

Viscosity of Moderately Concentrated Solutions of Polymethyl-Methacrylate in Methyl-Methacrylate

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ABSTRACT: A Haake[®] viscometer with the NV cup-and-bob sensor is used to measure the viscosity, η , of polymethyl methacrylate (PMMA) solutions in methyl methacrylate (MMA) at several polymer concentrations, weight-average molecular weights, and temperatures, and under nonreacting conditions. Six polymer samples having different average molecular weights are prepared by polymerizing MMA in a 1-L batch reactor using 2,2'-azoisobutyronitrile (AIBN) as the initiator. Our earlier experimental data (at moderate concentrations of the polymer) on the viscosity of PMMA solutions in MMA under

reacting conditions is also used. Two general correlations are developed between $\frac{\eta}{\eta_{\text{sol}}}$ and $C_{\text{poly}}M_w^{0.76}$ with the parameters obtained using genetic algorithm. The tuned correlations for viscosity can be used over an extended range of monomer conversions for model-based state estimation and on-line optimal control of the bulk polymerization of MMA. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2139–2144, 2008

Key words: cup-and-bob assembly; Haake[®]-NV sensor; Martin equation; polymethyl-methacrylate; viscosity

INTRODUCTION

It is well known that viscosity plays a very important role in the processing of polymers. What is not as well appreciated is that it is equally important in polymerization, in the power required for stirring batch and special reactors (e.g., wiped-film reactors), in reactive extrusion, in controlling the bubble formation and entrapment in stirred reactors, etc. A considerable body of literature exists on the viscosity of dilute polymer solutions and its use in both the analytical determination of the average molecular weights as well as for testing out various statistical mechanical theories (see, for example, Refs. 1 and 2). Similarly, data (and correlations) on the viscosity of moderately concentrated polymer solutions and melts has been well documented (for example, Refs. 3 and 4), and correlated with^{5–9} the stiffness of the backbone bonds, temperature, concentration, molecular weight, polymer–solvent thermodynamic interactions, etc. The viscosities of solutions of polymethyl-methacrylate (PMMA) in dimethyl formamide have been reported by Shakhovskaya et al.¹⁰ over a range of temperatures. Tager et al.^{11,12} found that the viscosity of PMMA solutions in toluene (a good solvent) is lower

than that in dihexyl oxalate (a poor solvent). Dreval' et al.¹³ have observed the variation of the viscosity of PMMA in various solvents using the concept of free volume. Roven'kova et al.¹⁴ have suggested several equations to correlate data, e.g., those of Berlin, Huggins, Budtov, Kreisa, Heller, Doi, etc. Fedors,¹⁵ Rao,¹⁶ and Kasaai et al.¹⁷ have worked with the Martin^{18,19} and the Lyons-Tobolsky²⁰ expressions, which describe the variation of the viscosity of polymer solutions over extended ranges of polymer concentration (dilute and moderately concentrated). Similarly, Cross²¹ has suggested a single equation using the critical molecular weight for chain entanglement. Models for polydisperse polymer systems have been proposed by Nicheti and Manas-Zloczower²² and Baillagou and Soong.²³ The viscosity normally increases linearly with increase in the polymer concentration. Entanglements between polymer chains begin to form when the dimensionless Berry number (product of the intrinsic viscosity, η_{int} , and the polymer concentration, C_{poly}) increases beyond unity, and they increase sharply when $C_{\text{poly}}\eta_{\text{int}} > 10$. The viscosity goes up significantly at this point.

Several studies have been reported recently on the viscosity of polymer solutions in their monomer. These are extremely important in the design of bulk polymerization reactors. In fact, Mankar et al.²⁴ developed a viscometer-reactor assembly and took extensive experimental data on the viscosity of reacting polymethyl-methacrylate-methylmethacrylate (PMMA-MMA) systems. They used their data to develop an extended Martin correlation²⁴ for this

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system. They then used this correlation [along with experimental data on the histories (variation with time, t) of the viscosity of the reaction mass and the temperature] to sense the state (monomer conversion and average molecular weights) of the polymerization mass, on-line. They also developed a model-based optimal predictive control strategy to negate the effects of "disturbances" of the temperature. Sangwai et al.²⁵ extended this work recently to non-isothermal reactors and to reactors with intermediate addition of initiator (AIBN), conditions which are commonly met with in industry. Rho et al.²⁶ have developed similar on-line inferential state estimation models and adaptive model-predictive control algorithms for PMMA using a batch polymerization reactor. The Williamson^{27,28} model is another excellent and robust (not very sensitive to parameters) model for the viscosity of reacting systems. Curteanu and Bulacovschi²⁸ used this model to predict the viscosity of the bulk polymerization of PMMA-MMA system. All these recent studies emphasize the importance of developing robust models for the viscosity of reactive systems that can explain data over extended ranges of monomer conversions and average molecular weights. This study is an attempt along this direction.

In this work, a cup-and bob viscometer is used to measure the viscosity of nonreacting PMMA-MMA solutions at low-to-moderate polymer concentrations. In addition, our earlier experimental data²⁵ on the viscosity of the PMMA-MMA system during near-isothermal polymerization in the viscometer-reactor assembly (at higher polymer concentrations) are used to develop two correlations, the extended Martin correlation and the Lyons-Tobolsky equation for this system that are applicable over a much wider range of monomer conversions than reported so far.

VISCOSITY MEASUREMENT

Experimental setup

A Haake[®] (Gebrueder Haake GmbH, Karlsruhe, Germany) viscometer with the NV cup-and-bob assembly is used to measure the viscosity of (nonpolymerizing) PMMA-MMA solutions at different (constant) temperatures. This sensor can measure viscosities from 1×10^{-3} to 1×10^3 Pa s. The bob stops rotating automatically above the higher value so as to avoid damage to the measuring head. The NV system consists of a cup and a coaxial bell-shaped bob so that the sample is sheared on both the inside and outside surfaces of the rotor. The cup has an insert through which a liquid at a controlled temperature flows. A 222-1133 Haake[®] temperature vessel (for sensor system) is fitted on the outside of the cup. Water at controlled temperature also flows in

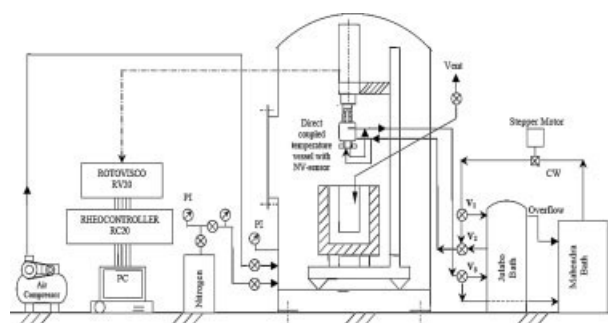


Figure 1 Schematic of the Haake[®] viscometer setup.

this. These help to maintain the sample at the desired temperature measured by a PT-100 sensor. A Julabo[™] (F10-MH, Julabo Labortechnik GmbH, Seelbach, Germany) and a Mahendra[®] Ultra Cryostat (Mahendra Scientific Instruments Manufacturing, Kanpur, India) temperature control bath are used for this purpose. The temperature is controlled to within $\pm 0.2^\circ\text{C}$.

The complete viscometer assembly is placed inside a pressurized vessel. Nitrogen is used for this purpose since there is no polymerization taking place. Pressurization is necessary to suppress the vaporization of monomer from the PMMA-MMA solutions at the temperatures used. The pressure used is taken to be about 10 times the vapor pressure of pure MMA, calculated using the Antoine equation²⁹ (P used = 1.5, 2.5, and 3.5 bar for temperatures of 50, 60, and 70°C , respectively). It is assumed that the presence of polymer does not lower the vapor pressure. This gives a safe upper value of the pressure. Figure 1 shows the details of the pressurization scheme as well as the temperature control system used for the experiment.

The cup-and-bob assembly is calibrated using double distilled water (viscosity = 10^{-3} Pa s at 20°C). The calibration factors are tuned such that the fluctuations in the viscosity of water are within $\pm 1.5\%$. The calibration factors obtained are $A = 1.7787$ Pa/% τ and $B = 22.89321$ s⁻¹/% τ .

Experimental procedure

Six samples of PMMA were obtained by polymerizing purified MMA (Central Drug House, New Delhi, India, LR, 99.0% purity) in a 1-L stainless steel stirred batch reactor^{24,30,31} at different conditions (initiator loadings, temperature, time of polymerization, etc) given in Table I. Table I also gives the monomer conversion, x_m (measured using gravimetry²⁴) and the weight average molecular weight, M_w [measured²⁴ using a calibrated Schott-Gerate (Schott Instruments GmbH, Mainz, Germany) 50101 Ubbelohde viscometer] of the polymer samples with-

TABLE I
Details of the Experiments

Polymerization conditions				Details of the samples withdrawn			
I_0 (mol/m ³)	P bar	Near-isothermal T (K)	RPM of the anchor agitator	Time of reaction at withdrawal (min)	Monomer conversion, x_{mr} of the withdrawn sample ^a	M_w of the withdrawn sample ^a	Symbols used
15.48	10	323.15	50	90	0.0915	1 005 530	□
		333.15		46	0.111	624 681	△
		343.15		24	0.1321	341 461	○
25.8		323.15		83	0.109	781 375	×
		333.15		54	0.168	439 462	◇
		343.15		27	0.191	245 934	+

^a Measured experimentally.

drawn from the reactor. These samples are quenched immediately in benzene (with a pinch of hydroquinone) at room temperature so as to stop the polymerization. Dilute solutions of the PMMA in benzene are precipitated using methanol and the polymer is filtered and dried. The dried polymer is dissolved in purified^{23,24} MMA, with a small amount of hydroquinone added (to prevent thermal polymerization at the test temperatures) to give homogeneous solutions of PMMA-MMA of the desired concentration. The original polymer solution is diluted with 4 mL of MMA each time after about 8–9 mL is taken out for use in the NV assembly. This is continued till the polymer concentration becomes about 2–3% w/w. In all, 132 values of viscosity were generated with these six polymer samples (with values of M_w as given in Table I), extending over 50–70°C and polymer concentrations of 12.04–166.9 kg m⁻³. The polymer produced is not monodisperse and is typical of that produced in industrial systems (with a PDI of a little over³² 2.0). This is not a major drawback since the correlation developed is to be used for polymerization reactor design and control.

The shear rates used are varied from about 20 s⁻¹ for solutions having higher concentrations to about 2200 s⁻¹ for very dilute solutions. An extra precaution is required when filling the NV assembly with concentrated polymer solutions so as to avoid drying of the polymer. A low shear rate of 20–30 s⁻¹ is applied as soon as the NV cup is tightened to the 222-1133 Haake[®] temperature vessel. Sufficient (relaxation) time is given before actually measuring the viscosities, as per the recommendation of Matsuo et al.³³

In addition to the present data on nonreacting systems, two sets of experimental viscosity data on the PMMA-MMA system from Sangwai et al.²⁵ during polymerization (at near-isothermal, NI, conditions, viz., NI-60 at $I_0 = 15.48$ and 25.8 mol m⁻³; 29 data points each) are also used in developing the two cor-

relations. These are at higher polymer concentrations ranging from 183.1 to 556.6 kg m⁻³.

RESULTS AND DISCUSSION

The extended Martin equation^{24,34}

One of the correlations developed in this work is the extended Martin equation.^{24,34} The viscosity, η , of the polymer solution, is given by

$$\eta = \eta_{\text{sol}} [1 + \eta_{\text{int}} C_{\text{poly}} \exp\{d_0 + d_1(\eta_{\text{int}} C_{\text{poly}}) + d_2(\eta_{\text{int}} C_{\text{poly}})^2\}] \quad (1)$$

In this equation, η_{sol} is the viscosity of the pure solvent, MMA, at the same temperature, C_{poly} is the concentration of the polymer, η_{int} is the intrinsic viscosity of a dilute (in the limit of $C_{\text{poly}} \rightarrow 0$) polymer solution of PMMA in benzene at 30°C, and $d_0 - d_2$ are parameters to be fitted to experimental data. η_{int} is given for the MMA-PMMA system by the Mark-Houwink equation with the parameters given by Cohn-Ginsberg et al.³⁵

$$\eta_{\text{int}} (\text{m}^3 \text{kg}^{-1}) = 5.2 \times 10^{-6} M_w^{0.76} \quad (\text{for } M_w \geq 35,000 \text{ kg kmol}^{-1}) \quad (2)$$

Clearly, η_{int} is used as a measure of M_w in eq. (1). This equation, along with eq. (1), gives

$$\frac{\eta}{\eta_{\text{sol}}} = 1 + C_{\text{poly}} M_w^{0.76} [\exp\{d_0^* + d_1^*(C_{\text{poly}} M_w^{0.76}) + d_2^*(C_{\text{poly}} M_w^{0.76})^2\}] \quad (3)$$

where $d_0^* - d_2^*$ are curve-fit parameters that are independent of T, C_{poly} , and M_w . C_{poly} is obtained for the experimental data in this study using gravimetry, whereas M_w is obtained using dilute solution visc-

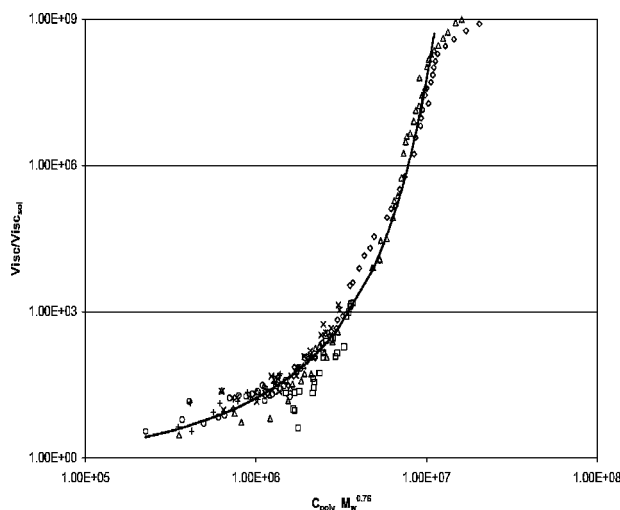


Figure 2 Plot of the solution-viscosity/solvent-viscosity as a function of $C_{\text{poly}}M_w^{0.76}$. Solid curve is the fitted extended Martin equation (eq. 3). Legend for the points are given in Table I.

ometry. For the data of Sangwai et al.²⁵ under reactive conditions, C_{poly} is obtained using

$$C_{\text{poly}} = (1 - \phi_m)\rho_p \quad (4a)$$

$$\phi_m = \frac{(1 - x_m)/\rho_m}{(1 - x_m)/\rho_m + x_m/\rho_p} \quad (4b)$$

$$\rho_m = 966.5 - 1.1(T - 273.15) \quad (4c)$$

$$\rho_p = 1200 \text{ kg m}^{-3} \quad (4d)$$

In this equation, ϕ_m is the volume fraction of the monomer, ρ_p is the density of the pure polymer, and ρ_m is the density of the pure monomer.^{36,37} Both C_{poly} and M_w are obtained using the kinetic model³⁶ for MMA polymerization.

The viscosity, η_{sol} , of the pure monomer is given by Yaws³⁸ as follows:

$$\log_{10}\eta_{\text{sol}} = J_1 + J_2/T + J_3T + J_4T^2 \quad (5)$$

where J_1 – J_4 are constants²⁴ equal to -7.7825 , $7.3478 \times 10^2 \text{ K}$, $1.0258 \times 10^{-2} \text{ K}^{-1}$, and $-1.1343 \times 10^{-5} \text{ K}^{-2}$, respectively.

The parameters, d_0^* , d_1^* , and d_2^* , in eq. (3) have been tuned using the experimental data on six sets of nonpolymerizing systems for relatively low concentrations of the polymer concentration. In addition, two sets of good data of Sangwai et al.²⁵ for the NI-60 polymerization runs (for $[I]_0 = 15.48$ and 25.8 mol m^{-3}) involving moderately concentrated PMMA solutions is used. Single-objective (simple) genetic algorithm (SGA³⁹) is used with 2000 generations for minimizing the sum-of-square errors between the experimental values and the model-predicted values. The optimal values of these parameters are found to be

$d_0^* = -12.03185$, $d_1^* = 9.21 \times 10^{-7}$, and $d_2^* = 4.57 \times 10^{-14}$. A plot of $\frac{\eta}{\eta_{\text{sol}}}$ against $C_{\text{poly}}M_w^{0.76}$ is shown in Figure 2. It is observed that data beyond values of $C_{\text{poly}}M_w^{0.76}$ of about 1.1×10^7 do not fit this correlation too well. Indeed, Sangwai et al.²⁵ have indicated that the extended Martin correlation is not too good for high values of $C_{\text{poly}}M_w^{0.76}$. A parity plot of the data for $C_{\text{poly}}M_w^{0.76} \leq 1.1 \times 10^7$ is shown in Figure 3. Interestingly, a single (common) correlation works well over almost the entire domain of interest and is recommended for use in reactor design for $2.25 \times 10^5 \leq C_{\text{poly}}M_w^{0.76} \leq 1.1 \times 10^7$.

The Lyons-Tobolsky equation^{20,28}

The Lyons-Tobolsky^{20,28} equation is given by

$$\frac{\eta}{\eta_{\text{sol}}} = \left[1 + (C_{\text{poly}}\eta_{\text{int}})\exp\left(\frac{k_H(C_{\text{poly}}\eta_{\text{int}})}{1 - bC_{\text{poly}}}\right) \right] \quad (6)$$

which, on using eq. (2), gives

$$\frac{\eta}{\eta_{\text{sol}}} = \left[1 + a^*C_{\text{poly}}M_w^{0.76}\exp\left(\frac{k_H^*C_{\text{poly}}M_w^{0.76}}{1 - b^*C_{\text{poly}}}\right) \right] \quad (7)$$

The tuned values of the three parameters are given by

$$\begin{aligned} k_H^* &= 1.4898 \times 10^{-6} \\ a^* &= 5.2 \times 10^{-6} \\ b^* &= 3.25 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1} \end{aligned} \quad (8)$$

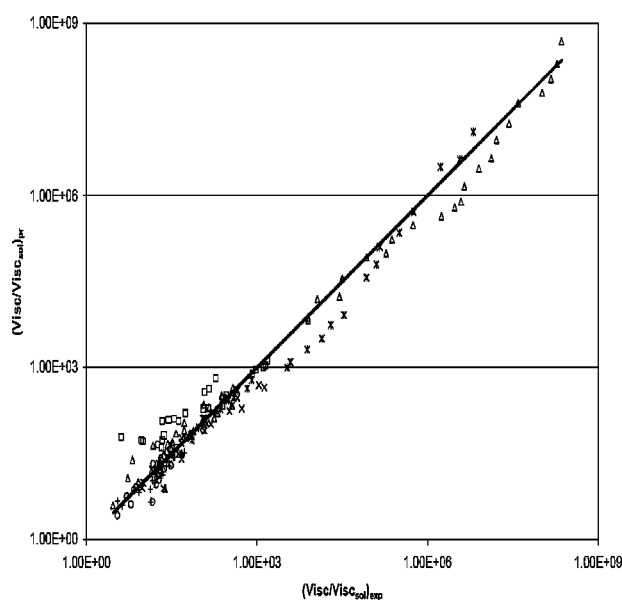


Figure 3 Parity plot of the viscosities determined experimentally versus model (eq. 3)-predicted values. Legend same as in Figure 2/Table I.

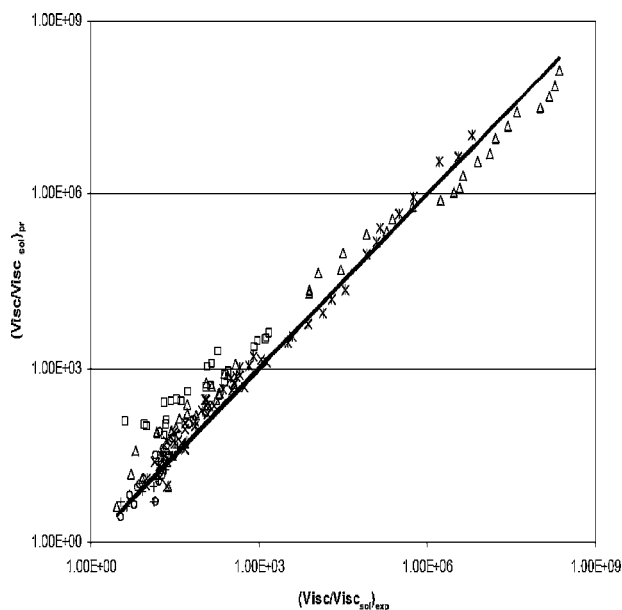


Figure 4 Parity plot of the viscosities determined experimentally versus model (eq. 7)-predicted values. Legend same as in Figure 2/Table I.

Figure 4 gives the parity plot for $C_{\text{poly}}M_w^{0.76} \leq 1.1 \times 10^7$ for this correlation. It is observed that the agreement of data with this correlation is equally satisfactory.

CONCLUSIONS

Experimental data is generated for the viscosity of PMMA-MMA systems at three different temperatures (50, 60, and 70°C) in the relatively low concentration region. This data is used along with some earlier experimental data (Sangwai et al.²⁵) on reactive PMMA-MMA systems in the higher concentration region. Two global correlations are developed for the viscosity which is equally good. These are applicable over an extended range of conditions.

NOMENCLATURE

a^*, b, b^*	parameters in eqs. (6) and (7)
C_{poly}	concentration of polymer (kg m^{-3})
d_0, d_1, d_2	empirical parameters in the viscosity correlation (eq. 1)
d_0^*, d_1^*, d_2^*	empirical parameters in the viscosity correlation (eq. 3)
k_H, k_H^*	parameters in eqs. (6) and (7)
M_w	weight-average molecular weight (kg kmol^{-1})
x_m	(molar) monomer conversion in batch reactor [$\equiv 1 - (M/M_0)$]

Greek letters

$\dot{\gamma}$	shear rate (s^{-1})
η	viscosity of the polymer solution (Pa s)
η_{int}	intrinsic viscosity ($\text{kg}^{-1} \text{m}^3$)
η_{sol}	viscosity of the pure solvent (monomer) (Pa s)
ρ_m, ρ_p	density of pure (liquid) monomer and polymer at temperature, T (kg m^{-3})
ϕ_m	volume fraction of monomer

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