

Stereoselective association between isotactic poly(methyl methacrylate) and syndiotactic poly(methacrylic acid)

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An extensive viscometric investigation has been carried out into the stereo-association between isotactic poly(methyl methacrylate) (it-PMMA) and syndiotactic poly(methacrylic acid) (st-PMAA) in different solvents and solvent mixtures. Solvent media were classified into three types, A, B and C, depending on their decreasing ability to promote complex formation. In all 'complexing' solvents (type A and B), even in the best one consisting of a mixture of 83 vol % ethanol and 17 vol % water, only one of the four possible cross-combinations of tactic PMMA and PMAA can associate. This stereoselectivity was confirmed by a calorimetric (d.s.c.) study of the glass transition of the various mixtures in the bulk. The it-PMMA/st-PMAA complex, although it is weaker, resembles the well known it/st-PMMA stereocomplex in many respects. It is suggested that association occurs primarily due to stereo-complementarity of the components involving interaction of the ester groups of it-PMMA with the α -methyl groups of st-PMAA and not to hydrogen bonding via the carboxyl groups of st-PMAA.

INTRODUCTION

It can be said that complexes between isotactic and syndiotactic poly(methyl methacrylate) (it/st-PMMA) represent the first example of a synthetic polymer by which two polymers of different stereochemical configuration associate. Since their discovery¹, many papers have been devoted to their association behaviour, structure, and properties in the liquid as well as in the solid phase, especially in the last decade².

We have found that it-PMMA can also associate in an analogous manner with syndiotactic poly(methacrylic acid) (st-PMAA) in *N,N*-dimethylformamide (DMF)³. Surprisingly, the diastereoisomeric combination of it-PMAA and st-PMMA does not associate in any way³. Therefore, the complex formation between PMMA and PMAA may be called stereo-selective.

In continuation of a preliminary report³ results on the association behaviour of it-PMMA and st-PMAA under various conditions and some properties of the complex are presented in this paper.

EXPERIMENTAL

Materials

It-PMMA and st-PMMA were synthesized according to established procedures^{4,5}. The polymers were purified by repeated precipitation of dioxane and DMF solutions in water.

It-PMAA was prepared by acid hydrolysis of finely powdered it-PMMA with 96% H₂SO₄⁶ at 25°C for about 3 days. Shorter reaction times yielded partly hydrolysed it-PMMA (co-it-MMA/MAA copolymers). They were purified by precipitation of methanol or DMF solutions in ether.

St-PMAA was obtained by ⁶⁰Co radiation polymerization of a 20 vol % solution of dry methacrylic acid in dry isopropyl alcohol at -78°C⁷. Partly hydrolysed st-PMMA (co-st-

MMA/MAA copolymers) were produced by hydrolysis with 96% H₂SO₄ for various reaction times at 45°C⁸. Maximum hydrolysis was 85%.

Low syndiotactic PMAA (low st-PMAA) was prepared by polymerizing methacrylic acid with bis(*p*-tert-butyl-cyclohexyl) peroxydicarbonate as initiator at a concentration of 0.5 mol % with respect to monomer. The reaction was performed in DMF at 25°C, using a weight ratio of 1 part methacrylic acid to 4 parts DMF. The solvents, 'Bakergrade' DMF from Baker Chemicals (Deventer, Holland), *para*-dioxane, and 2-methoxyethanol from Merck (Darmstadt, Germany) were employed without further purification.

Characterization of polymers

Average molecular weights (\bar{M}_v) were determined using the relation $[\eta] = 4.8 \times 10^{-5} \bar{M}_v^{0.80}$ in chloroform at 25°C for the PMMA⁹ and $[\eta] = 242 \times 10^{-5} \bar{M}_v^{0.51}$ in methanol at 26°C for the PMAAs¹⁰ ($[\eta]$ in dl/g). Occasionally \bar{M}_v of PMAA was determined after methylation of PMAA to PMMA with diazomethane¹¹ in DMF at room temperature.

Tacticities of PMMA samples were measured from 60 MHz p.m.r. spectra¹². The tacticity of PMAA samples was measured as PMMA after methylation with diazomethane.

The degree of hydrolysis, α , of PMMA samples was determined by dissolving 30 mg of polymer in 10 ml 0.1 N LiOH, to which 60 mg LiCl was added. The excess of LiOH was back-titrated potentiometrically with 0.1 N HCl. If the polymer sample was difficult to dissolve, α was calculated from its p.m.r. spectrum in *d*₆-DMSO, by taking the ratio of the areas of ester- and α CH₃-proton resonances, respectively:

$$1 - \alpha = A_{\text{COOCH}_3} / A_{\alpha\text{CH}_3}$$

If there was a serious overlap of the α CH₃- and β CH₂-proton resonances, then

$$1 - \alpha = 5A_{\text{COOCH}_3} / 3(A_{\alpha\text{CH}_3} + A_{\beta\text{CH}_2})$$

Table 1 Characterization of polymers

Polymer*	$\bar{M}_v \times 10^{-3}$	(mm) [†]	(mr) [†]	(rr) [†]
<i>it</i> -PMMA-13	90	0.90	0.07	0.03
<i>it</i> -PMMA-70	182	0.91	0.08	0.01
<i>it</i> -PMMA-74	620	0.93	0.06	0.01
<i>it</i> -PMMA-75	381	0.92	0.06	0.02
<i>it</i> -PMMA-78	830	0.96	0.02	0.02
<i>it</i> -PMMA-206	119	0.93	0.05	0.02
<i>it</i> -PMMA-216	25	0.90	0.08	0.02
<i>st</i> -PMMA-202	470	0.02	0.09	0.89
<i>it</i> -PMAA-2	464	0.89	0.08	0.03
<i>st</i> -PMAA-7	30	0.00	0.11	0.89
<i>st</i> -PMAA-10	13	0.01	0.10	0.89
<i>st</i> -PMAA-20	369	0.01	0.05	0.94
low <i>st</i> -PMMA-2	170	0.03	0.27	0.70

* *it* = isotactic, *st* = syndiotactic, PMMA = poly(methyl methacrylate), PMAA = poly(methacrylic acid); [†] (mm) = meso (isotactic) triads, (mr) = (heterotactic) triads, (rr) = racemic (syndiotactic) triads

The different polymers used are listed in Table 1.

Miscellaneous measurements

Viscometric measurements at constant time intervals (which allowed us to follow association with time) were carried out automatically in a Lauda Viscotimer (Schott u. Gen., Mainz, Germany) to which two Tempotac time controls (SAIA AG, Murten, Switzerland) were connected. Solutions of PMMA and PMAA (0.3 g/dl) were brought to the measuring temperature required and rapidly mixed in the desired ratio into an appropriate Ubbelohde viscometer. The lowest pump pressure (40 mmHg pressure) was applied to prevent possible destruction of association sites by shear forces³. Refractive indices were measured in a LI-3-interferometer from Zeiss-Jena, Germany, using a 20 mm cell.

Turbidity measurements were carried out using a Cenco-TNO light scattering apparatus equipped with an electrically heated cell. The intensity of the scattered light was measured at an angle of 90° as a function of temperature to obtain gel melting points.

Thermograms of 25 mg samples in aluminium pans with a loose lid were recorded on scanning using a Perkin-Elmer DSC-1B differential scanning calorimeter at a scan speed of 8°C/min. The inflection point of the c_p jump was taken as T_g . Samples were prepared by mixing 0.3 g/dl solutions of the polymer components in DMF or ethanol/H₂O (83 vol % ethanol) at 25° and 45°C, respectively, such that the base molar ratio of *it*-PMMA and *st*-PMAA was 1:1. After 5 days the gel or precipitate was isolated by centrifugation. Non-complexing 1:1 polymer mixtures were coprecipitated from DMF in ether. All samples were dried at 60°C *in vacuo* before scanning.

Powder X-ray diffractograms were obtained with a Philips diffractometer at a scan speed of 0.5°/min and an aperture angle of 0.5°; CuK α radiation was used.

RESULTS AND DISCUSSION

Association in DMF

Association of dilute solutions of *it*-PMMA and *st*-PMAA in DMF always led to viscosity enhancement, the maximum enhancement being at a 1:1 base molar ratio of the polymer components. This is illustrated in Figure 1 in which the relative change in viscosity number or reduced viscosity

$\Delta\eta_{red}$, is plotted versus the base mole fraction of *st*-PMAA, x_s . When the difference Δn between the refractive indices of mixtures and solvent, respectively, is plotted versus x_s , again maximum deviation of Δn from additivity occurred at $x_s = 0.5$. In view of these results further examinations were carried out, mainly with 1:1 polymer compositions.

The viscosity enhancement rate which reflects the velocity of association, increased with the average molecular weight of the polymer components³. In all instances the initial rate, $\dot{\eta}_{red} \equiv d\eta_{red}/dt$, appeared to be approximately constant over a few hours. Furthermore, it was found that the logarithms of $\dot{\eta}_{red}$ for three different *st*-PMMA were linear functions of \bar{M}_v of *it*-PMMA.

Viscosity enhancement was also greatly affected by temperature. According to Figure 2 for one combination

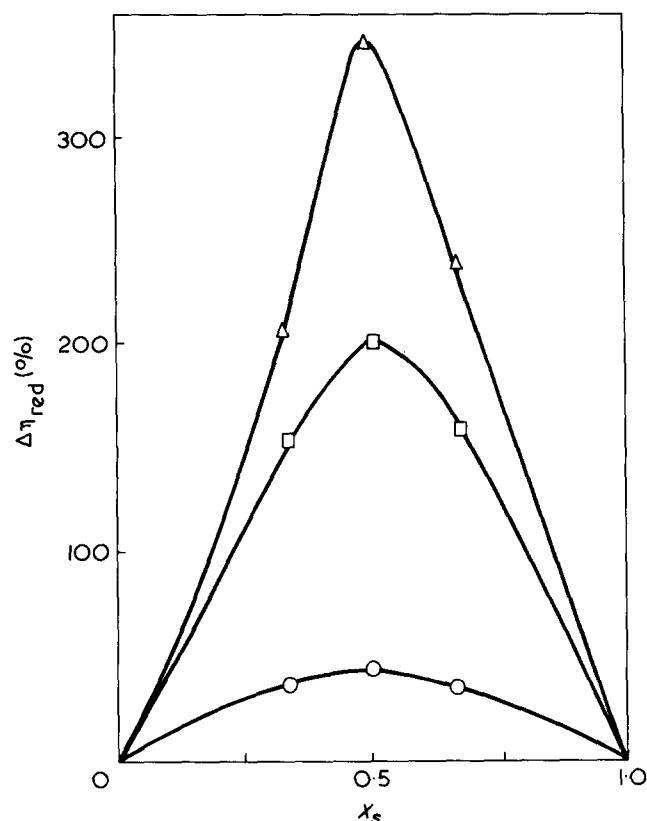


Figure 1 Relative change in viscosity number vs. base molar composition of *it*-PMMA-75 and *st*-PMMA-20 in DMF with a total polymer concentration of 0.3 g/dl at 25.0°C after ○, 1 h; □, 4 h; △, 8 h

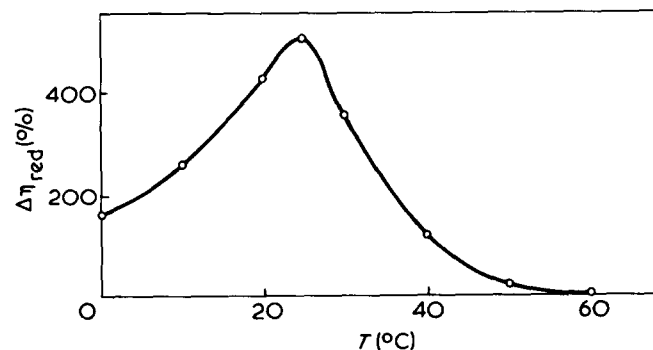


Figure 2 Temperature dependence of relative change in viscosity number of a 1:1 complex between *it*-PMMA-13 and *st*-PMAA-7 in DMF after an association time of 24 h. Total polymer concentration = 0.3 g/dl

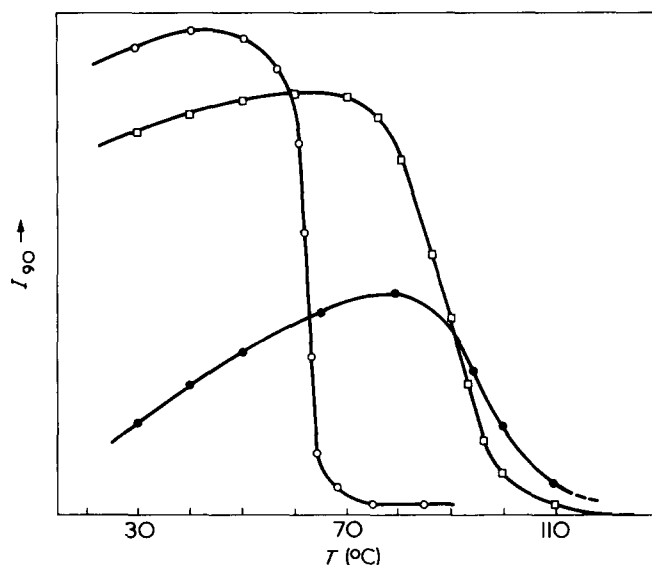


Figure 3 Scattered light intensity at an angle of 90° vs. temperature of: \circ , 1:1 complex of *it*-PMMA and *st*-PMAA in DMF; \square , 1:1 and 1:2 complex of *it*- and *st*-PMMA in DMF; \bullet , 1:1 complex of *it*- and *st*-PMMA in toluene. Total polymer concentration = 0.3 g/dl. Heating rate = $2^\circ\text{C}/\text{min}$

there was a maximum enhancement at about 25°C after an association time of 24 h.

The diminishing enhancements below 25°C may be a consequence of formation of less loose (denser) gel particles whereas the situation above 25°C is simply caused by production of decreasing amounts of (looser) complexes until association is completely suppressed at around 60°C , the dissociation temperature of the complex or gel melting temperature T_{gm} . This could also be obtained by detecting the disappearance of turbidity on heating or its appearance on cooling. At a heating (cooling) rate of $2^\circ\text{C}/\text{min}$ a T_{gm} of 63°C can be read from *Figure 3*. At a lower rate of $0.5^\circ\text{C}/\text{min}$ T_{gm} was 61°C . This was much lower than the T_{gm} of the *it*/*st*-PMMA complex which was 89°C in DMF and 95°C in toluene (*Figure 3*). Hence, association in DMF between *it*-PMMA and *st*-PMAA is weaker than between *it*- and *st*-PMMA.

The relation between these two systems is demonstrated further by a viscometric study of the association between *it*-PMMA and progressively hydrolysed *st*-PMMA's which are in fact cosyndiotactic MMA/MAA copolymers. *Figure 4* shows the results in DMF as a function of composition after two hours. With increasing MAA content of hydrolysed *st*-PMMA the depression, which is caused by formation of compact 1:2 *it*/*st*-PMMA complexes¹³, becomes more and more counteracted by a tendency to elevate η_{red} as a consequence of the creation of less dense network-like structures. It is nevertheless striking that association, even with highly hydrolysed *st*-PMMA, still produced pronounced negative deviations of η_{red} with minima around a 1:2 ratio ($x_s \approx 0.7$) in spite of the short average sequence length of MMA units. This is in sharp contrast with the association of *it*-PMMA with low *st*-PMMA containing about 70% syndiotactic triads, which only led to viscosity enhancements¹⁴. It seems therefore that, regarding the association ability of *st*-PMMA, a high degree of syndiotactic triads is more imperative than replacing MMA units by MAA or possibly other units. On these grounds it is tempting to suggest that the α CH_3 groups of the syndiotactic component play a role during association instead of its acid or ester groups.

Association between *st*-PMMA and progressively hydrolysed *it*-PMMA, i.e. co-isotactic MMA/MAA copolymers, were also studied to some extent. About 15% substitution of MMA by MAA units was sufficient to suppress association completely. Consequently, *it*-PMMA is much more sensitive to chemical modification than *st*-PMMA with respect to association ability. This suggests that the ester groups of *it*-PMMA are essential for association.

Association in other media

Solvents have a large influence on association. We have divided solvents into three types¹⁵ with respect to the stereo-complex formation between *it*- and *st*-PMMA at room temperature. In type A solvents viscosity reduction takes place due to strong association, in type B viscosity enhancement is due to weak association, and in type C solvents there is no association. We shall apply this classification to the present system of *it*-PMMA and *st*-PMAA.

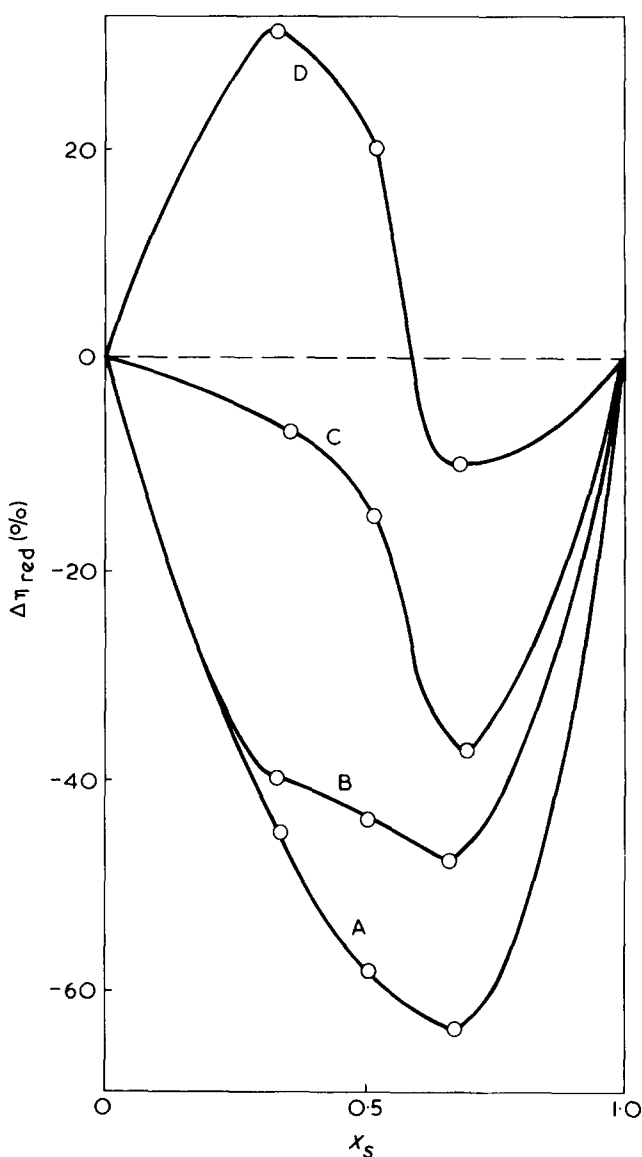


Figure 4 Relative change in viscosity number vs. base molar composition of *it*-PMMA-70 and partly hydrolysed *st*-PMMA-202. Degree of hydrolysis: A, 0%; B, 12%; C, 43%; D, 64%. Association time = 2 h. Total polymer concentration = 0.3 g/dl. Temperature = 25.0°C

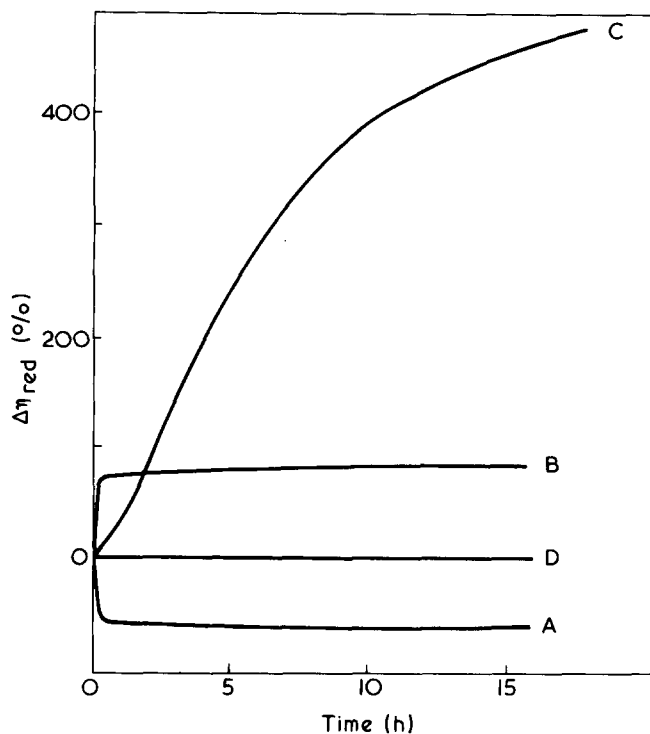


Figure 5 Time dependence of relative change in viscosity number during association of 1:1 base mole mixtures of *it*-PMMA-75 and *st*-PMAA-10 in: A, 83 vol % EtOH/H₂O; B, 2-ME; C, DMF; D, no association. Total polymer concentration = 0.3 g/dl. Temperature = 25.0°C, except in EtOH/H₂O (45.0°C)

Strictly speaking, no type A solvent has yet been found. However, a mixture of 83 vol % of ethanol in water (for short EtOH/H₂O) at 45°C, which is about the θ temperature for *it*-PMMA, conformed to an A type medium in so far as association led to a turbid solution which lowered the η_{red} (Figure 5, curve A). The minimum value of η_{red} c.q. $\Delta\eta_{red}$, appeared at a 1:2 ratio ($x_s \approx 0.67$ in Figure 6). At higher temperatures up to 70°C only a small shift of this minimum to higher *st*-PMAA contents was observed. The occurrence of a minimum at a 1:2 ratio is analogous to that in the association of *it*/*st*-PMMA in A solvents, which points to the formation of a 1:2 complex. DMF, the solvent which we used extensively, can be called a B type solvent. Others are *N,N*-dimethylacetamide (DMA) and dimethyl sulphoxide (DMSO). In DMA and DMSO η_{red} was comparatively smaller than in DMF, but in all three solvents viscosity could rise continuously over many hours to high η_{red} values (Figure 5, curve C).

Another class of B solvents is characterized by a large η_{red} but a rather low constant end value of η_{red} which was attained within a relatively short time (Figure 5, curve B). Such behaviour was apparent in the lower members of (di)ethylene glycol monoalkylether, HO-CH₂CH₂-(OCH₂CH₂)-OR, the one employed most in our experiments being ethylene glycol monomethyl ether or 2-methoxyethanol (2-ME).

Because of the different behaviour with respect to the time dependence of η_{red} , the B solvents were subdivided into a B1 type – the glycolethers – and a B2 type – DMF, DMA, and DMSO. In B2 solvents, weak local association between *it*-PMMA and *st*-PMMA occurs slowly, producing loose fluctuating networks. On the other hand, in B1 solvents association is believed to be more rapid and stronger, leading to denser networks. As in DMF, maximum viscosity enhancements in 2-ME were obtained at $x_s = 0.5$.

As to type C solvents, pyridine belongs approximately to this class, i.e. association does not take place (Figure 5, curve D). It should be remarked that in none of the mentioned solvents, not even in EtOH/H₂O, association occurred between *st*-PMMA and *it*-PMAA, *it*-PMMA and *it*-PMAA, or between *st*-PMMA and *st*-PMAA.

Thermal properties of PMAAs and their mixtures with PMMAs

It is known that PMAAs do not have a T_g below their decomposition temperatures (>180°C)¹⁶. Between ~180° and 260°C dehydration¹⁷ occurs, being fastest in the case of *it*-PMAA¹⁸. PMAAs dehydrated at 240°C over a period of 4 min turned out to possess T_g s (Table 2). A higher syndiotacticity of the anhydropolyacid (an-PMAA) increased T_g but decreased solubility in DMF due to intermolecular dehydration.

If the non-complexing mixtures, *st*-PMMA/*it*-PMAA, *st*-PMMA/*st*-PMAA, and *it*-PMMA/*it*-PMAA, including those with *at*-PMAA, were scanned, the T_g of the PMMA component (42°C for *it*- and 120°C for *st*-PMMA) appeared on the first scan. This was joined by the T_g of an-PMAA on rescan

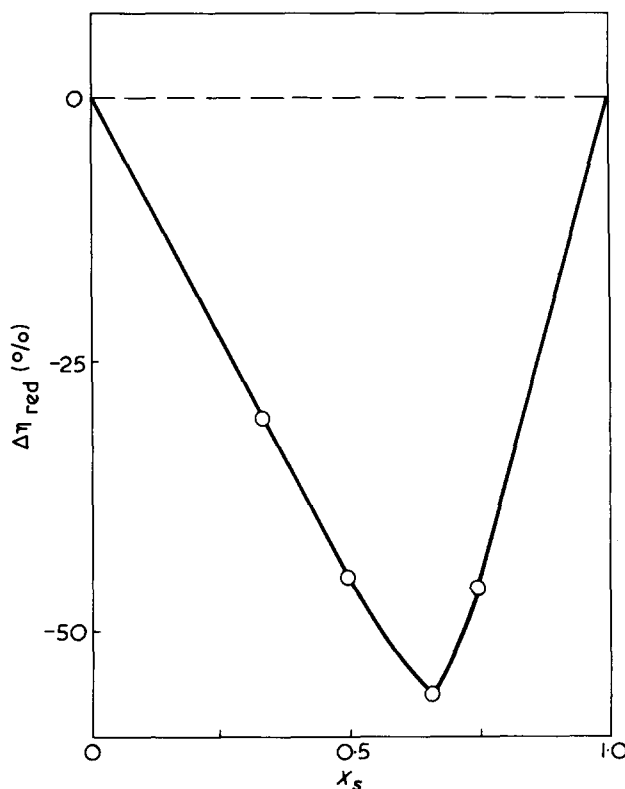


Figure 6 Relative change in viscosity number vs. base molar composition of *it*-PMMA-75 and *st*-PMAA-20 in 83 vol % EtOH/H₂O at 45.0°C after ½ h. Total polymer concentration = 0.3 g/dl

Table 2 Characterization of anhydropoly(methacrylic acids)

Precursor polymer	Triads	Anhydro-polymer	T_g (°C)	Soluble in DMF
<i>it</i> -PMAA-2*	0.89 (mm)	<i>it</i> -an-PMAA	140	Yes
<i>at</i> -PMAA-12†	0.51 (rr)	<i>at</i> -an-PMAA	167	Yes
low <i>st</i> -PMAA-2	0.70 (rr)	low <i>st</i> -an-PMAA	171	Swelling
<i>st</i> -PMAA-20	0.94 (rr)	<i>st</i> -an-PMAA	180	No

* $\bar{M}_v = 464\,000$, † $\bar{M}_v = 248\,000$, (mm) = 0.12, (mr) = 0.37

provided the mixture was heated above 180°C in the previous scan. A complex of *it*-PMMA and *st*-PMAA did not show the T_g of *it*-PMMA as long as the sample was not heated above 180°C. Only when dehydration of *st*-PMAA could take place above 180°C, a rescan gave the T_g values of *it*-PMMA and *st*-an-PMAA, signifying that the complex had dissociated because of dehydration, and that the new combination of liberated *it*-PMMA and *st*-an-PMAA was incompatible. T_m could not be detected for the complexes, although they possessed some crystallinity.

Crystallinity of complexes

A powder diffractogram of an *it*-PMMA/*st*-PMAA complex is composed of a central peak at $2\theta = 15^\circ$ flanked by two shoulders at $2\theta = 12^\circ$ and 18° , respectively, none of which is present in crystallized *it*-PMMA¹⁹. *St*-PMAA has not been crystallized so far. The 2θ values correspond to interplanar spacings of 0.59, 0.74 and 0.49 nm, respectively. Detailed data, including those of fibre diagrams, will be published in another paper concerning the structure of stereocomplexes²⁰.

POSSIBLE NATURE OF THE STEREO-ASSOCIATION

Of the four possible cross combinations between tactic PMMA and PMAA, only the one between *it*-PMMA and *st*-PMAA can form complexes. Because of this stereoselectivity we may exclude hydrogen bonding between ester and carboxyl groups playing a primary role. This argument is confirmed by the fact that *it*-PMMA and *st*-PMAA also associate in DMSO which breaks hydrogen bonds. This property of DMSO has been applied for instance, to suppress complex formation between PMAA and poly(*N*-vinylpyrrolidone)²¹.

Furthermore, if carboxyl and ester groups were intimately involved one should expect that strong complexes would be produced through a combined action of cooperativity and hydrogen bonding. This is not in agreement with the low T_{gm} of about 60°C, nor is it with respect to infra-red spectra of the dry complexes which do not indicate the presence of hydrogen bonds.

From experiments with cotactic MMA/MAA copolymers (Figure 4) it has been suggested that the α CH₃ groups of the syndiotactic polymer are involved in the association process. In this connection the hydrophobic or rather solvophobic interaction of α CH₃ groups of *st*-PMAA may cause its rapid association with *it*-PMMA in the strongly polar medium, EtOH/H₂O. It further appeared that in this medium the increase in pH on mixing *st*-PMAA with increasing quantities of *it*-PMMA was only about half of the pH increase on mixing PMAA with poly(ethylene oxide) which has been proved to associate by hydrogen bonding²².

Finally, comparative studies of X-ray fibre diagrams of *it*/*st*-PMMA and *it*-PMMA/*st*-PMAA complexes indicate that the structures are very similar²⁰ which should not be the case if hydrogen bonding plays a significant role in the complex formation of *it*-PMMA and *st*-PMAA. Therefore, it may well be that the stereo-association proceeds through interaction of α CH₃ groups of the syndiotactic polymers (PMMA and PMAA) with the ester groups of *it*-PMMA.

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