

Association of stereoregular poly(methyl methacrylates): 4. Further study on the composition of the stereocomplex

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The formation of the stereocomplex of highly isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA) was investigated in dilute solution by viscometry, osmometry, turbidimetry and n.m.r. Crystalline stereocomplexes, isolated from dilute and concentrated mixed solutions or formed by annealing in bulk, were investigated by X-ray diffraction and d.s.c. X-ray diffraction showed that all complexes, in whatever way or from whatever it/st ratio they were made, have the same crystalline structure. Moreover, all stereocomplexes showed a melting point which was independent of the it/st ratio. All this evidence means that only one type of stereocomplex exists. In dilute solutions the maximum deviations of reduced viscosity and osmotic pressure as well as the maximum turbidity were obtained at the composition it/st = 1/2. The same ratio could be derived from the maximum crystallinity after prolonged annealing of the mixture in bulk at 140°C, as determined by d.s.c. So contrary to previous statements¹ it is now considered that the real stereocomplex from it- and st-PMMA always possesses a composition it/st = 1/2. Comparing the X-ray fibre patterns of oriented stereocomplex with the fibre patterns of pure it- and st-PMMA showed that the stereocomplex has a structure different from that of the components.

INTRODUCTION

On mixing solutions of isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA) in suitable solvents a stereocomplex is formed by association of isotactic and syndiotactic sequences. This phenomenon has been investigated by several authors using various techniques e.g. viscometry, turbidimetry^{1,3-6}, light scattering^{7,8}, high resolution and broad line n.m.r.^{9,10}, sedimentation in an ultracentrifuge^{8,11}, calorimetry^{2,12} and dynamic mechanical^{2,13} and dielectric measurements¹⁴. From these measurements it was concluded that the solvent type has an influence on complex formation. It appeared that the solvents could be divided into three groups: (a) strongly complexing, (b) weakly complexing and (c) non-complexing solvents (see *Table 1*). It was also found that methyl methacrylate (MMA) can polymerize to predominantly syndiotactic PMMA in the presence of it-PMMA as a template^{15,16} in strongly complexing solvents.

In previous papers we concluded from calorimetric and dynamic mechanical measurements² that the complex formation of it- and st-PMMA can also occur in bulk. X-ray diffraction shows that the stereocomplex is crystalline^{17,18} but until now it has not been possible to establish the crystal structure completely. Liquori *et al.*¹⁷ proposed a model for the stereocomplex in which the flat syndiotactic chain lies in the grooves of the isotactic 5_1 -helices. Tadokoro *et al.*¹⁹ assume that the it-PMMA structure must be a double helix, and suggest a similar double-stranded structure for the stereocomplex. To us, the phenomenon of template polymerization of MMA along it-PMMA^{15,16} is difficult to understand, using Liquori's model.

The ratio of it-PMMA and st-PMMA in the stereocomplex is still a point of controversy. Most investigators mention a composition with an iso-syndio ratio of 1/2^{4,5,11,12,24}, but ratios of 1/1 and 1/1.5 are also reported^{9,10,20-23}. In order to find the real composition and to give an indication of the structure we prepared stereocomplexes of it- and st-PMMA in bulk as well as in solution. The results of viscometry, osmometry, turbidimetry, microcalorimetry, n.m.r. and X-ray diffraction on these stereocomplexes are described and discussed in this paper.

EXPERIMENTAL

The polymers used are listed in *Table 2*. All it-PMMA's were synthesized with phenylmagnesium bromide as catalyst²⁵. it-4, -5 and -6 were obtained by fractionation of it-PMMA, which was first extracted with hot methanol in a modified Soxhlet apparatus for 24 h to remove the low molecular weight part. The fractionation was performed on

Table 1 Classification of solvents by their ability to give stereocomplex formation between it- and st-PMMA

Type A Strongly complexing		Type B Weakly com- plexing	Type C Non-complexing
Dimethylformamide	Acetone	Toluene	Chloroform
Methylisobutyrate	Acetonitrile	Benzene	Dichloromethane
Dimethylsulphoxide	Tetrahydrofuran	Dioxane	
Tetrachloromethane	MMA monomer		

Table 2 Data on PMMA polymers applied for stereocomplex formation

PMMA polymer	$\bar{M}_v \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	I-H-S
it-1	500	20	95- 4- 1
it-2	400	—	94- 5- 1
it-3	1090	110	97- 3- 0
it-4	250	140	95- 4- 1
it-5	50	—	93- 6- 1
it-6	130	70	94- 5- 1
st-1	550	250	1- 9-90
st-2	380	—	1-10-89
st-3	1000	—	2-10-88
st-4	230	120	1- 5-94
st-5	50	—	0-10-90
st-6	130	40	0-16-84

the insoluble part by the precipitation method using acetone as solvent and methanol as precipitant; it-3 was merely extracted. st-1 and -2 were synthesized with triethylaluminum-titanium-tetrachloride as catalyst²⁶; st-3, -4, -5 and -6 were prepared from st-poly(methacrylic acid) samples by methylation with diazomethane in DMF solution, and subsequent precipitation in water. These st-poly(methacrylic acid) samples were directly obtained by radiation-polymerization of the monomer in isopropyl-alcohol^{27,28}, except st-poly(methacrylic acid) yielding st-6, which was prepared by a method described by Kabanov *et al.*²⁹. The \bar{M}_v was measured in chloroform at 25°C using the relation $[\eta] = 4.8 \times 10^{-5} \bar{M}_v^{0.80}$. \bar{M}_n was determined in toluene at 35°C with an automatic osmometer (Hallikainen). The tacticities of the PMMA's were measured on 5–10 wt% solutions in *o*-dichlorobenzene at 160°C by 60 MHz n.m.r. spectroscopy with a Jeol C-60 HL apparatus.

Reduced viscosities of mixed it/st-PMMA solutions were measured 10 min after mixing the separate it- and st-PMMA solutions in a Landa Viscotimer (Schott u. Gen., Mainz). The osmotic pressure measurements on mixed solutions in toluene and DMF were performed with the Hallikainen osmometer at 35°C. U.v. spectra of the mixed solutions in acetonitrile and dioxane were recorded with an Optica CF4R spectrophotometer in the region 200–400 nm. The turbidities of 0.1 wt % it/st-PMMA solutions in acetone were measured at a wavelength of 450 nm with a Jouan spectrophotometer.

Solid stereocomplexes were prepared by mixing 3 wt % solutions in chloroform at different compositions and precipitating in petroleum-ether (b.p. 40°–60°C). The mixtures were dried in vacuum for several days at room temperature. Annealing of the samples was performed at various temperatures and for various lengths of time. Stereocomplexes were also obtained from dilute solution after mixing 0.2 wt % DMF or acetone solutions of it- and st-PMMA at different it/st ratios at 55° or 40°C, respectively. After 3 weeks the crystallized material was isolated from the solutions in a centrifuge (25 000 g) and dried in vacuum at room temperature for several days.

Finally, stereocomplexes were prepared in concentrated solution by mixing 5 wt % DMF solutions. Because complex formation occurs immediately at such concentration, the mixed solutions were heated to the boiling temperature of DMF (155°C) in order to dissociate the complexes and to attain good mixing. The hot solutions were poured into a U-formed tube at 120°C. After cooling to room temperature the formed gels could easily be removed from the tube. The gels contained about 90–95% solvent and were stretched about 500–800% in a Zwick electronic tensile testing

machine. The oriented fibres were then annealed at constant length at 140°C where crystallization occurs.

The crystalline powders and fibres were analysed with a Statton-photographic X-ray camera using Ni filtered CuK α radiation. The optical densities of the films were measured by an Optronics optical densitometer

The melting behaviour of the stereocomplexes was studied with a differential scanning calorimeter (Perkin–Elmer DSC-2) at 10°C/min. The temperature scale was calibrated with high purity metal standards.

RESULTS

To find the real composition of the stereocomplex, we first had to decide whether more than one type of stereocomplex is formed depending on the method of preparation. Therefore different samples made by mixing it- and st-PMMA at various ratios in dilute and concentrated solution and in bulk were examined by d.s.c. and X-ray diffraction. Material crystallized from dilute solution showed melting endotherms with maxima at 206–215°C depending on solvent, on crystallization temperature and to only a small extent on composition. Materials crystallized in bulk gave smaller endotherms at lower temperatures, T_m depending only on the crystallization temperature T_c . The maximum area of the endotherm of the bulk mixtures was about half the area of the endotherm of the same mixtures isolated from dilute solution.

In Figure 1 the melting temperature T_m is plotted against the crystallization temperature T_c above 140°C for bulk samples with different it/st ratios. From this Hoffman–Weeks plot we deduced that the it/st ratio had no influence on T_m and we found an equilibrium-melting temperature of the stereocomplex $(T_m)_0 = 260^\circ\text{C}$ by extrapolating to $T_m = T_c$. At temperatures T_c below 140°C two adjacent melting endotherms were found, which could be ascribed to primary and secondary crystallization of the stereocomplex³⁰. X-ray diffraction was performed on samples made in bulk or in dilute solution and the powder diffractograms were compared for materials with different it/st ratios. Crystalline stereocomplexes obtained by stretching gels were also analysed by X-ray diffraction. The X-ray fibre pattern of the stereocomplex with it/st = 1/2 is drawn in Figure 2, while the fibre patterns of stereocomplexes with different it-/st ratios are compared in Figure 3.

The above results indicated that the same stereocomplex

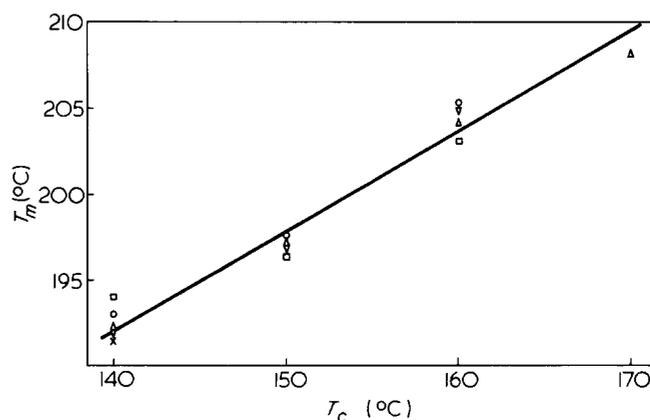


Figure 1 Melting temperature T_m as a function of crystallization temperature T_c for stereocomplexes in different mixtures of it-PMMA-2 and st-PMMA-2; it/st ratios: 1/4 (X); 1/2 (∇); 1/1 (○); 2/1 (△); 4/1 (□)

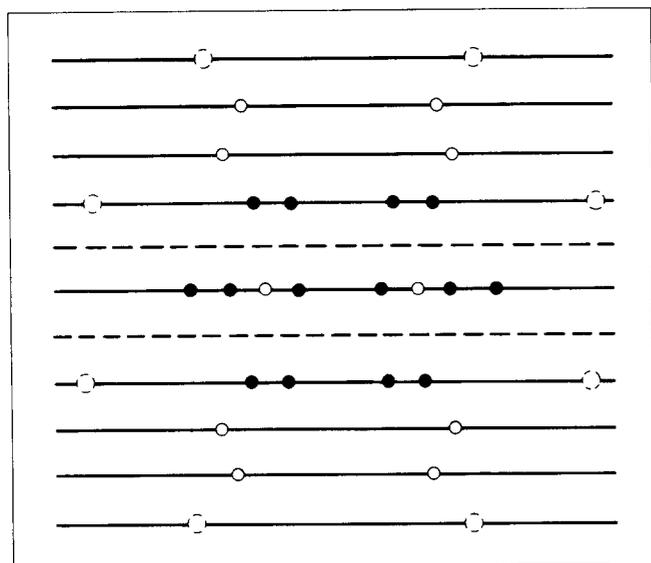


Figure 2 Schematic representation of the X-ray fibre diffractogram of stereocomplex from it-PMMA-2 and st-PMMA-2; intensities: high (●); low (○); very low and broad (◐)

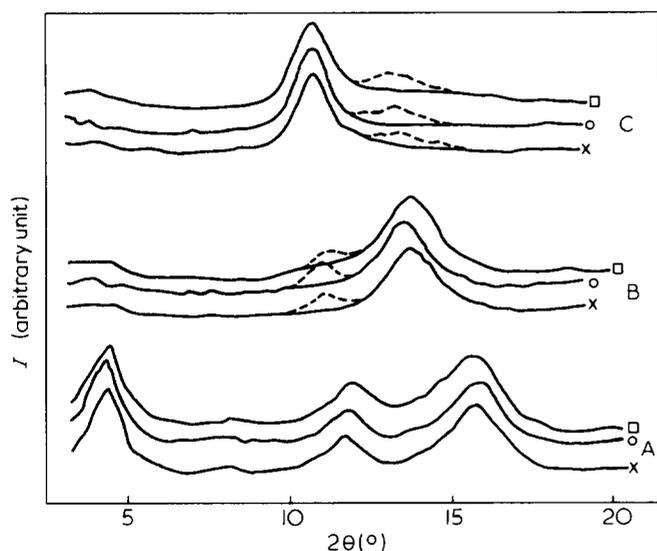


Figure 3 Intensities I versus diffraction angle 2θ measured by scanning the X-ray fibre diffractograms of stereocomplex from it-PMMA-2 and st-PMMA-2 at angles of A, 0° , B, 45° and C, 63° with the equator; it/st ratios: 2/1 (X); 1/1 (○); 1/2 (□)

structure is formed under all conditions. The following experiments are directed to discovering the composition of this stereocomplex.

In Figure 4 the reduced viscosities η_{sp}/c of different mixtures of it- and st-PMMA in type A solvent, DMF, are plotted against the weight fraction X_s of st-PMMA at $c = 0.2$ g/dl. From these measurements we see the influence of molecular weight on the initial viscosity behaviour, e.g. 10 min after mixing the separate solutions. In all cases a minimum arises at the same ratio it/st = 1/2.

Figure 5 shows the results of an osmotic pressure study of the apparent number-average molecular weight of mixtures of it- and st-PMMA in the type B solvent, toluene, at different concentrations in relation to the additive value, $(\bar{M})_{add}$ ($1/(\bar{M})_{add} \equiv \sum w_i/M_i$). The same pattern of curves was obtained for measurements in DMF, which is a type A solvent. Again the maximum effect occurs at the ratio it/st = 1/2.

Complex formation was also investigated by u.v.-spectroscopy in dilute acetonitrile solution as described by Liquori *et al.*¹⁷, who found an increase in absorption at 212 nm for mixtures of it- and st-PMMA with a maximum at it/st = 1/2. However, by measuring the spectrum over a broader wavelength range we found that the measurements are disturbed by precipitation of stereocomplex causing a very strong scattering of the incident light. So, we concluded that the maximum absorption at it/st = 1/2 is caused by a maximum turbidity and not by extra light absorption by the stereocomplex.

From mixed solutions in type A solvent, acetone (total concentration 0.2 g/dl), with iso-syndio ratios of 1/2 and 1/1 almost all the material precipitated. Other ratios, 4/1, 2/1 and 1/4, gave a much smaller yield. N.m.r. study of the

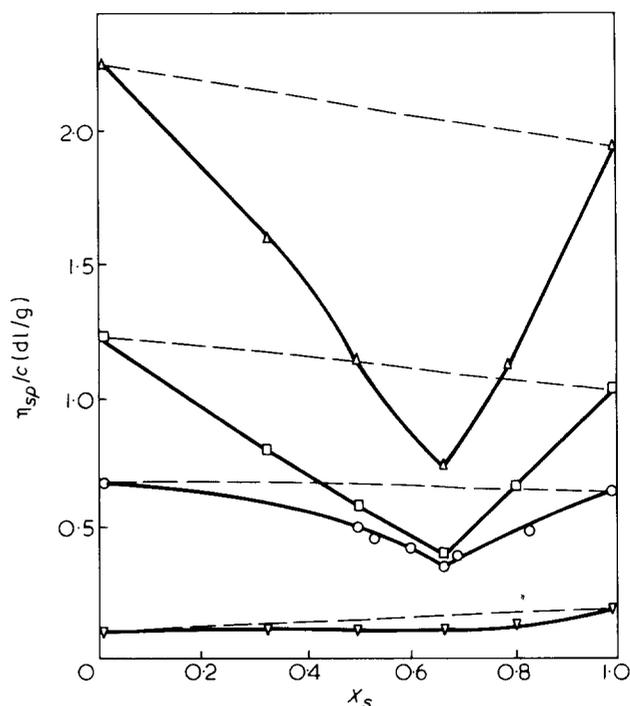


Figure 4 Reduced viscosity η_{sp}/c vs. weight fraction st PMMA (X_s) for mixtures of it- and st-PMMA of different average molecular weights in DMF measured 10 min. after mixing; it-3 + st-3 (Δ); it-1 + st-1 (\square); it-4 + st-4 (\circ); it-5 + st-5 (\blacksquare) (temperature 25°C ; PMMA concentration 0.2 g/dl)

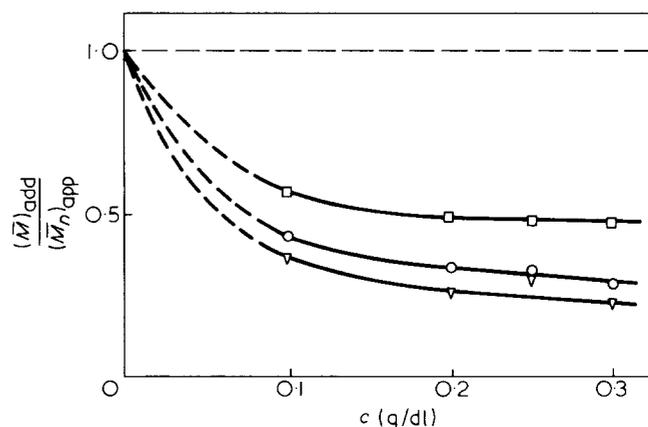


Figure 5 Increase of average molecular weight $(\bar{M}_n)_{app}$ due to stereoassociation measured by osmometry as a function of total concentration c for mixtures of it-PMMA-6 and st-PMMA-6 in toluene at 35°C , 30 min. after mixing; it/st ratios: 2/1 (\square); 1/1 (\circ); 1/2 (∇)

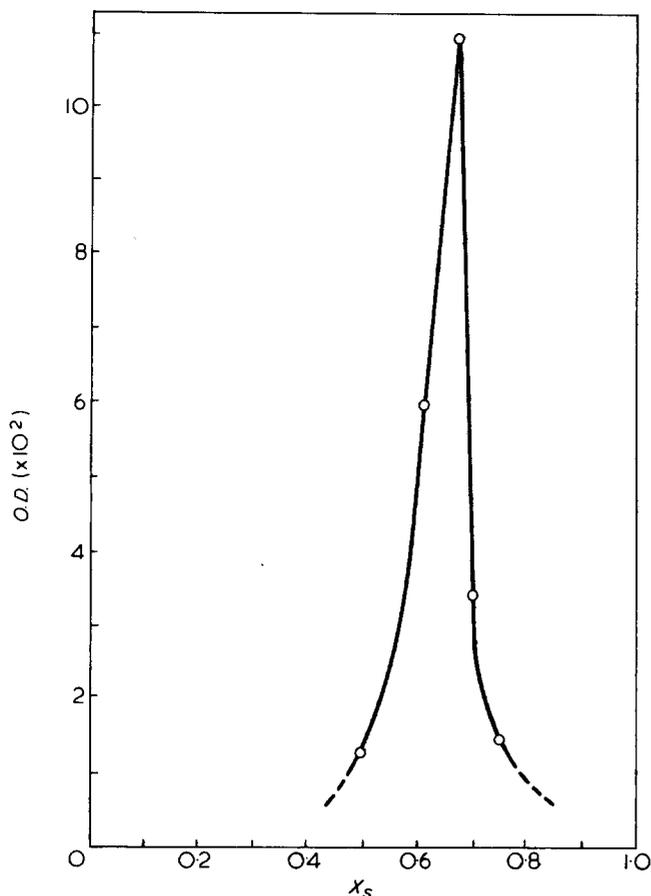


Figure 6 Optical density of 0.1% (w/v) mixed solutions of it-PMMA-4 and st-PMMA-4 in acetone vs. weight fraction st-PMMA (X_s) measured at 450 nm 2 h after mixing

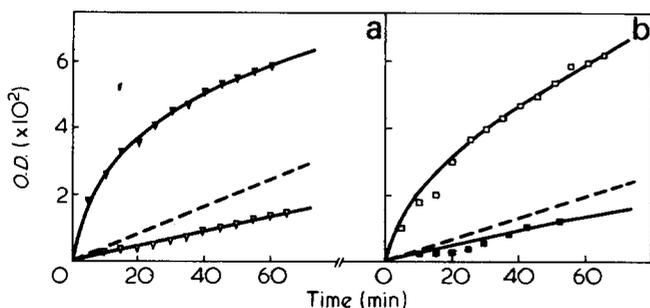


Figure 7 Increase of the optical densities of the mixed solutions with it/st ratios 4/6 (a) or 3/7 (b) from Figure 6 after addition of extra it-PMMA (∇ and \square , resp.) or st-PMMA (\blacktriangledown and \blacksquare , resp.). The total polymer concentration remained 0.1 g/dl. The dotted lines resemble the continuing increase of the optical densities without addition of extra it- or st-PMMA

supernatant solutions showed the presence of an excess of it-PMMA in mixtures 4/1 and 2/1 and an excess of st-PMMA in the mixture 1/4.

The optical density of mixtures of it- and st-PMMA, as measured by turbidimetry, is plotted against the weight fraction st-PMMA (X_s) in Figure 6. The very sharp peak at it/st = 1/2 is striking for these dilute solutions of highly tactic materials. The measurements were performed 2 h after mixing acetone solutions of 0.1 g/dl. In addition we see in Figure 7 the influence of adding extra st- or it-PMMA to mixtures with it/st = 4/6 and 3/7 at this moment.

Finally, the influence of the crystallization time on the area of the melting endotherm for different bulk mixtures of it- and st-PMMA was investigated. Annealing took place

at $T_c = 140^\circ\text{C}$, which was known to be the best temperature for complex formation². Although the melting peak temperatures hardly changed with time the areas of the endotherms increased noticeably as shown in Figure 8. At short annealing time the maximum crystallinity was found around it/st = 1/1 as before², but after longer times the maximum clearly shifts towards it/st = 1/2.

DISCUSSION

Experiments in bulk (Figure 1) showed that the it/st ratio has no particular influence on the melting temperature T_m of the stereocomplex for samples crystallized at the same temperature T_c . This is the first indication that the same complex structure is present irrespective of the composition of the bulk sample. The absence of depression of the melting point of the stereocomplex by excess of it- or st-PMMA leads to the conclusion that the binary interaction parameter of the stereocomplex with it- and st-PMMA is zero. This conclusion is based upon the relation between the melting point depression and the interaction parameter for a mixture of two polymers as applied by Nishi and Wang³¹. Stereocomplexes obtained from dilute solution had somewhat higher melting temperatures and crystallinities than stereocomplexes obtained in bulk. This can be explained by assuming that the complex formation can take place more selectively in dilute solution than in bulk. However, from X-ray diffraction it appeared that in bulk as well as dilute solution, all compositions yield the same crystalline structure. Comparing the X-ray powder diagram of complex from bulk with that of complex from dilute solution we saw differences

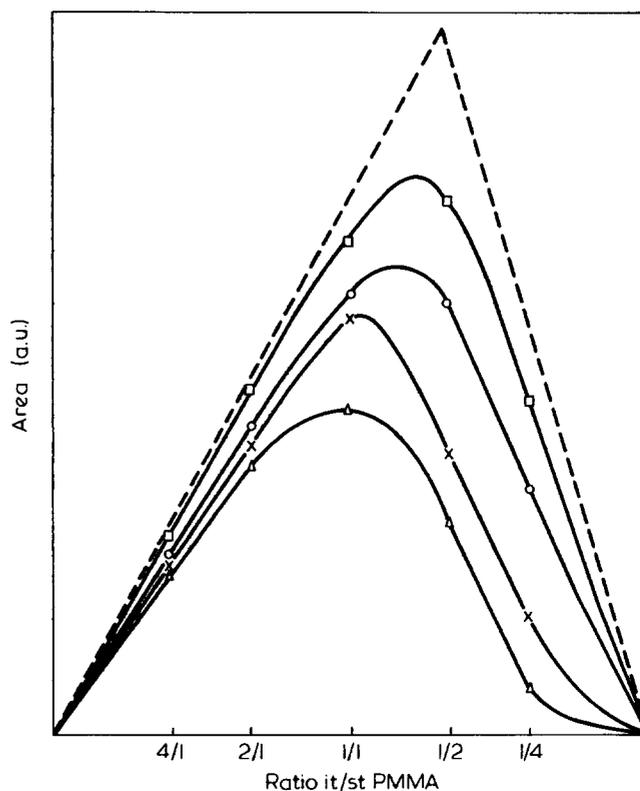


Figure 8 Specific area of the melting endotherms of stereocomplex as a function of the it/st ratio in bulk mixtures of it-PMMA-2 and st-PMMA-2 after different crystallization times: 4 h (\blacktriangle); 16 h (X); 4 days (\circ); 2 weeks (\square)

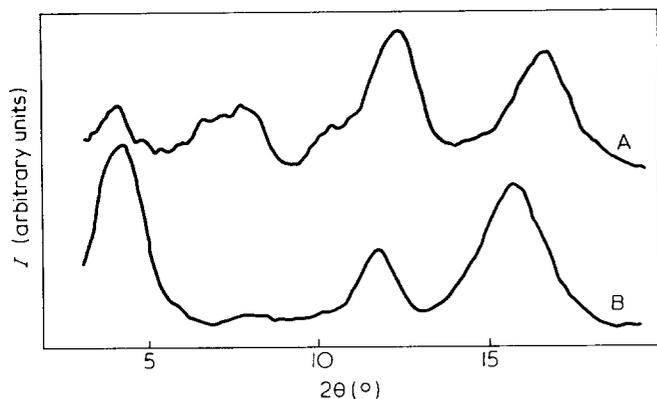


Figure 9 Intensities I of the equatorial reflections vs. diffraction angle 2θ on the X-ray fibre diffractograms of st-PMMA (A) and PMMA stereocomplex (B) respectively

which could only be explained by considering differences in perfection or dimensions of the crystals. The X-ray fibre patterns of samples obtained from concentrated gels (Figure 2) demonstrate that it is possible to stretch the complex in such a way that oriented crystallization can occur during subsequent annealing. Again we see that the it/st ratio has no influence on the shape of the pattern (Figure 3). So, it is evident that the same stereocomplex is formed irrespective of the initial it/st ratio and the method of preparation.

In order to determine the real composition of the complex we performed some experiments in dilute solutions, using PMMA samples with higher tacticities and narrower molecular weight distributions than before³. Considering the viscosity behaviour (Figure 4) we noticed no real differences from the former measurements. In type A solvents we still found, even with samples of very different molecular weights, a minimum reduced viscosity at an it/st ratio of 1/2. In addition, the osmotic pressure studies also pointed to a maximum association at it/st = 1/2 in type A as well as in type B solvent (Figure 5). Moreover, the optical density of mixtures of it- and st-PMMA in acetone, measured by turbidimetry at very low concentration, showed a very sharp maximum at it/st = 1/2 (Figure 6).

We may conclude from the above results that in dilute solution, most association occurs at an it/st ratio of 1/2, indicating also a 1/2 ratio in the stereocomplex itself. This conclusion was supported by the effect of addition of it- or st-PMMA to their mixtures in acetone as shown in Figure 7. The optical density immediately started to increase more rapidly, if the addition shifted the overall composition towards the it/st ratio of 1/2, whereas a retarding effect was seen if the overall composition shifted away from the it/st ratio of 1/2. In our opinion this rapid effect proves that the stereocomplex is always formed by one part it-PMMA and two parts st-PMMA, whatever the composition of the mixture is.

In bulk, however, the situation is not so simple. Figure 8 shows that the crystallinity of the samples, as measured by d.s.c., appears again to be dependent on the composition. However, it was somewhat confusing that we found a maximum crystallinity in compositions richer in it-PMMA than corresponding with the it/st ratio 1/2*. The application of

* Hatada *et al.*³² showed by n.m.r. experiments that the chains of it-PMMA ($T_g = 40^\circ\text{C}$) are much more mobile than those of st-PMMA ($T_g = 120^\circ\text{C}$). This might be the reason why the bulk crystallization at 140°C of the stereocomplex proceeded initially faster in compositions with excess of it-PMMA than in compositions around the it/st ratio 1/2.

longer annealing times revealed that the crystallinities at these compositions hardly increased, which is in contrast to compositions rich in st-PMMA. Therefore, the maximum crystallinity in Figure 8 shifts towards higher st-PMMA contents with a limit again at an it/st ratio of 1/2 for infinite annealing time. As the melting temperatures hardly changed during prolonged annealing, the increase of crystallinity should be attributed to formation of new stereocomplex crystals rather than to improvement of existing ones. Consequently we may conclude from the position of the final maximum that in bulk, just as in dilute solution, the PMMA stereocomplex is formed by one part of it-PMMA and two parts of st-PMMA.

This conclusion is in contradiction to a statement in one of the previous publications from this laboratory¹. At that time, the lack of sufficiently crystalline pure st-PMMA led us to assume wrongly that the crystalline fraction consisted of stereocomplex with an it/st ratio of 1/1 together with solvent stabilized st-PMMA. However, recently we obtained strongly crystalline st-PMMA by crystallization of oriented films in suitable solvent vapours as described by Tadokoro *et al.*³³. The X-ray fibre pattern of such films revealed that the structure of the stereocomplex is not only quite different from that of it-PMMA¹ but also different from that of st-PMMA. So, we were able to exclude the presence of separate st-PMMA crystals in mixtures of it- and st-PMMA. This is demonstrated by the equatorial optical density curves in Figure 9.

Consequently, we now think that the double melting reported before¹ should not be attributed to separate crystals of st-PMMA and stereocomplex, but to stereocomplex crystals of different quality, perhaps formed by primary and secondary crystallization. The same double melting phenomena were observed after crystallization in bulk at low crystallization temperatures (see Results). In both cases, X-ray analysis, after heating to a temperature just between both melting peaks, did not reveal the disappearance of crystalline st-PMMA but only the partial melting of stereocomplex.

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