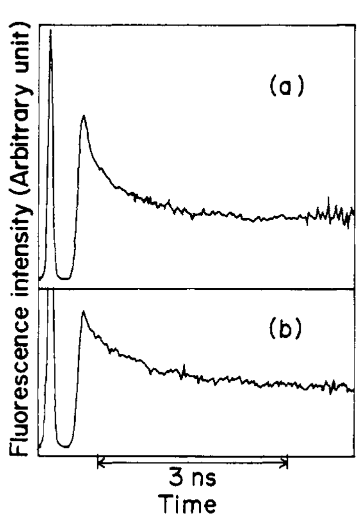

Figure 3. Fluorescence rise and decay curves of PV5BCz(r) (a) and PV5BCz(c) (b) in MTHF solution. A B-370 filter was used.

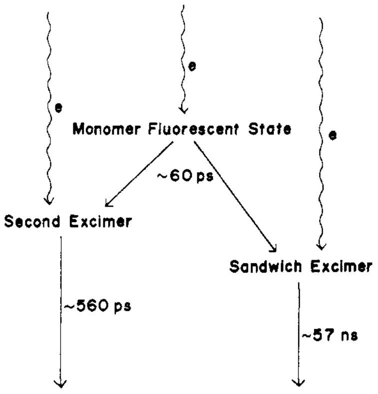

Figure 4. Scheme for excimer formation of PV5BCz(r). See text.

state may possibly be assigned to an excited state trapped in a chromophore that takes a different conformational and configurational structure. Energy migration from this molecule to excimer-forming sites, which may be coupled to a slight movement of the main chain or side groups, determines the time constant of 60 ps. Although the rise curve of the second excimer was not observed directly, it is reasonable to assume that the latter excimer is formed in a way similar to that of the sandwich excimer. The second excimer-forming site may be produced more easily in the ground state than the sandwich excimer. All these sites can be covered by energy migration represented by the process e, since the mean degree of polymerization of the present systems is small. The process of the conversion from the second excimer to the sandwich excimer was not observed and accordingly can be excluded. In the case of PV5BCz(c), the "second excimer" is replaced by another monomer fluorescent state. This excited chromophore may not take such a geometrical structure as that of the second excimer because of its isotactic sequence.

The present dynamic behavior of PV5BCz can be compared with those of PVCz and is summarized as follows. (1) The yield of the instantaneous formation of the sandwich excimer of PV5BCz system is relatively large compared to that of PVCz. (2) The sandwich excimer formation process from the monomer fluorescent state observed in the PV5BCz(r) is similar to that of PVCz except that its formation rate is 2 orders of magnitude larger than that of PVCz. (3) The second excimer does not form the sandwich excimer, which is common to both polymers. Results 1 and 2 may be explained by the difference of the steric restraints produced in the ground state. The sandwich excimer forming site of PV5BCz is more easily formed compared to that of PVCz because of its more bulky group, and a slight conformational change is enough to produce the excimer state. In order to establish the excimer formation mechanism of PVCz and related polymers proposed here, detailed studies involving solvent, viscosity, and temperature effects should be made.

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Akira Itaya* and Ken-ichi Okamoto

Department of Chemical Engineering
Faculty of Engineering, Yamaguchi University
Ube, Yamaguchi 755, Japan

Hiroshi Masuhara,* Noriaki Ikeda, and Noboru Mataga

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

Shigekazu Kusabayashi

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

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Coil-Globule Transition of a Single Polystyrene Chain in Dioctyl Phthalate

The collapse of a polymer coil, the so-called coil-globule transition, has been treated in several theoretical papers.[1-7] The coil-globule transition can be either continuous or

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discrete, depending on the chain stiffness.[7] For a flexible polymer having infinite molecular mass, one assumes that the coil–globule transition will be of the second order just at the Θ point;[6] for polymers with a finite molecular mass, the transition region should be broader the shorter the chains. Until very recently, experimental observations of such transitions were lacking, as the transition is obscured by intermolecular chain aggregation. In reality, individual macromolecules can exist in the completely globular state only at concentrations[8,9] too low to be examined experimentally. Only the onset of such a transition was observed in polymer solutions of polystyrene with the extreme molecular mass $M_w = 4.4 \times 10^7$ (the dimensions of M_w are g/mol), where the transition region is very narrow.[10] The development of the method of quasi-elastic light scattering in recent years[11,12] has made possible the determination of chain dimensions also in very dilute solutions. Tanaka and co-workers successfully used this method in an investigation of the coil–globule transition in the systems polystyrene ($M_w = 2.6 \times 10^7$)–cyclohexane[13,14] and polyacrylamide ($M_w = (5\text{–}6) \times 10^6$)–water–acetone.[15] Attempts to study the collapse of the coil by employing optical and viscometric methods for polymers having lower molecular mass have failed so far (for example, ref 16 and 17). By using small-angle neutron scattering, Nierlich, Cotton, and Farnoux reported an indistinct coil–globule transition of polystyrene with a very low molecular mass (M_w = 29 000).[18]

This paper shows that the coil–globule transition can be adequately characterized also at higher concentrations in a viscous solvent at low temperatures. Under such conditions, the dynamic processes of aggregation are slowed down so much that the measurements can be performed also below the binodal temperatures.

The samples were prepared by using polystyrene (PS) produced by Pressure Chemical Co., $M_w = 2 \times 10^6$ and polydispersity $M_w/M_n = 1.30$ (producer's data). Dioctyl phthalate (DOP), carefully purified, dried, and redistilled twice, was used as the viscous solvent. The Θ temperature of the system polystyrene–dioctyl phthalate is[19] 22.0 °C. The concentrations of solutions measured lay between 1×10^{-4} and 8×10^{-4} g cm^{-3}. The coil–globule transition was investigated by quasi-elastic light scattering and conventional elastic light scattering. In the former method, a He–Ne Spectra Physics 125A laser was used as the light source and a Hewlett-Packard 3721A was used in the signal processing (for details, see ref 20). The elastic light scattering was measured with a commercial Sofica apparatus adapted for measurements at temperatures below 20 °C. In both cases the accuracy of temperature control was better than 0.1 °C. The following cycle was used in the elastic light scattering measurements: the sample was first heated above the Θ temperature (for ~15 min) and then quickly cooled by dropping it into a thermostated immersion liquid; after 15–25 min, the scattering was measured. At the lowest concentration (~1×10^{-4} g cm^{-3}) the excess scattering was twice that of the solvent alone. The intensity measurements were evaluated by means of the Zimm plot down to 9 °C and by an analysis of the angular dependence only of the intensity of scattered radiation (11 values) at lower temperatures;[21] our interest was mainly concentrated on the determination of the radius of gyration, R_G, and the second virial coefficient, A_2. The hydrodynamic radius, R_H, was determined from the measured autocorrelation curves by a standard procedure using the Stokes–Einstein formula.[11]

Measurement with the Sofica apparatus provided also a "dynamic" coexistence curve of the system PS–DOP (Figure 1). At a given concentration, the temperature taken as the cloud point was that at which the light intensity measured at $\theta = 30°$ increased in consecutive measurements (after ca. 5 min) by more than 3%. For the sake of comparison, the same figure shows the coexistence curve of the PS–cyclohexane system.[13,22] To reduce the coexistence curve to a single master curve for a given polymer–solvent system,[23] the results are presented in the coordinates $\tau M^{1/2}$ vs. $cM^{1/2}$, where $\tau = (T - \Theta)/T$; this allows us to compare data on samples having different molecular masses. The figure shows that in the system PS–DOP the dynamic coexistence curve is markedly shifted to higher concentrations, thus providing an unusually wide temperature range for the investigation of collapsed coils. We attribute this phenomenon to the high viscosity of the solvent (e.g., at 2 °C, η = 295 cP). Slowing down the formation of aggregates by several orders of magnitude after the temperature has been reduced below the binodal allows us to measure at temperatures close to the spinodal.

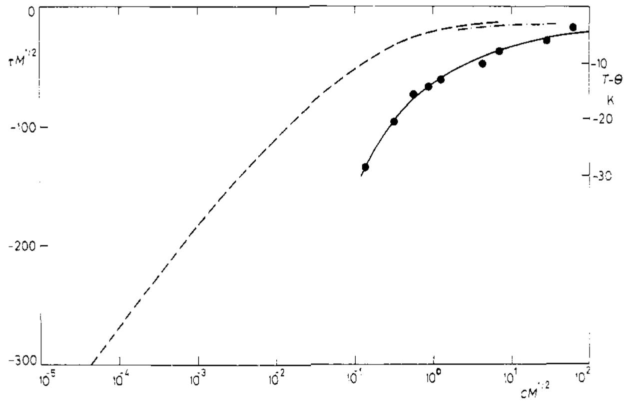

Figure 1. Dynamic coexistence curve in the system polystyrene ($M_w = 2 \times 10^6$)–dioctyl phthalate (points). For the sake of comparison, the same curves are given in the same universal coordinates for the system polystyrene–cyclohexane as published by Swislow et al.[13] (– – –) and Shultz et al.[22] (–·–).

Figure 2 shows the temperature dependence of the radius of gyration and hydrodynamic radius of the chain, R_G and R_H, respectively, and of the corresponding expansion factors $\alpha_G = R_G/R_{G\Theta}$ and $\tilde{\alpha}_H = R_H/R_{G\Theta}$. The expansion factors were calculated considering the unperturbed dimensions to be independent of temperature; for the given range of temperatures the relative error in $R_{G\Theta}$ is <0.8%. At low temperatures (<–4 °C), R_G decreased below 15 nm, which made its determination from the angular dependence of the intensity of scattered light unreliable. This is why the asymptotic region of collapse cannot be analyzed by using a sample with the molecular mass $M_w = 2 \times 10^6$. Our measurements give $R_{G\Theta}/M^{1/2} = 33 \times 10^{-10}$ cm mol$^{1/2}$ g$^{-1/2}$, in good agreement with the reported data for other solvents ((28.2–31.7) $\times 10^{-10}$ cm mol$^{1/2}$ g$^{-1/2}$ [24]). The experimental results in Figure 2 were fitted to the modified Sanchez formula describing the coil–globule transition:[14]

$$\frac{14\phi_G}{3N}(1 - \alpha_G^2) = \sigma\left(\frac{\Theta}{T} - 1\right)\phi_G^2 - \frac{2}{3}\phi_G^3 - \frac{1}{2}\phi_G^4 \quad (1)$$

where ϕ_G is the volume fraction of a chain of N segments and σ is a thermodynamic factor. Since $\phi_G = \phi_0/\alpha_G^3$, α for the total collapse condition can be written as $\alpha_{G_{\min}} = \phi_0^{1/3}$. The experimentally observed transition region is somewhat broader than the theoretical one, which may be due to the polydispersity of the polystyrene used ($M_w/M_n \approx 1.3$). The best fit is presented in Figure 2 as a solid line. The value

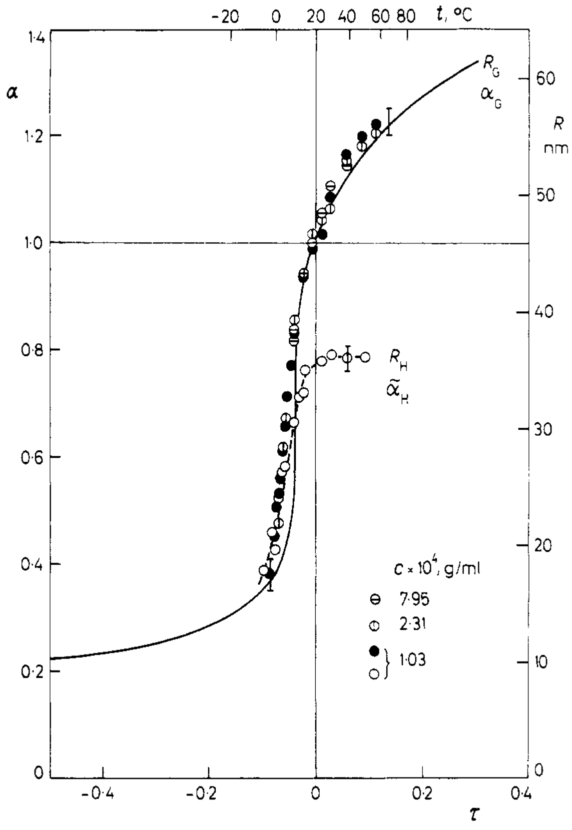

Figure 2. Dependence of the radius of gyration (R_G) and hydrodynamic radius (R_H) of the chain and of the expansion factors α_G and $\tilde{\alpha}_H$ on the temperature t and on the reduced temperature τ. The solid line indicates the best fit of α_G as a function of τ according to formula 1. The best fit parameters are $\sigma = 1.72$, $N = 9.6 \times 10^{-4} M_w$, $\alpha_{G_{\min}} = 2.41 M_w^{-1/6}$, and $\Theta = 20.5$ °C.

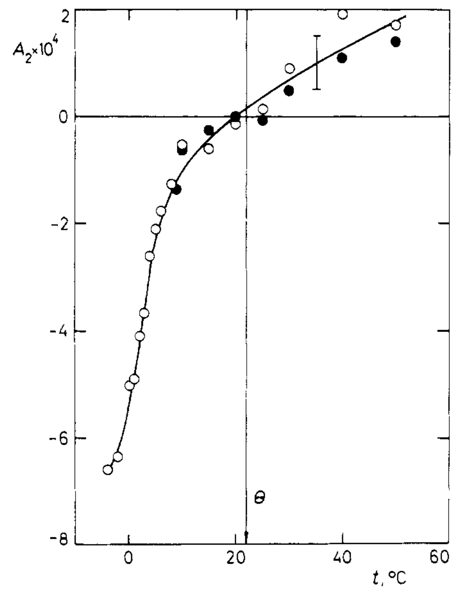

Figure 3. Temperature dependence of the second virial coefficient A_2 obtained by extrapolation (●) $c \to 0$, $\theta \to 0$ (Zimm plot) and (○) $\theta \to 0$ for $c = 1.03 \times 10^{-4}$ g/mL; for details, see text.

of the constant $\sigma = 1.72$ is smaller than that given for the system polystyrene–cyclohexane ($\sigma = 4$[14]). The Θ temperature obtained by fitting formula 1 is lower by 1.5 °C than that reported in the literature.[19] Figure 2 also demonstrates that $R_{H\Theta}/R_{G\Theta} \approx 0.77$, which is in good agreement with experimental results for polystyrene in Θ solvents.[25] This value is about 14% higher than that derived in the nondraining limit[26] (0.665).

The Zimm plots also provided the molecular mass and the second virial coefficient A_2 (Figure 3), both down to 9 °C ($\tau = -4.08 \times 10^{-2}$). The molecular mass is temperature independent within the limits of experimental error. An approximate value of A_2 for a dilute solution (1.03×10^{-4} g cm^{-3}) was determined at a single concentration only from the relation $Kc/R_{\theta=0} = 1/M_w + 2A_2c$, where $1/M_w = Kc/R_{\theta=0}$ at $\Theta = 22.0$ °C. The A_2 values thus obtained for $t \geq 9$ °C are in good agreement with the results obtained from the Zimm plot (cf. Figure 3); we assume, therefore, that they are reliable also at temperatures below 9 °C. No information concerning the third virial coefficient can be obtained on this level of analysis of our results.[3]

The method of slowing down of dynamic processes by using a viscous solvent allowed the coil–globule transition to be observed with polystyrene having the molecular mass $M_w = 2 \times 10^6$. If the asymptotic region of collapse is to be observed, one must use a polymer having a higher molecular mass, or a shorter wavelength. Such experiments will be described in a forthcoming paper.

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Petr Štěpánek, Čestmír Koňák, and Blahoslav Sedláček*

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
162 06 Prague 6, Czechoslovakia

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