

Infra-red spectroscopic investigation of bulk-crystallized *trans*-1,4-polyisoprene

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Crystallization from the melt of *trans*-1,4-polyisoprene was followed using Fourier-transform infra-red spectroscopy. The spectral subtraction factor *versus* time was obtained at the crystallization temperature and after cooling to 25°C for fractions and for the parent material. Crystallization of the β crystal form was followed at 36 and 43°C and of the α form at 43 and 51°C. Samples crystallized at 25°C and subsequently annealed at 43°C were also monitored. The amorphous fraction for pre-nucleated melt-crystallized α -form-containing samples increased with molecular weight at the crystallization temperature and after cooling to 25°C. Samples containing the β crystal form showed a molecular-weight dependence at a crystallization/annealing temperature of 43°C that disappears upon cooling the sample to 25°C. The results are discussed in terms of lamellar surface disorder and lamellar thickness distribution.

(Keywords: polyisoprene; crystallization; infra-red spectroscopy; molecular-weight effect)

INTRODUCTION

Many flexible-chain polymers crystallize to form single lamellae or lamellar aggregates with dimensions that depend on the molecular weight and crystallization conditions^{1,2}. Associated with the crystalline stems in the lamella is an amorphous component, which can include chain folds, chain ends and interlamellar traverses^{3,4}. During crystallization, two phenomena, molecular segregation and lamellar thickening, are believed to occur depending on the molecular weight, molecular-weight distribution and crystallization conditions, and can lead to different lamellar thickness distributions^{4,5}. Upon heating or cooling an isothermally crystallized sample, additional crystallization can take place^{1,5}. Possible sites for this additional process include the lamellar surfaces and any segregated amorphous component present. Further investigation of crystallization, especially in bulk systems, is necessary for a complete understanding of these various effects.

The infra-red spectra of various quiescently crystallized flexible-chain polymers have been shown, using spectral subtraction techniques, to be principally a composite of the amorphous spectrum, as obtained for a melted sample, and a spectrum containing many relatively sharp bands and characteristic of the crystal form(s) present⁶. By using a conformationally independent band and spectral subtraction, the amounts of amorphous and crystalline components have been quantitatively determined⁷. It should also be possible to follow the effects of thermal history on the crystalline/amorphous content by simultaneously recording the infra-red spectrum; this should allow a separation of the effects of isothermal crystallization from the melt and post-crystallization thermal treatments.

For the polymer used in the current study, *trans*-1,4-polyisoprene (TPI), two crystal forms, orthorhombic (β) and monoclinic (α), which can exist simultaneously, have been identified^{8,9}. Fourier-transform infra-red spectra (*FTi.r.*) have been obtained for solution-crystallized specimens from -145°C to the melting point. The absorbance area for the C=C stretching band at 1650–1665 cm⁻¹ was found to be the same, within experimental error, for solution-crystallized samples at 25°C and above the melting point⁷. This suggests that this band is conformationally independent, allowing its use for determination of the crystalline/amorphous content. The effects of molecular weight and crystallization temperature on the crystalline/amorphous content for TPI crystallized from solution have been studied using density, *FTi.r.* and surface reaction/¹³C n.m.r. techniques^{10,11}. The crystallinity, detected by dilatometry, for unfractionated TPI resulting from bulk crystallization at various temperatures has been reported¹².

In the work to be presented below, *FTi.r.* was used to monitor the crystalline/amorphous content of thin TPI samples during isothermal melt crystallization and annealing treatment and after post-crystallization cooling to room temperature. An unfractionated sample of TPI and various fractions therefrom were used. Conditions were such that only one crystal form, either α or β , was detected. The effect of molecular weight on the crystalline/amorphous content was found to depend on the crystal form/morphology, the crystallization temperature and the thermal history. The results are discussed in terms of lamellar surface disorder and lamellar thickness distribution. The spectra subtraction method apparently failed for samples monitored after short annealing times at 43°C and having low apparent crystallinities.

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EXPERIMENTAL

Synthetic (99%) *trans*-1,4-polyisoprene (TPI) with $M_w = 2 \times 10^5$ and $M_n = 4 \times 10^4$ was used as the unfractionated sample. Fractions from this material with 100% *trans* content were obtained using a toluene solution/methanol precipitation system¹¹; M_v for the fractions employed were found to be 8.3×10^4 , 2.8×10^5 , 4.9×10^5 and 6.1×10^5 from viscosity measurements using toluene solutions.

All polymer samples used for melt crystallization experiments were first crystallized from hexane solution at 25°C in the presence of 0.2% dissolved antioxidant; mats were obtained by filtration, washing and drying. Melt-crystallized films were prepared from these mats using various thermal histories. In one procedure the solution-crystallized mat was heated for 1 h at 75°C between NaCl plates in a thermostated FTi.r. heating cell in the spectrometer and then cooled to 25, 36 or 43°C. In another procedure samples prepared at 25°C were subsequently annealed in the heating cell at 43°C. In a third procedure crystal mats under vacuum were heated to 90°C for 1 h followed by residence in a constant-temperature bath at 55°C for a 2-week period; these were cooled to room temperature and then heated in the FTi.r. cell to 65°C followed immediately by crystallization in the cell at either 43 or 51°C. For all of the above preparations, when the FTi.r. spectrum showed no further change with time, the samples were cooled to 25°C.

Spectroscopic measurements were carried out using a Digilab FTS40 Fourier-transform infra-red spectrometer at 4 cm⁻¹ resolution at frequencies from 500 to 4000 cm⁻¹. The crystal form was identified and the crystallinity determined from the infra-red spectrum^{7,13}. Two infra-red methods, used previously with solution-crystallized polydiene samples, were employed to determine the crystallinity. Both methods depend on subtraction of an amorphous spectrum taken at 60°C from the spectrum for the semicrystalline sample taken

at either the crystallization temperature or at 25°C. In one method, the subtraction factor, the fraction of total spectrum intensity needed to remove the amorphous component, is used to obtain the crystalline and amorphous fractions¹³. In the other method the absorbance of the C=C stretching band at 1660–1670 cm⁻¹ is measured for the semicrystalline specimen before and after subtraction of the amorphous component⁷.

To obtain melting temperatures, differential scanning calorimetry measurements were made on 3–5 mg samples with a Du Pont 1090 thermal analyser at 10°C min⁻¹. An indium standard was used for calibration.

RESULTS

Infra-red spectra at 25°C for two 43°C melt-crystallized samples of the same TPI fraction are given in Figure 1. Spectrum (b) is characteristic of a composite of amorphous and β crystalline forms. Spectrum (a) was obtained for a sample with a different precrystallization history and is characteristic of a composite of amorphous and α crystalline forms. These spectra contain the same number of bands at peak frequencies within 1 cm⁻¹ as found for solution-crystallized samples containing the same crystalline form⁷. However, relative intensity differences in some bands occur between solution- and melt-crystallized samples because of crystallinity differences. The band at 1660–1670 cm⁻¹, used previously to determine the crystallinity of solution-crystallized TPI samples, was found in this study of melt-crystallized specimens to remain constant in area at temperatures from 25 to 65°C. Absorbances for the 1660–1670 cm⁻¹ band were the same at 0 and 25°C.

FTi.r. spectra were taken as a function of time after cooling from the melt at 75°C to constant crystallization temperatures of 43 and 36°C for unfractionated and fractionated TPI. Upon reaching the crystallization

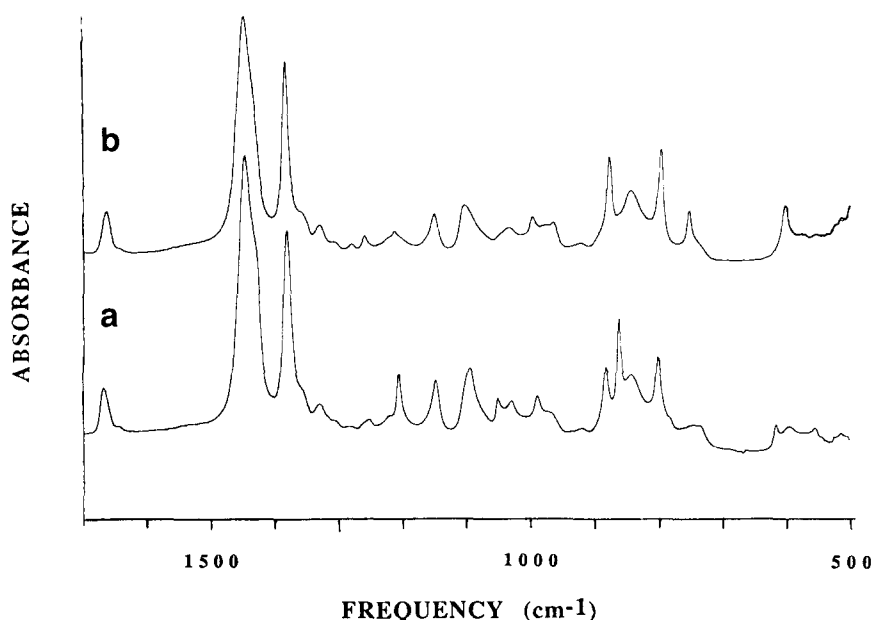


Figure 1 FTi.r. spectra at 25°C for TPI ($M_v = 610000$) bulk-crystallized at 43°C: (a) pretreated by cooling from 90°C to 55°C for 2 weeks followed by cooling to 25°C and heating to 65°C; (b) by cooling from 75°C

temperature of 43°C, the FTi.r. spectrum is the same as that observed at 60°C for an amorphous sample. Sharp bands, characteristic of the β crystal form, appeared at later times superimposed on the amorphous spectrum. Computer subtraction of the amorphous component was carried out for each spectrum. As time elapsed, the band at 876 cm^{-1} , characteristic of the β crystal form, increased in intensity and the amorphous band at 842 cm^{-1} decreased; the rate of these changes decreased with time, becoming zero. The band at 1665–1670 cm^{-1} remained constant in absorbance as the crystallization progressed. Successful subtraction implies that the system is composed of only two components and therefore the computer subtraction factor at each time could be taken as the amorphous melt-like fraction¹³. When the crystallization temperature is 36°C, the β crystal form is evident immediately. Subtraction factors as a function of time at 43 and 36°C are given in Figures 2 and 3, respectively. To test the completeness of the crystallization, additional experiments were carried out using samples melted and cooled under vacuum outside the spectrometer to either 36 or 43°C for time periods of 4 and 10 days (36°C) and 5, 10 and 20 days (43°C). No changes in the spectra were observed with time. There are no clear trends in the final values of the subtraction factor for 16 of the 18 samples studied in the FTi.r. cell (see Figures 2 and 3). The average deviation, ± 0.01 , is within the experimental uncertainty. The final values of the subtraction factor for the samples having $M_v = 6.1 \times 10^5$ crystallized at 43°C are significantly larger than all the others. After cooling all samples to 25°C, the subtraction factor decreased to 0.61 ± 0.02 for samples crystallized at 36°C and 0.60 ± 0.01 for all samples

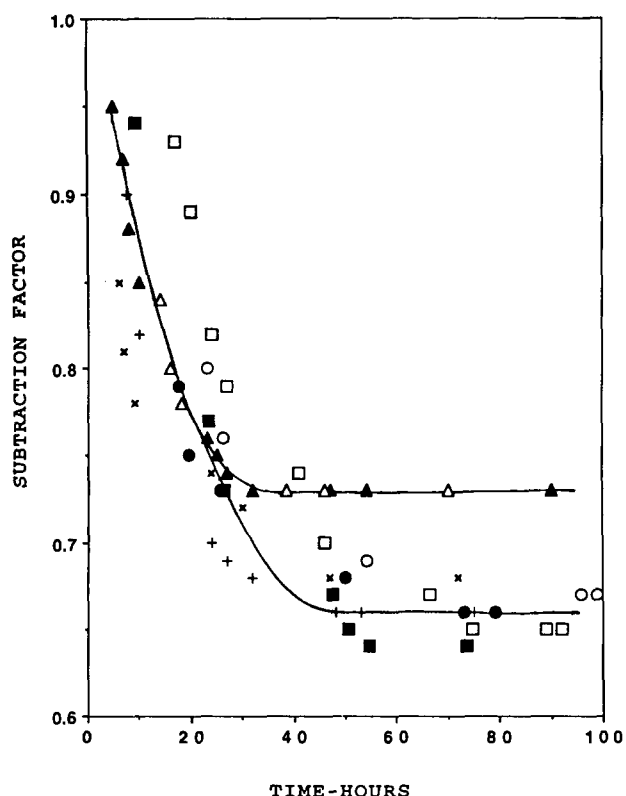


Figure 2 FTi.r. subtraction factor vs. time for TPI bulk-crystallized at 43°C after cooling from 75°C: (O, ●) unfractionated; (+, x) $M_v = 83\,000$; (□, ■) $M_v = 280\,000$; (Δ, ▲) $M_v = 610\,000$

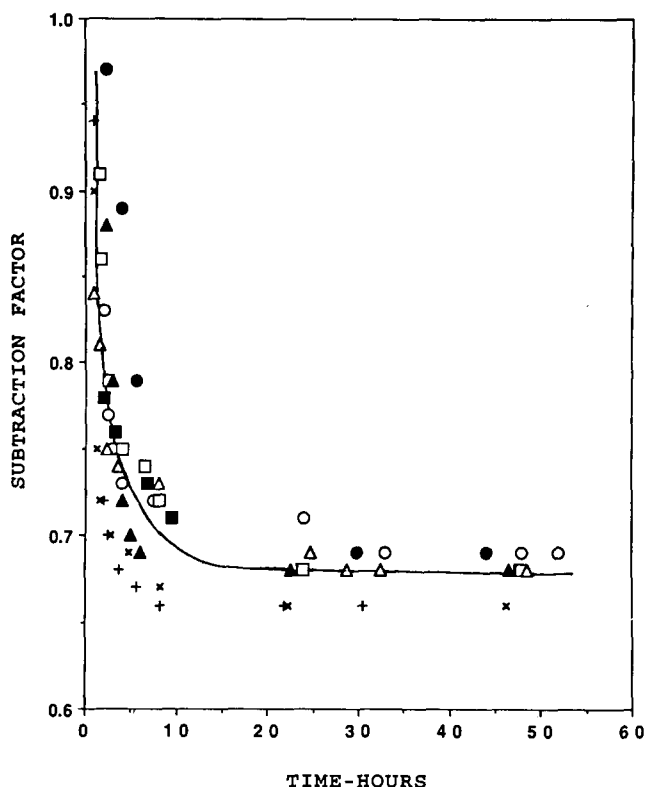


Figure 3 FTi.r. subtraction factor vs. time for TPI bulk-crystallized at 36°C after cooling from 75°C (symbols as in Figure 2)

crystallized at 43°C. Samples crystallized by cooling directly to 25°C from 75°C had values of 0.66. Using the conformationally independent band at 1665 cm^{-1} , an absorbance ratio for the crystalline part (A_c) to the total band (A_t) at 25°C for many of the samples crystallized at 43 and 36°C was obtained from the computer. Amorphous fractions ($1 - A_c/A_t$) obtained from the absorbance were all lower than the subtraction factors by 0.03–0.06 units. Correction of the subtraction factor for the increase in the number of absorbers present in the beam, caused by the crystallization and cooling processes, was made by multiplying by the ratio of the amorphous density at 60°C to the sample density at 25°C. This correction yielded values for the subtraction factor at 25°C in agreement with $1 - A_c/A_t$ within ± 0.02 units.

When samples crystallized from the melt at 25°C are heated to 43°C (the d.s.c. melting temperature), the band at 876 cm^{-1} , characteristic of the β crystal form, decrease markedly in intensity, almost disappearing completely; after an hour this band increases in absorbance with time. Subtracted spectra for these samples at various times are given in Figure 4. Particularly at times between 1 and 7 h these spectra are not the same as those obtained at long annealing times or those obtained for 25, 36 and 43°C crystallized samples. The more obvious differences in the spectra are an additional band at 840 cm^{-1} and a lowering of the intensity of the 962 cm^{-1} band (the 840 and 962 cm^{-1} bands are marked with arrows in Figure 4). The subtraction factor versus time for 43°C annealed samples is given in Figure 5. The final values depend on molecular weight, with the unfractionated and the highest-molecular-weight samples having about the same factors, which are higher than those for the other two samples. Upon cooling to 25°C, all four samples attain the same value, 0.60 ± 0.01 . Correction of this for

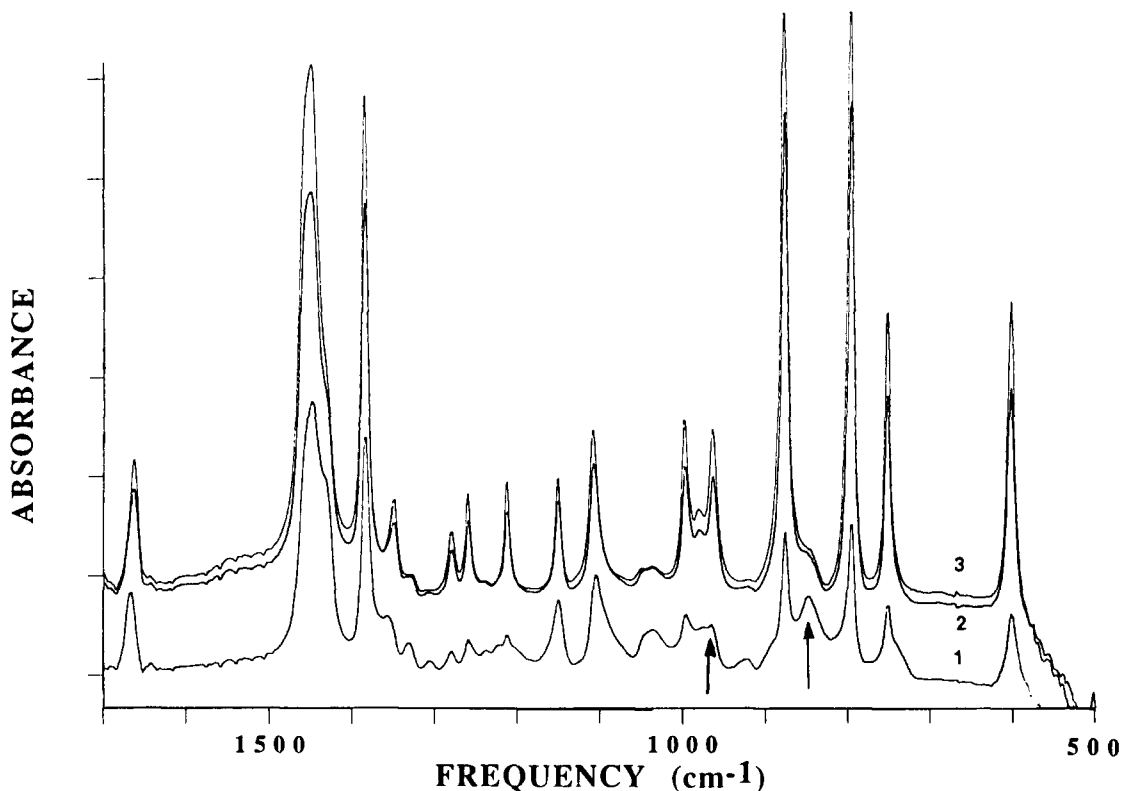


Figure 4 FTIR spectra after subtraction (using an amorphous spectrum taken at 60°C) for TPI heated to 75°C, bulk-crystallized at 25°C and then heated to 43°C: (1) for 1 h; (2) for 7.3 h; and (3) for 58 h. (Arrows mark the bands at 840 and 962 cm⁻¹)

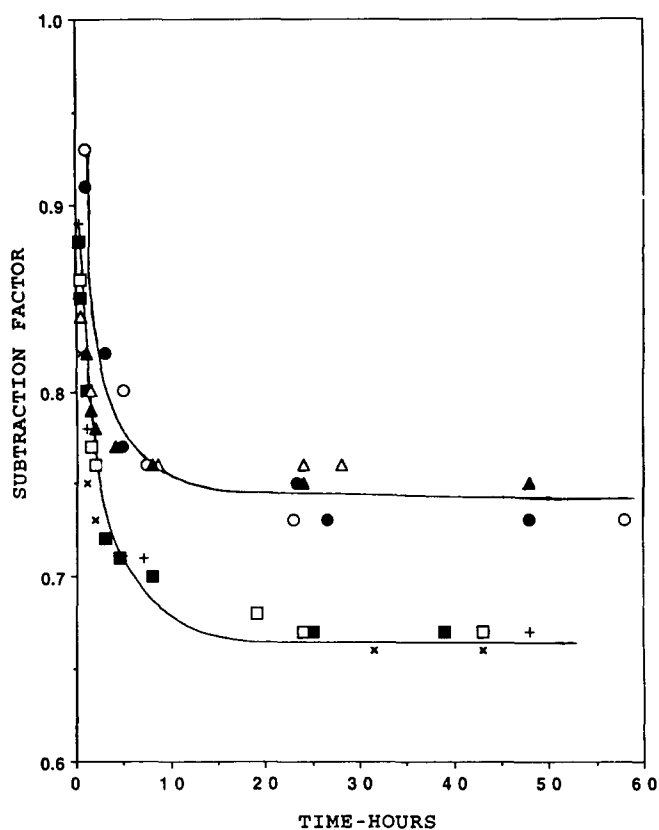


Figure 5 FTIR subtraction factor vs. time for TPI heated to 75°C, bulk-crystallized at 25°C and then heated to 43°C (symbols as in Figure 2)

the number of scatterers present gives a value of 0.56 ± 0.01 , in agreement with that of 0.57 ± 0.01 from the absorbance ratio. When each of these samples is heated to 43°C a second time, the amorphous fraction increases to the final subtraction factors observed at the

end of the initial annealing period. Additional measurements using a specimen with $M_v = 4.9 \times 10^5$ were obtained, with the results agreeing within experimental error at $T_a = 43^\circ\text{C}$ and after cooling to 25°C with those for the unfractionated and $M_v = 6.1 \times 10^5$ specimen.

To obtain TPI samples containing the α crystal form a pre-nucleation technique was used. Subtraction factor-time curves for samples crystallized at 43 and 51°C are given in Figures 6 and 7. The slopes of these curves taken at 51°C vary with the molecular weight. The final values observed depend on molecular weight, the subtraction factor increasing with increasing molecular weight at both temperatures. Cooling to room temperature is accompanied by a decrease in subtraction factor.

Corrected final subtraction factors (amorphous fraction) at the crystallization or annealing temperature (T_c and T_a , respectively) are given in Table 1. The corrected amorphous fractions at 25°C are given in Table 2. Each value given is an average for two samples. A comparison of amorphous fractions in Table 1 at the same T_c or T_a (43°C) shows some molecular-weight dependence, but with agreement in values at the lowest and highest molecular weights for the three types of samples. From the results given in Tables 1 and 2, it is found that upon cooling from T_c or T_a to 25°C the decrease in amorphous fraction observed varies from 0.05 to 0.16. The largest changes are exhibited by the fraction with the highest molecular weight crystallizing in the β form. The amorphous fraction at 25°C increases with molecular weight for the α -containing specimens but remains essentially constant within experimental error for the 43°C melt-crystallized and the 43°C annealed β samples.

D.s.c. measurements were carried out for most of the samples studied. Some representative scans are given in

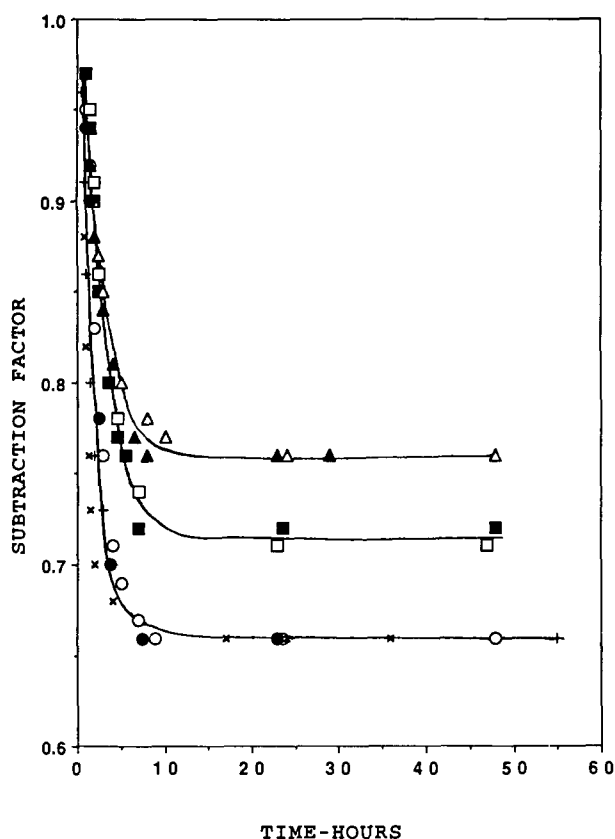


Figure 6 FTi.r. subtraction factor vs. time for TPI pretreated by cooling from 90°C to 55°C for 2 weeks followed by cooling to 25°C and heating to 65°C then crystallized at 43°C (symbols as in Figure 2)

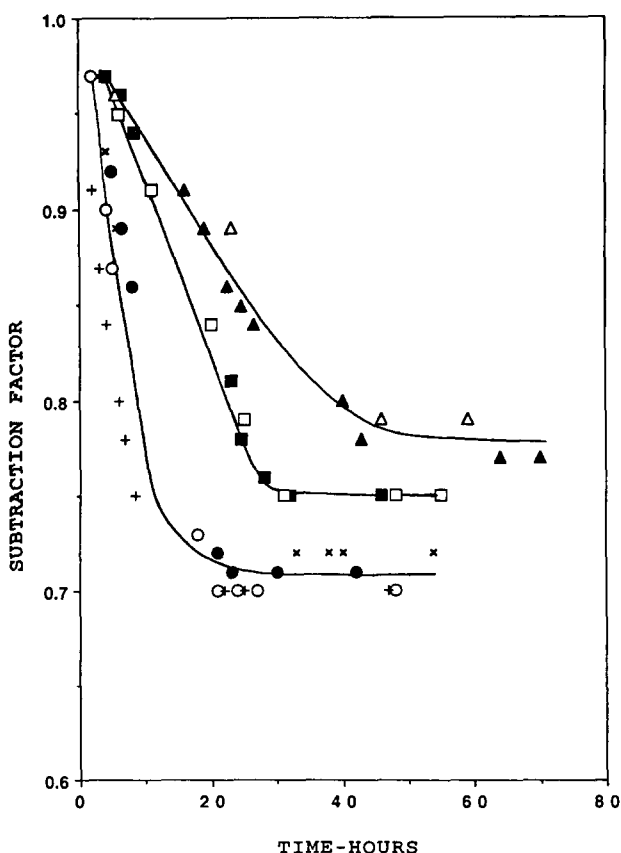


Figure 7 FTi.r. subtraction factor vs. time for TPI pretreated by the procedure in the legend for Figure 6 then crystallized at 51°C (symbols as in Figure 2)

Table 1 Corrected amorphous fractions at T_c

Sample	T_c or T_a (°C)	Amorphous fraction		
		Melt-cryst. β form	Prenucleated α form	Annealed β form
Unfract.	25	0.62	—	—
Unfract.	36	0.66	—	—
8.3×10^4		0.62	—	—
2.8×10^5		0.65	—	—
6.1×10^5		0.64	—	—
Unfract.	43	0.63	0.61	0.69
8.3×10^4		0.63	0.61	0.63
2.8×10^5		0.61	0.67	0.63
4.9×10^5		—	—	0.70
6.1×10^5		0.70	0.71	0.71
Unfract.	51	—	0.65	—
8.3×10^4		—	0.66	—
2.8×10^5		—	0.70	—
6.1×10^5		—	0.73	—

Table 2 Corrected amorphous fraction at 25°C

Sample	T_c or T_a (°C)	Amorphous fraction		
		Melt-cryst. β form	Prenucleated α form	Annealed β form
Unfract.	25	0.62	—	—
Unfract.	36	0.61	—	—
8.3×10^4		0.54	—	—
2.8×10^5		0.59	—	—
6.1×10^5		0.58	—	—
Unfract.	43	0.56	0.55	0.55
8.3×10^4		0.55	0.55	0.56
2.8×10^5		0.54	0.59	0.58
4.9×10^5		—	—	0.56
6.1×10^5		0.58	0.63	0.55
Unfract.	51	—	0.53	—
8.3×10^4		—	0.53	—
2.8×10^5		—	0.57	—
6.1×10^5		—	0.59	—

Table 3 T_m and T_{endo} for TPI samples^a

Sample (mol. wt)	T_c (°C)	T_m (°C)		T_{endo} (°C)	
		β	α	β	α
Unfract.	25	43	—	47	—
Unfract.	36	43	—	48	—
6.1×10^5		43	—	47	—
Unfract.	43	46	55	52	60
8.3×10^4		47	56	51	59
6.1×10^5		45	49	52	57
Unfract.	25/43 ^b	46	—	49	—
8.3×10^4		44	—	48	—
6.1×10^5		44	—	48	—
Unfract.	51	—	61	—	63
8.3×10^4		—	59	—	65
6.1×10^5		—	57	—	64

^aAverage of two or more determinations with a precision of $\pm 1^\circ\text{C}$

^bSample crystallized at 25°C, annealed at 43°C and cooled to 25°C

Figure 8. Single endotherms were observed for all samples but one. The exception was the low-molecular-weight α -containing sample crystallized at 43°C, which showed additional overlapping components at lower temperatures (see Figure 8). Melting and endotherm temperatures are given in Table 3; averages of two or more values

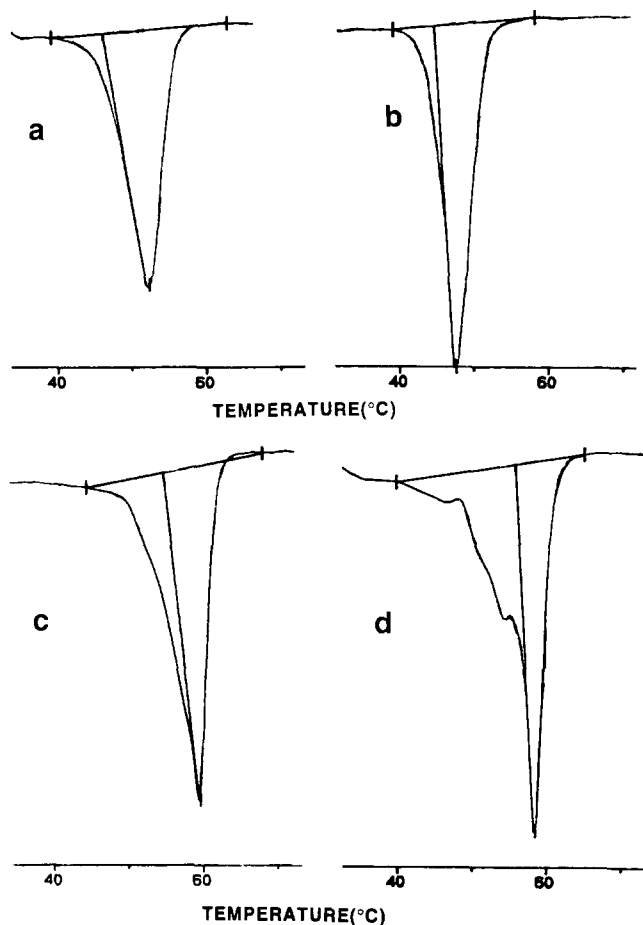


Figure 8 D.s.c. scans for melt-crystallized TPI: (a) β form crystallized at 43°C and cooled to 25°C, unfractionated sample; (b) β form crystallized at 25°C, heated to 43°C and cooled to 25°C, fraction with $M_n = 8.3 \times 10^4$; (c) α form crystallized at 43°C and cooled to 25°C, unfractionated sample; and (d) same as (c) except a fraction with $M_n = 8.3 \times 10^4$ used

were taken. The α -form-containing samples crystallized at 43°C show a significant decrease in T_m with increasing molecular weight.

DISCUSSION

An earlier investigation of crystallinity for solution-crystallized TPI showed a close agreement in values obtained from density measurements and from FTi.r. spectra, using the ratio of the absorbance of the 1665–1670 cm^{-1} double-bond stretching band after and before spectral subtraction of the amorphous component¹¹. In the present work the 1665–1670 cm^{-1} band was found to be conformation-independent from 0 to 65°C for melt-crystallized TPI samples. It was also found that the amorphous fractions obtained from the subtraction factor and absorbance methods, as described above, were in close agreement, provided a correction for a change in the number of absorbers is made in the former method. The subtraction factor method was used previously to find crystallinities of solution-crystallized *trans*-1,4-polybutadiene¹³. This method for determining crystalline or amorphous fractions should be applicable to any partially crystalline polymer that can be melted without decomposition. Neither the subtraction factor nor absorbance methods of determining amorphous fraction depend on a calibration. Use of either method does assume that the sample is a two-component system

with an amorphous part having the same conformational composition as that present in the melt.

In the present work the two-component assumption was found to be generally valid; subtraction of the amorphous component from spectra obtained after complete crystallization gave α or β crystal spectra identical to those for the subtracted spectrum from solution-crystallized samples. The two-component assumption does not appear to hold at short crystallization times for β TPI samples annealed near the melting point. The $\text{CH}_2\text{-CH}_2$ bond in amorphous TPI can take up either the *trans* or *gauche* conformation. The β and α crystal forms contain only *trans* CH_2CH_2 conformations^{8,9}: β TPI ($ST\bar{S}$ conformation) has an infra-red band at 877 cm^{-1} , assigned to the out-of-plane $=\text{C-H}$ vibration; α TPI ($CT\bar{S}CT\bar{S}$ conformation) exhibits a doublet at 862 and 882 cm^{-1} assigned to this vibration¹⁴. In amorphous TPI a broad band at 842 cm^{-1} with shoulders at 860 and 884 cm^{-1} are observed. The 842 cm^{-1} band has been attributed to the various conformations containing *gauche* $\text{CH}_2\text{-CH}_2$ bonds¹⁵. Therefore, the additional band at 840 cm^{-1} in the subtracted spectrum for 43°C annealed β TPI in the present work is believed to be indicative of an excess of *gauche* CH_2CH_2 conformations over those usually present in the amorphous component for TPI specimens. At latter times the excess of *gauche* CH_2CH_2 conformations in the annealed β samples is converted to *trans* and the extra spectral component after subtraction diminishes in relative intensity.

The FTi.r. subtraction factor *versus* time plot follows the conformational conversion from the amorphous state to a particular crystal form. The rate of this conversion is given by the slope of the plot. The appearance of these plots was found in this work to depend on the crystallization temperature, the method of crystal nucleation and in some cases the molecular weight. For all samples in either crystal form the higher-molecular-weight fraction has the largest amorphous fraction (corrected final subtraction factor) at 43°C. In light of the behaviour on cooling to 25°C and of the reversibility on reheating to 43°C, the higher amorphous fraction for the β samples at T_c is most likely caused by differences at the fold surface or in the amorphous interlamellar parts. The presence of a segregated low-molecular-weight amorphous component at the crystallization/annealing temperature for the higher-molecular-weight samples could also lead to a larger amorphous fraction for these. However, this presence would be expected in both of the unfractionated samples. Since the amorphous fractions for these two samples are clearly different (see Table 1), the presence of a segregated amorphous component is not considered likely. The molecular-weight dependence of the amorphous fraction for the α -containing samples at T_c is still apparent on cooling the samples to 25°C and, therefore, is possibly partially due to a different cause from that responsible for the differences with molecular weight for β form samples at T_c .

The effect of molecular weight on crystallinity at T_c and 25°C for narrow polyethylene fractions was reported on earlier¹⁶. At T_c the crystallinity becomes strongly molecular-weight-dependent at molecular weights between 10^5 and 10^6 and the increase in crystallinity on cooling to 25°C increases markedly in that range and above. The results of this investigation on melt-crystallized TPI are therefore generally consistent with

that work. The lamellar thickness distribution for polyethylene was investigated using transmission electron microscopy as a function of molecular weight and crystallization temperature¹⁷. This distribution was shown to be strongly dependent on these parameters for that polymer. However, to date, this type of study has not been carried out for TPI in either crystal form.

The appearance of single melting endotherms for bulk-crystallized TPI, observed for most samples in this study, is not in agreement with earlier work¹⁸. The single endotherms observed are a consequence of using isothermal crystallization conditions and only nucleating one form, α or β , in a particular crystallization. The increase in amorphous fraction with molecular weight for the α -containing samples melt crystallized at 43°C is accompanied by a 7°C decrease in melting temperature. The overlapping melting endotherms observed for the lowest-molecular-weight fraction crystallized at 43°C (see Figure 8) is indicative of the presence of more than one dominant lamellar thickness. For the α -containing samples crystallized at 51°C the amorphous fraction change with molecular weight is similar to those in samples crystallized at 43°C, but the melting behaviour is different; only one endotherm is present and there is no change of T_m with molecular weight within experimental uncertainty.

Of particular interest is that at 25°C the β -crystal-containing samples exhibit no clear dependence of amorphous fraction on molecular weight. Apparently all of these samples have similar lamellar thickness distributions. In agreement with this explanation the β -containing TPI samples prepared at 43°C have a T_m that is independent of molecular weight and thermal history within the experimental uncertainty.

The morphologies of the α - and β -crystal-containing specimens cooled to 25°C have been studied and are found to be different¹⁹. The α form yields spherulites while the β form gives sheaf-like and disordered structures. It is possible that these morphological differences are causing some of the observed changes of crystallinity with molecular weight.

FTi.r. crystallinities previously reported for both α and β solution-crystallized specimens of unfractionated TPI show an increase in amorphous fraction upon heating from 25 to 50°C and a decrease on cooling to -30°C¹⁵. The decrease in amorphous fraction taking place on cooling melt-crystallized TPI samples from T_c to 25°C is in general agreement with the increase in this parameter previously observed upon heating the dried solution-crystallized lamellar mats. During solution crystallization any completely amorphous chains present after the crystallization process at 30°C is over should have been removed in the extensive washing that preceded collection of the sample by filtration. Therefore the crystallinity increase observed on cooling those samples after drying must be due to fold or interlamellar traverse ordering. Fold surface ordering is therefore one possible cause of the crystallinity increase observed upon cooling melt-crystallized samples from T_c to 25°C. A segregated amorphous component at T_c could also crystallize on cooling to 25°C. The possible presence of a segregated amorphous component in melt-crystallized TPI samples at the crystallization temperature was discussed above and considered unlikely. Further evidence for the absence of an appreciable amount of segregated material is the observation of single melting endotherms for all β crystal

samples subsequently cooled to 25°C and for the α -containing samples crystallized at the highest temperature used (51°C). Lamellae resulting from crystallization of a segregated component would be expected to have a smaller thickness than that of the lamellae crystallizing at T_c , particularly for those crystallized at the highest T_c , and therefore to have a lower melting temperature. This would lead to two d.s.c. endotherms if the lamellar thicknesses of the two components are significantly different.

A comparison of the amorphous fraction for unfractionated β TPI crystallized from the melt with those obtained from solution crystallization without⁷ and with stirring²⁰ shows differences that can be related to the change in supercooling taking place. The degree of supercooling for melt-crystallized samples is $T_m^* - T_c$ and for solution-crystallized is $T_d^* - T_c$, where T_m^* is the equilibrium melting point and is taken as 83°C²¹ and T_d^* is the equilibrium dissolution temperature and is approximated by T_d found for stirrer-crystallized TPI²⁰. Amorphous fractions for stirrer-crystallized, quiescent solution-crystallized and melt-crystallized are 0.22, 0.39 and 0.56, while the supercoolings are 12, 28 and 40°C, respectively. As expected, an increase in amorphous fraction with increasing degree of supercooling is observed.

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