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THERMAL, VISCOMETRIC AND LIGHT SCATTERING MEASUREMENTS FROM PMMA/POLYSTYRENE/TOLUENE SYSTEMS

I. KATIME *, R. VALENCIANO and M. ANASAGASTI

Grupo de Propiedades Termodinamicas de Macromoleculas en Disolucion, Departamento de Quimica Fisica, Facultad de Ciencias, Universidad del Pais Vasco Apartado 644, Bilbao (Spain)

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ABSTRACT

Anionic and monodisperse polystyrenes of several molecular weights were investigated by means of laser light scattering and viscometric analysis in the isorefractive polymer/solvent mixture poly(methyl methacrylate)/toluene. It was found that the radius of gyration and intrinsic viscosity was strongly dependent on the concentration of poly(methyl methacrylate). Deviations from additivity of intrinsic viscosity values were established.

Differential thermal analysis (DTA) reveals the existence of two different glass transition temperatures, T_g, for the polystyrene/poly(methyl methacrylate) blends corresponding to the glass transition temperature for each separate polymer.

INTRODUCTION

In recent years there has been a lot of interest in polymer blends and polymer compatibility and several reviews of miscible polymer mixtures have been published on the subject [1–4].

When two polymer species are dissolved in a common solvent, they often display extreme incompatibility, even at rather low concentrations [5–8]. This phenomenon is called incompatibility. Incompatibility denotes the phenomenon whereby solutions of different polymers in the same solvent do not mix but separate into two phases. Upon decreasing the polymer concentrations and/or increasing the temperature the incompatibility disappears and two-phase systems transform into one-phase systems.

Because of the very small combinatorial entropy of mixing, polymers are normally not compatible unless the polymers are chemically very similar or there is a specific interaction between them. The compatibility of polymer–polymer systems is the exception rather than the rule.

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* Address for correspondence: Artaza 35-5°G, Lejona (Vizcaya), Spain.

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In this paper we report studies on polystyrene poly(methyl methacrylate) mixtures in toluene obtained by viscometry, laser light scattering and differential thermal analysis.

EXPERIMENTAL

The PMMA sample was prepared by free radical polymerization in benzene solution, initiated with 1,2-azobisisobutyronitrile. This sample was fractionated using its solubility in the benzene/methanol system and one fraction was used. This fraction has $\overline{M}_n = 129\,000$ and $\overline{M}_w = 156\,000$.

The polystyrene (PS) samples were obtained by anionic polymerization in THF, using cumyl potasium as initiator. Three samples were used for physical measurements. Their weight-average molecular weights are:

PS1	$\overline{M}_n = 130\,000$	$\overline{M}_w = 140\,000$
PS2	$\overline{M}_n = 330\,000$	$\overline{M}_w = 356\,000$
PS3	$\overline{M}_n = 1\,100\,000$	$\overline{M}_w = 1\,220\,000$

As solvent we used solutions of PMMA/toluene of different concentrations. Toluene (Cepsa) was previously distilled. The solutions were prepared in %(w/v). The concentration range was 0.5 to 2.5 g ml^{-1} in PMMA.

The dynamic calorimetric measurements were carried out using a Mettler TA 2000 differential thermal analysis (DTA) instrument, calibrated by the determination of the heat of fusion of indium. The experiments were carried out in aluminium crucibles with the tops perforated in order to facilitate contact with the atmosphere. The polymer films quantities used were approximately 10 mg for each experiment. The determination of melting temperature were carried out by placing the crucible in the furnace.

The absolute temperature was calculated from the equation

$$T_{s_1} = T_{p_1} - \tau(\mathrm{d}T_p/\mathrm{d}T) + \Delta U_1/S$$

where T_{s_1} is the sample temperature at point T_1, T_p is the program temperature at point T_1 (°C), τ is an intrinsic DTA constant, $\mathrm{d}T_p/\mathrm{d}T$ is the heating rate, ΔU_1 is the signal at point T_1 (μV) and S is the sensitivity of the thermocouple.

Laser light scattering measurements were carried out, at 298 K, with a modified FICA light scattering photometer where both light source and optical block of the incident beam were replaced by a He–Ne laser Spectra Physics model 157, which emits at 633 nm, with a power of 3 mW. The photogoniodiffusometer was calibrated with benzene using natural light and taking the Rayleigh ratio as $R_B = 8.96 \times 10^{-6}$ cm^{-1} [9]. All solutions were clarified by centrifugation for 2 h in a preparative Sorvall at 14000 rpm.

The refractive indices of the solvent were measured with a Abbe refractometer at 298 K and 633 nm. dn/dc, at 633 nm and 298 K, were measured in a Brice-Phoenix differential refractometer using a light source a He–Ne laser Spectra physics, model 156, which emits with a power of 3 mW.

All measurements of laser light scattering were made using Polystyrene concentrations ranging between $1\text{–}4 \times 10^{-3}$ g ml^{-1}.

The viscosities were measured at 298 K with a Ubbelohde suspended level viscometer suitable for dilutions in situ previously calibrated. Kinetic energy corrections were made applicable. Values of limiting viscosity number, $[\eta]$, were determined from the Huggins and Kramer equations by plotting η_{sp}/c and ln η_r/c versus c and extrapolating to zero concentration by the least squares method.

The viscosity measurements were made using polystyrene concentrations ranging between 0.2–0.5 g dl^{-1}.

Data treatment

The laser light scattering measurements carried to apparent weight average molecular weights, M^*, apparent second virial coefficients, A_2^*, and the radius of gyration, R_g.

Values of M^*, A_2^* and R_g were calculated using the usual Zimm Plot procedure. The experimental data are treated by the computer Commodore C-64. The plots traced by an Itoh 4800C plotter.

Absolute Second virial coefficients, A_2, were determined by means of the expression $A_2 = A_2^* M^*/M$.

The experimental viscosity data were similarly treated by computer.

DISCUSSION

This study was performed to illustrate the interactions that occur between polymers in solution. Initially it was anticipated that one could observe major differences of polymer interactions if the size, shape and polymer type were altered. This is the main reason for changing the molecular weight of both polymers. We have chosen one atactic PMMA sample of molecular weight $\overline{M}_w = 156\,000$ and three anionic and monodisperse polystyrenes with molecular weights of 1.10×10^6 (PS1), 3.30×10^5 (PS2) and 1.30×10^5 (PS3), respectively.

As can be seen in Fig. 1, the intrinsic viscosity of the three systems decreases as the PMMA concentration in the mixture increases. A concentration is ultimately reached from which no reproducible result can be obtained. This threshold concentration depends on polystyrene molecular weight decreasing when molecular weight decreases. This behaviour is contrary to that expected. The threshold concentrations are located at 2, 3 and 4 per cent, respectively, for polystyrenes PS3, PS2 and PS1.

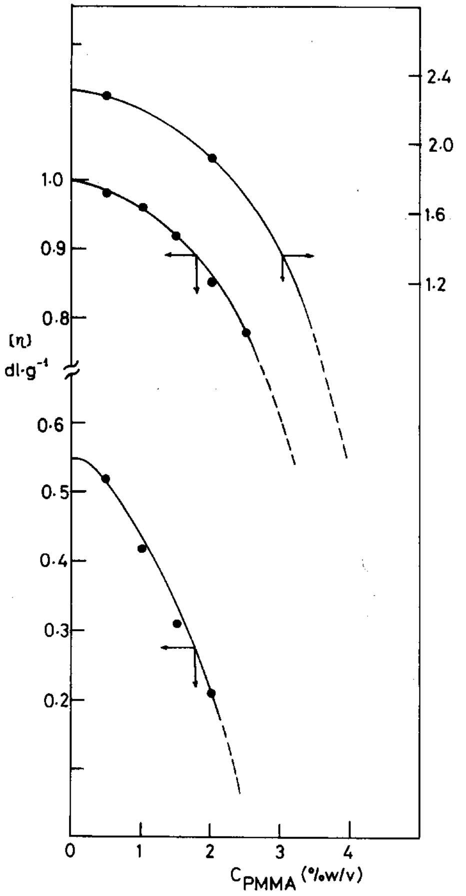
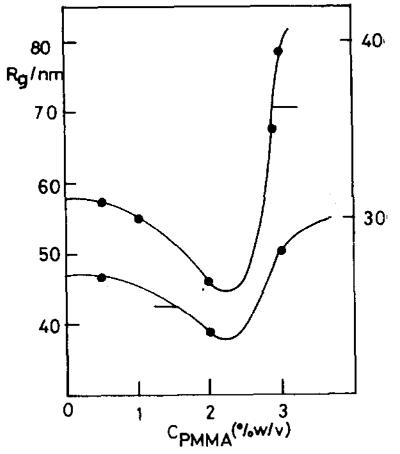


Fig. 1. Dependence of the intrinsic viscosity, [η], of solutions of a mixture of polystyrene and PMMA in toluene on the composition of PMMA in the mixture.

Williamson and Wright [10] suggested that the positive deviation from the additivity rule may be regarded as indicating good compatibility of the polymer pair, while the negative deviation shows that compatibility is poor. As can be seen in Fig. 1, the system PS/PMMA shows negative deviations, i.e., between PS and PMMA there exists no compatibility.

To determine the influence of PMMA on hydrodynamic properties of polystyrenes, we have employed one of the excluded volume theories, the Stockmayer–Fixman one [11]. This theory allows us to calculate the dimensions parameter, K_θ, and the interaction parameter B.

Figure 3 shows that as PMMA concentration increases, the K_θ parameter decreases a great deal. This indicates that the presence of the second polymer in the solution, provokes repulsive interactions in the system. The effect of these interactions is a contraction of the macromolecular coil of polystyrene due to the fact that polystyrene–polystyrene and PMMA–PMMA contacts



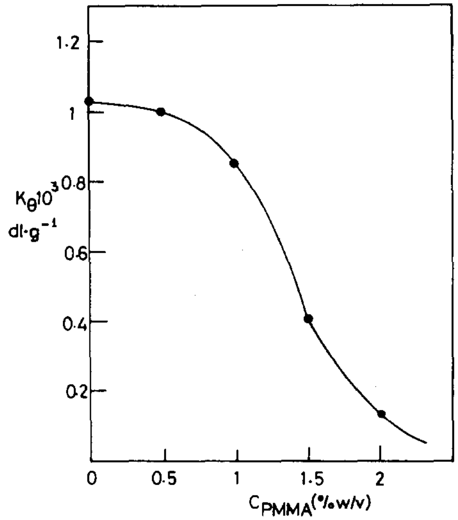


Fig. 2. Variation of radius of gyration of polystyrene as a function of PMMA concentration.

Fig. 3. Dependence of the K_θ parameter of polystyrene on proportion of PMMA in the mixture.

are more favourable than the polystyrene–PMMA ones.

In order to verify that this is what really occurs in our system, we have measured the mean radius of gyration of polystyrene at several PMMA concentrations using laser light scattering.

For this system, the PMMA molecules do not contribute to the light scattering intensity because the dn/dc of the PMMA/toluene system is approximately zero [12]. Polystyrene, therefore, is the only species that scatters light. The results obtained clearly show a similar behaviour to that observed by viscometry, that is, the mean radius of gyration decreases as the PMMA concentration increases in the system (Fig. 2). This indicates that the macromolecular coil of polystyrene becomes more compact due to the incompatibility of both polymers.

At PMMA concentrations higher than 2% the molecular weight and mean radius of gyration again increase, as a consequence of aggregation phenommena occurring between polystyrene coils.

According to the model of Krigbaum and Wall [13] we can determine whether two polymers show compatibility from viscosity data using the expression

$$\Delta b_{23} = b_{23} - b_{23}^{*} \tag{1}$$

where b_{23} represents the interaction between the polystyrene (3)-poly(methyl methacrylate) (2), which can be calculated from the empirical equation [14]

$$b_{23} = P\overline{M}^{*Q}$$

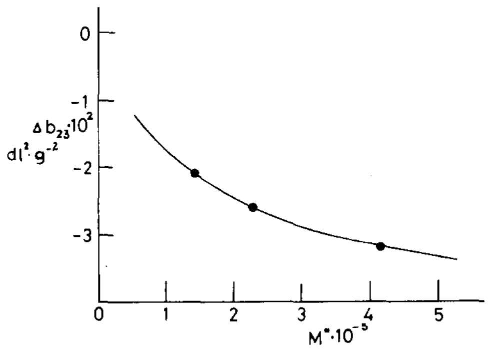
where P and Q are constant and $\overline{M}^*$ is the geometric mean of the molecular weights of the two polymers. For our system $P = 28.3\ 10^{-10}$ mol dl^2 g^{-3} and $Q = 1.45$ [15].

The b_{23}^* interaction parameter can be calculated from;

$$b_{23}^* = (b_{22} b_{33})^{1/2} \tag{2}$$

where b_{ii} are interaction parameters of the type polystyrene–polystyrene or PMMA–PMMA and are equal to $k_H[\eta]^2$, where k_H is the Huggins' constant. This b_{23}^* interaction parameter can be considered as a theoretical value of the system, thus eqn. (1) gives information about the compatibility or incompatibility of the system. Negative values of Δb_{23} are found in systems containing incompatible polymers, while values of b_{23} refer to attractive interaction and compatibility [16]. As can be seen in Fig. 4 these two polymers are not compatible and this incompatibility increases as molecular weight increases.

Several methods of measuring compatibility are available. One of the most sensitive methods of determining whether a two phase structure exists in a polymer blend is by measuring the glass transition within the mixture. If mixing has occurred then one glass transition, usually intermediate between those of the two components is found. If the polymers exist in separate domains then separate transitions of the two phases are obtained. In the PS/PMMA system we have found, over the whole composition interval investigated, two glass transition temperatures, corresponding to the polystyrene and poly(methyl methacrylate), respectively (Fig. 5).



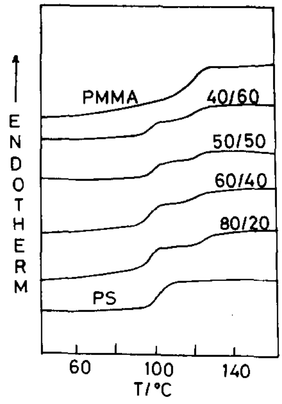


Fig. 4. Plot of the b_{23} parameter against geometric mean of molecular weight, M^*, for PS/PMMA blends in toluene.

Fig. 5. DTA scans of PS/PMMA blends. The weight ratios of PS/PPMA are indicated. The heating rate was 10°C min^{-1}.

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