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Evaluation and Interpretation of Ptitsyn-Eizner Parameter λ in Dilute Solutions of Poly[2-methoxy-4,6-di-(p,p′-isopropylidene Diphenyloxy)-s-triazine] and Other Polymers with Aromatic Backbone

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ABSTRACT

Dilute solution data on poly[2-methoxy-4,6-di-(p,p'-isopropylidene diphenyloxy)-s-triazine] have been analyzed by the Ptitsyn-Eizner theory. The rigidity parameter λ has been estimated. λ varies with the nature of the solvent. The temperature dependence of λ has also been investigated. The parameter λ has been compared with other polymers containing "long bonds."

INTRODUCTION

The rigidity of a polymer chain is generally described by a parameter σ, defined as $\sigma = \langle R_0^2 \rangle / \langle R_{of}^2 \rangle$, obtainable from measurements on dilute solutions. $\langle R_{of}^2 \rangle$ is the mean-square end-to-end distance corresponding to completely free internal rotations. However, a deduction based on the value of such a parameter is deemed valid only if the polymer sample comprises linear chains with flexibility imparted by rota-

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tions about valence bonds without distortion of valence angles. Such a situation is not obtained in the case of polymers containing aromatic structures in the backbone. Moreover, determination of $\langle R_0^2 \rangle$ from viscosity measurements implies application of some excluded volume theories with all their limitations.

Leon et al. [1, 2] have shown that the Ptitsyn-Eizner [3] theory of semirigid chains can be successfully employed to estimate macromolecular chain flexibility. Ptitsyn and Eizner proposed a λ parameter as a measure of chain flexibility in their original work. The calculation of this parameter for the so-called flexible polymers of high molecular weight can be made from the expression [1, 2]

$$\frac{M}{[\eta]} = \left(\frac{\pi}{3}\right)^{1/2} \frac{45}{64\,(3 - \sqrt{2})} \left(\frac{M_0}{b}\right)^2 \frac{1}{\phi_0 r_0 \lambda} + \frac{1}{\phi_0 (b)^3} \left(\frac{M_0}{2\lambda}\right)^{3/2} M^{1/2} \qquad (1)$$

where r_0 is the hydrodynamic radius of the monomer, b is the monomeric unit length, M_0 is the molecular weight of the monomer, M is the molecular weight of the polymer, ϕ_0 is Flory's universal constant ($= 2.87 \times 10^{23}$), and $[\eta]$ is the intrinsic viscosity in mL/g. According to this relation, a plot of $M[\eta]^{-1}$ against $M^{1/2}$ would be linear. Such a linear relation can be employed to estimate the λ parameter. Leon et al. have shown that the unperturbed dimensions can be calculated if λ is known under theta conditions by the following relation [1, 2]:

$$\lambda = \frac{M_0}{2b^2 \phi_0^{2/3}} K_\theta^{2/3} \qquad (2)$$

These authors have observed that the experimental value of K_θ and the values calculated from knowledge of λ under theta conditions agree very well for high molecular weight polymers (polystyrene, polyethylene, polymethyl methacrylate, etc.) with no aromatic moiety in the backbone [1, 2].

It has been observed by the present author that solutions of poly[2-methoxy-4,6-di-(p,p'-isopropylidene diphenyloxy)-s-triazine], hereafter abbreviated at PMIPT, behave as if it is made of flexible chains [4]. Its solution viscosity data can be adequately represented by the relations involving viscosity functions based on excluded volume theories. This polymer comprises polymer chains with ether linkages between the s-triazine ring and the benzene ring. It was thought of interest to examine the applicability of the Ptitsyn-Eizner [3] theory, devised for semirigid chains in the form advocated by Leon et al., [1, 2], to the relevant experimental data about this polymer. Such experimental data [5-7], reported in the literature for polymers with aromatic rings in the backbone of the polymer chains, are also analyzed in terms of Relations (1) and (2). This work forms the subject matter of the present communication.

EXPERIMENTAL

PMIPT was synthesized by a reported method [4]. The characteristics of various fractions of PMIPT obtained from viscometry, osmometry, and gel permeation chromatography have been reported [4].

RESULTS AND DISCUSSION

The $[\eta]$ and $\overline{M}_w$ data on PMIPT fractions under different experimental conditions were analyzed according to Eq. (1). The plots are shown in Fig. 1. The plots are linear. The correlation coefficient estimated by the least-squares treatment is found to be around 99.9%. This justified the validity of this treatment for flexible polymers. The values of λ calculated from the slopes of the $M [\eta]^{-1}$ vs $M^{1/2}$ plots based on the data under different experimental conditions are tabulated in Table 1 along with the polymer-solvent interaction parameter B and exponent ν of the MHKS relation, $[\eta] = KM^{\nu}$. Literature data on the polycarbonates of bisphenol-A [5], polysulfone [6], and poly(2,6-dimethyl-1,4-phenylene oxide) [7] were also analyzed in terms of the Eq. (1). The corresponding λ values are tabulated in Tables 2, 3, and 4, respectively, with the values of the B and ν parameters. The values of parameter B were obtained by the application of the modified Stockmayer-Fixman extrapolation method [8].

Examination of the data presented in Tables 1-4 reveals that the Ptitsyn-Eizner parameter λ depends on the nature of the solvent. For PMIPT, λ is equal to 1.64 in chloroform and 0.52 in a 1,2-dichloroethane:n-butanol (62:38 v/v) mixture, a theta solvent at 30°C. This indicates that λ is not strictly a structural parameter governed only by the nature of the chain. The variation is quite similar to that of B and ν. Such behavior is found for all the polymers examined. Like B and ν, the value of the parameter λ increases under normal circumstances with an increase in the solvent power of the solvent.

The variation of λ with polymer-solvent interactions is explicable on the basis of the wormlike chain model [9] used by Ptitsyn and Eizner [3]. According to this, λ is related to the angle between two monomeric units by the expression

$$\lambda = -\frac{1}{\ln \overline{\cos \alpha}} \qquad (3)$$

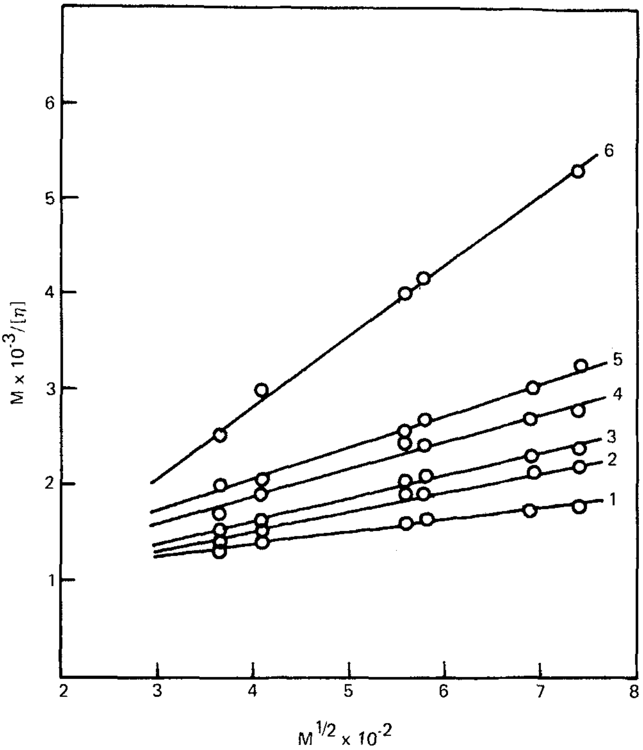

FIG. 1. Plots of $M/[\eta]$ versus $M^{1/2}$ for poly[2-methoxy-4,6-di-(p,p'-isopropylidene diphenyloxy)-2-triazine] in chloroform (1), 1,2-dichloroethane (2), 85:15 (v/v) 1,2-dichloroethane:n-butanol (3), 75:25 (v/v) 1,2-dichloroethane:n-butanol (4), 62:38 (v/v) 1,2-dichloroethane:n-butanol (6), and anisole (5) at 30°C.

where $\overline{\cos \alpha}$ is the cosine of the mean angle between the chain segments; therefore, λ depends on chain extension. An increase in the value of λ indicates a decrease in the value of α. This suggests that greater extension of the macromolecule can be due to greater rigidity or to an increase in polymer-solvent interactions which make the chain more extended. At theta conditions the polymer-solvent interactions vanish and λ becomes a true characteristic of chain flexibility.

The polymer-solvent interaction for a given polymer depends both on the nature of the solvent and the temperature. Hence, like B and ν, the parameter λ is also likely to vary with temperature. The temperature dependence of λ for PMIPT in different solvents is portrayed in Fig. 2. The variation of λ with temperature is found to be linear and is described by the relation

$$\lambda = A + CT \tag{4}$$

where A and C are constants. Generally, λ increases with temperature, but for solutions of PMIPT in 1,2-dichloroethane and methylene chloride, it diminishes, like the value of B, with an increase in temperature. Thus the parameter λ depends on temperature. However, there is no direct dependence of λ on solvent-polymer interactions since the former also depends on the macromolecular chain flexibility.

TABLE 1. λ, B, and ν Values for Poly[2-methoxy-4,6-di-(p,p'-isopropylidene diphenyloxy-s-triazine] (PMIPT) in Several Solvents at 30°C

Solvent	λ	$B \times 10^{27}$ cm^3	ν
Chloroform	1.64	4.15	0.74
Anisole	0.88	1.19	0.67
Methylene chloride (MC)[a]	1.11	2.28	0.68
Dichloroethane (DCE)	1.26	2.83	0.71
DCE:n-Bu (85:15)[b]	1.13	2.29	0.68
DCE:n-Bu (75:25)	0.98	1.74	0.65
DCE:n-Bu (62:38)	0.52	0.04	0.50

[a] At 25°C.
[b] Volume composition.

TABLE 2. λ, B, and ν Values for Bisphenol A Polycarbonate in Several Solvents at 25° [5]

Solvent	λ	$B \times 10^{28}$ cm^3	ν
Chloroform	2.36	1.04	0.82
Methylene chloride	2.67	1.10	0.81
Dichloroethane	1.52	0.60	0.78
Dioxane	1.77	0.86	0.71
THF	1.54	0.61	0.67
Cyclohexanone	1.14	0.25	0.62
Dioxane/cyclohexane	0.84	0.08	0.50

TABLE 3. λ, B, and ν Values for Polysulfone in Several Solvents [6]

Solvent	Temperature (°C)	λ	$B \times 10^{27}$ cm^3	ν
Chloroform	25	0.90	3.37	0.72
THF	25	0.58	0.86	0.58
DMF	25	0.51	0.41	0.55
DMSO	105.5	0.43	0.00	0.50

TABLE 4. λ, B, and ν Values for Poly(2,6-dimethyl-1,4-phenylene) Oxide in Several Solvents at 25°C

Solvent	λ	$B \times 10^{27}$ cm^3	ν
Toluene	2.39	2.02	0.68
Chlorobenzene	2.32	1.76	0.66
Chloroform	2.43	1.83	0.64

The fact that λ for a polymer under theta conditions is characteristic only of chain flexibility and that its variation with temperature is linear allows one to determine the theta temperature for a polymer-solvent system using Relation (4). Knowledge of λ under theta conditions allows calculation of the unperturbed dimensions using Eq. (2). For PMIPT, K_θ calculated from the λ value at theta conditions turns out to be 0.136 mL/g which is very nearly the same as the experimental value of 0.135 mL/g. For polycarbonate from bisphenol A, Moore et al. [5] obtained a value of 0.214 mL/g and Eq. (2) affords a value of 0.225 mL/g for K_θ. For polysulfone, Allen et al. [6] obtained a value of 0.145 mL/g and Eq. (2) leads to a value of 0.143 mL/g for K_θ. Thus K_θ values obtained from Eq. (2) from knowledge of λ under theta conditions agree well with the published values. Such agreement has also been found for a number of polymers.

It is noted that polyethers containing aromatic rings in their backbone have lower λ values than polymers containing no aromatic rings in their backbone [1, 2]. Such polymers are more flexible in solution. Their relatively greater flexibility may be attributed to the greater separation between consecutive ether links in the polymer chains.

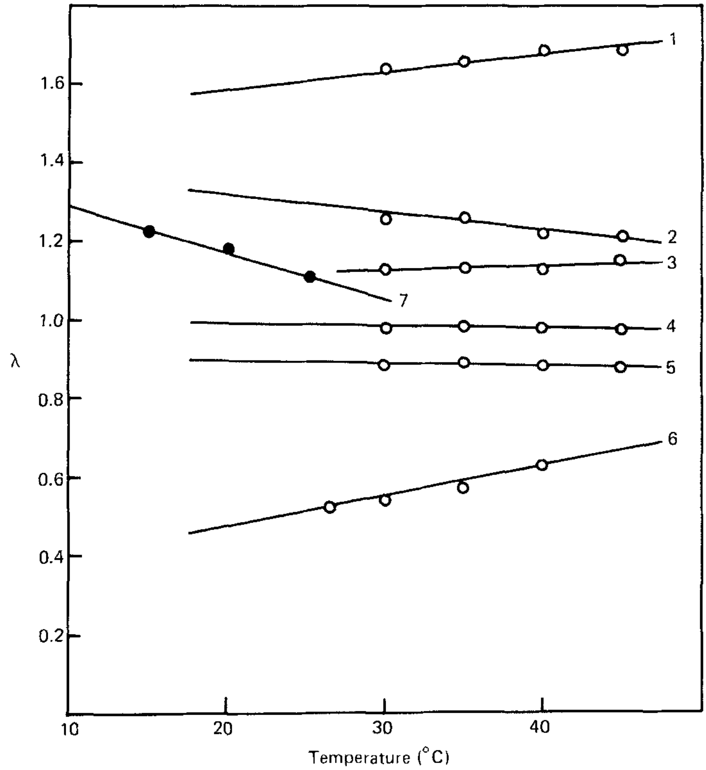

FIG. 2. Temperature dependence of λ for poly[2-methoxy-4,6-di-(p,p'-isopropylidene diphenyloxy)-s-triazine] in chloroform (1), 1,2-dichloroethane (2), 85:15 (v/v) 1,2-dichloroethane:n-butanol (3), 75:25 (v/v) 1,2-dichloroethane:n-butanol (4), 62:38 (v/v) 1,2-dichloroethane: n-butanol (6), anisole (5), and methylene chloride (7).

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