

Viscosity Studies on Polypropylene Glycol and Its Blend¹

K. Venkatramanan^{2,3} and V. Arumugam⁴

Viscosity studies have been made on polypropylene glycol (PPG) of different molar masses [500, 1000, 2000] in both low and medium concentration ranges [lower concentration range 0 to 1% (w/v) and medium concentration range 1 to 10% (w/v)] in toluene, in the temperature range of 303 to 333 K. The effect of concentration on the activation energy of flow was calculated. It was observed that the activation energy of flow is greater for molar masses of 1000 and 2000 than that of the solvent. The effect of molar mass was also analyzed, and it was indicated that in PPG, a molar mass of 1000 might represent a transition state for the molecule from one shape to another shape. An attempt has also been made to blend PPG 2000 with PPG 500 (concentration 1% (w/v)), for various compositions of the blend. The miscibility nature of the blend was analyzed through viscosity studies and other techniques. The blend showed immiscibility. In this study the activation energy of flow for PPG in toluene was calculated and also the miscibility of two molar masses of PPG was investigated through viscosity studies. This work clearly shows that a viscosity study can be used for analyzing the miscibility of two polymers.

KEY WORDS: activation energy; blend; compatibility; polypropylene glycol; toluene; transition state; viscosity.

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² Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya (Deemed University), Enathur, Kanchipuram – 631 561, Tamilnadu, India.

³ To whom correspondence should be addressed. E-mail: venkat_kannan@yahoo.com

⁴ Biophysics Laboratory, Central Leather Research Institute, Adyar, Chennai – 600 020, India.

1. INTRODUCTION

Viscometry is one of the simplest methods for studying the interactions and properties of polymer–polymer systems in solutions. Attractive interactions increase the viscosity of these systems. The temperature dependence of the viscosity of polymer solutions has been of great interest for a long time since the work of Moore and Brown [1], Moore and Murphy [2], Fort and Moore [3] and Moore [4]. The Arrhenius equation can be extended to dilute polymer solutions as for a pure liquid. Many researchers [5, 6] have observed that the apparent activation energy of flow and the pre-exponential term depend not only on the molar mass and concentration but also on the polymer chain stiffness and coil expansion. It has been reported that the difference between the activation energy for the solutions and for the solvent is much higher than for flexible chains.

Moore's equation has been applied to poly (β -naphthyl methacrylate) dissolved in different solvents by Niezette et al. [6]. They have also tried to express the pre-exponential term in terms of the Mark-Houwink and Fox-Flory constants. Viscosity and ultrasonic studies on polyethylene glycol in benzene have been reported by Arumugam et al. [7]. The conformational behavior of PPG oligomers in various solvents has been reported by Sandell and Goring [8].

Polymer blending is one of the most commercially significant areas for the development of new polymer materials. The ultimate goal of polymer blending is a practical one of achieving commercially viable polymers with either unique properties or lower cost than some other means might provide. Polypropylene glycol (PPG), the simplest propylene oxide based polyol is a commonly used polymer for various applications. It finds its applications as a hydraulic fluid, rubber lubricant, antifoam agent, etc. The advantage of using viscosity measurements for investigating polymer miscibility has been demonstrated by several researchers [9–14].

In the present study an attempt has been made to test Moore's equation for PPG of different molar masses and also to study the compatibility of PPG 2000 with PPG 500 using viscosity measurements.

2. MATERIALS AND METHODS

PPG samples of molar masses of 500, 1000, and 2000 were provided by Manali Petro Products, Chennai. Polymer solutions were prepared by dissolving these polymers in toluene to give concentrations of 0.1, 0.25, 0.5, 0.75, 1, 2, 5, 7, and 10% (w/v). The viscosity studies were carried out in a Ubbelohde viscometer in the temperature range of 303 to 333 K, and the timings were measured accurately using a digital stop watch (0.01 s).

The viscometer was kept in a temperature-controlled water bath (uncertainty of $\pm 0.5^\circ\text{C}$) during the experiment. The density of the solutions was measured using a gravimetric method at various temperatures using an ultra-thermostat (uncertainty of $\pm 0.5^\circ\text{C}$). All the weighings were done using a single-pan digital electronic balance (uncertainty of ± 0.1 mg).

2.1. Blend Preparation

In the present study, PPG 2000 is blended with PPG 500 at 1% (mass%) concentration. The compositions of the blend PPG 2000:500 were in the following ratios 1:0, 0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8, and 0:1 (uncertainty $\pm 0.5\%$). Refractive index studies were performed using an Abbe refractometer (Model G, Carlzeiss, uncertainty of $\pm 0.5\%$).

3. RESULTS AND DISCUSSION

The Arrhenius expression can be used for pure solvents and also for dilute polymer solutions. According to Moore [4],

$$\eta = Ae^{Q/(RT)}, \quad (1)$$

where Q is the apparent activation energy of flow in kJ, A is a pre-exponential term with activation entropy significance, R is the universal gas constant in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and T is the temperature in K. The logarithm of this equation leads to a linear relationship;

$$\ln \eta = \ln A + (Q/R)1/T. \quad (2)$$

Figure 1 shows the variations of $\ln \eta$ with the inverse of temperature for PPG 500. The plots of PPG 1000 and 2000 are also similar to these plots. Generally a drastic change in the ($\ln \eta$) viscosity indicates a conformational transition of the polymer chain. The straight line indicates that the viscosity did not change in this temperature range (303 to 333 K) [6]. In all cases $\ln \eta$ values increase with concentration and also with temperature. The activation energy is given by the slope of these curves. The variation of Q with concentration C is given in Fig. 2. It can be seen from Fig. 2 that the dependences fit a straight line, and the corresponding slope and intercept values are determined. The activation energy of flow follows the equation,

$$Q = Q_0 + K_e MC, \quad (3)$$

where K_e is a constant, M is the molar mass, C is the concentration, and Q_0 is a constant dependent on the polymer and its molar mass. The effect

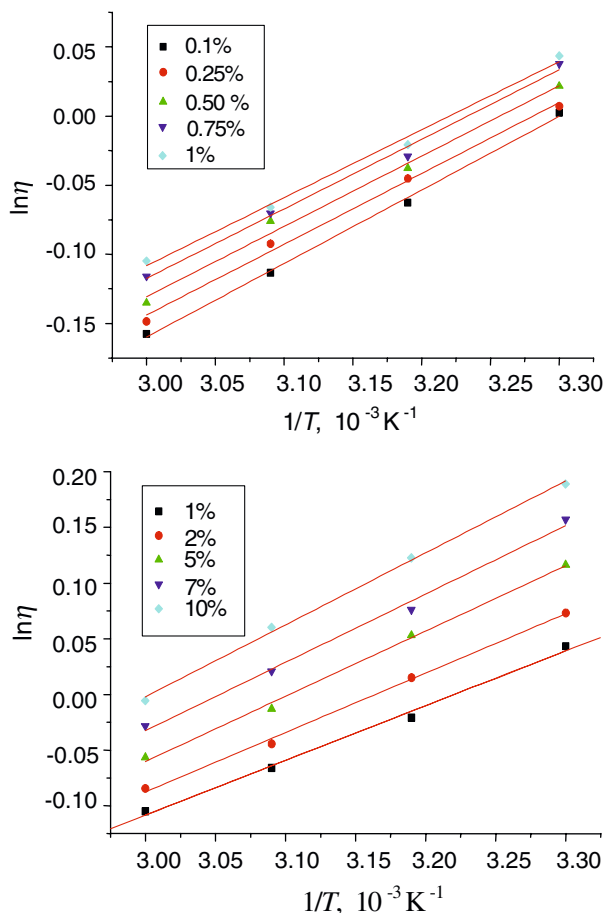


Fig. 1. Variation of $\ln \eta$ with $1/T$ in the temperature range 303 to 333 K for low and medium concentration ranges (mass%) of PPG 500 in toluene.

of concentration was noted while plotting Q against concentration (Fig. 2). Hence, for the sake of convenience, it was decided to divide the concentrations into two ranges, viz., lower range 0.1 to 1% and medium range 2 to 10% (mass %).

The intercepts of $\ln \eta$ versus $1/T$ plots give the A values, i.e., the pre-exponential terms. The variation of A with concentration and molar mass is given in Fig. 3. The $\ln A$ versus concentration curves show that the general trend is a straight line. PPG shows a decreasing trend with an increase

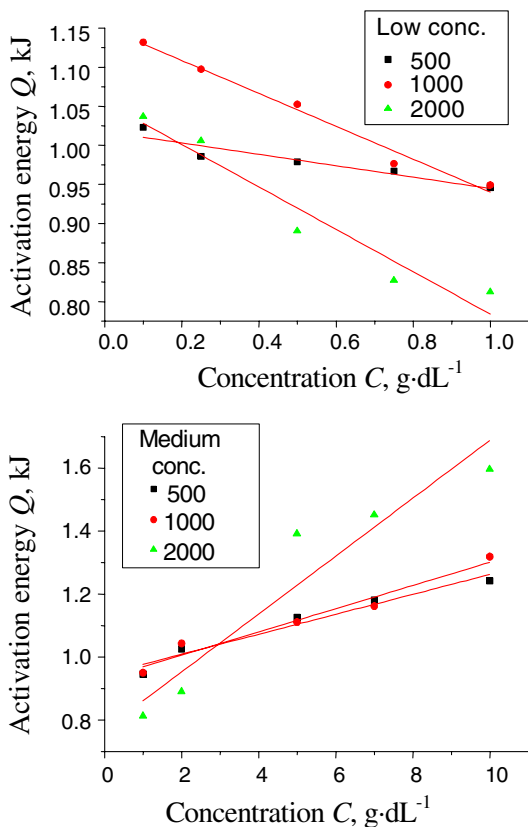


Fig. 2. Variation of activation energy Q with concentration C for PPG of different molar masses in toluene.

in concentration as can be seen from Fig. 3. If the plot is drawn between activation energy Q and concentration C , according to Eq. (3), we can get the value of Q_0 from the intercept and the slope will give the value of $K_c M$. The general trend seems to be the same, although the values are different in both graphs. It can be observed that the activation energy of flow is greater for molar masses of 1000 and 2000 than that of the solvent. According to Niezette et al. [6], such a behavior is expected for flexible chain polymers. Sandell and Goring [8] have reported that the polypropylene chain is flexible and can be bent into a flat compact coil with chain lengths as short as five repeating units. However, they have reported the disk-coil configuration as most suitable for only aqueous PPG solutions. In organic solvents the conformation of the oligomer chain would depend

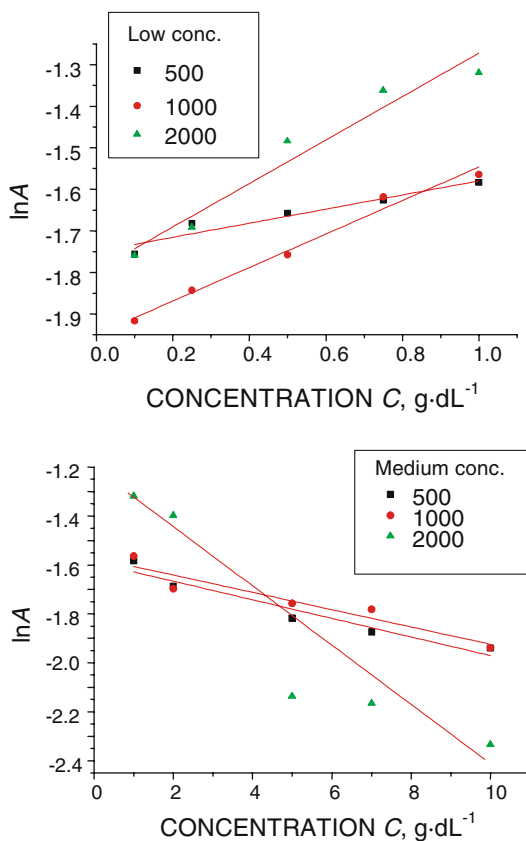


Fig. 3. Variation of the pre-exponential term $\ln A$ with concentration C for PPG of different molar masses.

on the nature of the solute–solvent interactions, Van der Waals forces, and also on the solute–solute interactions. It has been reported by Sandell and Goring that for molar masses greater than 500, PPG in benzene assumes a random coil configuration. Meyerhoff [15] has suggested that at low molar masses the configurations change from a random coil to a rotational ellipsoid shape. From Figs. 4 and 5, we understand that the behavior of PPG is different for molar masses below and above 1000. So we can infer that in PPG's, a molar mass of 1000 may represent the transition state for a change of behavior. A plot between $K_e M$ and molar mass M shows that for lower concentrations (0 to 1%), the value of $K_e M$ decreases with M , and vice versa for higher concentrations, which is shown below.

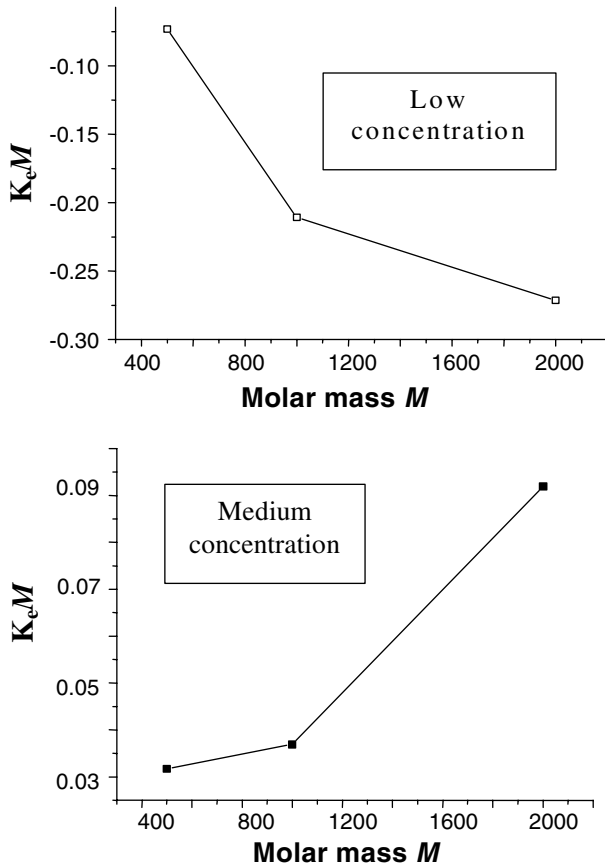


Fig. 4. Variation of $K_c M$ with different molar masses M of PPG.

4. BLENDS

When two or more polymers are mixed in a single continuous solid product, the composition is generally referred to as a polymer blend or polyblend. Singh and Singh [16] have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Rajulu [17] carried out ultrasonic and viscometric investigations of cellulose acetate/PMMA blends in solution and reported that the immiscible blend shows an S-type behavior. Sun et al. [18] have suggested a viscometric method to study polymer-polymer miscibility. The viscosity study (Fig. 6) shows that the blend is semicompatible. The viscosity method is simple, and it offers very useful information about the relationship

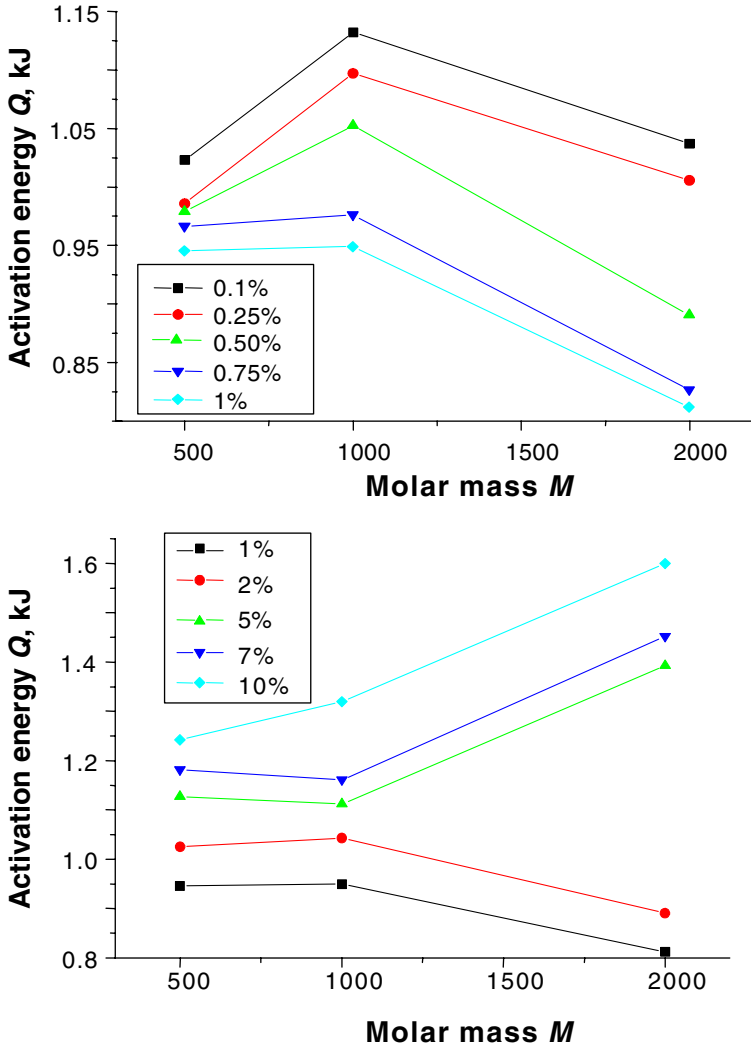


Fig. 5. Variation of activation energy Q with different molar masses M of PPG in toluene.

between dilute solution properties and the bulk structure of the polymer blend. The basic idea of using viscosity as a parameter for compatibility determination of polymer blends lies in the fact that in solution the repulsive interactions may cause shrinkage of polymer coils resulting in a viscosity of the polymer mixture that is lower than the value calculated from

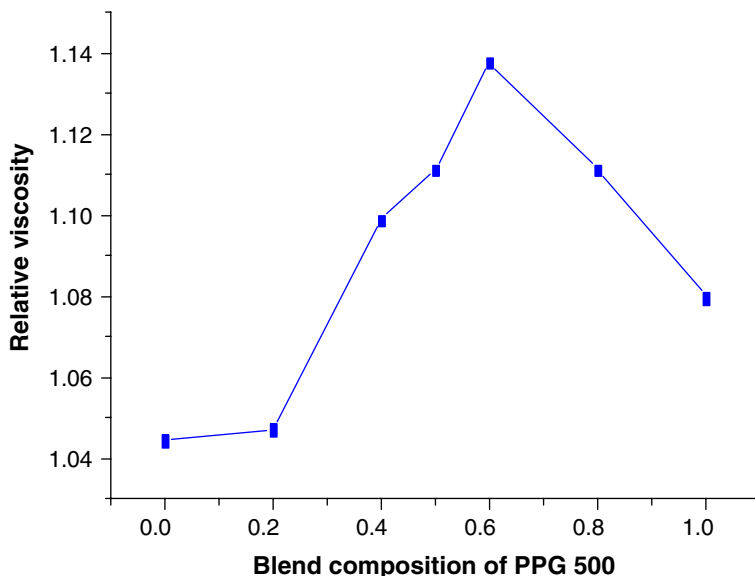


Fig. 6. Variation of relative viscosity η with the composition of PPG 500 in the blend PPG 2000:500 in toluene at 303 K.

viscosities of the pure components based on the assumption of the additive law.

Viscosity measurements may indicate the miscibility of a polymer blend. Das and Banerjee [19] have used a few empirical and semiempirical equations for predicting the miscibility of polymer blends based on viscosity, viz., the additive rule, log additive rule, and free volume additive rule. Three significantly different behavior patterns may be observed in the blends. In a compatible blend, the rheology represents an ideal mixing of the two components, which is very rare. The other two behaviors are represented by blends having a viscosity higher or lower than their components. For miscible blends a number of empirical and semiempirical equations predicting the viscosity of polymer blends have been proposed while achieving varying degrees of success.

The additive rule of mixtures is given by

$$\eta_b = m_1 \eta_1 + m_2 \eta_2, \quad (4)$$

$$\log \eta_b = m_1 \log \eta_1 + m_2 \log \eta_2, \quad (5)$$

$$1/(\log \eta_b) = m_1(1/\log \eta_1) + m_2(1/\log \eta_2) \quad (6)$$

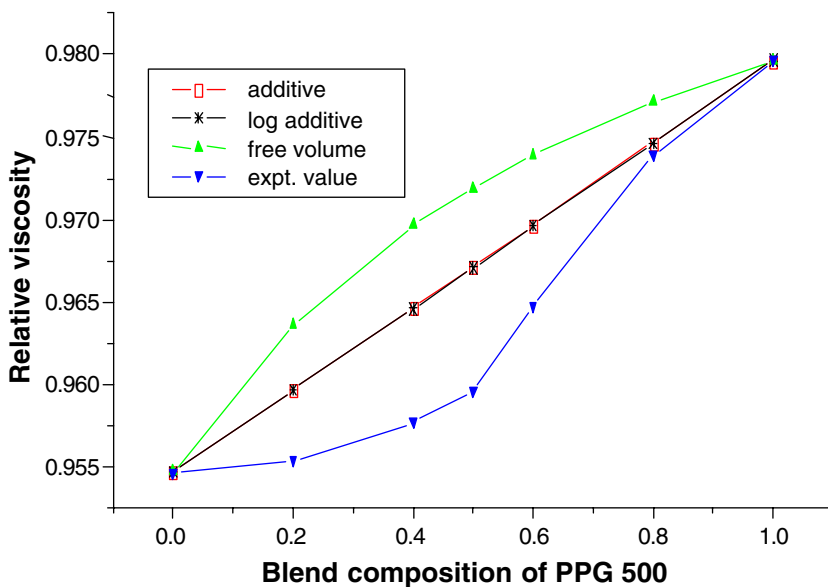


Fig. 7. Variation of relative viscosity η with the composition of PPG 500 using additive rule at 303 K.

where η_b is the viscosity of the blend, η_1 and η_2 are the viscosities of components 1 and 2, respectively, and m_1 and m_2 are the mass fractions of components 1 and 2, respectively.

Utracki and Kamal [20] have described the complexity of the viscosity composition behavior of polymer blends. Using rheological data, they are divided into three categories depending on the deviations from the log additive rule, i.e., (a) positive deviations, (b) negative deviations, and (c) positive and negative deviations. The negative deviation of the log additive rule in the case of immiscible blends was reported by Plochocki [21].

From Fig. 7, we can observe that the experimental values show negative deviations and they are closer to log additive values, which represent negative interactions, which in turn causes the macromolecules to shrink. This shows that the blend is immiscible.

Sun et al. [18] have proposed an interaction parameter α , based on the viscosity data of the component systems. The sign of parameter α can be used to predict the miscibility of the polyblend; when $\alpha > 0$, the blend is miscible, and when $\alpha < 0$, it is immiscible. In order to confirm the immiscibility of the blend, the α values (Table I) were determined by the usual methods [18, 22]. The values are negative, confirming the immiscible nature of the blend. Density studies (Table I) show that the variation

Table I. Composition of the Blend PPG 2000:500 in Toluene at 303 K

Blend composition (PPG 2000:500)	Relative viscosity, (η)	Density ($10^{-3}\text{kg}\cdot\text{m}^{-3}$)	Refractive Index	Interaction parameter (α)
1:0	1.07972	0.86131	1.4925	0
0.8:0.2	1.11121	0.86131	1.4920	-0.045833
0.6:0.4	1.13767	0.85949	1.4918	-0.0418585
0.5:0.5	1.11121	0.86131	1.4918	-0.0384816
0.4:0.6	1.09886	0.86131	1.4920	-0.0314124
0.2:0.8	1.04719	0.85949	1.4920	-0.0172649
0:1	1.04439	0.86131	1.4913	0

is not linear with an increase in composition of PPG 500, and, hence, it may be concluded that the blend is immiscible.

4.1. Optical Studies

Refractive index is a useful technique to analyze polymer blends. Rajulu et al. [23] studied the miscibility of PVC-PMMA blends using a refractometric technique. In the present study, the variation between refractive index and blend composition is non-linear (S-type), which shows the incompatibility (Table II).

5. CONCLUSION

The effect of concentration on the activation energy of flow was calculated for PPG 500, 1000, and 2000. It was observed that the activation energy of flow is greater for molar masses of 1000 and 2000 than that of 500. The effect of molar mass was analyzed from the plot between $K_e M$ and molar mass (M), which indicated that for lower concentrations, the value of $K_e M$ decreases with M and vice versa for higher concentrations. This showed that in PPG, a molar mass of 1000 might represent the transition state for the molecule from one shape to another shape. The miscibility nature of the blend PPG 2000:500 was also analyzed through viscosity studies and other techniques. The blend showed immiscibility.

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Table II. $\ln\eta$ Values for PPG of Molar Masses 500, 1000, and 2000 in Toluene in the Temperature Range of 303 to 333 K at Different Concentrations (g/dl) (mass%)

Molar mass of PPG	$1/T$ (10^{-3}K^{-1})	0.1%	0.25%	0.5%	0.75%	1%	2%	5%	7%	10%
500	3.30	0.00245	0.00708	0.02158	0.03750	0.04343	0.07319	0.11628	0.15720	0.18929
	3.19	-0.06268	-0.04530	-0.03785	-0.02937	-0.02073	0.01515	0.05283	0.07622	0.12272
	3.09	-0.11336	-0.09228	-0.07637	-0.07052	-0.06591	-0.04445	-0.0131	0.02076	0.06053
1000	3.00	-0.15760	-0.14856	-0.13549	-0.11601	-0.10487	-0.08441	-0.0567	-0.0283	-0.00566
	3.30	0.03051	0.04826	0.05235	0.06312	0.07409	0.09892	0.15848	0.2226	0.33365
	3.19	-0.04571	-0.03795	-0.02159	-0.01249	-0.00822	0.02226	0.07445	0.12588	0.2377
2000	3.09	-0.09605	-0.07556	-0.05378	-0.03547	-0.02171	-0.01784	0.03148	0.08552	0.18283
	3.00	-0.14849	-0.12867	-0.11945	-0.09838	-0.08573	-0.06795	-0.0191	0.03595	0.12406
	3.30	0.03121	0.04852	0.05950	0.06306	0.07670	0.13425	0.25674	0.32800	0.41136
3.19	-0.05580	-0.04663	-0.02857	-0.00145	0.02910	0.07745	0.16367	0.23593	0.30064	
	3.09	-0.09167	-0.07257	-0.05245	-0.02598	-0.01802	0.0232	0.09563	0.16873	0.2352
3.00	-0.13547	-0.11577	-0.08539	-0.07179	-0.04812	-0.00118	0.03897	0.09908	0.15703	

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