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Multiple melting behavior of poly(epichlorohydrin) enantiomorphs

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Differential scanning calorimetry (DSC) studies demonstrate that the multiple melting behavior observed in both *R* and *S* enantiomorphs of poly(epichlorohydrin), their equimolar blend and the stereoblock copolymer form follows two distinctly different patterns, depending on the crystallization conditions. Isothermal crystallization at *large* undercoolings results in primary crystallites which during the heating scan undergo a process of melting/recrystallization and final melting, evidenced by a *triple* melting peak endotherm with the shape and position of the highest melting peak strongly dependent on scanning rate. By comparison, isothermal crystallization at *small* undercoolings yields primary and secondary crystallized material which melts with a *double* peak endotherm, the shape of which depends strongly on the crystallization time, with no indication of reorganization during the scan. These melting behavior observations support previous suggestions about the role of enantiomorphism in the crystallization of the stereoblock copolymer. Characteristic slow overall rates of crystallization of poly(epichlorohydrin) make this polymer an ideal subject for the study and refinement of multiple melting in polymers.

1. Introduction

Semicrystalline polymers often exhibit more than one maximum in the melting endotherm. This so-called multiple melting behavior can result from the fusion of material of different levels of crystallite perfection (order), e.g., multiple crystal lattice types and multiple morphologies (folded- and partially extended-chain crystallites) which exist in the sample prior to the thermal analysis. Alternatively, when the polymer sample passes through the annealing temperature region during the thermal analysis scan, the experimental conditions may permit the occurrence of structural rearrangements typical of annealing behavior. In this case, concurrent endothermic melting and exothermic structural rearrangement processes of comparable rate can result in an overall, complex demonstration of multiple melting peaks; the superposition of an exothermic trough on a larger endotherm can appear in the DSC heating trace as multiple melting peaks.

Historically, Bair *et al.* [1] first demonstrated the potential of polymer lamellar crystallites (lamellae) to undergo some form of annealing process *during* the DSC heating scan, and demonstrated its effect on the appearance of the melting trace, in their investigations of the multiple melting peak behavior of polyethylene single lamellae. When the polyethylene sample was first cross-linked by irradiation, thereby rendering the lamellar surface molecules immobile and preventing lamellar perfection by thickening, the DSC trace was reduced to only a single peak endotherm. Roberts [2] presented the first clear demonstration of the anneal-type rearrangements taking place during the thermal analysis heating scan using poly(ethylene terephthalate) (PET). A distinct exotherm was displayed in the DSC trace when the heating scan of the isothermally crystallized sample was interrupted and the temperature was held constant between the two endothermic peak temperatures. In addition, the results of varying heating rate experiments demonstrated that with increasing heating rate, a proportionately smaller amount of crystallites had sufficient time to recrystallize during the DSC scan, thus accounting for the accompanying increase in the magnitude of the lower temperature endotherm. Such reorganization of crystallites during the thermal analysis scan is commonly the source of the similar multiple melting behavior exhibited in polymers, as described in the early studies of isotactic polystyrene [3–5], and poly(butylene terephthalate) [6].

In some polymer systems, the characteristic reorganization processes are more convoluted. For example, in isothermally crystallized syndiotactic polypropylene reorganization of the crystalline material during

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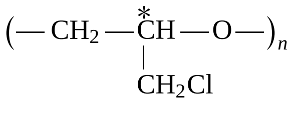
the DSC heating scan can involve changes to both the surface and the internal structure of the crystallite. The pseudo-chiral chains can alter their packing at the unit cell level to achieve the more stable antichiral packing, in a type of solid diffusion process driven by the lower energy configuration of this latter arrangement [7]. In a recent paper from this laboratory [8], complimentary DSC and variable temperature solid state ^{13}C NMR studies of quench-cooled isotactic polypropylene provided another example of intricate reorganization. Dramatic changes to the crystalline phase NMR spectra of samples at temperatures between the two endotherm maxima observed by the DSC were attributed to the interconversion of the α_1 and α_2 crystal forms during annealing conditions.

Structural rearrangements have been ruled out as the source of multiple melting endotherms in some polymers, such as of *trans*-1, 4-polyisoprene [9] and poly(vinylidene fluoride) [10], for which it has been shown that different crystal structures exist in the sample prior to thermal analysis. In some cases, multiple melting behavior has been ascribed to a combination of both morphology and reorganization [11, 12].

DSC thermograms are therefore not necessarily a direct reflection of the state of the material prior to thermal analysis. When available, the use of simultaneous DSC and structural analytical methods such as X-ray diffraction permit unequivocally the resolution of concomitant melting and recrystallization processes. The feasibility of performing simultaneous DSC and small-angle X-ray scattering measurements was first demonstrated by Russell and Koberstein, using polyethylene [13]. In another study using poly(ether ester ketone), the combination of DSC, small-angle and wide-angle X-ray scattering analyses has clearly demonstrated that the low temperature peak of the multiple endotherm marks the point at which the original isothermally formed crystallites become unstable, and the onset of melting and recrystallization [14]. One of the first successes of the new dynamic or modulated DSC technique has been the ability to resolve the thermal contributions that result from the reorganization processes, such as in the case of PET [15].

In this paper, we present our DSC investigation of the multiple melting behavior observed in the optically pure polyenantiomers poly(R-epichlorohydrin) (PRECH) and poly(S-epichlorohydrin) (PSECH), their equimolar blend, and the stereoblock poly(R, S-epichlorohydrin) (i-PRSECH) having repeat units with the chemical structure



$$\left(-\mathrm{CH_2}-\overset{*}{\underset{\substack{|\\ \mathrm{CH_2Cl}}}{\mathrm{CH}}}-\mathrm{O}-\right)_n$$

In our previous studies on the spherulite radial growth rate kinetics [16] and the spherulite morphology [17] of these optically active polyethers, it was found that the chiral centers in the backbone actively influence the development of the overall spherulite. Results of the preceding studies on PECH led to the suggestion that during isothermal crystallization from the melt, opposite-sense (R and S) chains and opposite-sense chain segments are effectively rejected from the lamellar growth front in the equimolar blend and stereoblock polymer, respectively. Such a stereoselective mechanism would clearly affect the degree of order and thus influence the metastability of the resulting crystallites (lamellae). The aim of the present thermal behavior investigation was to test and compare the thermal metastability of each of the polyenantiomers of PECH, their equimolar blend, and the stereoblock polymer in an effort to further explore the distinctions among them.

2. Experimental

The synthesis and characterization of the isotactic poly(R, S-epichlorohydrin) (i-PRSECH), and the optically active poly(S-epichlorohyrin) (PSECH), poly(R-epichlorohydrin) (PRECH), and the preparation of their equimolar blend have been described elsewhere [16]. The $\bar{M}_w$ values of the polymers, determined by gel permeation chromatography (GPC), were found to be ca. 450 000, with a polydispersity value of 1.6 for both PRECH and PSECH, and 1.4 for i-PRSECH. An equilibrium melting temperature of 136 °C has been determined for the poly(epichlorohydrin) polymers.

The Perkin-Elmer DSC-7 differential scanning calorimeter employed in the present investigation was calibrated for temperature and peak area using indium and octadecane standards. For the DSC experiments the sample weights were in the range of 1.70 to 1.80 mg. In all cases, the positions of the peaks in the thermograms are reported as the temperature at the peak maximum. Scanning rates used in a particular experiment are reported in the text or accompanying Figure caption; for the so-called quench-cooled samples a nominal rate of 120 °C/min was employed. Crystallization temperatures (T_c) and the corresponding undercoolings (ΔT) are used interchangeably throughout the text.

3. Results and discussion

Figs. 1(b) and (c) contain representative DSC heating traces of the polyenantiomer PSECH and the stereoblock i-PRSECH, respectively, subsequent to a quench-cool from the melt. The PSECH displays a single crystallization exotherm at ca. 25 °C and on continued heating there appears a single melting endotherm at 112 °C. The equimolar polyenantiomer blend (not shown) displays the same transition temperatures as the polyenantiomers, with a somewhat broader crystallization exotherm. Although the heating curve for the stereoblock is similar to those for the polyenantiomers, the corresponding exotherm and endotherm temperatures are shifted to ca. 50 and 106 °C, respectively. For all of these samples no crystallization occurred during the quench-cool from the melt, as can be inferred from the slow cool DSC trace shown in Fig. 1(a).

The "first-melt" DSC heating curves (20 °C/min) of the as-polymerized polyenantiomers PRECH and PSECH, and of the isolated stereoblock i-PRSECH fraction exhibit two melting endotherms (Fig. 2). The DSC trace of the stereoblock in (a) possesses a dominant lower temperature peak and an overall broader endotherm than those of the polyenantiomers, shown in

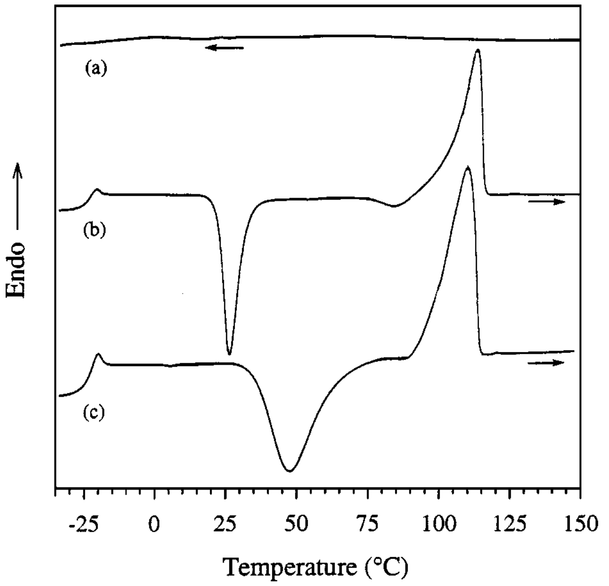


Figure 1 DSC cooling thermogram of (a) P*S*ECH (scanning rate = 20 °C/min), (b) heating thermograms of P*S*ECH, and (c) *i*-P*RS*ECH both quench-cooled from the melt (heating rates = 10 °C/min).

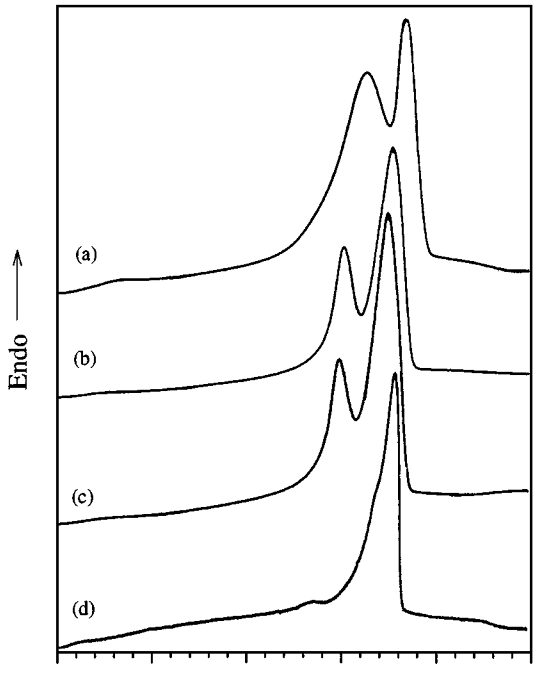


Figure 2 DSC first-melt thermograms of (a) the as-fractionated *i*-P*RS*ECH, (b) the as-polymerized P*R*ECH, and (c) the as-polymerized P*S*ECH, all heated at a rate of 20 °C/min. In (d) the as-polymerized P*S*ECH is heated at a rate of 5 °C/min.

(b) and (c). In addition, the higher melting temperature peak of the stereoblock endotherm falls at a slightly higher temperature than that of the polyenantiomers, probably as a result of the fractionation during separation from the atactic material, which was not required for the polyenantiomers. At a slower heating rate of 5 °C/min, the first-melt DSC curve of P*S*ECH shown in (d) displays a single peak, high melting temperature endotherm at a slightly higher temperature that has an indication of a shoulder on the low temperature side. The significance of this endotherm becomes clearer when all of the results have been presented and therefore further discussion of it is in the Summary section.

3.1. Effect of heating rate

To study the effect of heating rate on the observed melting behavior, samples of P*S*ECH and the equimolar polyenantiomer blend, isothermally crystallized at 90 °C ($\Delta T = 46$ °C) for 60 min, were heated at rates ranging from 1.2 to 40 °C/min (Fig. 3). At heating rates of $\leq$10 °C/min the polymers exhibit triple melting peak endotherms. The first peak, which is indicated with an arrow, tends to be somewhat obscure at low heating rates and its position is relatively insensitive to changes in heating rate. For both samples, with increasing heating rate the magnitude of the middle melting temperature peak increases and the middle and highest melting temperature peaks shift in opposite directions, which conforms to previous findings for other polymers [3, 10, 18, 19, 20]. The shifts are depicted in Fig. 4 for P*S*ECH, where the data have been extrapolated to

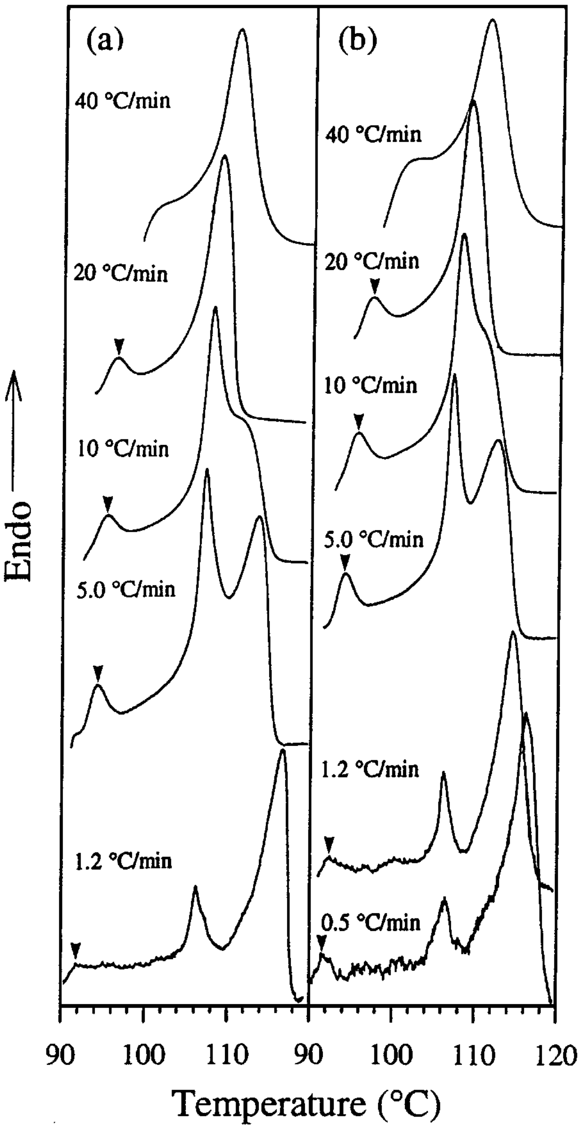


Figure 3 DSC thermograms of (a) P*S*ECH and (b) the equimolar polyenantiomer blend, isothermally crystallized at 90 °C for 1 h and heated at varying rates.

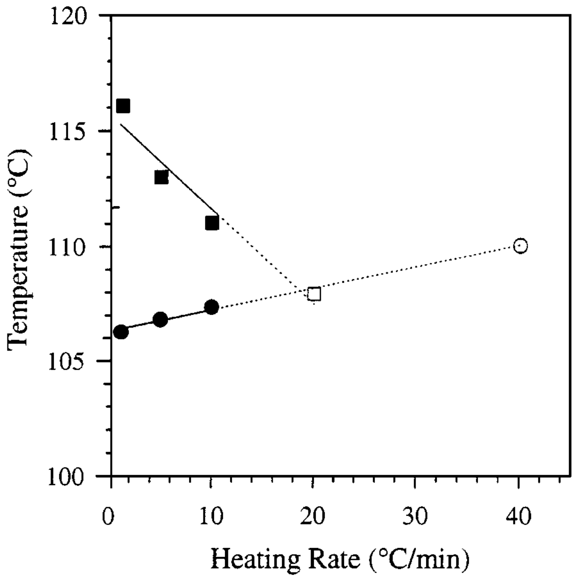


Figure 4 The middle (●) and highest (■) melting peak temperatures as a function of DSC heating rate for P*S*ECH isothermally crystallized at 90 °C for 1 h.

TABLE I Heats of fusion of PECH crystallized at 90 °C for different times

Heat of fusion, ΔH (J/g)			
i-P*RS*ECH	50/50 Blend	P*S*ECH	Crystallization time
Trace	1.6	3.6	15 min
Trace	2.3	5.6	20 min
Trace	9.7	n.d.	30 min
1.4	30	32	1 h
11	37	39	2 h
37	45	43	20–22 h

predict the absence of the highest melting temperature endotherm at a heating rate of ca. 20 °C/min; indeed, a single peak is obtained at a heating rate of 40 °C/min.

With increasing heating rate the sample passes through the annealing temperature region so quickly that there is insufficient time for reorganization (i.e., melting and recrystallization) of the original material. Consequently, the extent of reorganization decreases and the highest temperature melting material (reorganized material) melts at progressively lower temperatures. The middle melting temperature peak represents the temperature at which the original isothermally-formed crystallites become unstable, i.e., the onset of (partial) melting and recrystallization [14, 21, 22]. Its observed shift to higher melting temperatures with increasing heating rate has traditionally been explained in two ways: (1) In one explanation, the shift to higher temperature is rationalized entirely in terms of superheating [22]. With increasing heating rate, more of the original imperfect material remains and it is presumed inherently susceptible to the problems of thermal conductivity. (2) A second rationale for double melting temperature endotherms, which has been put forward by Rim and Runt [21], is schematically well presented elsewhere [21, 22] and is therefore not reproduced here. In essence, the observed multiple melting endotherm is considered to be the net illustrative effect of three thermal processes: the melting of the original imperfect crystallites, the recrystallization of some or all of this material, and finally the melting of the recrystallized material. With increasing heating rate, the contributions of the reorganization process are increasingly restricted. This minimizes the recrystallization exotherm and thus the melting endotherm of the recrystallized material so that the resultant overall endotherm displays a large lower melting temperature peak. Moreover, the net effect of the recrystallization exotherm is to shift the melting peak of the original material to lower temperatures as a consequence of competing simultaneous processes. The slower the heating rate, the larger the recrystallization exotherm and consequently the more down-shifted the melting peak of the original material becomes. Thus, this explanation is self-consistent with the heating rate dependence of the shape and magnitude of *both* middle and highest melting temperature peaks, depicting both the upward and downward shifts in the two melting temperature peaks as consequences of a complex, composite melting endotherm. This mechanism takes into account the limits of DSC; specifically, it is recognized that the observed thermogram is not only a function of the thermal processes ongoing in the sample, but also an algebraic sum of the endo- and exothermic transitions.

In the present case the results presented in Figs. 3 and 4 are consistent with the second explanation given above. Superheating of the original material may be a factor only at intermediate and higher heating rates. A weakness of the superheating rationale (1) is the dismissal of this phenomenon as a factor in the position of the highest melting temperature peak. Clearly, with increasing heating rate the reorganized material represented by the highest melting temperature peak becomes increasingly like the original imperfect material so that it should be sensitive to the same problems of superheating. However, superheating of this material is contrary to the observed *decrease* in melting peak temperature. In this case the question must be asked, why is the high melting temperature peak observed experimentally to be more sensitive to the change in heating rate. Naturally, at excessively high heating rates superheating of the intrinsically insulating polymer sample will play a role and the elevation of the single peak endotherm in the 40 °C/min scan in Fig. 4 may well be such an artifact (of superheating).

Table I contains the heats of fusion of P*R*ECH, the equimolar polyenantiomer blend, and the stereoblock samples, all isothermally crystallized at 90 °C ($\Delta T = 46$ °C) for different periods of time. In accordance with the spherulite growth rates reported previously [17], the overall rate of crystallization of the polyenantiomer exceeds that of the equimolar polyenantiomer blend. Even after a crystallization period of 20–22 h, the heat of fusion attained by the stereoblock polymer is only ca. 85% that attained by the other polymers.

3.2. Partial heating experiments

The technique of partial heating, for these purposes, was originally practiced by Lemstra [3] in an attempt to provide incontrovertible evidence of recrystallization

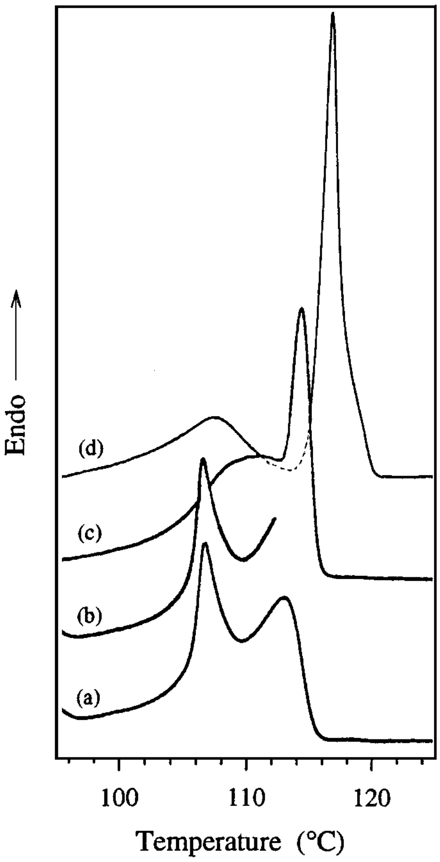


Figure 5 DSC thermograms of P*R*ECH isothermally crystallized at 90 °C for 1 h and (a) heated at 5 °C/min, (b) heated at 5 °C/min until high temperature peak, (c) same as (b) and immediately quench-cooled to 90 °C and subsequently heated at 5 °C/min, and (d) same as (b) and held at the high temperature peak for 56 min, quench-cooled to 90 °C, and heated at 5 °C/min. The DSC traces are presented in a *y*-shifted fashion but are all on the same scale.

during heating in the thermal analysis of isotactic polystyrene. Typically, the sample is heated to a temperature just above the lower melting temperature peak, quench-cooled, and reheated to complete melting. If the double melting behavior results from the melting of two distinct crystal systems, then only the higher melting temperature peak is expected to remain upon subsequent reheating, with the *same* heat of fusion as in the original DSC trace.

Partial heating experiments were performed on P*S*ECH, and the results are depicted in Fig. 5. The sample was isothermally crystallized at 90 °C ($\Delta T =$ 46 °C) for 60 min (i.e., *incompletely*) in the DSC chamber, and subsequently heated at a scanning rate of 5 °C/min (Fig. 5(a)). The highest temperature peak appears at ca. 112 °C. The experiment was repeated with a new sample but the heating was stopped at 112 °C (Fig. 5(b)). The sample was then *immediately* quench-cooled to the original T_c and after an isothermal period of 1–2 min, required for the DSC to equilibrate, a non-interrupted heating scan was recorded (Fig. 5(c)). A broad endotherm precedes the 'stop' temperature, indicating that not all of the material which had melted has also recrystallized by that point in the original heating scan, and probably recrystallized upon quenching. The higher melting temperature peak has shifted to ca. 114 °C, and has both sharpened and increased in magnitude upon reheating. It is expected that with a sufficiently long anneal at the 'stop' temperature the partially melted material would reorganize into the material represented by the highest melting temperature peak; then the subsequent heating trace should contain much less of the broad, lower temperature endotherm. Hence, the experiment was repeated with a new sample for which the temperature was held constant, at 112 °C, for 56 min before quench-cooling the sample to the original T_c. The subsequent non-interrupted heating curve (Fig. 5(d)) shows a small, broad peak followed by the high melting temperature peak which exhibits a dramatic narrowing in shape, and a shift in position to above 116 °C. The area under the high melting temperature peak in (d) is greater than that in (a), indicating that a longer exposure to the anneal conditions at 112 °C results in a greater amount of recrystallization.

It is of note that the highest temperature melting peak is not simply representative of the melting of material isothermally crystallized at the stop/hold temperature. The area under the highest melting temperature peak in Fig. 5(d) is an order of magnitude larger than the area under the full melting endotherm of a sample isothermally crystallized at approximately the same T_c for 24 h (see Fig. 7(a)). In addition, the position of the highest temperature peak in Fig. 5(d) is lower than that of the isothermally crystallized sample in Fig. 7(a), indicating that the lamellae of the former have not thickened to the same extent as those formed in the isothermally crystallized sample. Clearly, the heating trace in Fig. 5(d) is representative of a recrystallization process which occurs during the scan, and which can occur to a greater extent if the sample is held isothermally for a sufficient time period.

In a separate experiment, a sample of P*S*ECH was isothermally crystallized at 90 °C for 60 min in the DSC chamber, and subsequently heated at a scanning rate of 5 °C/min. The scan was halted and the sample was held isothermally at the temperature of the observed minimum between the two endothermic peaks in Fig. 5(a). After ca. 42 min the heating scan was resumed. The complete DSC trace, shown in Fig. 6, gives clear evidence of an exotherm in the isothermal hold region, supporting the proposal that recrystallization events occur during the DSC scan. Similar exotherms have been reported in relatively few cases [2]. Completion of melting of the sample results in a double melting peak endotherm. It is important to note that it would take *more than a week* to completely crystallize the sample at a T_c of 110 °C. Therefore, the area of the endotherm following the isothermal hold in Fig. 6 is related to a recrystallization process and not simply to the primary crystallization of the original sample.

3.3. Effect of crystallization temperature

The effect of varying the crystallization temperature, (T_c), or undercooling, (ΔT), on the shape and position of the melting endotherms of P*R*ECH, the equimolar polyenantiomer blend, and the stereoblock polymer is demonstrated with the collection of DSC curves in

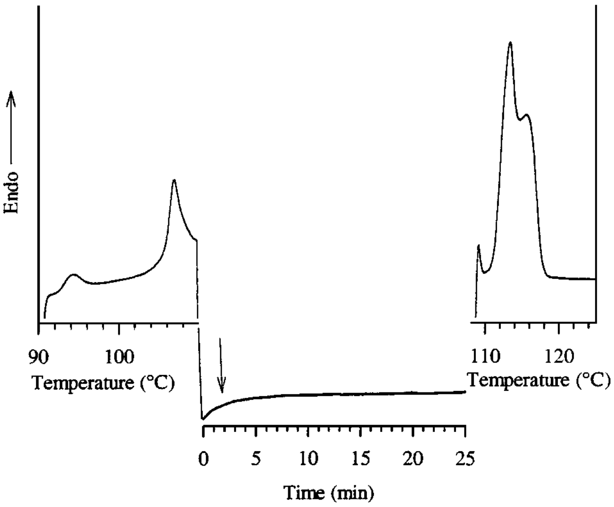


Figure 6 DSC thermogram of P*R*ECH isothermally crystallized at 90 °C for 1 h and heated at a 5 °C/min until 110 °C, held isothermal 42 min, and then resumed heating at 5 °C/min. (The arrow indicates exotherm (see text).)

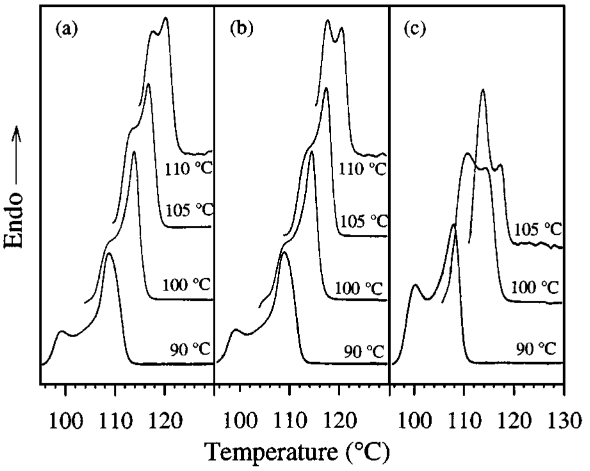


Figure 7 DSC thermograms of (a) P*R*ECH, (b) the equimolar polyenantiomer blend, and (c) *i*-P*RS*ECH samples isothermally crystallized at T_c for ca. 24 h and subsequently heated at 20 °C/min. For the purposes of demonstration, the vertical scale of some of the endotherms has been enlarged.

Fig. 7. The samples were isothermally crystallized for ca. 24 h at eight different undercoolings, ranging from 46 to 20 °C, and were subsequently heated at a scanning rate of 20 °C/min from the crystallization temperature. At a ΔT of 28 °C ($T_c = 110\,^\circ\text{C}$), the stereoblock polymer does not crystallize to any significant degree after 24 h so that the smallest ΔT employed for this sample was 33 °C ($T_c = 105\,^\circ\text{C}$). Typically, the stereoblock samples were of much lower crystallinity than the polyenantiomers or the equimolar polyenantiomer blend. With increasing T_c the degree of crystallinity dropped dramatically, so that for the purpose of demonstration only, the vertical scale of some of the endotherms in Fig. 7 has been enlarged.

At a given ΔT, all of the polymers exhibit *double* melting peak endotherms at the same temperatures, but the ratio of the areas of the two melting temperature peaks differs; the lower melting temperature peak becomes progressively dominant with increasing T_c (decreasing ΔT). The ratio of the lower to higher melting temperature peak is consistently higher for the stereoblock polymer than in the other polymers. The effect of varying ΔT on the melting profiles of the equimolar polyenantiomer blend and P*R*ECH is essentially the same, until the smallest ΔT of 28 °C ($T_c = 110\,^\circ\text{C}$) is employed. At this ΔT the lower melting temperature endotherm is very slightly more dominant for the blend, whereas for P*R*ECH the area is greater under the higher melting temperature peak. Far less subtle is the distinction between the melting profile of the stereoblock and that of either P*R*ECH or the equimolar polyenantiomer blend. For the stereoblock, the area under the lower melting temperature peak is prominent at undercoolings as great as 38 °C ($T_c = 100\,^\circ\text{C}$).

3.4. A second source of multiple melting

As shown in Fig. 3, for samples crystallized at relatively large undercoolings a *triple* melting peak endotherm is observed during subsequent melting, and the shapes of the middle and highest melting temperature peaks are strongly dependent on heating rate. By a direct comparison of the 20 °C/min scan in Fig. 3(a) with the heating scan of samples crystallized at 90 °C, shown in Fig. 7(a), it can be seen that the relatively weak, first peak in the heating curves in Fig. 3 appears as the lower melting temperature peak in Fig. 7. The significance of this peak is addressed later. Similarly, the second peak in Fig. 3 appears as the higher peak in Fig. 7. A third melting temperature peak is evident in Fig. 3 only at heating rates of 10 °C/min and lower, and results from a continuous recrystallization of the second melting temperature peak material during the heating scan. Such a peak does not appear in any of the DSC traces in Fig. 7.

All of the double melting endotherms shown in Fig. 7 were collected using a heating rate of 20 °C/min. It was shown in Fig. 3 that a sample isothermally crystallized at 90 °C does not undergo melting/recrystallization during the heating scan at this rate. The tendency for recrystallization to occur during heating is even less for samples which have been isothermally crystallized at smaller undercoolings. In fact, as demonstrated in Fig. 8, which compares the heating curves obtained at 20 °C/min in (a) and at 5 °C/min in (b) of a sample of the equimolar blend isothermally crystallized at 110 °C for 24 h, there is no reorganization even during the slower scan. The double melting endotherm in Fig. 7 must be a direct reflection of the distribution of crystallites present in the sample *before* thermal analysis. Thus, the results of the varying heating rate experiments (Fig. 3) and the varying T_c experiments (Fig. 7) demonstrate *different* sources of multiple melting behavior.

In a thermal behavior investigation of *i*-poly(*R*, *S*-epichlorohydrin), Janeczek *et al.* [23] reported the presence of three melting peaks in the thermogram of samples crystallized at 60 °C. Although varying heating rate studies were not performed on the samples, the results of a WAXD analysis excluded the possibility of more than one crystal type. Therefore, isothermal crystallization at small undercoolings results in at least two distinct levels of crystallite perfection.

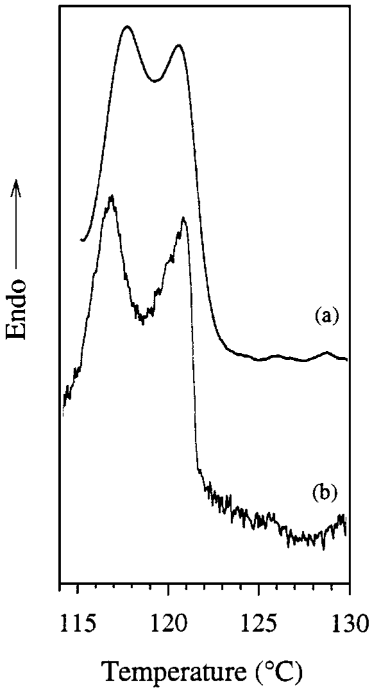


Figure 8 DSC heating thermogram of the equimolar blend sample isothermally crystallized at 110 °C for 24 h and heated at (a) 20 °C/min and (b) 5 °C/min. (Both thermograms calibrated with indium at 20 °C/min.)

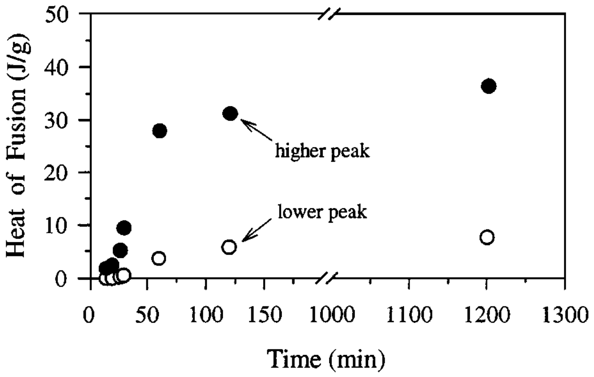


Figure 9 Plot of the partial heats of fusion of the lower and higher melting temperature peaks in the DSC heating scan (20 °C/min) of P*R*ECH, isothermally crystallized at 90 °C for varying periods of time.

To further investigate the source of the double melting endotherm behavior, different samples of P*R*ECH were isothermally crystallized at 90 °C for various periods of time, ranging from 2 min to ca. 24 h. Each sample was subsequently heated at a scanning rate of 20 °C/min immediately following crystallization. The plot of the areas of the resulting double melting peak endotherms as a function of crystallization period, in Fig. 9, shows that the higher melting temperature peak is representative of material which develops before and at a faster rate than that represented by the lower melting temperature peak. A similar crystallization period dependence of the specific heat of fusion has been reported by Lemstra *et al.* [4] in their study of the multiple melting behavior of *i*-polystyrene. They attributed the two levels of perfection, represented by the lower and higher melting temperature peaks of the samples crystallized at relatively small undercoolings, to the presence of subsidiary and dominant (more perfect) lamellae, respectively.

During isothermal crystallization, *secondary crystallization* involves initially rejected material, subsequent to the initial formation of the dominant lamellae, with the development of subsidiary lamellae which, through branching, fill the spaces between the former [24]. In recent cases, where the higher melting temperature peak is observed to develop before the lower one, the former has been associated with the melting of the secondary lamellae [24–27]. For example, this interpretation was used to explain the similar effects of varying the T_c on the multiple melting behavior in poly(ethylene succinate) and was substantiated by evidence from scanning electron microscopy [27]. A highly branched spherulitic structure was observed to develop in the samples only after a crystallization period of at least that equal to the time required for the appearance of the lower melting temperature endotherm in the DSC.

Some authors have described the melting process as morphologically the reverse of the isothermal crystallization process, with respect to the assignment of lower and higher melting temperature peaks to the subsidiary and dominant lamellae, respectively [28]. In the present system, at high crystallization temperatures (small undercoolings), the lower melting temperature peak is dominant in the heating curves (Fig. 7) of all of the samples; this suggests an increased amount of branching and/or filling-in between the dominant lamellae in the spherulitic structure. Furthermore, the lower melting temperature peak is consistently larger in the DSC curves of the stereoblock polymer and probably reflects an enhancement of the subsidiary lamellae in the spherulite, in accord with the observed relatively slower rate of overall crystallization. In addition, this correlates with the previously reported morphological observation of decreasing long range order in neighboring lamellae with the addition of the opposite-sense enantiomorph, either in a physical blend or covalently as in the stereoblock polymer.

4. Summary and conclusions

Multiple melting behavior which results from exothermic processes that occur during heating is a manifestation of the effects of anneal-type conditions during the thermal analysis scan. In principle, the detection of such a dynamic mechanism of competing processes, i.e., melting and recrystallization, can be successful only by analysis on a time frame similar to these events. Most probably, multiple melting is characteristic of most, if not all semicrystalline polymers. The choice of experimental conditions is equally critical as the sample thermal history in thermal behavior investigations. A comparison of the effect of varying the heating rate on the “as-polymerized” sample, i.e., the results presented in Figs 2(b) and (c), with the trend observed in the isothermally crystallized sample in Fig. 3 demonstrates the critical nature of the sample history in this type of analysis. It is particularly useful to examine the 20 and 5 °C/min heating scans of each sample. At a heating rate of 20 °C/min both samples melt with a double melting peak endotherm. However, when the heating rate is lowered to 5 °C/min, the as-polymerized sample melts with what is essentially a single melting peak while the isothermally crystallized sample melts with a triple melting peak endotherm. Indeed, the double melting peak endotherms obtained at a heating rate of 20 °C/min, for the two different samples, each arise for different reasons.

Fig. 3 demonstrates that at a heating rate of 20 °C/min there is insufficient time of exposure of the sample to anneal-type conditions to permit recrystallization. Thus, the melting profile is representative only of the melting of the originally present subsidiary lamellae (the low peak) and dominant lamellae, without the presence of a third, highest melting peak. Changing to a lower heating rate of 5 °C/min, the isothermally crystallized sample now has sufficient time to permit annealing of some of the dominant lamellae to form higher melting material, as evidenced by a triple melting endotherm.

Evidently, there is no endothermic peak due to the melting of subsidiary lamellae in the 20 °C/min heating scan of the as-polymerized sample in Fig. 2. Rather, what is clearly demonstrated by the convergence of the endotherm to a single melting peak upon decreasing the heating rate is that for the as-polymerized sample the rate of melting and recrystallization is sufficiently high so that it is detected even during a heating scan of 20 °C/min; this gives rise to a double melting endotherm. Thus, heating the as-polymerized sample at 5 °C/min provides sufficient time so that everything is annealed into higher melting material, giving rise to the single peak endotherm.

The characteristic rates of crystallization and reorganization of PECH are well within the normal practical analysis conditions of the DSC. Depending on both the experimental parameters and sample thermal history, different sources of multiple melting can be manifested and resolved in the same DSC trace. PECH is thus very amenable to the study of the phenomenon of multiple melting. Perhaps it is not by coincidence that the preponderance of multiple melting studies have been reported for those polymer systems with similar (relatively slow) rates of crystallization, i.e., on the order of normal DSC scanning conditions, such as *i*-polystyrene and PET.

Two sources of multiple melting behavior are active in PECH depending on the thermal history of the sample and the heating rate: (1) Upon melting subsequent to crystallization at relatively large undercoolings, the originally formed dominant lamellae are subject to recrystallization at slow heating rates (ca. $\leq$10 °C/min). A triple melting peak endotherm results with the lowest temperature peak corresponding to the melting of subsidiary lamellae; the middle and highest peaks representing the continuous melting and recrystallization of the dominant lamellae with their shape and position strongly dependent on heating rate. (2) At much smaller undercoolings, the drive to recrystallize during heating of the original high-melting crystallites is minimal, if not zero, and the highest melting peak is absent. A double melting peak endotherm is observed, the appearance of which is more sensitive to crystallization time due to the excessively slow isothermal crystallization kinetics, and the processes of primary and secondary crystallization can be resolved.

The results of previous studies [16, 17] on the crystallization kinetics of P*S*ECH, P*R*ECH and the equimolar blend have conferred strong support to the premise of a stereoselective mechanism active at the lamellar growth front in the blend, i.e., a rejection of opposite-sense chains from a specific enantiomer lamella. Investigation into the spherulite surface morphology provided unequivocal evidence that *R* and *S* chains of the equimolar blend do not form spherulites of *R* and spherulites of *S*, respectively, during isothermal crystallization [17]. Therefore, at the lamellar level the equimolar polyenantiomer blend and either of the pure polyenantiomer component systems are quite similar. Since the melting-recrystallization which occurs during the thermal analysis scan occurs at the lamellar level, then the thermal profile of the blends would be similar to that of the pure enantiomers. This is demonstrated in Fig. 3 where a change in heating rate effects very similar responses to the appearance of the triple melting endotherms of the P*S*ECH and the blend samples.

Ultimately, the observed differences in the overall bulk crystallization kinetics among all of the PECH polymers are related to their structural differences; namely, the enantiomorphic relationship between the components in the equimolar polyenantiomer blend, and to the nature of the inherent defect sites which covalently link the chain segments of opposite sense in the stereoblock polymer chain. The proposed increase in branching of the dominant lamellar framework in the *i*-P*RS*ECH stereoblock relative to the other polymers may be attributed to the chemical nature of the chain. Specifically, during isothermal crystallization, an opposite-sense stereosegment of the chain, introduced by a defect site, may present a less crystallizable entity and consequently be rejected from the main crystallite growth front, thus enhancing the formation of subsidiary lamellae.

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