Stereocomplex formation of PMMA in cosolvent mixtures

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In this paper we have studied the stereocomplex formation of PMMA in the following cosolvent mixtures: acetronitrile/CCl_4, acetonitrile/butyl chloride and butyl chloride/CCl_4. We have found that, when the cosolvent power of the binary mixture increases, the complexing capacity decreases. These results can be explained by taking into account the excess Gibbs free energy, G^E, and the order of the liquids.

Keywords Stereocomplex; excess Gibbs free energy; cosolvent mixture; PMMA; self-association; complexing capacity

INTRODUCTION

In the last few years, the formation of PMMA stereocomplexes has been extensively studied[1-12]. The ester group of the isotactic chain and the α-methyl group of the syndiotactic chain are mainly responsible for complex formation, as Bosscher *et al.*[10] reported.

Stereocomplexes are produced both in bulk and in solution. In this sense, the solvents can be classified into three groups: the strongly complexing type A, the weakly complexing type B, and the non-complexing type C.

When cosolvent mixtures are used, the association of heterotactic PMMA decreases when cosolvent power of the mixture increases, as Katime *et al.*[13] and Horta *et al.*[14] have reported. In this work, the influence of cosolvency on stereocomplex formation of isotactic and syndiotactic PMMA is studied.

EXPERIMENTAL

Carbon tetrachloride (Merck), acetonitrile (Fluka) and n-butyl chloride (C. Erba) were purified by standard procedures and freshly distilled before use.

Solvent mixtures were made up by volume. The refractive indices of the solvents and of the binary solvent mixtures were measured with an Abbé refractometer at 298K.

The isotactic PMMA sample was prepared by polymerization of MMA (Fluka) in toluene at low temperature with phenylmagnesium bromide as initiator[15].

The synthesis of syndiotactic PMMA sample used here has already been described[16].

The weight-average molecular weights, $\bar{M}_w$, of the samples were 6.6×10^5 and 1.7×10^5, respectively.

Stereocomplexes were prepared by mixing, in a ratio of 1 to 2, $0.2 \, g \, dl^{-1}$ i- and s-PMMA solutions in the binary mixture. The mixed solutions were kept in a thermostatically controlled bath at 30.0° ± 0.05°C for one day. The precipitate was separated from the solution in a centrifuge using an acceleration of $22000 \times g$ and then dried in vacuum at room temperature for several days.

The melting behaviour of the stereocomplexes was studied with a Mettler D.T.A. apparatus at a heating rate of $5°C \, min^{-1}$.

A modified Ostwald viscometer was used. The kinetic energy correction was less than 0.3% and, therefore, was neglected. Fluctuations of the temperature were less than ±0.02°C. Reduced viscosities, η_{sp}/c, were measured on sample solutions at 0.2% (w/v) polymer concentration.

RESULTS AND DISCUSSION

The formation of PMMA stereocomplex has been attributed mainly to the interactions between the ester group of the isotactic form and the α-methyl group of the syndiotactic form[10]. This behaviour has been studied in pure solvents, with the observation that these play an important role. Here, the influence of cosolvent mixtures on stereocomplex formation is discussed.

In *Figure 1* is presented the percentage of stereocomplex obtained at different compositions of the cosolvent mixtures acetonitrile/carbon tetrachloride, acetonitrile/butyl chloride and butyl chloride/carbon tetrachloride. The plots show a high yield of complex formation ($\simeq 95\%$) in pure solvents, indicating that the specific interaction between the two tactic forms is nearly complete. On the other hand, when the composition of the binary mixture approaches its solvency maximum, a decrease of the yield of stereocomplex is observed, indicating that the interactions are impeded. This behaviour depends on the cosolvent mixture used, as shown in *Figure 1*.

The behaviour can be explained as follows. The three liquids used are strongly complexing. On the one hand, the complexing capacity of acetonitrile and butyl chloride can be explained by taking into account their self-association capacities (liquid order)[17] which therefore prevent interaction with the polymer, in spite of their large dipole moments ($\mu = 3.44$ and $\mu = 1.90$ D, respectively); for this reason these liquids behave as theta solvents of

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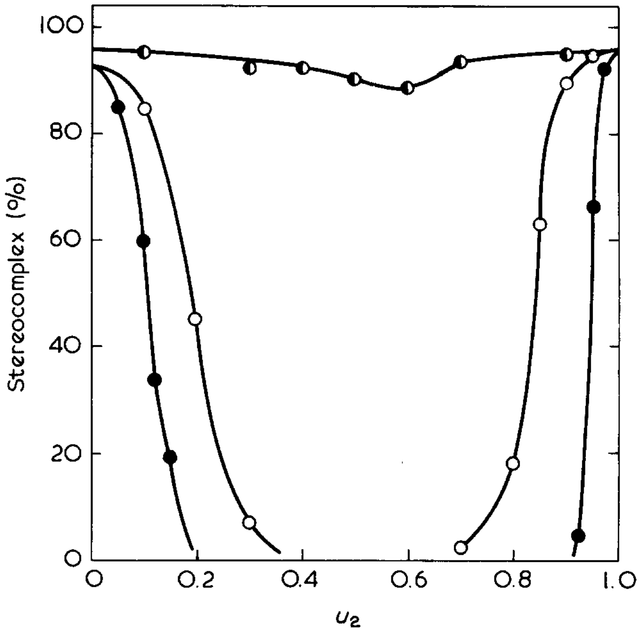

Figure 1 Stereocomplex percentage as a function of the composition of the binary mixtures: acetonitrile/carbon tetrachloride (●), acetonitrile/butyl chloride (○) and butyl chloride/carbon tetrachloride (◑) (u_2 = volume fraction of the second component of each mixture)

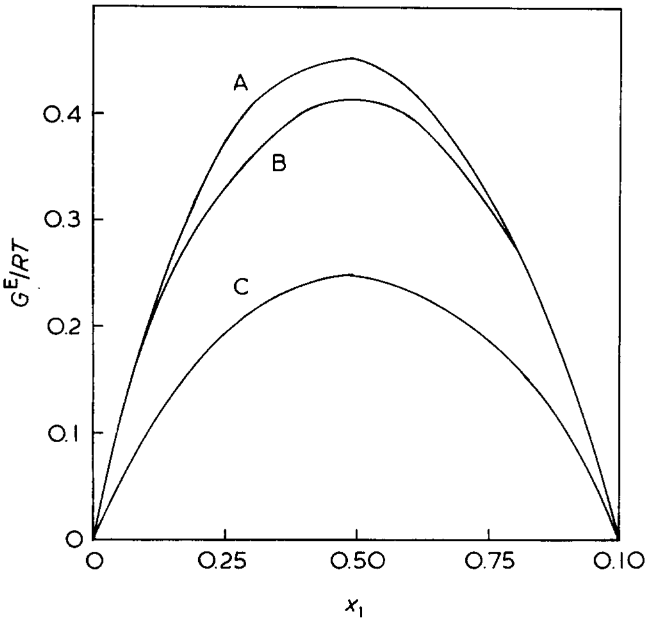

Figure 2 G^E/RT values *versus* mole fraction, x_1, for the different cosolvent binary mixtures: acetonitrile/carbon tetrachloride (curve A), acetonitrile/butyl chloride (curve B) and butyl chloride/carbon tetrachloride (curve C)

PMMA[18,19]. On the other hand, the complexing character of carbon tetrachloride is due to its non-polar character, and does not show specific interactions.

When a second liquid is added to the system, the associations are partially broken, making the interactions with the polymer easier[20]. This is reasonable if we take into account the excess Gibbs energies for these mixtures[21–23], as shown in *Figure 2*. It is well known that positive values of G^E indicate an incompatibility between liquids. Therefore, when adding a polymer to the mixtures, those with higher G^E values will display greater solvating power[24–26].

The thermograms of the stereocomplexes in the solid state show two melting peaks, the areas of which depend on the composition of the binary mixture (*Figure 3*). When the solvating power of the cosolvent mixture is increased, the area of the first peak decreases, leading to the possibility of its disappearance. This behaviour can be explained using the model of Challa *et al.*[5], which supposes two stages in the complexation. In the first, some chains are strongly joined, leading to primary stereocomplex particles. In the second stage, the chain non-associated segments interact weakly with themselves. When the solvating power of the mixture is increased, the interactions in the second stage (Challa model) are impeded, leading to a decrease in the intensity of the first peak of the thermogram (*Figure 3*).

Figure 1 shows that in the composition intervals $0.2 < u_2 < 0.9$ for the acetonitrile/carbon tetrachloride system and $0.4 < u_2 < 0.7$ for acetonitrile/butyl chloride, the precipitate does not appear. In order to verify whether this behaviour is due to lack of complexation, some viscosity measurements were carried out. As an example, the reduced viscosity in the cosolvent mixture acetonitrile/butyl chloride at $u_2 = 0.6$ ($\eta_{sp}/c = 1.47\,\mathrm{dl\,g^{-1}}$) is higher than the value expected ($\eta_{sp}/c = 0.82\,\mathrm{dl\,g^{-1}}$).

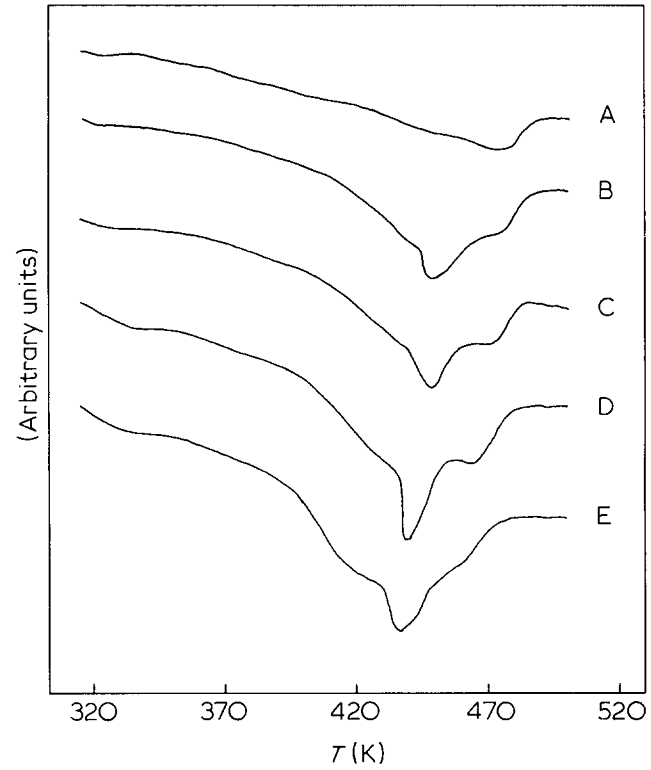

Figure 3 Thermograms of different stereocomplexes obtained at different compositions of the binary mixture acetonitrile/butyl chloride, where the volume fraction of the second component is u_2 = 0.80 (curve A), 0.85 (curve B), 0.90 (curve C), 0.95 (curve D) and 1.00 (curve E)

Table 1 Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture acetronitrile/carbon tetrachloride (u_2 = volume fraction of second component)

u_2	0	0.05	0.10	0.13	0.15	0.95	0.97	1.0
T_{m1} (°C)	183	177	175	175		179	166	155
T_{m2} (°C)	195	195	199	203	205	201	198	187

Table 2 Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture acetonitrile/butyl chloride (u_2 = volume fraction of second component)

u_2	0	0.10	0.20	0.30	0.70	0.80	0.85	0.90	0.95	1.0
T_{m1} (°C)	183	176	176	173		173	175	174	164	162
T_{m2} (°C)	195	196	201	204	207	201	201	197	191	187

Table 3 Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture butyl chloride/carbon tetrachloride (u_2 = volume fraction of second component)

u_2	0	0.10	0.30	0.40	0.50	0.60	0.70	0.90	1.0
T_{m1} (°C)	162	160	159	159	159	162	161	157	155
T_{m2} (°C)	187	187	189	189	191	191	192	191	187

Therefore, the strongly cosolvent mixtures can behave as non-complexing solvents.

The temperature of melting changes with the composition of the binary mixture, as shown in *Tables 1–3*. The first melting peak, T_{m1}, is always between those corresponding to the pure liquids, while the second melting temperature, T_{m2}, increases when the composition of the mixture approaches its solvency maximum[27,28]. This increase of T_{m2} is explained by the expansion of the chains produced by the polymer–solvent interactions. In that case, according to steric effects, there is a higher probability of a greater number of consecutive unions occurring between the chains' polar groups, leading to greater stability.

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