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Supercritical CO_2-Induced Stereocomplex Formation of Highly Stereoregular Isotactic Poly(methyl methacrylate) and Syndiotactic Poly(methyl methacrylate) Blends

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ABSTRACT: Crystalline stereocomplexes of highly stereoregular isotactic poly(methyl methacrylate) (*it*-PMMA; mm = 97.2%) and syndiotactic poly(methyl methacrylate) (*st*-PMMA; rr > 86.1%) blends formed by treatment with supercritical CO_2 at pressures from 5 to 25 MPa and at temperatures in the 30−170 °C range were investigated by means of differential scanning calorimetry (DSC) measurements as a function of treatment temperature, pressure, and *it*-PMMA/*st*-PMMA mixing ratio. The ΔH of the stereocomplex had a maximum at 33 wt % *it*-PMMA content, in agreement with stereocomplexes formed in some solvents and in bulk thermal annealing methods. For the case of over 50% *it*-PMMA content, two endothermic peaks, $T_m{}^1$ and $T_m{}^3$, were detected. Examination of the effect of heating rate from 5 to 40 °C/min on the DSC results showed that the melting temperatures, $T_m{}^1$ and $T_m{}^3$, corresponded to the fringed micellar structure and the lamellar crystallites of the complexed sections, respectively. For 33% or less *it*-PMMA content, the crystalline stereocomplex formed by supercritical CO_2 had only one endothermic peak that occurred over a narrow temperature range, which was comparable with that obtained by thermal annealing or solvent treatment.

Introduction

Stereocomplex formation between isotactic poly(methyl methacrylate) (*it*-PMMA) and syndiotactic poly(methyl methacrylate) (*st*-PMMA) has been investigated as early as 1958[1] and by various methods, all of which have been reviewed by Spevacek et al.[2] and te Nijenhuis et al.[3] Stereocomplex formation between *it*-PMMA and *st*-PMMA occurs in organic solvents, and moreover, the chemical nature of the solvent can have considerable influence on the stereocomplex formation. Solvents for complex formation can be divided into three groups according to their effect on the reduced viscosity: strongly complexing solvents (e.g., dimethylformamide (DMF), acetonitrile, tetrachloromethane); weakly complexing solvents (e.g., toluene, benzene); and noncomplexing solvents (e.g., chloroform, dichloromethane).[4,5] Katime et al.[6] have studied the stereocomplex formation in the mixture of two strongly complexing solvents, such as acetonitrile/tetrachloromethane. Their results indicated that when the composition of cosolvent mixtures leads to an increase in the excess Gibbs free energy, the complexing capacity decreases. Bistac et al.[7] proposed a tentative explanation of the solvent effect by invoking the Lewis acid−base concept. The acidic or basic character of a given solvent was studied simultaneously with its strength of complexation, and the results allowed the authors to propose a relationship between these two parameters. The influence of the solvent on the aggregation and crystallization behavior, however, still needs further research.

It was well-known that the stereoregularity of PMMA influences the crystalline stereocomplex morphology.[2,3] Stereocomplexes consisting of *it*-PMMA with low stereoregularity (mm = 80−83%) and *st*-PMMA with low stereoregularity (rr = 55−77%) induced by thermal annealing and solvent treatment exhibit only one endothermic peak by DSC measurement. For the case of the highly stereoregular *it*-PMMA (mm > 91%) and *st*-PMMA (rr > 88%) blends, however, stereocomplexes exhibit multiple endothermic peaks, which are affected by the annealing temperature, solvent characteristics, and *it*-PMMA/*st*-PMMA mixing ratios.[6,8−10]

Supercritical CO_2 ($T_c = 31.1$ °C, $P_c = 7.38$ MPa) has been identified as a solvent that can plasticize many glassy polymers and semicrystalline polymers.[11] Mizoguchi et al. have reported on the plasticizing effect of CO_2 on PET and on the effect of crystallization resulting from longer CO_2 exposure times and on the increased crystallization rates for PET/CO_2 solutions above the glass transition temperature, T_g, compared with thermally crystallized PET.[12] Furthermore, in the presence of supercritical CO_2 and methanol entrainer, methyl-substituted poly(aryl ether ether ketone) exhibits a crystalline structure with a single and sharp melting peak at above 229 °C, which is not observed when thermal treatment is used.[13] Syndiotactic polystyrene undergoes a number of solid−solid transitions in supercritical CO_2 that do not occur with solvent treatment or thermal annealing.[14] For example, planar mesophase to β form, α form to β form, and γ form to β form transitions can be brought about under appropriate conditions of temperature and CO_2 pressure. These studies show that polymers treated with supercritical fluids can influence the crystalline structure formation and phase transition in ways that are not observed through solvent treatment or thermal annealing.

We reported that the crystalline stereocomplex formation between low strereoregular *it*-PMMA (mm =

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Table 1. Characteristics of the Polymer Samples

			tacticity (%)[b]		
sample	$10^{-4}M_n$[a]	M_w/M_n[a]	mm	mr	rr
*it*1	3.62	10.06	81.0	9.6	9.4
*it*2	1.89	1.07	97.2	2.3	0.5
*st*1	5.58	1.93	6.7	36.1	57.2
*st*2	2.03	1.16	0.9	12.0	87.1
*st*3	4.04	1.03	0.5	12.4	87.1
*st*4	12.05	1.05	1.5	12.4	86.1
*st*5	16.30	1.06	0.0	8.2	91.8
*st*6	30.70	1.19	0.6	9.9	89.6

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

81.0%) and *st*-PMMA (rr = 57.2%) occurred in supercritical CO_2 and that the crystalline stereocomplex induced by supercritical CO_2 contributed to the superior morphology of the microcellular foams obtained, compared with amorphous PMMA.[15] In this study, we use the highly stereoregular PMMA samples, *it*-PMMA (mm = 97.2%) and *st*-PMMA (rr > 86.1%), and examine the effect of supercritical CO_2 on the crystalline stereocomplex formation. The effect of the stereoregularity on the crystalline stereocomplex morphology is investigated by means of DSC measurements as a function of treatment pressure, temperature, and the ratio of *it*-PMMA/*st*-PMMA.

Experimental Section

Materials. The *it*-PMMA samples with low stereoregularity, *it*1, were prepared by an anionic polymerization technique.[16] The *it*-PMMA samples with high stereoregularity, *it*2, were prepared in toluene at −78 °C with *t*-BuMgBr as initiator according to a method reported by Hatada et al.[17] The *st*-PMMA samples with low stereoregularity, *st*1, were prepared by a conventional free radical polymerization technique. The *st*-PMMA samples with high stereoregularity and low molecular weight, *st*2, were prepared in toluene solvent at −78 °C with *t*-BuLi/Et_3Al (1/3) initiator according to the procedure reported by Hatada et al.[18] The *st*-PMMA samples with high stereoregularities and high molecular weights, *st*3 to *st*6, were prepared in toluene solvent at −78 °C with $[Cp^*_2SmH]_2$ as initiator according to a method reported by Yasuda et al.[19]

Characterization of the polymer samples prepared is given in Table 1. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (DSC). Tacticities were determined by α-CH_3 signals intensities obtained by ^{1}H NMR spectroscopy. Further details on the characterization are given in ref 15. The molecular weight, the molecular weight distribution, and the tacticity of the prepared PMMAs are listed in Table 1.

Sample Preparation. Samples were prepared for treatment by solvent casting. Amorphous PMMA films were prepared by casting a 8 wt % dichloromethane solution of *it*-PMMA and *st*-PMMA in various ratios onto an aluminum cup. To remove all solvent, the films were dried for 1 day at room temperature and afterward dried for 1 day at room temperature under vacuum. Before treatment with supercritical CO_2 or thermal annealing, all films obtained were heated at 250 °C for 10 min and cooled quickly to reduce any solvent or thermal histories.[20]

Supercritical CO_2 Treatment. A high-pressure apparatus[15] was used for supercritical CO_2 treatment. CO_2 was pressurized by means of two HPLC pumps (Milton Roy Co., NSI-33R). The pressure was controlled with a back-pressure regulator (Tescom Co., Minneapolis, 26-1765-24-065). The pressure of the sample was measured to within 0.1 MPa with a precision Bourdon gauge (Nagano Keiki Seisakusho, Ltd., Tokyo, GP35-141). Samples (20 × 20 × 0.100 mm) were loaded into an autoclave (34 cm^3 inner volume) preheated in an air bath (Tabai Espec Co., Osaka, LC-112). The temperature of the air bath was controlled to within 1 K. Air remained in the autoclave was removed by purging with CO_2. The autoclave was pressurized with CO_2 at pressures ranging from 5 to 25 MPa and maintained at the desired temperature for a given period of time. The time for introducing CO_2 was several minutes, and the CO_2 depressurization rate was 5 MPa/h, which was manually controlled with a metering valve. By using this procedure, the sample obtained was a transparent film without any visible bubbles.

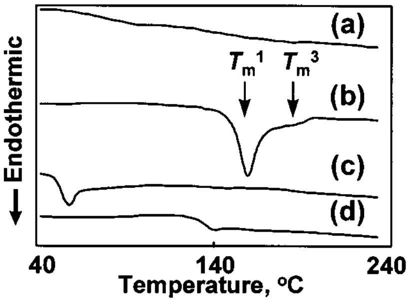

Figure 1. DSC thermograms of high stereoregularity PMMA films treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. Heating rate 10 °C/min. (a) *it*2/*st*4 (50/50) untreated, (b) *it*2/*st*4 (50/50), (c) *it*2 only, and (d) *st*4 only.

Analysis. Differential scanning calorimetry (DSC) was carried out with a TA instruments MDSC 2910 that was calibrated with indium. The procedure used was that reported in previous work.[15] After loading about 9 mg 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 in the melting endotherm. The heat of melting, ΔH, was determined by peak area of the melting endotherm.

Results and Discussion

Multiple Melting Points of the Stereocomplex. Figure 1 shows the DSC thermograms of the high stereoregular PMMA samples, *it*2 (mm = 97.2%)/*st*4 (rr = 87.1%) (50/50 wt/wt) blend, *it*2 only, and *st*4 only, treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. An untreated sample (Figure 1a) is shown for reference. Low stereoregular sample (*it*1 (mm = 81.0%)/*st*1 (rr = 57.2%)) films treated at the same condition had a single endothermic peak at about 160 °C as observed in the literature.[15] The high stereoregular blend samples (Figure 1b) exhibited two endothermic peaks at about 160 and 185 °C. It is well-known that multiple endothermic peaks in the temperature range from 120 to 220 °C, denoted as $T_m{}^1$, $T_m{}^2$, and $T_m{}^3$, have been reported in the literature for blends of high stereoregular *it*-PMMA/*st*-PMMA.[8,9,21,22] The $T_m{}^2$ with a small endothermic peak was assigned to the decomposition of complexed sections formed during DSC measurements.[8] Several explanations for the existence of $T_m{}^1$ and $T_m{}^3$ have been proposed. One author proposed[21] that upon heating the solvent-stabilized *st*-PMMA crystallites first melt at $T_m{}^1$, and this is then followed by melting of the stereocomplex crystallites at $T_m{}^3$. Another group proposed[22] that the crystallized *it*-PMMA chains melt at $T_m{}^1$ which is then followed by melting of the stereocomplex crystallites ($T_m{}^3$) that have crystallized more or less simultaneously with *it*-PMMA chains. In this work, only the DSC thermograms of the *it*2 and the *st*4 films had a very small endothermic peak near T_g with a maximum at 58 and 140 °C, respectively. These maxima can be attributed to the enthalpy of relaxation. No large endothermic peaks over the temperature range from 120 to 220 °C were observed. Form

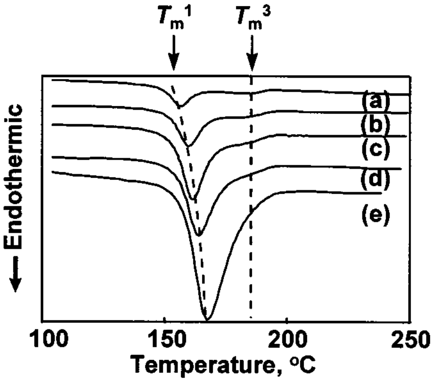

Figure 2. DSC thermograms of high stereoregular PMMA films (*it*2/*st*2 = 50/50) treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. Heating rate: (a) 5, (b) 10, (c) 15, (d) 20, and (e) 40 °C/min.

the results in Figure 1, it is clear that the two endothermic peaks of the high stereoregularity blend samples induced by high-pressure CO_2 treatment corresponded to the melting of neither the solvent-stabilized *st*-PMMA crystallites nor the *it*-PMMA crystallites.

Figure 2 shows the DSC thermograms of the *it*2/*st*2 (50/50wt/wt) blend, which was treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h, with various heating rate on DSC measurements. The effect of heating rate on the DSC results, superheating characteristics, of the stereocomplex consisting of *it*2 and various molecular weight *st*-PMMA (rr > 86.1%) samples that have been treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h are summarized in Table 2. The higher melting temperatures represented as T_m^3 were independent of the heating rate and *st*-PMMA molecular weight. On the other hand, the lower melting temperatures represented as T_m^1 increased with the heating rate in the range 5−40 °C/min. Figure 3 shows T_m^1 of the stereocomplex consisting of *it*2/*st*2 blend films as a function of heating rate. The superheating characteristics of T_m^1 did not depend on the molecular weight or the stereoregularity of the *st*-PMMA used. Schomaker and Challa[8,9] have investigated the multiple endothermic peaks of stereocomplexes in detail and proposed the occurrence of two crystallization modes. According to their work,[8] the superheating characteristics of the two types of crystallites are different since T_m of the fringed micellar structure increases with the heating rate in DSC measurements, in contrast to T_m of the lamellar crystallites, which is essentially independent of the heating rate. Our results indicated that the T_m^1 and T_m^3 corresponded to the fringed micellar structure and the lamellar crystallites of the complexed sections, respectively, due to differences in superheating characteristics.

Figure 4 shows the effect of treatment temperature, T_t, on the T_m^1, T_m^3, and ΔH of the stereocomplex of *it*2/*st*4 (50/50) blend films obtained by supercritical CO_2 treatment at 20 MPa for 6 h. Although T_m^3 did not depend on T_t in the temperature range 30−130 °C, T_m^3 was found to be linearly dependent on T_t above 150 °C. While no endothermic peaks could be detected above 110 °C for the case of the low stereoregular PMMA samples (*it*1/*st*1),[15] lamellar crystallites were obtained from the high stereoregular PMMA samples (*it*2/*st*4) in the temperature range 30−170 °C. We estimate that the lamellar crystallites with high melting temperature could not be formed by the same conditions as because of the low stereoregularity. On the other hand, T_m^1 was not detected on the blend films treated with supercritical CO_2 above 150 °C, and T_m^1 was found to be linearly dependent on T_t with a slope of 0.42 over the temperature range 30−130 °C. According to Hoffman et al.,[23] a slope near unity is indicative of fringed micellar structure, and a slope of about 0.5 suggests the formation of lamellar crystallites. For the case of crystallization from *it*-PMMA/*st*-PMMA DMF system, however, although the slope of the lower melting temperature (T_m^1) vs T_t was 0.17,[21] the T_m^1 corresponds to the fringed micellar crystallites due to superheating characteristics.[9] The reason why the slope of T_m^1 vs T_t was less than unity is probably due to the influence of DMF or CO_2, which can act as a plasticizer. For the case of crystallization of *it*-PMMA, it was reported that the slopes of T_m vs T_t influenced by solvent concentration and that the slope obtained by thermal treatment was larger than that of the *o*-xylene solvent treatment.[24] The polymer concentrations of the *it*-PMMA/*st*-PMMA DMF system[21] were very low, being about 0.2 wt %, and the amount of CO_2 sorbed into the *it*-PMMA/*st*-PMMA blend films can be estimated to be less than 20 wt % at the given experimental conditions,[25] which means that the polymer concentrations of *it*-PMMA/*st*-PMMA CO_2 system is estimated to be about 80 wt %. We estimated that the slope of T_m^1 vs T_t was less than unity because of the influence of the amount of plasticizer, either DMF or CO_2, which affects the mobility of the polymer.

Figure 5 depicts the influence of treatment pressure on of the stereocomplex of *it*2/*st*4 (50/50) blend films induced by supercritical CO_2 treatment at 70 °C for 6 h. The T_m^1 and ΔH of the stereocomplex increased with increasing treatment pressure at the given experimental conditions and attained a constant value above 20 MPa, in agreement with previous results for the low stereoregular samples.[15] The T_m^3, however, did not depend on the treatment pressure over the range of conditions studied. The amount of CO_2 sorbed in the polymer generally increases with increasing treatment pressure at a given temperature, and the CO_2 that is sorbed can act as a plasticizer for the polymer.[26] Our results indicate that a certain amount of CO_2 was needed for the stereocomplex formation at below T_g.

Influence of *it*-PMMA and *st*-PMMA Mixing Ratio. Figure 6 shows the DSC thermograms of *it*2/*st*4 blend films with various *it*-PMMA and *st*-PMMA mixing ratios treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. In the range of 50−100% *it*-PMMA content, the stereocomplex obtained had two endothermic peaks with one of the peaks being very broad over the 155−190 °C range. The stereocomplex consisting of less than 33% *it*-PMMA content had a single sharp endothermic peak between 160 and 170 °C, indicating the absence of a wide distribution of crystal sizes. These results indicate that the crystalline stereocomplex consisting of less than 33% *it*-PMMA content had similar size crystallites.

The T_m^1 and T_m^3 of the stereocomplex as a function of *it*-PMMA content are shown in Figure 7. The T_m^1 and T_m^3 increased when the *it*-PMMA content decreased and were independent of the stereoregularity of *it*-PMMA and *st*-PMMA, in agreement with previous observations of solvent-induced stereocomplex formation.[10] Although no endothermic peak was detected for the high stereoregular *it*2 sample treated at these conditions (Figure 1c), one endothermic peak at 150 °C was detected for the given experimental conditions for the case of the *it*1

Table 2. Effect of Heating Rate on T_m^1, T_m^3, and ΔH of the Stereocomplexes Obtained with Supercritical CO_2 at 20 MPa and 70 °C for 6 h[a]

	5 °C/min[b]			10 °C/min[b]			15 °C/min[b]			20 °C/min[b]			40 °C/min[b]		
st-PMMA sample	T_m^1 (°C)	T_m^3 (°C)	ΔH (J/g)	T_m^1 (°C)	T_m^3 (°C)	ΔH (J/g)	T_m^1 (°C)	T_m^3 (°C)	ΔH (J/g)	T_m^1 (°C)	T_m^3 (°C)	ΔH (J/g)	T_m^1 (°C)	T_m^3 (°C)	ΔH (J/g)
*st*2	156.5	184.5	22.0	159.8	185.7	21.7	161.5	185.4	21.3	164.0	186.0	21.3	167.8	*c*	20.6
*st*3	156.9	184.6	21.6	160.8	185.7	21.6	162.2	185.4	21.2	164.0	186.0	21.8	169.5	*c*	21.2
*st*4	155.9	183.8	18.7	159.2	185.7	21.0	161.7	185.4	21.2	164.2	186.0	20.4	167.2	*c*	20.4
*st*5	158.3	185.2	19.4	161.6	185.7	19.9	163.3	185.4	20.0	166.6	186.0	19.9	172.5	*c*	19.4
*st*6	157.9	185.3	17.5	161.0	185.7	17.6	162.9	185.4	19.1	166.3	186.0	17.7	170.5	*c*	18.6

[a] All samples were prepared with high stereoregularity *it*-PMMA, *it*2, and *st*-PMMA of various molecular weights. [b] Heating rate on DSC measurement. [c] Overlap with T_m^1.

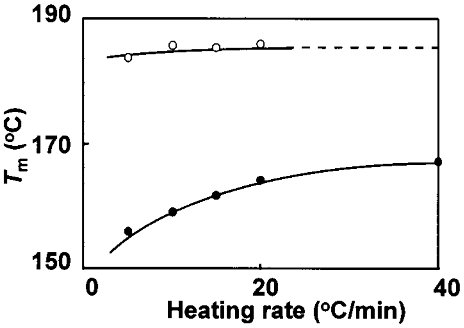

Figure 3. T_m^1 and T_m^3 as a function of heating rate, employing *it*2/*st*2 (50/50) blend film treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. T_m^1(●), T_m^3(○).

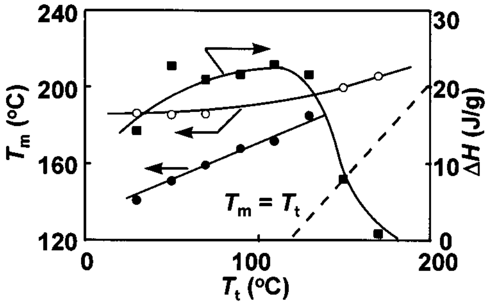

Figure 4. T_m^1, T_m^3, and ΔH of the stereocomplex of *it*2/*st*4 (50/50) blend films treated with supercritical CO_2 at 20 MPa for 6 h as a function of crystallization temperature T_t: T_m^1 (●), T_m^3 (○), ΔH (■).

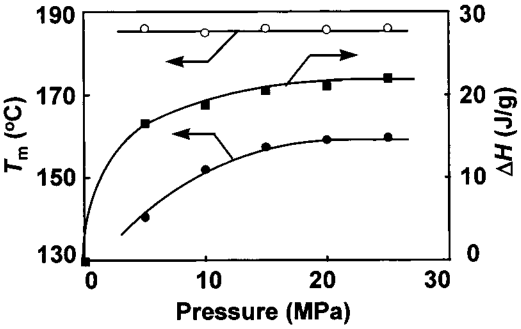

Figure 5. T_m^1, T_m^3, and ΔH of the stereocomplex of *it*2/*st*4 (50/50) blend films treated with supercritical CO_2 as a function of pressure at 70 °C for 6 h. T_m^1 (●), T_m^3 (○), ΔH (■).

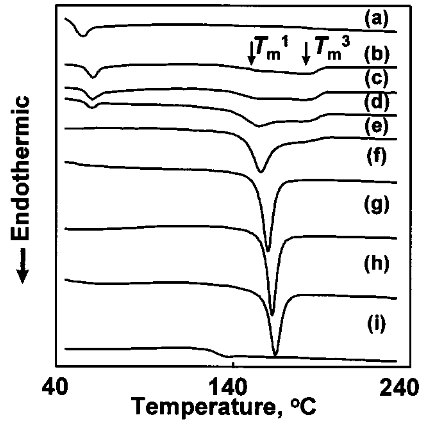

Figure 6. DSC thermograms of *it*2/*st*4 blend films treated with supercritical CO_2 at 20 MPa and 70 °C for 6 h. Heating rate: 10 °C/min. *it*2/*st*4 (wt/wt) = (a) 100/0, (b) 80/20, (c) 75/25, (d) 67/33, (e) 50/50, (f) 33/67, (g) 25/75, (h) 20/80, and (i) 0/100.

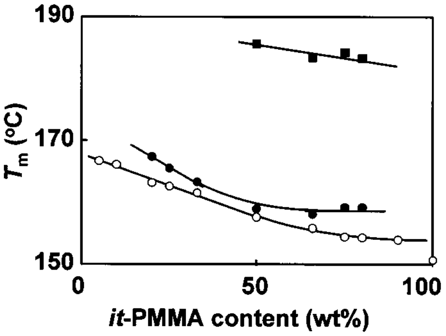

Figure 7. T_m^1 and T_m^3 of the stereocomplex induced by supercritical CO_2 as a function of *it*-PMMA content at 20 MPa and 70 °C for 6 h. T_m^1 of *it*2/st4 (●), T_m^3 of *it*2/*st*4 (■), T_m^1 of *it*1/*st*1 (○).

sample.[15] We estimated that the stereocomplex formation between isotacitic sequences and syndiotacitic sequences occurred because of the presence of irregular sequences made up of 9.4% rr triad sequences in the *it*1 sample, as shown in Table 1. Figure 8 shows the effect of *it*-PMMA content on the ΔH and the ratio $\Delta H_3/\Delta H$ of the stereocomplex obtained by supercritical CO_2 treatment at 20 MPa and 70 °C for 6 h. Because ΔH of the stereocomplex has a maximum for 33 wt % *it*-PMMA, a suitable content of *it*-PMMA for the stereocomplex formation for high-pressure CO_2 treatment is probably 33 wt %, which is similar for thermal annealing and solvent treatment.[5] Hatada et al.[27,28] observed the stereocomplex formation process precisely using conventional GPC, using uniform *it*-PMMA with high stereoregularity (mm > 97%) and *st*-PMMA with high stereoregularity (rr > 91%), which had been isolated by means of preparative supercritical fluid chromatography. Their results indicate that the initial stage of stereocomplex formation involves the association of a single molecule of *it*-PMMA and a single molecule of *st*-PMMA. In the final stage, that is, in the equilibrium state, of stereocomplex formation consisting of high stereoregular PMMA used, it seems reasonable that a suitable mixing ratio for *it*-PMMA/*st*-PMMA is 1/2 according to numerous investigations.[2,3] For the case of stereocomplex formation induced by supercritical CO_2

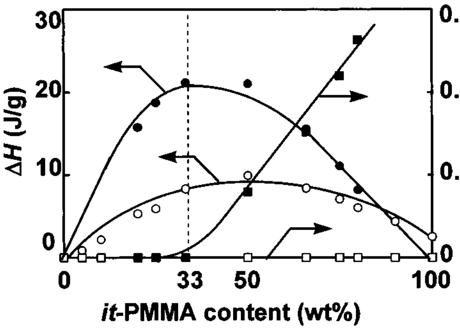

Figure 8. ΔH and $\Delta H_3/\Delta H$ of the sterecomplex induced by supercritical CO_2 as a function of *it*-PMMA content at 20 MPa and 70 °C for 6 h. ΔH of *it*2/*st*4 (●), $\Delta H_3/\Delta H$ of *it*2/*st*4 (■), ΔH of *it*1/*st*1 (○), $\Delta H_3/\Delta H$ of *it*1/*st*1 (□).

treatment, the T_m and ΔH attained equilibrium in about 6 h.[15] Our results indicated that the suitable mixing ratio of the stereocomplex induced by supercritical CO_2 for *it*-PMMA/*st*-PMMA was 1/2, in agreement with the equilibrium state of stereocomplexes formed in some solvents and in bulk thermal annealing method. The ratio $\Delta H_3/\Delta H$, which gives the relative intensity of T_m^1 and T_m^3, depended on the mixing ratio as mentioned above (Figure 6). For the case of 33% *it*-PMMA content, the crystalline stereocomplex obtained by thermal annealing and solvent treatment for both blends have broad melting temperatures.[8,10] The crystalline stereocomplex of 33% *it*-PMMA content induced by supercritical CO_2 had only one sharp endothermic peak, which was not observed by solvent treatment or thermal annealing.

Kazarian et al. reported that polymers possessing electron-donating functional groups exhibit specific interactions with CO_2, most probably of which are of a Lewis acid−base nature.[29] Recently, Bistac et al.[7] reported that the ability of a solvent to promote stereocomplex formation depends on the solvent's basicity. In other words, PMMA does not favor polymer self-association in acidic solvents, such as chloroform, whereas PMMA promotes polymer self-association in basic solvents, such as DMF and benzene. Our results indicate that supercritical CO_2 can be either a strong or weak complexing solvent, although supercritical CO_2 acts as a Lewis acid. The solubility parameter of PMMA, δ_{PMMA}, is about 19 $MPa^{-1/2}$ at 25 °C, whereas the solubility parameters of strong or weak complexing solvents are in the range 18−25 $MPa^{-1/2}$, and the solubility parameter of noncomplexing solvent, chloroform, is 19.6 $MPa^{-1/2}$ at 25 °C.[30] Furthermore, all strong, weak, and noncomplexing solvents reported dissolve PMMA molecules independent of stereoregularity without mixing *it*-PMMA/*st*-PMMA. However, the solubility parameters of CO_2, δ_{CO_2}, in the temperature range 30−190 °C and the pressure range 5−30 MPa were treated 0−15 $MPa^{-1/2}$ evaluated from equations in the literature[31] (Figure 9). It was also well-known that supercritical CO_2 is a weak solvent for some polymers such as polyethylene, poly(acrylic acids), poly(methyl methacrylate), and polystyrene and that supercritical CO_2 can act as only a plasticizer for these polymers despite the low solubility.[32] Considering the large difference between δ_{CO_2} and δ_{PMMA} and the solubility of PMMA in supercritical CO_2, we estimated that the interactions between CO_2 and PMMA appear to be smaller than those reported between strong or weak complexing solvents and PMMA and that CO_2 acts as a complexing solvent over a range of temperatures because CO_2 molecules do not inhibit the interaction between *it*-PMMA and *st*-PMMA, although supercritical CO_2 acts as a Lewis acid.

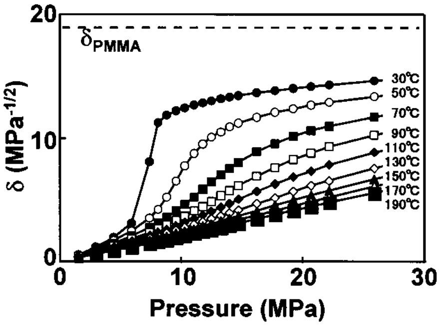

Figure 9. Solubility parameters of CO_2 at various temperatures and pressures calculated by the equation of state of Pang and McLaughlin.[31] The solubility parameter of PMMA (δ_{PMMA}) is about 19 $MPa^{-1/2}$.[30]

Conclusions

Crystalline stereocomplexes of highly stereoregular *it*-PMMA (mm = 97.2%) and *st*-PMMA (rr > 86%) blends were formed by treatment with CO_2 at pressures in the 5−25 MPa range and over temperatures from 30 to 170 °C. DSC measurements indicated that the ΔH of the stereocomplex had a maximum for 33 wt % *it*-PMMA content, in agreement with stereocomplexes formed in some solvents and in bulk thermal annealing methods. For the case of over 50% *it*-PMMA content, two endothermic peaks, T_m^1 and T_m^3, were detected. The data were analyzed according to the theory of Schomaker,[8] and it was concluded that T_m^1 and T_m^3 corresponded to the fringed micellar structure and the lamellar crystallites of the complexed sections, respectively. The treatment pressure did not influence the T_m^3 at constant treatment temperature, although T_m^3 increased with increasing the treatment temperature at 20 MPa. Crystalline stereocomplexes of less than 33% *it*-PMMA content that were treated with CO_2 had only one sharp endothermic peak, comparable with those obtained by thermal annealing and solvent treatment.

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