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ferroelectric β-PVF$_2$ structure is adopted. Below ~71 mol % VF$_2$, a second structure reflecting the increasing influence of tetrafluoroethylene groups is also seen; the relative population of this phase increases at the expense of the β-PVF$_2$ structure as the VF$_2$ content drops, and below ~35 mol % the structure becomes characteristic of PTFE.

In terms of solid-state transformations, these copolymers also exhibit a continuous spectrum of behavior. Compositions containing $\geq$83 mol % VF$_2$ do not undergo phase transformations but retain their ferroelectric β-structure at all temperatures between ambient and the melting point, during both heating and cooling. Between ~82 and 72 mol % VF$_2$, discrete and reversible Curie transitions are obtained, of the same type as seen previously in trifluoroethylene copolymers and involving the same kind of paraelectric structure (i.e., disordered through the introduction of $g^{\pm}$ bonds). Below ~72 mol %, the increasing F$_4$E content introduces more disorder into the lattice and reduces the stability of the ferroelectric phase. This results from expansion of the interchain lattice as a result of the larger van der Waals volume of the CF$_2$ group; not only are successive CF$_2$ units sterically restricted from adopting exact trans arrangements, but the accompanying intermolecular expansion also renders energetically easier the introduction of gauche$^{\pm}$ rotations in the remainder of the chain. This manifests itself in smearing out of the Curie transitions and in coexistence of the two phases over broad ranges of temperature. Eventually, in the region below ~35 mol % VF$_2$, the structure becomes typical of PTFE and the ferroelectric phase is no longer obtained.

As described recently,[9] in the compositional range where Curie transformations are observed, the ferroelectric-to-paraelectric transition temperatures increase linearly with VF$_2$ content and coincide with the melting temperature in a copolymer of ~82 mol % VF$_2$. This explains the absence of Curie transformations at higher VF$_2$ contents and allows extrapolation to 100 mol % VF$_2$. Such extrapolation led[9] to a temperature of 195–197 °C as that where the Curie transition of PVF$_2$ homopolymer would be centered and was in qualitative agreement with previous predictions from VF$_2$ copolymers with trifluoroethylene.[17]

Registry No. (VF$_2$)(F$_4$E) (copolymer), 25684-76-8.

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Quantitative Investigation of the Amorphous and Crystalline Components in *trans*-1,4-Polyisoprene from Solution

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ABSTRACT: *trans*-1,4-Polyisoprene structures in the α and β crystalline forms with various morphologies were prepared by using different crystallization procedures. The effects of molecular weight, crystallization temperature, and annealing treatment on the crystalline stem length and the noncrystalline traverse length were investigated by using epoxidation in suspension followed by carbon-13 solution NMR. Preliminary studies were carried out to determine the optimum conditions for quantitative reaction of the double bonds at the lamellar surfaces. Results were obtained suggesting that for many liquids penetration of partially reacted lamellas can take place from the lateral surfaces; reactant concentration and time were also shown to be important and conditions were found that gave agreement between the fraction reacted and the noncrystalline fraction from infrared and density measurements. Interlamellar traverses were detected in multilamellar structures with the amount increasing with increasing molecular weight. The nature of chain folding in the *trans*-polydienes is discussed.

Introduction

trans-1,4-Polyisoprene, TPI, crystallizes from solution in either the α or the β form as single folded-chain lamellas, overgrown curved lamellas, or more complex structures that include lamellar stacks and spherulites.[1-6] Determination of crystallinity by density[3,4] and by solid-state carbon-13 NMR[7] measurements showed that a sizable noncrystalline component (35–50%) is present in dried crystal mats. In single lamellas this noncrystalline component is expected to be at the lamellar surfaces as chain folds and noncrystallizing chain ends. For multilamellar structures interlamellar chain traverses may also be present. The amount of the total surface component in TPI samples can be quantitatively evaluated in suspension

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by chemical reaction with the double bonds. In earlier work[3,4] some solution-crystallized α-TPI preparations were reacted in suspension with *m*-chloroperbenzoic acid (MCPBA) to form an epoxide and the extent of reaction was evaluated by proton NMR. More recently, a carbon-13 NMR method has been developed to determine directly the average fold size and the crystalline stem length in addition to the extent of reaction.[8] It was believed of interest to use this carbon-13 NMR analysis to study the effects of polymer molecular weight and crystallization conditions on the nature of the noncrystalline component in solution-crystallized TPI. When using chemical reactions to study the fold surfaces, one assumes that (i) all noncrystalline portions are completely reacted, (ii) the lateral surfaces are negligibly small compared to the total area, and (iii) the reaction does not penetrate into the crystalline core of the lamellas. Earlier epoxidation and electron microscopic results suggested that some penetration of the crystalline core took place, dependent on the reaction conditions.[3] Therefore, in addition to using the newly developed carbon-13 NMR method to analyze the reaction products for various preparations, it was considered important to explore the effects of reaction conditions on the results of the epoxidation reaction and to choose the optimum reaction parameters.

The work to be presented below consists of two parts. In the first part, the effects of the choice of reaction liquid and of the relative concentrations of reactants on the epoxidation results are examined by using unfractionated and fractionated synthetic TPI crystallized from solution in the β form. Using carbon-13 NMR, the resulting products were analyzed in solution in terms of an average reacted block length, $\langle B \rangle$, an average unreacted block length, $\langle A \rangle$, and a fraction of reacted double bonds, F_e. In the second part of this work, TPI fractions were crystallized under different conditions, giving the α or β form and morphologies that included single lamellas, sheaves, and spherulites. These structures were epoxidized in suspension under optimum conditions and analyzed by carbon-13 NMR analysis to obtain values of $\langle A \rangle$, $\langle B \rangle$, and F_e. The amount of the noncrystalline component in these crystals was also obtained from density and FTIR measurements. The effects of crystallization conditions and molecular weight on TPI crystallization were investigated. The effects of annealing on some of the TPI structures and evidence for the existence of tie molecules between lamellas are also presented and discussed.

Experimental Section

Samples. Synthetic *trans*-1,4-polyisoprene (Polysciences, Inc.), found earlier[9] by gel permeation chromatography to have $M_n = 3.5 \times 10^4$ and $M_w/M_n = 4.8$ and by carbon-13 NMR to have a trans content of 99%, was used. Fractions of 100% trans content were obtained by precipitation from toluene solution with methanol, as described previously.[5]

Crystallization. Crystallization of unfractionated TPI was carried out from 1% (w/v) amyl acetate solution heated to 90–95 °C for 1 h; the solution was cooled to 60 °C, then placed in a 0 °C bath, and left undisturbed for 24 h. The resulting suspension was heated to 20 or 30 °C at an average rate of 0.06 °C/min, left at that temperature for 40 h, and then filtered and washed with fresh amyl acetate at the same temperature to remove any material which might not be crystallized. This procedure is referred to below as 0/20 or 0/30. A small portion was dried below the final annealing temperature for X-ray analysis or for density measurements. The remaining part was suspended in the selected liquid for epoxidation. The X-ray pattern, DSC endotherm, and IR spectrum showed the crystalline part of these preparations to be in the β form.

Two crystallization procedures were employed with the fractionated synthetic TPI samples and are referred to as the precooling and the direct method, respectively. In the precooling method, a 0.1% TPI solution was heated to 90–95 °C for 1 h and then cooled in a 0 °C bath to bring about precipitation; the crystal–liquid mixture was heated again at a rate of 0.15 °C/min to the minimum redissolution temperature, T_r, followed by cooling to a desired crystallization temperature, T_c. By carefully controlling T_r (32–36 °C depending on the molecular weight), this procedure yields single β lamellas of uniform size when using amyl acetate as a solvent and α single lamellas when using hexane as a solvent. In the direct method, the heated TPI solution was cooled directly in a constant-temperature bath at the desired temperature for crystallization. The 0/20 or 0/30 procedures, described above, were also used in crystallization of fractionated TPI. This yields overgrown curved lamellas in the β form with one or a few layers, regardless of the molecular weight; direct crystallization at 20 or 25 °C leads to a mixture of sheaves and spherulites or large round structures, respectively.[5]

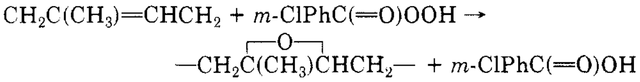
Table I
Carbon-13 NMR Assignments Used for Analysis of TPI-Epoxidized TPI Block Copolymers[a]

assignment[b,c]	chem shift, ppm vs TMS	assignment[b,c]	chem shift, ppm vs TMS
IIE (C_4)	23.76	EEI & EEE (C_1, m, r)	35.17, 35.54
III & EII (C_4)	26.77	EII (C_1)	36.33
IEE & EEE (C_4, m, r)	24.42, 24.57	IEE (C_1)	38.78
EEI (C_4)	27.47	III & IIE (C_1)	39.75

[a] Assignments as given in ref 8. [b] I represents an isoprene unit and E an epoxidized isoprene unit. [c] The carbon atom numbering is given in the text.

In all the cases, antioxidant 2246, 2,2-methylenebis(4-methyl-6-*tert*-butylphenol), was added (0.2 g/L) to the solution to prevent possible oxidation of the polymer during heating and crystallization.

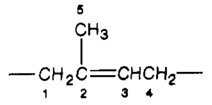
Epoxidation. Reaction of the TPI crystals, prepared as given above, was carried out in suspension in selected liquids at 0 °C with *m*-chloroperbenzoic acid (MCPBA) present in molar ratios of [MCPBA]/[DB] = 1–4. The reaction occurring is



$$\mathrm{CH_2C(CH_3){=}CHCH_2} + m\text{-}\mathrm{ClPhC({=}O)OOH} \rightarrow -\mathrm{CH_2\overset{\frown O \frown}{C(CH_3)CH}CH_2}- + m\text{-}\mathrm{ClPhC({=}O)OH}$$

After epoxidation, the reaction product was filtered and washed repeatedly with fresh suspension liquid at 0 °C. Drying was carried out at 0 °C for 2–3 days then at room temperature.

Carbon-13 NMR Measurement. The 50.32-MHz carbon-13 NMR spectrum of each preparation was obtained with an IBM WP 200-SY NMR system on about 10% (w/v) solutions in $DCCl_3$ by using TMS as an internal standard and a spectral width of 8333 Hz in 32K of memory. Gated broad-band proton decoupling with NOE was used. The delay time between pulses was 20 s. The number of scans collected ranged from 800 to 10 000, but in most cases it was 2500–3000. These experimental parameters were believed to be appropriate to obtain quantitative results.[8] The pertinent carbon-13 NMR assignments for TPI-epoxidized TPI copolymers as made earlier[8] and used in this work are given in Table I; the numbering of the carbon atoms in the repeat unit is as follows:



$$-\underset{1}{\mathrm{CH_2}}\underset{2}{\overset{\overset{5}{\mathrm{CH_3}}|}{\mathrm{C}}}{=}\underset{3}{\mathrm{CH}}\underset{4}{\mathrm{CH_2}}-$$

Crystallinities. Crystallinity measurements by density were carried out with a water–ethanol gradient column. A crystalline density for β-TPI of 1.02 g cm^{-3} [10] and an amorphous density of 0.905 g cm^{-3} [11] were used.

Crystallinity measurements by FTIR were carried out by using a Bio-Rad FTS-40 FTIR instrument. Samples were made by filtration of the suspended structures onto a Teflon membrane in a filter funnel. The method, developed in these laboratories,[12] employed the C=C stretching band at 1664–1670 cm^{-1}. A 100% crystalline spectrum was obtained from the sample spectrum by computer subtraction of an amorphous spectrum taken at 65 °C. The amorphous band at 843 cm^{-1} was used as a subtracting reference. The crystallinity was then calculated from the ratio of the absorbance at 1664–1670 cm^{-1} for the 100% crystalline part to that for the total sample by xeroxing, cutting, and weighing. At least two subtraction determinations were made for each measurement.

DSC and X-ray Measurements. DSC measurements were made with a Du Pont 1090 Thermal Analyzer by using a heating rate of 10 °C/min and 2–5-mg samples. Values of heat of fusion, ΔH_f, were obtained by computer calculation using the interactive DSC data analysis program. Wide-angle X-ray diffraction photographs were recorded with a 57.3-mm diameter cylindrical camera to identify the crystal form(s).

Morphology. Morphologies of the preparations were observed in suspension with a Zeiss microscope having interference contrast optics. A Cambridge Stereoscan S4 scanning electron microscope was used for viewing OsO_4-fixed structures prepared as described elsewhere.[5] Single lamellas dried and shadowed with Au/Pd were viewed with a Philips EM300 electron microscope.

Results

TPI lamellas and more complex lamellar structures in suspension are expected to react mainly at the surfaces, leading to the formation of segmented block copolymers. If reaction at the surface is complete, the average unreacted sequence of monomer units, $\langle A\rangle$, characterizes the average number of monomer units in a chain traverse through the crystal core and the average reacted sequence of monomer units, $\langle B\rangle$, characterizes an average of the number of monomer units in the folds, in noncrystallizing chain ends and in interlamellar traverses. Equations for the calculation of $\langle A\rangle$, $\langle B\rangle$, and F_e, the fraction of the double bonds at the surface, by using carbon-13 NMR resonances were given earlier for epoxidation of TPI lamellas.[8] In the present work this analysis was carried out by using both of the methylene carbons, C_1 and C_4 (see above for labeling of repeat unit). From the C_1 resonances the equations are

$$\langle A\rangle = 1 + 2[\mathrm{II(I\ or\ E)}]/([\mathrm{IEE}] + [\mathrm{EII}]) \quad (1)$$

$$\langle B\rangle = 1 + 2[\mathrm{EE(E\ or\ I)}]/([\mathrm{IEE}] + [\mathrm{EII}]) \quad (2)$$

$$F_e = \langle B\rangle/(\langle A\rangle + \langle B\rangle) \quad (3)$$

where the square brackets signify areas under the particular resonance. For the calculations from the C_4 resonances the equations used for $\langle A\rangle$ and $\langle B\rangle$ differ from the above because the EEI and (E or I)II resonances are not completely separable. The equations used are

$$\langle A\rangle = ([\mathrm{(E\ or\ I)II}] + [\mathrm{EEI}])/[\mathrm{IIE}] \quad (4)$$

$$\langle B\rangle = 1 + [\mathrm{(I\ or\ E)EE}]/[\mathrm{IIE}] \quad (5)$$

The assignments for the resonances cited in eq 1–5 are given in Table I. The data given below are averages of the results for the C_1 and C_4 carbons.

The effects of the reaction medium on the epoxidation of lamellar TPI samples in suspension will be considered first. Results mainly at two reaction times for 15 different reaction mediums were obtained for unfractionated TPI, crystallized from amyl acetate solution at 0 °C and then heated slowly to 30 °C in the crystallization liquid. The molar ratio of MCPBA to double bonds in the sample, [M]/[D], was 1 and the concentration was 5.5 g L^{-1}. In Figure 1, $\langle A\rangle$ and $\langle B\rangle$ are given for the reaction in each liquid with the liquids being grouped according to their functionality. Starting from the left-hand side of the figure the points given correspond to 1-butanol, octanol, 2-ethoxyethanol, methanol, ethanol, 3-pentanone, 2-pentanone, methyl ethyl ketone, acetone, 4-methyl-2-pentanone, ethyl acetate, methyl acetate, propyl acetate, amyl acetate, and butyl acetate. $\langle B\rangle$ changes from 4 to 16 and F_e changes from 0.23 to 0.50 with a change of medium at constant reaction time (14 days), whereas $\langle A\rangle$ fluctuates by ±12%. When acetate esters are used, a longer reaction time (21–28 days) leads to increases in $\langle B\rangle$ as shown and increases in F_e up to 0.60 with $\langle A\rangle$ fluctuating by ±6%. The noncrystalline content of this sample, as measured by density, was 0.37. For all of the acetate esters used, F_e exceeds the noncrystalline content after 14 days of reaction. The dissolution temperatures of a TPI lamellar sample suspension epoxidized to 35% were measured in nine liquids by using a heating rate of 1 °C/h. The results for seven of these are included in Figure 1. The sample was insoluble in the other two liquids, methanol and 1-butanol, at all temperatures up to the boiling point. It can be observed that as the dissolution temperature for the epoxidized lamellas decreases, $\langle B\rangle$, as obtained by reaction carried out in that liquid, increases.

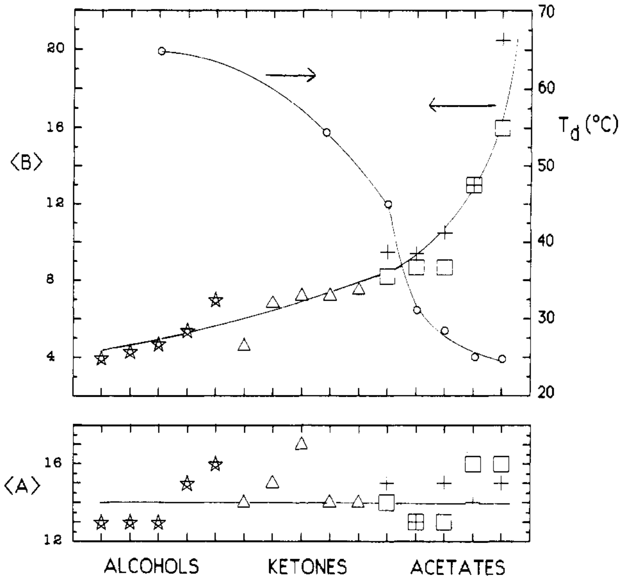


Figure 1. Effect of reaction medium on $\langle A\rangle$ and $\langle B\rangle$ after TPI epoxidation. Reaction for 14 days: alcohols (☆; ketones (△); acetates (□). Reaction for 21 days: acetates (+). The specific liquids are listed in the text. The dissolution temperatures, T_d, for 2-ethoxyethanol, acetone, and five acetate esters are also shown (○).

Table II
Values of $\langle A\rangle$, $\langle B\rangle$, and F_e of Epoxidized β-TPI Lamellas at Different [M]/[D] Ratios[a]

medium	[M]/[D][b]	time, days	F_e	$\langle B\rangle$	$\langle A\rangle$
acetone	1	14	0.34	7.2	14
	3	10	0.36	8.2	15
		20	0.42	10.5	15
	4	10	0.41	10.0	15
1-butanol	1	14	0.23	4.0	13
	3	10	0.36	8.9	16
		13	0.38	9.5	15
		17	0.38	9.0	15
		20	0.38	9.3	15

[a] Unfractionated TPI crystallized from amyl acetate at 0 °C and heated to 30 °C in the suspension liquid followed by resuspension and epoxidation at 0 °C. [b] The concentrations at [M]/[D] = 1, 3, and 4 were 5.5, 7.6, and 10.1 g L^{-1}, respectively.

The quantity of MCPBA used was found to affect the epoxidation reaction. At lower [M]/[D] in media that are poor solvents the reaction was incomplete, leading to lower $\langle A\rangle$ and $\langle B\rangle$. Reaction results at higher [M]/[D] in three of these liquids are shown in Table II and in Figure 2. $\langle B\rangle$ and also F_e increase with reaction time while $\langle A\rangle$ remains constant when using either acetone or 2-ethoxyethanol as the suspension liquid. $\langle B\rangle$ remains constant after 13 days,

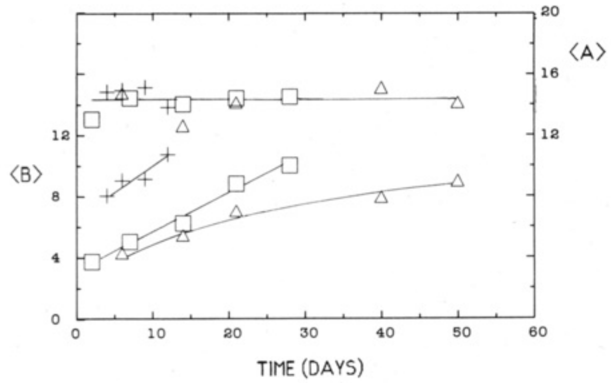


Figure 2. Effect of reaction time and reactant ratio on the unreacted ⟨*A*⟩ and reacted ⟨*B*⟩ block lengths for TPI lamellas epoxidized in 2-ethoxyethanol. [M]/[D]: 1 (△); 2 (□); 4 (+).

Table III
Heat of Fusion by DSC of β-TPI and Epoxidized TPI at Different Reaction Levels

medium	sample	$1 - W_c$[a]	F_e	ΔH_f, J/g[b]
2-ethoxyethanol	β single lamellas, T_c = 20 °C, M_v = 2.6 × 10^5	0.38	0	74 ± 2
			0.26	72 ± 2
			0.40	62 ± 3
2-ethoxyethanol	β curved overgrown lamellas, T_c = 0/30 °C, M_v = 2.6 × 10^5	0.39	0	75 ± 1
			0.34	72 ± 1
			0.40	71 ± 1
			0.48	65 ± 1
1-butanol	β curved overgrown lamellas, T_c = 0/30 °C, T_c = 0/30 °C, unfractionated	0.37	0	76 ± 3
			0.38	76 ± 2[c]

[a] Fraction of noncrystallized portion by density using $\rho_c = 1.02$. [b] Mean of at least four measurements; weight correction for the O atoms of the oxirane according to F_e. [c] Average of five preparations at the same reaction conditions to a similar reaction level at different times (10–20 days).

however, when the reaction is carried out in 1-butanol; also in this liquid F_e reached and did not exceed the density value for the noncrystalline content.

Heat of fusion measurements were carried out on unepoxidized and epoxidized lamellas as listed in Table III. The heat of fusion values, ΔH_f, are averages of at least four measurements. Preparations reacted in 2-ethoxyethanol show a gradual decrease in ΔH_f with increasing F_e until the latter parameter reaches $1 - W_c$ whereupon ΔH_f drops more rapidly. ΔH_f remains constant when 1-butanol is used as the reaction medium. Infrared spectra were obtained for TPI preparations after epoxidation in 1-butanol. The amorphous band at 842 cm^{-1} disappears and the band, attributed to C═C stretching, can be eliminated by subtraction of the crystalline component; both of these observations suggest that the surface reaction was complete.

The principal purpose of the present study was to investigate the effects of molecular weight and crystallization conditions, and therefore the morphology, on the crystalline stem length and the noncrystalline traverse length for TPI structures crystallized from solution. The epoxidation medium chosen for this was 1-butanol at [M]/[D] = 3. From the preliminary studies given above these were found to be the best conditions for completion of the reaction in a reasonable time (8–14 days) and for the avoidance of crystal core penetration and of cross-linking. As a test of the completeness of reaction, F_e values measured for 15 preparations, differing in molecular weight and/or crystallization conditions, were compared with noncrystalline values from both infrared and density measurements. The F_e values ranged from 0.33 to 0.49; the values from infrared agreed within 0.02 units and those from density within 0.03, suggesting that the surface reaction is complete without further unwanted effects. The preparations studied include: (i) single lamellas in the β crystalline form prepared by the precooling method at crystallization temperatures of 20 and 30 °C in amyl acetate (Figure 3); (ii) overgrown curved β lamellar structures crystallized from amyl acetate by cooling directly to 0 °C; these were then heated slowly in the crystallization liquid (0.06 °C/min) to 20, 30, and 32 °C and annealed for various time periods (Figure 4); (iii) α lamellas (one preparation) crystallized by precooling in hexane solution at 25 °C; (iv) α sheaves/spherulites crystallized from amyl acetate at 25 °C (Figure 5). For the latter preparations it was necessary to employ a longer reaction time in order to obtain constant values. All preparations were epoxidized in suspension and the products subjected to carbon-13 NMR measurements. Twenty-nine different

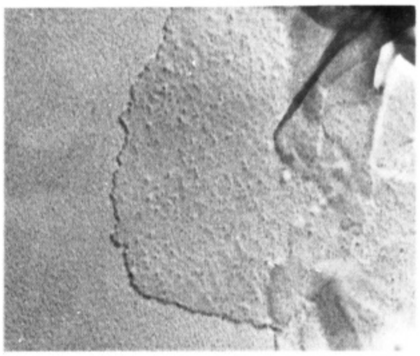


Figure 3. Transmission electron micrograph of a β-TPI lamella crystallized from 0.1% amyl acetate solution at 20 °C, reacted with OsO_4, dried, and Au/Pd shadowed.

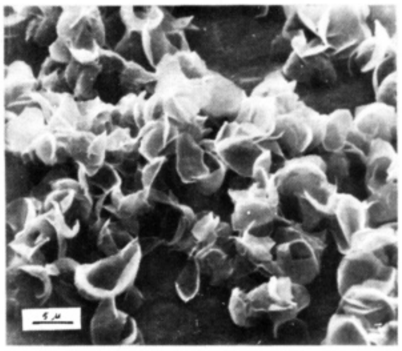


Figure 4. Scanning electron micrograph of β-TPI curved lamellas from 1% amyl acetate solution cooled to 0 °C. The resulting suspension was heated at 0.6 °C/min to 30 °C, kept at 30 °C for 48 h, reacted with OsO_4, dried, and gold coated.

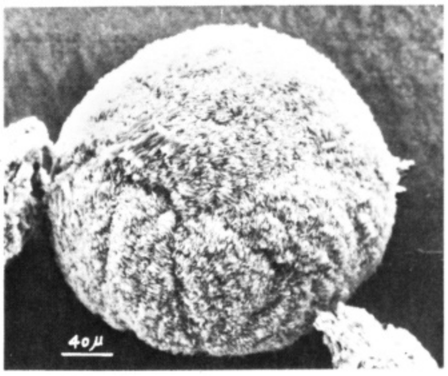


Figure 5. Scanning electron micrograph of α-TPI spherulite crystallized from 1% amyl acetate solution at 25 °C (M_v = 2.6 × 10^5) for 4 days, reacted with OsO_4, dried, and gold coated.

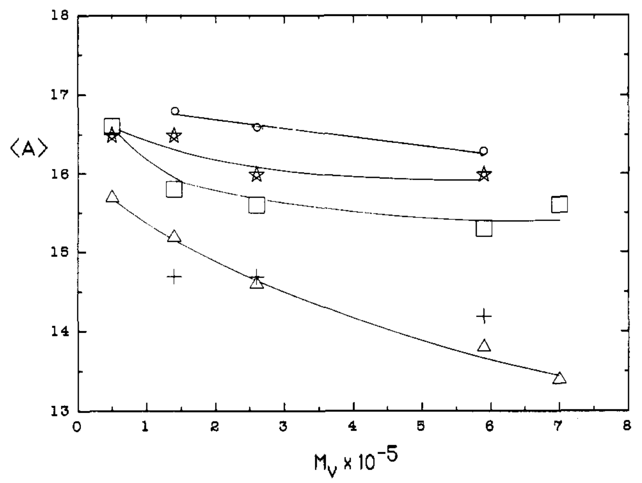


Figure 6. Unreacted block length ⟨A⟩ versus molecular weight for single and multilamellar TPI structures: (○) β single lamellas, T_c = 20 °C; (☆) same but T_c = 30 °C; (△) overgrown curved β lamellar structures, cooled to 0 °C, heated slowly to 20 °C and left at 20 °C for 40 h; (□) same but final temperature was 30 °C; (+) α sheaves/spherulites, T_c = 25 °C.

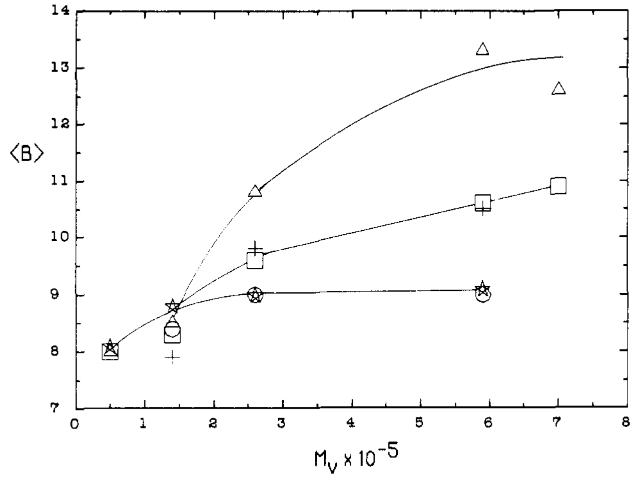


Figure 7. The reacted block length ⟨B⟩ versus molecular weight for single and multilamellar TPI structures. Same legends as Figure 6.

preparations were investigated. Four of these were studied in triplicate, 18 in duplicate, and seven as single determinations. The result for each sample was a mean of data for the C_1 and C_4 carbons. The precision for the duplicate and triplicate determinations as well as for each C_1/C_4 pair was ±5% for both ⟨A⟩ and ⟨B⟩.

⟨A⟩ and ⟨B⟩, obtained as a function of molecular weight, are given in Figures 6 and 7, respectively, for β single lamellas, β overgrown lamellas, and α sheaves/spherulites. All the samples studied show a decrease in the average stem length, ⟨A⟩, with increasing molecular weight; however, this is within the precision limits expected for these measurements except for the overgrown curved β lamella sample cooled to 0 °C and annealed to 20 °C for 40 h, for which it corresponds to a 0.9 nm change. The ⟨A⟩ values are in the order single β lamellas > overgrown curved β lamellas annealed at 30 °C > α spherulites > β curved lamellas annealed at 20 °C. The change observed in ⟨A⟩ with a change in the morphology is largest at the highest molecular weight and corresponds to 1.3 nm. For the five samples studied ⟨B⟩ shows a value of 8.3 ± 0.3 at the lower molecular weights but then exhibits wide divergences at larger values. For the sample cooled to 0 °C and annealed to 20 °C a 50% change occurs with a 14-fold molecular weight increase. The single lamella samples show about a 10% change initially then level off.

Other experiments, not recorded in Figures 6 and 7, were also carried out. These included the use of longer annealing times for treatment of the overgrown curved β lamellas, annealing to 20 °C and then to 30 °C, annealing to 32 °C, the use of higher concentrations, and the preparation of α single lamellas. Increasing the annealing time at 20 and at 30 °C from 40 h to 1 week caused no significant change in ⟨A⟩ for samples with M_v from 1.4 × 10^5 to 5.9 × 10^5. With this change in annealing time a significant decrease in ⟨B⟩ occurs for one sample; for the sample with M_v of 5.9 × 10^5 annealed at 20 °C ⟨B⟩ decreases by 2 units. The results of the following treatments did not differ significantly from those for the samples annealed at 30 °C for 40 h: (i) annealing for 2 weeks at 30 °C (M_v = 5.9 × 10^5), (ii) annealing at 20 °C for 40 h followed by an increase to 30 °C for 1 week (M_v = 2.6 × 10^5), (iii) annealing at 32 °C for 40 h (M_v = 2.6 × 10^5), and (iv) change of the crystallization concentration to 3, 4, and 5% (w/v) with crystallization at 0 °C and annealing at 30 °C for 40 h (M_v = 2.6 × 10^5). One preparation of α single lamellas was prepared by precipitation from 0.1% hexane solution at 25 °C by using the precooling technique; these yielded ⟨A⟩ = 16 and ⟨B⟩ = 8.6 monomer units.

Discussion

It was found in this study that when TPI lamellar structures in suspension are epoxidized both the average reacted block length, ⟨B⟩, and the fraction reacted, F_e, depend on the liquid medium. When acetate esters are used, F_e exceeds the noncrystalline fraction calculated from density measurements, suggesting that penetration of the crystalline core of the lamellas occurs. Since ⟨A⟩ keeps relatively constant while ⟨B⟩ increases, this penetration must take place principally from the lateral surfaces. The double bonds in the chains at the lateral surfaces are expected to react immediately. If the attractive forces between the epoxidized chains and the liquid medium exceed those between epoxidized TPI and TPI units and if the folding is mainly to nearby sites along an exposed fold plane, the reacted lateral chains could separate or loosen from the rest of the crystal and allow reaction of the next row of chains formerly inside the crystalline core. This would give a mixture of block copolymer and completely epoxidized TPI chains or chain sequences. As the amount of completely reacted chain sequences increases, ⟨B⟩ would increase but ⟨A⟩ would not change. The results of the dissolution temperature experiments for a 65/35 TPI/epoxidized TPI block copolymer in various liquids (see Figure 1) support this mechanism. It was found that all of the acetate esters used have lower dissolution temperatures for the epoxidized lamellas than for the unreacted lamellas and as the dissolution temperature decreases, F_e obtained in that medium increases. Even in liquids with relatively high dissolution temperature, such as acetone and 2-ethoxyethanol, a separation or loosening occurs at higher [M]/[D] and longer time. The DSC results shown in Table III are another indication that epoxidized chains separate from the lateral surfaces, causing additional reaction. Although the heat of fusion could be affected by the fold thickness,[13] it is unlikely that this occurs in this study, since the average unreacted block length did not change as F_e increased. The ΔH_f decrease implies a decrease of crystallinity occurring due to conversion of the TPI units in crystal traverses to noncrystallizing epoxidized units as the reaction proceeds. The electron microscopy studies carried out earlier[3] on α-TPI lamellas epoxidized in amyl acetate showed considerable erosion at the sides as well as the formation of holes in the interior part after reaction. The dissolution temperature for epoxidized TPI in amyl acetate is low and therefore appreciable loss of the lamellar side portion would be expected. The amount of reaction taking place during hydrochlorination of TPI lamellas was found to depend on the reaction medium used.[14] Penetration from the lateral surfaces was also reported in a study of chlorination of polyethylene lamellas.[15]

As discussed above, penetration from the side favors the presence of chain folding at the crystal surface to nearby sites. The presence of large amounts of folding to sites not in adjacent rows is expected to hold the outside lateral crystal traverses in place and therefore lead to less penetration from these surfaces.

The attainment of constant values for F_e with reaction time, in agreement with independent measures of the noncrystalline fraction for the various TPI structures, suggests that reaction at the fold surfaces is complete and that significant penetration of the crystal core is not taking place. Under these conditions the values of $\langle A \rangle$ and $\langle B \rangle$ obtained can be equated with characteristics of the original lamellar structures. $\langle A \rangle$ is directly related to the average crystalline stem length and therefore to the average thickness of the crystalline core. $\langle B \rangle$ characterizes all of the lamellar features available for reaction, which includes fold surfaces, lateral surfaces, noncrystallizing chain ends, and interlamellar traverses. From the dimensions of the lamellas investigated herein the lateral surface area is estimated to be 2% or less of the total and therefore this effect can be ignored. For the single β lamellas $\langle B \rangle$ and F_e show increases with increasing molecular weight over the lower part of the range studied. Similar changes, observed by density measurements for α-TPI lamellas, were attributed previously to the presence of very short noncrystallizing chain ends.[4] $\langle B \rangle$ for β-TPI lamellas becomes constant at 9 for higher molecular weights and therefore this value is equated to the average fold length. A 10 °C change in crystallization temperature causes little or no change in the average fold length; α- and β-TPI lamellas have similar values for this parameter. The average fold length from this work is about 2 times that reported for α-TPI lamellas from hydrochlorination/carbon-13 NMR results[14] and exceeds by a 16% value resulting from use of the epoxidation/carbon-13 NMR method.[8] The F_e values reported in the hydrochlorination study were about 40% lower than the noncrystalline content from density. In light of the present study and current results of the hydrochlorination method, it is now believed that complete reaction was not obtained in the earlier hydrochlorination work.

In a recent comparable study of chain folding in *trans*-1,4-polybutadiene, TPBD, containing 1% cis units and having M_v of 2×10^4, $\langle B \rangle$ ranged in value from 5 to 9, depending mainly on the crystallization temperature, T_c.[16] The change in fold length with T_c was attributed to the rejection of cis and accompanying trans units from the crystal core during the crystallization process; the amount of trans unit rejection was expected to increase with increasing crystalline stem length, accounting for the increase in $\langle B \rangle$ with increasing T_c. A statistical treatment assuming a mixture of relatively short folds having a length B' with folds containing rejected units and having a variable length up to a value of $\langle A \rangle - 1$ was developed to calculate the crystallinity;[17] agreement with experiment was found for $B' = 3$–4. The value for $\langle B \rangle$ found for TPI must be compared with B' for TPBD since the presence of cis units was not detected for the TPI fractions used. The average fold length for β-TPI lamellas is, therefore, two- to threefold larger than that for TPBD. The characteristic ratio, as obtained from solution property measurements for randomly coiled chains, is 1.3 times larger for TPI[18] than for TPBD;[19] this latter difference was attributed principally to the suppression of gauche states about CH_2CH_2 bonds in TPI due to the presence of the methyl group.[19] The chains in the crystal core are farther apart for TPI than for TPBD, due again to the presence of the methyl group in the former. Both this and the gauche suppression effect could contribute to the difference in fold length for the two polymers. However, for a TPI lamella with a β-form crystal core the minimum number of monomer units necessary for an adjacent 120 or 010 fold is three, as obtained from molecular models. Therefore, the $\langle B \rangle$ value of 9 suggests that a significant amount of nonadjacent but nearby and/or loose adjacent reentry folding occurs.

Table IV
Fraction of Noncrystalline TPI Units in Interlamellar Traverses

preparation	$M_v \times 10^{-5}$	F_t
overgrown curved β lamellas annealed at 30 °C	1.4	0
	2.6	0.05
	5.9	0.2
α sheaf/spherulites	2.6	0.1

Multilamellar TPI structures in the α and in the β crystalline forms were investigated in the present study. The $\langle B \rangle$ values depend upon molecular weight and on the details of crystallization and annealing; they exceed those found for single lamellas by as much as 50% at the largest molecular weights used. This change could be due to larger folds and/or to the presence of interlamellar linkages. The decrease in $\langle B \rangle$ with an increase in the annealing temperature from 20 to 30 °C or by annealing for a longer time at 20 °C (these processes being carried out in the crystallization liquid) is accompanied by a similar increase in $\langle A \rangle$. This suggests that significant fold tightening occurs during the annealing process. However, the agreement in $\langle B \rangle$ values for preparations annealed at 30 °C for various time periods with that annealed at 32 °C suggests that the folds have reached an optimum value. This fold length should be similar to that measured for single lamellas and any excess in $\langle B \rangle$ value should be due to interlamellar traverses longer than the fold length. This conclusion is supported by the $\langle B \rangle$ value differences between α sheaves/spherulites and α lamellas. There is a difference in the concentrations used for single lamella preparation (0.1%) and multilamellar structure preparation (1%) which could contribute to the difference in B values measured. However, no effect of concentration on A or B was found in this work in the 1–5% range. A recent study of TPBD structures showed no concentration effects in the 0.05–5% region.[16] The $\langle B \rangle$ excess for overgrown curved β lamellas annealed at 30 °C and for α sheaves/spherulites can be used to calculate the fraction of monomer units in interlamellar traverses longer than the fold length, F_e(traverses), as follows:

$$F_e(\text{traverses}) = 2(\langle B \rangle - \langle B \rangle_0)/(\langle B \rangle + \langle B \rangle_0) \qquad (6)$$

where $\langle B \rangle_0$ is the value for single lamellas prepared from the same polymer. The values obtained are given in Table IV. The fraction of noncrystalline monomer units in interlamellar traverses increases with molecular weight. This is believed to be due to an increase in the number of these traverses at the expense of chain folds with increasing molecular weight. This result is in qualitative agreement with thermal analysis results for melt-crystallized polyethylene.[20] In order to estimate the average length of the interlamellar traverses the fraction of these traverses (F_t) must be known. This latter fraction can be obtained by a statistical "gambler's ruin" calculation.[21] Carrying out this calculation using input parameters for the sample prepared from material with $M_v = 5.9 \times 10^5$ by cooling to 0 °C and annealing at 30 °C gives 0.07. From the equation

$$\langle B\rangle = F_t\langle B\rangle_t + (1 - F_t)\langle B\rangle_0 \tag{7}$$

the average length of an interlamellar traverse, $\langle B\rangle_t$, for this sample is estimated as 30. However, this method predicts that F_t decreases with an increase in the noncrystalline content. This is unlikely since the noncrystalline content increases with molecular weight and therefore F_t increases with increasing noncrystalline content in this work.

Conclusions

The results of this study lead to the following conclusions:

1. The extent of reaction for TPI lamellas is dependent on the liquid medium used due to the possibility of crystal penetration from the lateral surfaces. Segmented block copolymers containing unreacted TPI sections and epoxidized TPI sections can be prepared by using 1-butanol as the reaction medium.

2. Tie molecules are detected in multilamellar TPI structures. The amount of these interlamellar linkages increases with increasing molecular weight.

3. The fraction of reacted double bonds determined by carbon-13 NMR is in good agreement with the fraction of the noncrystalline component from FTIR measurements and from density.

4. The average number of monomer unit per fold for the lamellas grown in this study is 9. The epoxidation results favor nearby reentry chain folding.

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Electrochemical Doping Reactions of the Conducting Ladder Polymer Benzimidazobenzophenanthroline (BBL)

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ABSTRACT: The electrochemical reactivity of films of the title polymer is examined by using cyclic voltammetry, coulometry, and spectroelectrochemistry. In contact with acidic aqueous $(Bu_4N)_2SO_4$ buffer, BBL voltammetry exhibits two redox steps corresponding to the sequential reduction of the unprotonated and the protonated forms of BBL connected by a $pK_a = 2.2$. The reductions consume overall one electron and one proton per BBL monomer site. The (more positive) reduction of unprotonated BBL is proposed to involve protonation at the carbonyl to yield a quinone/hydroquinone form; reduction of the protonated BBL is proposed to involve protonation of imine sites to yield a quinone/quinoimine form of the polymer. The quinone/quinoimine form is the more electrically conductive form of doped BBL.

The electrochemical reactivity of electrically conductive polymers[1] is an important aspect of their synthesis by electropolymerization, of their oxidation or reduction (i.e., doping) into a conducting state, of understanding their electronic structure, and of their application to energy storage or electrochromism.

This paper presents a study of the electrochemical reactivity of the polymer poly[(7-oxo-*7H,12H*-benz[*de*]imidazo[4′,5′:5,6]benzimidazo[2,1-*a*]isoquinoline-3,4:11,12-tetrayl)-12-carbonyl], mercifully abbreviated BBL. This polymer is a member of the structurally diverse class of materials called ladder polymers, which are double-stranded, highly conjugated macromolecules. Ladder polymers have only recently experienced significant investigation;[2] there are now reports of significant electrical conductivities and other attractive properties such as liquid crystallinity and high thermal stability, to 500 °C in the case[3,4] of BBL.

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