Macromolecules 1984, *17*, 1634-1636

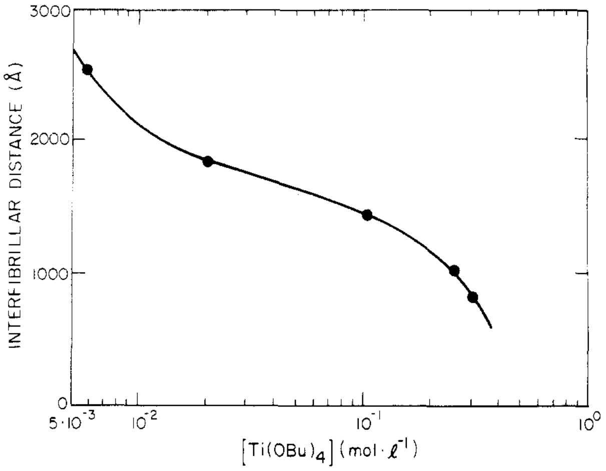

Figure 3. Interfibrillar distance in polyacetylene films as a function of [Ti(OBu)$_4$] (catalyst aging time at rm = 1 h, Al/Ti = 4, P_{AC} = 69 cmHg, t_p = −78 °C).

formation of larger fibrils. This process is mainly affected by the concentration of the catalyst solution, its aging time, and the polymerization temperature.

An important characteristic in polyacetylene films is the variation of its interfibrillar distance with the experimental conditions of the reaction. The average distance[9] between the fibrils throughout the film is measured on two-dimensional micrographs assuming that the three-dimensional fibril growth on the surface of the Ziegler-Natta catalyst solution is homogeneous. A slight decrease in the interfibrillar distance is observed when the fibril diameter increases. The decrease in this parameter becomes significant when the catalyst concentration is increased as shown in Figure 3. These results can be explained by the increase in the number of the active centers on the surface of the catalyst solution which gives closer fibrils when the polymerization occurs. The data shown in Figure 3 are consistent with the density measurements performed on the same films (Table I).

The last parameter is of importance, particularly when electrochemical doping of the polymer is involved. The surface area, which varies with the interfibrillar distance, is the main factor in determining the current density of polyacetylene batteries that have been studied and developed for few years.[10]

In conclusion, the kinetics of growth of polyacetylene film and fibrils show that the experimental conditions of the polymerization are very important in the determination of the polymer density, porosity, and fibril diameter and have to be taken into account when it is doped and characterized.

Registry No. Ti(OBu)$_4$, 5593-70-4; AlEt$_3$, 97-93-8; polyacetylene (homopolymer), 25067-58-7; acetylene, 74-86-2.

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Received March 20, 1984

Kinetics of the Cooperative Complex Formation and Dissociation of Poly(acrylic acid) and Poly(oxyethylene)

The formation of complexes between poly(carboxylic acids) and polymeric hydrogen bond acceptors such as poly(oxyethylene) or poly(vinylpyrrolidone) in aqueous solution has been investigated over a number of years.[1] The association is a cooperative process; since there is only a small *difference* between the stability of hydrogen bonds of these polymers with the aqueous medium and the stability of the interpolymer hydrogen bonds, a large number of the interpolymer bonds must form to yield a stable complex. Complex stability is thus a steep function of the length of the shorter of the interacting chains.

In 1977, Anufrieva et al.[2] showed that if one of the interacting polymers carries a fluorescent label, its displacement from the polymer complex by an unlabeled polymer can be monitored by the change in the depolarization of fluorescence. More recently, Chen and Morawetz[3] studied the kinetics of such a "complex interchange" using poly(acrylic acid) (PAA) labeled with the dansyl chromophore, which fluoresces very weakly in water but strongly in organic media.[4] It was found that complexation of labeled PAA with poly(oxyethylene) (POE) leads to a large increase in fluorescence intensity. Displacement of labeled PAA from the complex by the unlabeled polymer could, therefore, be followed by the decay in the emission.

We have now found that the change in fluorescence intensity of dansyl-labeled PAA when it participates in complex formation can also be used to follow the kinetics of complexation and of complex decomposition. Since these are relatively fast processes, a stopped-flow apparatus had to be used for their study. Unless stated otherwise, experiments were carried out at 25 °C, at pH 2.7, and in the presence of 1 M NaCl. Polymer complexation was studied by mixing 4 × 10^{-4} N PAA labeled with 1.8 mol % of dansyl groups[3] with an equal volume of a POE solution. Complex decompositions were followed after solutions of the dansyl-labeled complex were mixed with a buffer at a pH at which the complex is known to be unstable.

Complexation of PAA with an excess of POE (molecular weight ~20 000) was found to be biphasic with the fluorescence intensity I varying with time t as

$$\ln\,[(I - I_\infty)/(I_0 - I_\infty)] = \alpha \exp(-k_{\mathrm{obsd}}t) + (1 - \alpha)\exp(-k'_{\mathrm{obsd}}t)$$

Table I lists the parameters obtained at various concentrations of POE and at various temperatures. Assuming that the fast process can be represented by a simple scheme

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB}$$

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Table I
Parameters of Complex Formation Kinetics in the PAA–POE System[a]

10^2[POE], mol·L^{-1}	25 °C			32 °C			36.5 °C			42 °C		
	k_{obsd}, s^{-1}	k'_{obsd}, s^{-1}	α	k_{obsd}, s^{-1}	k'_{obsd}, s^{-1}	α	k_{obsd}, s^{-1}	k'_{obsd}, s^{-1}	α	k_{obsd}, s^{-1}	k'_{obsd}, s^{-1}	α
0.4	0.11	0.030	0.59	0.17	0.037	0.63	0.29	0.060	0.60	0.34	0.066	0.64
0.8	0.28	0.035	0.62	0.32	0.044	0.68	0.41	0.061	0.63	0.48	0.067	0.70
1.5	0.43	0.042	0.68	0.52	0.051	0.73	0.67	0.066	0.70	0.73	0.071	0.73
2.0	0.57	0.047	0.72	0.67	0.067	0.78	0.72	0.074	0.75	0.95	0.079	0.78

[a] [PAA*] = 4×10^{-4} N; pH 2.7; 1 M NaCl.

Table II
Rate Constants for the Decomposition (k_{-1}, s^{-1}) of Complexes PAA (4×10^{-4} N)–POE (4×10^{-3} N)[a]

pH[b]	19 °C	25 °C	32 °C	42 °C
3.85	18.1	20.3	23.7	27.6
5.08		24.3	26.5	
6.37		51.8		

[a] Original pH 2.7. [b] Final pH.

Table III
Activation Parameters for Association (a) and Complex Decomposition (d) in the PAA–POE System[a]

$\Delta H_a^{\ddagger}$, kcal mol^{-1}	$\Delta H_d^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S_a^{\ddagger}$, eu	$\Delta S_d^{\ddagger}$,[b] eu
3.7	2.8	−35.9	−43

[a] Initial [POE]/[PAA] = 10, pH 2.7, 1 M NaCl. [b] Final pH 3.85.

it can be shown that for [B] ≫ [A] the apparent first-order rate constant is given by $k_{obsd} = k_1[B] + k_{-1}$. Figure 1, a typical plot of k_{obsd} against [POE], shows that k_{obsd} is in fact linear in the POE concentration for [POE]/[PAA] > 10. While k_1 values could be obtained from such plots with high precision, the intercepts are too small to yield reliable k_{-1} data.

When the solution of the PAA–POE complex was mixed with an equal volume of buffers (ionic strength 0.4) to raise the pH to values at which the complex is dissociated, the decay in the fluorescence was found to follow first-order kinetics. Table II lists rate constants obtained at varying final pH as well as the temperature dependence of the rate constants observed at pH 3.85. It may be noted that the rate of complex decomposition changes relatively little between pH 3.85 and 5.08 but increases much more sharply when the pH is further raised to 6.37. According to Kotliar's data[5] of the titration of poly(acrylic acid) in the presence of 1 M uni-univalent electrolyte, the degree of ionization is 0.175 at pH 3.85, 0.566 at pH 5.08, and 0.854 at pH 6.37. It would seem, therefore, that the rate of complex dissociation rises much more abruptly at high degrees of ionization.

Table III lists the activation parameters for the formation and the decomposition of the PAA–POE complex. The small $\Delta H_a^{\ddagger}$ corresponding to the polymer association indicates that the initial formation of an interpolymer hydrogen bond is diffusion controlled. The large negative value of $\Delta S_a^{\ddagger}$ may be interpreted as a consequence of the extensive change in the conformation of the chain molecules required to allow a number of hydrogen bonds sufficient for complex stability to be formed. The activation enthalpy for the dissociation of the complex, $\Delta H_a^{\ddagger}$, should contain a large contribution proportional to the number of interpolymer hydrogen bonds which must be exchanged for hydrogen bonds with water. Unfortunately, we have no way of estimating the magnitude of this enthalpy corresponding to a single hydrogen bond.

We believe that this is the first study of the rate of formation and decomposition of complexes of flexible-chain molecules other than formation[6] or the decomposition[7] of the double-helical structures of DNA or synthetic polynucleotides. The situation is quite different in our case since we need not be concerned with problems associated with the winding and unwinding of the double helix. Also, although Russian workers such Zezin et al.[8] claimed to have shown that complex formation involves the intimate association of contiguous monomer residues, we find their argument unconvincing on stereochemical grounds.

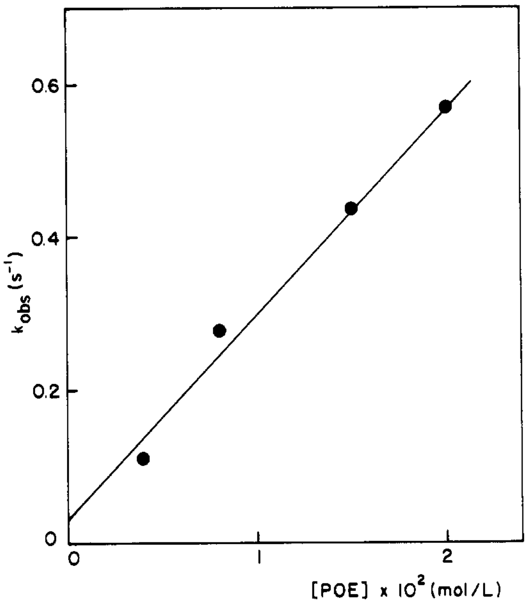

Figure 1. Dependence of the rate constant for complex formation, k_{obsd}, on the POE concentration in the PAA–POE system.

Experimental Section. Stopped-Flow Device. The apparatus was built in the Department of Biological Chemistry, University of Michigan, and described by Becvar.[9] This instrument initiates reactions by mixing reactants at a point separated in position and thus in time from the observation point. The time interval, called the dead time, during which the reaction proceeds without being observed, was ~1.5 ms. The intensity of scattered light, measured after mixing of unlabeled PAA solution with POE solution, was less than 3% of the fluorescence intensity and it was time independent. Thermostated solutions (±0.1 °C) were excited at 340 nm and the fluorescence intensity was measured by using a Corning glass filter no. CS 3-70.

Acknowledgment. We are indebted to the National Science Foundation, Polymers Program, for financial support of this study by Grant DMR-77-05210.

Registry No. PAA, 9003-01-4; POE, 25322-68-3.

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Received February 13, 1984

Slow-Mode Diffusion of Poly(vinylpyrrolidone) in the Semidilute Regime

The overlap concentration, c^* $(=1/[\eta])^1$, is for molecules with $M_w > 10^5$, still a rather low concentration, and solutions with $c^* < c < c^\dagger$ are therefore called semidilute,[1,2] where $c^\dagger = (6^{3/2}/8N_A)(K^{5/2}/K_\Theta{}^4)$ indicates the crossover to concentrated solutions,[3] with K defined by $\langle R^2\rangle = KM^{6/5}$ and K_Θ by $\langle R^2\rangle_\Theta = K_\Theta M$. Our main understanding of semidilute solutions is due to de Gennes,[2] who applied scaling arguments for a description of this regime. A key parameter is the correlation length ξ, which defines a mean distance between two points of entanglement. It becomes shorter with increasing concentration and is given by[2,4]

$$\xi = a(c/c^*)^{-0.75} \qquad \text{for } c > c^* \tag{1}$$

where a is a length parameter that is difficult to calculate quantitatively. For lower concentrations the correlation length is

$$\xi = \langle R^2\rangle^{1/2} \qquad \text{for } c < c^* \tag{2}$$

where $\langle R^2\rangle$ is the mean square end-to-end distance. Beyond c^* a slow decrease to the unperturbed dimensions is predicted with a power law for the mean square radius of gyration

$$\langle S^2\rangle \sim (c/c^*)^{-0.25} \tag{3}$$

for individual chains in a good solvent.[5-7]

In *dilute solutions* only one translational diffusive motion is expected to which the Stokes–Einstein relationship can be applied

$$D = \frac{kT}{6\pi\eta_0}\,\frac{1}{R_h} \tag{4}$$

which defines a hydrodynamically effective radius of the coil. *Beyond* c^* de Gennes predicts two modes of diffusive motions, i.e., (i) a fast mode, which is given by[2]

$$D_{\text{coop}} \sim kT/6\pi\eta_0\xi \tag{5}$$

and (ii) a slow mode, which should follow[8]

$$D_{\text{self}} \sim N^{-2}(c/c^*)^{-1.75} \tag{6}$$

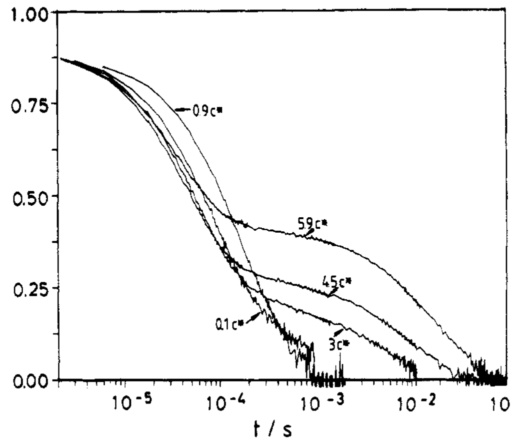

Figure 1. Time correltion function (TCF) $g_1(t)$ for five concentrations of PVP in water at a scattering angle of $\theta = 90°$; M_w 57×10^4; $c^* = 0.00731$ g cm^{-3}.

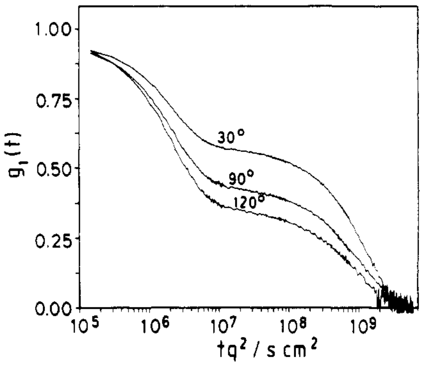

Figure 2. $g_1(t)$ as a function of tq^2 for the same sample as in Figure 1 for three different scattering angles, where $q = (4\pi/\lambda)\sin(\theta/2)$.

Self-diffusion is conceived here as a motion of the chain along its contour length (reptation). Hwang and Cohen[9] introduce two further diffusion coefficients, i.e., D_s, the translational diffusion coefficient of the solvent, and D_{cm}, which they associate with a center-of-mass diffusion (however, see below.)

We have carried out dynamic light scattering (LS) measurements on poly(vinylpyrrolidone) (PVP) in aqueous and ethanolic solutions. These are both good solvents, and we have indeed found a fast and a slow mode of motion at $c > c^*$, but only one mode in the dilute regime. This behavior is shown in Figure 1 for five typical concentrations of a polymer with $M_w = 57 \times 10^4$ (LS), $M_n = 27.4 \times 10^4$ (OS), and $A_2 = 4.60 \times 10^{-4}$ cm^3 mol g^{-2} (LS) in water. For the two concentrations c_1 and $c_2 < c^*$ we obtain a time correlation function (TCF) that decays approximately as a single exponential. For the concentrations c_3 to $c_5 > c^*$ a slower decay of the TCF becomes apparent in addition to the fast one and becomes more and more prominent with increasing concentration. Both modes are essentially diffusive since the characteristic relaxation times occur, for measurements at different angles, at the same value of q^2t. The amplitudes, however, depend on the scattering angle and have been extrapolated to zero angle (see Figure 2). Similar TCF have been found recently by Nose and Tanaka[10] for PMMA in 2-butanone. The diffusivities of the modes can be evaluated quantitatively by the program CONTIN provided by Provencher[11] and are plotted in Figure 3 against c/c^* for the PVP samples shown in Figures 1 and 2. We find in both solvents for the fast and the slow modes an exponent of +0.60 and −1.50, respectively. Both exponents are lower in value than +0.75 and −1.75 predicted by de Gennes for an entangled system. Experimental data

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