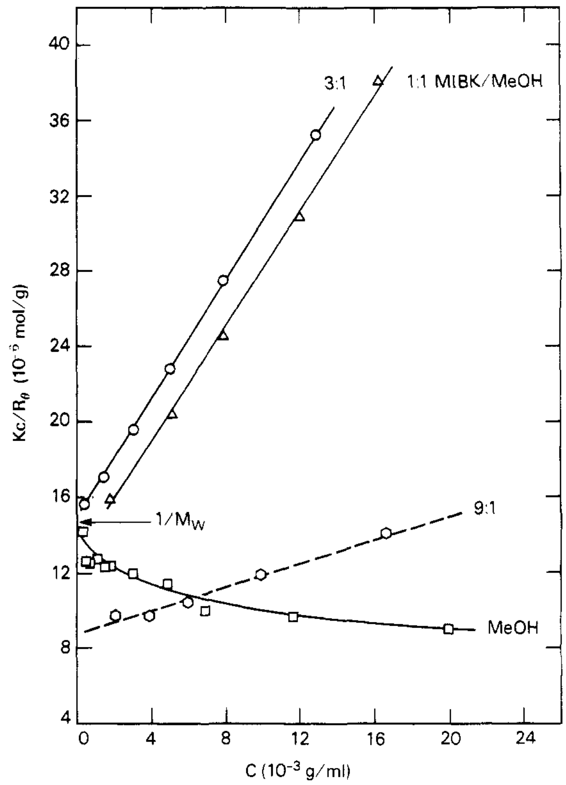

Figure 5. Light scattering plots for PVB in MIBK/MeOH mixtures at room temperature. All data were taken on solutions that had been heated for at least 2 h at no less than 50 °C. For the 1:1 and 9:1 MIBK/MeOH solvents, only the most concentrated solution was heated. Immediately after cooling, the most concentrated solution was used to prepare the solutions of lower concentration by dilution.

permanently. The scattering plot obtained at ~24 °C a full 3 weeks after heating (□) lies well above that initially obtained at this temperature (○). If these solutions are considered largely nonaggregated during the later readings at ~24 °C, then the negative slope of this plot (negative A_2) is evidence that MeOH is a very poor solvent for PVB at this temperature. Negative values of A_2 indicate very poor solvents, a slope of zero occurs in Θ solvents, while in good solvents A_2 is strongly positive.

The best solvent we have found for PVB is acetic acid. Scattering data, shown in Figure 3, obtained before (○) and after heating for 2 h at 80 °C (△) yield nearly identical plots. Thus, there appears to be only a slight amount of aggregation in this solvent prior to heating. The intercept is very close to that determined in MeOH at 50 °C and therefore most likely represents the true value of $1/M_w$ for our PVB sample.

Scattering measurements at 44 °C in MIBK are also shown in Figure 3 (□). The slope of this plot is nearly zero. The intercept is well below that obtained in MeOH and acetic acid. The value of M_w calculated from this intercept is almost 3 times larger than the true value, indicating that the solutions are strongly aggregated even at this elevated temperature. Linear scattering plots that yield excessively high M_w values have been previously observed for PVB in several solvents and also have been attributed to aggregation.[12]

Aggregation of PVB was also observed in a solvent mixture of 3:1 MIBK/MeOH by volume (see Figure 4 (○)). Heating, cooling, and remeasuring the scattering yielded a curve (△) that is shifted upward and has a 27% greater slope. After allowing these solutions to stand 1 month, additional scattering data (□) was taken that indicates that the most dilute solutions did not reaggregate. More concentrated solutions reaggregated to an extent that increased with concentration. Nonetheless, the strong positive slope of the plots in Figure 4 is evidence that the solvent mixture is an excellent one for PVB even though each solvent individually is a poor solvent. Such systems are not uncommon[18] and are termed "cosolvents".

Scattering plots obtained after heating from PVB in various solvent mixtures of MIBK and MeOH are shown in Figure 5. The intercepts of these plots may differ from $1/M_w$ due to polymer aggregation or selective adsorption of one of the two solvents by the polymer. Aggregation can only lower the intercept below $1/M_w$. Selective adsorption alters the intercept according to[19]

$$M^*/M = [1 + \alpha_a(\mathrm{d}n_0/\mathrm{d}\phi_1)/(\mathrm{d}n/\mathrm{d}c)_{\phi_1}]^2 \qquad (6)$$

where M is the true molecular weight and M^* is the apparent value (computed from the intercept of the scattering plot). If MeOH is taken to be solvent 1, then α_a is the selective adsorption coefficient for MeOH and $\mathrm{d}n_0/\mathrm{d}\phi_1$ is the change in refractive index of the solvent mixture with

Table II
A_2 vs. Solvent at Room Temperature after Heating[a]

solvent	$A_2 \times 10^{-4}$, mL·mol/g^2
acetic acid	10.4
3:1 MIBK/MeOH	7.9
1:1 MIBK/MeOH	7.8
9:1 MIBK/MeOH	1.6
MeOH	*b*
MIBK	insoluble

[a] All data were taken on solutions that had been heated for at least 2 h at no less than 50 °C. For the 1:1 and 9:1 MIBK/MeOH solvents, only the most concentrated solution was heated. Immediately after cooling, the most concentrated solution was used to prepare the solutions of lower concentration by dilution. [b] This scattering plot was too nonlinear for accurate determination of A_2. However, A_2 was negative.

the volume fraction of MeOH; $(\mathrm{d}n/\mathrm{d}c)_{\phi_1}$ is the specific refractive index increment at constant solvent composition—what we have previously denoted simply $\mathrm{d}n/\mathrm{d}c$. Since in mixtures of MIBK and MeOH $\mathrm{d}n_0/\mathrm{d}\phi_1$ is negative, selective adsorption of MeOH by the polymer (positive α_a) lowers the apparent molecular weight (raises the intercept). Thus, both aggregation and selective adsorption of MIBK can lower the intercept of a scattering plot below $1/M_w$. If the plot for the 1:1 mixture is assumed to be unaffected by aggregation, then the intercept of this plot indicates a slight selective adsorption of MIBK by the PVB ($\alpha_a = -0.07$). The selective adsorption coefficient can be used to determine the probability that a given repeat unit has a solvent molecule "adsorbed" to it.[20]

$$x_1 = \alpha_i M_0/\bar{V}_i \qquad (7)$$

where M_0 is the molecular weight per repeat unit (60 for PVB of the composition shown in Figure 1) and $\bar{V}_i$ is the partial molar volume of solvent i (i = a for MeOH, i = b for MIBK). In the 1:1 solvent, $\alpha_b = -\alpha_a = 0.07$; therefore $x_b = 0.03$, or there are 3 adsorbed MIBK molecules for every 100 PVB repeat units. The intercept above $1/M_w$ obtained in the 3:1 MIBK/MeOH mixture can only by attributed to selective adsorption of MeOH ($\alpha_a = 0.03$, $x_a = 0.04$). The true value of α_a in this solvent is greater than this computed value if any aggregates were present in these solutions. Since MeOH is selectively adsorbed in the 3:1 MIBK/MeOH solvent, it is safe to assume it is even more strongly adsorbed in the 9:1 solvent mixture. Therefore, the low intercept obtained in the 9:1 MIBK/MeOH solvent mixture cannot be attributed to selective adsorption. Selective adsorption of MeOH raises the intercept. Instead, the low intercept must be attributed to aggregation in this solvent.

The second virial coefficients measured in various solvents at room temperature after heating are given in Table II. In the absence of aggregation and selective adsorption, a ranking by quality of solvents for PVB would follow the order of A_2 values. As A_2 increases, the solvent becomes better. However, since these effects were not completely absent in the data used to construct Table II (particularly in the 9:1 solvent mixture), the solvent ranking given in this table must be considered tentative.

B. Intrinsic Viscosity. Due to the complicating effects of aggregation and selective adsorption on the A_2 values determined by light scattering, another means was sought to characterize the quality of solvents for PVB. The alternate means chosen was intrinsic viscosity measurements. Theory relates the intrinsic viscosity to the polymer chain dimensions through the expression[21]

$$[\eta] = \Phi(\langle r^2\rangle_0/M)^{3/2} M^{1/2} \alpha^3 \qquad (8)$$

where Φ is a universal constant—the same for all polymer molecules, M is the polymer molecular weight, $\langle r^2\rangle_0$ is the mean square end-to-end distance in the unperturbed or Θ state, and α is the expansion factor for the chains defined as $\alpha \equiv \langle r^2\rangle^{1/2}/\langle r^2\rangle_0^{1/2}$. For a given polymer, the larger values of α indicate a better solvent. If $\langle r^2\rangle_0$ is assumed unaffected by the solvent, then $[\eta]$ varies only with α (Φ and M being constant), and therefore $[\eta]$ is a relative measure of solvent quality. From Schulz–Blaschke plots such as that shown in Figure 6, $[\eta]$ and the Schulz–Blaschke constant, k_{SB}, were determined.

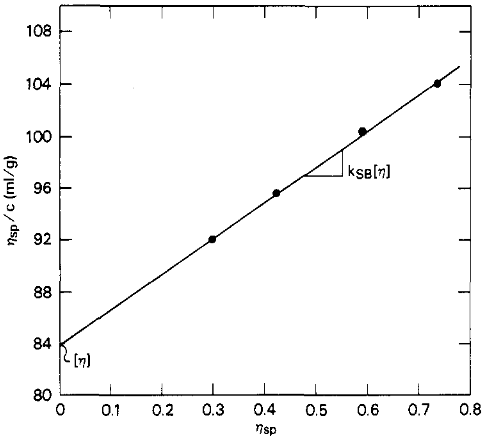

Figure 6. Schulz–Blaschke plot for PVB in 1:1 MIBK/MeOH at 25 °C.

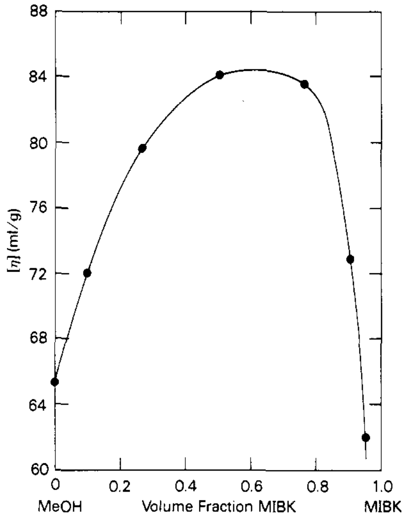

Figure 7. Intrinsic viscosity of PVB in MIBK/MeOH mixtures at 25 °C.

A previous investigation[12] found that the presence of aggregates had no measurable effect on $[\eta]$ for PVB in THF. The same value of $[\eta]$ was obtained regardless of whether or not solutions were heated prior to measurement. The same heat treatment reduced the apparent molecular weight (from light scattering measurements) by ~30% and increased A_2 up to 50%.[22] We made measurements on heated and unheated solutions of PVB in pure MeOH and 9:1 MIBK/MeOH and also found no effect on $[\eta]$. The lack of any effect of heat treatment on $[\eta]$ again supports the conclusion that aggregates have a minimal influence on the intrinsic viscosity. This conclusion has also been reached by other investigators studying different systems in which polymer aggregation occurs.[23,24]

The intrinsic viscosity of PVB is shown as a function of solvent composition for various MIBK/MeOH mixtures in Figure 7. Since $[\eta]$ increases with α (see eq 8), the solvent is better at higher $[\eta]$. Apparently, most mixtures

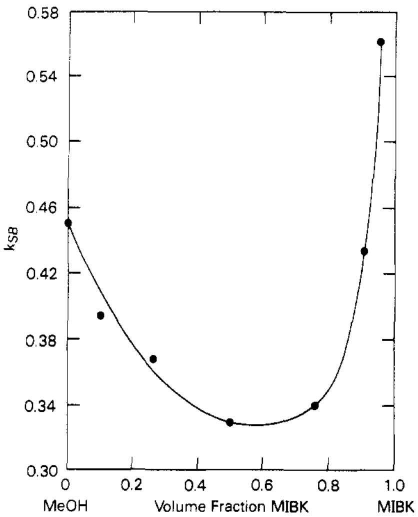

Figure 8. Schulz–Blaschke constant for PVB in MIBK/MeOH mixtures at 25 °C.

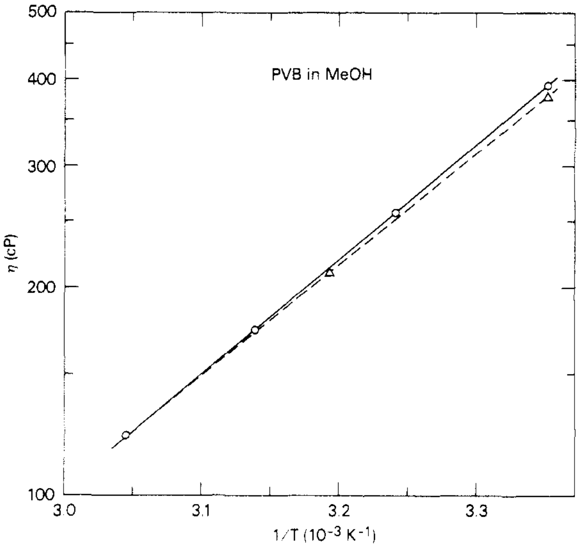

Figure 9. log η vs. $1/T$ for 0.1187 g/mL (at 25 °C) PVB in MeOH on the heating (○, —) and cooling (△, ---) cycles.

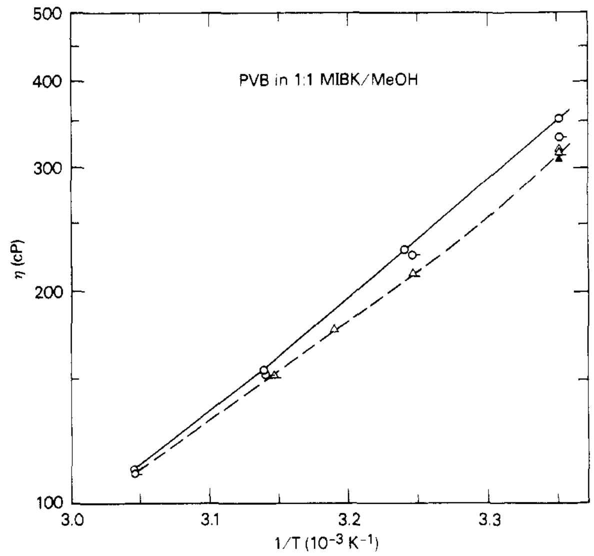

Figure 10. log η vs. $1/T$ for 0.1185 g/mL (at 25 °C) PVB in 1:1 MIBK/MeOH. The first heating cycle (○, —) and first cooling cycle (△) were separated by 15 h. After 72 h elapsed, the second heating cycle (○, pip) and second cooling cycle (△, pip, ---) were conducted, between which 15 h elapsed. Immediately after temperature equilibration at the end of the second cooling cycle, the datum ▲ was taken.

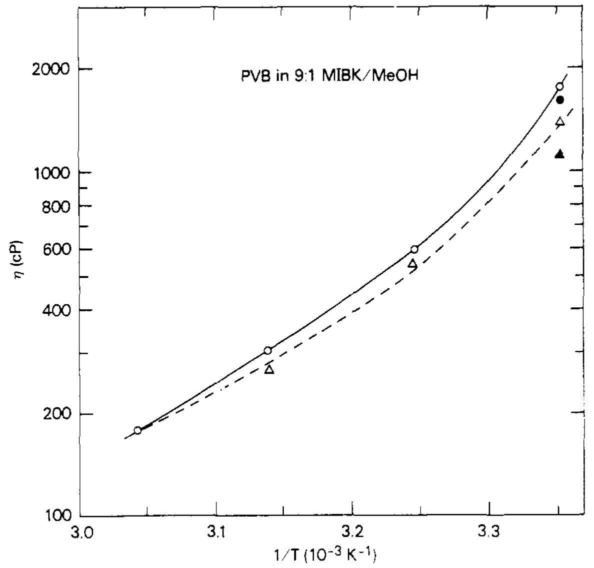

Figure 11. log η vs. $1/T$ for 0.1188 g/mL (at 25 °C) PVB in 9:1 MIBK/MeOH on the heating (○, —) and cooling (△, ---) cycles. The datum ▲ was taken immediately after temperature equilibration at the end of the cooling cycle. The datum ● was taken 12 days later.

of MIBK and MeOH are better solvents for PVB than either pure solvent. Values of k_{SB} are also related to solvent quality, becoming smaller in better solvents.[15] A plot of k_{SB} vs. solvent composition is shown in Figure 8. As expected, it is similar to Figure 7, but inverted. From the data of Figure 7, PVB should have a weak selective adsorption of MIBK in a 1:1 solvent mixture and weak adsorption of MeOH in a 3:1 MIBK/MeOH solvent mix. These predictions are in accord with light scattering data discussed previously. The intrinsic viscosity data is also consistent with the second virial coefficient data in Table II in indicating that the 1:1 and 3:1 MIBK/MeOH mixtures are nearly equally good solvents for PVB, the 9:1 mix is a worse solvent, but it is still better than pure MeOH.

Problems with solution filtration sometimes arose. In solvent mixtures containing more than 50% MIBK, no more than a few milliliters of the polymer solution could be forced through a 0.5-μm filter before it clogged. This, despite the fact that there were no visible undissolved particles. The problem was remedied by heating each solution at 50 °C for 12 h prior to filtering. In the 95% MIBK solution, even this was not sufficient. This solution was heated to 70 °C and filtered while still warm. Even so, it became difficult to filter after ~10 mL had been dispensed. These filtering difficulties were probably due to aggregates that were dispersed upon heating.

C. Viscosity of 12% PVB Solutions. The viscosity of 12% PVB solutions was measured at temperatures from 25 to 55 °C with as solvents pure methanol, 1:1 MIBK/MeOH by volume, and 9:1 MIBK/MeOH. The results are shown in Figures 9–11. There is some hysteresis in these plots; higher viscosities are obtained on the cycle of increasing temperature than on the decreasing temperature cycle. The extent of this hysteresis increases with the MIBK content of the solvent. In all plots, data indicated by open points were obtained once η had stabilized to the extent that it was changing less than ~$^1/_2$% per hour. No detectable change in η with time was observed in pure MeOH. In the 1:1 MIBK/MeOH solvent, changes were barely detectable except at 25 °C on the cooling cycle where the increase in η with time was pronounced. In the solvent containing 9:1 MIBK/MeOH viscosity changes of

Table III
Viscosity of 12% PVB Solutions (Summary of Figures 9-11)

solvent	solvent quality ranking	η at 25 °C, cP most aggregated[b]	 least aggregated[c]	% diff	A_A,[a] kcal/mol most aggregated[b]	 least aggregated[d]
MeOH	3	391.3	378.2	3.5	7.6	7.2
1:1 MIBK/MeOH	1	352.8	308.1	14.5	7.6	6.6
9:1 MIBK/MeOH	2	1674.3	1114.1	50.3	19.5	8.6

[a] E_A = 2.19 kcal/mol in pure MIBK and 2.57 kcal/mol in pure MeOH. [b] Start of heating cycle. [c] End of cooling cycle, immediately after temperature equilibration. [d] Start of cooling cycle.

at least several percent were observed at each temperature and on both cycles before the viscosity stabilized. However, the viscosity was not affected by the measurement process. Repeated flow time measurements caused no detectable change in solution viscosity.

We attribute the hysteresis in Figures 9–11 to the presence of supramolecular structures or aggregates. The extent of aggregation is reduced upon heating but increases slowly when cooled. Notice in Figure 11 that even 12 days after completing the cooling cycle the viscosity had not risen to its initial value. Eventually, however, it might have. Thus, with enough patience, the heating and cooling cycles might coincide.

The extent of aggregation is apparently affected far more by solvent polarity than solvent quality. A measure of aggregation is given in Table III. Here is shown the percentage difference between the "most aggregated" (initial) 25 °C viscosity and the "least aggregated" 25 °C viscosity (measured at the end of the cooling cycle immediately after temperature equilibration). This measure of the extent of aggregation increases with the MIBK content of the solvent. On the basis of the intrinsic viscosity data shown in Figure 7, pure MeOH is a poorer solvent than either solvent mixture, yet PVB aggregates the least in it. A 1:1 ratio of MIBK and MeOH is nearly the optimum solvent ratio for PVB, still aggregation occurs. It is in the solvent of intermediate quality, the 9:1 mixture, where aggregation is most severe. Aggregation increases with solvent nonpolarity, seemingly independent of solvent quality. This finding is consistent with our previous observation that filtration difficulties were more severe in solvents containing a greater percentage of the relatively nonpolar MIBK. We conclude that the polar alcohol groups in the PVB molecules (see Figure 1) are instrumental in aggregate formation. The better a solvent is for these highly polar alcohol units, the less tendency there is for the molecules to associate. Since these units, however, represent a relatively minor portion of the chains (weight fraction 19%), the best solvents for these polar units may be poor solvents for the chain overall. Aggregation phenomena that are not related to thermodynamic solvent quality have previously been reported.[23,25] We believe that the combined measurements of dilute solution properties and concentrated solution viscosities for PVB in these solvents provide exceptionally strong evidence of this behavior.

The solvent composition effects not only the hysteresis or history dependence of the viscosity but also its magnitude and temperature dependence. The viscosity was ~10% higher using pure MeOH as the solvent than when a 1:1 MIBK/MeOH mixture was used. However, the 9:1 solvent mixture produces the highest solution viscosity by more than a factor of 4. (A solution using a 19:1 MIBK/MeOH solvent mixture was so viscous it would barely flow in the flask in which it was prepared.) The apparent activation energy for flow

$$E_A \equiv \partial \ln \eta / \partial (1/RT) \qquad (9)$$

was also much higher using 9:1 MIBK/MeOH solvent mixture, especially at the start of the heating cycle (most aggregated conditions). These effects cannot be attributed to differences in solvent viscosity as this property varies by only 1.3% amongst these mixtures, being lowest in the 1:1 mix. The activation energy for solvent flow was not measured but should be similar for all three solvents as the values of E_A for pure MeOH (2.57 kcal/mol) and pure MIBK (2.19 kcal/mol) are very close.[26]

A surprising feature of the results in Table III is that the best solvent (1:1 MIBK/MeOH) yields a lower solution viscosity than the worst solvent (MeOH) despite greater aggregation in the better solvent. The viscosity of a semidilute polymer solution may be expressed as the product of a structure factor F and friction factor ζ

$$\eta = F\zeta \qquad (10)$$

The structure factor includes the effects of chain size and overlap. The friction factor accounts for all other contributions of η, the most important being the segmental mobility. At a given polymer concentration, F depends primarily on molecular weight, while ζ depends on temperature.[2] Variation in η with solvent can arise through differences in ζ or through changes in excluded volume interactions that increase the chain dimensions and hydrodynamic screening length, thus affecting F. The influence of the solvent on F depends on the degree of chain overlap. The concentration c^* where overlap begins is $c^* \cong 0.77/[\eta]$.[27] Thus, our solutions are all at $c \geq 10c^*$, and the polymer coils strongly overlap. At such high concentration of polymer, the chain dimensions and therefore F should be nearly the same in all solvents.[27] In any case, any residual influence of solvent quality would lower the ratio $F_{\mathrm{MeOH}}/F_{1:1}$ below 1 and therefore could not account for the observation $\eta_{\mathrm{MeOH}}/\eta_{1:1} > 1$. Instead, the higher viscosity obtained with MeOH must be attributed to a larger value of ζ.

A higher relative viscosity (η/η_s) in poor solvents than in good ones has been reported with both polar polymers such as poly(methyl methacrylate),[5] ethylcellulose,[6] poly(vinyl chloride–acetate) copolymers,[7] as well as with the nonpolar polystyrene[5,10] and poly(α-methylstyrene).[11] In contrast, the steady-state compliance of poly(α-methylstyrene) solutions is independent of solvent quality.[11,28,29] The above two observations led Isono and Nagasawa[11,30] to propose that solvent quality influences the solution viscosity through its effect on the strength of polymer entanglements rather than their number. Entanglements are stronger in poorer solvents. This explanation is consistent with our observation that the activation energy for flow (under least aggregated conditions) is higher in the poorer solvent MeOH (7.2 kcal/mol) than in the better 1:1 mixture (6.6 kcal/mol). The stronger the entanglements, the higher the activation energy for flow. It should be noted that this entanglement effect must be separate from the aggregation phenomenon in PVB solutions since it follows solvent quality not solvent polarity. The viscosity is lower with the better 1:1 MIBK/MeOH solvent than in

MeOH despite increased aggregation.

With the least polar solvent, 9:1 MIBK/MeOH, aggregation dominates the viscosity behavior. This solvent is of intermediate quality, between pure MeOH and the 1:1 mixture. Still, the viscosity is greatest using the 9:1 mix at all temperatures, by up to a factor of 4. The effect of temperature on the aggregation in the 9:1 MIBK/MeOH solution is so large that the ln η vs. $1/T$ curve becomes significantly nonlinear. An apparent E_A determined when the solution is most highly aggregated is more than twice those measured in other solvents, and even at the highest temperature (55 °C), the apparent E_A is still much larger than in the 1:1 mixture or in MeOH. Aggregation affects both the friction factor ζ and the structure factor F. It alters ζ through its effect on the segmental mobility and F through its effect on the apparent molecular weight. Association of portions of the chains through hydrogen bonding results in a weak, reversible cross-linking, which raises the apparent molecular weight.

Summary and Conclusions

The viscosity and its temperature dependence of semidilute (12% (wt/v)) PVB solutions were strongly affected by the solvent. The viscosity in the poorer solvent MeOH was higher than in the good solvent 1:1 MeOH/MIBK despite greater aggregation in the latter solvent. This is due to a larger friction coefficient in MeOH, which it has been suggested may be due to tighter entanglements in this poorer solvent. This explanation is consistent with the observed higher activation energy for flow using this solvent. The solution viscosity using the 9:1 solvent mixture was dramatically higher, as was its temperature dependence due to severe aggregation. η vs. $1/T$ curves were highly nonlinear in the 9:1 solvent, in contrast with MeOH and the 1:1 mixture, as the degree of aggregation decreased with increasing temperature. The intrinsic viscosity measured in these solvents was insensitive to the state of aggregation. It is concluded that aggregation is via association of the hydroxyl groups of PVB since aggregation did not decrease with solvent quality but rather with solvent polarity. Aggregates dispersed and reformed slowly—weeks may be required to reach equilibrium at room temperature.

Appendix

Temperature Dependence of the Specific Refractive Index Increment. We start with the usual Gladstone–Dale formula for the refractive index of a mixture[31]

$$(n-1)/\rho = \sum_i w_i k_i \qquad (1A)$$

where n and ρ are the refractive index and density of the mixture, w_i is the weight fraction of component i, and k_i is its specific refractive energy. The specific refractive index increment is

$$\nu \equiv \frac{\delta n}{\delta c} = \frac{\delta n}{\delta(w_2\rho)} = \frac{\delta n}{\delta w_2}\,\frac{\delta w_2}{\delta(w_2\rho)} \qquad (2A)$$

where subscript 2 denotes the polymer and 1 will denote the solvent, but since

$$\frac{\delta(w_2\rho)}{\delta w_2} = \rho + w_2\frac{\delta\rho}{\delta w_2} \qquad (3A)$$

where $w_2 \ll 1$ and $\delta\rho/\delta w_2 < 1$, while $\rho \sim 1$, we can write

$$\frac{\delta(w_2\rho)}{\delta w_2} \cong \rho \qquad (4A)$$

and thus eq 2A becomes

$$\nu \cong \frac{1}{\rho}\,\frac{\delta n}{\delta w_2} \qquad (5A)$$

Substituting eq 1A into eq 5A for n and writing the result for a two-component mixture of polymer (2) and solvent (1), we obtain

$$\nu \cong \frac{1}{\rho}\Big(\sum_i w_i k_i\Big)\frac{\delta\rho}{\delta w_2} + \frac{\delta}{\delta w_2}(w_1k_1 + w_2k_2) \qquad (6A)$$

or

$$\nu \cong \frac{1}{\rho}\Big(\sum_i w_i k_i\Big)\frac{\delta\rho}{\delta w_2} + (k_2 - k_1) \qquad (7A)$$

The temperature derivative of this expression is

$$\frac{\delta\nu}{\delta T} \cong \Big(\sum_i w_i k_i\Big)\left[\frac{1}{\rho}\left(\frac{\delta}{\delta T}\left(\frac{\delta\rho}{\delta w_2}\right)\right) + \left(\frac{\delta\rho}{\delta w_2}\right)\left(-\frac{1}{\rho^2}\right)\times\left(\frac{\delta\rho}{\delta T}\right)\right] \qquad (8A)$$

Equation 8A follows without approximation from eq 1A and 5A. It can be recast into the more usable form, shown as eq 4, by assuming (1) ρ is linear in w_2 and thus $\delta\rho/\delta w_2 \cong \rho_2 - \rho_1$ and (2) $n \cong n_1$, $\rho \cong \rho_1$, and $\delta\rho/\delta T \cong \delta\rho_1/\delta T$ since the solutions are very dilute. Equation 8A then becomes

$$\frac{\delta\nu}{\delta T} \cong \left(\frac{n_1 - 1}{\rho_1}\right)\left[\frac{1}{\rho_1}\left(\frac{\delta\rho_2}{\delta T} - \frac{\delta\rho_1}{\delta T}\right) - \frac{(\rho_2 - \rho_1)}{\rho_1{}^2}\left(\frac{\delta\rho_1}{\delta T}\right)\right] \qquad (9A)$$

where eq 1A has also been used to substitute for $\sum w_i k_i$.

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Hydrogen Bonding in Polymers. 2. Infrared Temperature Studies of Nylon 11

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ABSTRACT: Fourier transform infrared temperature studies of a semicrystalline polyamide, nylon 11, are presented. From previous studies of an amorphous nylon, we demonstrated that the absorptivity coefficient of the hydrogen bonded N–H stretching mode was a very strong function of the strength of the hydrogen bond. Accordingly, area changes in the N–H stretching envelope as a function of temperature were not solely the result of hydrogen bonded N–H groups transforming the "free" groups. This result is also applicable to semicrystalline nylons. As a result, significant errors exist in the previously reported thermodynamic parameters obtained from infrared studies. Emphasis has been placed in this study on the N–H stretching and amide I modes of nylon 11. The two regions yield different information. The hydrogen bonded N–H stretching frequency does not exhibit separable features attributable to ordered and disordered hydrogen bonded conformations but rather reflects the overall distribution of hydrogen bonded strengths. In contrast, the amide I mode is conformationally sensitive through dipole–dipole interactions, and separate bands can be identified that are assigned to ordered and disordered hydrogen bonded conformations. Finally, in both regions of the spectrum, bands attributable to "free" (non-hydrogen bonded) amide groups are discernable.

Introduction

In a recent paper[1] we reported the results of an infrared temperature study of an amorphous polyamide. There were several significant conclusions arising from this work. Changes occurring in the N–H stretching region of the spectrum with temperature had been misinterpreted in the past. The strong dependence of the absorption coefficient with the strength of the intermolecular hydrogen bond had not been fully appreciated. This led to an overestimation of the fraction of hydrogen bonded amide groups that transform to "free" groups upon increasing the temperature. Furthermore, subsequent estimations of thermodynamic parameters associated with hydrogn bond dissociation in polyamides and analogous materials were subject to unacceptable error. Our interpretation of the N–H stretching region of the spectrum of the amorphous nylon was supported by results obtained in the amide I, II, and V regions.

The above studies were performed deliberately on an amorphous polyamide to reduce the complexity due to crystallinity. However, most nylons are semicrystalline in the condensed phase at ambient temperatures. Furthermore, we considered it essential to establish whether the effects observed in the amorphous nylon also occur in the semicrystalline materials. Nylon 11 was chosen for this study because of its relatively low melting point, which reduces the problems of degradation at elevated temperatures.

Schroeder and Cooper[2] have previously employed infrared spectroscopy to study nylon 11 and a series of semicrystalline nylons. The main thrust of their paper concerned the use of infrared spectroscopy to obtain thermodynamic parameters associated with hydrogen bond dissociation. More recently, Garcia and Starkweather[3] used a comparable approach for nylon 6,6. In both cases estimations of the enthalpy of dissociation of hydrogen bonds appear high (8–12 and about 14 kcal mol^{-1} N–H, respectively). The question arises "are these values high because of a misinterpretation of the infrared spectral changes occurring with temperature?". Our primary concern in this paper is to reexamine the infrared spectrum of semicrystalline nylons.

Experimental Section

Poly(aminoundecanoic acid), or more commonly, nylon 11, was kindly supplied by the E.I. Du Pont de Nemours Co. The polymer exhibits a glass transition temperature of approximately 45 °C and a crystalline melting point of 196 °C, as determined by differential scanning calorimetry.

Samples for infrared analysis were prepared by casting films from a 1% (w/v) solution of the polymer in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) onto potassium bromide windows at room temperature. Following evaporation of the majority of the solvent, the samples were placed in a vacuum oven at 100 °C for 12 h to remove residual solvent and moisture and then immediately transferred to the temperature cell contained in the spectrometer.

Spectra were acquired on a Digilab Model FTS-15E Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal-averaged, and the spectra were stored on a magnetic disc system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. The film used in this study was sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.[4] Spectra recorded at elevated temperatures were obtained with a Micristar heat controller. This device has a reported accuracy of ± 0.1 °C.

Thermal analysis was performed on a nylon 11 sample prepared under identical conditions with that used for the infrared studies. A Perkin-Elmer differential scanning calorimeter (DSC-2) coupled with a Perkin-Elmer computerized data station was employed.

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