

## INTERPRETATION OF THE INTRINSIC VISCOSITY–TEMPERATURE DEPENDENCE ON THE BASIS OF THE EXCLUDED VOLUME ANALYSIS

Maria BERCEA\* and Simona MORARIU

“Petru Poni” Institute of Macromolecular Chemistry  
41-A Grigore Ghica Vodă Alley, 700487 Iași, Roumania

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The variation of  $\ln[\eta]$  with temperature for poly(methyl methacrylate) and copolymers of 2-(*o*-chlorophenyl)-4-methylene-1,3-dioxolane with methyl methacrylate is discussed using the theories of excluded volume effect. Both  $d \ln \langle r_0^2 \rangle / dT$  and  $\Theta$  temperature are evaluated from this analysis.

### INTRODUCTION

The behaviour of macromolecules in solution at different temperatures is dependent on the chemical nature of the polymer and solvent, which influences the interactions between chain elements, on the one hand, and between polymer and solvent, on the other hand. The thermodynamic properties of polymer solutions can be explained in terms of the excluded volume.<sup>1</sup> In some cases, with increasing of temperature the polymer chains gain enough energy to overcome the potential barrier between low-energy and high-energy rotational isomeric states and undergo a transition between these two states.<sup>2-4</sup>

The intrinsic viscosity is often used to characterize the dimensions of macromolecules in dilute solution. The polymer conformation is influenced by different possible interactions, which are conveniently divided in two classes: *short-range interactions*, which occur between neighbouring atoms or groups and *long-range interactions*, attractive and repulsive forces between segments widely separated in a chain (occasionally approaching one other) and between polymer segments and solvent molecules. These interactions are discussed in terms of the excluded volume effect.

Generally, the unperturbed dimensions, originally assumed to be independent of temperature and solvent, represent a characteristic of the polymer chain and the coefficient  $d \ln \langle r_0^2 \rangle / dT$  was estimated from  $K_\theta$  values measured in several  $\theta$  solvents (single or mixed) with theta temperature over a suitable range. However, a small effect of the solvent on the chain conformation may overlap the effect of the temperature<sup>5</sup> and values of  $\langle r_0^2 \rangle / M$  are slowly affected by the nature of the solvent, whereas in single solvent measurements the temperature range can affect the value of the  $\langle r_0^2 \rangle / M$  ratio.

In this paper, the qualitative features of the intrinsic viscosity as a function of temperature in the case of homopolymers and some random copolymers is interpreted on the basis of the excluded volume analysis.

### THEORY

It is often reported that the intrinsic viscosity  $[\eta]$  is a linear function of temperature (T) over a given range of temperatures. Analyzing different polymer-solvent systems, a relatively large scattering of the

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\* Author for correspondence. Tel.: +40232-217454; Fax: +40232-211299; E-mail: bercea@icmpp.ro

experimental data can be observed.<sup>6</sup> Consequently, a refined analysis is required to determine  $d \ln[\eta]/dT$ . Thus, the following equation is considered:

$$[\eta]_T = K_{\theta,T} \times M^{1/2} \times \alpha^\gamma \quad (1)$$

where  $[\eta]_T$  is the intrinsic viscosity at a temperature  $T$ ,  $K_{\theta,T}$  – unperturbed dimensions parameter, considered dependent on temperature,  $M$  – molecular weight of the polymer,  $\alpha$  – expansion factor and  $\gamma$  – a parameter to which the value 3.0 was assigned.

The derivation of the equation (1) in respect of temperature gives:

$$\frac{d \ln[\eta]_T}{dT} = \delta + \gamma \frac{d \ln \alpha}{dT} \quad (2)$$

where:

$$\delta = \frac{d \ln K_{\theta,T}}{dT} \quad (3)$$

Various theories relate the expansion factor  $\alpha$  to the excluded volume parameter  $z$  by equations of the form:

$$f(\alpha) = A \times z \quad (4)$$

where  $A$  is a constant. The equation (4) is derived in function of temperature and one obtains:

$$\frac{d \ln \alpha}{dT} = \frac{1}{\kappa} \times \frac{d \ln z}{dT} \quad (5)$$

where:

$$\kappa = \frac{d \ln f(\alpha)}{d \ln \alpha} \quad (6)$$

In theta conditions, the polymer chains are expected to exhibit Gaussian statistics over all molecular weight range. The Mark-Houwink relationship for the unperturbed state is given by:

$$[\eta]_\theta = K_\theta \times M^{0.5} \quad (7)$$

The proportionality of  $[\eta]_\theta$  to  $M^{0.5}$  over several decades of  $M$  has been confirmed by different investigations.<sup>5</sup> The dependence of  $(\langle r_o^2 \rangle / M)_\infty$  on the solvent quality is reflected in the value of  $K_\theta$ , which is considered as a characteristic of the polymer homologous series:

$$\left( \frac{K_\theta}{\phi_o} \right)^{2/3} = \frac{\langle r_o^2 \rangle}{M} \quad (8)$$

where  $\phi_o = 2.51 \cdot 10^{21} \text{ mol}^{-1}$  for intrinsic viscosity expressed in  $\text{dL} \cdot \text{g}^{-1}$ .

From equations (2), (5) and (8) one finds:

$$\frac{d \ln[\eta]_T}{dT} = \frac{3}{2} \times \frac{d \ln \langle r_o^2 \rangle}{dT} + \frac{\varepsilon}{\kappa} \times \frac{d \ln z}{dT} \quad (9)$$

The parameter  $\varepsilon$  values were calculated for different systems using the polymer and solvent densities as well as the temperature coefficients of these quantities. The obtained values of  $\varepsilon$  were around  $1 \cdot 10^{-4}$ . If the term  $\frac{d \ln \langle r_o^2 \rangle}{dT}$  is considered to be independent on temperature, its value can be obtained by determining the

constant part of the temperature coefficient  $\frac{d \ln[\eta]_T}{dT}$ .

The temperature coefficient of the mean square unperturbed length, *i.e.*,  $\frac{d \ln \langle r_0^2 \rangle}{dT}$ , gives important information on the chain conformation and it can be obtained directly, by determining  $\langle r_0^2 \rangle$  at several temperatures. The temperature coefficient seldom exceeds  $1 \cdot 10^{-3} \text{ deg}^{-1}$ . If the chosen solvent offers theta point over a suitable range of temperatures, the effect of temperature on the macromolecular dimensions is likely to be masked by specific effects of the solvents, even though these may be quite small.<sup>7</sup> The light scattering method is not recommended for the investigated samples, important errors in experimental evaluation of the root-mean-square radius of gyration in the unperturbed state appearing. However, reliable values of  $\frac{d \ln \langle r_0^2 \rangle}{dT}$  can be obtained by determining the temperature coefficient of the intrinsic viscosity in perturbed state using an athermal solvent. Another method applied to determine  $\frac{d \ln \langle r_0^2 \rangle}{dT}$  involves measurement of the stress–temperature coefficient of the amorphous polymers converted into a network by cross-linking and maintained at fixed strain (as for example simple elongation).

In good solvent the dynamic properties of the polymer chains are governed by the excluded volume effect. Adding solvent to the pure polymer, the macromolecular coil dimensions increase until the maximum expansion is reached for an isolated chain (infinite dilution). As a consequence, both inter- and intramolecular interactions manifest and, as the solvent quality increases, the segments become more and more open. When the segments belonging to different molecules are completely separated, the effect of intermolecular contacts differs from that of intramolecular ones. Unexpected behaviour can be detected in the case of random copolymers, when the conformation of the macromolecule in a dilute solution tends to a few preferred states, the most stable being characterized by minimum energy.

The excluded volume parameter  $z$  can be expressed as a function of temperature as:

$$z = 2\Psi \left( \frac{3}{2\pi} \right)^{3/2} \left( \frac{\bar{v}_2^2}{V_1 N_A} \right) \left( \frac{M}{\langle r_0^2 \rangle} \right)^{3/2} \left( 1 - \frac{\Theta}{T} \right) M^{1/2} \quad (10)$$

where:

$$\Psi = \frac{A_2 M^2}{4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}} \quad (11)$$

$V_1$  is the molar volume of the solvent,  $\bar{v}_2$  – partial specific volume of the polymer,  $N_A$  – Avogadro number and  $\Theta$  – theta temperature.  $A_2$  represents the second virial coefficient and  $\langle S^2 \rangle$  the mean square radius of gyration.

From the equation (10) one can obtain:

$$\frac{d \ln z}{dt} = d \ln \left( \frac{\bar{v}_2^2 / V_1}{dT} \right) - \delta + \frac{\Theta}{T(T - \Theta)} \quad (12)$$

By substituting in the equation (9), finally the following relation can be obtained:

$$\left\{ T \left[ \left( \frac{d \ln [\eta]_T}{dT} - \delta \right) \left( \frac{\kappa}{\gamma} \right) - \varepsilon + \delta \right] \right\}^{-1} = Y = \frac{T}{\Theta} - 1 \quad (13)$$

Various excluded volume theories give the expressions for  $f(\alpha)$  and  $\kappa$ . Thus, according to the Flory theory:<sup>7</sup>

$$f(\alpha) = \alpha^5 - \alpha^3 \quad \text{and} \quad \kappa = \frac{5\alpha^2 - 3}{\alpha^2 - 1} \quad (14)$$

The Fixman theory<sup>8</sup> predicts:

$$f(\alpha) = \alpha^3 - 1 \text{ and } \kappa = \frac{3\alpha^3}{\alpha^3 - 1} \quad (15)$$

Kurata-Stockmayer-Roig theory<sup>9</sup> gives the following dependences:

$$f(\alpha) = \frac{(\alpha^3 - \alpha)(3\alpha^2 + 1)^{3/2}}{\alpha^3} \text{ and } \kappa = \frac{9\alpha^4 - 3\alpha^2 + 2}{(\alpha^2 - 1)(3\alpha^2 + 1)} \quad (16)$$

The values of the expansion factor  $\alpha$  can be obtained from the relations:<sup>10</sup>

$$\alpha = \left( \frac{[\eta]_T}{[\eta]_{\theta,T}} \right)^{1/\gamma} \quad (17)$$

$$\ln[\eta]_{\theta,T} = \ln[\eta]_{\theta,T_0} + \delta(T - T_0) \quad (18)$$

where  $[\eta]_{\theta,T_0}$  and  $\ln[\eta]_{\theta,T}$  are the values of the intrinsic viscosity under theta conditions at temperatures  $T_0$  and  $T$ , respectively. The value of  $[\eta]_{\theta,T_0}$  is experimentally obtained.

## RESULTS AND DISCUSSION

Fig. 1 presents the  $\ln[\eta]_T$  as a function of temperature for poly(methyl methacrylate) (PMMA) and poly[(2-(*o*-chlorophenyl)-4-methylene-1,3-dioxolane)-*co*-methyl methacrylate] (CPMD-*co*-MMA) samples with different CPMD contents and molecular weights (Table 1) in carbon tetrachloride as solvent. PMMA chains in carbon tetrachloride are in the unperturbed state at 27°C and, above theta temperature, the macromolecular chains are more opened due to the polymer-solvent interactions, as reflected by the increase of the intrinsic viscosity with increasing temperature. For all copolymer samples  $[\eta]$  decreases slowly with increasing temperature, suggesting an improvement of solvent quality due to the CPMD sequences. The slope of this dependence increases with increasing CPMD content and for sample 4, having 18.4% CPMD, the highest slope is obtained. Thus, the viscosity-temperature behaviour of copolymer solutions depends on the chemical structure of the copolymer and on the change of the physical interactions under the influence of both temperature and comonomer nature.

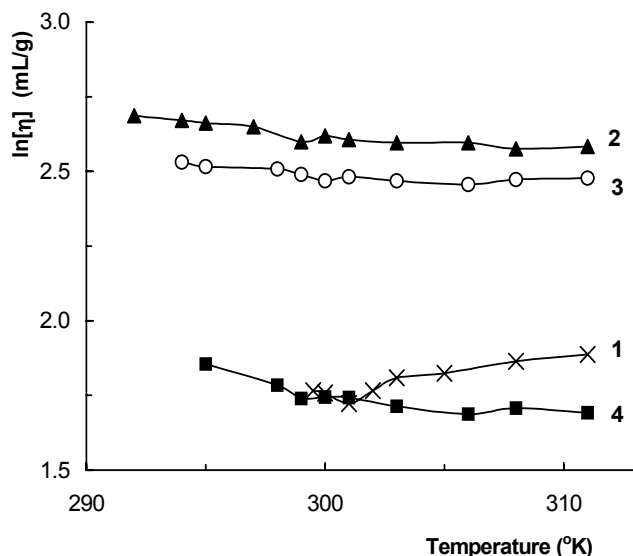


Fig. 1 – Dependence of  $\ln[\eta]$  on temperature for solutions of PMMA (Sample 1, Table 1) and CPMD-*co*-MMA (Samples 2-4, Table 1) in  $\text{CCl}_4$ .

Table 1

The characteristics of the studied samples

Sample	CPMD in copolymer (molar fraction)	$M_n \times 10^{-3}$ ( $\text{g} \times \text{mol}^{-1}$ )	$M_w/M_n^a$
1	0.000	14.0	1.51
2	0.044	14.2	1.50
3	0.067	13.6	1.61
4	0.184	7.7	1.60

<sup>a</sup> Estimated by GPC

The curves shown in Fig. 1 can be represented by polynomials in  $T$ , as follows:

$$\ln[\eta]_T = a_0 + a_1T + a_2T^2 + \dots + a_mT^m \quad (19)$$

By differentiating the equation (19), one can find:

$$\frac{d \ln[\eta]_T}{dT} = a_1 + 2a_2T + 3a_3T^2 + \dots + ma_mT^{m-1} \quad (20)$$

The comparison of the equations (9) and (20) reveals that  $\frac{d \ln \langle r_o^2 \rangle}{dT}$  can be evaluated as  $\frac{2}{3}a_1$  and that numerically  $2a_2T + 3a_3T^2 + \dots + ma_mT^{m-1}$  is equal to  $\frac{\epsilon}{\kappa} \times \frac{d \ln z}{dT}$ . Values of  $\frac{d \ln \langle r_o^2 \rangle}{dT} = \frac{2}{3}a_1$  are given in Table 2.

Table 2

Values of  $\frac{d \ln \langle r_o^2 \rangle}{dT}$  and theta temperature determined for the studied samples in  $\text{CCl}_4$

Sample	$\frac{d \ln \langle r_o^2 \rangle}{dT} \times 10^3$ ( $\text{deg}^{-1}$ )	Theta temperature ( $^{\circ}\text{K}$ )	
		from Fig. 3	experimental
1	0.0469	299.12	299.0 <sup>11</sup>
2	-0.1520	297.08	298.2 <sup>4</sup>
3	-0.4353	299.29	299.1 <sup>4</sup>
4	-0.4057	289.77	-

The least squares polynomials can be used to give numerical values of  $d \ln[\eta]_T$  at a given temperature, as required on the left side of equation (9). Using the excluded volume theories in the calculation of the right-hand side of equation (9), the total slope can be then interpreted according to this relation.

The expressions of  $\kappa$  from the equations (14)–(16) are plotted as a function of  $\alpha$  in Fig. 2. It can be seen that the Fixman theory gives values closed to the Kurata-Stockmayer-Roig ones, whereas the differences between the Flory theory and the other two theoretical approaches considered in this study are higher. These differences become important especially for  $\alpha > 1.2$ .

According to equation (13), the plot of  $Y$  vs.  $T$  should be linear, of intercept  $-1$  on the  $Y$ -axis and  $\Theta$  on the  $T$ -axis. Fig. 3 presents the  $Y$ - $T$  dependences for the investigated samples and the obtained values of  $\Theta$  temperatures are given in Table 2. A good agreement can be seen between the calculated  $\Theta$  temperature and the experimental data obtained previously by turbidimetry.<sup>4,11</sup>

The concept of  $\Theta$  temperature for solutions of copolymers has not exactly the same meaning as in the case of homopolymers. Theta condition cannot be easily established because the excluded volume interactions exist between both like and unlike segment pairs. It is possible to obtain experimentally the critical mixing temperature for an infinite molar mass or the temperature at which the second virial coefficient vanishes for a given copolymer-solvent system, and this temperature can be operationally

identified with the  $\Theta$  temperature. Yet, it is very difficult to realize experimentally similar conditions with those corresponding to  $\Theta$  temperature of a homopolymer solution; as the interactions between like and unlike segments have to vanish simultaneously. For random copolymers an average binary cluster integral is assumed, which vanishes in the unperturbed state.

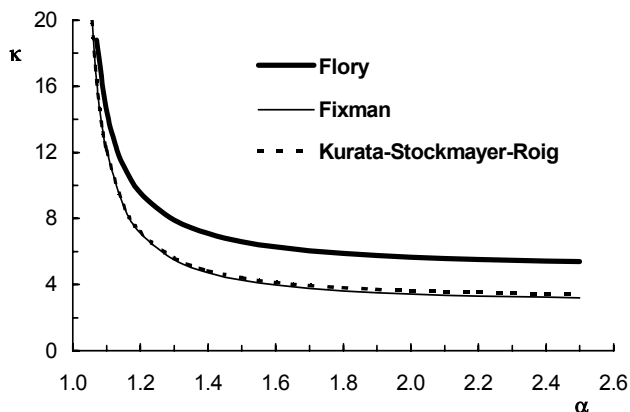
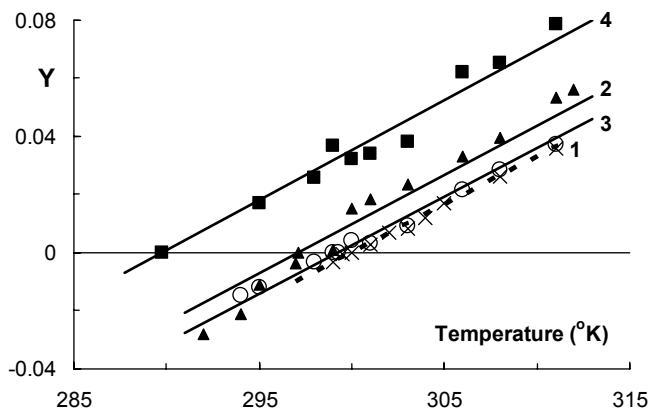


Fig. 2 – The parameter  $\kappa$  given by different excluded volume theories as a function of the expansion factor  $\alpha$ .

Fig. 3 – Plots of  $Y$  [eq. (13)] vs. temperature, according to the theory of Flory [eq. (14)] for the studied samples.



## EXPERIMENTAL

The synthesis of 2-(*o*-chlorophenyl)-4-methylene-1,3-dioxolane (CPMD) and the radical copolymerization of methyl methacrylate (MMA) with CPMD were previously reported.<sup>2</sup> Three samples of CPMD-*co*-MMA were selected for the present study (Table 1).

The weight average molecular weights ( $M_w$ ) and the number average molecular weights ( $M_n$ ) were obtained by gel permeation chromatography (GPC) using a PL-EMD 950 Evaporative Mass Detector equipped with 2×PLgel 5  $\mu$ m MIXED-C, 300×7.5 mm columns.  $\text{CHCl}_3$  (flow rate of 0.7  $\text{mL}\cdot\text{min}^{-1}$ ) was used as eluent.

Viscometric measurements were performed with an Ubbelohde type capillary viscometer requiring no corrections for the flow kinetics or hydrostatic pressure in carbon tetrachloride solutions. The temperature control of the bath was  $\pm 0.02^\circ\text{C}$ . Flow times were reproducible to within 0.05 s. Intrinsic viscosities were obtained using the Huggins method, in the domain of concentrations for which the relative viscosity is in the range  $1.2 < \eta_r < 1.8$ .

## CONCLUSIONS

An analysis of the intrinsic viscosity data over a temperature range where the dependence  $\ln[\eta]_T$  as a function of  $T$  is non-linear requires the excluded volume theories. The Flory, Kurata-Stockmayer-Roig and Fixman theories are considered, giving satisfactory results for random copolymers. The Flory theory is proved to be very useful to be applied for estimating the  $\Theta$  temperature. This analysis becomes very important especially when the theta condition is difficult to realize or even not accessible experimentally. The investigations must be extended over a temperature range as wide as possible when large changes of  $d\ln[\eta]_T / dT$  are expected.

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