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A study on the transition of linear polymer dimension from theta to collapsed regime by intrinsic viscosity measurement for poly(ethyl methacrylate) in isopropyl alcohol

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The intrinsic viscosity of poly(ethyl methacrylate) in isopropyl alcohol (propan-2-ol) around the theta (θ) temperature was measured using a capillary viscometer. Contraction and collapse were observed below the θ temperature. Because of experimental difficulties around the cloud point, mathematically curve-fitted experimental points were obtained instead of experimental data at lower temperatures. The temperature dependence of the intrinsic viscosity can be represented by a master curve in a plot of $\alpha_\eta^3|\tau|\bar{M}_w^{1/2}$ ($g^{1/2}\,mol^{-1/2}$) vs. $|\tau|\bar{M}_w^{1/2}$ ($g^{1/2}\,mol^{-1/2}$), where $\alpha_\eta = ([\eta]_T/[\eta]_\theta)^{1/3}$ is the viscosity expansion factor and $\tau = (T-\theta)/T$ is the reduced temperature. A universal plot of reduced viscosity vs. reduced blob parameter (N/N_c) shows the attainment of the collapsed state below the θ temperature. The results in this work have been compared with previously published results.

(Keywords: poly(ethyl methacrylate); intrinsic viscosity; polymer dimension)

INTRODUCTION

The average dimension and conformation of a polymer chain in solution vary with the nature of the polymer and the solvent quality[1]. In a good solvent, the polymer chain expands due to repulsive intramolecular interactions[2,3]. The transition of a flexible polymer chain from random-coil behaviour at the theta (θ) temperature to a collapsed globule at lower temperatures occurs in a poor solvent[4–13]. However, in many polymer–solvent systems, phase separation occurs not only below the upper critical solution temperature (*UCST*) but also above the lower critical solution temperature (*LCST*), which often appears near the gas–liquid critical temperature of the solvent[14,15].

Many experimental results related to the collapsed regime based on static and hydrodynamic properties of polymer solutions, especially using polystyrene as the polymer and cyclohexane as the solvent, have been reported[16–22]. The coil–globule transition is observed in various natural and synthetic gels as well as in polyacrylamide polymers[23–30].

Recently, the author has reported the thermodynamic interaction parameters of poly(ethyl methacrylate)–isopropyl alcohol and the temperature coefficient of the dipole moment of poly(ethyl methacrylate) in different solvents[31,32].

The aim of the present study is to observe the coil expansion around the θ temperature and polymer contraction at temperatures below the θ temperature ($\theta = 36.9°C$) of the poly(ethyl methacrylate) (PEMA) chain in isopropyl alcohol (propan-2-ol, IPA). The results of this work were compared with previously published results. For this purpose, the intrinsic viscosities $[\eta]$ of a PEMA sample were determined over a wide temperature range around the θ temperature in IPA, which is a θ solvent for this polymer at 36.9°C. Because of experimental difficulties around the cloud point, experiments for the PEMA–IPA pair at lower temperatures could not be performed. Therefore, mathematically curve-fitted experimental points were obtained instead of experimental data at lower temperature.

THEORETICAL BACKGROUND

Theoretical studies show that, in order to describe the collapsed state of a single polymer chain correctly, not only intramolecular interactions but also intermolecular interactions must be taken into account near to and below the θ temperature[24,33,34]. The expansion factor α is related to a chain dimension R as $\alpha = R(T)/R(\theta)$, where R can be either the hydrodynamic radius R_h or the radius of gyration R_g. The intrinsic viscosity expansion factor is given by:

$$\alpha_\eta^3 = [\eta]_T/[\eta]_\theta \qquad (1)$$

where $[\eta]_T$ and $[\eta]_\theta$ represent the intrinsic viscosities in ordinary and θ solvents, respectively.

In the past few years, it has been shown in several works[20–22] that the temperature dependence of intrinsic viscosity can be represented by a master curve in a plot of $\alpha^3|\tau|\bar{M}_w^{1/2}$ *versus* $|\tau|\bar{M}_w^{1/2}$, where $\tau=(T-\theta)/T$ is the reduced temperature and $\bar{M}_w$ is the weight-average molecular weight.

According to the temperature blob theory[35,36], the expansion factors α_s (radius of gyration) and α_h (hydrodynamic radius) have the following asymptotic limits in the collapsed regime, for $T<\theta$:

$$\alpha_s = 1.161(N/N_c)^{-1/6} \qquad (2)$$

$$\alpha_h = 1.481(N/N_c)^{-1/6} \qquad (3)$$

where (N/N_c) is the reduced blob parameter. The value of α_η is between α_s and α_h. Additional experimental work carried out on polystyrene shows that the relation:

$$\alpha_\eta^3 = \alpha_g^2\alpha_h \qquad (4)$$

is valid between the various expansion factors[9,20,22,37]. Combination of equations (2), (3) and (4) yields the following equation for the viscosity expansion factor:

$$\alpha_\eta = 1.259(N/N_c)^{-1/6} \qquad (5)$$

On the basis of the temperature blob theory[38], a polymer chain of N monomers is viewed as a succession of blobs, each containing N_c monomers. The ratio (N/N_c) is directly related to experimentally measurable quantities and given by the following equation[37]:

$$\frac{N}{N_c} = \frac{\tau^2\bar{M}_w}{M_0(A^*N_1)} \qquad (6)$$

where M_0 is the molecular weight of one monomer and N_1 is the number of monomer units in a statistical segment. A^*N_1 is a prefactor that depends on the nature of the solvent and monomer structure but is independent of the molecular weight of the polymer chain. The prefactor (A^*N_1) is an adjustable parameter that can be defined empirically from a comparison of theory and experiment[37]. Combination of equations (5) and (6) yields an equation that can be written as:

$$(A^*N_1) = h^2/(3.98M_0) \qquad (7)$$

In the collapsed regime, we can set the plateau height to be h in a plot of $\alpha^3|\tau|\bar{M}_w^{1/2}$ *versus* $|\tau|\bar{M}_w^{1/2}$.

EXPERIMENTAL

Poly(ethyl methacrylate) (PEMA) was obtained from Polysciences. The molecular weight ($\bar{M}_w$) was determined as 2.7×10^5. The molecular-weight distribution was found as 1.7 using a g.p.c. method. Isopropyl alcohol (IPA), a θ solvent of PEMA, was purified by fractional distillation twice. An Ubbelohde-type capillary viscometer was used for intrinsic viscosity measurements. The viscometer was immersed in a constant-temperature bath controlled to ±0.005°C over a temperature range of 30.5–42°C.

Intrinsic viscosities were determined using the following equation:

$$[\eta] = \lim_{c\to 0}(\eta_{sp}/c) \qquad (8)$$

where $\eta_{sp}=(\eta-\eta_0)/\eta_0$ is the specific viscosity, η and η_0 are the polymer solution viscosity and solvent viscosity, respectively, and c is the polymer concentration. Nine η_{sp}/c values around the θ point were defined for initial concentrations of PEMA from 1×10^{-3} to $3\times10^{-3}\,\mathrm{g\,ml^{-1}}$. Intrinsic viscosity values were calculated by least-squares linear fitting of the experimental data. Details of the experimental procedure were given in ref. 32. To study the PEMA–IPA system at sufficiently low temperature, intrinsic viscosities over a temperature range of 33–30°C (per 0.5°C) were measured in the dilute solution regime ($c<9\times10^{-5}\,\mathrm{g\,ml^{-1}}$) and determined using the following approximation: $[\eta]=\eta_{sp}/c$. The cloud point was observed to start at 30.5°C.

RESULTS AND DISCUSSION

Experimental results of intrinsic viscosities of a PEMA sample at various temperatures are given in *Table 1*. In *Figure 1*, the expansion factor α, defined in terms of intrinsic viscosities in equation (1), is plotted again T/θ for PEMA in IPA solution. Continuous contraction and collapse of PEMA chains in IPA at temperatures below the θ state can be clearly observed from *Figure 1*. Since the cloud point of the polymer was observed at a temperature of 30.5°C, accurate measurement was possible up to 31°C.

Chu and coworkers have studied the transition of a

Table 1 Intrinsic viscosities of PEMA in IPA around the θ temperature (36.9°C)

T (°C)	$[\eta]$ (dl g^{-1})	α
30.5[a]	0.165	0.827
31	0.158	0.812
31.5	0.166	0.825
32	0.161	0.816
32.5	0.166	0.826
33	0.185	0.856
34	0.210	0.892
35	0.240	0.933
36	0.267	0.967
36.5	0.273	0.974
36.9	0.295	1.000
38	0.292	1.000
40	0.302	1.007
42	0.309	1.015

[a] Cloud point was observed to start at this value

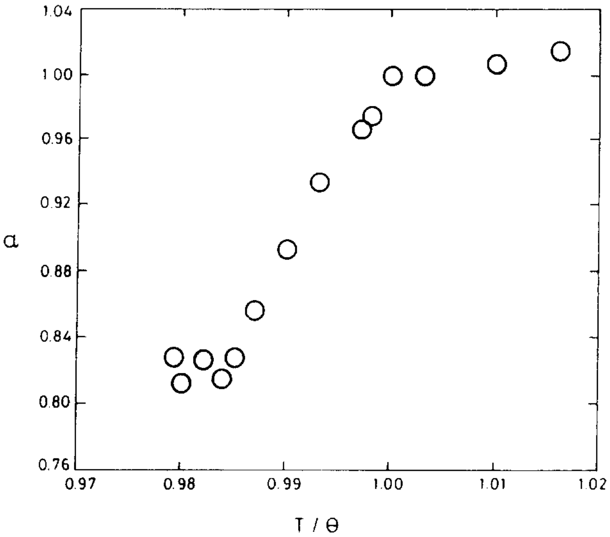

Figure 1 The experimental values of expansion factor *versus* temperature for PEMA sample in IPA

polymer dimension from θ to collapsed state for polystyrene–cyclohexane (PS–CH) and polystyrene–methyl acetate (PS–MA) using light scattering techniques as well as intrinsic viscosity measurements of dilute polymer solutions[16–20]. I observed that all of the master curves in plots of $\alpha^3|\tau|\bar{M}^{1/2}$ ($g^{1/2}\,mol^{-1/2}$) vs. $|\tau|\bar{M}_w^{1/2}$ ($g^{1/2}\,mol^{-1/2}$), which represent the temperature dependence of the expansion factor, can be approximated by a polynomial expression given by:

$$f(x) = a_0 + ax_1 + \cdots + a_n x_n \qquad (9)$$

There is increasing difficulty and error at very low temperatures and very low concentrations. Therefore, a suitable curve to find the asymptotic plateau was fitted to experimental results of PEMA solution in IPA using the polynomial approximation given in equation (7).

As an example, the experimental data given in ref. 20 and a fitting curve for the PS–CH system are shown in *Figure 2*. The polynomial coefficients are given in *Table 2* for some polymer–solvent pairs. The asymptotic plateau values of fitting curves using polynomial coefficients in *Table 2* were found to be almost the same as those obtained from the results of experimental data in refs. 20 and 16. The asymptotic plateau value calculated from the fitting curve of experimental data in ref. 20 is found to be 24.4, as shown in *Figure 2*. Expansion factors of PEMA in IPA at 30.5–28.5°C were calculated using the polynomial coefficients in *Table 2*.

Table 2 Polynomial coefficients for several polymer–solvent systems

Degree	PS–CH[20]	PS–MA[17]	PEMA–IPA
0	0.0659868	0.186030	0.128898
1	0.883181	0.849984	0.806714
2	2.16129×10^{-3}	1.14912×10^{-3}	−0.02970065
3	-3.68507×10^{-4}	-4.52107×10^{-5}	–
4	3.32131×10^{-6}	1.37241×10^{-5}	–

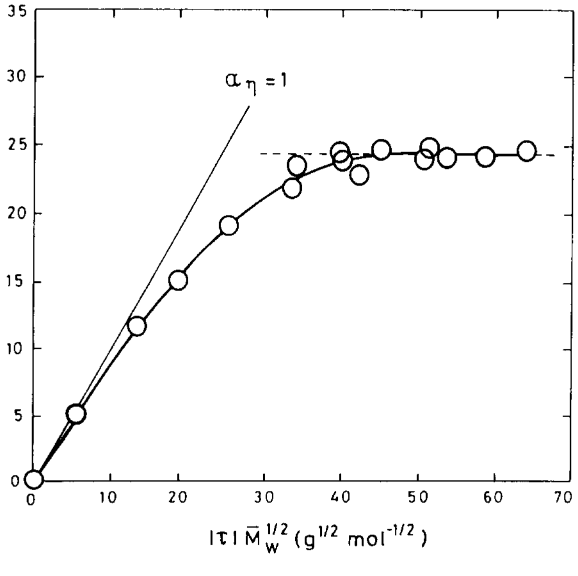

Figure 2 Plot of the scaled expansion factors $\alpha_\eta^3|\tau|\bar{M}_w^{1/2}$ of viscosity as a function of scaled reduced temperature $|\tau|\bar{M}_w^{1/2}$ for PS–CH data from ref. 20. The asymptotic plateau region is denoted by a broken line. In this region the $\alpha_\eta^3|\tau|\bar{M}_w^{1/2}$ value is $\sim 24.4\,g^{1/2}\,mol^{-1/2}$. The theoretical curve is denoted by a full line

Table 3 Expansion factors of PEMA in IPA around the θ temperature[a]

T(°C)	α^3	$\lvert\tau\rvert\bar{M}_w^{1/2}$	$\alpha_\eta^3\lvert\tau\rvert\bar{M}_w^{1/2}$	(N/N_c)	$\alpha_\eta(N/N_c)^{1/6}$
*28.5	0.385	14.47	5.58	27.43	1.26
*29	0.413	13.56	5.60	24.07	1.26
*29.5	0.440	12.67	5.58	21.04	1.26
*30	0.462	11.95	5.52	18.69	1.25
*30.5	0.492	10.91	5.39	15.60	1.25
30.5	0.566	10.91	6.18	15.60	1.30
31	0.536	10.08	5.41	13.30	1.25
31.5	0.562	9.19	5.16	11.07	1.23
32	0.545	8.31	4.53	9.04	1.18
32.5	0.565	7.48	4.22	7.32	1.15
33	0.628	6.59	4.14	5.70	1.14
34	0.711	4.90	3.49	3.14	1.08
35	0.813	3.20	2.60	1.34	0.98
36	0.905	1.51	1.16	0.30	0.79
36.5	0.925	0.67	0.62	0.06	0.61
36.9	1.000	0.0	0.0	–	–
38	1.003	–	–	0.40	0.90
40	1.024	–	–	1.75	1.11
42	1.047	–	–	8.48	1.45

[a] Values indicated with asterisk (*) obtained from fitting curve

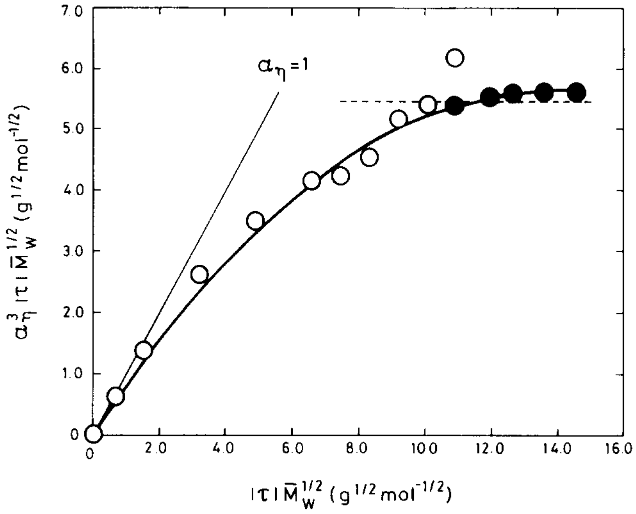

Figure 3 Plot of the scaled expansion factors $\alpha_\eta^3|\tau|\bar{M}_w^{1/2}$ of viscosity as a function of scaled reduced temperature $|\tau|\bar{M}_w^{1/2}$ for PEMA in IPA: (○) experimental results, (●) theoretical results. Asymptotic plateau region, which is denoted by a broken line, is $\alpha_\eta^3|\tau|\bar{M}_w^{1/2} \simeq 5.5\,g^{1/2}\,mol^{-1/2}$. The theoretical curve is denoted by a full line

Results for the scaled reduced temperature $|\tau|\bar{M}_w^{1/2}$ and scaled expansion factor $\alpha_\eta^3|\tau|\bar{M}_w^{1/2}$ obtained from intrinsic viscosity measurements of PEMA in IPA are collected in *Table 3*. In addition, calculations at lower temperature were performed by using the polynomial equation. In the same table, calculated $\alpha_\eta(N/N_c)^{1/6}$ values in the region not far from the lowest experimental point are indicated by asterisks.

Figure 3 shows the variation of scaled expansion factor of intrinsic viscosity with scaled reduced temperature of the PEMA–IPA system. As can be seen clearly in *Figure 3*, the behaviour of the polymer chain is far away from the unperturbed state line ($\alpha_\eta = 1$). In the PEMA sample studied in this work, the universality of polymer coil contraction in the coil–globule transition is also present as in the case of PS–CH[19–21] and PS–MA systems[17]. The collapsed regime started at about $|\tau|M_w^{1/2} =$

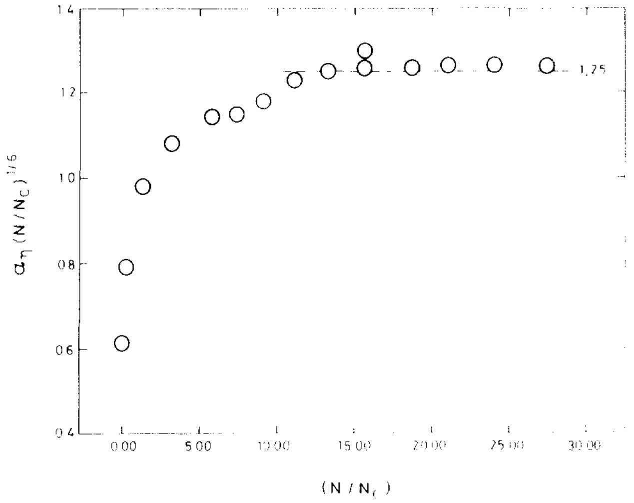

Figure 4 Universal plot of reduced viscosity size (α_η) *versus* reduced blob parameter (N/N_c) for PEMA–IPA system

$10\,g^{1/2}\,mol^{-1/2}$ for the PEMA–IPA pair. We used the value of $|\tau|M_w^{1/2} = 12\,g^{1/2}\,mol^{-1/2}$ to compute the average plateau value. In order to construct a more universal plot, the reduced blob parameter (N/N_c) should be used as the x axis instead of the scaled reduced temperature. From experimental results for PEMA in the collapsed regime and combination of equations (6) and (7) we have:

$$\frac{N}{N_c} = \frac{\tau^2 M_w}{114(0.067)} \tag{10}$$

Figure 4 shows a universal plot of the reduced expansion factor $\alpha_\eta(N/N_c)^{1/6}$ *versus* reduced blob size (N/N_c). Although the plateau value for the scaled expansion factor in the collapsed regime of PEMA is different from that of PS, our asymptotic value (1.25) of viscosity size (α_η) for PEMA in IPA is almost the same as the reported literature value for PS–CH[20], and it is in agreement with blob theory prediction with $\alpha_\eta^3 = \alpha_s^2 \alpha_h = 2.0$. Experimental prefactor values of viscosity size were determined as 1.29 (ref. 21), 1.27 (ref. 38) and 1.26 (ref. 22) by different research groups for polystyrene–cyclohexane (PS–CH) and poly(4-chlorostyrene)–n-propylbenzene (PPCS–nPB) systems. The value of prefactor (A^*N_1) was calculated as 0.067 from the asymptotic height of $\alpha_\eta^3|\tau|M_w^{1/2}$ for PEMA in IPA in this work using equation (7). The values of prefactor for PS–MA (addition of 1 wt% antioxidant), PS–MA, PS–CH and PPCS–nPB have been published as 19 (ref. 17), 9.9 (ref. 17), 1.6 (ref. 16) and 4 (ref. 22) below the θ temperature, respectively.

CONCLUSION

A universal plot of reduced viscosity size $\alpha_\eta(N/N_c)^{1/6}$ *versus* reduced blob parameter (N/N_c) shows the attainment of the collapsed state below the θ temperature for the PEMA–IPA system. As can be seen from the results of various prefactors calculated for several polymer–solvent systems, the value of prefactor (A^*N_1) depends not only on the solvent quality (good or poor solvent) but also on the chemical nature of the solvent used.

The author reported recently different results for the thermodynamic interaction parameters of PEMA and PS chains in a θ solvent[32,39]. These results suggest that there are some extra repulsive forces in the PEMA–IPA system due to the hydroxyl group of IPA.

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