Contraction of Polystyrene Molecules in Dilute Solution below the Θ Temperature

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ABSTRACT: Diffusion constants of polystyrene in cyclohexane were measured at temperatures equal to and less than the Θ temperature. The change in hydrodynamic radius with temperature was determined for polymers with molecular weights ranging from 5×10^4–4.4×10^7. The results are consistent with a mean field model of coil contraction and with scaling laws as applied to this problem. The data show that hydrodynamic radii vary less sharply with changes in temperature below the Θ point than radii of gyration. This is consistent with the idea that excluded volume effects are more prominent for monomer units which are widely spaced on the polymer molecule than for those which are relatively close to each other.

The concept of good and bad solvent in polymer solutions is linked to temperature, the Θ temperature representing the point at which attractive and repulsive forces compensate. In a Θ solvent, the polymer chain can be fairly represented as a Gaussian coil obeying random flight statistics. For most polymer–solvent pairs (where solution is endothermic), the coil expands on heating and contracts on cooling. There is a temperature range between the Θ temperature and the point of precipitation in which the polymer remains in solution. In this region, which is a function of both molecular weight and concentration, chain contraction can be investigated. The temperature range is narrow, but may be increased by use of highly dilute solutions.

There is a great body of experimental information on chain configuration at and above the Θ temperature. Fewer studies have been carried out below the Θ temperature, and systematic investigations of chain collapse as a function of both molecular weight and temperature are lacking. In this work we present measurements of the hydrodynamic radius (R_H) of polystyrene in cyclohexane for temperatures below $T = \Theta$ over a molecular weight range 5×10^4–4.4×10^7.

The first attempt to develop a consistent theory of chain collapse was that of Ptitsyn,[1] who used an extension of the Flory theory[2] of excluded volume. A very similar analysis has also been presented by de Gennes.[3] The subject has been treated by Massih and Moore[4] and by Moore.[5] A series of papers dealing with the problem have been presented by I. M. Lifschitz and collaborators,[6-9] including a recent review article.[10] A diagrammatic analysis using cluster expansions has been offered by Miyakawa and Saito,[11] and an illuminating discussion of the collapsing polymer as a condensing gas has been given by Domb.[12] In the modern theory of excluded volume, the radius of gyration, R_g, is proportional to N^ν where N is the number of statistical segments in the chain. In a Θ solvent, $\nu = 0.5$, in a good solvent, $\nu \approx 0.6$; a "best" recent estimate based on renormalization group methods has $\nu = 0.588$.[13] In a poor solvent, $\nu = 0.333$. The crossover from Θ conditions to a good or poor solvent occurs in a region of temperature which becomes progressively narrower as the polymer molecular weight increases. Accordingly, the ratio $R_g\ (T = \Theta \pm \epsilon)/R_g(T = \Theta)$ changes precipitously as N becomes large, exhibiting a behavior which can be regarded as a phase transition. There is, however, no agreement on whether the transition is first or second order, and the transition is abrupt, in principle, only in the limit of large N.

Experimental observation of chain collapse was first made by Katchalsky and Eisenberg,[14] who pointed out that poly(methacrylic acid) was highly contracted at low pH. Birshtein et al.[15] studied poly(methacrylic acid) in methanol–water mixtures and demonstrated changes in intrinsic viscosity by a factor of 20 or more by varying the methanol/water ratio. This phenomenon, confirmed by Anufrieva et al.,[16] was attributed to the special role played in hydrophobic interactions. Cuniberti and Bianchi[17] measured light scattering from a sample of polystyrene in cyclohexane and from a sample of poly(acrylic acid) in dioxane. Poly(acrylic acid)–dioxane solutions exhibit chain collapse as temperature increases, an inverse behavior signaling desolvation and an entropy increase with increasing temperature. They found much greater changes in the dimensions of poly(acrylic acid) with temperature than of polystyrene. This arises, in our opinion, from solvophobic effects in poly(acrylic acid) solutions since the CH_2CH and COOH groups have very different affinities for the solvent. Iwasa et al.[18] have shown that the intrinsic viscosity of poly(vinyl acetate) in carbon tetrachloride drops sharply below the Θ temperature, and this decrease is more rapid for polymers of higher molecular weight. By means of small-angle X-ray scattering, Chiba et al.[19] showed that the radius of gyration of poly(*p*-chlorostyrene) of $M_w = 5.5 \times 10^5$ in *n*-propylbenzene decreases about 10% before precipitation over a temperature range extending to 16 °C below the Θ temperature.

Slagowski, Tsai, and McIntyre[20] examined the radius of gyration of a very high molecular weight polystyrene ($M_w = 4.4 \times 10^7$) in cyclohexane in the neighborhood of the Θ temperature and found rapid changes in R_g in a narrow temperature range above and below the Θ temperature. A decrease in temperature of 1.4 °C below $T = \Theta$ produced a decrease in R_g of over 40%. This is still quite far from chain collapse since R_g at the lowest temperature measured is 1210 Å, while a collapsed sphere would have a radius of gyration of 198 Å.

Nierlich, Cotton, and Farnoux[21] have studied the R_g of a polystyrene sample of molecular weight 29 000 in deuteriocyclohexane below $T = \Theta$ by small-angle neutron scattering. Their measurements were carried out at a concentration of 3.4×10^{-3} g/mL, and the lowest temperature attained before precipitation was 26.8 °C below the Θ point. They found a radius of gyration at $T = \Theta$ of 51.8 Å, and R_g decreased 13.4% in the range of temperature studied. The radius of gyration of a compact sphere of polystyrene of this molecular weight is 17 Å.

Our objective in this investigation was to observe polymer contraction in a poor solvent. Since, in some cases, contraction is enhanced in materials which contain chemical groups on the polymer of vastly different polarity, it was desirable from our point of view to select a polymer in which there were no special solvophyllic or solvophobic interactions in order that the experiment would illustrate general properties of polymer–solvent interactions unperturbed by effects unique to a particular substance.

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Since measurements were to be performed near the point of precipitation, it was desirable to work with polymers with a relatively narrow molecular weight distribution to see a maximum effect, and it was important to use a method of measurement which was sensitive enough to yield precise measurements in solutions of low concentration. For this reason, we chose polystyrene since samples of narrow molecular weight dispersion are available. Photon correlation spectroscopy was chosen as a method of measurement; by this procedure one obtains accurate values of the diffusion constant, and therefore molecular radii. The determination can be performed in highly dilute solution. Cyclohexane, a Θ solvent for polystyrene at 35.4 °C, was selected as the solvent.

Experimental Section

Samples and Sample Preparation. The polymer samples were obtained from the Pressure Chemical Co. In addition, two samples of molecular weight 7×10^6 and 4.4×10^7 were studied. These were a gift from Professor L. J. Fetters of the University of Akron. Cyclohexane (Gold Label Spectrophotometric of the Aldrich Chemical Co.) was used as received.

Most solutions of the polymer were prepared and filtered through Gelman Alpha Metrecel filters (0.45 μm) into a square 1-cm quartz cell and allowed to settle for 24 h or longer before measurement. The two solutions of highest molecular weight (7×10^6 and 4.4×10^7) were prepared by filtering the solvent and dissolving the polymer in the filtered solvent. This procedure was used to avoid the possibility of fracturing the polymer molecule in the filtration process.

The cell containing the filtered solution was placed in a thermostat containing ethylene glycol as the cooling fluid. The refractive indices of ethylene glycol, cyclohexane, and quartz do not differ greatly from each other, and therefore stray reflections from cell–liquid interfaces were markedly reduced.

Scattering Measurements. The polymer solutions were illuminated with light at 4416 Å from a 25-mW RCA helium–cadmium laser. The scattered light was monitored with an RCA 31034A phototube. The photocurrent was passed through a Mech-Tronics 511 photon discriminator and an RC filter and fed into a Honeywell SAI 48 400 point correlator. The correlation functions were fit to a single exponential decay, using a nonlinear least-squares fitting program. The measured relaxation time, τ_r, was related to the polymer diffusion coefficient by

$$\tau_r = (2Dq^2)^{-1}$$

where q, the magnitude of the scattering vector, is given by

$$q = 4\pi n \sin(\Theta/2)/\lambda$$

where Θ is the scattering angle and n is the refractive index of the solvent. Most measurements were made at scattering angles between 20 and 30°; however, a few measurements were made at other angles to confirm the q^{-2} dependence of the relaxation time. The correlation functions of samples above the precipitation point fit well to a single-exponential decay, and measured diffusion coefficients were reproducible to ±2%. The onset of polymer precipitation was signaled by an increase in scattering intensity and a nonexponential correlation function. For reasons explained above, measurements were made at the lowest concentrations possible when the temperature was close to the precipitation point. The minimum practical concentration of polystyrene was a function of molecular weight and ranged from 1.5×10^{-3} g/mL for $M = 50\,000$ to 10^{-5} g/mL for $M = 4.4 \times 10^7$. At the lowest concentrations, long averaging times (up to 16 h) were necessary to obtain reasonable signal-to-noise ratios.

Theoretical Background

A hydrodynamic calculation of the diffusion constant of a polymer molecule in dilute solution was carried out by Kirkwood,[22] who showed that

$$D/kT = (1/6\pi\eta_0)((1/N^2)\sum_{i,j}^{N}{}'\langle R_{ij}^{-1}\rangle) + 1/(N\zeta) \quad (1)$$

D is the diffusion constant, k is Boltzmann's constant, T is the absolute temperature, η_0 is the solvent viscosity, N is the number of statistical chain elements in a single polymer chain, ζ is a segmental friction constant, and R_{ij} is the distance between segment i and segment j. $\sum'$ designates a sum over all pairs i and j except $i = j$, and $\langle\ \rangle$ represents an ensemble average over all polymer molecules in the solution. The final term in eq 1 is small and will be dropped in what follows. A hydrodynamic radius R_H is defined by

$$D = kT/(6\pi\eta_0 R_H) \quad (2)$$

which, when taken together with eq 1, yields

$$R_H^{-1} = (1/N^2)\sum_{i,j}{}'\langle R_{ij}^{-1}\rangle \quad (3a)$$

Note that the radius of gyration of a polymer molecule may be written as

$$R_g^2 = (1/2N^2)\sum_{i,j}\langle R_{ij}^2\rangle \quad (3b)$$

The excluded volume theory, in a mean field approximation, was proposed by Flory for polymer coils expanded in a good solvent. A calculation, similar in spirit, can be developed for a negative excluded volume, using the Flory result. This contains an additional term which becomes significant in the partially collaped coil. This calculation was carried through by Ptitsyn et al.[1] and further analyzed by de Gennes,[3] leading to the result

$$\alpha^5 - \alpha^3 - K_1/\alpha^3 = K_2 N^{1/2}\tau \quad (4a)$$

$$\tau = (T - \Theta)/\Theta \quad (4b)$$

K_1 and K_2 are constants which are independent of molecular weight and T. α was originally defined by Flory to be the ratio of the root mean square end-to-end distances of a polymer chain in a good solvent to a polymer chain in a Θ solvent, $\alpha^2 = \langle R_N^2\rangle/\langle R_N^{0\,2}\rangle$, but α may be considered to be the ratio of any characteristic linear dimension such as R_g/R_g^0 or R_H/R_H^0. The superscript 0 refers to the value at the Θ point. Clearly, eq 4a does not apply at $T = \Theta$; it is intended for temperatures appreciably below the Θ point. If we designate an arbitrary linear measure of the molecule by R, eq 4a at sufficiently large $N^{-1/2}\tau$ yields

$$R \sim N^{3/5}\tau^{1/5} \text{ for } T > \Theta \quad (5a)$$

$$R \sim N^{1/2} \text{ for } T = \Theta \quad (5b)$$

$$R \sim N^{1/3}(-\tau)^{-1/3} \text{ for } T < \Theta \quad (5c)$$

In the development of scaling relationships in dilute polymer solution, Daoud and Jannink[23] show that R is given by (see eq 19 of that paper)

$$R \sim |\tau|^{-1} f(N^{-1}\tau^{-2}) \quad (6)$$

The dominating term of $f(N^{-1}\tau^{-2})$ is $(N\tau^2)^k$. Recognizing from eq 5a through 5c that k takes on the values of $^3/_5$, $^1/_2$, and $^1/_3$ for T greater than, equal to, or less than Θ, respectively, we find that eq 6 yields the same exponents of τ given in eq 5a, 5b, and 5c. It is worthy of note that coil dimensions calculated from the Flory mean field calculation and from the scaling laws of Daoud and Jannink are mutually consistent. Whether or not the mean field values of k are exact, the scaling arguments lead to

$$(R/R_0) \sim (N\tau^2)^k \quad (7)$$

In the asymptotic limit ($N\tau^2$ large) both R_g and R_H should obey the same scaling law. However, when $N\tau^2$ is not sufficiently large, this is not necessarily the case. For

Table I
Characterization of Polystyrene Samples[a]

sample no.	M	M_w/M_n	R_H^0, Å	k_D, mL/g
1	5.0×10^4	≤ 1.06	52	14
2	9.6×10^4	≤ 1.06	73	20
3	2.4×10^5	≤ 1.06	117	27
4	3.9×10^5	≤ 1.06	149	45
5	2.2×10^6	$\leqslant 1.2$	339	70
6	7.2×10^6	≈ 1.1	525	140
7	4.4×10^7	≈ 1.1	1360	

[a] R_H^0 and k_D are measured at 35.4 °C in cyclohexane.

example, the diffusion coefficient and the radius of gyration appear to obey different scaling laws in good solvents. Recently papers by Weill and des Cloizeaux[24] and by Akcasu and Han[25] have interpreted these discrepancies in good solvents by excluded volume theory in terms of the "blob" model of a polymer molecule. The blob model in the dilute solution limit is based on the thesis that excluded volume effects are negligible if the spacing between segments is small. Excluded volume appears as an interaction between blobs, and since the number of blobs is proportional to $N\tau^2$, the same scaling laws as above are obtained. It should be understood that the "blob" is a poetic representation of a gradual effect, and its expression as an abrupt change in chain statistics is a distinct oversimplification.

Asymptotic laws derived for polymers of infinite molecular weight apply in a restricted range for polymer molecules of finite molecular weight, and this range is much broader for the radius of gyration than it is for the hydrodynamic radius. The reason for this is that the statistical weight of long spacings on a polymer molecule is greater in R_g than it is in R_H, a fact which is obvious from the definitions given in eq 3a and 3b. Weill and des Cloizeaux and Akcasu and Han point out that molecular weight dependence of both diffusion constants of polymers in solution and intrinsic viscosities are fully understandable since R_H reaches its asymptotic value in a range of molecular weight higher than that normally studied.

This argument, designed for polymers in a good solvent, also applies when the excluded volume is negative. Short intersegmental spacings remain more or less Gaussian ($R_{ij} \sim |i - j|^{1/2}$), while distances between widely separated segments vary with a lower power of $|i - j|$. Owing to the high statistical weight of short spacings, R_H will be further from the asymptotic limit than R_g at any finite value of molecular weight.

Results

In Table I, molecular weights, a polydispersity index, M_w/M_n, diffusion constants of polystyrene in cyclohexane at the Θ temperature in the zero concentration limit, and the variation of the diffusion constant with concentration at the Θ temperature, k_D, are listed. k_D is defined by

$$D_0^0 = D_c^0(1 + k_D c + O(c^2)) \tag{8}$$

D_c^0 is the diffusion constant at $T = \Theta$ at finite concentration, and D_0^0 is its limiting value at zero concentration. At other temperatures we use the symbols D_c and D_0. Our measurements at $T = \Theta$ are in accord with an earlier study of King et al.[26] The magnitude of k_D is greater at $T < \Theta$ than that found at $T = \Theta$. Measurement of k_D below $T = \Theta$ is difficult because the concentration range is limited. Nevertheless, D_0 is determined accurately since $k_D c$ is small at the concentration measured, ±1% in the best cases and ±2% for the most difficult. Hydrodynamic radii are calculated from eq 2, using diffusion constants in the limit of zero concentration. The viscosity of cyclohexane as a function of temperature was taken from Rossini et al.[27] The results are presented in Figure 1. Changes in R_H with temperature are slight except for substances of high molecular weight. According to scaling laws (eq 6), R_H/R_H^0 is a function of $M\tau^2$ regardless of the molecular weight. The data are plotted as a function of $M\tau^2$ in Figure 2 and exhibit a remarkable consistency for a molecular weight range of three orders of magnitude. Most of the higher values of $M\tau^2$ in Figure 2 relate to high molecular weight samples. This region could not be easily reached for the substances of lower molecular weight since the solution concentration necessary for measurement brought about molecular aggregation and precipitation.

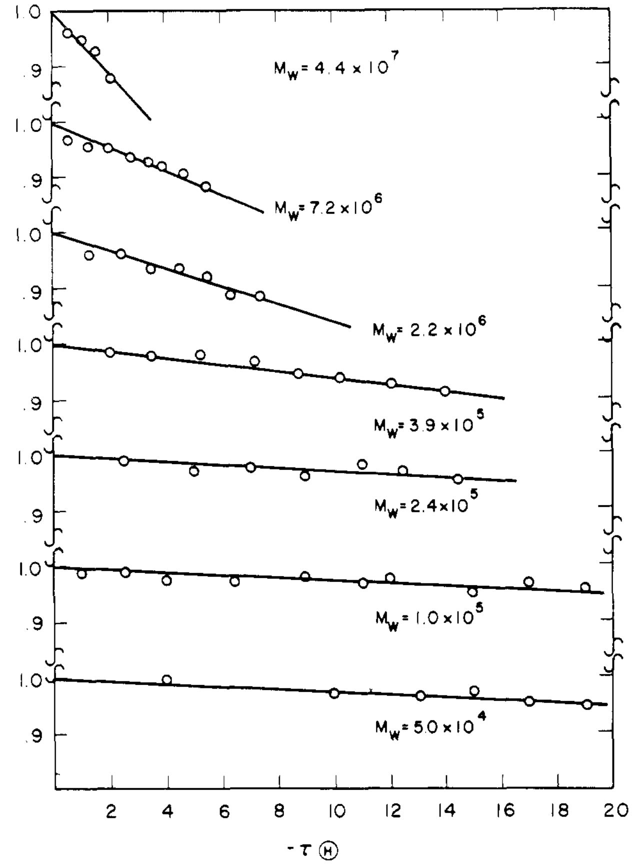

Figure 1. R_H/R_H^0 for polystyrene in cyclohexane as a function of temperature. Measurements are derived from diffusion constants at and below the Θ temperature.

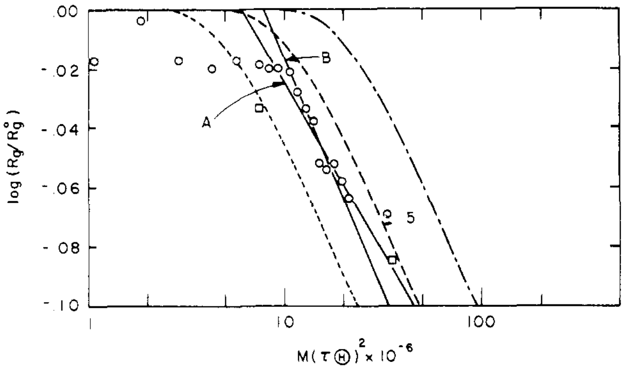

Figure 2. Log (R_H/R_H^0) vs. $M(\tau\Theta)^2$ for $M_w = 5.0 \times 10^4$ (○), 1.0×10^5 (□), 2.4×10^5 (△), 3.9×10^5 (▽), 2.2×10^6 (◇), 7.2×10^6 (●), and 4.4×10^7 (■): (- - -) $\alpha n = 0.25$; (— — —) $\alpha n = 0.5$; (- — -) $\alpha n = 1.0$. The solid line is based on eq 9.

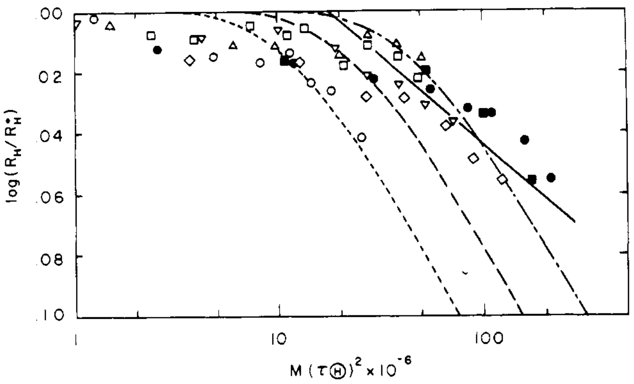

Figure 3. Log (R_g/R_g^0) vs. $M(\tau\Theta)^2$ for $M_w = 2.9 \times 10^4$ (○) (ref 21) and 4.4×10^7 (□) (ref 20): (- - -) $\alpha n = 0.25$; (— — —) $\alpha n = 0.5$; (- — - —) $\alpha n = 1.0$. The solid lines are based on eq 10a and 10b.

A plot of R_g/R_g^0 vs. $M\tau^2$ is shown in Figure 3. This is based on neutron scattering experiments by Nierlich et al.[21] and by light-scattering results of Slagowski et al.[20] All data fall on a smooth curve except for the lowest temperature point of Slagowski et al. which is not plotted.

Taking the straight line in Figure 2 as representative of the hydrodynamic radius of polystyrene in the partially collapsed state and using the polystyrene sample of molecular weight 4.4×10^7 as a reference point we find the equation

$$R_H = 0.273M^{0.446}(-\tau)^{-0.108} \tag{9}$$

A similar result can be obtained for the measurements of R_g. Unfortunately, the data are sparse. Line A is fitted to the data of light scattering ($M = 4.4 \times 10^7$) plus neutron scattering ($M = 2.9 \times 10^4$), and line B is fitted to the neutron scattering experiments only. The reference point of both lines is $R_H^0 = 51.8$ (Table I of ref 21) for the sample of $M = 29\,000$. We find

$$R_g = 0.467M^{0.398}(-\tau)^{-0.204} \text{ for curve A} \tag{10a}$$

$$R_g = 0.589M^{0.348}(-\tau)^{-0.304} \text{ for curve B} \tag{10b}$$

Equations 9, 10a, and 10b only fit the experimental points for $M\tau^2$ sufficiently large. We note that the exponents in eq 10b are close to those derived for the collapsed chain (eq 5), as already has been mentioned by Nierlich et al.[21] Light-scattering and neutron-scattering measurements over a wider range of molecular weight are required to achieve a more accurate determination of the exponents.

It is significant that the exponents of eq 9 show that R_H of the partially collapsed chain deviates less from the Θ state than does R_g. This is exactly what has been found for polymers in good solvents, and it appears that the "blob" model applies satisfactorily for T less than Θ as well. We can derive expressions for R_g/R_g^0 from eq 9 and 25 of ref 25, using $\nu = {}^1/_3$,

$$R_g/R_g^0 = \left[x^2(3 - 2x) + 18x^{1/3}\left(\frac{1 - x^{5/3}}{5} - \frac{1 - x^{8/3}}{8}\right)\right]^{1/2} \tag{11a}$$

$$R_H/R_H^0 = \frac{4}{x^{1/2}}\left[2(3 - x) + 9\left(\frac{x^{-2/3} - 1}{2} - \frac{x^{-2/3} - x}{5}\right)\right]^{-1} \tag{11b}$$

$x = (A\alpha n/M\tau^2)$ where A is the monomer molecular weight, n is the number of monomer units in a statistical segment, and α is related to the binary cluster integral (see eq 6 and ref 25). The product αn is generally treated as an adjustable parameter. The experimental values of R_H/R_H^0 and R_g/R_g^0 are compared to the predictions of eq 11a and 11b in Figures 2 and 3 for different values of αn. As can be seen from these figures, both the radius of gyration and the hydrodynamic radius agree qualitatively with the predictions of the "blob" model for sufficiently high $M\tau^2$. The value for αn for chain contraction is between 0.5 and 1.0, while Akcasu and Han found a value of 4 for chain expansion. This is apparently related to differences in the temperature dependence of the binary cluster integral above and below the Θ temperature.

The diffusion experiments are consistent with a shrinkage of polymer coils below the Θ temperature. The effect is not very large, and the coils are very far from a collapsed globule. It is certainly possible that a coil collapse would occur at lower temperature than we have studied. This would require a much more sensitive experimental method which would yield accurate results at polymer concentrations lower than those we have used.

While this paper has applied the "blob" concept to emphasize that R_g changes more drastically with chain expansion than R_H, this is not a new idea. Stockmayer and Albrecht,[29] in a perturbation theory of excluded volume, showed that R_H expands less than R_g.

A recent analysis of chain statistics above and below $T = \Theta$ has been presented by Sanchez,[30] and he has fit the data of Slagowski et al.[20] to his theory. His method does not distinguish between R_H and R_g as far as we can see.

Conclusions

The decrease of the hydrodynamic radius of polystyrene in cyclohexane with decreasing temperature has been measured for materials varying in molecular weight by three orders of magnitude. These results are in reasonable agreement with scaling laws, with all results fitted to a single master curve. Comparison of the decrease of the hydrodynamic radius with the decrease of the radius of gyration below the Θ temperature shows that changes in R_g are greater than changes in R_H. This is qualitatively in accord with the "blob" model which has been applied to polymer expansion in good solvents by Weill and des Cloizeaux[24] and by Akcasu and Han.[25]

Notes Added in Proof. Nishio et al.[31] have shown that poly(acrylamide) molecules decrease abruptly in size upon increasing the acetone content in an acetone–water mixture. This is similar to the rapid decrease in viscosity of solutions of methacrylic acid in water–methanol solutions observed by Anufrieva et al.[16]

Swislow et al., working at very low polymer concentrations, have observed a coil–globule transition in cyclohexane solutions of polystyrene ($M_w = 2.7 \times 10^7$) below the Θ temperature. The volume fraction of a single polymer molecule within a sphere of radius R_H is 2.7×10^{-3} at the Θ temperature and 4.2×10^{-2} after collapse.

Post and Zimm[33] have developed a model of chain collapse similar to those of Ptitsyn et al.[1] and deGennes[3] which they apply to experimental observations on DNA. A related analysis has also been carried out by Frisch and Fesciyan.[34]

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Chromism in Polydiacetylene Solutions and Crystals

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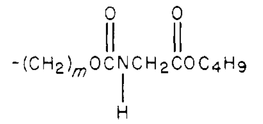
ABSTRACT: A planar–nonplanar conformational transition is reported for two weakly-soluble, urethane-substituted polydiacetylenes. These results strongly support the intramolecular hydrogen-bonding model which has been used to explain this conformational transition for highly soluble polymers of this type. A comparison of the chromism associated with the solution phase conformational transition with the thermochromism observed in crystalline polydiacetylenes suggests that the interplay of intra- and intermolecular interactions is importantly involved in the thermochromic phase changes.

A planar–nonplanar conformation transition has been reported recently[1] for solutions of polydiacetylenes, (=RC—C≡C—CR=), with substituent groups (R) of the form



$$-(CH_2)_mOC(=O)N(H)CH_2C(=O)OC_4H_9$$

where m = 3 (poly3BCMU) or m = 4 (poly4BCMU). These materials are quite soluble in $CHCl_3$, yielding a yellow solution with a lowest energy optical transition (E_0) at ~21 500 cm^{-1}. This E_0 value is considerably blue shifted compared to the normal crystalline value (E_0 ~ 16 000 cm^{-1})[2] due to a nonplanar backbone conformation. This nonplanar conformation probably consists of a statistical distribution of 90° rotations about the single bond in the backbone, which interrupts the backbone conjugation but allows maximum utilization of the entropy content of the R group in the stabilization of the solution phase. On addition of a nonsolvent such as hexane dramatic, reversible color changes occur: yellow → blue ($E_0 = 21\,300 \rightarrow 16\,000$ cm^{-1}) for poly3BCMU and yellow → red ($E_0 = 21\,700 \rightarrow 18\,800$ cm^{-1}) for poly4BCMU. The proposed mechanism for the chromism is based on *intramolecular* hydrogen bonding between the C=O and N—H groups on adjacent urethane substituents. This leads to a planar or near planar backbone configuration, hence the dramatic red shift in the E_0 transition. Strong evidence for this mechanism is provided by infrared spectroscopy.[1,2] The (butoxycarbonyl)methyl group plays no role in this mechanism.

In this paper, we demonstrate that polydiacetylenes with simple urethane substituents of the form $-(CH_2)_mOC(O)NHC_6H_5$ also show the chromic transition. Comparison to crystal spectra[3-5] yields some information on the origin of the different E_0 values for the m = 3 and 4 cases. The relevance of these results to the thermochromic phase changes in polydiacetylene crystals is discussed.

The polydiacetylenes chosen for this investigation were polyTCDU (m = 4) and polyDDU (m = 3). Solutions were prepared by stirring the mixtures at 100 °C in dimethylformamide (DMF) for a few hours. The solutions were then filtered, since there was always an insoluble fraction of roughly 30%. Polymer concentrations of ~10^{-4} mol/L were achieved in this manner (mol refers to mol of polymer repeat units). These solutions were stable with respect to precipitation for at least 6 months. No attempt was made to establish the molecular weights of the dissolved polymer, though it is likely that only the relatively low molecular weight portion of the sample is soluble. Both polymers were soluble to about the same extent in dimethyl sulfoxide. The spectroscopic experiments reported here were limited to the UV–visible portion of the spectrum, since solvent interference and low polymer concentrations prevented meaningful infrared spectroscopy.

Addition of a nonsolvent which is misible in DMF, such as $CHCl_3$ or methanol, produces color changes in an analogous manner to the BCMU polymers. Absorption spectra are shown in Figure 1 for polyDDU in DMF/$CHCl_3$ and in Figure 2 for polyTCDU in DMF/methanol for various volume fractions of DMF in $CHCl_3$ or methanol (V_{DMF}). The V_{DMF} values for the color transitions are independent of polymer concentration. E_0 values are compared in Table I. In the nonplanar conformation, all