

VISCOMETRIC STUDY OF POLY(METHYL METHACRYLATE) AND POLYSTYRENE BLENDS IN DIFFERENT SOLVENTS

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Abstract The intermolecular interaction between poly(methyl methacrylate) (PMMA) and polystyrene (PS) in tetrahydrofuran (THF) and *N,N'*-dimethyl formamide (DMF) solvents was studied at 28°C using a dilute solution viscometry method. Solvent is believed to play a key role in characterizing the viscosity behavior of the polymer solution. The intrinsic viscosity and viscosity interaction parameter were experimentally measured for the binary (solvent/polymer) and for the ternary systems in two solvents. The compatibility of the polymer mixture was discussed in terms of the sign of Δb_m . The results show that the compatibility of PMMA/PS blend in DMF is larger than that in THF.

Keywords Viscometry, Compatibility, PMMA/PS blend

INTRODUCTION

The study of viscosity on a ternary system which is composed of two different polymers and a solvent is a very interesting subject, mainly due to its simplicity and importance in the characterization of the intermolecular interaction between the two different polymers in solution^[1–18]. Polymer-polymer compatibility has been extensively studied by several techniques, such as differential scanning calorimetry, dynamic mechanical measurements, neutron scattering, inverse gas chromatography, electron microscopy, light scattering and others^[19]. Dilute-solution viscometry (DSV) is the best technique to study polymer-polymer compatibility^[12, 13, 20–26]. The effectiveness of this method relies on the assumption that the repulsive or attractive intermolecular interaction between two different polymers in solution (polymer(1)-polymer(2) interaction) have a great influence on the viscosity of the polymer solution. The two polymers are dissolved in a common solvent, so their hydrodynamic volumes are affected by the solvent selected. The intermolecular interaction between the two different polymers in solution may also play a key role in characterizing the viscosity behavior of ternary system to which little attention has been devoted^[27–29].

As is well known, the intermolecular interaction in ordinary polymer solution (polymer (1) –solvent) can be either repulsive or attractive, depending on the solvent selected^[30]. Therefore, in order to perform DSV measurements, the influence of solvent on the intermolecular interaction between the two different polymers in solution should be also taken into account. The viscosity behavior of PMMA/PS in benzene at 20°C has also been studied^[31]. It was found that these two polymers were incompatible due to the repulsive interactions existing between them.

In the present work, the viscosity measurement of PMMA, PS and PMMA/PS blends in, THF and DMF has been studied. The compatibility of the polymer mixture is evaluated through the sign of Δb_m .

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EXPERIMENTAL

Materials

PMMA with average molecular weight 350,000 g/mol and PS with average molecular weight of 29,300 g/mol were purchased from Aldrich (USA). THF and DMF were used as received.

Viscometric Measurements

All measurements were performed at $28^\circ\text{C} \pm 0.1$ using a Cannon-Fenske type capillary viscometer. The stock solutions of each ternary or binary system were made by dissolving the polymer samples in filtered solvents (THF and DMF) up to concentration of 1.0 g/dL. Five sample solutions of lower concentrations were prepared by adding appropriate aliquots of solvent to the stock solution. For each solution 12 mL of the solution was loaded to minimize drainage errors to the viscometer and placed in the thermostat. The elution time of each solution was then determined as the average of several readings. The dilution finished after the solution volume reached 21 mL. Kinetic energy corrections were taken into account for the evaluation of the intrinsic viscosity $[\eta]$ and viscometric interaction parameter, b , which were determined by extrapolation to infinite dilution (zero solute concentration) and from the slope of the linear plots, respectively, of Huggins plots, *i.e.* η_{sp}/c versus c .

RESULTS AND DISCUSSION

Viscosity measurements on the ternary system can be carried out by two methods. The first method, the polymer-solvent method, is performed by putting polymer A (referred to as the probe polymer) in solution containing a constant concentration of polymer B (referred to as the matrix polymer)^[32]. This method has received more attention in recent years^[24, 33–35]. The second method is carried out by putting the polymer A and polymer B simultaneously in a pure solvent. It is well known that the measurement of the intrinsic viscosity of polymer A and polymer B in solution is important, because the intermolecular interaction between polymer A and B is enhanced.

Krigbaum and Wall developed the following equation for mixed polymer solution^[18]:

$$\eta_{sp, m} = [\eta]_1 c_1 + [\eta]_2 c_2 + b_{11} c_1^2 + 2 b_{12} c_1 c_2 + b_{22} c_2^2 \quad (1)$$

where $\eta_{sp, m}$ is the specific viscosity of the mixed polymer solution, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosity of polymer components 1 and 2, respectively; c_1 and c_2 are the concentrations of components 1 and 2, respectively, and b_{11} , b_{22} are the specific interaction parameters of components 1 and 2 in the binary system (polymer-solvent). b_{12} is the specific interaction parameter of components 1 and 2 in solution (ternary system) which is expressed as:

$$b_{12} = (b_{11} b_{22})^{1/2} \quad (2)$$

Equation (2) is also applicable for binary systems in which there is no interaction between polymer 1 and 2. On the other hand the interaction between polymer 1 and 2 is expressed by Eq. (3):

$$\Delta b = b_{12} - (b_{11} b_{22})^{1/2} \quad (3)$$

Or can be written in another form,

$$\Delta b_m = b_m^{\text{exp}} - b_m^{\text{theor}} \quad (4)$$

where m indicates the polymer mixture, Δb is the intermolecular interaction between polymer 1 and 2 and is considered as a good criterion to predict the polymer-polymer compatibility^[4, 14, 36]: $\Delta b > 0$ indicates that both polymers are compatible, whereas $\Delta b < 0$ indicates that they are incompatible.

Figures 1 and 2 show the plots of the reduced viscosity η_{sp}/c versus c for PMMA, PS and PMMA/PS blends with a weight fraction of 0.50 in THF and DMF at 28°C . All the plots are linear. On extrapolating η_{sp}/c to zero concentrations, both $[\eta]$ and the viscometric interaction parameter, b , can be obtained, which are tabulated in Tables 1 and 2. Since the $[\eta]$ of PMMA and PS in THF is larger than that of PMMA and PS in DMF, we could

conclude that THF is a better solvent for both PMMA and PS. Therefore, the polymer-solvent interaction in THF is larger than that in DMF, which lead to swelling of the polymer chains in solution and thus increases the intrinsic viscosity of the polymer solution. On the other hand, the $[\eta]$ values of PMMA in THF and DMF are larger than the $[\eta]$ values of PMMA/PS in the same solvents at 1:1 wt% blend as shown in Tables 1 and 2. A reasonable explanation is that the repulsive interactions between PMMA and PS in THF and DMF would increase the intermolecular excluded volume and the contraction of PMMA/PS coils in solvent and thus decrease the $[\eta]$.

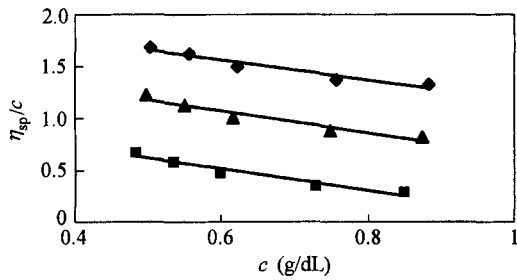


Fig. 1 Plots of reduced viscosity (η_{sp}/c) versus concentration for PMMA, PS and PMMA/PS blends with the weight fraction of 0.50 in THF at 28°C
◆ PMMA; ■ PS; ▲ PMMA/PA (0.50)

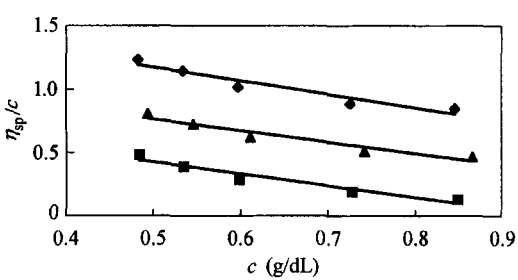


Fig. 2 Plots of reduced viscosity (η_{sp}/c) versus concentration for PMMA, PS and PMMA/PS blend with the weight fraction of 0.50 in DMF at 28°C
◆ PMMA; ■ PS; ▲ PMMA/PA (0.50)

A comparison of the experimental and theoretical values of b_m could give useful information about the interactions between polymer pairs. The negative values of b in Table 2 indicate that the polymer chains prefer to interact between themselves, and Δb_m indicates the degree of polymer-polymer compatibility.

Table 1. Viscosity data for PMMA and PS in THF and DMF as solvents at 28°C

Solvent	$[\eta]$	b	$[\eta]$	b
	PMMA	PMMA	PS	PS
THF	2.156	-0.984	1.144	-1.049
DMF	1.711	-1.073	0.819	-0.842

Table 2. Experimental and theoretical viscometric data for the ternary mixture PMMA/PS in THF and DMF as solvents at 28°C

Solvent	W_2	$[\eta]_m^{exp}$	b_m^{exp}	$[\eta]_m^{id}$	b_m^{id}	Δb_m
THF	0.25	1.433	-1.067	1.398	-1.033	-0.034
	0.50	1.710	-1.062	1.651	-1.017	-0.045
	0.75	1.912	-1.091	1.904	-1.001	-0.090
DMF	0.25	1.002	-0.892	1.101	-0.972	0.080
	0.50	1.216	-0.906	1.304	-1.006	0.099
	0.75	1.381	-0.906	1.507	-1.039	0.134

According to Eqs. (1)–(4), the intermolecular interaction parameters, b_{11} , b_{22} , b_{12} (b_m) and Δb_m for various weight fractions of polymer-polymer mixture in THF and DMF solvents can be determined and their results are also given in Tables 1 and 2. The compatibility data in Fig. 3 show the variation of Δb_m with different weight fractions of PMMA and PS mixtures in THF and DMF, respectively. It can be seen that PMMA is slightly compatible with PS in DMF in all composition ranges while PMMA is incompatible with PS in THF in all composition ranges. The incompatibility between PMMA and PS in PMMA/PS blend in THF could be attributed to the strong repulsive intermolecular interactions between the polymer chains in THF.

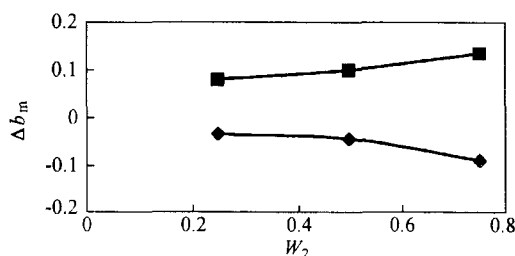


Fig. 3 Plots of the compatibility magnitude vs. different weight fractions for PMMA/PS blends in THF and DMF at 28°C

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