

Stereocomplex formation between *isotactic* PMMA and *syndiotactic* polymers of methacrylates of straight-chain alcohols

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Summary

Stereocomplex formation between *isotactic* (*iso*-) poly(methyl methacrylate) (PMMA) and *syndiotactic* (*syn*-) polymers of methacrylates of straight-chain alcohols such as ethyl, propyl, butyl and allyl alcohols was found to occur in acetone to form gel. The solid complexes recovered from the gels in acetone showed endotherms in their DSC thermograms due to the melting of the complexes. The melting points of the complexes are 143.0°C, 125.4°C, 101.5°C and 141.5°C, respectively. The X-ray powder patterns of these complexes showed reflection peaks at $2\theta=4.3-4.4^\circ$ and $6.8-10.6^\circ$. The former reflections are commonly observed for all stereocomplexes including PMMA stereocomplex and should correspond to the fiber period. The degree of the latter decreased as the size of ester group increased, corresponding to the increasing distances between two double-stranded helices, if we adopt the Challa's double-stranded helical model for the stereocomplex.

Introduction

It has been well known that *isotactic* (*iso*-) and *syndiotactic* (*syn*-) poly(methyl methacrylate) (PMMA) chains associate to form a crystalline stereocomplex, the concept of which was first introduced by Liquori et al¹⁾. The structure of the stereocomplex has long been studied by several scientists and recent investigations^{2,3)} indicated double-stranded helix models in which a helix of *iso*-PMMA chain with a small radius is surrounded by a *syn*-PMMA helical chain with a large radius. In these models, the ester groups of *syn*-PMMA chain are all pointing outward, and thus modification of the ester groups of the *syn*-polymer chain would have much smaller influence than that of ester groups of the inner *iso*-polymer chain. However, only a limited number of stereocomplexes of polymethacrylates other than PMMA have been so far reported; stereocomplex between *iso*-PMMA and *syn*-poly(isobutyl methacrylate)⁴⁾ and that between *iso*-PMMA and *syn*-poly(methacrylic acid)⁵⁾.

Recently, we found that the stereocomplex formation took place in solid and in toluene between *iso*-PMMA and *syn*-polymethacrylates having primary alkyl ester groups with branching at β -position such as benzyl,

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methallyl and cyclopropylmethyl groups⁶). *syn*-Polymers of methacrylates of straight-chain alcohols other than *syn*-PMMA such as poly(ethyl methacrylate) (PEMA) did not form the complex with *iso*-PMMA under the same conditions.

It has been recognized that formation of PMMA stereocomplex in bulk is a less selective process than in solution, and yields smaller and less regular crystalline regions⁷). Bosscher et al. reported that stereocomplex formation between *iso*-PMMA and *syn*-poly(isobutyl methacrylate) was successful in dimethylformamide solution but not in solid⁴), though we found that the complex formation between them was possible in solid⁶). These results suggest that the complex formation in complexing solvents proceeds better than that in solid, but there have been no examples that the complex formation is possible only in solution.

After the extensive studies on better conditions for the complex formation, we found that stereocomplex formation between *iso*-PMMA and *syn*-polymers of methacrylates of straight-chain alcohols such as ethyl, propyl, butyl and allyl alcohols took place in acetone which falls into a category of strong complexing solvent⁸). The present results suggest that the complex formation in acetone is a superior way for the preparation of stereocomplex between *iso*-PMMA and *syn*-polymethacrylate.

Experimental

Materials: *iso*-PMMA was prepared by polymerizing methyl methacrylate (MMA) with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -60°C ^{9,10}) ($M_n=33030$, $M_w/M_n=1.25$, $mm:mr:rr = 97:2:1$). *syn*-PMMA was obtained with $t\text{-C}_4\text{H}_9\text{Li}-(\text{C}_2\text{H}_5)_3\text{Al}$ ($\text{Al/Li}=3/1$ mol/mol) in toluene at -78°C ¹¹). Other *syn*-polymethacrylates were obtained with $(\text{C}_2\text{H}_5)_3\text{Al-R}_3\text{P}$ ($\text{R}=\text{ethyl or phenyl}$, $\text{Al/P}=2/1$ mol/mol) in toluene at -78°C ¹²). Characteristics of the *syn*-polymethacrylates are summarized in Table 1.

Table 1 Stereocomplex formation between *iso*-PMMA and several *syn*-polymethacrylates in acetone^a

Ester group	DP ^b	Syndiotactic polymethacrylate				Stereocomplex		
		$\frac{M_w}{M_n}$	Tacticity(%)			Tg	Melting point(°C)	ΔH^c (cal/g)
			mm	mr	rr	(°C)		
CH ₃ ^d	330	1.25	97	2	1	51	—	—
CH ₃	226	1.26	3	8	89	120	175.5	5.84
CH ₃ CH ₂	141	1.32	1	10	89	74	143.0	5.27
CH ₃ CH ₂ CH ₂	135	1.41	0	11	89	34	125.4	4.47
CH ₃ CH ₂ CH ₂ CH ₂	135	1.41	0	9	91	15	101.5	2.14
CH ₂ =CHCH ₂	421	1.43	0	10	90	44	141.5	3.80

^a The complex was prepared in acetone without annealing; unit mole ratio of *iso*-PMMA and *syn*-polymethacrylate being 1:1.

^b Degree of polymerization. ^c Heat of fusion. ^d *iso*-PMMA.

Preparation of stereocomplex between *iso*-PMMA and *syn*-polymethacrylate: *iso*-PMMA and *syn*-polymer of methyl, ethyl, propyl, butyl or allyl methacrylate were dissolved in acetone under reflux for 30 min and the solution was allowed to cool at a certain temperature to form gel; room temperature for *syn*-PMMA, 0°C for *syn*-polymers of ethyl, butyl and allyl methacrylates and -20°C for *syn*-poly(propyl methacrylate). The solid stereocomplex was obtained by evaporating the acetone from the gel under vacuum at room temperature. The amounts of remaining acetone in the blend were less than 1.5 wt%.

Measurement: Differential scanning calorimetric analysis was performed with a Rigaku DSC 8230 calorimeter at a heating rate of 10°C/min. X-ray powder pattern was obtained with a Rigaku model RAD-ROC X-ray diffractometer.

Results and Discussion

As mentioned in the Experimental section, an equimolar amount of *iso*-PMMA and *syn*-poly(ethyl methacrylate) (PEMA) formed gel in acetone at 0°C while no gel formation took place in toluene at any temperatures. In Figure 1 is shown the DSC thermogram of the polymer blend obtained from the gel in acetone (Figure 1C), together with the thermograms for *iso*-PMMA and *syn*-PEMA recovered from the acetone solutions by evaporation of the solvent (Figures 1A and 1B). An endothermic peak was observed with a maximum

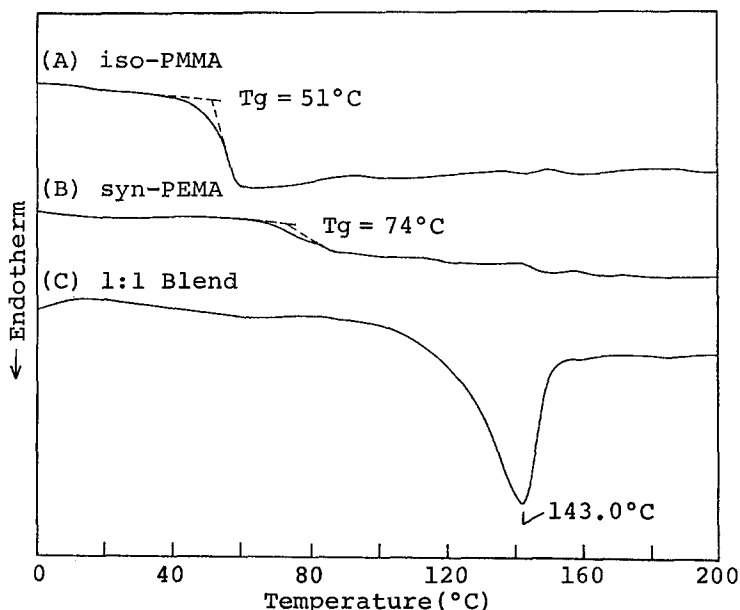


Figure 1. DSC thermograms of *iso*-PMMA(A), *syn*-PEMA(B) and 1:1 blend of *iso*-PMMA and *syn*-PEMA(C) recovered from acetone solutions (Heating rate 10°C/min).

temperature of 143.0°C while the glass transition due to *iso*-PMMA and *syn*-PEMA almost disappeared in the DSC thermogram of the 1:1 blend. The peak at 143.0°C disappeared in the second run of the measurement while two glass transitions were observed at 51°C and 76°C due to *iso*-PMMA and *syn*-PEMA, respectively. These results indicate that the peak is ascribed to the melting of the crystalline complex formed between *iso*-PMMA and *syn*-PEMA in acetone.

iso-PMMA may crystallize under certain conditions; for example, that annealed at 80°C for 72h showed a melting point of 138°C in the DSC thermogram which is close to the melting point of the complex between *iso*-PMMA and *syn*-PEMA formed in acetone. However, *iso*-PMMA recovered from acetone solution did not show any DSC peak due to the melting point. X-ray powder pattern of the *iso*-PMMA also indicates amorphous nature of the polymer (Figure 2A). The blend of *iso*-PMMA and *syn*-PEMA showed a crystalline reflection pattern as shown in Figure 2B. The reflection at $2\theta=4.32^\circ$, corresponding to an interplanar distance of 20.5 Å, is close to an equatorial reflection for the stereocomplex formed between *iso*-PMMA and *syn*-PMMA²). The results indicate that the crystalline phase in the blend of

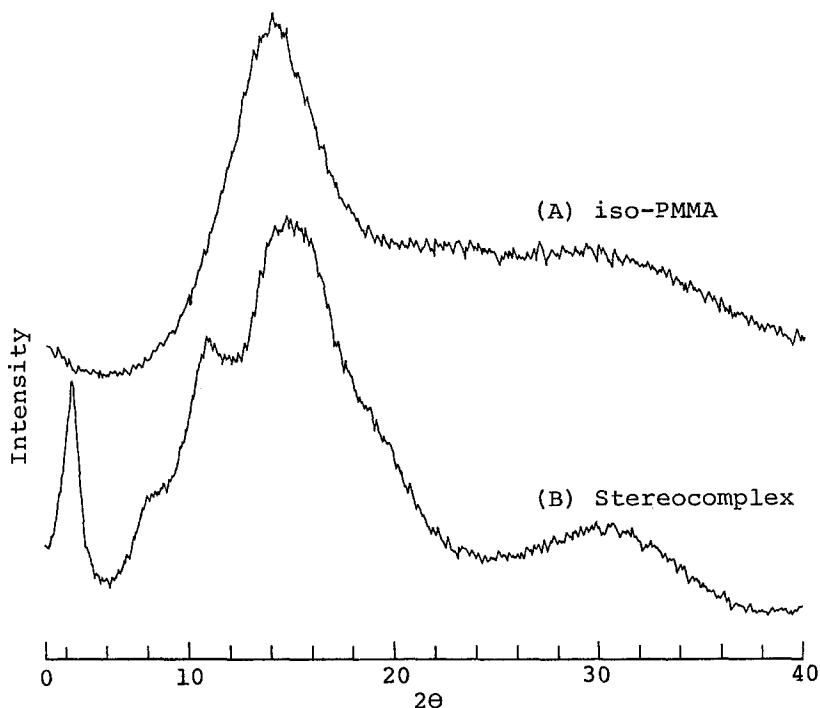


Figure 2. X-ray powder patterns of *iso*-PMMA recovered from acetone solution (A) and a stereocomplex between *iso*-PMMA and *syn*-PEMA(1:1) formed in acetone without annealing (B).

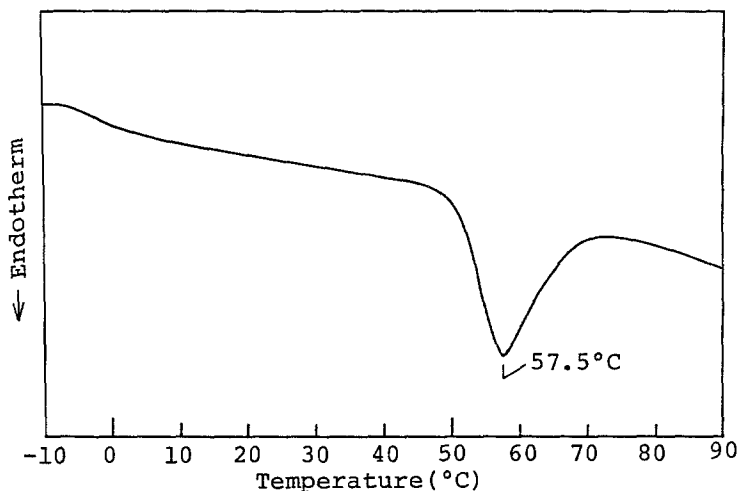


Figure 3. DSC thermogram of a 1:1 mixture of *iso*-PMMA and *syn*-PEMA in 3-heptanone (conc. = 10wt%, heating rate 10°C/min).

iso-PMMA and *syn*-PEMA obtained from acetone solution is due to a new stereocomplex formed between these two polymers, whose structure may resemble that of PMMA stereocomplex.

As mentioned previously, the complex formation between *iso*-PMMA and *syn*-PEMA in acetone resulted in gel formation. Similar phenomena were observed in several aliphatic ketones such as 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone and 3-heptanone. The melting point of the gel formed in 3-heptanone was found to be 57.5°C by DSC measurement (Figure 3). DSC measurement of the gel in acetone was not successful owing to smaller difference between the boiling point of the solvent and the melting point of the gel.

syn-Polymers of several methacrylates such as propyl, butyl and allyl methacrylates which do not form crystalline complexes with *iso*-PMMA in the solid state, formed stereocomplexes in acetone. As the ester group became longer (methyl < ethyl < propyl < butyl), the melting point and the heat of fusion became smaller as shown in Table 1. The decreasing order of the melting point of the complexes is the same as that of glass transition temperature for *syn*-polymers. The results suggest that the flexibility of alkyl ester group affects the stability and structure of the complexes. Thus the stereocomplexes having different melting points can be prepared from *iso*-PMMA and *syn*-polymers of methacrylates of straight-chain alcohols.

The X-ray powder patterns of the stereocomplexes of *iso*-PMMA and the *syn*-polymers are shown in Figure 4. The weak reflections at about 2θ of 4.35° are commonly observed for all the stereocomplexes of *iso*-PMMA and *syn*-polymethacrylates, and should correspond to the fiber periods of the crystals³). The other weak peaks in the range of 2θ from 6.8 to 10.6°,

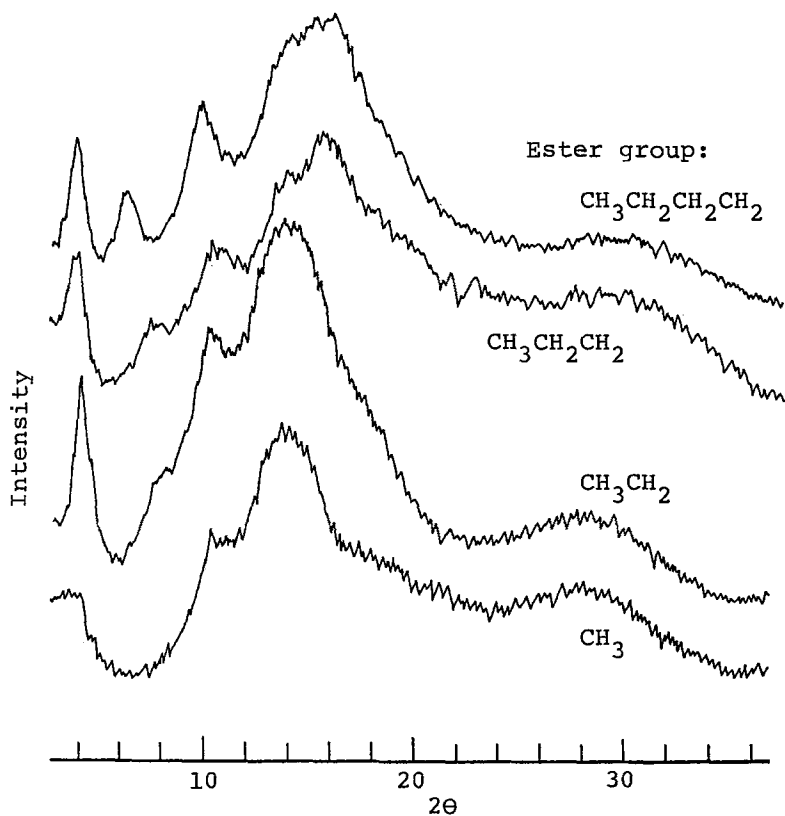


Figure 4. X-ray powder patterns of stereocomplexes of *iso*-PMMA and various *syn*-polymethacrylates formed in acetone without annealing.

Table 2 Stereocomplex formation between *iso*-PMMA and *syn*-poly(MMA-*ran*-EMA) in acetone^a

MMA/EMA in polymer ^b		Syndiotactic poly(MMA- <i>ran</i> -EMA)				Stereocomplex		
Mn ^c	Mw ^c Mn	Tacticity(%) ^b			Tg (°C)	Melting point(°C)	ΔH ^d (cal/g)	
		mm	mr	rr				
100/0	87200	1.75	2	8	90	127	196.1	9.91
66/34	80000	1.31	0	10	90	110	181.0	9.10
46/54	87000	1.29	0	10	90	101	165.8	7.69
34/66	80400	1.34	0	10	90	92	158.6	7.29
0/100	58800	1.29	3	8	89	82	147.9	6.05

^a The complex was prepared in acetone without annealing; unit mole ratio of *iso*-PMMA and *syn*-copolymer being 1:1.

^b Determined by ¹H NMR. ^c Determined by GPC. ^d Heat of fusion.

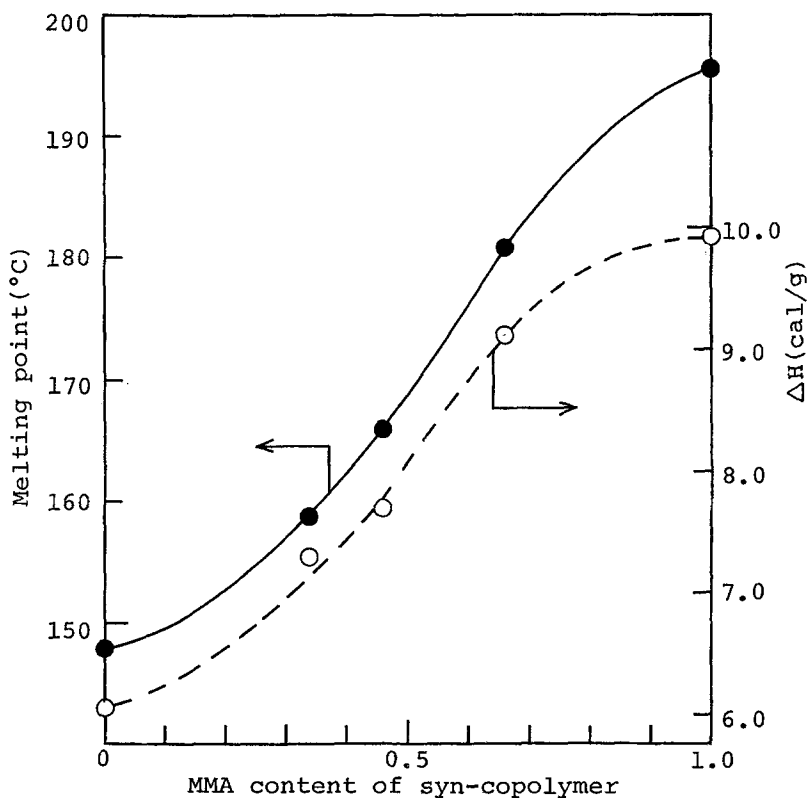


Figure 5. Effect of composition of syn-poly(MMA-ran-EMA) on the melting point and heat of fusion of the stereocomplex formed with *iso*-PMMA in acetone without annealing.

which shift to lower angle as the ester groups become bulkier, may correspond to the distance between two double-stranded helices, in the case that the Challa's double-stranded helical model is valid for these new stereocomplexes; as the ester group of outer *syn*-polymer becomes longer, the distance between adjacent double-stranded helices becomes larger.

Blends of *iso*-PMMA and *syn*-random copolymers of MMA and EMA with various copolymer compositions formed crystalline stereocomplexes when mixed in acetone, but not in the solid state with annealing. The characteristics of the *syn*-copolymers are summarized in Table 2. The melting point depended on the copolymer composition and increased as the MMA content increased (Figure 5). These results suggest that the melting point of stereocomplex involving *syn*-copolymer can be finely controlled by changing the copolymer composition.

The present results indicate that a large variety of *syn*-polymers of methacrylates with straight-chain alcohols can form crystalline stereocomplexes with *iso*-PMMA. In the previous communication⁶) we reported stereo-

complex formation between *iso*-PMMA and *syn*-polymethacrylates of primary alkyl esters with branching at β -position. From these results, it is obvious that the structure of the complex can be widely altered by changing the ester group of *syn*-polymers. Further details of the investigation will be published in the near future.

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