

Effects of temperature on the infra-red spectrum of partially crystalline *trans*-1,4-polyisoprene

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Fourier-transform infra-red spectra were taken for semicrystalline solution-crystallized *trans*-1,4-polyisoprene at various temperatures from -145°C to the melting temperature (60 – 65°C) and in the melt to 110°C . Changes were followed by use of difference spectra. A decrease in amorphous content with decreasing temperature down to about -30°C and an increase in this parameter with temperature to 60°C were followed quantitatively. Crystal-field splitting of a CH_2 scissoring band was observed at -145°C . Changes in conformationally sensitive amorphous bands at temperatures above 65°C were used for tentative assignment of components of these bands.

(Keywords: infra-red spectroscopy; *trans*-1,4-polyisoprene; polymer conformation; polymer crystallization)

INTRODUCTION

Lamellae and lamellar structures of *trans*-1,4-polyisoprene (TPI) crystallized from solution have been investigated recently using various techniques^{1–6}. Semicrystalline samples containing either an orthorhombic (β -form) crystal component⁷ or a monoclinic (α -form) crystal component⁸ have been characterized by Fourier-transform infra-red spectroscopy^{5,6}, density^{1,2}, solid-state ^{13}C nuclear magnetic resonance⁹, and reaction in suspension^{1–4,6}. The effects of molecular weight and crystallization conditions on the amorphous fraction, the average fold length and the crystalline stem length have been investigated⁴; the average fold length of 9 that is found suggests that tight adjacent folding does not occur in TPI lamellae. This is not a general result since similar studies on 99% *trans*-, 1% *cis*-1,4-polybutadiene lamellar structures give a minimum fold length of 5¹⁰. Further investigations of the amorphous component in TPI are therefore of interest.

The infra-red spectrum of TPI, crystallized from solution, has been obtained at room temperature and the 100% crystalline component obtained by subtraction of a spectrum taken on the melt⁵. This method was developed and applied to many semicrystalline polymers earlier¹¹. Single-chain normal-coordinate calculations have been carried out for both α - and β -TPI and band assignments made^{5,12} and a correlation between the two spectra given⁵. The amorphous spectrum of TPI has also been assigned by correlation of it with the 100% α - and β -form spectra⁵ and the effects of chemical reactions at the lamellar surfaces on the infra-red spectrum at room temperature investigated⁶.

In the present work Fourier-transform infra-red spectroscopy is employed to investigate solution-crystallized TPI at various temperatures over the -145 to 110°C

range. Some of the changes that occur are best followed by difference spectroscopy and are explained in terms of conformational conversions and changes in amorphous content, respectively.

EXPERIMENTAL

Unfractionated synthetic *trans*-1,4-polyisoprene (Polysciences Inc.) was crystallized from 1% amyl acetate solution by precipitation at 0°C and slow heating in the crystallization liquid to 30°C , yielding stacks of curved semicrystalline lamellae with the crystalline portions in the β -form. Semicrystalline samples with the crystalline component in the α -form were obtained from the same material by cooling a 1% amyl acetate solution directly to 30°C . All samples were washed with fresh amyl acetate and mats formed by filtration using Teflon filters followed by drying at room temperature.

Infra-red measurements were made using a Digilab FTS 40 Fourier-transform infra-red spectrometer at 4 cm^{-1} resolution from 500 to 4000 cm^{-1} at various temperatures from -145 to 110°C . Measurements below room temperature were made while cooling and then upon reheating to room temperature; the cooling process took 2.5 h for a 170°C temperature change. Measurements above room temperature were made using a thermostatted heating cell.

RESULTS

Infra-red spectra taken in the 700 to 1700 cm^{-1} region at room temperature and at -145°C for semicrystalline TPI, containing an all α -form crystalline phase, are given in *Figure 1*. Spectra obtained at the same two temperatures for another semicrystalline sample with an all β -form crystalline phase are shown in *Figure 2*. For samples containing either the α - or β -crystalline form many of the bands increase in height with decreasing temperature.

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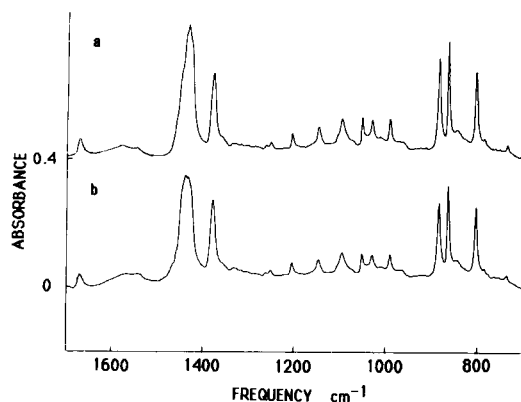


Figure 1 Infra-red spectra for solution-crystallized α -form-containing *trans*-1,4-polyisoprene from 700 to 1700 cm^{-1} : (a) at -145°C and (b) at 25°C

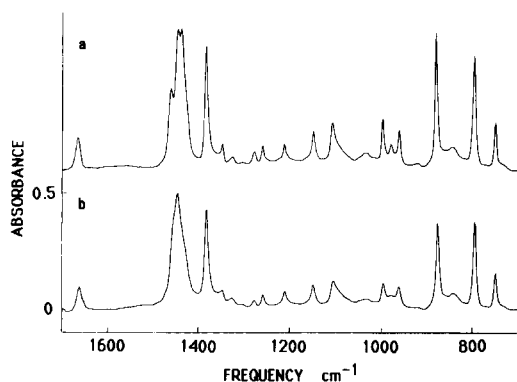


Figure 2 Infra-red spectra for solution-crystallized β -form-containing *trans*-1,4-polyisoprene from 700 to 1700 cm^{-1} : (a) at -145°C and (b) at 25°C

The low-temperature spectrum for the β -TPI-containing sample shows a splitting of the band at 1447 cm^{-1} with a shoulder at 1455 cm^{-1} into a doublet at $1439/1447\text{ cm}^{-1}$ and an overlapping singlet at 1462 cm^{-1} . For the β -form sample non-symmetrical narrowing of 11 cm^{-1} for the band at 1105 cm^{-1} and of 3 cm^{-1} for the bands at 997 , 978 , 962 cm^{-1} and a frequency change of $+4\text{ cm}^{-1}$ for the 877 cm^{-1} band are observed. A narrowing of the band for the α -form sample at 1030 cm^{-1} by 3 cm^{-1} occurs.

The changes with temperature taking place in the spectrum for a particular sample can best be seen if difference spectra are used. Difference spectra for semi-crystalline TPI containing the β -crystalline form, obtained in each case by subtracting the room-temperature spectrum from that at a particular temperature between room temperature and -145°C , are shown in Figure 3. Some sharp negative changes closely associated in frequency with sharp positive changes are observed in this figure along with increases in the heights of all bands originally present with decreasing temperature. The negative/positive changes are caused by the frequency shifts with or without narrowing from one side of the band only, as noted above. A symmetrical band narrowing would appear as a negative/positive/negative effect. Many of these changes appear in the portions of the spectra associated with the crystalline component

Partial subtraction of a spectrum taken for an amorphous TPI sample in the melt from each of those obtained in the -145 to 60°C region was carried out in order to

remove the contribution of the amorphous component in the semicrystalline sample spectrum and to yield a spectrum characteristic of the crystal form present only. This subtraction was successful for spectra taken at all temperatures except those below -120°C . Small broad bands are present in the subtracted spectrum taken below -120°C not found in those taken at higher temperatures. The subtraction factor necessary to remove successfully the amorphous component upon cooling a β -form-containing sample changed from 0.31 at room temperature to 0.24 at -28°C and then remained at 0.24–0.25 down to -120°C ; when this sample was heated a subtraction factor of 0.28 at 23°C was necessary. For an α -form-containing sample the subtraction factor decreased from 0.17 at 28°C to 0.13 at -22°C and remained at this value down to -110°C ; upon heating, the factor at -21°C was 0.13 and at 25°C it was 0.16. Heating a β -form-containing sample to 60°C from 25°C in one of two different runs caused an increase in the subtraction factor from 0.97 to 1.53. Amorphous fractions were calculated from the subtraction factors on an absolute basis by using the room-temperature crystallinity values from infra-red spectroscopy, obtained earlier⁶. The amorphous fraction is plotted vs. temperature for α - and β -form-containing samples in Figure 4. An increase in amorphous fraction with increasing temperature commences at about -30°C for both types of sample.

Heating a partially crystalline TPI sample from room temperature to the melting temperature (60 – 65°C) leads to the loss of the sharp crystalline bands and the retention of the superimposed broad amorphous bands. Spectra obtained at 65 and 110°C from 500 to 1300 cm^{-1} are given in Figure 5; decreases in band intensities are observed upon heating above T_m with the magnitude of this depending on the band. The detailed changes taking place upon heating the melt can best be followed by a difference spectrum, as given in Figure 6. Minima in this spectrum are observed at 740 , 800 , 844 , 862 , 882 , 972 , 988 , $1030/1050$, $1090/1105$, 1148 and $1202/1220/1235$. These minima do not all occur at a frequency that corresponds to a band maximum; many of them take place within a complex band contour (compare Figures 5 and 6). Using different reference temperatures, 65 and 70°C , it can be seen that some of these changes are not gradual but take place just above T_m . The components of conformationally

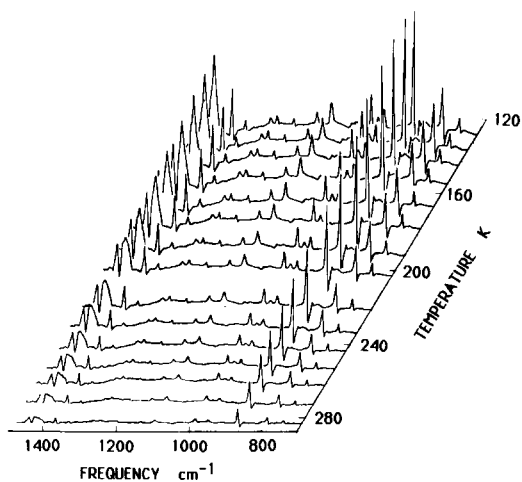


Figure 3 Difference spectra for solution-crystallized β -form-containing *trans*-1,4-polyisoprene from 700 to 1500 cm^{-1} . Absorbance spectrum taken at temperature T minus spectrum taken at 25°C

dependent bands at 800–810, 840–890, 970–985, 1100–1105 and 1200–1235 cm^{-1} are listed and identified in Table 1. The most intense band component is marked with an asterisk. The conformational assignments given in this table will be discussed below in more detail. Deconvolution of three of the above bands in the 65 and

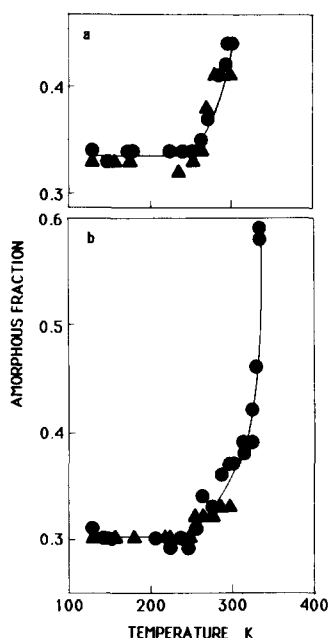


Figure 4 Amorphous fraction vs. temperature from infra-red spectra for solution-crystallized *trans*-1,4-polyisoprene: (a) α -form-containing sample, (●) cooling, (▲) heating; (b) β -form-containing sample, (●) cooling and heating from 25°C, (▲) heating to 25°C

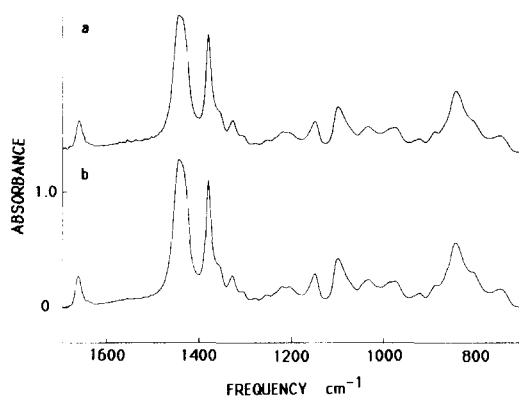


Figure 5 Infra-red spectra from 700 to 1700 cm^{-1} for *trans*-1,4-polyisoprene in the melt: (a) 110°C, (b) 65°C

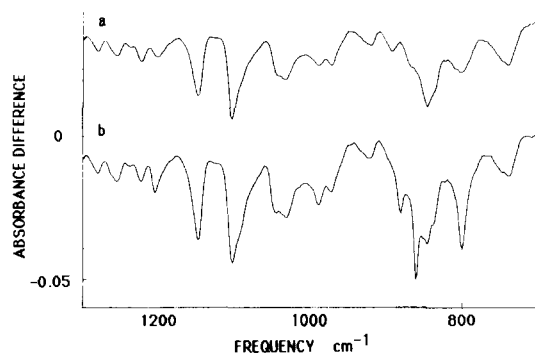


Figure 6 Difference spectra from 700 to 1300 cm^{-1} for *trans*-1,4-polyisoprene in the melt: (a) spectrum obtained at 110°C minus spectrum obtained at 70°C; (b) spectrum obtained at 110°C minus spectrum obtained at 65°C

Table 1 Infra-red frequencies and band component assignments for *trans*-1,4-polyisoprene in the melt

Absorbance spectra frequencies (cm^{-1})	Difference spectra ^a frequencies (cm^{-1})		Conformational assignment
	Ref. temp. 65°C	Ref. temp. 70°C	
800	800	800 808	<i>trans</i> <i>gauche</i>
840*	824 838 844	824 838*	<i>cis/gauche</i> <i>gauche</i> <i>gauche</i>
860	862*	—	<i>trans</i>
887	882	868 890	<i>trans</i> <i>trans</i>
972*	972	972	<i>gauche</i>
984	988*	988	<i>trans</i>
1099	1090 1105*	1090 1105*	<i>gauche</i> <i>trans</i>
1204	1204*	1202	<i>trans</i>
1220	1220	1220*	<i>gauche</i>
1235	1235	1235	

* Denotes largest component of a band

^a Difference spectra were obtained by subtracting the spectrum taken at the reference temperature from the spectrum taken at 110°C

110°C spectra was carried out and the frequencies found to be: (i) 827, 842, 868, 890, (ii) 958, 972, 987 and (iii) 1205, 1220, 1235 cm^{-1} .

DISCUSSION

The infra-red spectrum for semicrystalline TPI obtained from solution is composed of relatively sharp bands characteristic of the crystalline component overlapping with broader bands due to the amorphous component, the latter appearing as in the spectrum taken just above the melting point⁵. The 100% crystalline spectrum that results depends on the crystalline form present; all bands appearing can be explained using single-chain normal-coordinate analysis⁵. It is therefore assumed that the amorphous component in partially crystalline TPI has the same conformational distribution as found just above the melting point. The appearance of sharp bands for the crystalline component is a consequence of the restrictions on the C–C bond conformations which can be *cis* (C), *gauche* (G), *skew* (S) or *trans* (T). For the CH_2 – CH_2 bond in *trans*-1,4-polyisoprene either the *gauche* or *trans* conformations are probable. For α -TPI a $CTSC\bar{T}\bar{S}$ conformational sequence is present and for β -TPI the sequence is $ST\bar{S}$ with the CH_2 – CH_2 bond in the *trans* (T) conformation. For amorphous TPI more than one energetically allowed single-bond conformation is possible¹³. These include the extended conformations (T) which are the most probable: STS , $ST\bar{S}$, CTS , $\bar{S}T\bar{S}$, $\bar{S}T\bar{S}$ and $CT\bar{S}$; the less probable folded conformations (G); SGS , $\bar{S}GS$, $SG\bar{S}$, $\bar{S}G\bar{S}$, $\bar{S}G\bar{S}$, $\bar{S}G\bar{S}$ and $\bar{S}G\bar{S}$; and the least probable folded conformations: CGS , $CG\bar{S}$, $CG\bar{S}$ and $C\bar{G}\bar{S}$. It is expected that changes in temperature above the glass transition temperature ($\sim -65^\circ\text{C}$) will lead to conformational changes in amorphous TPI with lower temperatures favouring the more probable conformations. In chain-folded lamellae, as in bulk amorphous material, conformations containing *gauche* units must be present even at low temperatures.

In the present work changes in both amorphous and crystalline infra-red spectral bands with temperature were observed. The changes in the amorphous bands can be summarized as follows: (i) a proportional decrease in band intensities upon cooling from room temperature to about -30°C and an increase upon heating to 60°C ; (ii) no change between about -30 and -120°C ; (iii) the appearance of additional weak band components from -120 to -145°C ; and (iv) decreases in intensity with heating the melt from 65 to 110°C ; these latter changes depend on the frequency and do not necessarily involve a complete band.

In the present work the proportional changes in all of the amorphous bands ((i) above) are interpreted quantitatively in terms of changes in the amorphous content with temperature using the multiplication factor necessary to remove the amorphous portion from the total spectrum at any given temperature. This is then expressed in terms of the amorphous content by using the crystallinity obtained at room temperature with a subtraction of the amorphous contribution to the mixed mode attributed to $\text{C}=\text{C}$ stretching⁶. The β -TPI structures used in this work are stacks of curved lamellae (see figure 4 of ref. 4). For fractions crystallized in the same way average non-crystalline traverse lengths (folds and intermolecular traverses) of 8 to 11, depending on molecular weight, were found⁴. Since single β -TPI lamellae contain folds with average lengths of 8–9 monomer units, the amorphous chain units in the curved lamellae structures are principally in the chain folds. This, of course, assumes that no adsorbed non-crystalline material is present in these structures at room temperature. The intensity changes observed by FTi.r. for both α - and β -TPI suggest that, as the temperature decreases from 30 to -30°C , an increase of ~ 2 monomer units per crystal traverse occurs in the number having the conformation characteristic of the crystal form present. This increase is accompanied by a decrease in the number of units having all other conformations found in the amorphous chain-fold regions and should result in a tighter, more ordered, fold. In modelling the fold the amorphous segments nearest the crystal stems are expected to be in an extended conformation (CTS or STS) different from that for the crystal stem units¹⁴. Assumption of the crystal conformation by units on adjacent chain segments in the folds would lead to a lower energy for these units due to interchain interactions. If the amorphous units nearest the crystal stem change to and remain in the crystal conformation, an overall decrease in the number of monomer units per fold with a similar increase in the number of monomer units in the crystal stem would result. The FTi.r. results suggest that these conformational transitions, wherever they occur in the chain, are reversed upon reversing the temperature change and cease about 40°C above the glass transition temperature for bulk material.

Upon heating β -TPI from -30 to 60°C an increase in amorphous content occurs. This type of change, referred to as premelting, has been observed for melt-crystallized polyethylene^{15,16}. The increase in amorphous content for polyethylene was found by low-angle X-ray scattering to be accompanied by first a decrease in the average crystal stem length and then, close to the melting point, an increase in this parameter while the thickness of the amorphous and the 'transition' layers increased over the whole temperature range¹⁵. The decrease in the average

crystal stem length with increasing temperature suggests a fold-surface melting phenomenon and supports the supposition above that the conformational changes occurring in TPI as observed by FTi.r. are taking place at the fold/crystal stem interface. Crystallite melting starting at the sides as well as that at the fold surfaces could also occur, particularly at higher temperatures. However, the reverse process is not taking place in TPI below 25°C unless adsorbed amorphous chains are present.

In previous work the fraction of monomer units at the lamellar surfaces was determined by epoxidation in *n*-butanol suspension at 0°C , followed by ^{13}C n.m.r. in solution⁴. The fraction epoxidized was found to agree within experimental error with the non-crystalline fractions at 25°C , as obtained from density and from infra-red measurements on dried samples. In making this comparison it was assumed that the crystallinity did not change for dried samples in the temperature range from 25 to 0°C or upon resuspension in *n*-butanol. The present results show that the first assumption is not correct.

The specific decreases in intensity of components of complex amorphous bands that occur upon heating the melt can be explained in terms of *trans* to *gauche* conformational changes in the $\text{CH}_2\text{-CH}_2$ sequences and therefore allow tentative assignment of portions of a complex band contour to such conformations. Vibrational mode assignments for the amorphous spectrum of TPI were made earlier on the basis of overlap with crystalline bands identified using single-chain normal-coordinate analysis⁵. Some modes were assigned more than one frequency and are therefore expected to be conformationally dependent. These include the $=\text{CH}$ out-of-plane bending mode with at least three components at 842 , 860 and 884 cm^{-1} and the $=\text{CH}$ in-plane bending mode with at least two components at 1205 and 1220 cm^{-1} . The asymmetric band at 1099 cm^{-1} and the shoulder at 800 cm^{-1} also appear from the present work to be conformationally sensitive. Furthermore, the two bands at 976 and 987 cm^{-1} , previously assigned to two different modes¹, are now believed to be components of the same CH_3 rocking mode. In making conformational assignments to components of an amorphous band contour, it is expected that those parts associated with *trans* conformations of the $\text{CH}_2\text{-CH}_2$ sequence will have frequencies close to those found for the two crystalline forms. These should also show larger decreases with increasing temperature directly above the melting point. The various components of the amorphous bands for TPI, as assigned in this work, are listed in Table 1. These are categorized into the three groups as discussed above: those identified with the various CTS or STS conformations (*trans*), those identified with SGS conformations (*gauche*) and in one case that identified with CGS conformation. Deconvolution of the components in the amorphous bands at $840\text{--}890$, $970\text{--}990$ and $1205\text{--}1235\text{ cm}^{-1}$ yielded frequencies in agreement with those given in Table 1. The intensity shifts occurring in the $1664\text{--}1672\text{ cm}^{-1}$ band, assigned principally to $\text{C}=\text{C}$ stretching, are not believed to be due to conformational changes. There is a bond length change of about 4% between the α - and β -forms^{7,8} which causes a shift in vibration frequency. The average $\text{C}=\text{C}$ bond length in amorphous TPI is not known but the current results suggest that it differs from that for either of the two crystalline forms.

No reasonable explanation for the weak broad bands

appearing for semicrystalline samples with either an α - or a β -crystalline component at temperatures about 50°C below the glass transition temperature is available at this time.

The changes in the components of the spectrum associated with the crystalline component in semicrystalline TPI upon cooling from room temperature includes intensity increases, small shifts in frequency and decreases in bandwidth as well as splitting at low temperatures of the CH₂ bending band at 1450 cm⁻¹ for the β -crystalline form. The intensity increase with decreasing temperature down to -22°C is caused at least in part by the conformational changes occurring in the amorphous component, as discussed above. The selective frequency shifts, bandwidth changes and additional intensity increases can best be explained in terms of the contraction of the crystal lattice with cooling, leading to stronger interchain interactions.

The 1450 cm⁻¹ band was previously predicted to contain two overlapping bands, one due to CH₂ scissoring and the other to CH₃ asymmetric bending⁵. The spectrum for the β -form-containing material at low temperatures given in the present work shows a splitting into a doublet at 1439/1447 cm⁻¹ tentatively assigned to the CH₂ scissoring and a singlet at 1462 cm⁻¹ assigned to CH₃ asymmetric bending. The doublet splitting of the CH₂ scissoring band is believed to be caused by crystal-field splitting, as observed for polyethylene¹⁷ and for *trans*-1,4-polybutadiene¹⁸.

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