

# The influence of ester groups on the stereocomplex formation between different polyalkylmethacrylates

F. Bosscher, D. Keekstra and G. Challa

Laboratory of Polymer Chemistry, State University of Groningen, Nyenborgh 16, Groningen, The Netherlands

(Received 2 January 1980)

Isotactic poly(ethyl methacrylate) (it-PEMA) and syndiotactic poly(isobutyl-methacrylate) (st-PiBMA) were synthesized to investigate the stereocomplex formation with syndiotactic and isotactic poly(methyl methacrylate) (st- and it-PMMA) respectively. A d.s.c. study pointed out that it-PEMA and st-PMMA form incompatible mixtures whereas st-PiBMA and it-PMMA form compatible mixtures in which stereocomplex formation can occur as indicated by viscometry and X-ray diffraction. These results confirm the idea that the methyl ester groups of the isotactic chain and the  $\alpha$ -methyl groups of the syndiotactic chain are responsible for stereocomplex formation.

## INTRODUCTION

Since the first paper of Liquori *et al.* in 1965<sup>1</sup> much research effort has been dedicated to the complex formation of isotactic and syndiotactic poly(methyl methacrylate) (it- and st-PMMA). In the search for other complex forming systems, Lohmeyer *et al.*<sup>2</sup> found that stereoregular poly(methacrylic acid) (PMAA) and PMMA formed complexes only if the first polymer has the syndiotactic and the second the isotactic configuration. In order to explain this stereoselectivity they suggested that the methyl ester groups of the isotactic polymer and the  $\alpha$ -methyl groups of the syndiotactic polymer are responsible for the complex formation. To test this idea, some other stereoregular poly(alkyl methacrylates) were prepared and their complexing ability investigated.

## EXPERIMENTAL

The polymers used are listed in Table 1. It-PMMA and it-poly(ethyl methacrylate) (it-PEMA) were synthesized with phenylmagnesium-bromide as catalyst<sup>3</sup>, st-PMMA and st-poly(isobutyl-methacrylate) (st-PiBMA) with  $\text{AlEt}_3/\text{TiCl}_4$  as catalyst<sup>4</sup>.  $\bar{M}_v$  of it- and st-PMMA were measured in chloroform at 25°C using  $[\eta] = K \times \bar{M}_v^a$ , in which  $K = 4.8 \times 10^{-5} \text{ dl g}^{-1}$  and  $a = 0.8$ .

$\bar{M}_v$  of it-PEMA was measured in butanone at 23°C with  $K = 2.83 \times 10^{-5} \text{ dl g}^{-1}$  and  $a = 0.79$ <sup>5</sup>. For st-PiBMA no Mark-Houwink parameters were available, therefore  $\bar{M}_w$  was measured at room temperature in DMF using a Malvern laser light scattering apparatus.

The tacticities of it- and st-PMMA were derived from the  $\alpha$ -methyl peaks obtained for 5–10 wt % solutions in *o*-dichlorobenzene at 160°C by 60 MHz n.m.r. spectroscopy with a Jeol C-60 HL apparatus. Because of overlap of the  $\alpha$ -methyl protons and ester-methyl protons the ratio *I:H:S* could not be calculated in this way for it-PEMA and st-PiBMA, and the Fourier-transform n.m.r. technique described by Hatada *et al.*<sup>6</sup> had to be applied.

Figures 1 and 2 show the proton Fourier transform n.m.r. spectra of it-PEMA and st-PiBMA respectively. The spectra were recorded at 58°C in  $\text{CDCl}_3$  (1 wt % polymer solutions) on a Varian XL-100 FT-n.m.r. spectrometer by using a  $(90^\circ - T)_n$  pulse sequence, where  $T = 10 \text{ s}$  and  $n = 8$ .

By choosing the pulse sequence  $(180^\circ - t - 90^\circ - 10 \text{ s})_8$ , where  $t = 420 \text{ ms}$  and  $t = 250 \text{ ms}$  for it-PEMA and st-PiBMA respectively, the longitudinal magnetization of the ester-methyl signal was zero, and the tacticity could be measured from the three splittings in the  $\alpha$ -methyl resonance (insertion of Figures 1 and 2).

Thermal analyses of blends, obtained by coprecipitation from a common non-complexing solvent, were performed with a d.s.c.-2 (Perkin-Elmer). The reduced viscosities of mixed solutions in various solvents were compared with the additive values in order to indicate complex formation. Stereocomplexes precipitated from such solutions and were isolated by centrifugation. After drying, the stereocomplexes were investigated by d.s.c. and X-ray powder diffraction. For details of sample preparation, viscometry, X-ray and thermal analysis refer to Vorenkamp *et al.*<sup>7</sup>.

## RESULTS AND DISCUSSION

The measurements of the glass transition temperatures,  $T_g$ , of mixtures of it-PEMA and st-PMMA do not show any influence of composition on  $T_g$ ; both  $T_g$  of it-PEMA (15°C) and  $T_g$  of st-PMMA (131°C) remain unaffected. It

Table 1 Data on polymers applied for complex formation

	$\bar{M}_v \times 10^{-3}$	<i>I - H - S</i>
it-PMMA	400	94 - 5 - 1
st-PMMA	380	1 - 10 - 89
it-PEMA	115	93 - 5 - 2
st-PiBMA	650 ( $\bar{M}_w$ )	3 - 6 - 91

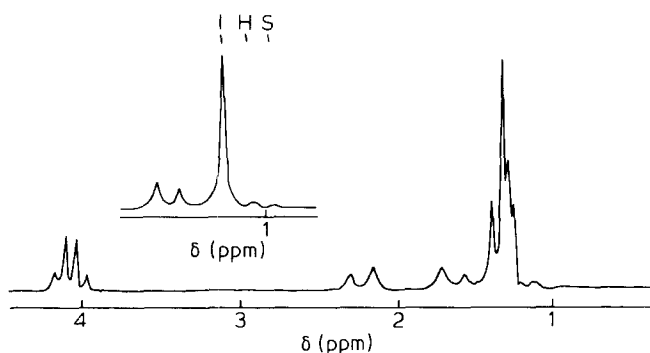


Figure 1 100 MHz FT-n.m.r. spectrum of 1 wt % it-PEMA in  $\text{CDCl}_3$  at  $58^\circ\text{C}$ . The insertion corresponds to the peak-eliminated spectrum around  $\delta = 1.2$  ppm., using a pulse sequence of  $(180^\circ - 420 \text{ ms} - 90^\circ - 10 \text{ s})_g$

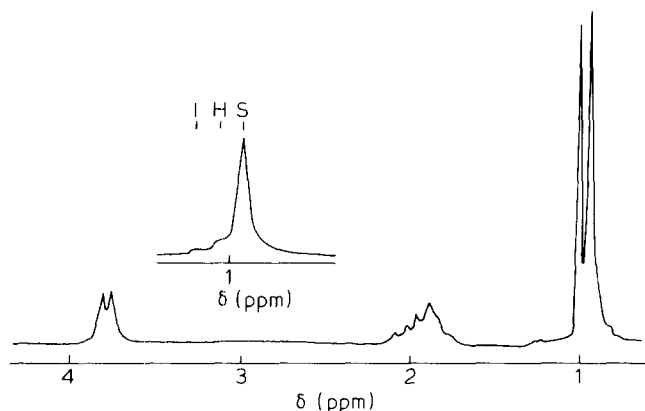


Figure 2 100 MHz FT-n.m.r. spectrum of 1 wt % st-PiBMA in  $\text{CDCl}_3$  at  $58^\circ\text{C}$ . The insertion corresponds to the peak-eliminated spectrum around  $\delta = 1$  ppm., using a pulse sequence of  $(180^\circ - 250 \text{ ms} - 90^\circ - 10 \text{ s})_g$

can therefore be concluded that it-PEMA and st-PMMA form incompatible mixtures and there occurs no complex formation at all.

In mixtures of it-PMMA and st-PiBMA a single  $T_g$  intermediate to the  $T_g$ 's of pure it-PMMA ( $38^\circ\text{C}$ ) and pure st-PiBMA ( $67^\circ\text{C}$ ) was measured. In this case it was concluded that the two polymers are compatible. If complex formation occurred in bulk one should also expect some endotherm for dissociation of the complex. However, after annealing samples at different temperatures no such endotherm could be observed. Only after very long annealing at  $120^\circ\text{C}$ , for 18 days at least, an endotherm was found at  $160^\circ\text{C}$ . However, X-ray powder diffraction showed that this endotherm was not descendent from a crystalline complex but from crystalline pure it-PMMA (Figures 3a, b). So, in bulk at  $120^\circ\text{C}$  a phase separation took place caused by crystallization of it-PMMA from the homogeneous blend. The reduced viscosity  $\eta_{sp/c}$  of different mixtures of it-PMMA and st-PiBMA, measured in DMF at  $c = 5 \times 10^{-3}$  basemol  $\text{dl}^{-1}$  and  $11^\circ\text{C}$ , showed a small negative deviation of about 9% compared with the additive value. Although we cannot observe a sharp minimum in  $\eta_{sp/c}$  versus composition, as in the case of it- and st-PMMA<sup>7</sup>, the results indicate some complex formation. Therefore, an attempt was made to isolate complexes of it-PMMA and st-PiBMA by precipitation from  $5 \times 10^{-3}$  basemol  $\text{dl}^{-1}$  solutions in DMF of different compositions during 14 days at  $4^\circ\text{C}$ . After working up these complexes showed a melting endotherm of  $153^\circ\text{C}$ , independent of the composition. The X-ray

powder diffractogram, Figure 3c, proved that this crystalline material is not pure it-PMMA. The X-ray diffraction pattern of a weakly oriented fibre, obtained by stretching of a 10 wt% gel in DMF, indicated that the reflection at  $2\theta = 4^\circ 11'$ , corresponding to an interplanar distance of 2.11 nm, is an equatorial reflection just as for the stereocomplex of it- and st-PMMA<sup>7</sup>. It is, therefore, very likely that it-PMMA and st-PiBMA form a stereocomplex comparable with the stereocomplex of it- and st-PMMA. For the sake of completeness,  $T_g$ 's of mixtures of it-PEMA and st-PiBMA were also measured. In these mixtures of different composition unchanged values of  $T_g$  for each component, 15 and  $67^\circ\text{C}$  respectively were observed. So as expected it-PEMA and st-PiBMA do not form compatible mixtures.

## CONCLUSION

The fact that only it-PMMA forms stereocomplexes with both st-PMMA and st-PMAA stimulated the investigation of the complexing ability between other polyalkylmethacrylates. By substituting the methyl ester of it-PMMA with another small ester, viz the ethyl ester, complex formation with st-PMMA disappears and the two components, it-PEMA and st-PMMA, form incompatible mixtures as was the case for it-PMAA and st-PMMA.

However, after transforming the methyl ester of the st-PMMA into an even bulkier isobutyl ester, complex formation takes place, and crystalline stereocomplex can be isolated. Table 2 gives a summary of the different stereoregular polyalkylmethacrylate pairs and their complexing abilities. It can, therefore, be concluded that:

1. Stereocomplex formation occurs if the isotactic chain is PMMA and the syndiotactic chain is either PMMA or PiBMA or PMAA.
2. Both the X-ray diffraction patterns of the stereocomplex of it-PMMA and st-PiBMA and of it-PMMA

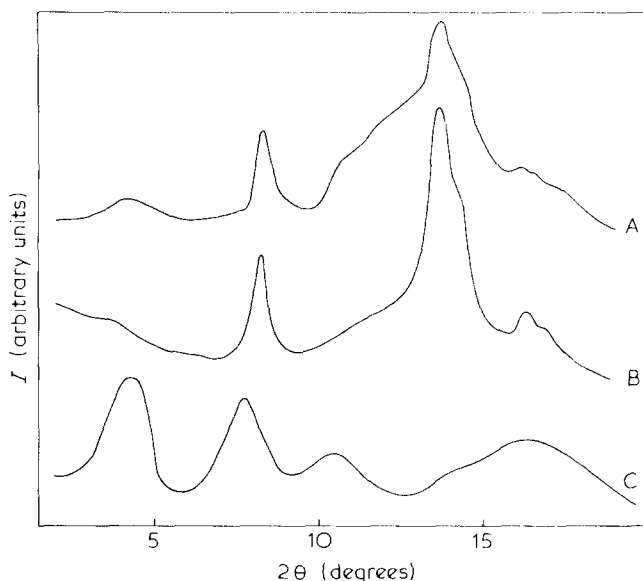


Figure 3 X-ray powder diffractograms of A — blend of it-PMMA and st-PiBMA after annealing at  $120^\circ\text{C}$  for 18 days; B — pure it-PMMA crystallized at  $120^\circ\text{C}$  for 14 days; C — stereocomplex of it-PMMA and st-PiBMA precipitated from DMF at  $4^\circ\text{C}$  during 14 days

Table 2 Complexing ability of different polyalkylmethacrylate pairs

	st-PMMA	st-PiBMA
it-PMMA	Yes	Yes
it-PEMA	No	No

and st-PMAA<sup>8</sup> agree with the x-ray diffraction pattern of the stereocomplex of it- and st-PMMA, so the structures of the three stereocomplexes are basically the same.

These conclusions confirm the suggestion of Lohmeyer *et al.*<sup>2</sup> that stereo-association proceeds through interaction of the methyl ester groups of it-PMMA and the  $\alpha$ -CH<sub>3</sub> groups of the syndiotactic polymers, e.g. PMMA, PiBMA and PMAA.

## ACKNOWLEDGEMENTS

The assistance of Drs. D. M. Kok and Ir. O. Piepers of the department of Organic Chemistry during the FT-n.m.r. measurements is gratefully acknowledged.

## REFERENCES

- 1 Liquori, A. M., Anzuino, G., Coiro, V. M., D'Alagni, M., de Santis, P. and Savino, M. *Nature* 1965, **206**, 358
- 2 Lohmeyer, J. H. G. M., Tan, Y. Y., Lako, P. and Challa, G. *Polymer* 1978, **19**, 1171
- 3 Goode, W. E., Owens, F. H., Feldmann, R. P., Snijder, W. H. and Moore, J. H. *J. Polym. Sci.* 1960, **46**, 317
- 4 Abe, H., Imai, K. and Matsumoto, M. *J. Polym. Sci. (c)* 1968, **23**, 469
- 5 Chinai, S. N. and Samuels, R. J. *J. Polym. Sci.* 1956, **19**, 463
- 6 Hatada, K., Ohta, K., Okamoto, Y., Kitayama, T., Umemura, Y. and Yuki, H. *J. Polym. Sci. (Polym. Lett. Edn.)* 1976, **14**, 531
- 7 Vorenkamp, E. J., Bosscher, F. and Challa, G. *Polymer* 1979, **20**, 1262
- 8 Lohmeyer, J. H. G. M., Thesis, Groningen, 1979