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Treatments of intrinsic viscosity and glass transition temperature data of poly(2,6-dimethylphenylmethacrylate)

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Abstract

A useful relationship, $\ln(T_g) = \ln(T_{g,\infty}) - m[\eta]^{-\nu}$, between intrinsic viscosity and glass transition temperature for a series of homologous polymers was obtained by combining the Mark–Houwink–Kuhn–Sakurada (MHKS) relation for intrinsic viscosity and molecular mass, and the Fox–Flory equation for glass transition temperature and number-average molecular mass. This relationship was applied to poly(2,6-dimethylphenylmethacrylate) (PDMPh) in a variety of solvents (ideal to good) such as toluene, tetrahydrofuran/water, tetrahydrofuran, and chlorobenzene systems. The parameter α estimated by this procedure in toluene, tetrahydrofuran/water, tetrahydrofuran, and chlorobenzene systems are 0.50_6, 0.51_1, 0.56_7, and 0.67_3, respectively which are in agreement with those of Mark–Houwink–Kuhn–Sakurada values by less than 5% differences. The $T_{g,\infty}$ quantity estimated from this equation also is within the standard deviation of that obtained from the Fox–Flory method. The m quantity is increasing as the thermodynamic quality of the solvent improves, therefore, m may be considered as an indicator of coil conformations in a given solvent.

Keywords: Glass transition temperature; Intrinsic viscosity; Poly(2,6-dimethylphenylmethacrylate); Polymethacrylate derivative

1. Introduction

The aims of this work are to:

(a) investigate the relationship between T_g, and $[\eta]$, for the homologous poly(2,6-dimethylphenylmethacrylate) (PDMPh) series;
(b) estimate the $T_{g,\infty}$ using T_g and $[\eta]$ relationship and comparing with that of the Fox–Flory method [27];
(c) estimate α values from Eq. (5) and compare with the reported values [3];
(d) interpret m as a factor related to the conformation of the polymeric chain in the solution.

The intrinsic viscosity of macromolecules in dilute solutions is a measure of their hydrodynamic average size, form, and shape in the solution [1–10]. Many studies could be found that explore empirical relationships between coil dimensions of synthetic polymers with their intrinsic viscosity [1–15]. The most frequently used relationship between intrinsic viscosity, $[\eta]$, and the weight-average molecular weight, $\langle M_w\rangle$, is Mark–Houwink–Kuhn–Sakurada (MHKS) equation:

$$[\eta] = K_\alpha \langle M_w\rangle^\alpha \tag{1}$$

where the parameter α is a measure of thermodynamic power of solvent and K_α a measure of coil volume for an unperturbed condition or ideal solvent.

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Numerous researchers [1–12] have demonstrated the validity of MHKS equation applied to random coiled polymers for molecular weights ranging several orders of magnitude. By increasing thermodynamic strengths of solvents, the magnitude of coefficient α would increase while the magnitude of K_α would decrease. Generally for random coil flexible polymer molecules, the value of α would be between 0.50 and 0.80. For non-flexible and rigid (worm- or rod-like) macromolecules higher values of α, larger than or equal to unity has been observed. Thus the numerical value of α provides information concerning polymer conformation as well [1–14].

The validity of the Fox–Flory relationship between glass transition temperature, T_g, and number-average molecular weight, $\langle M_n\rangle$, for a homologous series of polymers has also been confirmed by a large number of investigators [16–29]. The well-known Fox–Flory equation (Eq. (2)) and its approximated form, (Eq. (3)) are the most frequently used relationships to relate the glass transition temperature with the number-average molar mass of a homologous series of a polymeric chain [17,18]:

$$T_g = T_{g,\infty}\, e^{-b/\langle M_n\rangle} \tag{2}$$

where b is a constant related to apparent energy of activation for a viscous fluid, proportional to exponent of the Fox–Flory equation for E_T [17] and independent of molecular weight of polymer. For simplicity, instead of Eq. (2) normally Eq. (3) is used:

$$T_g = T_{g,\infty} - \frac{k}{\langle M_n\rangle} \tag{3}$$

where k is a constant related to the nature of the polymer and $T_{g,\infty}$ represents the glass transition temperature obtained by extrapolation of $\langle M_n\rangle$ to infinity.

The nature of the glass transition temperature according to Cowie is a subject for considerable controversy and speculation. The phenomenon is rather a complex process to analyze. Most experimental evidences, however, tend to support the idea that T_g represents an iso-free volume state, with the free volume contribution at T_g. The available free volume can be altered either by addition of diluents or by increasing the number of chain ends in the system, each chain end presumably creates more free volume than a segment in the interior of the chain [16].

Replacing $\langle M_w\rangle = I\langle M_n\rangle$ in Eq. (1), rearranging for $\langle M_n\rangle$, substituting the $\langle M_n\rangle$ value into Eq. (2), taking the logarithm and rearranging one obtains:

$$\ln(T_g) = \ln(T_{g,\infty}) - IbK^{1/\alpha}[\eta]^{-1/\alpha} \tag{4}$$

Rewriting $m = IbK^{1/\alpha}$ and $\nu = 1/\alpha$ in Eq. (4), one obtains Eq. (5) which represents a linear relationship between $\ln(T_g)$ and $[\eta]^{-\nu}$ for a set of homologous polymer series:

$$\ln(T_g) = \ln(T_{g,\infty}) - m[\eta]^{-\nu} \tag{5}$$

2. Experimental

The monomer 2,6-dimethylphenylmethacrylate was synthesized by the reaction of methacryloyl chloride with corresponding phenol in the presence of triethylamine in benzene solution. The monomer was purified by several redistillations at reduced pressures. The PDMPh was obtained by radical polymerization of a 10% solution of monomer in benzene using 2,2′-azobisisobutyronitrile as a radical initiator at 333 K. The crud polymer was purified by precipitation in methanol. The narrow fractions of polymer were obtained by fractionation using toluene as a solvent and methanol as a precipitant. The number- and weight-average molecular masses were determined by size exclusion chromatography. The efflux time of the polymer solution and solvent was measured by a Desreux–Bischoff dilution capillary viscometer at 298 K. The intrinsic viscosities of the samples were determined through Huggins and Kraemer methods. A Perkin-Elmer differential scanning calorimeter, DSC-7, was used to determine the glass transition temperature of the samples. The samples were preheated under nitrogen to have the same thermal history. Table 1 summarizes the experimental data for five selected fractions of the PDMPh that are used in this work.

3. Results and discussions

3.1. Ideal solvent

Under the theta (θ) conditions [1–4] in which there are no excluded volume effects, Eq. (1) could be

Table 1
Physical characteristics of five selected fractions of PDMPh for the study of the relationship between glass transition temperatures and intrinsic viscosity in various solvents

$\langle M_w \rangle$ (kg/mol)	$\langle M_n \rangle$ (kg/mol)	T_g (K)	$[\eta]$ (dl/g)			
			Toluene	THF/ water	THF	CB
332	289	449.0	0.452	0.348	0.605	0.692
106	85	434.0	0.251	0.238	0.300	0.420
57	43	425.0	0.187	0.164	0.207	0.270
34	30	420.0	0.150	0.134	0.150	0.160
19	13	388.0	0.112	0.099	0.110	0.113

Table 2
$T_{g,\infty}$, and m from Eq. (7) in the indicated theta-solvents systems, calculated $m = bK_\theta^2$, and the $T_{g,\infty}$ values from the Fox–Flory method [27] for PDMPh

Systems	Property			
	Eq. (7)		Calculated m $(\mathrm{dl/g})^{1/2}$	Fox–Flory $T_{g,\infty}$ (K)
	$T_{g,\infty}$ (K)	m		
Toluene	451	13	12	450
THF/water	450	11	11	

written as:

$$[\eta]_\theta = K_\theta \langle M \rangle^{1/2} \tag{6}$$

where $[\eta]_\theta$ is the intrinsic viscosity under theta-conditions. It has been confirmed by numerous investigators [1–11] that the intrinsic viscosity, $[\eta]$, is proportional to the square root of the average molar mass, $\langle M \rangle^{1/2}$, over several decades of molar mass.

Under ideal conditions Eq. (5) can be written as,

$$\ln(T_g) = \ln(T_{g,\infty}) - m[\eta]_\theta^{-2} \tag{7}$$

Based on Eq. (7), a graph of the $\ln(T_g)$ versus $[\eta]_\theta^{-2}$ yields the numerical values of $\ln(T_{g,\infty})$, and $m = IbK_\theta^2$ as the intercept and the slope, respectively. Also, the slope $m = bK_\theta^2$ could be obtained from the graph of $\ln(T_g)$ versus $I[\eta]_\theta^{-2}$. The plots of $\ln(T_g)$ against $I[\eta]_\theta^{-2}$ for PDMPh in toluene (a single theta-solvent) and THF/water (a binary theta-mixture systems) is presented in Fig. 1.

The quantities of m from the slopes, the calculated $m = bK_\theta^2$, and $T_{g,\infty}$ estimated from the intercept of Fig. 1 along with the $T_{g,\infty}$ values obtained from the Fox–Flory relationship are tabulated in Table 2. The last value is reported from reference [27] for comparison of the results. The values of $T_{g,\infty}$ from the intercept agrees with that of the Fox–Flory (Eq. (2) or Eq. (3)) and m from the slope of the lines agree with calculated values ($m = bK_\theta^2$).

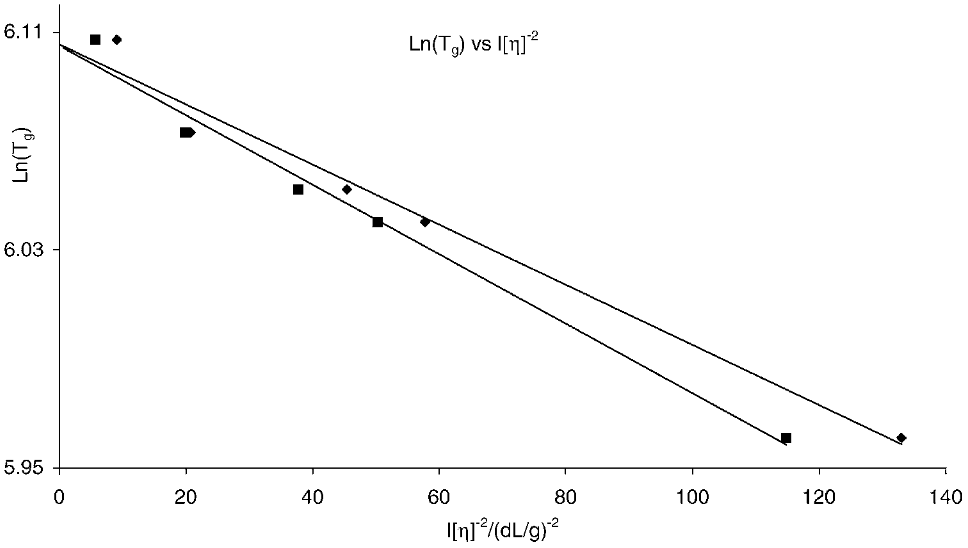

Fig. 1. Variation of $\ln(T_g)$ vs. $[\eta]_\theta^{-2}$ for PDMPh in ideal solvents: toluene (◆); and THF/water (■).

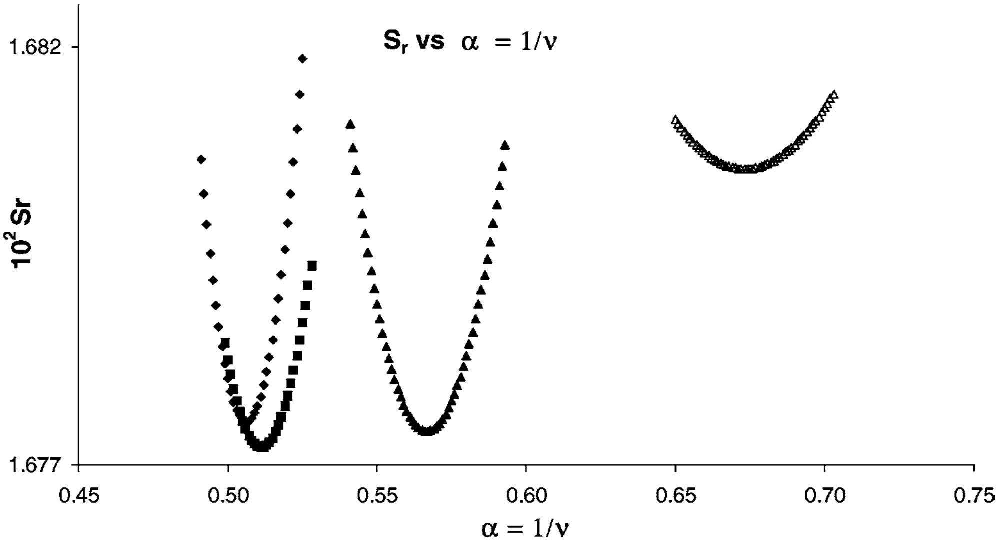

Fig. 2. Judicious numerical variation of S_r vs. suggested values of ν for PDMPh in toluene (◆), THF/water (■), THF (▲), and CB (×).

3.2. Non-ideal conditions

A plot of Eq. (5) could be a useful tool for estimating α, m and $T_{g,\infty}$ values for non-ideal systems, that mean, moderately good or good solvents, in which the quantity of α is not known. Supposing that there is a linear relationship between $\ln(T_g)$ and $[\eta]^{-\nu}$, and with the knowledge that $0.5 < \alpha = (1/\nu) < 0.8$ for a random flexible polymers such as PDMPh; a solution could be achieved by employing the method of least-squares, seeking the best straight line between experimental points of $\ln(T_g)$ versus $[\eta]^{-\nu}$ by judicious numerical approximation and reiteration methods. In order to fit a straight line to a set of experimental data, based on Eq. (5), for each suggested quantity of ν, only one standard deviation about regression (S_r) value exists. A smaller value of the S_r is indicative of a better fit of data to a straight line.

Table 3
KMHS' viscometeric parameters (presented for comparisons [3]), and calculated $m = bK_\alpha^{1/\alpha}$; α parameters estimated from Eq. (5) using minimum of S_r versus ν, and maximum of R^2 versus ν; and finally m and $T_{g,\infty}$ values from Eq. (5) with/without polydispersity correction for PDMPh in the indicated systems

Method	Parameter	Solvent			
		Toluene	THF/water	THF	CB
KMHS [3]	$10^4 K_\alpha$	7.80	7.50	3.31	1.84
	α	0.50	0.50	0.59	0.65
	$10^4 bK^{1/\alpha}$	12	11	24	34
Eq. (5)	α (minimum of S_r)	0.50_6	0.51_1	0.56_7	0.67_3
	α (maximum of R^2)	0.50_6	0.51_1	0.56_7	0.67_3
	$10^4 Im$	19	16	29	53
	$10^4 m$	14	11	20	38
	$T_{g,\infty}$	451	450	444	447
	$T_{g,\infty}$[a]	448	448	447	446

[a] Corrections made by polydispersity.

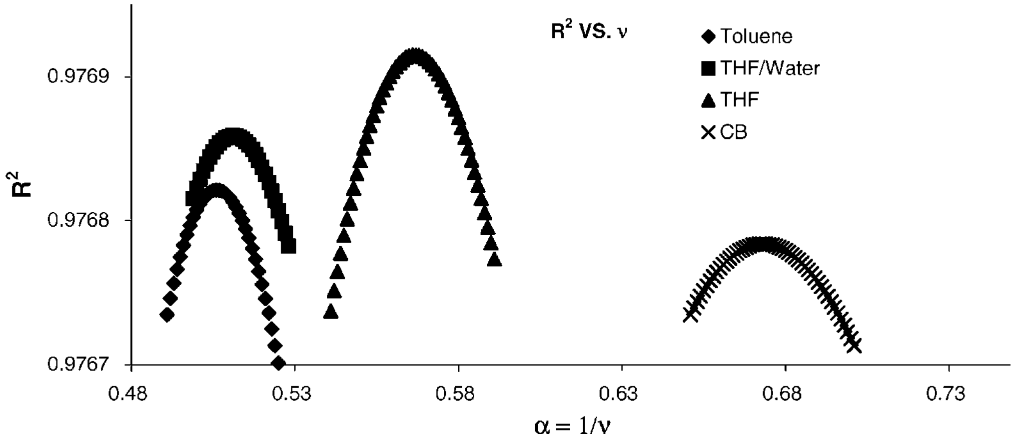

Fig. 3. Judicious numerical variation of suggested values of ν vs. R^2 for PDMPh in toluene (◆), THF/water (■), THF (▲), and CB (×).

A plot of S_r, against reiterated ν values would reach a minimum as can be seen in Fig. 2. The minimum corresponds to the best value of α and would generate the best line when $\ln(T_g)$ is plotted against $[\eta]^{-\nu}$ (Fig. 4). The estimated values of α are tabulated in Table 3. Also, the values of α from KMHS equation are shown for comparisons [3]. As Table 3 indicates, these values are in agreement with those of MHKS within 5%.

One can also use the square of correlation coefficient (R^2) as a criterion for the fitting of a straight line into a given set of data. A higher value of the R^2 indicates a better fit of data to a straight line. Fig. 3 represents the judicious numerical variation of R^2 versus suggested ν values based on the Eq. (5). The maximum of each curve yields the best ν value that fits to the straight line corresponding to experimental data of $\ln(T_g)$ against $[\eta]^{-\nu}$. The value of $\alpha = 1/\nu$ from this maximum may be considered as the best-estimated value of the MHKS' α as tabulated in Table 3. The corresponding α from this method is identical with the value from the previous method (S_r against ν).

Once the value of α is estimated, a graph of $\ln(T_g)$ versus $I[\eta]^{-1/\alpha}$ will yield $T_{g,\infty}$ and m values.

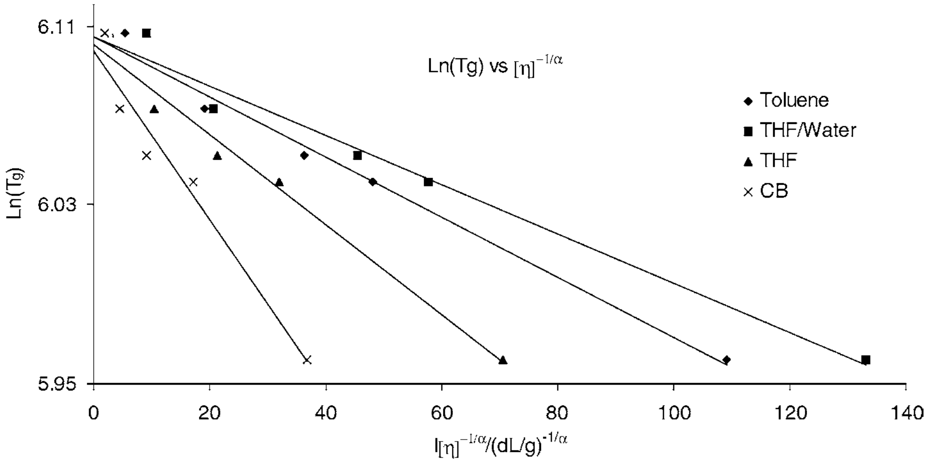

Fig. 4. $\ln(T_g)$ vs. $I[\eta]^{-1/\alpha}$ for PDMPh in toluene (◆), THF/water (■), THF (▲), and CB (×) systems.

Fig. 4 represents such a graph for PDMPh in toluene, THF/water, THF, and chlorobenzene (CB) systems.

Observing Fig. 4, one may assume that all systems would reach to a common intercept. Indeed, the least-square calculation also confirms the common intercept within the standard deviation as shown in the Table 3.

4. Conclusions

The units of slope m, based on Eq. (5), must be (volume/mass)$^{\nu}$, hence, m^{α} = volume/mass and equal to the specific volume of the segmental polymeric coil. It is an established fact that a random coil polymer expands more in a better solvent. Therefore, when the value of m increases by improving the quality of a solvent from poor to good one, this may indicate the expansion of the polymeric random coil. The m and α quantities are in agreement with respect to the thermodynamic quality of solvent. As the thermodynamic quality of the solvent improves, the value of α increases, and m also increases, indicating the expansion of the polymeric coil in a better solvent.

Hence, the parameter α and $T_{g,\infty}$ estimated from Eqs. (5) and (7) agree with those of Mark–Houwink–Kuhn–Sakurada and the Fox–Flory equation.

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