Studies of linear polymer dimensions of polystyrene in cyclohexane over a wide range of temperature by intrinsic viscosity

Bahattin M. Baysal*
Department of Chemical Engineering and Polymer Research Center, Boğaziçi University, 80815 Bebek-Istanbul, Turkey

and Nurseli Uyanık
Department of Chemistry, Technical University of Istanbul, 80626 Maslak-Istanbul, Turkey
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Intrinsic viscosities ([η]) of polystyrene solutions in cyclohexane above and below the θ temperature have been measured using a capillary viscometer. The viscosity measurements were performed on five polystyrene samples with molecular weights of 6.3×10^4, 9.0×10^4, 6.0×10^5, 2.8×10^6 and 10×10^6. A smooth and continuous contraction was observed below the θ temperature (34.5°C). The temperature dependence of $[\eta]$ can be represented by a master curve in a $\alpha_\eta^3|\tau|M^{1/2}$ ($\mathrm{g^{1/2}\,mol^{-1/2}}$) *versus* $|\tau|M^{1/2}$ ($\mathrm{g^{1/2}\,mol^{-1/2}}$) plot, where $\alpha_\eta=[\eta(T)]/[\eta(\theta)]^{1/3}$ is a viscosity expansion factor and $\tau=(T-\theta)/T$ is the reduced temperature. A universal plot of reduced viscosity (α_η) *versus* reduced blob parameter (N/N_c) shows the achievement of the collapsed state for the $T<\theta$ region. The prediction of the temperature blob theory is also verified for the $T>\theta$ region.

(Keywords: polystyrene; cyclohexane; intrinsic viscosity; polymer dimension)

INTRODUCTION

The temperature and molecular weight dependence of polymer dimensions and the transition of a flexible polymer chain from a random coil at the θ temperature to a collapsed globule in a poor solvent has attracted a lot of attention over the last two decades. The contraction of the polymeric chain is considered using both classical mean-field theories and other new approaches over a wide range of temperature. However, the nature of the transition of a flexible polymer chain from a Gaussian coil at the θ temperature to a collapsed globule in a poor solvent is still a matter of controversy from the point of view of theoretical as well as experimental results.

There has been extensive experimental information gathered on the dynamic and static properties of chain configuration at and above the θ temperature (at which polymer–segment and solvent attractive and repulsive forces compensate)[1–4]. The transition from random-coil behaviour in the θ state to a globule coil in the collapsed state has been the subject of many studies, particularly over the last decade[5–17].

Recently, Chu *et al.* have studied the transition of polymer dimensions from the θ to the collapse regime for polystyrene/cyclohexane and polystyrene/methyl acetate systems using static and quasi-elastic light scattering techniques as well as intrinsic viscosity measurements of dilute polymer solutions[18–22].

Polymer contraction is enhanced in materials which contain chemical groups on the macromolecule of vastly different polarity. The complete coil–globule transition is observed universally in various natural and synthetic gels as well as in polyacrylamide and several *N*-substituted acrylamide polymers[23–30]. Our objective in the present study is to observe the coil expansion and polymer contraction at above and below the θ temperature, respectively. For this purpose, the intrinsic viscosities of five polystyrene samples were examined over a wide range of temperature around the θ temperature (34.5°C) for this polymer–solvent system. In addition, since intrinsic viscosity of a polymer–solvent pair has been related to the interaction parameter χ in the limit of $v_2=0$, we used our viscosity data to calculate interaction parameters for the polystyrene/cyclohexane system[31].

THEORETICAL BACKGROUND AND EARLIER DEVELOPMENT

Intrinsic viscosity is given by the relationship[32]:

$$[\eta]=\Phi\langle r^2\rangle_0^{3/2}\alpha^3M^{-1} \tag{1}$$

which is applicable to flexible chains having molecular weight, M, of $>\sim10^4$, Φ is the Flory constant and the factor

$$\alpha=(\langle r^2\rangle/\langle r^2\rangle_0)^{1/2} \tag{2}$$

characterizes the extent to which polymer–solvent interactions expand the chain dimensions over their unperturbed values, and is thus unity in a θ solvent.

The viscosity expansion factor is given by the following relationship[33,34]:

$$\alpha_\eta^3=1+1.55z \tag{3}$$

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* To whom correspondence should be addressed

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The parameter z is the one commonly encountered in perturbation theories of the expansion factor, and is given by[35]:

$$z=(3/2\pi)^{3/2}BA^{-3}M^{1/2} \tag{4}$$

were B is related to the interaction parameter χ by:

$$B=\bar{v}^2(1-2\chi)/V_1N_A \tag{5}$$

where $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of solvent, and N_A is Avogadro's number.

It is well established that viscosity measurements performed on solutions under θ conditions can yield information on the unperturbed dimension with the aid of the following relations:

$$[\eta]=[\eta]_\theta\alpha_\eta^3 \tag{6}$$

$$[\eta]_\theta=K_\theta M^{1/2} \tag{7}$$

where $[\eta]$ and $[\eta]_\theta$ represent the intrinsic viscosities in ordinary and θ solvent, respectively. However, since the hydrodynamic radius of polymer chains increases less rapidly than the statistical radius as the excluded volume increases, theoretical considerations related to equations (3)–(5) clearly indicate that the expansion factors given in equations (1) and (6) are not identical, but $\alpha_\eta \leqslant \alpha$ (refs 36 and 37). For practical purposes, in our calculations we have preferred to use the following exponential type of[34,38]:

$$\alpha_\eta^3=\alpha^{2.43} \tag{8}$$

$$\Phi=\Phi_0(\alpha_\eta/\alpha)^3 \tag{9}$$

where[37]

$$\Phi_0=2.87\times10^{21}$$

The classical theoretical calculation is based on the consideration of the smoothed density representation of the polymer chain as a swarm of segments distributed about its centre of mass[32,39]. The temperature dependence of the expansion factor can be obtained from the following Flory equation given for the excluded volume effect[32,37]:

$$\alpha^5-\alpha^3=2C_M(1/2-\chi)M^{1/2} \tag{10}$$

where

$$C_M=(27/2^{5/2}\pi^{3/2})(\bar{v}^2/N_AV_1)(\langle r^2\rangle_0/M)^{-3/2}$$

and $\bar{v}$ is the (partial) specific volume of polymer, V_1 is the molar volume of solvent, χ is a parameter related to the local free energy of the polymer solvent interactions, the original value of the numerical constant has been decreased by one-half as suggested by an exact series expansion for small α values[37,40].

Sanchez proposed a mean field theory for polymer chains with excluded volume and attractive interactions in which the second and all higher order virial coefficients are approximated and retained[41]. By using the Hermans–Overbeek approximation[38,42], he derived the following explicit formula for the temperature dependence of the radius of gyration:

$$\frac{7v_2}{3N}(1-\alpha^2)=\tfrac{1}{2}\left(\frac{\theta}{T}\right)v_2^2+\ln(1-v_2)+v_2 \tag{11}$$

where v_2 is the volume fraction of a chain of N segments with radius of gyration S, and $\alpha=\langle S^2\rangle^{1/2}/\langle S_0^2\rangle^{1/2}$ is the expansion factor. Equation (11) suggests that the chain collapses for $(T/\theta)<1$ and $N\rightarrow\infty$, while $(T/\theta)>1$ requires $\alpha^2>1$, and the Flory form[32] of the expansion factor [equation (10)] is obtained. For the polystyrene/cyclohexane system, by using a very high molecular weight polystyrene ($M_W=4.4\times10^7$), agreement between theory and experiment has been observed[5,41].

Sun *et al.* have also observed the sharp transition of polystyrene ($M_W=2.6\times10^7$) in cyclohexane by monitoring the hydrodynamic radius by means of photon correlation spectroscopy[8]. They also calculated the expansion factor using equation (11) and obtained good agreement between experimental data and the mean field theory predictions[8].

Erman and Flory re-examined the change of dimensions in networks and linear macromolecules in order to find out the requirements for discontinuous collapse through a transition of first order in a poor solvent[17]. For this purpose, they derived the following form of the reduced chemical potential $\Delta\mu_1$ for the diluent in a mixture with chain segments connected to one another either as a coherent network or a single polymer chain

$$\Delta\tilde{\mu}_1=(\chi_1-\tfrac{1}{2})v_2^2+(\chi_2-\tfrac{1}{3})v_2^3+\cdots+(RT)^{-1}(\partial\Delta A_{el}/\partial n_1) \tag{12}$$

where v_2 is the volume fraction of polymer segments, χ_1 and χ_2, ... are functions of temperature and related to the interaction parameter χ by the following empirical relation:

$$\chi=\chi_1+\chi_2v_2+\chi_3v_2^2+\cdots \tag{13}$$

ΔA_{el} is the elastic free energy and n_1 is the number of molecules of the solvent. [In equation (12) the contribution to the chemical potential by the presence of ionic groups on the chains is omitted.] Erman and Flory have calculated the elastic contribution to the reduced chemical potential by relating the elastic free energy to the displacement between the ends of the linear chain molecules. They have also showed that after truncating the series in v_2 at its first (quadratic) term one obtains the classical Flory expression, equation (10), for the temperature dependence of the expansion factor[17].

In another theoretical approach the polymer collapse transition from six-fifths power law for the expanded polymer to two-thirds law for collapsed polymer is expressed utilizing probabilities in the partition function[15].

Recently, Chu *et al.* re-examined the polystyrene/cyclohexane and polystyrene/methyl acetate systems to study the coil-to-globule transition for flexible polymer chains[18,19]. They carefully considered the controversies about the existence and the order of transitions and the experiments providing conflicting results. The transition of the linear polymer dimension from the θ to the collapse regime was studied using light scattering and quasi-elastic light scattering techniques as well as intrinsic viscosity measurements[18–22]. They analysed their experimental results in the framework of the blob theory.

In the temperature blob theory[43,44], a polymer chain of N monomers is viewed as a succession of blobs, each containing N_c monomers. From the static definition of the expansion factors, α_s (of the radius of gyration) and α_h (of the hydrodynamic radius) have the following asymptotic limits:

For $T<\theta$ (poor solvent)

$$\alpha_s=1.161(N/N_c)^{-1/6} \tag{14}$$

$$\alpha_h=1.481(N/N_c)^{-1/6} \tag{15}$$

Table 1 Specification of polystyrene samples

Sample	M_w (g mol^{-1})	M_w/M_n	$[\eta]$[a] (dl g^{-1})
PS1	6.3×10^4	1.04	0.207
PS2	9.0×10^4	1.06	0.248
PS3	6.0×10^5	1.08	0.700
PS4	2.8×10^6	1.20	1.310
PS5	10×10^6	1.20	2.110

[a] In cyclohexane, 34.5°C

Table 2 Intrinsic viscosities (dl g^{-1}) for polystyrene in cyclohexane at various temperatures

	M_w (g mol^{-1})				
T (°C)	10×10^6	2.8×10^6	6.0×10^5	9.0×10^4	6.3×10^4
20.0	0.91	0.85	0.53	0.227	0.189
25.0	0.98	0.90	0.57	0.233	–
26.0	–	–	–	–	0.197
27.0	–	0.92	–	–	–
28.0	1.05	0.95	–	–	–
29.0	1.09	0.98	–	–	–
30.0	1.25	1.02	0.62	0.243	0.206
31.0	1.49	–	–	–	–
32.0	1.72	1.12	–	0.248	0.206
34.5(θ)	2.11	1.31	0.70	0.248	0.207
36.0	–	–	0.72	–	0.209
37.0	–	–	–	0.255	–
38.0	2.47	1.51	0.75	–	–
40.0	–	–	–	0.262	0.214
42.0	2.84	1.65	0.80	–	–
44.5	3.04	1.68	0.83	0.266	0.217
50.0	3.38	1.78	0.88	–	–
55.0	3.73	1.86	0.92	0.277	0.220
60.0	3.97	1.92	0.95	–	–
70.0	4.31	–	–	0.289	–

For $T > \theta$

$$\alpha_s = 0.923(N/N_c)^{0.1} \tag{16}$$

$$\alpha_h = 0.747(N/N_c)^{0.1} \tag{17}$$

The reduced blob parameter (N/N_c) is directly related to an experimentally measurable quantity by the following relation:

$$\frac{N}{N_c} = \frac{\tau^2 M_w}{M_0(AN_1)} \tag{18}$$

where M_0 is the molecular weight of one monomer and N_1 is the number of monomer units in a statistical segment. The prefactor (AN_1) is an adjustable parameter and should be determined empirically by comparison of theory and experiment.

EXPERIMENTAL

Polymers and solvents

Polystyrene samples were used without further fractionation (obtained from Polysciences Inc.). The specifications of the polymer samples used in this study are given in *Table 1*.

Reagent grade cyclohexane and benzene (Fluka AG) were purified by fractional distillation twice.

Viscosity measurements

A precision capillary viscometer (Cannon 50K-319) was used for the intrinsic viscosity measurements. The efflux times for ~1 ml benzene and cyclohexane were 178.0 s (25°C) and 260.25 s (34.5°C), respectively. The time precision was better than ±0.05 s. The viscometer was immersed in a constant temperature bath controlled to ±0.01°C over a temperature range of 20–70°C.

Procedure

The intrinsic viscosities were calculated using the following relation:

$$[\eta] = \lim_{C \to 0} (\eta_{sp}/C) \tag{19}$$

where the specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$, with η and η_0 being the polymer solution viscosity and the solvent viscosity, respectively, and C is the polymer concentration.

Five η_{sp}/C values were determined for the 4×10^{-3}–1×10^{-4} g ml^{-1} concentration range. Intrinsic viscosity values were obtained by least square linear fitting of the experimental data. Experimental $[\eta]$ values have a precision of $\pm 1\%$. For high molecular weight samples (PS3, PS4 and PS5), intrinsic viscosities at 20°C were carried out in a dilute solution regime (7×10^{-5} g ml^{-1}) and calculated using the following approximate relation: $[\eta] = \eta_{sp}/C$. For the highest molecular weight sample used (PS5), the cloud point was observed at only 1°C below the lowest measured temperature (20°C).

RESULTS AND DISCUSSION

The experimental results of intrinsic viscosities in cyclohexane for five polystyrene samples are reported in *Table 2* at various temperatures. *Figure 1* shows the temperature dependence of intrinsic viscosity for the abovementioned two-component system.

Conventional log–log plots for $[\eta]$ as a function of M_w are constructed and are illustrated in *Figure 2*. The plotted points for the cyclohexane solutions at the θ temperature (34.5°C) fall on a straight line and are

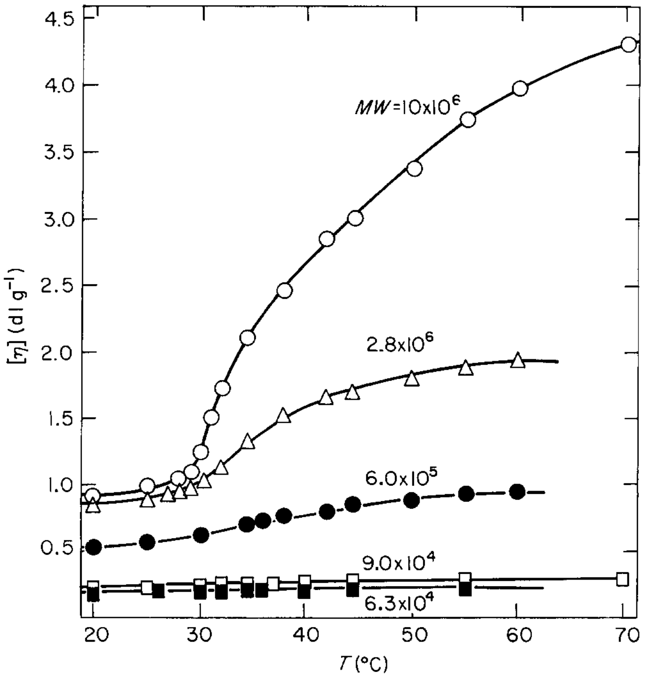

Figure 1 Intrinsic viscosity $[\eta]$ *versus* temperature for polystyrene in cyclohexane solutions. The polymers are identified by their molecular weights

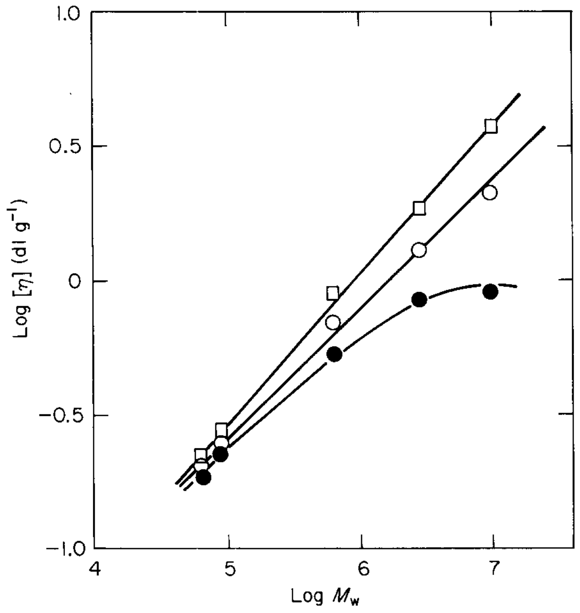

Figure 2 Relation between intrinsic viscosity $[\eta]$ and weight-average molecular weight M_w for polystyrene in cyclohexane. Viscosity data at: (○) the θ temperature (34.5°C); (□) 55°C; (●) 20°C

represented by the equation:

$$[\eta]_\theta = 9.12 \times 10^{-4} M_w^{0.48} \qquad (20)$$

Equation (20) is in agreement with the zero shear rate intrinsic viscosity results and combined literature data in cyclohexane at 34.5°C[45]. The data points for the same solutions at 55°C also follow a straight line which can be represented by the equation:

$$[\eta] = 4.63 \times 10^{-4} M_w^{0.56} \qquad (21)$$

The above value of $[\eta]$ in cyclohexane is slightly different than the reported[1] value of $2.30 \times 10^{-4} M_w^{0.608}$ in the same solvent at 44.5°C. Equation (21) indicates that cyclohexane is a slightly better solvent at 55°C for polystyrene compared to θ conditions. The poor solvent regime of cyclohexane at 20°C is illustrated by the downward bending of the log $[\eta]$ *versus* log M_w plot for polystyrene samples having molecular weights of $>6.0 \times 10^5$.

T<θ: contraction of a polymer chain

In *Figure 3*, the theoretical and experimental results for the temperature dependence of the dimensions of linear polystyrene chains in cyclohexane are presented. The theoretical values of the mean-squared linear expansion α^2 for polystyrene chains having molecular weight of 10×10^6 were calculated from two theoretical approaches:

(1) The predictions of a mean field theory based on the Hermans–Overbeek approximation were evaluated from equation (11)[41,42] and are illustrated in *Figure 3*. In an alternative evaluation of equation (10), since the main interaction between segments involves the large phenyl group side chains for polystyrene, the entropic change associated with segment–segment interactions is considered. For this calculation the following relation was used, by expanding the logarithmic term and truncating the higher terms in equation (10)[8]:

$$\frac{14}{3N}(1-\alpha^2) = \sigma\left(\frac{\theta}{T} - 1\right)v_2^2 - \tfrac{2}{3}v_2^3 \qquad (22)$$

where v_2 is the volume fraction of a chain of N segments, the expansion factor $\alpha = (v_\theta/v_2)^{1/3}$ and $\sigma = 1 - \Delta S/k_B$. For the totally collapsed state $\alpha_{\min} = v_\theta^{1/3}$. The dependence of N and $\alpha_{\min}$ on molecular weight is expressed as $9.6 \times 10^{-4} M_w$ and $2.41 M_w^{-1/6}$, respectively, and $\sigma = 4$ for this system[8]. The prediction of equation (22) is also plotted in *Figure 3* and depicted as solid curves for polystyrene chains in cyclohexane having molecular weights of 10×10^6 and 9×10^4 g mol^{-1}.

(2) The predictions of α^2 based on the reduced chemical potential for the diluent were carried out using the following relation[17]:

$$\Delta\tilde{\mu}_1 = 0 = (\chi_1 - \tfrac{1}{2})v_2^2 + (\chi_2 - \tfrac{1}{3})v_2^3 + \frac{1}{x}[(v_2^0)^{2/3}v_2^{1/3} - v_2] \qquad (23)$$

where, in addition to the abovementioned definitions, x represents the number of segments in the linear molecule and $v_2 = v_2^0\alpha^{-3}$ in the perturbed state. The last term in equation (23) was obtained by differentiation of the ΔA_{el} expression by relating the elastic free energy of a network to the displacement between the ends of a linear chain molecule[17]. χ_1 and χ_2 were calculated according to the equation of state theory for a binary mixture of solvent and polymer for each temperature. Parameters were obtained from various references[17,46,47]. Necessary adjustments were performed in order to bring the value of α to unity at $\theta = 34.5$°C. The number of segments in the polystyrene molecule was calculated as $x = (M_w/104) \times 2$. The value of v_2^0 was obtained from the relation $v_2^0 = 3/(4\pi\rho_e^3 P x^{1/2})$, where the dimensionless parameter P and the constant of proportionality ρ_e are taken as 1.5 and 2/3, respectively. Equation (23) was solved for v_2

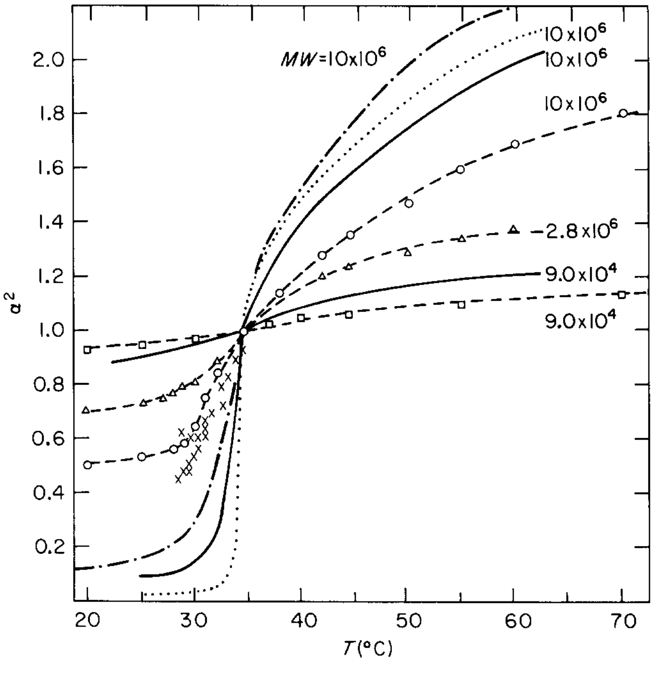

Figure 3 Comparison of theoretical and experimental values of the expansion factor α^2. Theoretical curves calculated from: (——) equation (22)[8]; (···) equation (23)[17]; (–·) equation (11)[41]. Experimental expansion factor of intrinsic viscosity for: (○) $M_w = 10 \times 10^6$; (△) $M_w = 2.8 \times 10^6$; (□) $M_w = 9.0 \times 10^4$. Crosses denote intrinsic viscosity data from reference 22. The broken lines for the experimental points are to guide the eye. For experimental points, the ordinate denotes $\alpha_\eta^{6/2.43}$ (see text)

and α^2 values were obtained as $\alpha^2 = (v_2^0/v_2)^{2/3}$ for each temperature. In *Figure 3*, the calculated theoretical curve of the temperature dependence of the mean-squared linear expansion of polystyrene in cyclohexane from equation (23) is illustrated as a dotted line.

The ordinate in *Figure 3*, α^2, denotes the mean-squared linear expansion factor [equation (2)], whereas experimental α_η^3 values were calculated from equation (6). In order to make a proper comparison, experimental values of the expansion factor were calculated by considering equation (8). That means that for experimental points the ordinate in *Figure 3* denotes $\alpha_\eta^{6/2.43}$. (In *Figure 3*, experimental data points for PS1 and PS3 are omitted for the sake of clarity.)

Table 3 Expansion factors of three polystyrene samples in cyclohexane from the θ temperature (34.5°C) to the collapsed regime at 20°C

T(°C)	α_η^3	$\lvert\tau\rvert M^{1/2}$	$\alpha_\eta^3\lvert\tau\rvert M^{1/2}$	N/N_c	$\alpha_\eta(N/N_c)^{1/6}$
		$M_w = 10 \times 10^6\,\mathrm{g\,mol^{-1}}$			
20.0	0.430[a]	156	67.1	116	1.67
25.0	0.467[a]	101	47.2	48.1	1.48
28.0	0.497[a]	68.2	33.9	22.1	1.33
29.0	0.518	57.6	29.8	15.7	1.27
30.0	0.592	46.9	27.8	10.4	1.24
31.0	0.709	36.4	25.8	6.28	1.21
32.0	0.817	25.9	21.2	3.18	1.13
34.5	1.00	0	0	–	–
		$M_w = 2.8 \times 10^6\,\mathrm{g\,mol^{-1}}$			
20.0	0.653[a]	82.8	54.1	32.4	1.55
25.0	0.687[a]	53.3	36.6	13.5	1.36
27.0	0.707	41.8	29.6	8.28	1.27
28.0	0.726	36.1	26.2	6.18	1.22
29.0	0.751	30.5	22.9	4.39	1.16
30.0	0.777	24.8	19.3	2.92	1.10
32.0	0.859	13.7	11.8	0.89	0.932
34.5	1.00	0	0	–	–
		$M_w = 6.0 \times 10^5\,\mathrm{g\,mol^{-1}}$			
20.0	0.755	38.3	28.9	6.95	1.26
25.0	0.814	24.7	20.1	2.88	1.11
30.0	0.881	11.5	10.1	0.63	0.887

[a] Possibility of coalescence

All of the abovementioned theoretical approaches predict that the collapse of a randomly coiled linear macromolecule in a poor solvent should occur[8,17,41] in this binary system over a range of ~2–3°C for a molecular weight of ~ 10 × 10⁶. Experimental data based on the viscosity measurements exhibit a continuous rather than a discrete transition even for a polystyrene sample having a molecular weight of 10 × 10⁶.

The contraction of the polystyrene coil will take place between the θ region and the coexistence curve where phase separation will take place[21]. We used dilute solutions to measure the variations of the radius of a single coil in a sufficiently large temperature range. For finite concentrations, single chain contraction and interpenetration of different chains are two competitive mechanisms before phase separation. In this study, the intrinsic viscosity measurements were always carried out in completely clear solutions except for the viscosity run which was done at 20°C using the polystyrene sample PS5 with a molecular weight of 10 × 10⁶. For this run, coalescence was observed if the temperature was decreased to 19°C.

Data for the scaled reduced temperature and scaled expansion factor of intrinsic viscosity are given in *Table 3* for three polystyrene samples having molecular weights over 6.0 × 10⁵. *Figure 4* shows the variation $\alpha_\eta^3|\tau|M_w^{1/2}$ of intrinsic viscosity with respect to the scaled reduced temperature $|\tau|M_w^{1/2}$. Literature values of intrinsic viscosity for the same system are also plotted for comparison[22]. $\alpha_\eta^3 = [\eta]_T/[\eta]_\theta$, and the collapsed state was observed as a plateau region in *Figure 4*. In the range $0 < |\tau|M^{1/2} < 10$ there exists a θ regime with the slope of $\alpha_\eta^3 \sim 1$ where the polymer chains remain essentially unperturbed. A

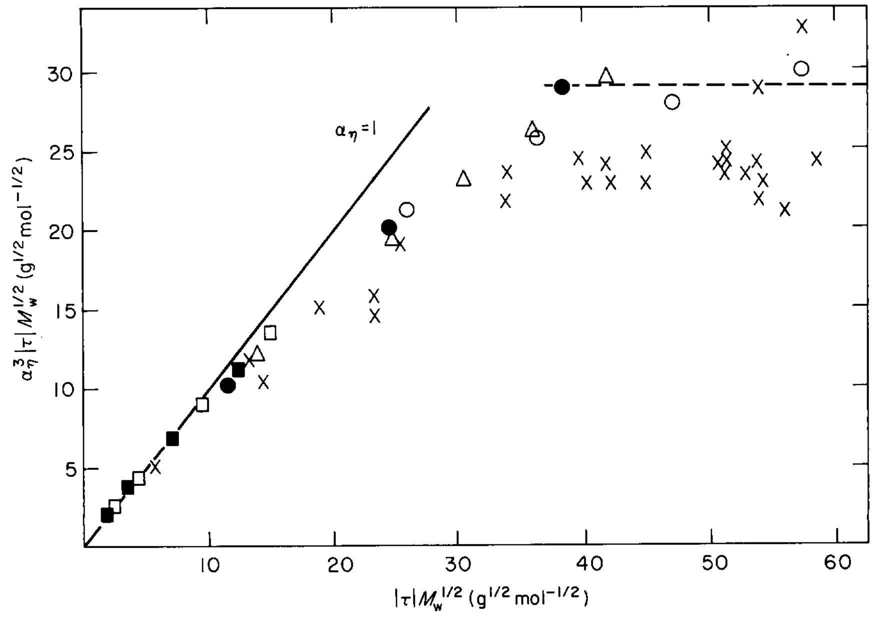

Figure 4 Variation of the scaled expansion factors $\alpha_\eta^3|\tau|M_w^{1/2}$ of viscosity as a function of scaled reduced temperature $|\tau|M_w^{1/2}$. The value of $\alpha_\eta^3|\tau|M_w^{1/2}$ at the asymptotic plateau region (– – –) is 29.0 g$^{1/2}$ mol$^{-1/2}$. The polymers are identified in *Figure 1*. Data is related to $T < \theta$ region. The scaled curve was obtained by using polystyrene with different molecular weights and at different concentrations

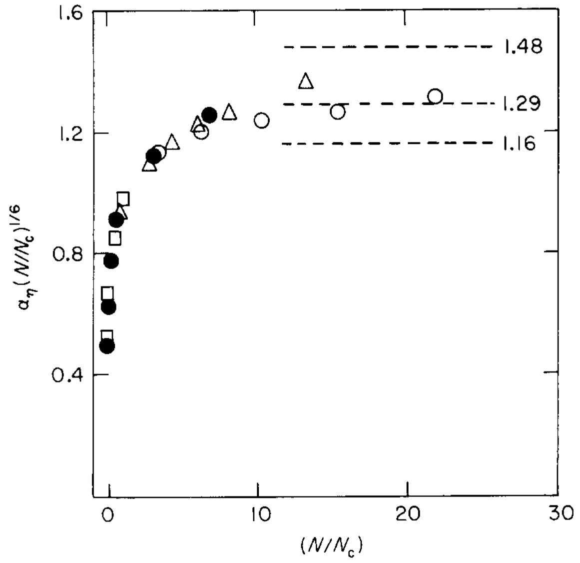

Figure 5 Universal plot of the reduced expansion factor $\alpha_\eta(N/N_c)^{1/6}$ as a function of the reduced blob parameter (N/N_c). The asymptotic plateau values reached by α_s $(=1.16)$ and α_h $(=1.48)$ are denoted by broken lines. The polymeric samples are identified in *Figure 1*

crossover behaviour was observed[18,22] between the θ regime and the collapsed regime with $10<|\tau|M^{1/2}<35$.

Our viscosity data are essentially in agreement with those reported by Chu *et al.*[22] and Perzynski *et al.*[14]. However, we determined a plateau value of $29.0\ \mathrm{g}^{1/2}\ \mathrm{mol}^{-1/2}$ instead of the reported literature values of 24.1 (ref. 22) and 27.0 (ref. 14).

In *Figure 4* some of our viscosity data have been excluded (see *Table 3*) since they crossed the coexistence curve in our reported concentration range[21,22].

We used the experimental values $|\tau|M^{1/2}>38$ (the beginning of the collapse regime) to compute the average plateau value. The polystyrene chains contracted to ~75% of the unperturbed θ state by using conventional intrinsic viscosity measurements.

Extensive experimental work carried out on polystyrene chains shows that the following relation:

$$\alpha_\eta^3=\alpha_s^2\alpha_h \tag{24}$$

between the definitions of the various expansion factors is valid[13,14,22,48]. By combining equations (14), (15) and (24) the following relation is obtained for the viscosity expansion factor:

$$\alpha_\eta=1.259(N/N_c) \tag{25}$$

Considering the experimental results based on intrinsic viscosities in the collapsed regime, $\alpha_\eta^3|\tau|M^{1/2}=29.0$, and the expectation of equation (25), we obtain:

$$\frac{N}{N_c}=\frac{\tau^2 M}{104(2.03)} \tag{26}$$

where $M_0=104$ is the molecular weight of styrene and the prefactor (AN_1) in equation (18), which may depend on polymer flexibility, is 2.03. The calculated values of the reduced blob parameters are included in *Table 3*.

Figure 5 shows a universal plot of the reduced expansion factor $\alpha_\eta(N/N_c)^{1/6}$ *versus* reduced blob size (N/N_c). All of our experimental data except those points in the coexistence curve could be represented by one master curve. The universality of polymer coil contraction in the coil-to-globule transition has been demonstrated by other workers[6,13,14,18–22].

Literature results of asymptotic collapse values of static size (α_s) and hydrodynamic size (α_h) predicted by equations (14) and (15), respectively, are represented by broken lines[18,19,43]. Our asymptotic value (1.29) of viscosity size (α_η) is a little higher compared to the reported literature value (1.23)[22]. However, it is in agreement with blob theory prediction with $\alpha_\eta^3=\alpha_s^2\alpha_h=2.00$, and a plateau value of 26 for $\alpha_\eta^3|\tau|M_w^{1/2}$.

$T>\theta$: crossover region from θ to good solvent conditions

The variation of the expansion factor as a function of temperature in the crossover region $(T>\theta)$ for linear polystyrene chains in cyclohexane which shows a progressive change from Gaussian to excluded-volume behaviour is also plotted in *Figure 3*. It will be seen that theoretical predictions[8,17,41] of the expansion factor are not in agreement with experimental results.

The values of the expansion factor and the blob parameter of polystyrene samples in cyclohexane above the θ temperature are given in *Table 4*. The blob parameters for the $T>\theta$ region are calculated from equation (18) using the value of the prefactor[12,43] $(AN_1)=4$. *Figure 6* shows a plot of $\alpha_\eta(N/N_c)^{-1/10}$ as a function of (N/N_c). The asymptotic limit is reached for large (N/N_c) values. However, the experimental value is found to be 0.773 which is somewhat higher than the theoretical value of 0.747 predicted for hydrodynamic size by equation (17)[43].

The thermodynamic interaction parameters χ_1 and χ_2 were evaluated from intrinsic viscosity measurements given in *Table 2* in the temperature range of 20–60°C and the results are reported in detail elsewhere[49].

In conclusion, we have found that the intrinsic viscosity measurement is sensitive enough to observe the contraction and the collapse of a polymer in solution. We have shown that our viscosity measurements were reproducible even without working in $\mu\mathrm{g\ ml}^{-1}$ concentrations

Table 4 Expansion factors of three polystyrene samples in cyclohexane above the θ temperature

T (°C)	α_η	N/N_c	$\alpha_\eta(N/N_c)^{-1/10}$
		$M_w=10\times10^6\ \mathrm{g\ mol}^{-1}$	
38.0	1.06	3.04	0.948
42.0	1.11	13.6	0.855
44.5	1.13	23.8	0.823
50.0	1.17	55.3	0.783
55.0	1.21	93.8	0.768
60.0	1.24	141	0.756
		$M_w=2.8\times10^6\ \mathrm{g\ mol}^{-1}$	
38.0	1.05	0.852	1.07
42.0	1.08	3.81	0.945
44.5	1.09	6.67	0.901
50.0	1.11	15.5	0.844
55.0	1.13	26.3	0.815
60.0	1.14	39.4	0.790
		$M_w=6.0\times10^5\ \mathrm{g\ mol}^{-1}$	
36.0	1.01	0.034	1.42
38.0	1.02	0.183	1.21
42.0	1.05	0.817	1.07
44.5	1.06	1.43	1.02
50.0	1.08	3.32	0.958
55.0	1.10	5.63	0.925
60.0	1.11	8.45	0.897

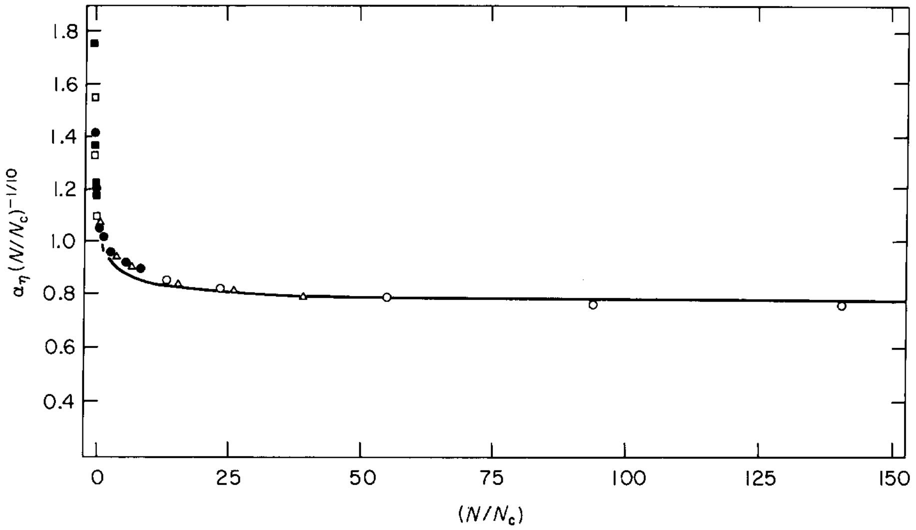

Figure 6 Plot of $\alpha_\eta(N/N_c)^{-1/10}$ of intrinsic viscosity as a function of the reduced blob parameter (N/N_c). The polymeric samples are identified in *Figure 1*. The solid curve corresponds to the blob theory by Akçasu and Han[43]

as in reference 22. In addition, experimental results have been presented for the $T > \theta$ and $T < \theta$ regions, and these have been compared with the results of existing theoretical calculations[8,17,41,43].

After this work was ready for submission, a new theory was offered by Birshtein *et al.* for coil–globule type transitions in polymers[50,51]. A comparison of our existing data together with additional experimental results progressing close to the θ temperature with recent theoretical predictions will be the subject of our next work.

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