Polymer Bulletin 23, 279–286 (1990)

Polymer Bulletin

Stereocomplex formation between isotactic PMMA and syndiotactic polymethacrylates in bulk and in solution

Tatsuki Kitayama, Nobutaka Fujimoto, Yoshio Terawaki, and Koichi Hatada

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, 560 Japan

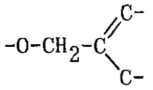
Summary

Blend of isotactic PMMA and syndiotactic poly(benzyl methacrylate) was found to form stereocomplex when annealed at 80°C. The blend showed endotherm in DSC thermogram due to the melting of the complex. The complex was also formed in toluene, which was evidenced by ^{1}H NMR spectroscopy and thermal analysis. Several syndiotactic polymers of substituted benzyl methacrylates and aliphatic methacrylates having primary alkyl ester group with branching at β-position, such as methallyl and cyclopropylmethyl methacrylates, were also found to form stereocomplexes with isotactic PMMA in bulk by annealing.

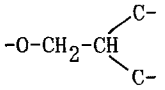
Introduction

It has been known that isotactic (iso-) and syndiotactic (syn-) poly(methyl methacrylate) (PMMA) chains associate to form a crystalline stereocomplex in certain solvents such as toluene, dimethylformamide and acetone, a concept of which was first introduced by Liquori *et al.* (1). The structure of the complex has long been investigated by several scientists but it is still not completely clear. From X-ray diffraction data and conformational energy calculations, Bosscher *et al.* (2) proposed that the stereocomplex is a double-stranded helix in which a helix of iso-PMMA chain with a small radius (a 30/4 helical conformation) is surrounded by a syn-PMMA helical chain with a large radius (a 60/4 helical conformation). Very recently, Schomaker and Challa (3) proposed another double-stranded helix model for the stereocomplex with a 9/1 helical symmetry and 18.9Å pitch. In these models, where the ester groups of syn-PMMA chain are all pointing outward, a modification of the ester groups of the syn-chain would have much smaller influence on the feasibility of stereocomplex formation than that of the ester groups of the inner iso-chain. However, only a limited number of stereocomplex of polymethacrylates other than PMMA have been so far reported; stereocomplex between iso-PMMA and syn-poly(isobutyl methacrylate) (PiBuMA) (4) and that between iso-PMMA and syn-poly(methacrylic acid) (5). Other reported pairs leading stereocomplexes are isotactic polymers of (R)- and (S)-*t*-butylthiiranes (6), isotactic polymers of (R)- and (S)-poly(α-methylbenzyl methacrylate)s (7), optically active polymers of (R)- and (S)-α-ethyl-α-methyl-β-propiolactones (8,9), optically active polymers of γ-benzyl L- and D-glutamates (10-12), and polymers of L- and D-lactides(13), all of which are the complexes between enantiomeric polymer chains.

In this work we examined polymethacrylates of primary alkyl esters with branching at β-position as syndiotactic component in the complex,



or



and found, using differential scanning calorimetry (DSC) and NMR spectroscopy, that the stereocomplex formation took place between these syndiotactic polymethacrylates and iso-PMMA. In this report, preliminary results mainly on the complex formation between syn-poly(benzyl methacrylate) (PBzMA) and iso-PMMA are described.

Experimental

Iso-PMMA was prepared by polymerizing methyl methacrylate (MMA) with *t*-C_4H_9MgBr in toluene at -60°C (14); Mn=33000, Mw/Mn=1.25. Syn-polymethacrylates were obtained with *t*-C_4H_9Li-R_3Al (R=ethyl or butyl, Al/Li=3 mol/mol) in toluene at -78°C (15). Characteristics of the syn-polymethacrylates are summarized in Table 1. Blends of the polymers were prepared by precipitating the mixtures in chloroform to hexane.

^1H NMR spectra were measured in toluene-d_8 on a JEOL JNM-FX100 spectrometer at 100 MHz. Differential scanning calorimetric analysis was performed with a Rigaku DSC 8230 at a heating rate of 10 $^oC\cdot min^{-1}$. X-ray powder diffractogram was obtained with a Rigaku model RAD-ROC X-ray diffractometer.

Results and Discussion

A blend of iso-PMMA and syn-PBzMA with a unit mole ratio of 1:1 was annealed at 80°C for 48h. DSC thermogram of the blend is shown in Figure 1 together with those for both components. Glass transitions observed in the thermograms of iso-PMMA and syn-PBzMA almost disappeared in the thermogram of the annealed blend, and a clear endotherm appeared with a maximum temperature of 109°C, which is attributed to the melting of the stereocomplex as described below.

Bosscher *et al.* reported that the complex between iso-PMMA and syn-PiBuMA was obtained by precipitation from dimethylformamide at 4°C during 14 days (4). They also described that the blend of iso-PMMA and syn-PiBuMA annealed at 120°C for 12 days showed endotherm at 160°C but the endothermic peak was attributed to the melting of crystalline iso-PMMA in the mixture. We also observed that iso-PMMA annealed at 80°C for 72h showed a melting point of 138°C in the DSC thermogram, which was almost 30°C higher than that observed for the blend. To make sure further whether the melting point of the blend is due to the stereocomplex or crystalline iso-PMMA, X-ray powder patterns of the iso-PMMA and the blend annealed at 80°C for 3 days were examined (Figure 2). The pattern of the iso-PMMA(Figure 2A) was similar to that of

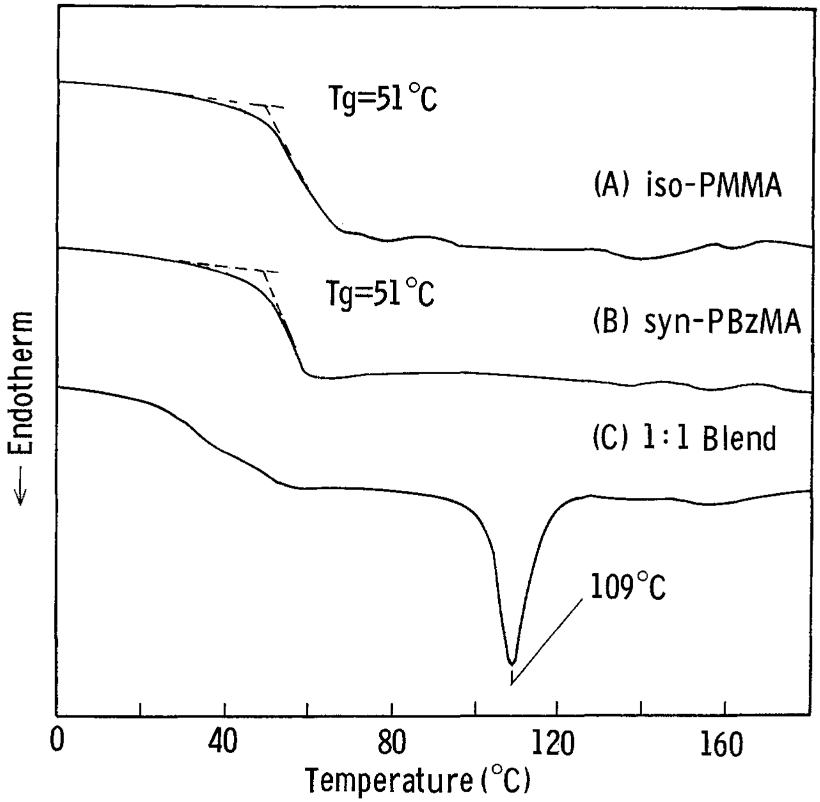


Figure 1 DSC thermograms of iso-PMMA (A), syn-PBzMA (B) and 1:1 mixture of iso-PMMA and syn-PBzMA annealed at 80°C for 48h (C) (Heating rate 10°C·min^{-1})

iso-PMMA reported by Bosscher *et al.* (4), and the pattern for the blend (Figure 2B) was completely different from the pattern of the iso-PMMA. The X-ray diffraction pattern of the blend showed weak reflections at $2\theta=4.2°$ and 6.4°, along with a strong one at 14.0°. The reflection at $2\theta=4.2°$, corresponding to an interplanar distance of 2.10 nm, is close to an equatorial reflection for the stereocomplex of iso-PMMA and syn-PMMA (16). These results indicate that the crystalline phase formed in the annealed blend of iso-PMMA and syn-PBzMA is not due to crystallized iso-PMMA but a new stereocomplex formed between these two polymers. The complex formation was attained more easily than in the case of iso-PMMA and syn-PiBuMA reported by Bosscher *et al.* (4).

The association between PMMA molecules in solution was elucidated by ^{1}H NMR spectroscopy(17–19). When association occurs between polymer molecules, the mobility of the protons of the polymer decreases and their high resolution NMR signals become too broad to be detected. Then the degree of

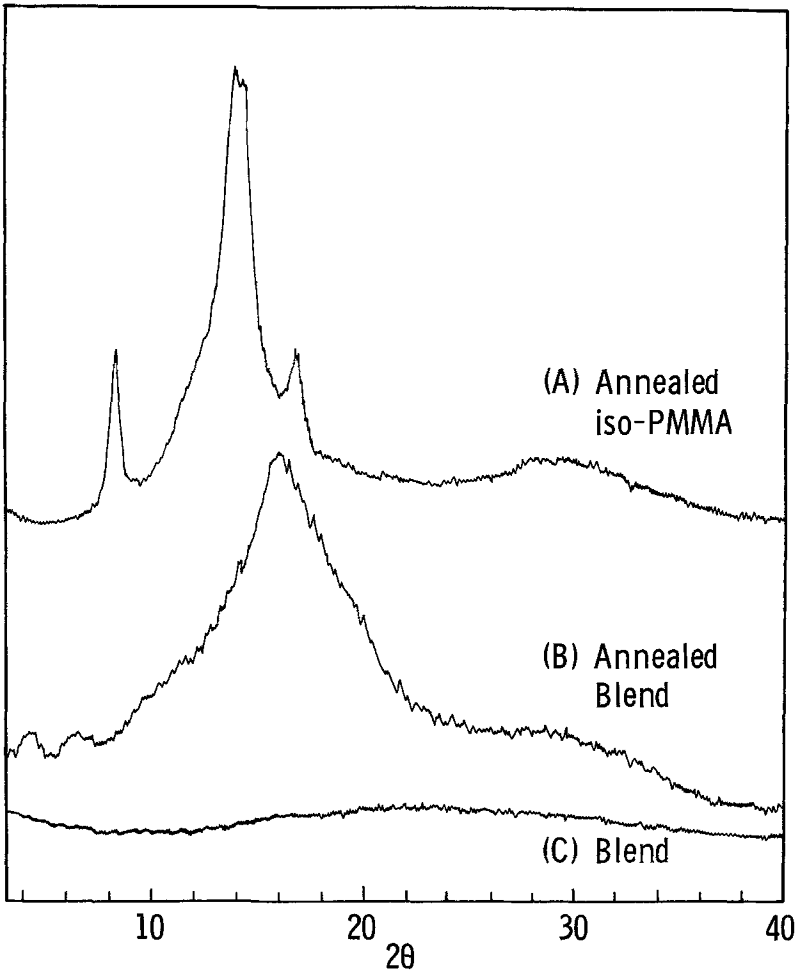


Figure 2 X-ray powder diffractograms of iso-PMMA (A) and the blend of iso-PMMA and syn-PBzMA (1:1) (B) both annealed at 80°C for 72h, and the blend without annealing (C)

association, *Da*, can be determined from the following equation;

$$Da = 1 - I/I_0.$$

Here, I represents the observed signal intensity and I_0 the intensity for the case in which no association takes place in the same solution at the same temperature. In this work, the value of I_0 was estimated using a solution of octane in toluene-d_8 containing the same amount of hydrogen as that in the polymer solution. ^1H NMR spectra were measured for iso-PMMA, syn-PBzMA and an equimolar mixture of iso-PMMA and syn-PBzMA in toluene-d_8. The summation of the intensities of all the signals was determined at various temperatures. The measurements were performed from lower to higher temperatures. Figure 3 shows the plots of *Da* values against temperature.

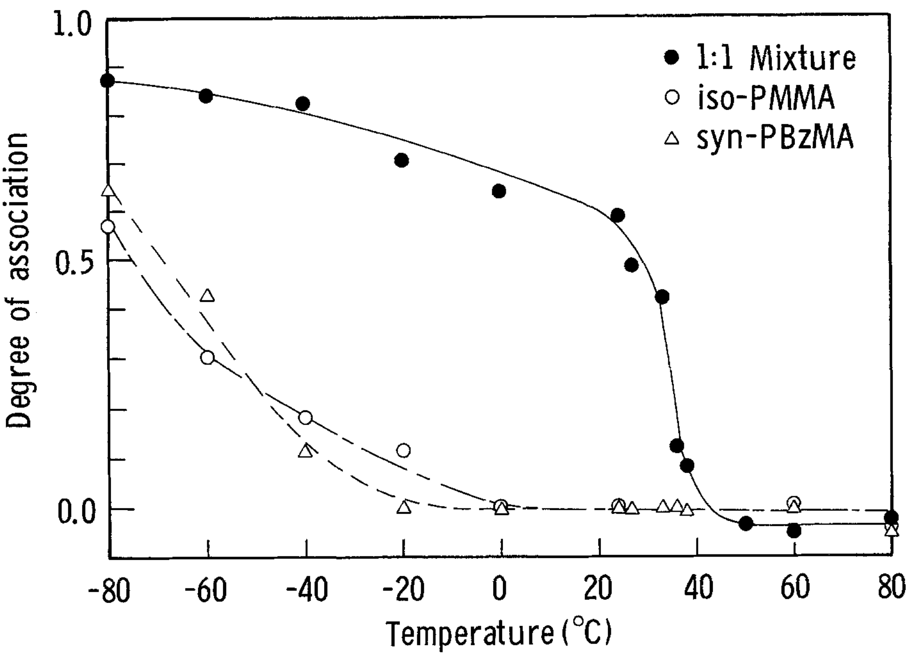


Figure 3 Degree of association of iso-PMMA(△), syn-PBzMA (o) and 1:1 mixture of iso-PMMA and syn-PBzMA (●) in toluene-d_8 at various temperatures (conc.=0.46–0.47 unit mol·l^{-1})

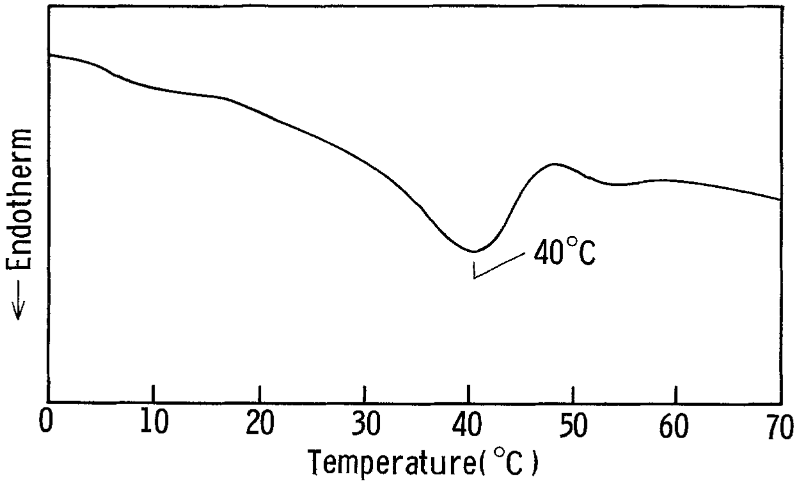
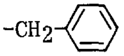
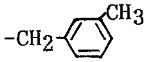
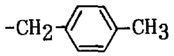
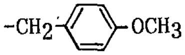
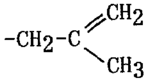
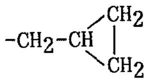
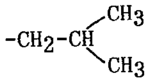


Figure 4 DSC thermogram of a 1:1 mixture of iso-PMMA and syn-PBzMA in toluene (conc.=10wt%, heating rate 10 °C·min^{-1})

Da values for iso-PMMA and syn-PBzMA increased below -40°C with a decrease in the temperature. At -80°C the syn-PBzMA showed larger *Da* than the iso-PMMA. The curve for the polymer mixture suggests that association between iso-PMMA and syn-PBzMA in toluene-d_8 began to occur rather sharply at around 30-40°C and the *Da* values became much larger than those for the individual polymer chains at lower temperatures. In fact, the NMR sample solution of the mixture formed gel at ambient temperature and the gel melted by human body heat. The gel melting temperature of this complex was about 20°C lower than that of the PMMA stereocomplex.

The gel melting point was also detected by DSC measurement. A 10% solution of a 1:1 mixture of iso-PMMA and syn-PBzMA showed endotherm with a maximum temperature of 40°C due to the melting of the gel (Figure 4). The temperature is close to that observed by ^{1}H NMR spectroscopy. These results clearly indicate that the stereocomplex between iso-PMMA and syn-PBzMA form in solution as well as in bulk similarly to the case of PMMA stereocomplex.

Table 1 Stereocomplex formation between iso-PMMA[a] and several syn-polymethacrylates in bulk[b]

Syndiotactic polymethacrylate							Stereocomplex	
Ester group	DP[c]	$\frac{Mw}{Mn}$	Tacticity(%)			Tg (°C)	Annealing temp.(°C)	Melting point(°C)
			mm	mr	rr			
$-CH_3$	226	1.26	2.7	8.6	88.7	120	150	189
	35	1.09	0.7	8.0	91.3	51	80[d]	109
	24	1.08	2.1	11.4	86.5	22	80	114
	55	1.08	2.2	11.1	86.7	53	80	121
	82	1.13	0.5	11.1	88.4	57	80	123
 $-CH_2-C(=CH_2)-CH_3$	41	1.13	2.0	5.3	92.7	15	120	146
	71	1.20	0.9	10.1	89.0	50	80	129
 $-CH_2-CH(CH_3)_2$	50	1.15	2.7	8.2	89.1	53	120	156

[a] DP=330, Mw/Mn=1.25, mm:mr:rr=97.3:1.7:1.0, T_g=51°C.

[b] Unit mole ratio of iso-PMMA and syn-polymethacrylate = 1:1. Blend was annealed for 24h.

[c] Degree of polymerization.

[d] Annealed for 48h.

Syndiotactic polymers of several substituted benzyl methacrylates also formed stereocomplex with iso-PMMA when the blends were annealed at 80 or 85°C (Table 1). The results indicate that substitution on the phenyl ring of PBzMA hardly affects the ability of complex formation and thus a wide variety of the stereocomplexes can be prepared between iso-PMMA and syn-polymer of substituted benzyl methacrylate.

The blend of iso-PMMA and syndiotactic polymer of methallyl, cyclopropylmethyl or isobutyl methacrylate also showed melting point due to stereocomplexes when annealed at 80 or 120°C (Table 1). The melting points of the complexes with syn-polymers of isobutyl (156°C) and methallyl (146°C) methacrylates are higher that those of the complexes with syn-polymers of benzyl methacrylate and its derivatives (109-123°C). All of the syn-polymethacrylates have branching at β-position in their ester groups. A blend of iso-PMMA and syn-poly(ethyl methacrylate) did not show melting point as long as it was annealed at 80 or 120°C for 48h.

As mentioned before, Bosscher *et al.*(4) claimed that the melting point observed for annealed blend of iso-PMMA and syn-PiBuMA was due to the melting of crystallized iso-PMMA. However, we found that the iso-PMMA showed melting point of 143°C when annealed under the same conditions as the blend of iso-PMMA and syn-PiBuMA, which is 13°C lower than the melting point of the annealed blend. We also observed that iso-PMMA and syn-PiBuMA formed gel easily in toluene at 0°C. These results suggest that the stereocomplex between these polymers should form in solid and in solution.

Table 1 indicates that the melting point of the complex can be controlled in a wide temperature range (from 109°C for syn-PBzMA to 189°C for syn-PMMA) by selecting an appropriate syndiotactic component.

Blends of iso-PMMA and syndiotactic random copolymers of MMA and BzMA with various compositions showed melting points in their DSC thermograms when annealed at 80°C. The melting point depended on the copolymer composition; the copolymer of higher MMA content showed higher melting point. A ternary blend of iso-PMMA, syn-PMMA and syn-PBzMA (unit mole ratio = 1:0.4:0.6) could also form crystalline phase when annealed at an appropriate temperature. When the blend was annealed at 80°C, at which temperature iso-PMMA and syn-PBzMA form stereocomplex as described above, it showed a melting point of 112°C. On the other hand, the blend annealed at 140°C showed a melting point of 175°C, which corresponds to the melting of PMMA stereocomplex. Therefore, the complexation in this ternary mixture could be controlled by the annealing temperature. Further details of these subjects will be published in the near future.

Since the first report on the stereocomplex formation appeared, it seems to have been believed that the pair of isotactic and syndiotactic polymers which can form the complex is limited to methyl ester even though a few exceptions have been reported (4, 5). However, the present work revealed that there should be a wide variety of stereocomplexes between iso-PMMA and syn-polymethacrylates and thus stereocomplex will have much more chance for the application to material design.

Acknowledgments

A part of this work was supported by a Grant-in-Aid for Scientific Research (No. 61430022) from the Ministry of Education, Science, and Culture of Japan. The authors are grateful to Mr. Tetsuo Yamamoto of Faculty of Science, Osaka University, for the measurements of X-ray powder diffractograms.

References

1. Liquori, A. M., Anzuino, G., Corio, V. M., D'Alagni, M., de Santis, P., Savino, A. *Nature*(London) (1965) **206**, 358
2. Bosscher, F., ten Brinke, G. T., Challa, G. *Macromolecules* (1982) **15**, 1442
3. Schomaker, E., Challa, G. *Macromolecules* (1989) **22**, 3337
4. Bosscher, F., Keekstra, D., Challa, G. *Polymer* (1981) **22**, 124
5. Lohmeyer, J. H. G. M., Tan, Y. Y., Lako, P., Challa, G. *Polymer* (1978) **19**, 1171
6. Dumas, P., Spassky, N., Sigwalt, P. *Makromol. Chem* (1972) **156**, 55
7. Hatada, K., Shimizu, S., Terawaki, Y., Ohta, K., Yuki, H. *Polym. J.* (1981) **13**, 811
8. Grenier, D., Prud'homme, R. E. *Macromolecules* (1983) **16**, 302
9. Prud'homme, R. E. In "Frontiers of Macromolecular Science" (Proc. 32nd IUPAC Int. Symp. Macromol.), Saegusa, T., Higashimura T., Abe, A. (eds), Blackwell Sci. Pub., Oxford, London, Edinburgh, Boston, Melbourne (1989) pp 55
10. Fukuzawa, T., Uematsu, I. *Polym. J.* (1974) **6**, 537
11. Matsushima, N., Hikichi, K., Tsutsumi, A., Kaneko, M. *Polym. J.* (1975) **7**, 382
12. Baba, Y., Kagemoto, A. *Macromolecules* (1977) **10**, 458
13. Ikada, Y., Jamshidi, K., Tsuji, H., Hyon, S-H. *Macromolecules* (1987) **20**, 904
14. Hatada, K., Ute, K., Tanaka, K., Okamoto, Y., Kitayama, T. *Polym. J.* (1986) **18**, 1037
15. Kitayama, T., Shinozaki, T., Sakamoto, T., Yamamoto, M., Hatada, K. *Makromol. Chem. Supplement* (1989) **15**, 167
16. Vorenkamp, E. J., Bosscher, F., Challa, G. *Polymer* (1979) **20**, 59
17. Spevacek, J., Schneider, B. *Makromol. Chem.* (1974) **175**, 2939
18. Spevacek, J., Schneider, B. *Makromol. Chem.* (1975) **176**, 729
19. Spevacek, J., Schneider, B. *Makromol. Chem.* (1975) **176**, 3409

Accepted December 28, 1989 S