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Studies on Equation-of-State Parameters and Linear Polymer Dimensions of Poly(*p*-chlorostyrene) in Diethylene Glycol Monobutyl Ether by Intrinsic Viscosity Measurements

Dolunay Şakar*

The Department of Chemistry, Yıldız Technical University, Davutpasa Campus,
Istanbul, Turkey

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Summary. Intrinsic viscosities, $[\eta]$, of poly(*p*-chlorostyrene) (*PPCS*) in diethylene glycol monobutyl ether (*DGMBE*) which exhibits an exothermic solubility behavior with the polymer were measured using an Ubbelohde type capillary viscometer between 25 and 85°C. Polymer solvent interaction parameters at infinite dilution (χ_1), exchange energy parameter ($\overline{X}_{12}$), exchange enthalpy (X_{12}), and entropy parameters (Q_{12}), of the *PPCS*/*DGMBE* pair were found at studied temperature range according to equation-of-state theory.

In the blob theory, dependence of $[\eta]$ on temperature can be scaled by a master curve in a plot of $\alpha_\eta{}^3|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ as the polymer coil contracts below the Θ-point, however, it can be scaled by a master curve in a plot of $\alpha_\eta{}^{-5}|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ as the polymer coil expands above the Θ-point in an endothermic solubility behavior. Since the studied *PPCS*/*DGMBE* system represents exothermic solubility behavior, the master curves of the system were plotted in $\alpha_\eta{}^3|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ as the polymer coil contracts above the Θ-point and in $\alpha_\eta{}^{-5}|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ as the polymer coil expands below the Θ-point. The universal plots of $\alpha_\eta(N/N_c)^{1/6}$ *versus* N/N_c and $\alpha_\eta(N/N_c)^{-1/10}$ *versus* N/N_c were plotted above and below Θ-point, respectively.

Keywords. Conformation; Solvent effect; Thermodynamics; Intrinsic viscosity; Poly(*p*-chlorostyrene).

Introduction

The average dimension and conformation of a polymer chain in solution vary with the nature of polymer-solvent pair. The polymer chain expands as the solvent becomes better. Several theoretical and experimental studies are present in

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* Corresponding author. E-mail: dolunaykar@yahoo.com

the literature [1]. The well-known of the presented theories are equation-of-state and thermal blob theory. Experimental studies by light scattering, diffusion, and intrinsic viscosities were performed to check the theories. However, all the studied polymer-solvent systems exhibit endothermic solubility [2–4]. In this study, poly(*p*-chlorostyrene) (*PPCS*) in diethylene glycol monobutyl ether (*DGMBE*) which exhibits exothermic solubility, were investigated by measuring its intrinsic viscosities at a temperature range of 25 to 85°C. The results were applied to the equation-of-state and thermal blob theories in order to observe the behavior of the *PPCS* chain in an exothermic solubility regime compared to in an endothermic regime. The thermodynamic parameters related to the polymer-solvent interaction were obtained. Then, a theoretical plot was drawn by using those parameters.

The intrinsic viscosity measurements were applied to the thermal blob theory. The chain contraction region above Θ-point in this study was compared to the chain contraction region below Θ-point in the endothermic solubility of the *PPCS* studied earlier.

Theoretical Background

Equation-of-State Theory

As the temperature of a polymer solution increases, the polymer coil expands in an endothermic solubility behavior, however it contracts in an exothermic solubility behavior. The dimension of the coil in the polymer solution passes through an unperturbed dimension at Θ-point as the temperature changes. The ratio of dimensional change of the coil is quantified by the thermal expansion factor, α_η [5–8] (Eq. (1)) where $[\eta]$ and $[\eta]_\Theta$ are the intrinsic viscosities at ordinary and Θ-temperatures, respectively.

$$[\eta] = [\eta]_\Theta \alpha_\eta^3 \tag{1}$$

The intrinsic viscosity of a polymer is related to the dimensions of its coil in the solution by Eqs. (2) and (3) where K_Θ and M are the chain unperturbed dimension constant and molecular weight of the polymer, respectively. Φ_o is the universal viscosity constant for chain polymers and has a value of $2.5\,10^{21}\,\text{mol}^{-1}$ if the intrinsic viscosity unit is g per $100\,\text{cm}^3$. $\langle r^2 \rangle_o$ is mean squared end-to-end distance of the unperturbed coil.

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

$$K_\Theta = \Phi_o (\langle r^2 \rangle_o / M)^{3/2} \tag{3}$$

Under non-theta conditions, α_η^3 is a function of the excluded volume parameter z (Eq. (4)).

$$\alpha_\eta^3 = 1 + 1.05z \tag{4}$$

The polymer-solvent interaction density B is related to z by Eqs. (5) and (6) where $\bar{\nu}$ is partial specific volume of the polymer, χ_1 is polymer-solvent interaction parameter in infinitely dilute polymer solutions, V_1^o is molar volume of the solvent, and N_A is Avogadro's number.

$$z = (3/2\pi)^{3/2}(B\Phi_o/K_\Theta)M^{1/2} \tag{5}$$

$$B = \bar{\nu}^2(1 - 2\chi_1)/V_1^o N_A \tag{6}$$

Total interaction parameter χ is defined in a whole concentration range in the theory as given by Eq. (7) [9] where $\theta_2(= (s_2/s_1)\varphi_2/[(s_2/s_1)\varphi_2 + \varphi_1])$ is the contact site fraction of the components and R is universal gas constant. φ_2 are defined as $(1 - \varphi_1)$. (s_2/s_1) is the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule.

$$\begin{aligned} RT\chi = {} & (p_1^* V_1^*/{\varphi_2}^2)\{3\tilde{T}_1 Ln[(\tilde{\nu}_1^{1/3} - 1)/(\tilde{\nu}^{1/3} - 1)] + \tilde{\nu}_1^{-1} - \tilde{\nu}^{-1}\} \\ & + (X_{12} - T\tilde{\nu}Q_{12})V_1^*{\theta_2}^2/\tilde{\nu}{\varphi_2}^2 \end{aligned} \tag{7}$$

χ can be expanded in a series of volume fraction of polymer φ_2 (Eq. (8)) where χ_1, χ_2, and χ_3 are thermodynamic interaction parameters which are a function of temperature. For infinitely dilute solutions, *i.e.* when φ_2 goes to zero, χ equals to χ_1.

$$\chi = \chi_1 + \chi_2\varphi_2 + \chi_3\varphi_2^2 + \cdots \tag{8}$$

According to the equation-of-state theory, χ_1 is determined in infinitely dilute polymer solutions as follows [10, 11] (Eqs. (9)–(11)) where the subscripts 1 and 2 indicate solvent and polymer, respectively, R is universal gas constant, α_1 is thermal expansion coefficient of the solvent, s_2/s_1 is ratio of surface areas of polymer segment to solvent molecule, X_{12} is exchange enthalpy, and Q_{12} is exchange entropy parameter and represent the exchange enthalpy and entropy of interaction for formation of a contact between a solute segment and solvent molecule, respectively.

$$\mathrm{Lim}_{\nu_2 \to o}\chi = \chi_1 = (p_1^* V_1^*/\tilde{\nu}_1 RT)[(A^2\alpha_1 T/2) + Y_{12}] - V_1^* Q_{12}(s_2/s_1)^2/R \tag{9}$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)X_{12}/p_1^* \tag{10}$$

and

$$Y_{12} = X_{12}(s_2/s_1)^2/p_1^* \tag{11}$$

X_{12} is assumed to be independent of temperature and Q_{12} can be adjusted for a particular system so as to have an agreement between a calculated quantity and an observed property under one set of conditions. V_1^*, p_1^*, and T_1^* are the characteristic molar volume, pressure, and temperature of the solvent and given by Eqs. (12)–(14) where $\tilde{\nu}$, $\tilde{T}$, and $\tilde{p}$ are reduced while those with asterisk are characteristic volume, temperature, and pressure, respectively, α is the thermal expansion coefficient defined by Eq. (15) and γ is the thermal pressure coefficient defined by Eq. (16).

$$\tilde{\nu}^{1/3} = (V/V^*)^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \tag{12}$$

$$\tilde{T} = T/T^* = (\tilde{\nu}^{1/3} - 1)/\tilde{\nu}^{4/3} \tag{13}$$

$$p^* = p/\tilde{p} = \gamma T\tilde{\nu}^2 \tag{14}$$

$$\alpha = (1/V)(\partial V/\partial T)_{p=o} \tag{15}$$

$$\gamma = (\partial p/\partial T)_{\nu} \tag{16}$$

If Eq. (9) is rearranged in the following form (Eq. (17)) and all equation-of-state parameters are assumed independent on temperature in the studied temperature range, Eq. (17) shows that the χ_1 versus $1/T$ plot must give a straight line. The slope and intercept of this line will give the following quantities:

Slope: $V_1^* X_{12}(s_2/s_1)^2/\tilde{\nu}_1 R$
Intercept: $(p_1^* V_1^* A^2 \alpha_1/2\tilde{\nu}_1 R) - (V_1^* Q_{12}(s_2/s_1)^2/R)$

$$\chi_1 = p_1^* V_1^* A^2 \alpha_1/2\tilde{\nu}_1 R - V_1^* Q_{12}(s_2/s_1)^2/R + V_1^* X_{12}(s_2/s_1)^2/\tilde{\nu}_1 RT \tag{17}$$

Effective exchange energy parameter is given by Eq. (18) [12].

$$\overline{X}_{12} = X_{12} - T\tilde{\nu}Q_{12} \tag{18}$$

Thermal Blob Theory

In the thermal blob theory, a polymer chain of N monomers is viewed as a succession of blobs each containing N_c monomers. It allows an approximate calculation of both dynamic and static reduced thermal expansion factors on chain configuration above and below Θ-temperature. The expansion factors α_s (radius of gyration) and α_h (hydrodynamic radius) reach the following asymptotic limits at high (N/N_c) values [13–14] (Eqs. (19) and (20)) where (N/N_c) is the reduced blob parameter.

$$\text{For } T\langle\Theta \quad \alpha_s = 1.161(N/N_c)^{-1/6}; \;\; \alpha_h = 1.481(N/N_c)^{-1/6} \tag{19}$$

$$\text{For } T\rangle\Theta \quad \alpha_s = 0.923(N/N_c)^{0.1}; \;\; \alpha_h = 0.747(N/N_c)^{0.1} \tag{20}$$

On the other hand, extensive experimental work carried out on polystyrene chains shows that the following relationship (Eq. (21)) between the various expansion factors is valid [3, 15–17].

$$\alpha_\eta^3 = \alpha_s^2 \alpha_h \tag{21}$$

By combining Eq. (21) with Eqs. (19) and (20), the following relationship (Eqs. (22) and (23)) for viscosity expansion factor is obtained for $T\langle\Theta$ and $T\rangle\Theta$, respectively.

$$\text{For } T\langle\Theta \quad \alpha_\eta = 1.26(N/N_c)^{-1/6} \tag{22}$$

$$\text{For } T\rangle\Theta \quad \alpha_\eta = 0.86(N/N_c)^{0.1} \tag{23}$$

Equations (22) and (23) indicate that $\alpha_\eta(N/N_c)^{1/6}$ and $\alpha_\eta(N/N_c)^{-0.1}$ reach asymptotic values as 1.26 and 0.86, respectively, at high N/N_c.

The ratio (N/N_c) is directly related to experimentally measurable quantities and given by Eq. (24) [2, 17] where τ is reduced temperature defined as $(T - \Theta)/T$, M_o

is molecular weight of the monomer, M is molecular weight of the polymer, and N_1 is number of monomer units in a statistical segment.

$$N/N_c = \tau^2 M/M_o(A^*N_1) \tag{24}$$

A^*N_1 is a prefactor and should be determined from the plateau heights in the master curves plotted as $\alpha_\eta^3|\tau|M^{1/2}$ against $|\tau|M^{1/2}$ as the chain contracts and $\alpha_\eta^{-5}|\tau|M^{1/2}$ against $|\tau|M^{1/2}$ as the chain expands as follows from Eqs. (25) and (26) where h and H are the plateau heights of the master curves in contraction and in expansion, respectively.

$$(A^*N_1) = h^2/(1.26^6 M_o) \tag{25}$$

$$(A^*N_1) = H^2/(0.86^{-10} M_o) \tag{26}$$

Results and Discussions

Experimental results of intrinsic viscosity of the *PPCS* in *DGMBE* and other calculated values at studied temperatures were listed in Table 1 for the contracted and in Table 2 for the expanded chains, respectively.

Thermal expansion factors, α_η obtained from Eq. (1) were plotted in Fig. 1. It can be seen that the polymer coil contracts with increasing temperature.

By means of Eqs. (2)–(6), polymer-solvent interaction parameter in infinite dilution, χ_1, was calculated and given in Fig. 2 at studied temperature range.

By assuming all equation-of-state parameters are constant at studied temperature range, exchange enthalpy, X_{12}, and exchange entropy, Q_{12}, parameters of the *PPCS-DGMBE* pair were estimated as $-155.23\,\mathrm{Jcm^{-3}}$ and $-0.46\,\mathrm{Jcm^{-3}K^{-1}}$, respectively. By using these parameters in the Eq. (7), the χ-interaction parameter was calculated for the whole composition range at Θ-point and plotted in the Fig. 3. The parameter χ moderately increases with the volume fraction of the polymer in the exothermic solubility although it considerably increases in an endothermic solubility [9]. An inversion point can be observed around $\varphi_2 = 0.4$.

It was shown by *Chu et al.* that $[\eta]$ of polymer chains can be scaled by a master curve in a plot of $\alpha_\eta^3|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ below the Θ-point as the chain contracts in an endothermic solubility behavior [18–20]. On the other hand, it was

Table 1. Intrinsic viscosity, $[\eta]$, thermal expansion factor, α_η, polymer-solvent interaction parameter, χ_1, scaled reduced temperature, $|\tau|M^{1/2}$, scaled expansion factor of intrinsic viscosity, $\alpha_\eta{}^{-5}|\tau|M^{1/2}$, of *PPCS* in *DGMBE* at temperatures below Θ-point

$\frac{T}{°\mathrm{C}}$	$\frac{[\eta]}{\mathrm{cm^3/g}}$	α_η	χ_1	$\|\tau\|M^{1/2}$	$\alpha_\eta{}^{-5}\|\tau\|M^{1/2}$	(N/N_c)	$\alpha_\eta(N/N_c)^{-1/10}$
25	26.06	1.36	0.35	43.74	9.31	1.57	1.30
30	19.72	1.24	0.41	34.45	11.72	0.97	1.24
35	19.21	1.23	0.42	25.46	8.97	0.53	1.31
40	18.38	1.21	0.42	16.76	6.41	0.23	1.40
45	16.06	1.16	0.45	8.33	3.97	0.06	1.54
50	10.33	1.00	0.50	0.16	0.16	0.00	–

Table 2. Intrinsic viscosity, $[\eta]$, thermal expansion factor, α_η, polymer-solvent interaction parameter, χ_1, scaled reduced temperature, $|\tau|M^{l/2}$, scaled expansion factor of intrinsic viscosity, ${\alpha_\eta}^3|\tau|M^{1/2}$, of *PPCS* in *DGMBE* at temperatures above Θ-point

$\frac{T}{°\mathrm{C}}$	$\frac{[\eta]}{\mathrm{cm}^3/\mathrm{g}}$	α_η	χ_1	$\lvert\tau\rvert M^{1/2}$	$\alpha_\eta^3\lvert\tau\rvert M^{1/2}$	(N/N_c)	$\alpha_\eta(N/N_c)^{1/6}$
50	10.33	1.00	0.50	0.16	0.16	0.00	0.00
55	8.78	0.95	0.51	7.76	6.61	0.11	0.66
60	5.12	0.79	0.55	15.44	7.67	0.43	0.69
65	8.82	0.95	0.51	22.89	19.60	0.95	0.94
70	6.18	0.84	0.54	30.13	18.08	1.64	0.91
75	6.72	0.87	0.53	37.16	24.24	2.49	1.01
80	4.05	0.73	0.56	43.99	17.30	3.49	0.90
85	5.27	0.80	0.55	50.63	25.90	4.63	1.03

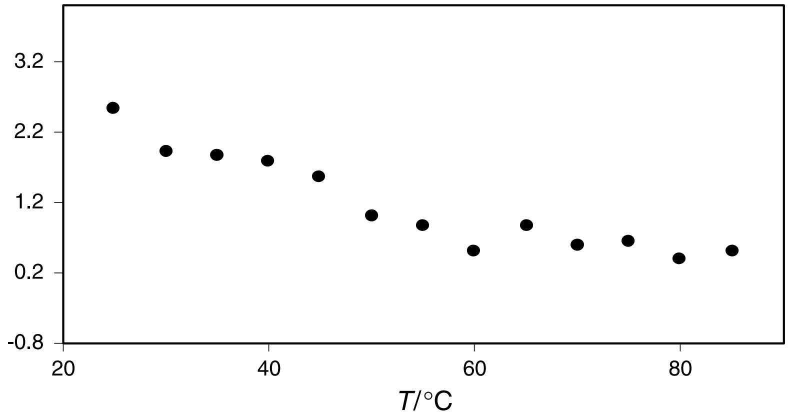

Fig. 1. Variation of viscosity expansion factor of *PPCS* in *DGMBE* below and above Θ-temperature (50.1°C)

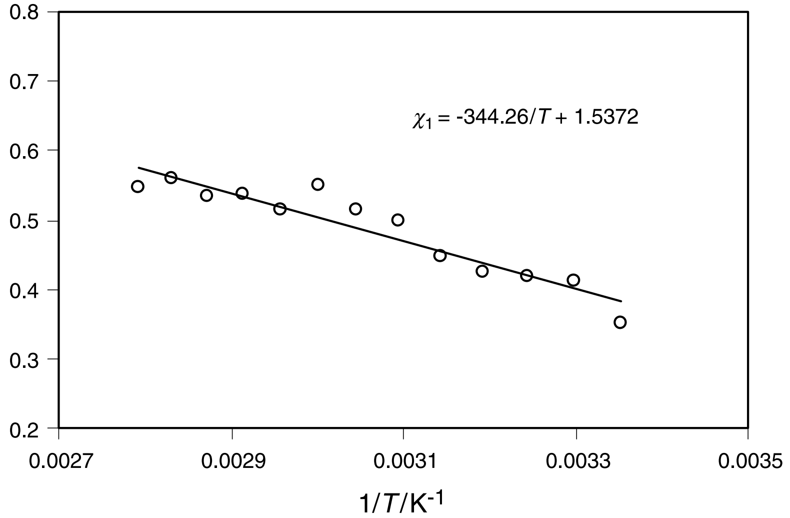

Fig. 2. Variation of polymer-solvent interaction parameter at infinite dilution, χ_1, with temperature

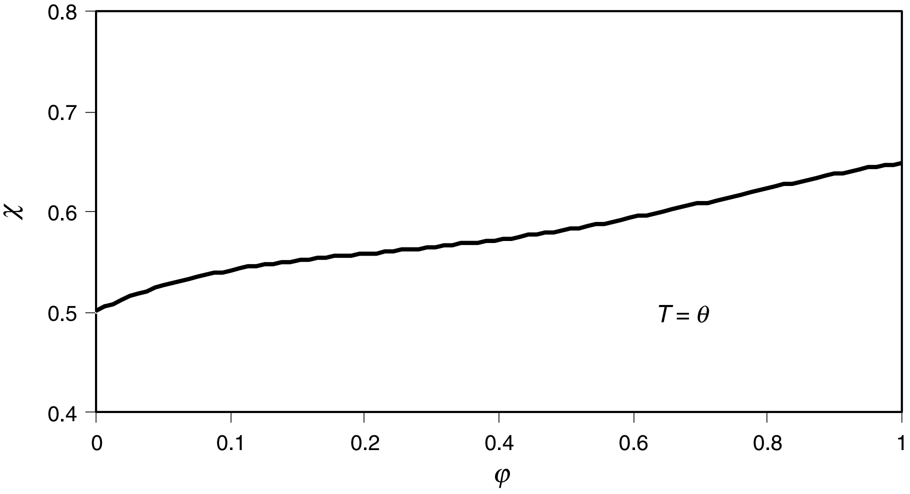

Fig. 3. Polymer-solvent interaction parameter, χ, calculated according to Eq. (7) in various volume fractions of the polymer at Θ-point

shown by *Yilmaz* and *Baysal* that $[\eta]$ of polymer chains can be scaled by a master curve in a plot of $\alpha_\eta^{-5}|\tau|M^{1/2}$ *versus* $|\tau|M^{1/2}$ above the Θ-point as the chain expands in an endothermic solubility behavior [21]. As known, in an exothermic solubility behavior, the polymer chain expands below Θ-point but it contracts above Θ-point contrary of endothermic solubility. Since the solubility of *PPCS-DGMBE* system is exothermic, the master curve of ◊ the system was plotted as $\alpha_\eta^{-5}|\tau|M^{1/2}$ against

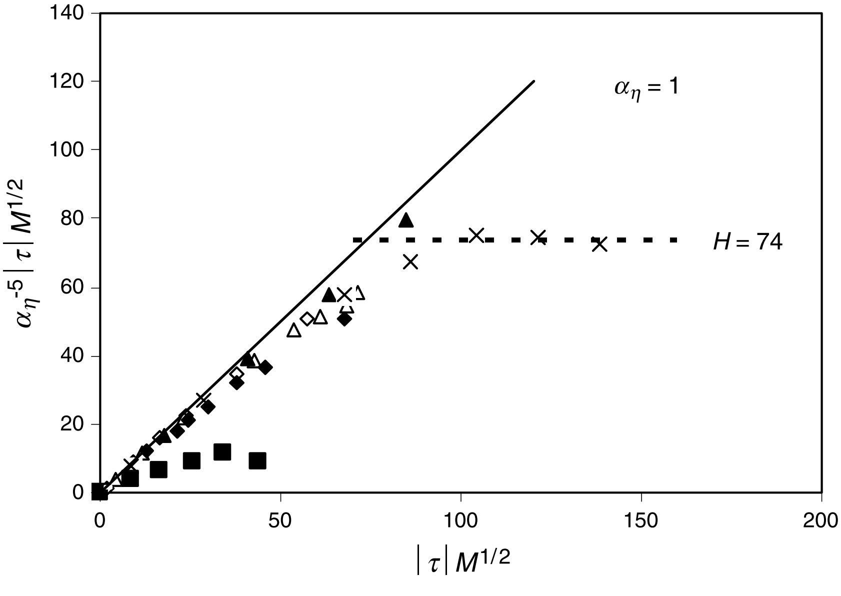

Fig. 4. Plot of scaled expansion factor $\alpha_\eta{}^{-5}|\tau|M^{1/2}$ of intrinsic viscosity as a function of scaled reduced temperature $|\tau|M^{1/2}$ for expanded *PPCS* with different molecular weights in various solvents; symbols are as follows: 1.75×10^6 gmol^{-1} in n-propylbenzene (x), 1.75×10^6 gmol^{-1} in isopropylbenzene (Δ), 6.5×10^5 gmol^{-1} in n-propylbenzene (▲), 2.7×10^5 gmol^{-1} in isopropyl benzene (◇), 2.7×10^5 gmol^{-1} in benzene (◆), 2.7×10^5 gmol^{-1} in *DGMBE* (■)

$|\tau|M^{1/2}$ in Fig. 4 with the parameters in Table 1 below Θ-point which the chain expand and it was compared with curves of *PPCS* chains expanded in other solvents reported earlier. Similarly, the master curve of the system was plotted as $\alpha_\eta^3|\tau|M^{1/2}$ against $|\tau|M^{1/2}$ in Fig. 5 using the parameters in Table 2 above Θ-point which the chain contract and it was compared with curves of *PPCS* chains contracted in other solvents reported earlier. It is obviously seen that data obtained in this study do not superpose on the data reported earlier for the endothermic polymer-solvent systems of *PPCS*, even in the *Gaussian* region. It seems that the expansion and contraction mechanism are different in the endothermic and exothermic solubility behavior in polymer-solvent systems. The ratio of contraction and expansion in this study is higher than those obtained for endothermic solubilities.

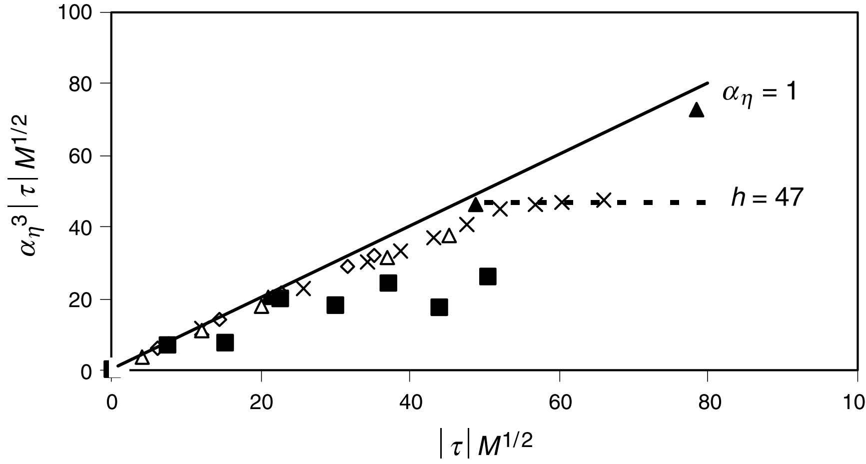

Fig. 5. Plot of scaled expansion factor $\alpha_\eta^3|\tau|M^{1/2}$ of intrinsic viscosity as a function of scaled reduced temperature $|\tau|M^{1/2}$ for contracted *PPCS* with different molecular weights in various solvents; symbols are related to polymeric samples and solvents identified in Fig. 4

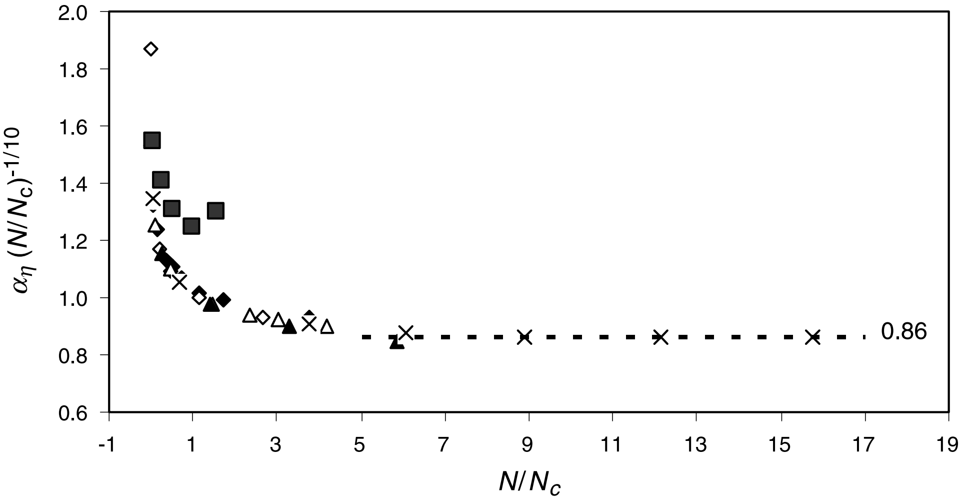

Fig. 6. Variation of $\alpha_\eta(N/N_c)^{-0.1}$ as a function of reduced blob parameter (N/N_c); symbols are related to polymeric samples and solvents identified in Fig. 4

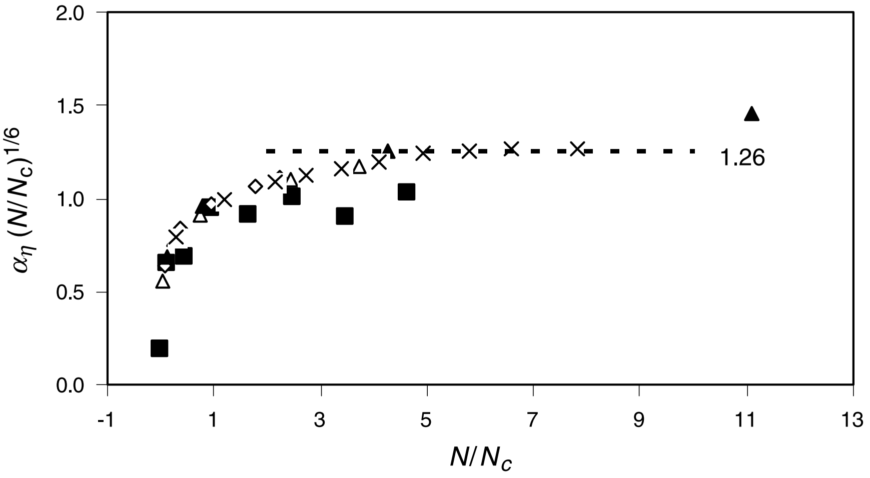

Fig. 7. Variation of $\alpha_\eta(N/N_c)^{1/6}$ as a function of reduced blob parameter (N/N_c); symbols are related to polymeric samples and solvents identified in Fig. 4

Since the scaled expansion factors in this study did not reach the plateau, the plateau heights given in the Figs. 4 and 5 were used to calculate A^*N_1 using Eqs. (25) and (26), respectively. Figures 6 and 7 show the plots of $\alpha_\eta(N/N_c)^{-0.1}$ and $\alpha_\eta(N/N_c)^{1/6}$ as a function of reduced blob parameter, (N/N_c), for expanded and contracted chains, respectively. The points in this study are far away from the points reported earlier. This suggests that the thermal blob theory can not explain polymer-solvent systems exhibiting exothermic solubility behavior.

Experimental

PPCS was synthesized in the laboratory with the viscosity molecular weight of 270000 g mol^{-1}. *DGMBE* was purchased from Merck A.G. as a reagent grade chemical. A home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ±0.01°C was used for intrinsic viscosity measurements. The intrinsic viscosity of the polymer solution was determined by means of Eq. (27) where $\eta_{sp} = (\eta - \eta_o)/\eta_o$ is specific viscosity, η and η_o are viscosity of polymer solution and solvent, respectively, and c is the polymer concentration.

$$[\eta] = \lim_{c\to 0}(\eta_{sp}/c) \qquad (27)$$

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