

# Viscosity, molecular weight and concentration relationships at 298 K of low molecular weight *cis*-polyisoprene in a good solvent

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## Abstract

A series of six well characterised homopolymers of *cis*-polyisoprene (PIP) ranging from 1180 to 115,000 molecular weight were utilised to explore viscosity and the scaling relationship between viscosity and concentration in dodecane (good solvent). For each polymer molecular weight, the relative viscosity of PIP in dodecane at 298 K was measured at several polymer concentrations using capillary viscometry. The linear extrapolation of experimental data based on Huggins, Kramer, Martin and Schulz-Blaschke equations was used to find the intrinsic viscosity at infinite dilution for each polymer molecular weight. The single-point method of evaluation of the intrinsic viscosity was also used for comparison. The Mark-Houwink fit of the data gave power index of 0.72 indicating that dodecane is good solvent for PIP and the latter exists in solution as open flexible coil. Both the radius of gyration and critical chain overlap concentration,  $c^*$ , were derived from measured intrinsic viscosities. Plot of the relative viscosities versus the scaled concentration  $c/c^*$ , resulted in single curve with slope value  $4.44 \times 10^{-2}$  and correlation coefficient  $r^2 = 0.996$ , indicating good linear fit. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Critical chain overlap concentration; Hydrodynamic radius; Intrinsic viscosity; Mark-Houwink equation; Radius of gyration; Relative viscosity; Root-mean-square end-to-end distance; Stockmayer-Fixman equation; Viscometry

## 1. Introduction

In our previous work, we have studied the rheological and phase separation properties of sterically stabilised poly(methyl-methacrylate) (PMMA) latex particles in non-aqueous non-adsorbing polymer solution [1–3]. The non-adsorbing polymer and solvent were *cis*-polyisoprene (PIP) and dodecane, respectively. Both the phase separation behaviour and rheology of the dispersions depended heavily on the molecular weight and concentration of the PIP. In this current communication, we report some solution properties of PIP in dodecane at 298 K derived from viscometry data.

Viscometric methods are based on the fact that the viscosity of a liquid to which a polymer is added increases proportionally with the volume of the polymer. Viscosity provides a wealth of information relating to size of the polymer molecule in solution, including the effects upon chain dimensions of polymer, structure, molecular shape, degree of polymerization and

polymer–solvent interactions. Most commonly, however, it is used to estimate molecular weight of a polymer. This involves the use of semi-empirical equations which have to be established for each polymer/solvent/temperature system analysis of samples whose molecular weights are known.

Absolute measurements of viscosity are not essential in dilute solution viscosity since it is only necessary to determine the viscosity of a polymer relative to that of the pure solvent. The limiting or intrinsic viscosity  $[\eta]$ , quantity is related to the molecular weight of the polymer by the semi-empirical Mark-Houwink equation,

$$[\eta] = KM_v^\alpha \quad (1)$$

where  $K$  and  $\alpha$  are constants for a given polymer, solvent and temperature. Generally,  $0.5 < \alpha < 0.8$  for flexible random coils in a good solvent,  $0.8 < \alpha < 1.0$  for inherently stiff molecules (e.g. cellulose derivatives, DNA, etc.) and  $1.0 < \alpha < 1.7$  for highly extended chains (e.g. polyelectrolytes in solutions of very low ionic strength) [4].

The methods which have been used can be divided into those involving extrapolation of experimental data (EED) at a series

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of concentrations and those involving estimation of  $[\eta]$  from a single viscosity measurement and the method is called the single-point method of evaluation (SPME).

In EED method, the viscosity of a dilute solution can be described by either any or a combination of the following equations [5]:

$$\text{Huggins equation : } \frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \quad (2a)$$

$$\text{Kraemer equation : } \frac{\ln \eta_r}{c} = [\eta] - k_K[\eta]^2 c \quad (2b)$$

$$\text{Schulz-Blaschke equation : } \frac{\eta_{sp}}{c} = [\eta] + k_{SB}[\eta]\eta_{sp} \quad (2c)$$

$$\text{Martin equation : } \ln\left(\frac{\eta_{sp}}{c}\right) = \ln[\eta] + k_M[\eta]c \quad (2d)$$

where  $\eta_r$  is the relative viscosity,  $\eta_{sp} = \eta_r - 1$  is the specific viscosity,  $c$  is the polymer concentration, and  $k_H$ ,  $k_K$ ,  $k_{SB}$  and  $k_M$  are the respective constants.  $\eta_{sp}$  is dependent on concentration and interaction forces. Plots of  $\eta_{sp}/c$  against  $c$  ( $\ln \eta_r/c$  against  $c$ ,  $\eta_{sp}/c$  against  $\eta_{sp}$  and  $\ln(\eta_{sp}/c)$  against  $c$ ) are straight lines with the intrinsic viscosity as the intercept provided that the concentrations are not too high. The respective constants  $k_H$ ,  $k_K$ ,  $k_{SB}$  and  $k_M$  can be calculated from the slope and depend on the solution state, temperature and polymer structure. Each of EED equations has limitations in its application. For instance, the Huggins equation strictly above applicable when  $[\eta]c \ll 1$ . At higher concentrations, experimental data show upward curvature when plotted according to this equation. The Krammer equation is an approximation of the Huggins equation, from which it may be derived assuming  $\eta_{sp} \ll 1$ . It has been suggested that  $k_H + k_K = 0.5$ , when the approximation is satisfactory for the Kraemer and Huggins equations [5]. The Schulz-Blaschke equation was deduced empirically. Experimental data plotted according to this equation show downward curvature as the concentration increases, though such plots are usually linear at higher concentrations than those obtained by application of the Huggins equation. Similar observations have been made with regard to the Martin equation, which was also deduced empirically.

The inconvenience of extrapolation methods for routine analysis has given rise to considerable interest in estimation of  $[\eta]$  from a single specific viscosity measurement, particularly when  $[\eta]$  need only evaluated approximately. In the SMME, the fol-

lowing equations are often used [5]:

$$\text{Solomon and Ciut\u00e1 : } [\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} c^{-1} \quad (3a)$$

$$\text{Deb and Chatterjee : } [\eta] = [3(\ln \eta_r - \eta_{sp} + 0.5\eta_{sp}^2)]^{1/3} c^{-1} \quad (3b)$$

$$\text{Ram Mohan Rao and Yaseen : } [\eta] = [\eta_{sp} + \ln \eta_r](2c)^{-1} \quad (3c)$$

These equations are only valid for use with good polymer-solvent pairs, as observed in practice [5].

## 2. Experimental

The *cis*-polyisoprene, together with the characterisation data by membrane osmometry (MO), intrinsic viscometry (IV), gel permeation/size exclusion chromatography (GPC/SEC) and low angle laser light scattering (LALLS), was supplied by Polymer Laboratories Ltd, UK. These methods were used to characterise the polymers for number-average ( $M_n$ ), weight-average ( $M_w$ ), viscosity-average ( $M_v$ ) and z-average ( $M_z$ ) molecular weights, and molecular weight distribution or polydispersity ( $M_w/M_n$ ). The polymers used were fairly monodispersed ( $M_w/M_n < 1.10$ ). The characterisation data are given in Table 1. The dodecane was supplied by Sigma-Aldrich. The polymers and dodecane were used, as supplied, without further purification.

A stock polymer solution was prepared by weighing PIP into a volumetric flask. The flask was then two thirds filled with dodecane. Dissolution of the polymer was done by suspending the flask with contents in a Dawe ultrasonic bath for at least 10 min. Such a time period was found to be enough to completely dissolve the polymer at concentrations used which were fairly low. The flask was finally filled to the mark and once again shaken in an ultrasonic bath for 3–4 min. Solutions with varying concentrations were prepared by pipetting the stock solution into 25 cm<sup>3</sup> volumetric flasks and diluted to the mark with dodecane.

The relative viscosity,  $\eta_r$ , is related to the flow times  $t$  and  $t_0$  and densities  $\rho$  and  $\rho_0$  for the solution and pure solvent, respectively, by the equation,

$$\eta_r = \frac{t}{t_0} \frac{\rho}{\rho_0} \quad (4)$$

Using the lowest molecular weight polymer for which the magnitude of  $\rho/\rho_0$  could be more significant, the densities of the

Table 1  
Molecular weight (in g mol<sup>-1</sup>) characterization data for PIP as supplied by Polymer Laboratories Ltd.

Batch no.	MO ( $M_n$ )	IV ( $M_v$ )	LALLS ( $M_w$ )	GPC/SEC ( $M_n$ )	GPC/SEC ( $M_w$ )	GPC/SEC ( $M_z$ )	$M_w/M_n$	Assigned ( $M_p$ )	Adopted code
20323-4	+	1203	+	1085	1165	1180	1.08	1180	P1K
20328-1	+	8308	+	7893	8061	8075	1.03	8000	P8K
20332-4	+	29103	+	27117	27943	28340	1.03	28300	P28K
20332-2	29240	31257	30720	30441	31137	31537	1.03	31500	P31K
20335-2	+	87862	+	85088	86942	85942	1.02	86000	P86K
20335-3	108000	110000	111251	111251	113314	113271	1.02	115000	P115K

+ According to the information provided by the supplier the technique not used or unapplicable.

Table 2  
Evaluated intrinsic viscosity values by extrapolation of experimental data (EED) method

Polymer code	$M_v$	$[\eta]$ ( $\text{cm}^3 \text{g}^{-1}$ )				
		Huggins	Kramer	Martin	Schulz-Blaschke	Mean value
P1K	1202	2.61	2.63	2.82	2.97	2.75
P8K	8308	12.40	12.40	12.40	12.38	12.39
P28K	29103	25.78	25.75	25.80	25.82	25.79
P31K	31257	33.55	33.52	33.68	33.45	33.55
P86K	87862	55.74	55.55	55.70	55.67	55.66
P115K	110000	70.14	70.13	70.17	70.20	70.17

solutions and solvent were measured and found to be the same within the experiment error. This was taken to mean that the contribution by  $\rho/\rho_0$  to  $\eta_r$  was negligible at concentrations used for capillary viscometry and so  $\eta_r$  was simply set to be equal to  $t/t_0$ .

The flow times of PIP solutions were measured with a Cannon-Fenske-type viscometer clamped to holder and suspended in a water bath at 25 °C. A 10  $\text{cm}^3$  volume of sample was pipetted into the viscometer for each determination, and the time of flow between two marks measured. The flow time used in all subsequent calculations of  $\eta_r$  was the average of at least five readings which agreed to within  $\pm 0.5$  s. To minimise any possible effects of polymer adsorption [6], equilibrium was allowed to be attained with the most concentrated solution and then measured the flow time with a fresh portion of the solution. Flow times of decreasing concentration solution series were performed, and finally the solvent flow time measured. It has been observed that provided the value of the adsorbed layer thickness remains constant throughout these measurements, the effect of the adsorbed layer will be minimised. Data at several polymer concentrations were used to determine  $[\eta]$  ( $\text{cm}^3 \text{g}^{-1}$ ) by the EED and SPME procedures.

### 3. Results and discussion

Fig. 1 shows a plot of the relative viscosity,  $\eta_r$ , as a function of concentration of PIP,  $c$ , of different molecular weights. The intrinsic viscosity  $[\eta]$ , values calculated gave roughly the same values irrespective of the equation used. Hence, a mean value for a given polymer molecular weight were used for further data analysis (Tables 2–4).

In general, the Mark-Houwink equation is linearised by plotting  $\ln[\eta]$  against  $\ln M_v$  from which the constants  $\alpha$  and  $K$  are

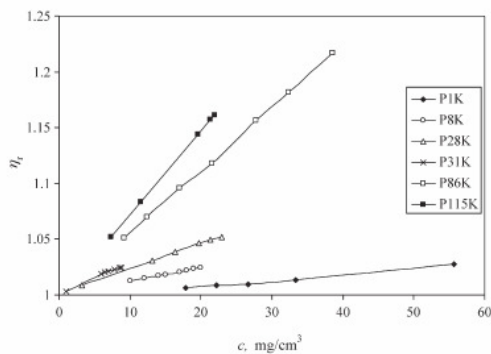


Fig. 1. Plot of relative viscosity with concentration for the different molecular weight polymers of PIP in dodecane.

Table 3  
Evaluated intrinsic viscosities using single-point method

Polymer code	$M_v$	Mean $[\eta]$ ( $\text{cm}^3 \text{g}^{-1}$ )			
		SC	DC	RY	Mean value
P1K	1202	3.92	3.93	3.93	3.93
P8K	8308	12.18	12.20	12.20	12.19
P28K	29103	23.46	23.53	23.53	23.51
P31K	31257	29.97	30.02	30.02	30.00
P86K	87862	53.74	54.24	54.27	54.08
P115K	110000	69.96	70.63	70.65	70.41

SC: Solomon and Ciuta, DC: Deb and Chatterjee, RY: Ram Mohan Rao and Yaseen.

Table 4  
Characteristic properties of PIP in dodecane

Polymer code	$[\eta]_0$ ( $\text{cm}^3 \text{g}^{-1}$ )	$[\eta]$ ( $\text{cm}^3 \text{g}^{-1}$ )	$\alpha_{\eta^a}$	$R_h$ (nm)	$R_{g0}^a$ (nm)	$R_g^a$ (nm)	$c^*$ ( $\text{g cm}^{-3}$ )
P1K	4.59	3.61	1.10(0.94)	0.9	1.0(1.1)	1.1(1.1)	0.261
P8K	12.03	11.49	1.15(1.04)	2.4	3.2(2.9)	3.2(3.1)	0.0720
P28K	22.52	26.86	1.24(1.13)	4.9	5.6(5.5)	7.0(6.2)	0.0243
P31K	23.34	28.23	1.30(1.13)	5.2	5.9(5.8)	7.7(6.6)	0.0204
P86K	38.13	58.31	1.37(1.20)	9.3	10.6(9.6)	14.5(11.6)	0.00832
P115K	43.78	68.37	1.41(1.23)	10.8	12.3(11.1)	17.4(13.6)	0.00644

<sup>a</sup> Values in brackets represent chain solution properties calculated from theoretical approximations due to van Krevelen [9].

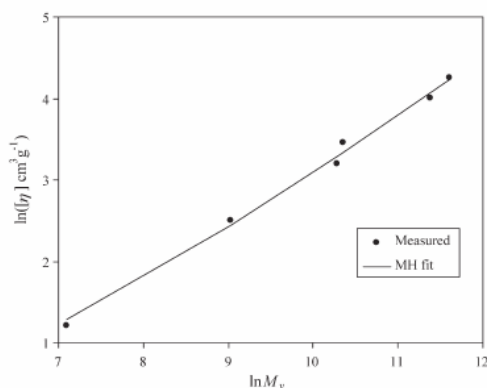


Fig. 2. The Mark-Houwink (MH) plot of the measured intrinsic viscosity data.

determined. Theoretically, this plot should not be linear over a wide range of  $M_v$ , so that  $\alpha$  and  $K$  values should not be used for polymers with  $M_v$  outside the range defined by the calibration samples. In the range  $1180 \leq M_w \leq 115,000$ , data seem to show curvature especially at lower  $M_v$ . It is known that macromolecules of  $M_v < 10^4 \text{ g mol}^{-1}$  and higher molecular weight samples do not exhibit a linear variation of  $\ln[\eta]$  against  $\ln M_v$ . A curvature at low  $M_v$  is often observed due to the non-Gaussian character of short flexible chains [5,6]. A relationship which is also valid for low molecular weights can be established by inserting a correction term  $b_\eta$  in the limiting viscosity. On plotting  $[\eta]$  versus  $M_v$   $[\eta] = b_\eta$  is obtained at  $M_v = 0$ . If  $\ln([\eta] + b_\eta)$  is plotted as a function of  $\ln M_v$ , a straight line is obtained even for low molecular weights. For high values of the limiting viscosity,  $b_\eta$  is so small that it can be neglected and the  $[\eta]$ – $M_v$ –relationship applicable to high molecular weights is obtained. Correcting with  $b_\eta = 1.0 \text{ cm}^3 \text{ g}^{-1}$  obtained from a plot of  $[\eta]$  against  $M_v$  for our data gave a fairly linear plot over the entire range of molecular weight studied. The modified Mark-Houwink  $[\eta]$ – $M_v$ –relationship allowing for low molecular weight rigidity for PIP in dodecane at 25 °C and plotted in Fig. 2 was thus found to be:

$$[\eta] = 1.0 + 0.0158M_v^{0.72} \quad (5)$$

The power index 0.72 indicates that dodecane is a good solvent for PIP and the later in solution exist as open and highly expanded flexible random coils [7]. The solubility rule supports this finding that dodecane is good solvent for PIP. A polymer, according to the rule, is soluble in a given solvent if the absolute value of the difference between the solubility parameters of the solvent and polymer is less than or equal to  $3.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ , assuming that the molar volume of solvent is equal to  $100 \text{ cm}^3 \text{ mol}^{-1}$  and as long as the polymer is non-polar and does not form hydrogen bonding in the solvent, the factors that can cause deviation from the rule of thumb [8]. The solubility parameter of dodecane is  $16.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$  and that of PIP has been found to be in the range  $16.2$ – $20.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$  and was calculated to be  $17.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$  using van Krevelen estimations

[9]. Using the solubility parameter calculated, the difference is approximately  $1 \text{ J}^{1/2} \text{ cm}^{-3/2}$ , which is less than the rule of thumb value. Furthermore, the solvent–interaction parameter  $\chi$  using van Krevelen data gave a value of 0.474 [10]. The interaction parameter  $\chi \approx 0.5$  implies that the polymer in a given solvent will have a random coil (or close to) configuration, which ultimately makes it easier to calculate the radius of gyration. These two theoretical results, according to polymer solution theory, confirm the experimental observation above that dodecane is good solvent for PIP.

In the range  $2 \times 10^4 < M_w < 10^7$ , Hirata et al. [11] have plotted their and other workers' data for PIP using the Mark-Houwink equation and found that they all fitted closely by the equation [12,13],

$$[\eta] = 0.0159M_v^{0.747} \text{ cm}^3 \text{ g}^{-1} \quad (6)$$

in good solvents (e.g. cyclohexane, toluene, etc.), regardless of the difference in solvent power or in temperature, and

$$[\eta]_o = 0.132M_v^{0.5} \text{ cm}^3 \text{ g}^{-1} \quad (7)$$

at theta temperature or in theta solvent. (e.g. 1,4-dioxane at 34 °C and at 31.2 °C). The slight difference in the value of the constant  $\alpha$  found may be due to smaller molecular weight range which was used in this work and also, most of the solvents used and reported in the literature are better solvents for PIP than dodecane [9]. The value of  $[\eta]$  for a given polymer depends on the thermodynamic quality of the solvent. In a good solvent, the polymer–solvent contacts are preferred and the value of  $[\eta]$  is high, whereas in poor solvents polymer–polymer contacts are preferred and lead to lower values of  $[\eta]$ . A description of the intramolecular interactions of polymer chains in dilute solutions is given by the equations of Fox and Flory [14].

Estimation of ideal chain dimensions from hydrodynamic measurements ( $[\eta]$ ) obtained in good solvents requires one of the graphical procedures [15]. The most familiar of these, the Stockmayer-Fixman plot [6], presumes that the viscosity expansion factor is  $\alpha_\eta^3 (\alpha_\eta^3 = [\eta]/[\eta]_o)$  in the Fox–Flory relation, which represents deviation from the unperturbed condition and which depends on the interaction between repeat units. The corresponding  $[\eta]$  data obtained from evaluation of the modified Mark-Houwink constants from the polymer samples with were used to plot as shown in Fig. 3 the linear form of the Stockmayer-Fixman equation given as follows:

$$\frac{[\eta]}{M_v^{0.5}} = K_0 + 0.51\Phi BM_v^{0.5} \quad (8)$$

where  $K_0$  is the conformational parameter,  $B$  is the long-range interaction parameter and  $\Phi$  is the Flory constant.  $B$  is a measure of the extent of the solvent–polymer interaction and thus, depends upon the chain structure and polymer–solvent interactions but is a constant for a given polymer–solvent–temperature system.

The conformational parameter  $K_0$  is related to the unperturbed dimension called root-mean-square end-to-end distance,

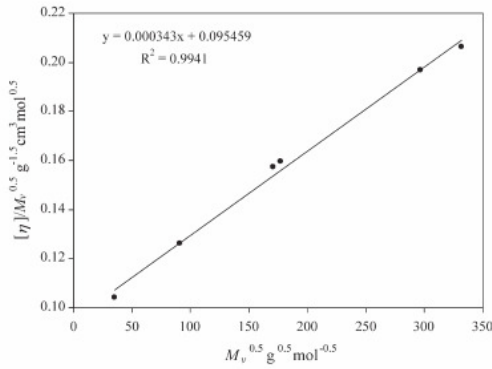


Fig. 3. The Stockmayer-Fixman plot of intrinsic viscosity data of PIP in dodecane from modified Mark-Houwink equation.

$(h^2)_0^{1/2}$ , by the equation [16,17],

$$K_0 = \Phi_0 \left( \frac{(h^2)_0}{M_v} \right)^{3/2} \quad (9)$$

With  $\Phi = 2.5 \times 10^{23} \text{ mol}^{-1}$  [5], this gave the conformational parameter,  $K_0 = 9.41 \times 10^{-2} \text{ cm}^3 \text{ mol}^{0.5} \text{ g}^{-1.5}$  and  $B = 2.72 \times 10^{-27} \text{ cm}^3 \text{ mol}^2 \text{ g}^{-2}$ . Using Eq. (10), the relation between the root-mean-square end-to-end distance for unperturbed chain,  $(h^2)_0^{1/2}$ , and  $M_v$  was found to be,

$$(h^2)_0^{1/2} = 7.22 \times 10^{-9} M_v^{1/2} (\text{cm}) \quad (10)$$

The hydrodynamic radius  $R_h$  is determined assuming the polymer the polymer coils are hard spheres so that when the polymer coil concentration is represented in terms of a volume fraction is the Einstein value of 2.5. This gives an equivalent hard sphere hydrodynamic radius expression of the chain [2],

$$R_h = \left( \frac{1}{2.5 N_A} \frac{3[\eta]M_w}{4\pi 10^6} \right)^{1/3} \quad (11)$$

The *dilute* and *semidilute* regimes in polymer solution theory are separated by the critical chain overlap concentration,  $c^*$ . This crossover concentration between the dilute and the *semidilute* regimes represents the concentration at which the polymer coils begin to touch or overlap. Various theoretical models have been suggested to estimate  $c^*$  [18–20]. According to the Vincent et al. model [18],  $c^*$  can be estimated from chain dimensions as follows:

$$c^* = \frac{M_w}{b^* R_g^3 N_A} \quad (12)$$

where  $N_A$  is the Avogadro number,  $M_w$  is the molecular weight,  $R_g$  is the perturbed radius of gyration and  $b^*$  is a constant and is equal to 5.63 for hexagonal close packing of polymer coils. In a good solvent, the unperturbed radius of gyration,  $R_{g0}$ , is usually a better estimate of the chain dimensions than the root-mean-squared end-to-end,  $(h^2)_0^{1/2}$ , as it accounts for the

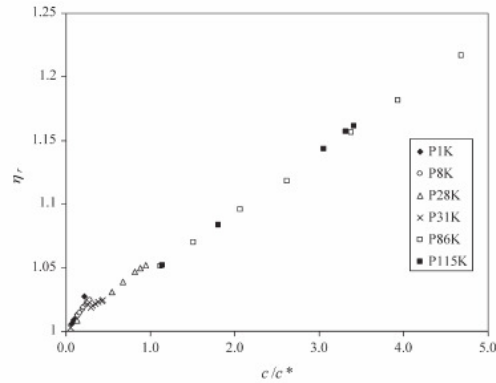


Fig. 4. Plot of relative viscosity with scaled polymer concentration for the different molecular weight polymers (slope =  $4.44 \times 10^{-2}$ , correlation coefficient,  $r^2 = 0.996$ ).

hydrodynamic radius,  $R_h$  (assuming non-draining condition), based on the Kirkwood-Riseman theory [6]

$$R_{g0} = \frac{R_h}{0.875} \quad (13)$$

where the hydrodynamic radius was calculated using Eq. (11) but more appropriately it can be determined by dynamic light scattering measurements [19]. The radius of gyration,  $R_g$ , of the chain in dodecane has also been estimated using the Stockmayer-Fixman equation. The calculated  $c^*$  values together with  $[\eta]$ ,  $\alpha_\eta$ ,  $R_h$ ,  $R_{g0}$  and  $R_g$  values for the PIP polymer studied are given in Table 4. It can be seen that  $c^*$  decreases with increasing molecular weight as the lower molecular weight chains, that have lower occupied hydrodynamic volume, require a higher concentration to overlap, as is expected.

To facilitate better interpretation of the variation of the slopes plots of  $\eta_r$  versus  $c$  shown in Fig. 1 for different polymers, the relative viscosity is replotted with the concentration re-scaled by the theoretically determined values of  $c^*$  (corresponding to each  $M_w$ ) as shown in Fig. 4. The variation in slopes is completely eliminated in the polymer molecular weight range and concentrations studied resulting in a single curve of slope value  $4.44 \times 10^{-2}$  with correlation coefficient  $r^2 = 0.996$ , indicating good linear fit. Often such scaling of data results in a curve with two regimes being indicated by the change in the slope of the trend in the data. Based on literature [20,21], these regimes correspond to *semidilute unentangled* and *semidilute entangled*, respectively. The first crossover between the two regimes is taken to mark the onset of the critical chain overlap concentration where the polymer chains topologically constrain each other and begin to entangle. These regimes were not observed in this study. However, there is slight deviation from linearity at low  $c/c^*$  which in our case is dominated by contributions by polymers P1K ( $M_w = 1180$ ) and P8K ( $M_w = 8000$ ). This is not surprising because even their effects, especially P1K, on rheology and phase separation of PMMA systems with higher polymer weights studied previously [1–3]. For instance, the

polymer PIK acted more like a solvent than a polymer. It did not induce phase separation and reduced the Bingham yield stress on addition to dispersion. On the other hand, higher molecular weight polymers induced phase separation and metastable phases.

Table 4 also gives the calculated chains dimensions,  $R_{g0}$  and  $R_g$ , purely based on theoretical approximation procedures due to van Krevelen [9]. In this procedure, the solubility parameters are estimated using the group additivity approach from the knowledge of structural group contributions. The solubility parameters are used to determine the constants in the Mark-Houwink and Stockmayer-Fixman equations. The Flory-Huggins theory is used to predict the solvent/polymer interaction parameter,  $\chi$ , or the second virial coefficient,  $A_2$ . From these theoretical predictions, the radius of gyration can be estimated under theta and non-theta conditions. A detailed step-by-step procedure is given in van Krevelen [9].

The agreement between the van Krevelen theoretical predictions and our results is remarkably good although theoretical values seem to be lower as the molecular weight of the polymer increases. This is inevitable because of the crude approximations and assumptions made in the theoretical treatment of viscometry data. The van Krevelen expansion coefficient,  $\alpha_s$ , estimation theory seems to give a value less than unity for the lowest molecular weight polymer. This is unrealistic because it would imply that the polymer coils shrink in good solvent. To avoid this, the expansion coefficient was, hence, assumed to be unity.

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