

Supercritical CO₂-Induced Stereocomplex Formation of Highly Stereoregular Isotactic Poly(methyl methacrylate) and Syndiotactic Poly(methyl methacrylate) Blends: Effect of Molecular Weight on Crystalline Structure

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ABSTRACT: Crystalline stereocomplexes of highly stereoregular isotactic poly(methyl methacrylate) (*it*-PMMA) and syndiotactic poly(methyl methacrylate) (*st*-PMMA) blends formed by treatment with supercritical CO₂ were investigated by means of differential scanning calorimetry (DSC) measurements as a function of PMMA molecular weight. The rates of stereocomplex formation obtained with supercritical CO₂ treatment were faster than those obtained by thermal treatment. The higher rates of stereocomplex formation can be attributed to the plasticizing effect of CO₂ molecules in the PMMA. The heat of melting of the stereocomplex (ΔH) decreased with increasing PMMA molecular weight and was found to be independent of *it*-PMMA and *st*-PMMA mixing ratio. For the case of *it*-PMMA/*st*-PMMA of 1:1, the stereocomplexes obtained by thermal and CO₂ treatment had two endothermic peaks. The relative intensity of the second endothermic peak ($\Delta H_2/\Delta H$) decreased with increasing PMMA molecular weight and showed stronger dependence on *it*-PMMA molecular weight than on the *st*-PMMA molecular weight.

Introduction

Stereocomplex formation between isotactic poly(methyl methacrylate) (*it*-PMMA) and syndiotactic poly(methyl methacrylate) (*st*-PMMA) has been investigated by methods which were reviewed by Spevacek et al.¹ and te Nijenhuis.² The formation of the crystalline stereocomplex between *it*-PMMA and *st*-PMMA is known to occur in bulk thermal treatment as well as in organic solvents (solvent treatment). It is well-known that multiple endothermic peaks, or so-called T_m^1 , T_m^2 , and T_m^3 , occur for blends of highly stereoregular *it*-PMMA/*st*-PMMA on differential scanning calorimetry (DSC) measurements.^{3–5} Schomaker and Challa investigated this phenomenon in detail and proposed the occurrence of two crystallization modes.^{3,4} They suggested that $T_m^2 \sim 166$ °C with a small endothermic peak can be assigned to the decomposition of complexed sections formed during DSC measurements. Further, those authors proposed that $T_m^1 \sim 175$ °C corresponds to the melting of complexed sections partly organized into small fringed micellar clusters of the complex sections and that $T_m^3 \sim 186$ °C corresponds to the melting of lamellar crystallites of the complexed sections. For the case of stereocomplex formation occurred in organic solvent, they also reported that the melting temperature, T_m^1 and T_m^3 , and the relative intensity of the second endothermic peak, $\Delta H_2/\Delta H$, depend on the weight fraction of *it*-PMMA and/or the molecular weight of *it*-PMMA and *st*-PMMA.^{4,5} For the case of bulk thermal annealing, however, there are no reports on the effect

of the weight fraction of *it*-PMMA and the molecular weight on the stereocomplex structure in detail probably due to the slow stereocomplex formation rates.³

Carbon dioxide (CO₂) is nonflammable, nontoxic, and relatively inexpensive and has a moderate critical temperature and pressure ($T_c = 31.1$ °C, $P_c = 7.38$ MPa), which make it a convenient solvent for many applications, such as polymerization, foaming, and processing agents. The advantage of using supercritical CO₂ in polymer engineering includes its ability to plasticize many glassy polymers and semicrystalline polymers and lower their glass transition temperature, T_g . Chiou et al. reported on the plasticizing effect of CO₂ dissolved in poly(ethylene terephthalate) (PET) and the resulting crystallization.⁶ Mizoguchi et al. reported that the crystallization rates of PET in high-pressure CO₂ at temperature below T_g are faster than that for thermal annealing at temperature above T_g .⁷ Plasticizing effects of CO₂ on the crystallization rates of syndiotactic polystyrene (sPS) have been found to be similar to those observed for PET.⁸ For the case of amorphous poly(aryl ether ether ketone) (PEEK), CO₂-induced crystallization occurs at 10 MPa and 100 °C, and the degree of crystallinity depends on the molecular weight of PEEK used.⁹ For polycarbonate (PC), CO₂ dissolution results in a higher degree of crystallization for low molecular weight samples than for high molecular weight.¹⁰

We have reported that crystalline stereocomplex formation occurs in supercritical CO₂ and that the crystalline stereocomplex induced by supercritical CO₂

Table 1. Polymer Sample Characterization

sample	10 ⁻⁴ <i>M_n</i> ^a	<i>M_w</i> / <i>M_n</i> ^a	tacticity (%) ^b		
			mm	mr	rr
<i>it</i> 2	1.89	1.07	97.2	2.3	0.5
<i>it</i> 3	5.18	1.36	97.1	2.3	0.6
<i>it</i> 4	15.60	1.24	97.5	2.5	0.0
<i>it</i> 5	24.90	1.27	97.8	2.2	0.0
<i>st</i> 2	2.03	1.16	0.9	12.0	87.1
<i>st</i> 3	4.04	1.03	0.5	12.4	87.1
<i>st</i> 4	12.05	1.05	1.5	12.4	86.1
<i>st</i> 5	16.30	1.06	0.0	8.2	91.8
<i>st</i> 6	30.70	1.19	0.6	9.9	89.6

^a Measured by GPC with *at*-PMMA standards calibration.^b Calculated by ¹H NMR.

contributes to the superior morphology of the microcellular foams obtained,¹¹ because the crystalline structures of some crystalline polymers, PET, and a blend of polyethylene and polypropylene play a major role in the morphology of the microcellular foams. Therefore, it is very important to understand the mechanism regarding crystalline stereocomplex structure induced by supercritical CO₂. For the case of stereocomplex formation of highly stereoregular *it*-PMMA and *st*-PMMA with narrow molecular weight distribution, we found that a fringed micellar structure and lamellar structure were formed and that the melting temperatures (*T_m*¹ and *T_m*³), the heat of melting (ΔH), and the relative intensity of the second endothermic peak ($\Delta H_3/\Delta H$) depended on the weight fraction of *it*-PMMA as well as thermal and solvent treatment.¹² However, there was no report concerning about the effect of the molecular weights of *it*-PMMA and *st*-PMMA on the crystalline structures induced by supercritical CO₂ treatment. Since the morphology of microcellular foams is particularly affected by crystalline morphology, it is important to investigate the relationship between the molecular weight and the crystalline structures, that is, fringed micellar structure or lamellar structure. This study deals with the effect of the molecular weight of highly stereoregular PMMA with narrow molecular weight distribution, *it*-PMMA (*M_n* = (1.89–24.90) × 10⁴, *M_w*/*M_n* < 1.36) and *st*-PMMA (*M_n* = (2.03–30.70) × 10⁴, *M_w*/*M_n* < 1.19), on the crystalline structures, *T_m*¹, *T_m*³, ΔH , and $\Delta H_3/\Delta H$, by means of DSC measurements. Furthermore, we compare with the crystalline structure obtained by other methods, especially thermal treatment in air at ambient pressure.

Experimental Section

Materials. The *it*-PMMA sample with low molecular weight, *it*2, was prepared in toluene at –78 °C with *t*-BuMgBr as initiator according to a method reported by Hatada et al.¹³ The *it*-PMMA samples with high molecular weight, *it*3 to *it*5, were prepared in toluene at –78 °C with Yb[C(SiMe₃)₃]₂ as initiator according to a method reported by Yasuda et al.¹⁴ The *st*-PMMA sample with low molecular weight, *st*2, was prepared in toluene at –78 °C with the *t*-BuLi/Et₃Al (1/3) initiation system reported by Hatada et al.¹⁵ The *st*-PMMA samples with high molecular weight, *st*3 to *st*6, were prepared in toluene at –78 °C with the [Cp*₂SmH]₂ initiation system reported by Yasuda et al.¹⁶ The molecular weight, the molecular weight distribution, and the tacticity of the PMMAs prepared are listed in Table 1. Number-average molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) were measured by gel permeation chromatography (GPC). Tacticities (mm, mr, and rr) were determined by α-CH₃ signal intensities obtained by ¹H NMR spectroscopy. Details on the characterization of these samples have been reported elsewhere.¹¹

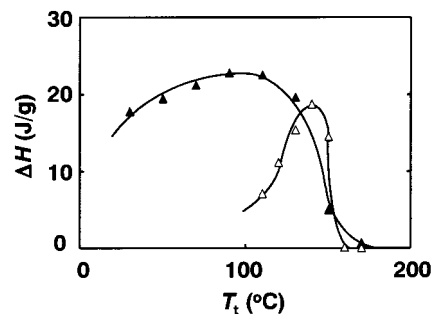


Figure 1. ΔH of the stereocomplex of *it*2/*st*4 (mixing ratio: 1/2) blend films as a function of treatment temperature, *T_t*. Supercritical CO₂ treatment at 20 MPa for 6 h: \blacktriangle . Thermal treatment in air at atmospheric pressure for 480 h: \triangle .

The amorphous PMMA films were prepared by casting an 8 wt % dichloromethane solution of *it*-PMMA and *st*-PMMA in various mixing ratios in an aluminum cup. To remove all solvent, the film was dried for 1 day at room temperature and afterward dried for 1 day at room temperature under vacuum. Before treatment with supercritical CO₂ or thermal treatment, all films were heated at 250 °C for 10 min and cooled quickly to erase any solvent or thermal histories.¹⁷ No samples exhibited endothermic peaks corresponding to the melting of the stereocomplex as measured by DSC.

Supercritical CO₂ Treatment and Thermal Treatment Procedure. A high-pressure apparatus¹¹ was used for supercritical CO₂ treatment. Further details on the procedure are given in ref 12. Thermal treatment procedure was carried out as follows. Thermal treatment samples, which were weighed in DSC pans, were left in an air bath with the temperature being controlled to within 1 °C. The samples were brought to the desired temperature at rate of 10 °C/min and kept at that temperature for a given period of time.

Analyses. DSC was carried out with a TA instruments MDSC 2910 that was calibrated with indium. After loading each sample into the DSC, the temperature was brought to 0 °C and maintained at that temperature for 1 min. The thermograms were recorded at a heating rate of 10 °C/min. The melting temperature, *T_m*, was determined from the maximum of the melting endothermic peak. The heat of melting, ΔH , was determined by the peak area of the melting endotherm. For the case of two endothermic peaks detected, *T_m*¹ and *T_m*³ represented the first peak corresponding to the fringed micellar crystal and the second peak corresponding to the lamellar crystal, respectively. The relative intensity of the second peak, $\Delta H_3/\Delta H$, was calculated from the ratio of the peak area, *T_m*³, and the total area of the two endothermic peaks.^{4,12}

Results and Discussion

Stereocomplex at a 1/2 *it*-PMMA/*st*-PMMA Mixing Ratio. For the case of thermal treatment, it is well-known that stereocomplexes form below 130 °C and have two endothermic peaks, and the stereocomplex induced by thermal annealing above 140 °C has only one endothermic peak.³ For the case of high-pressure CO₂ treatment at 20 MPa and over a temperature range of 30–170 °C, stereocomplexes consisting of less than 33% *it*-PMMA content had only one large endothermic peak with narrow temperature range.¹² Moreover, we reported that the *T_m*¹ and ΔH of the stereocomplex increased with increasing treatment pressure and attained a constant value above 20 MPa and that the *T_m*³ did not depend on the treatment pressure. Therefore, Figure 1 shows the ΔH of the stereocomplex of *it*2/*st*4 (1/2) blend films formed by supercritical CO₂ treatment at 20 MPa and thermal treatment at ambient pressure as a function of treatment temperature, *T_t*. The ΔH of the stereocomplex induced by thermal treatment had a

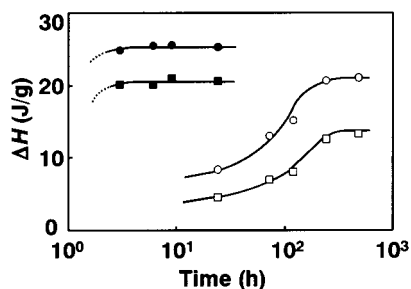


Figure 2. Enthalpy changes of stereocomplex *it*-PMMA/*st*-PMMA (mixing ratio: 1/2) as a function of treatment time. Supercritical CO₂ treatment at 90 °C and 20 MPa: *it2/st2* (●), *it5/st2* (■). Thermal treatment in air at 140 °C and atmospheric pressure: *it2/st2* (○), *it5/st2* (□).

maximum at 140 °C, whereas the ΔH that resulted from supercritical CO₂ treatment had a maximum at 90 °C. Our results indicated that the supercritical CO₂-induced stereocomplexes formed at lower temperatures and over a wider treatment range than those formed by thermal treatment. Considering the data, the CO₂ molecules probably dissolved in the *it*-PMMA/*st*-PMMA amorphous blends and acted as a plasticizer, which lowered the T_g . Watkins et al.^{18,19} reported that the phase separation of homogeneous blends between polystyrene and poly(vinyl methyl ether) at temperatures more than 90 °C below the ambient pressure lower critical solution temperature (LCST) upon sorption of less than 3.3 wt % CO₂, because of a disparity in the free volumes of these polymer components induced by CO₂. We assumed that the stereocomplex formation was induced by enhanced mobility of *it*-PMMA and *st*-PMMA.

Figure 2 illustrates the ΔH of the stereocomplex of *it*-PMMA/*st*-PMMA (1/2) induced by supercritical CO₂ treatment at 20 MPa and 90 °C and thermal treatment in air at 140 °C as a function of treatment time. Mixtures of *it*-PMMA and *st*-PMMA treated with CO₂ completely formed crystalline stereocomplexes within 3 h, even though the temperature was below T_g . The rates of the stereocomplex formation induced by supercritical CO₂ treatment were faster than those induced by thermal treatment at above T_g , regardless of *it*-PMMA molecular weight. The rates of stereocomplex formation, however, were not influenced by molecular weight, for both crystallization conditions of supercritical CO₂ treatment and thermal treatment. According to literature data,^{20,21} the pressure coefficient of T_g (dT_g/dp) is about -11.8 °C/MPa, which was higher than the dT_g/dp , -8.5 °C/MPa, for PET and sPS over the same pressure range. This plasticizing effect of CO₂ on the crystallization rates for semicrystalline polymers was reported for PET and sPS.^{7,8} Our results indicate that the CO₂ molecules in the *it*-PMMA and *st*-PMMA blend films act as an intensive plasticizer and that they increase the stereocomplex formation rates, independent of the polymer molecular weight.

Figures 3 shows the DSC thermograms of the stereocomplexes consisting of various molecular weights of *it*-PMMA and *st*-PMMA (*st2*). At the given experimental conditions for supercritical CO₂, the stereocomplexes exhibited a single endothermic peak, independent of the molecular weight of *it*-PMMA. The results show that the ΔH values were depend on the molecular weight of *it*-PMMA and furthermore that the ΔH values decreased as the molecular weight of *it*-PMMA increased. For the case of the various molecular weight of *st*-PMMA with *it*-PMMA (*it2*), the ΔH clearly decreased as the molec-

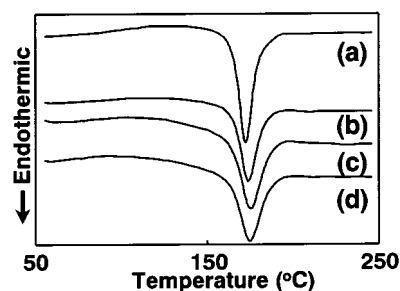


Figure 3. DSC thermograms of *it*-PMMA/*st*-PMMA (mixing ratio: 1/2) blend films treated with supercritical CO₂ at 90 °C and 20 MPa for 6 h. (a) *it2/st2*, (b) *it3/st2*, (c) *it4/st2*, (d) *it5/st2*. Heating rate was 10 °C/min.

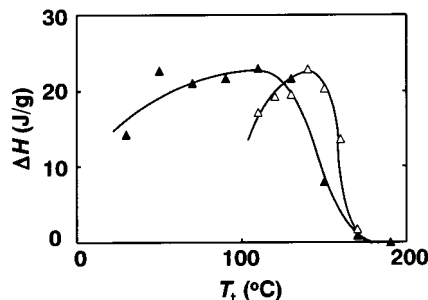


Figure 4. ΔH of the stereocomplex of *it2/st4* (mixing ratio: 1/1) blend films as a function of treatment temperature, T_t . Supercritical CO₂ treatment at 20 MPa for 6 h: ▲. Thermal treatment in air at atmospheric pressure for 480 h: △.

ular weight of *st*-PMMA increased. It has been reported that the molecular weights of *it*-PMMA and *st*-PMMA mixtures do not influence the ΔH of stereocomplex formation in dilute solutions of dimethylformamide (DMF).⁵ It was well-known that CO₂ molecules dissolve in PMMA and that the PMMA chains have a low affinity for CO₂.²² The amount of CO₂ dissolved into the *it*-PMMA/*st*-PMMA blend films can be estimated to be less than 20 wt % at the experimental conditions of this work based on methods in the literature.²³ This means that the polymer concentration of *it*-PMMA/*st*-PMMA–CO₂ systems is very high and probably close to 80 wt %. On the other hand, since the polymer concentrations of *it*-PMMA/*st*-PMMA–DMF system were very low being about 0.2 wt %, we assumed that the molecular weight did not influence the mobility of the polymer chains in the stereocomplex formation. We estimate that these differences in the molecular weight effect between supercritical CO₂ and DMF at atmospheric pressure occur depending on the mobility of the *it*-PMMA and *st*-PMMA chains under the experimental conditions of stereocomplex formation.

Stereocomplex Formation at a 1/1 *it*-PMMA/*st*-PMMA Mixing Ratio. As described above, stereocomplexes that formed below 130 °C thermal treatment conditions had two endothermic peaks detected by DSC.³ Stereocomplexes obtained by supercritical CO₂ treatment consisting of more than 33% *it*-PMMA content also exhibited two endothermic peaks.¹² Figure 4 shows that the ΔH of the stereocomplex of *it2/st4* (mixing ratio: 1/1) blend films formed by supercritical CO₂ treatment and thermal treatment as a function of T_t . The DSC data of stereocomplex at a 1/1 *it*-PMMA/*st*-PMMA mixing ratio obtained by thermal treatment and supercritical CO₂ treatment are summarized in Tables 2 and 3. For the each case of supercritical CO₂ and thermal treatment, the stereocomplexes obtained

Table 2. Summary of DSC Results for the Stereocomplex at a *it*-PMMA/*st*-PMMA (*it2/st4*) 1/1 Mixing Ratio Obtained by Thermal Treatment at *T_t* for 480 h

<i>T_t</i> (°C) ^b	DSC measurements ^a		
	<i>T_m</i> ¹ (°C)	<i>T_m</i> ³ (°C)	Δ <i>H</i> (J/g)
110	149.5	183.3	17.1
120	160.1	184.7	19.3
130	169.7	<i>c</i>	19.5
140	<i>d</i>	186.3	22.9
150	<i>d</i>	195.0	20.3
160	<i>d</i>	200.9	13.6
170	<i>d</i>	204.6	1.7

^a Heating rate 10 °C/min. ^b Treatment temperature. ^c Overlap with *T_m*¹. ^d Not detected.

Table 3. Summary of DSC Results for the Stereocomplex at a *it*-PMMA/*st*-PMMA (*it2/st4*) 1/1 Mixing Ratio Obtained by Supercritical CO₂ Treatment at *T_t* and 20 MPa for 6 h

<i>T_t</i> (°C) ^b	DSC measurements ^a		
	<i>T_m</i> ¹ (°C)	<i>T_m</i> ³ (°C)	Δ <i>H</i> (J/g)
30	140.8	186.2	14.3
50	151.0	185.3	22.7
70	159.0	185.7	21.0
90	167.6	<i>c</i>	21.7
110	171.7	<i>c</i>	23.0
130	185.1	<i>c</i>	21.6
150	<i>d</i>	199.7	8.0
170	<i>d</i>	205.9	0.9
190	<i>d</i>	<i>d</i>	0.0

^a Heating rate 10 °C/min. ^b Treatment temperature. ^c Overlap with *T_m*¹. ^d Not detected.

Table 4. Thermal Properties of the Stereocomplex *it*-PMMA/*st2* (*M_n* = 2.03 × 10⁴) (Mixing Ratio: 1/1) as a Function of *M_n* of *it*-PMMA

<i>it</i> -PMMA 10 ⁻⁴ <i>M_n</i> ^a	<i>T_t</i> (°C) ^b	thermal properties ^c			
		<i>T_m</i> ¹ (°C)	<i>T_m</i> ³ (°C)	Δ <i>H</i> (J/g)	Δ <i>H</i> ₃ /Δ <i>H</i>
1.89	110 ^d	153.1	184.5	18.0	0.325
5.18	110 ^d	153.8	183.4	15.6	0.260
15.60	110 ^d	152.5	182.9	14.6	0.144
24.90	110 ^d	152.7	186.4	13.6	0.136
1.89	50 ^e	152.5	185.2	22.8	0.197
5.18	50 ^e	152.7	181.5	22.5	0.105
15.60	50 ^e	153.2	185.1	22.0	0.118
24.90	50 ^e	153.6	<i>f</i>	20.7	0.000

^a Measured by GPC with *at*-PMMA standards calibration. ^b Treatment temperature of thermal treatment or supercritical CO₂ treatment. ^c Measured by DSC. ^d Thermal treatment in air at 110 °C and atmospheric pressure for 480 h. ^e Supercritical CO₂ treatment at 50 °C and 20 MPa for 6 h. ^f Not detected.

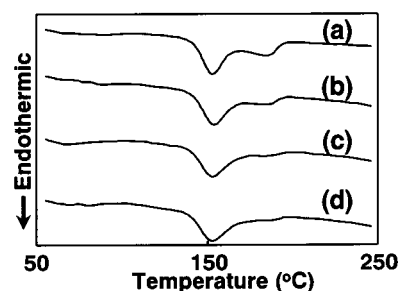
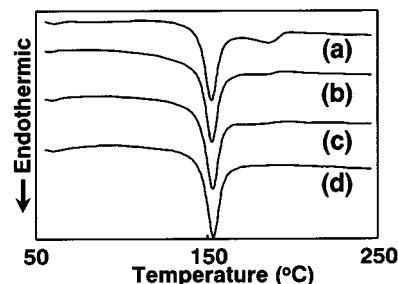
at below 130 °C have two endothermic peaks, but the *T_m*¹ was not detected on the blend films treated with supercritical CO₂ and thermal treatment above 140 °C. As shown in Tables 4 and 5, the melting points of the crystalline stereocomplexes *T_m*¹ and *T_m*³ were approximately 152 and 183 °C, respectively, for both the supercritical CO₂ treated (50 °C) and thermal treated (110 °C) material. In this second section, the effect of molecular weight of highly stereoregular PMMA on the multiple endothermic peaks of the stereocomplexes is examined.

Table 4 provides a summary of the thermal properties of the stereocomplexes with *it*-PMMA/*st2* (mixing ratio: 1/1) obtained by thermal treatment and supercritical CO₂. For *it*-PMMA/*st*-PMMA at a 1/1 mixing ratio, we confirmed that the stereocomplex formation required 3 h to reach its equilibrium state for CO₂ treatment and 480 h for thermal annealing. These equilibrium times

Table 5. Thermal Properties of the Stereocomplex *it2* (*M_n* = 1.89 × 10⁴)/*st*-PMMA (Mixing Ratio: 1/1) as a Function of *M_n* of *st*-PMMA

<i>st</i> -PMMA 10 ⁻⁴ <i>M_n</i> ^a	<i>T_t</i> (°C) ^b	thermal properties ^c			
		<i>T_m</i> ¹ (°C)	<i>T_m</i> ³ (°C)	Δ <i>H</i> (J/g)	Δ <i>H</i> ₃ /Δ <i>H</i>
2.03	110 ^d	153.1	184.5	18.0	0.325
4.04	110 ^d	152.6	186.4	17.4	0.342
12.05	110 ^d	151.3	186.0	17.3	0.313
16.30	110 ^d	152.9	189.5	14.8	0.329
30.70	110 ^d	152.2	189.0	13.6	0.322
2.03	50 ^e	152.5	185.2	22.8	0.197
4.04	50 ^e	152.7	185.2	21.8	0.184
12.05	50 ^e	151.0	185.3	22.7	0.175
16.30	50 ^e	154.0	188.3	21.3	0.176
30.70	50 ^e	153.9	189.2	20.3	0.177

^a Measured by GPC with *at*-PMMA standards calibration. ^b Treatment temperature of thermal treatment or supercritical CO₂ treatment. ^c Measured by DSC. ^d Thermal treatment in air at 110 °C and atmospheric pressure for 480 h. ^e Supercritical CO₂ treatment at 50 °C and 20 MPa for 6 h.

**Figure 5.** DSC thermograms of *it*-PMMA/*st*-PMMA (mixing ratio: 1/1) blend films annealed in air at 110 °C and atmospheric pressure for 480 h: (a) *it2/st2*, (b) *it3/st2*, (c) *it4/st2*, (d) *it5/st2*. Heating rate was 10 °C/min.**Figure 6.** DSC thermograms of *it*-PMMA/*st*-PMMA (1/1) blend films treated with supercritical CO₂ at 50 °C and 20 MPa for 6 h: (a) *it2/st2*, (b) *it3/st2*, (c) *it4/st2*, (d) *it5/st2*. Heating rate was 10 °C/min.

were also found for *it*-PMMA/*st*-PMMA at a 1/2 mixing ratio. Figures 5 and 6 illustrate DSC thermograms of the stereocomplexes, consisting of the various molecular weight *it*-PMMA, *it2* to *it5*, and *st*-PMMA(*st2*) with the *it*-PMMA/*st*-PMMA mixing ratio being 1/1. For both treatment conditions, the stereocomplex had two endothermic peaks at 152–154 and at 182–187 °C independent of the molecular weight of *it*-PMMA. The relative intensities of the second endothermic peak of the stereocomplexes obtained, Δ*H*₃/Δ*H*, however, were found to depend on the molecular weight of *it*-PMMA. Namely, the Δ*H*₃/Δ*H* values decreased as the molecular weight of *it*-PMMA increased. It has been reported that stereocomplexes consisting of *it*-PMMA with high molecular weight (*M_n* = 1 × 10⁶) and *st*-PMMA with high molecular weight (*M_n* = 1 × 10⁶) obtained by thermal treatment in the temperature range 120–140 °C do not exhibit *T_m*³ on DSC measurements.⁴ In other words, for

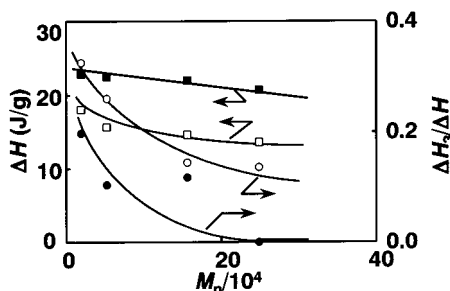


Figure 7. ΔH and $\Delta H_3/\Delta H$ of the stereocomplex as a function of M_n of *it*-PMMA. All samples were prepared at a *it*-PMMA/*st*2 mixing ratio of 1/1. Supercritical CO_2 treatment at 50 °C and 20 MPa for 6 h: ΔH (■), $\Delta H_3/\Delta H$ (●). Thermal treatment in air at 110 °C and atmospheric pressure for 480 h: ΔH (□), $\Delta H_3/\Delta H$ (○).

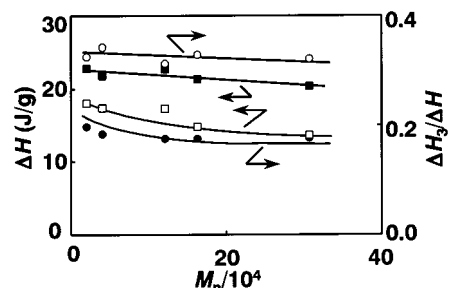


Figure 8. ΔH and $\Delta H_3/\Delta H$ of the stereocomplex as a function of M_n of *st*-PMMA. All samples were prepared at a *it*2/*st*-PMMA mixing ratio of 1/1. Supercritical CO_2 treatment at 50 °C and 20 MPa for 6 h: ΔH (■), $\Delta H_3/\Delta H$ (●). Thermal treatment in air at 110 °C and atmospheric pressure for 480 h: ΔH (□), $\Delta H_3/\Delta H$ (○).

high molecular weight *it*-PMMA and *st*-PMMA, the $\Delta H_3/\Delta H$ showed decrease with increasing M_n of PMMA for the case of thermal treatment. In our data, the dependence of $\Delta H_3/\Delta H$ on PMMA molecular weight for supercritical CO_2 treatment as well as thermal treatment shows the same trend and attributed this to the mobility of *it*-PMMA and *st*-PMMA chains under the given experimental conditions.

Figures 7 and 8 show the ΔH and the relative intensities of T_m^3 , $\Delta H_3/\Delta H$, of the stereocomplexes obtained by thermal annealing and CO_2 treatment as a function of the polymer (*it*-PMMA and *st*-PMMA) molecular weight. The thermal properties of the stereocomplexes with *it*2/*st*-PMMA (mixing ratio: 1/1) obtained by thermal treatment and supercritical CO_2 treatment are summarized in Table 5. For both cases, the ΔH depended on the molecular weight of *it*-PMMA or *st*-PMMA. These findings agree with the DSC results for stereocomplex prepared at an *it*-PMMA/*st*-PMMA mixing ratio of 1/2. The $\Delta H_3/\Delta H$ exhibited a greater dependence on the molecular weight of *it*-PMMA than *st*-PMMA. For DMF-induced stereocomplex formation, it is well-known that the $\Delta H_3/\Delta H$ values depend on the weight fraction of *st*-PMMA. That is, the $\Delta H_3/\Delta H$ values decrease as the molecular weight of *st*-PMMA increase.⁵ It has not been reported, however, that the $\Delta H_3/\Delta H$ has a stronger dependence on the molecular weight of *it*-PMMA than *st*-PMMA for both thermal and solvent treatments. This means that the formation of lamellar structure with higher melting temperatures was probably inhibited by the reduction in mobility of the *it*-PMMA chains. The reason for the differences in the molecular weight effect between *it*-PMMA and *st*-PMMA is still not clear.

Conclusions

Crystalline stereocomplexes of highly stereoregular PMMA with narrow molecular weight distribution, *it*-PMMA and *st*-PMMA, and blends formed by treatment with supercritical CO_2 were investigated by means of DSC measurements as a function of PMMA molecular weight. The rates of stereocomplex formation obtained by supercritical CO_2 treatment were faster than those obtained by thermal treatment because of the plasticizing effect of CO_2 molecules sorbed in PMMA. The rates of stereocomplex formation, however, seemed to be independent of the molecular weight for both thermal treatment and supercritical CO_2 treatment preparations. The ΔH of the stereocomplex induced by CO_2 decreased with increasing PMMA molecular weight, which is probably due to the mobility of *it*-PMMA and *st*-PMMA chains, as well as the PEEK- CO_2 system⁹ and the PC- CO_2 system.¹⁰ For the case of stereocomplexes prepared with *it*-PMMA/*st*-PMMA mixing ratios of 1/1, two endothermic peaks were observed for both supercritical CO_2 treatment and thermal treatment. Further, the $\Delta H_3/\Delta H$ decreased with increasing PMMA molecular weight and were found to depend on the molecular weight of *it*-PMMA more than *st*-PMMA. We can conclude that the formation of lamellar structures with higher melting temperatures seems to be inhibited by the reduction in mobility of the *it*-PMMA chains to a much greater extent than *st*-PMMA chains.

References and Notes

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