Table I
Model Parameters and Temperature Coefficients of Unperturbed Chain Dimensions for Various Polymers

polymer	κ_0	$\lvert\tau_0\rvert$	λ^{-1}, Å	T, K	$10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$, $\deg^{-1}$	
					calcd	obsd
PM	0.3[a]	0[a]	14.5[a]	413	−2.3	−1.2 to −1.0 (383–463 K)[f]
PDMS	2.6[b]	0[b]	20.7[b]	298	0.86	0.71–0.78 (313–373 K)[g]
POM	17[a]	25[a]	15.6[a]	303	−3.3	−2.6 to −0.46 (473 K)[h]
i-PP	3.5[c]	4.5[c]	14.2[c]	413	−2.2	−1.5 (~416 K)[i]
s-PP	7.5[c]	30[c]	26.2[c]	413	−2.4	−0.7 (~318 K)[j]
i-PS	11[a]	15[a]	26.4[a]	300	−3.3	
a-PS						−0.1 (293–427 K)[k]
s-PS	0.8[a]	2.3[a]	40.4[a]	300	−3.2	
i-PMMA	1.7[a]	1.4[a]	32.7[a]	300	−1.9	−2.3 (303–425 K)[l]
a-PMMA	2.75[d]	0.6[d]	44.6[d]	300	0.55	~0 (303–343 K)[m]
s-PMMA	4.4[a]	0.8[a]	65.6[a]	300	1.3	1.4 (307–378 K)[l]
PDLA	6.5[e]	0[e]	28.3[e]	300	2.8	

[a] See ref 5. [b] See ref 6. [c] See ref 1. [d] See ref 2. [e] See ref 7. [f] See ref 8–10; see also ref 3, p 45. [g] See ref 11; see also also ref 3, p 46. [h] RIS values; see ref 12. [i] See ref 13. [j] See ref 14. [k] See ref 15. [l] See ref 16 and 17. [m] See ref 17–19.

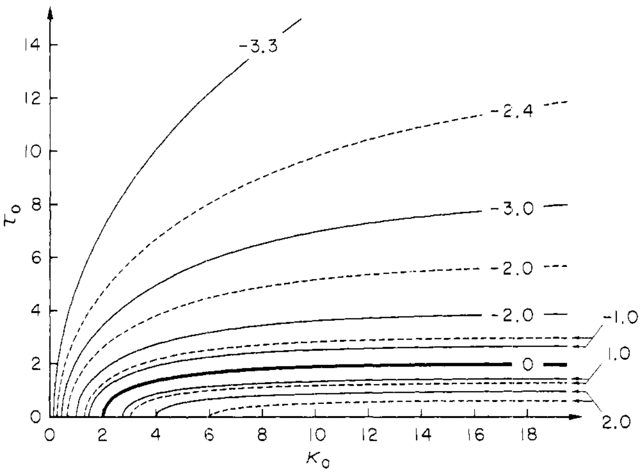

Figure 1. Contour map of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$ in a (κ_0, τ_0) plane. The full and broken curves are the contour lines at $T = 300$ and $T = 400$ K, respectively.

temperature coefficient is always equal to $-T^{-1}$ on the present assumption, as seen from eq 4.

It is interesting to see that the temperature coefficient is positive for PDMS, s-PMMA, and PDLA. In this connection, a contour map of the temperature coefficient in a (κ_0, τ_0) plane calculated from eq 4 is shown in Figure 1, where the full and broken curves are the contour lines at $T = 300$ and 400 K, respectively, the attached numbers indicating the values of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$. Along the heavy full curve 0, it vanishes at all temperatures. Comparing Figure 1 with Figure 3 of ref 21 or Figure 2 of ref 22, we see that the temperature coefficient becomes positive for typical HW chains. This is not difficult to understand, considering the fact that typical HW chains have locally *bent* backbones, which are straightened as the temperature is increased.

Our final remark is concerned with cellulose derivatives, for which observed values of $10^3(\mathrm{d}\ln\langle R^2\rangle_C/\mathrm{d}T)$ are −7 to −3 $\deg^{-1}$.[23] These large negative coefficients cannot be explained by means of eq 4 even if we assume the KP chain ($\kappa_0 = 0$), for which the negative temperature coefficient becomes a maximum in magnitude. This difficulty may be removed by taking into account the dependence of the force constant α on temperature. Then the factor T^{-1} on the right-hand side of eq 4 is replaced by $T^{-1} - \mathrm{d}\ln\alpha/\mathrm{d}T$. Thus we find that $10^3(\mathrm{d}\ln\alpha/\mathrm{d}T) \simeq -4$ to 0 $\deg^{-1}$ for cellulose derivatives (at $T \simeq 300$ K) if the KP chain is assumed. This result seems reasonable since it means that the temperature coefficient of Young's modulus is negative. However, it is difficult and also meaningless to give any more physical interpretation to such temperature coefficients of α.

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Kinetics of Polymer Complex Interchange in Poly(acrylic acid)–Poly(oxyethylene) Solutions

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Poly(acrylic acid) (PAA) and poly(oxyethylene) (POE) have long been known to form complexes in water solution.[1] Osada has studied the equilibrium of this process by using the pH shift accompanying complex formation.[1b] He has demonstrated the cooperativity of the association by the steep dependence of the complex stability on the chain length of the interacting polymers.

We have initiated a study of this complex by taking advantage of the emission characteristics of the dansyl moiety, which fluoresces much more intensely in organic media than in water.[2] We have found that aqueous solutions of dansyl-labeled PAA exhibit a large increase of fluorescence on complexation with POE, reflecting the

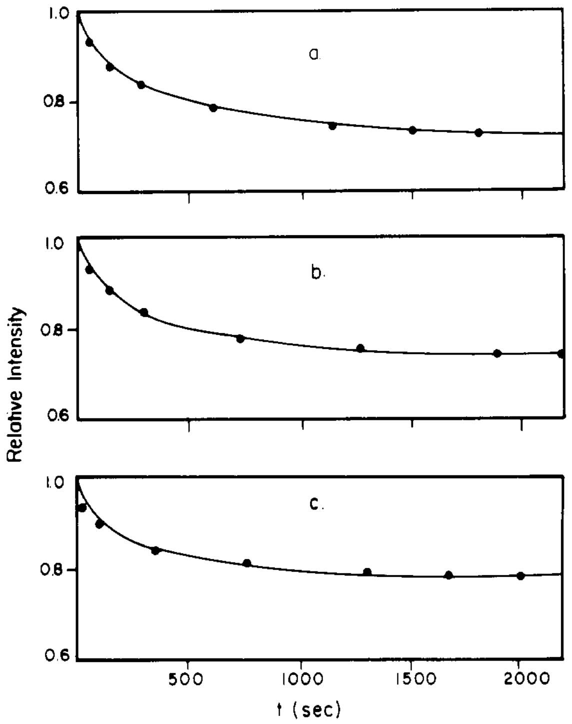

Figure 1. Time dependence of the emission intensity after the addition of unlabeled PAA to a solution containing dansyl-labeled PAA and POE ($\bar{M}_\eta$ = 77 000): (a) 1.54 M NaCl; (b) 1.00 M NaCl; (c) 0.56 M NaCl.

local exclusion of water. A study of the equilibrium properties of such systems will be reported later. Here we only wish to communicate results obtained when an excess of *unlabeled* PAA was added to the complex, using the decrease in fluorescence intensity to study the kinetics of the displacement of the labeled PAA by the unlabeled polymer.

Experimental Section

Two poly(oxyethylene) samples were used in this study. The first (J. T. Baker Chemical Co.) had an intrinsic viscosity in water at 30 °C of 0.327 dL/g, corresponding to $\bar{M}_\eta$ = 24 000. A second sample obtained from Dr. F. E. Bailey, Jr., of Union Carbide had $[\eta]$ = 0.81 dL/g, corresponding to $\bar{M}_\eta$ = 77 000. Dansyl chloride (Eastman Kodak) was reacted with an excess of ethylenediamine to obtain *N*-dansylethylenediamine (mp 149–151 °C). This compound was condensed with methacrylyl chloride to [(*N*-dansylamino)ethyl]methacrylamide (mp 136–136.5 °C). Acrylic acid was copolymerized with 0.85 mol % of the dansyl derivative, stopping the reaction at 29.5% conversion. Spectroscopic analysis showed that the copolymer contained 1.42 mol % of the dansyl-labeled monomer. The intrinsic viscosity in 0.5 M NaBr was 3.08 dL/g, corresponding to a molecular weight of 5.9×10^5. The unlabeled PAA used in this study had $[\eta]$ = 3.42 dL/g, corresponding to $\bar{M}_\eta = 6.9 \times 10^5$.

A Perkin-Elmer MPF-44B spectrofluorimeter was used to measure the emission intensity. Thermostated solutions were excited at 304 nm, the isosbestic point of the protonated and unprotonated dansyl chromophore. The emission was followed at 520 nm as a function of time after mixing an aqueous solution containing the POE complex with the dansyl-labeled PAA and a solution containing an excess of unlabeled PAA.

Results and Discussion

In an initial experiment 2.3×10^{-2} N unlabeled PAA was added to a solution containing 1.01×10^{-3} N labeled PAA and 1.17×10^{-2} base molar POE at pH 4.1 and at 25 °C. The emission intensity decreased by 16.7%, but the change was too fast to observe. The approach to equilibrium was slowed down substantially by reducing the temperature to 2 °C, the pH to 2.65 (0.002 M HCl), by using more dilute polymers, and by addition of sodium chloride. Figure 1 represents the time dependence of the emission intensity, I, after addition of 1.25×10^{-4} N unlabeled PAA to a solution containing 1.92×10^{-5} N PAA carrying 1.42 mol % of the dansyl label and 4.1×10^{-5} base molar POE, with NaCl concentrations of 0.56, 1.00, and 1.54 M. All kinetic curves corresponded to a biphasic process, i.e.,

$$(I - I_\infty)/(I_0 - I_\infty) = \alpha \exp(-kt) + (1 - \alpha) \exp(-k't)$$

where I_0 and I_∞ correspond to $t = 0$ and $t = \infty$. A typical first-order plot is shown in Figure 2 and the parameters α, k, and k' obtained with the various salt concentrations and with POE of two chain lengths are listed in Table I.

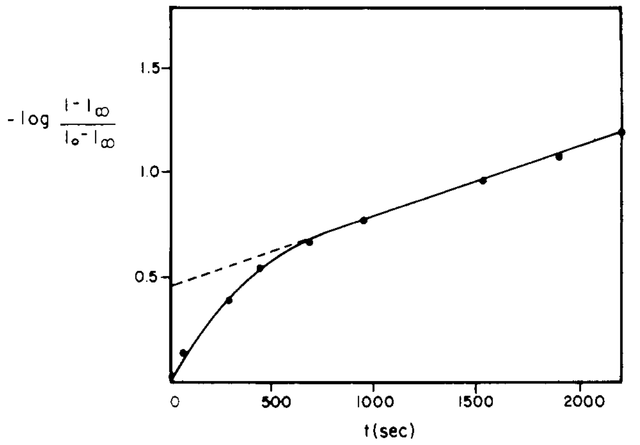

Figure 2. First-order plot of the decay of the emission intensity after addition of unlabeled PAA to a solution containing dansyl-labeled PAA and POE ($\bar{M}_\eta$ = 77 000) in 1.00 M NaCl.

Table I
Parameters Describing the Interchange of the PAA–POE Complex with PAA

mol wt of POE	concn of NaCl, M	k, s^{-1}	k', s^{-1}	α
24 000	1.54	0.0038	0.00031	0.70
24 000	1.00	0.0046	0.00072	0.68
24 000	0.56	0.010	0.0016	0.50
77 000	1.54	0.0038	0.00030	0.66
77 000	1.00	0.0047	0.00078	0.65
77 000	0.56	0.011	0.0015	0.51

The following points may be noted: (a) The kinetic data are insensitive to the chain length of the POE, although the stability of the POE–PAA samples increases sharply with an increasing chain length of POE.[1b] Thus the biphasic character of the exchange is not likely to be a reflection of the polydispersity of the interacting polymers. (b) An increasing salt concentration decreases the rate constants characterizing both the faster and the slower process. This is probably due to a decrease in the solvation of the complex.

We believe that this is the first study of the kinetics of a polymer complex interchange.

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Polymers in Mixed Solvents: Feasibility of Computing Binary and Ternary Interaction Parameters from Intrinsic Viscosities Only

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Usually, intrinsic viscosities $[\eta]$ of polymers in mixed solvents can be determined easily and reproducibly. As they depend on the thermodynamic interactions among components, it is attractive to estimate interaction parameters g directly from measurements of $[\eta]$ as a function of solvent composition u_2 (for g and u_2, see eq 1). This has been attempted, for example, by Cowie and McCrindle[1] and, more recently, by Dondos and Benoit.[2] They determined binary interaction parameters between polymer and nonsolvent, but without accounting for the existence of a ternary interaction parameter.

The inclusion of such a parameter in the phenomenological expression for the Gibbs free energy of mixing has been advocated convincingly by Pouchlý et al.[3,4] They were the first to determine the ternary interaction function, together with binary polymer–nonsolvent interaction parameters, by combining the results of total sorption (Y) measurements (light scattering, osmometry, and viscometry) and preferential sorption (λ) measurements (dialysis equilibrium).[3,4] Later, Chu and Munk[5] and Aminabhavi and Munk[6] developed methods to derive Y and λ, and thus binary and ternary interaction functions, from measurements with the analytical ultracentrifuge. Horta et al.[7,8] have given a statistical mechanical explanation for the ternary interaction function: it may be regarded as a modifier of binary parameters. Their explanation is based on an extension of the formalism outlined by Pouchlý and Patterson.[9]

The purpose of the calculations reported in this note is to investigate if an acceptable parameter g_{23} for the interaction between a polymer and a nonsolvent can be obtained together with the ternary interaction function from intrinsic viscosities only, even for the case of a "truncated" $[\eta]$–u_2 curve. Such curves may be restricted to the range $0.0 \leq u_2 \leq 0.5$, for instance, because of demixing.

Determination of binary and ternary interactions in this experimentally simple way (as compared to other methods[3–6]) would enable us to calculate and to understand tentatively a ternary (or rather pseudoternary[10]) isothermal demixing diagram for a polymer–solvent–nonsolvent system,[11] starting from the phenomenological expression of Pouchlý et al.[3,4] for the Gibbs free energy of mixing of such a system.

In order to verify our method, we calculated g_{23} and g_T from the extensive viscosity data of Munk et al.,[12] the interaction parameters of their systems being known independently, i.e., from combining the results of measurements[5,6] of second virial coefficients A_2 and preferential adsorption parameters λ.

Theory

We define the thermodynamic interaction parameters g_{ij} and g_T by the Gibbs free energy of mixing ΔG_m expressed as[3–5]

$$\Delta G_m/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_1)n_1\phi_2 + g_{13}(\phi_3)n_1\phi_3 + g_{23}(\phi_3)n_2\phi_3 + g_T(u_1,\phi_3)n_1\phi_2\phi_3 \quad (1)$$

where indices 1 and 2 denote solvent components and index 3 denotes polymer. Numbers of moles are denoted by n_i, volume fractions before mixing by ϕ_i, and solvent compositions by u_1 or u_2:

$$u_1 \equiv \phi_1/(\phi_1 + \phi_2)$$

$$u_2 \equiv \phi_2/(\phi_1 + \phi_2) \quad (2)$$

The notation g in this equation for the interaction parameters instead of the more usual[1–4,12] notation χ has been advocated by Koningsveld and Staverman,[10] who related χ to chemical potential rather than to Gibbs free energy. The g functions in (1) are functions not only of composition (as indicated) but also of molecular weight (distribution) and temperature.[10]

The g functions may be related to intrinsic viscosities $[\eta]$, and in turn derived from them, only through a nonthermodynamic molecular model such as, for instance, the Flory–Fox model,[13] which relates the molecular parameters molecular weight $\bar{M}_w$, unperturbed dimension K_θ, and linear expansion coefficient α to the thermodynamic total sorption parameter Y, a function of the interaction parameters g_{ij} and g_T. In the derivation of the Flory–Fox model, Y has been supposed to be independent of molecular weight, though Y should depend on it (through g). We assume, then, that a phenomenological, molecular weight dependent Y may be derived from $[\eta]$, using equations like those of the Flory–Fox model:

$$[\eta] = K_\theta \alpha^3 \bar{M}_w^{0.5}$$

$$\alpha^5 - \alpha^3 = 2C_M Y \bar{M}_w^{0.5} \quad (3)$$

with

$$C_M = 0.356(\bar{v}_3^2/V_1)K_\theta^{-1}$$

where $\bar{v}_3$ is the partial specific volume of the polymer and V_1 is the molar volume of component 1. (The constant C_M has been given in full elsewhere;[12,13] it has been calculated with 0.356 assuming a value of 2.5×10^{23} (cgsu) for Flory's universal viscosity constant Φ_0.)

A thermodynamically exact expression for Y in the limit $\phi_3 \rightarrow 0$ has been derived from (1) by Pouchlý et al. It reads in the g notation of Chu and Munk[5]

$$Y = \tfrac{1}{2}(b_{33} - u_1u_2b_{23}^2/b_{22}) \quad (4)$$

with

$$b_{22} = u_1 l + u_2 - u_1u_2\left\{2\left[g_{12} + (u_1 - u_2)\frac{\partial g_{12}}{\partial u_1}\right] - u_1u_2\frac{\partial^2 g_{12}}{\partial {u_1}^2}\right\}$$

$$b_{23} = (l g_{23}^\circ - g_{13}^\circ) + 1 - l - (u_1 - u_2)(g_{12} - g_T^\circ) + u_1u_2\left(\frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_T^\circ}{\partial u_1}\right)$$

$$b_{33} = u_1 + u_2 l + 2u_1u_2(g_{12} - g_T^\circ) - 2(u_1\chi_{13}^\circ + u_2 l \chi_{23}^\circ) - 2\chi_T^\circ u_1u_2$$

$$l = V_1/V_2 \text{ (molar volume ratio)}$$

$$\chi_{i3}^\circ = g_{i3} - (\partial g_{i3}/\partial \phi_3)^\circ$$

$$\chi_T^\circ = g_T^\circ - (\partial g_T/\partial \phi_3)_{u_1}^\circ$$

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