Stereo complexes in solutions of syndio- and isotactic poly(methyl methacrylate) mixtures: 2. Mutual interaction constant of stereo polymers

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The coefficient of interaction between syndiotactic and isotactic poly(methyl methacrylate) was determined at 25°C in solutions of a mixture of these two polymers in dioxan and chlorobenzene by using the method of instrinsic viscosity measurement in a 'polymer solvent'. In these systems where stereocomplexes are formed the coefficient is unusually high and depends on the solvent used.

Keywords Stereocomplexes; syndio- and isotactic poly(methyl methacrylate); mutual interaction constant

INTRODUCTION

This paper is a continuation of a preceding investigation[1] of solutions of mixtures of syndiotactic (s-PMMA) and isotactic (i-PMMA) poly(methyl methacrylates) in dimethylformamide, dioxan and chlorobenzene, where the formation of stereo complexes was investigated viscometrically and by the light scattering method as a function of time, of the ratio between stereo polymers and of their total concentration. The intensity of formation of stereo complexes differed from one solvent to another, being the strongest in dimethylformamide, medium in dioxan and the weakest in chlorobenzene. This was reflected, on the one hand, in the rate of change in viscosity at the beginning of the complex-forming process, and on the other, in the time needed for the stabilization of the complex.

In this study we describe the determination of the viscometric parameter k_{is} at 25°C which characterizes mutual interaction between syndiotactic and isotactic poly(methyl methacrylates) at this temperature as an analogy of a solution of a binary mixture of compatible polymers in a common solvent. For this purpose, the method of 'polymer solvent' was employed[2–9]. According to this method, the intrinsic viscosity of the polymer A, $[\eta_A]_B$, is determined in a number of variously concentrated solutions of polymer B which serve as solvents, and *vice versa*. For $[\eta_A]_B$ we have[8,9]:

$$[\eta_A]_B=\{[\eta_A]/(\eta_r)_B\}(1+2k_{AB}[\eta_B]c_B+\dots) \qquad (1)$$

here; $(\eta_r)_B$ is the relative viscosity of the polymer B at the concentration c_B, $[\eta_A]$ and $[\eta_B]$ are the intrinsic viscosities of the polymers A and B in a pure solvent. The constant k_{AB} is a criterion of interaction between macromolecules A and B. It may be obtained in two ways: (a) in the plot:

$$m=[\eta_A]_B(\eta_r)_B/[\eta_A] \qquad (2)$$

vs. reduced concentration $\tilde{c}=[\eta_B]c_B$, it is determined by the slope at the beginning. This procedure has an advantage in that at $\tilde{c}\to 0$ in the intercept on the y-axis is unity. A certain difficulty in the determination of the slope arises when the dependence becomes curved due to higher concentration terms. (b) The second procedure using the plot:

$$f=\{[\eta_A]_B(\eta_r)_B/[\eta_A]-1\}/2[\eta_B] \qquad (3)$$

vs. $\tilde{c}$ gives directly k_{AB} from the intercept on the y-axis. The case where the polymer B is the dissolved compound and the solution of the polymer A is the solvent, is treated similarly and gives the same value ($k_{AB}=k_{BA}$). The method of 'polymer solvent' reflects changes in the molecular dimensions of molecules of the polymer A due to molecules of the polymer B and is more reliable and exact in the determination of k_{AB} than direct calculation of this value using the interaction constant obtained from measurements of the intrinsic viscosity of a solution of a mixture of polymers at a constant ratio of both components.

In this study we attempted, by using the constant k_{AB} of a mixture of stereo polymers of poly(methyl methacrylate), to find out how strong the interaction is between polymer macromolecules of nonidentical type which

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Table 1 Characteristics of polymer samples

Polymer	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	Tacticity (content of triads in %) Syndio	Iso	Hetero
i-PMMA	1.28	1.04	8.5	74.3	17.2
s-PMMA	4.97	3.8	91.4	1.2	7.4

accompanies the formation of stereo complexes and whether this interaction depends on the solvent. Both procedures outlined above were used and compared with each other in the determination of k_{AB}.

EXPERIMENTAL

Preparation of polymer samples, their characterization and procedure used in the measurement have been reported in an earlier paper[1]. The molecular mass and tacticity of the polymers are given in *Table 1*.

Solutions used in the viscosity measurements were prepared in the following way: The polymer, whose solution was used as the solvent, was dissolved to give a series of solutions having concentrations ranging from 2.5 to 10 or 20×10^{-4} g cm^{-3}. After dissolution and filtration through a sintered glass filter G 2, the second polymer was dissolved in these solutions. The basic solutions were then diluted using the respective solution of the first polymer as solvent.

RESULTS AND DISCUSSION

The condition for obtaining the coefficient k_{AB} (or, for our system i-PMMA and s-PMMA, the constant k_{is}) by the viscometric measurement as described above is a linear dependence of the intrinsic viscosity of solution of the polymer mixture on weight fractions of the polymer components (additivity of their intrinsic viscosities). This may be fulfilled only in solutions not containing aggregated particles. In those systems where such aggregates are formed the required conditions can be achieved only at the beginning of a sufficiently slow aggregation process, when the solution still contains only unaggregated polymer macromolecules.

In the investigation of time dependences of the formation of stereo complexes of poly(methyl methacrylate) described in our earlier paper, the initial solutions were those in which the complexes were destroyed by heating to 80°–90°C for 20 min. The measurement of the intrinsic viscosity of mixtures at the three ratios of stereo polymers taken for the investigation (1:2, 1:1, 2:1) revealed that in solutions in dimethylformamide the formation of aggregates was so fast that even if the measurement took place within the shortest possible time after heating, the effect of the presence of desolvated stereo complexes with intrinsic viscosity lower than the additive value could already be perceived. For these reasons, the constant k_{AB} cannot be determined in such solvent. The additivity of intrinsic viscosities of polymer components immediately on heating of the solutions was satisfied only with dioxan and chlorobenzene solutions. This is why these solvents could be used in our study.

In dioxan, both the intrinsic viscosities of the syndiotactic polymer in solutions of the isotactic polymer, $[\eta_i]_s$, and *vice versa*, $[\eta_s]_i$, were measured (*Table 2*). The required relative viscosities $(\eta_r)_i$ and $(\eta_r)_s$ respectively were obtained by measuring polymer solutions in pure solvents at required concentrations. *Figure 1a* shows that due to the curved shape of the m vs. $\tilde{c}$ dependences (equation (2)), obviously caused by a strong influence of further terms of the series expansion (1), the constant k_{is} cannot be determined using their initial slopes. On the contrary, the plot of the parameter f vs. $\tilde{c}$ satisfies the purpose (*Figure 1b*). It was possible to draw straight lines through experimental points; by extrapolating these lines to $\tilde{c}=0$, a common intercept was cut out on the y-axis equal to $k_{is} = k_{si} = 2.7$. The different slopes of these straight lines indicate a differently strong effect of higher terms of the

Table 2 Intrinsic viscosities in 'polymer' solvents

Solutions in dioxan				Solutions in chlorobenzene*	
$c_s \times 10^4$ (g cm^{-3})	$[\eta_i]_s$ (cm^3 g^{-1})	$c_i \times 10^4$ (g cm^{-3})	$[\eta_s]_i$ (cm^3 g^{-1})	$c_s \times 10^4$ (g cm^{-3})	$[\eta_i]_s$ (cm^3 g^{-1})
0	74.2	0	96.6	0	67.5
2.5	78.9	2.5	99.3	2.5	69.0
5.0	85.6	5.0	101	5.0	69.2
7.5	92.8	7.5	108	7.5	72.4
10	106	10	109	10	73.3
–	–	20	124	–	–

* $[\eta_s]_i = 85.9$ cm^3 g^{-1}

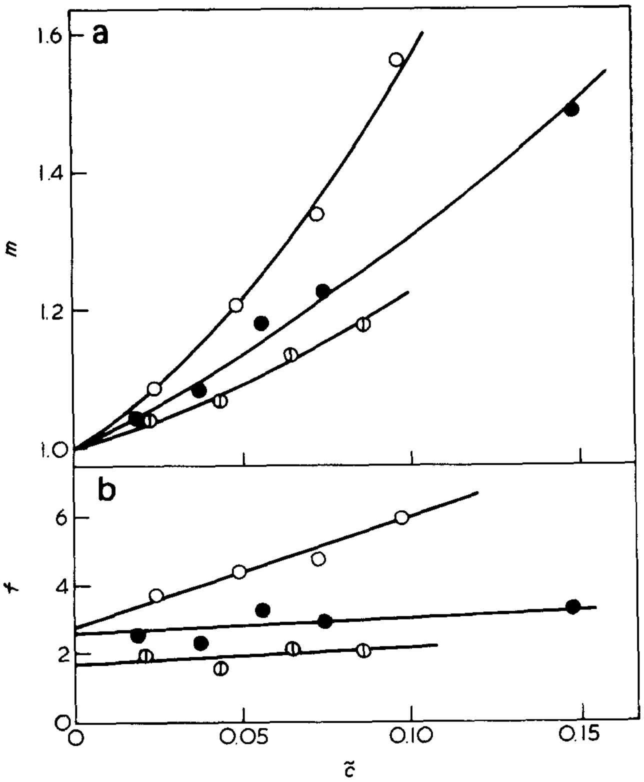

Figure 1 (a) Dependence of parameter m (Equation 2) on reduced polymer concentration $\tilde{c}$ (b) Dependence of parameter f (Equation 3) on reduced polymer concentration $\tilde{c}$. Solutions in dioxan (○) and chlorobenzene (◐): i-PMMA a solute, s-PMMA solutions as solvents; solutions in dioxan (●): s-PMMA as solute, i-PMMA solutions as solvents

series expansion (1) on the concentration dependence of viscosity of polymer mixtures if various ways of dilution are used.

Measurements in chlorobenzene were carried out only for the syndiotactic polymer dissolved in a solution of isotactic polymer used as solvent. The plot in *Figure 1a* for chlorobenzene is also curved, and therefore not suited for the determination of k_{is}. The plot f vs. $\tilde{c}$ (*Figure 1b*) is satisfactory, leading to $k_{is} = 1.6$.

The k_{is} values determined for both solvents used are unusually high. The k_{AB} coefficients reported in the literature[8] for pairs of the usual polymers are much lower ($\sim$0.2–0.3). The difference can be explained only by exceptionally strong interactions between syndiotactic and isotactic macromolecules of poly(methyl methacrylate). The lower k_{is} value for the solution in chlorobenzene compared with that in dioxan is in agreement with the weaker complex formation observed in our earlier experiments in the same solvent.

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