Macromolecules 1988, *21*, 2075–2079 **2075**

Infrared Spectral Correlations for Crystalline and Amorphous *trans*-1,4-Polyisoprene

Michal Gavish, Peter Brennan, and Arthur E. Woodward*

Chemistry Department, The City College and The Graduate School,
The City University of New York, New York, New York 10031. *Received June 2, 1987*

ABSTRACT: The infrared spectra for α- and β-*trans*-1,4-polyisoprene are compared, and a correlation is found between both the frequencies of their observed vibrational modes and their potential energy distribution from normal coordinate calculations for a single chain. Each band in the β spectrum corresponds to either one or two bands in the α spectrum. Correlation between each of the spectra of the two crystalline forms and the amorphous TPI is used to assign the infrared bands of the latter.

Introduction

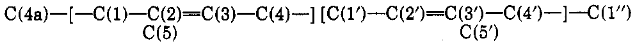
trans-1,4-Polyisoprene, TPI, precipitates from various solvents as single lamellas with crystalline cores and amorphous surfaces[1,2] or as multilamellar structures,[3,4] depending on the crystallization conditions. Two crystal forms, α and β, have been clearly identified for this polymer. The α-form has a monoclinic unit cell with two chains, each containing two repeat units.[5] The β-form has an orthorhombic unit cell with four chains, each containing one repeat unit.[6] Partially crystalline TPI can be prepared from solution with only the α-form, only the β-form, or both crystal forms present.[3] The nature of the fold surface in solution-crystallized TPI lamellas has been investigated by using quantitative chemical reactions in suspension coupled with carbon-13 NMR analysis.[7,8]

It was believed of interest to explore the application of Fourier transform infrared spectroscopy to the characterization of the crystalline and noncrystalline components in solution-crystallized TPI. Use of the infrared method depends on assignment of the spectral bands, as obtained by normal-coordinate calculations. Single-chain normal-coordinate calculations for α- and β-TPI were carried out previously by Petcavich and Coleman.[9] In that work assignments were given for the spectral bands for the β-form but only for a few of the bands for the α-form. In the present work, these calculations were repeated in order to obtain assignments for the latter. The force constant for the double bond was changed, and a unique force constant for the C–CH_3 bond was introduced. The geometry given for the α-form from X-ray analysis[5] was adopted in the present work; this differs from that used in the earlier calculations in the C–C bond length, in some of the bond angles and in all of the dihedral angles. The new force constants were also used in the analysis of the TPI β crystalline form in order to compare the calculated frequencies and the potential energy distributions with those for the α-form.

As the normal-coordinate analysis of TPI progressed, it was realized that a complete correlation existed between the observed infrared spectral frequencies for the two crystal forms. Each vibrational band in the spectrum for the β-form is correlated to a singlet in a few cases or to a doublet in the majority of cases in the spectrum of the α-form.

The spectral frequency correlation for the two crystalline forms was also extended to the bands in the amorphous spectrum. The relatively broad infrared bands observed are expected. However, since the conformations characteristic of the two crystal forms are also highly probable ones for the amorphous chain, overlap of the amorphous and crystalline bands must occur. This overlap can be used as a means of assignment of the amorphous bands in terms of the calculated assignment for the α- and β-crystalline structure.

Table I
Geometric Parameters of TPI



$$\mathrm{C(4a)—[—C(1)—\underset{C(5)}{C(2)}{=}C(3)—C(4)—]\,[C(1')—\underset{C(5')}{C(2')}{=}C(3')—C(4')—]—C(1'')}$$

bond length (Å)		bond angle, ψ (deg)		dihedral angle, τ (deg)	
		α-TPI			
C═C	1.38	ψ_{123}; $\psi_{1'2'3'}$	126.5	τ_{1234}; $\tau_{1'2'3'4'}$	180
C—C	1.53	ψ_{234}; $\psi_{2'3'4'}$	124.8	$\tau_{2341'}$; $\tau_{2'3'4'1''}$	8.6
C—H	1.09	$\psi_{341'}$; $\psi_{3'4'1''}$	111.4	$\tau_{341'2'}$	179.0
		ψ_{4a12}; $\psi_{41'2'}$	107.6	τ_{4a123}	111.0
		ψ_{235}; $\psi_{2'3'5'}$	125.2	$\tau_{41'2'3'}$	−111.0
		ψ_{534}; $\psi_{5'3'4'}$	120		
		HCH	109.5		
		CCH	109.5		
		C═CH	120		
		β-TPI			
C═C	1.33	ψ_{123}	120	τ_{1234}	180
C—C	1.54	ψ_{234}	125	τ_{4a123}	117
C—H	1.09	$\psi_{341'}$	109.5	$\tau_{2341'}$	−117
		HCH	109.5	$\tau_{341'2'}$	180
		CCH	109.5		
		C═CH	120		

Experimental Section

To obtain the β-crystalline form, we crystallized synthetic TPI from 1% (w/v) amyl acetate solution at 0 °C, followed by slow heating of the suspension liquid to 30 °C. This resulted in a morphology of curved stacks of overgrown lamellas with a semicrystalline structure.[3] The α-form was obtained by a precooling method of crystallization from 0.1% hexane solution that involves precipitation at 0 °C, redissolution at 32 °C, and crystallization at 20 °C. This resulted in semicrystalline lamellas with an ellipsoidal shape and pointed ends.

Mats were formed by filtration of the above suspension onto Teflon filters. These were dried at room temperature. The Fourier transform infrared spectra were obtained from 450 to 4000 cm^{-1} at 4 cm^{-1} resolution by using a Digilab FTS 40 spectrometer.

In order to obtain the amorphous spectrum, we placed one of the semicrystalline films in a heating cell and recorded its infrared spectrum at 65 °C. At this temperature, all the sharp peaks that are associated with the crystalline structure disappear from the spectrum, leaving a spectrum that contains broad bands only. This amorphous spectrum was then subtracted from both semicrystalline α- and β-spectra giving 100% crystalline spectra with no detectable amount of the other crystalline form.

Normal-coordinate calculations were carried out for TPI single chains in each of the two stable crystalline forms by using a computer program written by Boerio.[10,11] The molecular parameters of the α- and β-crystal structures were taken from earlier X-ray studies[5,6] and are summarized in Table I. The **F** matrices for the α and β repeat conformational units were constructed by transferring to them unrefined force constants from model compounds. Most of the force constants involving skeletal vibrations

0024-9297/88/2221-2075$01.50/0 © 1988 American Chemical Society

as well as the different methylene modes were transferred from *trans*-polybutadiene.[12] The force constants of the methyl group as well as those involving the double bond were transferred from *trans*- and *cis*-butene.[13,14] The set of force constants, as shown in Table II, was applied to both the α- and β-structures.

Table II
Valence Force Constants for TPI[a]

force constant	value	force constant	value	force constant	value
H_ϵ	0.910	$H_\xi{}^b$	0.611	$F_{K\xi}{}^c$	0.174
H_β	0.944	H_δ	0.540	$F_{\theta\theta}$	−0.032
Γ_1	0.344	H_φ	0.560	$F_{\theta\gamma}$	0.015
Γ_2	0.199	H_ψ	0.480	$F_{\varphi\psi}$	0.027
τ_D	0.328	τ_T	0.024	$F_{\epsilon\psi}$	−0.029
$F_{T\omega}$	0.419	$\tau_K{}^b$	0.0073	$F_{\omega\theta}$	−0.028
K_T	4.384	F_{DT}	0.094	$F_{\xi\xi}$	−0.031
$K_K{}^b$	4.672	F_{TR}	0.122	$f_{\theta\theta}{}^t$	0.010
$K_D{}^b$	7.901	F_{dd}	0.004	$f_{\theta\theta}{}^g$	−0.006
K_l	4.947	$F_{rr}{}^b$	0.037	$f_{\gamma\gamma}{}^t$	0.120
K_d	4.524	$F_{D\varphi}$	0.355	$f_{\gamma\gamma}{}^g$	−0.02
$K_r{}^c$	4.699	$F_{T\theta}$	0.341	$f_{\gamma\theta}{}^t$	0.008
H_ω	1.049	$F_{T\psi}$	0.333	$f_{\gamma\theta}{}^g$	0.029
H_γ	0.664	$F_{T\gamma}$	0.066	$f_{\omega\omega}{}^t$	0.080
H_θ	0.668	$F_{T\varphi}$	0.075	$f_{\omega\gamma}{}^t$	−0.045
$H_\zeta{}^b$	0.529			$f_{\omega\gamma}{}^g$	0.073

$K_T = K_R$ $F_{\gamma\gamma} = F_{\theta\theta}$ $F_{\epsilon\varphi} = F_{\epsilon\psi}$ $f_{\theta\gamma}{}^t = f_{\psi\gamma}$
$H_\alpha = H_\beta$ $\tau_T = \tau_R$ $f_{\gamma\gamma}{}^t = f_{\psi\theta}$ $f_{\theta\gamma}{}^g = f_{\varphi\theta}$
$F_{T\gamma} = F_{R\theta}$ $F_{\omega\gamma} = F_{\omega\theta}$ $f_{\omega\omega} = f_{\epsilon\epsilon}$ $f_{\theta\theta}{}^g = f_{\varphi\theta} = f_{\epsilon\omega}$
$F_{T\psi} = F_{D\epsilon}$ $F_{T\psi} = F_{D\psi}$ $f_{\omega\gamma}{}^g = f_{\epsilon\theta} = f_{\omega\psi}$

[a] The symbols for force constant definitions are taken from ref 15. The symbols for the internal coordinates for TPI are shown in Figure 1. All stretch force constants are in mdyn/Å; stretch–bend interactions are mdyn/rad; bend constants are in units of (mdyn·Å)/rad². Most force constants are transferred from *trans*-1,4-polybutadiene[12] unless otherwise noted. [b] Force constants transferred from *trans*- and *cis*-butene.[13,14] [c] Force constants transferred from polypropylene.[16]

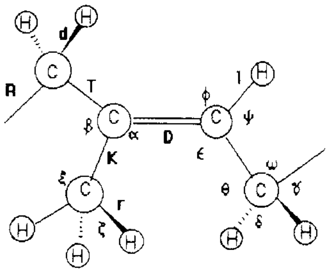


Figure 1. Internal coordinates of TPI repeat monomer unit.

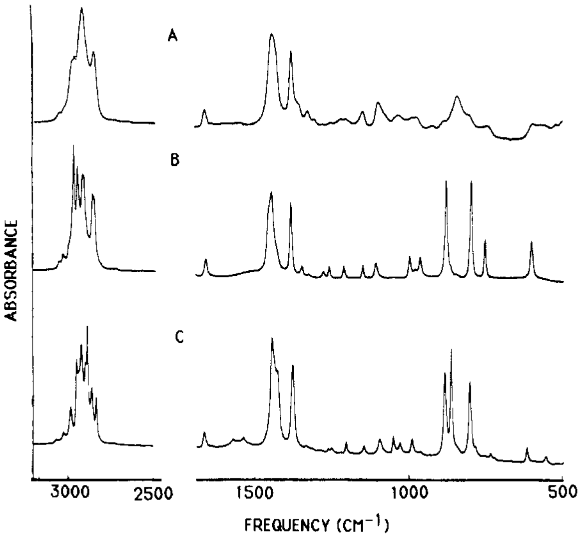


Figure 2. Infrared spectra of TPI in the 450–1700 and 2500–3100 cm⁻¹ regions: (A) amorphous TPI; (B) β-TPI; (C) α-TPI.

Table III
Correlation of Observed and Calculated α- and β-TPI Infrared Frequencies

β-TPI			α-TPI		
freq (cm⁻¹)		PED[a] (%)	freq (cm⁻¹)		PED[a] (%)
obsd	calcd		obsd	calcd	
3022	3019	99K_l	3018	3018, 3017	99K_l
2979	2959	100K_r	2970	2965, 2965	100K_r
2965	2957	100K_r	2941	2963, 2963	100K_r
2943	2921	100K_d	2918	2922, 2923	100K_d
2914	2918	100K_d	2879	2914, 2914	100K_d
2906	2887	99K_r	2872	2871, 2868	99K_r
2855	2847	99K_d	2851	2850, 2850	99K_d
2846	2841	99K_d	2830	2842, 2841	99K_d
1664	1670	72K_D, 12K_T	1672	1669, 1670	72K_D, 14K_T
			1579	1559	15K_T, 12K_K
			1540	1523	14K_T, 16K_K
1450	1463	93H_ζ	1450	1469	71H_δ, 18H_γ
	1463	91H_ζ		1463, 1463	92H_ζ
	1454	75H_δ		1462, 1462	92H_ζ
				1460	75H_δ, 11H_γ, 11H_θ
1430	1446	77H_δ	1430	1448	80H_δ, 11H_γ, 11H_θ
				1446	80H_δ, 10H_γ, 12H_θ
1384	1387	39H_ζ, 40H_ξ	1383	1377	28H_ζ, 32H_ξ, 18H_γ
				1373	41H_ζ, 47H_ξ
1348	1361	10H_ζ, 12H_ξ, 17K_T	1340	1347	38H_γ, 15H_θ, 15H_ζ, 17H_ξ
1324	1335	61H_γ, 18H_θ, 11f_{rr}	1320	1306	38H_γ, 32H_θ
1280	1322	45H_γ, 40H_θ	1280	1262	42H_γ, 51H_θ
				1256	56H_γ, 50H_θ
1260	1252	44H_γ, 45H_θ	1260	1248	41H_γ, 47H_θ
				1244	47H_γ, 49H_θ
			1250	1235	36H_γ, 40H_θ
				1230	52H_γ, 43H_θ
1212	1192	21H_φ, 24H_θ, 10K_T, 18H_γ	1205	1197	26H_ψ, 25H_φ, 16K_T, 14H_γ, 14H_θ
1150	1133	27H_γ, 39H_θ	1150	1166	21H_γ, 40H_θ, 12K_T
1107	1093	60K_T, 10H_θ	1105	1089	49K_T, 18H_ξ
			1099	1083	43K_T, 14H_θ, 11H_ξ
1058	1039	21K_T, 25H_ξ	1050	1051	15K_T, 38H_ξ, 10H_γ, 18H_θ
				1048	20K_T, 34H_ξ, 18H_θ
997	1010	33K_T, 23H_ξ	1030	1018	76K_T, 24H_ξ, −14$F_{T\omega}$
978	992	50H_ξ, 16K_T	992	995	51H_ξ, 26H_θ
				994	32H_ξ, 26H_θ
962	946	57H_ξ, 25K_T	965	964	60H_ξ,. 19K_T
				963	56H_ξ, 17K_T
877	865	42Γ_2, 24τ_D	882	886	41Γ_2, 27τ_D
			862	872	49Γ_2, 28τ_D
800	816	55K_K	800	816	20K_K, 19K_T
			780	810	23K_K, 20K_T
750	742	51H_γ, 21H_θ	750	770	24H_γ, 30H_θ, 12K_T
			730	750	51H_γ, 19H_θ, 10K_T
600	586	26H_β, 14H_ϵ, 20K_T	618	625	22H_β, 29H_ω, 19K_K
			555	573	27H_β, 17H_ω, 12K_K
474	514	36Γ_1, 15τ_D	490	505	34Γ_1, 17τ_D, 16H_β, 12H_ω
			470	490	36Γ_1, 19τ_D, 15H_β, 12H_ω
b	455	11H_β, 40H_ω, 12K_T		450	18Γ_1, 26H_β, 20H_ω, 12K_T
				441	17Γ_1, 11H_ϵ, 32H_ω, 10K_T
	373	67H_β, 12K_T		351	71H_β, 19H_ϵ
				316	78H_β, 16H_ϵ
	225	40H_ϵ, 31H_β		248	12H_β, 26H_ϵ, 28H_ω
				233	15H_β, 22H_ϵ, 17H_ω, 10K_T
	174	21Γ_1, 62H_ω		176	20H_ω, 25H_β, 16τ_D
				150	10K_T, 25H_β, 16τ_D
	119	31τ_R		106	22H_ω, 42τ_R
	90	40τ_R, 23τ_K		91	46τ_R
	85	95τ_K		86	95τ_K
				81	96τ_K

[a] Contributions to potential energy distribution of >10%. [b] Spectra not observed below 450 cm⁻¹ in this work.

Results and Discussion

The infrared spectra for amorphous TPI, 100% β, and 100% α are given in Figure 2 (A, B, and C, respectively)

Table IV
Correlation of the Observed Crystalline and Amorphous Infrared Frequencies[a]

β-TPI obsd freq (cm^{-1})	amorphous TPI obsd freq (cm^{-1})	α-TPI obsd freq (cm^{-1})	type of vibration
3022 (sh)	3015 (sh)	3018 (sh)	$\nu_s(=\mathrm{CH})$
2979 (sh)	2975 (sh)	2970 (s)	$\nu_{as}(\mathrm{CH_3})$
2965 (vs)	2961 (s)	2941 (vs)	$\nu_{as}(\mathrm{CH_3})$
2943 (vs)	2925 (vs)	2918 (vs)	$\nu_{as}(\mathrm{CH_2})$
2914 (vs)	2920 (vs)	2879 (vs)	$\nu_{as}(\mathrm{CH_2})$
2906 (vs)	2912 (vs)	2872 (vs)	$\nu_s(\mathrm{CH_3})$
2855 (s) 2846 (s)	2848 (s)	2851 (s) 2830 (s)	$\nu_s(\mathrm{CH_2})$
1664 (m)	1665 (m)	1672 (m)	$\nu(\mathrm{C{=}C})$
	1570 (vw)	1579 (w)	
	1540 (vw)	1540 (w)	
1450 (s)	1450 (s)	1450 (s)	$\delta(\mathrm{CH_2})$; $\delta_{as}(\mathrm{CH_3})$
1430 (sh)	1430 (sh)	1430 (sh)	$\delta(\mathrm{CH_2})$
1384 (s)	1383 (s) 1360 (m)	1383 (s)	$\delta_s(\mathrm{CH_3})$
1348 (m)	1329 (m)	1340 (m)	α: $\delta_s(\mathrm{CH_3}) + \gamma(\mathrm{CH_2})$ β: $\delta_s(\mathrm{CH_3}) + \nu(\mathrm{C{-}C})$
1324 (w)	1307 (sh)	1320 (w)	$\gamma(\mathrm{CH_2})$
1280 (w)	1281 (w)	1280 (w)	$\gamma(\mathrm{CH_2})$
1260 (m)	1253 (w-br)	1260 (w) 1250 (w)	$\gamma(\mathrm{CH_2})$
1212 (m)	1220 (w) 1205 (w)	1205 (m)	$\delta(=\mathrm{C{-}H})_{ip}$
1150 (m)	1150 (m)	1150 (m-w)	$\gamma(\mathrm{CH_2})$
1107 (m)	1099 (m-s, br)	1105 (sh) 1099 (m)	$\nu(\mathrm{C{-}C})$
1058 (vw)	1033 (m)	1050 (m)	$\gamma_r(\mathrm{CH_3}) + \nu(\mathrm{C{-}C})$
997 (m)	987 (m)	1030 (m)	$\nu(\mathrm{C{-}C}) + \gamma_r(\mathrm{CH_3})$
978 (w)	976 (m)	992 (m)	$\gamma_r(\mathrm{CH_3})$
962 (m)	924 (w)	965 (w)	$\gamma_r(\mathrm{CH_3})$
877 (s)	884 (sh) 860 (sh) 842 (s)	882 (s) 862 (s)	$\delta(=\mathrm{C{-}H})_{op}$
800 (s)	800 (sh)	800 (s) 780 (sh)	$\nu(\mathrm{C{-}CH_3})$
750 (m-s)	764 (m) 743 (m)	750 (w) 730 (w)	$\gamma_r(\mathrm{CH_2})$
600 (ms)	595 (m) 570 (m)	618 (m) 555 (m)	$\delta(\mathrm{C{=}C{-}C})$
474 (s)	520 (m) <505 (m)	490 (m) 470 (m)	$\delta(=\mathrm{C{-}CH_3})_{op}$

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.
[b] Abbreviations: ν, stretch; δ, bend; γ, twist, wag; γ_r, rock.

from 500 to 1700 and from 2500 to 3100 cm^{-1}. Frequencies and potential energy distribution calculated for bands in the 80 to 3100 cm^{-1} region are listed in Table III for 100% α-TPI and for 100% β-TPI; observed frequencies from 470 to 3022 cm^{-1} are also included in this table. In Table IV the observed frequencies for the amorphous bands from 500 to 3015 cm^{-1} are shown along with those for α- and β-TPI, as taken from Table III; band assignments, obtained from the potential energy distributions given in Table III, are included in Table IV.

Differences between the observed crystalline infrared spectra in this and the previous FTIR study of TPI[9] are seen for both the α- and β-forms. Bands not observed in the previous study of a sample that was predominantly α-TPI appear at 2830 (s), 1250 (w), 780 (sh), and 555 cm^{-1} (m) and those at 1010 and 604 cm^{-1} are absent in the present study. It is to be pointed out that the 604 cm^{-1} band is characteristic of the β-form. For the β-form the bands at 2980 (sh) and 1058 cm^{-1} (w) observed in the present study were previously not reported.[9]

In the present study close agreement (Δ = 3–6) between calculated and observed frequencies for the C=C stretching band in α- (1672 cm^{-1}) and β- (1664 cm^{-1}) crystalline forms occurs even though unrefined force constants were used. This agreement apparently reflects the appropriateness of the force constant for the C=C bond taken from a model compound containing a methyl group attached to one carbon atom in the double bond. For the β-form only one calculated frequency above 460 cm^{-1} deviates from the assigned observed value by more than 20 cm^{-1}; for the observed band at 1280 cm^{-1} Δ is 42. One large deviation in calculated and observed frequencies also occurs for α-TPI; the observed band is at 2879 cm^{-1} and Δ is 35. However, this and all other frequencies calculated for bands in the C–H stretching region are in close agreement with those calculated earlier.[9]

A comparison of the calculated potential energy distributions for both crystal forms shows many differences between this work and the earlier study.[9] For both crystal forms about half of these distributions differ. Principal discrepancies occur in the assignments for in-plane =C—H bending and for C—CH_3 stretching. In-plane =C—H bending was assigned at 1150 cm^{-1} for both forms; the present assignments at 1205 (α) and 1212 cm^{-1} (β) are in agreement with group frequency placement.[17] The assignment of the bands at 800 (α and β) and 780 cm^{-1} (α) to C–CH_3 stretching is unique to the present work and arises due to the introduction of a force constant characteristic of this particular bond. For the β-form the band at 1348 cm^{-1} was previously assigned[9] to CH_2 wagging and twisting whereas in the present work it is found to be a mixed mode containing CH_3 bending and C–C stretching. For the β-form the amount of mode mixing reported in the two works varies for the bands at 1384, 1051, 997, 978, and 962 cm^{-1}. In the 900–1400 cm^{-1} region for α-TPI the earlier calculations show contributions of C–C stretching not found in the present work.

The conformational repeat unit in α-TPI contains two chemical repeat units. Therefore, many of the calculated frequencies appear twice with the same or slightly different values. Most of the calculated frequencies given in Table III for α-TPI can be consecutively paired due to the same or closely similar potential energy distributions. Out of 59 calculated frequencies there are only five bands that are not paired. As reported previously,[9] the calculated pairs have the same or nearly the same frequencies in the 2800–3020 cm^{-1} region. In the range of 960–1700 cm^{-1} the frequency difference between members of each pair is 1–9 cm^{-1} except for the pair calculated at 1523 and 1559 cm^{-1}. Some pairing of frequencies in this region was given earlier;[9] however, it was generally not the same and was not as extensive as that shown in Table III. For bands with frequencies below 900 cm^{-1} the pair members differ in frequency by 9–52 cm^{-1}. Pairing in this frequency region was reported earlier[9] only for the 872 and 886 cm^{-1} bands.

For α-TPI each pair of calculated bands is represented by a single observed band at ambient conditions in the 960–3020 cm^{-1} range except for those at 1523 and 1559 cm^{-1} and 1105 and 1099 cm^{-1}. For α-TPI bands below 900 cm^{-1} each member of each pair is assigned to a corresponding observed frequency. The pair splitting is large enough in this region so that both bands are observed.

The infrared spectrum of α-TPI shows a larger number of bands than that for β-TPI (see Figure 2), due to the fact that the conformational repeat unit in the polymer chain in the α-form contains two monomer units and therefore has twice as many atoms as the conformational repeat unit in the β-form. Another difference between the two forms is in the geometric parameters (bond lengths, bond angles, and mainly dihedral angles) which causes some difference in the orientation of the normal coordinates and as a result a slight shift in their corresponding vibrational frequencies. Although the different geometries give rise to two different

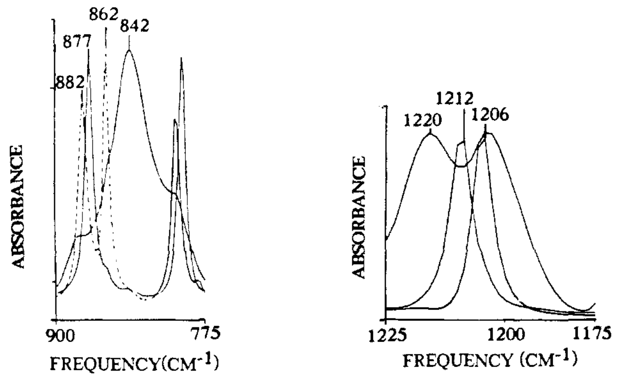


Figure 3. Overlap of correlate crystalline and amorphous TPI bands.

spectra for α- and β-TPI, the chemical structures are the same for both forms and therefore it should be possible to correlate the two spectra. Such a correlation is carried out in Table III by matching calculated and observed frequencies for the two forms having the same or similar potential energy distributions. In only two cases do substantial differences appear in the potential energy distribution for the correlated bands. These are for the calculated bands at 1361 (β) and 1347 (α) and at 174 (β), 176, and 159 cm^{-1} (α). It is observed that in most cases each frequency for the β-form is associated with two calculated frequencies for the α-form. There are four exceptions to this out of 34 calculated β-bands above 170 cm^{-1}. There are two bands above 170 cm^{-1} found for the α-form only (observed at 1579 and 1540 cm^{-1}). In most cases the observed band intensities for the two forms also approximately correlate, as seen in Figure 2. Exceptions occur where a band for β-TPI is associated with a single observed α-TPI band at 1050, 978, and 964 cm^{-1}. In all cases where an observed β-TPI band is associated with two observed α-TPI bands, the combined intensity of the latter two approximate that of the former. It is concluded that there is a direct correlation between the two structures both in their vibrational frequencies and in their assigned potential energy distribution.

Many polymers have more than one stable crystalline form, containing one or more monomer units per repeat conformational unit. Assuming that the correlations found for alpha and beta TPI have general validity, it should be possible using single-chain normal vibrational analysis to correlate the spectra for the various forms of a particular polymer. Each band in the spectrum of the crystal form with the smaller number of monomer units per repeat conformational unit should correlate to one or more bands in the spectra of the other forms containing more monomer units per conformational repeat unit.

It should be possible also to extend the above correlation to a mixture of chain conformations as found for the amorphous polymers. Each single band in the β-TPI spectrum and the single and double bands in the α-TPI spectrum should correlate with a series of amorphous bands that will closely overlap or split into adjacent modes and therefore appear as a broad band.

The use of normal-coordinate calculation for the assignment of the infrared spectrum for amorphous TPI is complicated by the number of conformations that are present. The C–C single bond conformations are restricted in the α- and β-crystalline structures to single values for each bond, which results in the $\mathrm{CTSCT\bar{S}}$ conformational sequence for the α-form and the $\mathrm{ST\bar{S}}$ sequence for the β-form. For amorphous TPI, on the other hand, other energetically allowed single bond conformations are possible.[18] These include the most probable conformations (STS, $\mathrm{\bar{S}TS}$, CTS, $\mathrm{ST\bar{S}}$, $\mathrm{\bar{S}T\bar{S}}$, and $\mathrm{CT\bar{S}}$), the less probable conformations (SGS, $\mathrm{\bar{S}GS}$, $\mathrm{\bar{S}\bar{G}S}$, $\mathrm{S\bar{G}S}$, $\mathrm{SG\bar{S}}$, $\mathrm{S\bar{G}\bar{S}}$, $\mathrm{\bar{S}G\bar{S}}$, and $\mathrm{\bar{S}\bar{G}\bar{S}}$), and the least probable conformations (CGS, $\mathrm{C\bar{G}S}$, $\mathrm{CG\bar{S}}$, and $\mathrm{C\bar{G}\bar{S}}$).

For the crystalline structures restriction of the position for each normal coordinate to one value leads to an infrared spectrum containing single sharp bands. When two positions exist, the infrared spectrum contains either sharp singlets or doublets. If a larger number of positions is possible, as is the case with the amorphous state, the infrared spectrum should contain groups of sharp singlets that overlap to form broad bands. However, since the possible C—C single-bond conformations for the amorphous chain include those allowed for the single bonds in α- and β-TPI, all of the spectral bands observed for the crystalline forms should fall completely within the frequency domains of the amorphous bands. The intensity maximum for a particular crystalline band will not necessarily coincide with that for the amorphous band with the same assignment due to the presence of other conformations. Therefore, the amorphous spectrum is assigned by a transfer of the potential energy distribution for the crystalline bands that are completely overlapped by an amorphous band. This correlation is shown for TPI in Table IV, along with band assignments for the two crystalline and the amorphous forms. For the 1450 cm^{-1} bands two separate modes are assigned, as shown. As noted above, α- and β-TPI have different assignments for the 1348 and 1340 cm^{-1} bands (1329 cm^{-1} for amorphous). The 1051 (α and β) and 1033 (amorphous) and the 962 (β), 924 (amorphous), and 964 (α) are mixed modes. Some of the amorphous bands, such as those at 3015, 2975, 1665, 1450, 1430, 1383, 1281, 1253, and 1150 cm^{-1}, have their maxima at the same or similar frequencies as those for both of the corresponding crystalline bands. In other cases, although overlap occurs the correlation is not as apparent, since the maxima in the crystalline spectra are shifted considerably from those in the amorphous spectrum. Examples of this are shown in Figure 3 and include the amorphous bands at 842 cm^{-1} with shoulders at 860 and 884 cm^{-1}, assigned to C–H out of plane bending, and the doublet at 1220 and 1206 cm^{-1}, assigned to C–H in plane bending. The amorphous bands, as assigned, are observed to overlap the α- and β-bands having the same assignments. In three cases one amorphous band corresponds to two observed α-TPI bands (amorphous bands at 1253, 1099, and 800 cm^{-1}). The intensities of corresponding amorphous and crystalline bands approximately agree as shown in Table IV.

Acknowledgment. We are grateful to Professor Paul Painter at The Pennsylvania State University for providing the computer program used. We also wish to acknowledge support of this research by the PSC/CUNY Faculty Research Award Program and by Grant RN 08168 from the MBRS/NIH Program.

Registry No. TPI, 9003-31-0.

References and Notes

(1) Keller, A.; Martuscelli, E. *Makromol. Chem.* **1972**, *151*, 189.
(2) Anandakumaran, K.; Herman, W.; Woodward, A. E. *Macromolecules* **1983**, *16*, 563.
(3) Kuo, C.; Woodward, A. E. *Macromolecules* **1984**, *17*, 1034.
(4) Xu, J.; Woodward, A. E. *Macromolecules* **1986**, *19*, 1114.
(5) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polymer Sci., Polym. Phys. Ed.* **1973**, *11*, 233.
(6) Bunn, C. W. *Proc. R. Soc. London, Ser. A* **1942**, *6*, 497.
(7) Schilling, F. C.; Bovey, F. A.; Anandakumaran, K.; Woodward, A. E. *Macromolecules* **1985**, *16*, 2688.

(8) Tischler, F.; Woodward, A. E. *Macromolecules* **1986**, *19*, 1328.
(9) Petcavich, R. J.; Coleman, M. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *16*, 2097.
(10) Boerio, F. J. Ph.D. Dissertation, Case Western Reserve University, Cleveland, OH, 1970.
(11) Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectrosopy and its Application to Polymeric Materials*; Wiley: New York, 1982.
(12) Neto, N.; DiLauro, C. *Eur. Polymer J.* **1967**, *3*, 645.
(13) Levin, I. W.; Pearce, A. R.; Harris, W. C. *J. Chem. Phys.* **1973**, 59, 3048.
(14) Levin, I. W.; Pearce, A. R. *J. Mol. Spectrosc.* **1974**, *49*, 91.
(15) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.
(16) Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1965**, *21*, 1527.
(17) Saunders, R.; Smith, D. *J. Appl. Phys.* **1937**, *6*, 497.
(18) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *69*, 6829.

FTIR Investigations of Crystallinity and Surface Reaction for *trans*-1,4-Polyisoprene Lamellar Structures Crystallized from Solution

Michal Gavish, Joseph Corrigan, and Arthur E. Woodward*

Chemistry Department, The City College and The Graduate School, The City University of New York, New York, New York 10031. *Received June 15, 1987*

ABSTRACT: Infrared studies of *trans*-1,4-polyisoprene (TPI) and of block copolymer derivatives were carried out. TPI lamellar structures were reacted in suspension so that their surfaces were modified while their crystalline cores remained unchanged. The reactions used were epoxidation and hydrochlorination of the double bond. The infrared spectra of the modified surface were obtained, and tentative band assignments were made. A procedure was developed to obtain the percent crystallinity of TPI lamellar structures from the infrared spectrum by using measurements of the relative intensity of the 1664–1670-cm^{-1} band in the crystalline and semicrystalline spectra. Effects of pressure on as-prepared and surface-modified TPI lamellar structures were observed.

Introduction

Lamellar structures of the polydienes *trans*-1,4-polybutadiene, TPBD, and *trans*-1,4-polyisoprene, TPI, have been obtained by crystallization from solution under a variety of conditions; these structures have been characterized morphologically by using optical and scanning electron microscopy.[1-4] The crystalline/amorphous character of some of these preparations have been studied by physical methods, such as density and solid-state carbon-13 NMR.[1,3,5,6] In addition to depending on the assumption of a two-phase model, the calculation of crystallinity from density requires accurate crystalline and amorphous densities. Since there is some disagreement in the value of the crystalline density for β-TPI,[7-9] the development of alternative methods for crystallinity determination is desirable. One method employed for crystallinity measurement is infrared spectroscopy. A convenient and unambiguous procedure is to use a single band for which the band shape, position, and intensity are independent, or nearly so, of overall crystalline and amorphous chain conformations. A band due principally to a vibration of a group of atoms held in a relatively rigid conformation is a logical choice. A method for the quantitative determination of the crystalline fraction in semicrystalline TPI was developed in the present study by using the infrared spectroscopic band assigned principally to the C=C stretching vibration. The values obtained from infrared spectroscopy are found to be in close agreement with those from density measurements.

For quantitative assessment of chain folding at lamellar surfaces, a direct method involving chemical reaction in suspension, followed by carbon-13 solution NMR, was developed.[10-12] The polydienes are well suited for this type of study, due to the susceptibility of the double bond present in each repeat unit to addition reactions. However, it is crucial that the reaction at the surface is complete and is confined to that region. Considerable effort has been expended to establish reaction conditions that lead to complete reaction of the lamellar surfaces without crystal core penetration or cross-linking taking place to an appreciable degree. Two reactions for the modification of TPI, epoxidation using *m*-chloroperbenzoic acid[11] and hydrochlorination,[12] have been investigated to date. It has been shown that both of these reactions can be carried out under conditions that give single products preserving the stereochemistry of the double bond, as characterized by carbon-13 NMR.[11,12] When one or the other of these reactions is taken to completion at the lamellar surfaces of solution-crystallized TPI structures in suspension, a product having chemically modified blocks alternating with unmodified blocks results.

In the present work it is found that dried mats of solution-crystallized samples subjected to reaction in suspension with either *m*-chloroperbenzoic acid or with HCl yield an infrared spectrum containing all the crystalline bands observed for the original lamellas combined with a new set of bands, obtainable by subtraction, characteristic of the reaction. The changes in the spectrum for the amorphous surface component caused by chemical modification are found to be consistent with the band assignment made by correlation with the crystalline assignments.[13]

The effect of pressure on the crystallinity of TPI structures and on the spectrum for surface-modified TPI was also investigated, with the same decrease in the crystalline component being observed at all pressures used.

Experimental Section

Surface Reactions. Unfractionated *trans*-1,4-polyisoprene, TPI, ($M_w = 1.7 \times 10^5$, $M_w/M_n = 4.8$)[14] was crystallized from 1% amyl acetate solution by precipitation at 0 °C and slow heating to 30 °C. Curved, overgrown, semicrystalline lamellas are obtained, with a crystalline core in the β form.[1]

TPI lamellas, suspended in 1-butanol, were reacted with an excess (3/1) of *m*-chloroperbenzoic acid at 0 °C for 5 days. TPI

© 1988 American Chemical Society