which is to increase the tt content of PVDF chains.

This control of the PVDF crystalline phase upon blending is not peculiar to mixtures with PMMA. Indeed, we have recently observed a similar crystallization behavior of PVDF in blends with some other compatible polymers, characterized by different chemical structures.[26] These new data will be discussed in detail in a forthcoming publication.

Acknowledgment. We thank Drs. L. Bosio and C. Chassagnard for their kind and helpful assistance in the X-rays and NMR experiments, respectively. This work was supported by the "Centre National de la Recherche Scientifique" through Grant ATP 983004.

Registry No. PVDF, 24937-79-9; PMMA, 9011-14-7; i-PMMA, 25188-98-1; s-PMMA, 25188-97-0; (VDF)(TrFE) (copolymer), 28960-88-5.

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Crystallization of Randomly Epoxidized *trans*-1,4-Polyisoprene

Jia-rui Xu 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 December 10, 1987*

ABSTRACT: Copolymers of *trans*-1,4-polyisoprene containing from 1 to 10% randomly placed epoxidized units were crystallized from solution. The crystal form from infrared spectroscopy, the DSC melting endotherm(s), and the reacted and unreacted block lengths, as obtained by surface epoxidation in suspension followed by carbon-13 solution NMR, were determined. Small amounts of oxirane units (1–2%) have no significant effect on the melting endotherm or block lengths but do change the crystal form and the redissolution temperature. Evidence for incorporation of oxirane units in the crystal core is discussed.

Introduction

The quantitative characterization of single lamellas and lamellar structures of *trans*-1,4-polybutadiene, TPBD, and *trans*-1,4-polyisoprene, TPI, has been carried out by using a surface reaction coupled with carbon-13 solution nuclear magnetic resonance measurements.[1–6] This procedure yields the fraction reacted and the average reacted and unreacted block lengths of the modified chains. For single lamellas at moderate to high molecular weight and with the proper choice of reaction conditions these parameters can be equated to the total surface fraction, the average fold length and the crystalline stem length, respectively. For multilamellar structures the reacted block length is equated to an average noncrystalline chain traverse length, characteristic of the folds and any interlamellar traverses present.

The effects of polymer molecular weight (M_v = 7000–36 000) and of crystallization solvent and temperature on the morphology, the crystallinity, the surface fraction, the crystalline stem length, and the average reacted block length have been studied for 99% trans-, 1% cis-1,4-polybutadiene crystallized from dilute solution.[2] The average reacted block length increased from 5 to 9 with a change in crystalline stem length from 15 to 24 but with the crystallinity remaining at 0.24–0.27; it was also found that within the detection limits the cis units present in the chains appear at the lamellar surfaces and that the measured parameters were independent of crystallization concentration up to 5%. Lamellas of a 88.5% trans-1,4-, 10% cis-1,4-, 1.5% 1,2-polybutadiene with $M_w = 4.6 \times 10^5$ were obtained from solution by using various crystallization conditions with gels being formed above a concentration of 0.7%.[3] All of the crystalline products from this sample gave an average reacted block length of 11 ± 1 and a crystalline stem length of 16 ± 1. It was also determined that about 5% of the cis units was incorporated in the crystal core and the remainder excluded and appearing at the lamellar surfaces.

TPI fractions, containing no detectable amounts of the other isomeric units, with molecular weights (M_v) of 0.5×10^5 to 7×10^5 were crystallized from solution by using conditions that individually give single β-form lamellas,

0024-9297/88/2221-2994$01.50/0

α-form lamellas, overgrown curved β-form lamellas, and α-form spherulites.[6] For the β-lamellas the average fold length increased from 8 to 9 with increasing molecular weight (M_v) from 50 000 to about 1.5×10^5 and then remained constant with M_v to 6×10^5. For the overgrown curved β-lamellas the average reacted block length increased with molecular weight and changed with crystallization conditions.

Except for the studies on the two polybutadiene isomeric copolymers described above, the parameters resulting upon crystallization of random copolymers, particularly the determination of the average fold length and the crystalline stem length as a function of copolymer composition, have not been investigated to date. Random copolymers can be easily prepared by epoxidation of TPI in solution.[4] The purpose of the present work was to investigate the effects of epoxidized TPI units in amounts from 1 to 10% on TPI crystallization. Fourier transform infrared and differential scanning calorimetry measurements were made on the as crystallized copolymers. These preparations were subjected to epoxidation in suspension followed by carbon-13 solution NMR. The results suggest that for low contents (1 and 2%) the epoxidized units are rejected from the crystal core but do not cause a significant change in the reacted and unreacted block lengths from those found for 100% TPI. The presence of larger amounts of epoxidized units (5–10%) yields some changes in melting endotherms and block lengths.

Experimental Section

Sample Preparation. Unfractionated TPI ($M_n = 3.5 \times 10^4$, $M_w/M_n = 4.8$), obtained from Polysciences, Inc., were used. Epoxidations were carried out with *m*-chloroperbenzoic acid in 1% chloroform solution with stirring for 1–2 h. The copolymer was precipitated in methanol, redissolved, reprecipitated repeatedly, and finally dried.

Crystallization. Crystallizations were attempted from 0.1% (w/v) solution by using a precooling method.[6,7] The sample is dissolved at an elevated temperature (T_d), the solution cooled to 0 °C giving precipitation (T_p), the temperature raised at an average rate of 0.3 deg/min until dissolution is observed (T_R), and the solution placed in a constant temperature bath (T_C) and left undisturbed for a 2–7-day period. Freshly distilled amyl acetate, 2-pentanone, and ethyl acetate/amyl acetate mixtures were used as solvents. Morphological observations were made on suspensions of crystallized structures by using a Zeiss photomicroscope equipped with interference contrast optics.

Infrared Spectroscopy. A Digilab FTS 40 Fourier Transform infrared spectrometer at 4 cm^{-1} resolution was used to obtain spectra in the 450–4000 cm^{-1} region on thin filtered and dried mats of the crystalline lamellar preparations.

Differential Scanning Calorimetry. Melting endotherms for the dried preparations were obtained with a Du Pont 1090 thermal analyser at a heating rate of 10 °C/min.

Suspension Epoxidation. The as prepared lamellas were resuspended in *n*-butyl alcohol and reaction was carried out with dissolved *m*-chloroperbenzoic acid, MCPBA, at 0 °C for 12–17 days by using [MCPBA]/[double bonds] = 3 and a starting polymer concentration of 7.6 g/L. The polymer reaction products were washed with fresh *n*-butyl alcohol at 0 °C and dried.

Carbon-13 Nuclear Magnetic Resonance. Carbon-13 NMR measurements at 75.47 MHz were carried out with an IBM NR/300 FT NMR. The samples were in 10% $DCCl_3$ solution containing TMS. A spectral width of 12 500 Hz in 32K memory with broad-band decoupling, a delay time of 5 s, and coaddition of 7000–9000 scans were used. Band intensities in the CH_2 region were obtained by machine integration.

Results

Four copolymers prepared to different oxirane contents were found by Carbon-13 solution NMR, using the methylene carbon peak assignments given earlier,[4,6] to contain 1.4, 2.2, 5.0, and 9.8% reacted units. The presence of NMR peaks assigned to sequences containing isolated reacted units and the absence of peaks assigned to two or more consecutive reacted units suggest that random placement of the epoxidized units occurs.

Table I
Crystallization Conditions and Properties for Random Copolymers of TPI and Epoxidized TPI[a]

oxirane content, %	cryst liquid[b]	T_R,[c] °C	T_c,[d] °C	cryst time, days	melting endotherm, °C prim.	melting endotherm, °C sec.	cryst form prim.	cryst form sec.
0	AA	33	20	2	52	57	β	α
1.4		31	20	3	52, 57	...	β, α	...
1.4		29	20	2	52, 57	...	β, α	...
1.4		29	10	2			β	...
2.2		29	20	3			α	...
2.2		26	20	2	58	...	α	...
2.2		26	10	2			β	...
5.0		25	20	7	57		α	...
5.0		24	20	7	57		α	...
5.0		19	10	2	51	...	α	...
5.0		20	10	2	51	...	α	...
9.8		3	0	7	...	...	...	...
9.8	50/50	22	10	5	48	...	α	...
9.8	AA/EA	22	10	5	48	...	α	...

[a] Crystallized from 0.1% solution by precooling method.[6] [b] Abbreviations: amyl acetate, AA; ethyl acetate, EA. [c] Redissolution temperature. [d] Crystallization temperature.

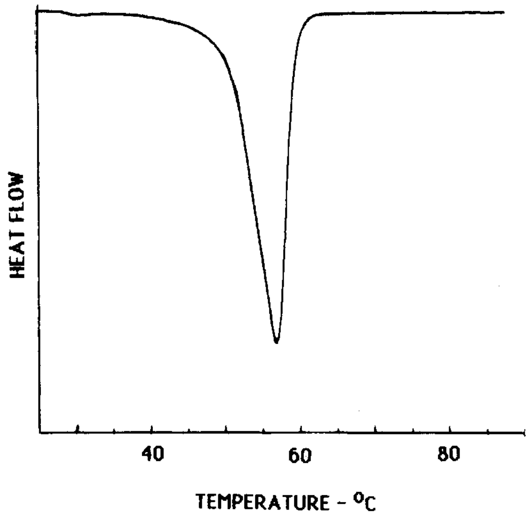

Figure 1. Melting endotherm for 5.0% solution epoxidized TPI crystallized from 0.1% amyl acetate solution at 20 °C.

Crystallization of the copolymers from solution was carried out by using the precooling method ($T_d \rightarrow T_p \rightarrow T_R \rightarrow T_c$) under conditions as given in Table I. It is observed that the minimum redissolution temperature, T_R, decreases with an increase in the oxirane content when the same solvent is used. The time necessary for initial nucleation, as well as the crystallization rate, was observed to increase with increasing oxirane content. For the copolymer with 9.8% oxirane the use of mixed solvents (ethyl acetate and amyl acetate) and a crystallization temperature of 10 °C were necessary in order to obtain useful yields. The morphology generally observed was multilamellar although single lamellas resulted for the copolymer with a 1.4% oxirane content crystallized at 10 °C from amyl acetate and for the copolymer with a 9.8% oxirane content crystallized at 10 °C from 50/50 amyl acetate/ethyl acetate.

A DSC scan for the copolymer with 5.0% oxirane content crystallized at 20 °C is given in Figure 1. An infrared spectrum for the copolymer containing 9.8% oxirane units

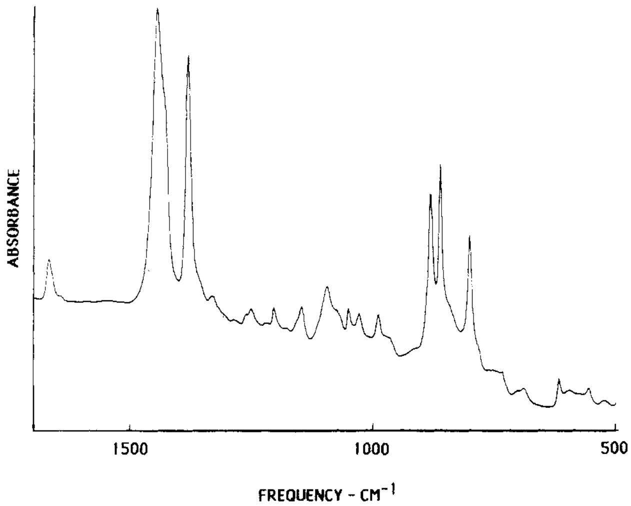

Figure 2. Infrared spectrum for 9.8% solution epoxidized TPI crystallized from 50/50 amyl acetate/ethyl acetate solution at 10 °C.

is given in Figure 2; the spectrum is mainly that of semicrystalline TPI in the α-form;[8] however, there are bands for epoxidized TPI present, at 1250, 1122, 1068, and 682 cm^{-1}. As shown in Table I, the melting endotherm(s) from DSC measurement is a function of the oxirane content and the crystallization temperature. One cause of the first effect is the change of crystal form that takes place with increasing oxirane content from predominantly β to completely α, as observed by using infrared spectroscopy. For crystallization from 1% amyl acetate at 20 °C an endotherm at 50–51 °C was previously associated with β-TPI and an endotherm at 58–59 °C with α-TPI.[7] At a crystallization temperature of 10 °C an endotherm at 47–50 °C was given for β-TPI; three TPI fractions, crystallized directly from 1% amyl acetate solution at 10 °C,[6] are found in this work to be principally in the β-form and to have major endotherms at 48–49 °C and smaller endotherms, indicative of the α-form, at 57–58 °C. For the copolymer with a 5% oxirane content in the α-form the melting endotherm for material crystallized at 10 °C is 6–7 deg lower; when crystallized at 20 °C, however, this material has a melting endotherm within 1 deg of those for polymers with 0, 1, and 2% oxirane content.

Crystallization of the four oxirane-containing copolymers was also attempted from 2-pentanone; it was observed that T_R decreases from 67 to 19 °C for oxirane contents of 1.4–9.8% with crystallization at 20 °C yielding the β-form at 1.4 and 2.2% oxirane contents and the α-form at 5.0% oxirane content.

Eight crystallized copolymer samples were epoxidized in suspension under conditions found earlier[6] to give complete reaction at the lamellar surfaces; carbon-13 NMR measurements were carried out on the products. The CH_2 resonances observed for all but one sample showed within experimental uncertainty only the presence of blocks of epoxidized (E) and nonepoxidized (I) units. For the copolymer containing 9.8% oxirane units crystallized from 50/50 amyl acetate/ethyl acetate at 10 °C a small resonance at 38.96 ppm, indicative of IEI sequences,[4] was detected along with a much more intense doublet at 38.87 and 38.76 ppm due to IEE sequences. It was not possible to determine the relative intensity of the 38.96 ppm resonance due to noise and the closeness of the larger doublet. This resonance was not detectable for the copolymer with the 5.0% oxirane content crystallized at 20 °C from amyl acetate. The average unreacted fold length, $\langle A \rangle$, the average reacted fold length, $\langle B \rangle$, and the fraction epoxidized, F_e, were calculated, as given previously,[4,6] from the resonances for the CH_2 carbons in the unreacted, the reacted and the junction regions; the values determined are given in Table II. $\langle A \rangle$, $\langle B \rangle$, and F_e for the copolymers containing 1.4 and 2.2% oxirane units are not significantly different from the values found for 100% TPI. At 5% oxirane content a decrease in $\langle A \rangle$ by 1–2 units and in $\langle B \rangle$ by about 1 unit occur. For the copolymer with a 9.8% oxirane content crystallized at 10 °C from 50/50 amyl acetate/ethyl acetate a relatively small $\langle A \rangle$ and large $\langle B \rangle$ result in a large F_e.

Table II
Suspension Epoxidation of Solution Crystallized Randomly Epoxidized *trans*-1,4-Polyisoprene

oxirane content, %	solv	T_c, °C	$\langle A \rangle$	$\langle B \rangle$	F_e
0[a]	AA	20	16	9	0.35
1.4		20	17	8.9	0.35
2.2		20	16	9.2	0.37
2.2		10	15	9.0	0.38
5.0		20	14	8.1	0.37
			14	8.4	0.38
5.0		10	13	8.3	0.39
9.8	50/50 AA/EA	10	10	9.9	0.50
			9.9	11	0.52

[a] values of $\langle A \rangle$, $\langle B \rangle$, and F_e are averages from previous results for fractionated samples.

Discussion

In this investigation oxirane units were randomly placed in the TPI chain in amounts of 1.4, 2.2, 5.0, and 9.8%. These copolymers were crystallized from solution by using a precooling method,[6] the melting endotherms were measured, and the crystal form was determined. The lamellar structures obtained by crystallization of the random copolymers were then epoxidized in suspension forming block copolymers of TPI and epoxidized TPI. Random incorporation of epoxidized TPI units in the TPI chain first affects the solubility of the polymer, as shown by the decrease in the redissolution temperature, T_R, starting at 1.4% oxirane content. The crystal form occurring during the crystallization is the second parameter affected, and this occurs at about 2.2% oxirane content. At larger oxirane contents (>5%) the melting endotherm and the average reacted and unreacted block lengths show changes. A relatively high rate of β-nucleus formation was reported previously.[9] Oxirane unit incorporation apparently slows this rate, allowing sole nucleation of the α-form. A new crystal form is not apparent even at 10% oxirane content.

The complete rejection of the oxirane units in the copolymer from the crystal core should leave the melting endotherm unchanged; it would also lead to the incorporation of these units in the reacted blocks during the suspension reaction. If this was occurring, the unreacted block length would be equal to the crystalline stem length and at high enough molecular weight for single lamellas the average reacted block length would equal the average fold length. If isolated oxirane units are included in the crystal core, the melting endotherm would be expected to decrease. The constancy of the melting endotherms for the copolymer containing 0, 1.4, and 2.2% oxirane units suggests that rejection does occur during crystallization. As discussed earlier,[6] an average fold length of 9 for TPI suggests a loose fold or a considerble amount of nearby nonreentrant folding. For 1.4 and 2.2% oxirane content in the copolymer rejection does not affect the fold length. Since, on the average, the number of repeat units between oxirane units would be 100 and 50, respectively, the observed constancy of the stem length is not unexpected. The decrease in both $\langle A \rangle$ and $\langle B \rangle$ for the copolymer with a 5.0% oxirane content suggests that some incorporation in the crystal core occurs at both T_cs used; however, IEI sequences were not detectable in one sample crystallized at 20 °C. There is on the average an oxirane unit every 20 isoprene units in the random copolymer, which could possible cause some restriction on $\langle A \rangle$. This oxirane content does not affect the melting endotherm when $T_c = 20$ °C but does cause a significant lowering of the endotherm for $T_c = 10$ °C. Before a complete explanation is given for this effect, further study is believed necessary.

For the copolymer with the largest oxirane content (9.8%) crystallized from a mixture of liquids the lower $\langle A \rangle$ is accompanied by a larger $\langle B \rangle$, suggesting enough oxirane unit rejection to affect the fold length. The average number of TPI monomer units between oxirane units in the copolymer with a 9.8% oxirane content is 10, the same as the measured unreacted block length. Evidence for a loss of kinetic control of the crystallization process due to the close spacing of foreign units was observed in the crystallization of a polybutadiene copolymer containing 88.5% trans 1,4, 10% cis 1,4, and 1.5% 1,2 units.[3] $\langle A \rangle$ for that copolymer was 11 ± 1 and $\langle B \rangle$ was 16 ± 1, independent of the conditions used. The amount of oxirane unit rejection from the TPI crystal core is apparently high but is not complete, since a small number of IEI units are probably present.

Aknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Support was also received from the PSC/CUNY Faculty Research Program and from the MBRS/NIH Program (Grant RN 08168). We gratefully acknowledge the aid of Irina Zemel in the analysis of some of the NMR results.

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Regulation of Supermolecular Structure of Amphiphilic Polymers by Means of the Langmuir–Blodgett Technique

Masayoshi Watanabe,* Yohzou Kosaka, Kiyoshi Oguchi,[1] Kohei Sanui, and Naoya Ogata*

Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan.

Received November 25, 1987

ABSTRACT: The formation of surface films of poly(vinyl alkylals) at the air/water interface, the transfer of these surface films to solid substrates by means of the Langmuir–Blodgett technique, and the structure of the transferred films have been investigated. Poly(vinyl alkylals) were prepared from atactic poly(vinyl alcohol) (isotactic diad, 53%) and several kinds of *n*-alkyl aldehydes. The spread of dilute benzene solutions (0.01 wt %) of the polymers at the air/water interface, followed by compression of the surface area, gave stable surface films with a limiting area of ~0.3 nm^2/average repeat unit, irrespective of the side-chain length and the degree of polymerization of the starting poly(vinyl alcohol). The surface films could be transferred to several kinds of solid substrates with a transfer ratio of unity to form Y-type built-up films. The thickness of the built-up films was proportional to the number of layers, and single-layer thickness increased with increasing side-chain length. The surface wettability of the built-up films changed alternatingly, depending on whether the number of layers was even or odd. These results indicated that the surface films were monolayers of polymers, with hydrophilic main chains spread over the air/water interface and hydrophobic side chains directed approximately normal to the interface. The transferred films maintained the oriented structure of the monolayers at the interface. If the monolayers were assumed to consist of two-dimensional polymer chains, ^{1}H NMR studies on the stereo structure of the polymers implied that the main chain had two-dimensionally coiled conformations. The results for the limiting area required that the polymer chains be packed very closely.

Introduction

Regulation of supermolecular structures of synthetic polymers is a very important problem, since the properties of the polymers are frequently influenced by their supermolecular structures as well as their molecular structures. The Langmuir–Blodgett (LB) technique is an excellent method for obtaining ultrathin films with a well-defined and controllable molecular assembly, and there has been much interest in LB films because of this molecular assembly.[2] Studies of LB films have been conducted primarily on amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long alkyl chains. However, there has been little study of built-up films consisting of surface films of preformed polymers,[3-12] although a great number of studies have been carried out on the surface films of polymers at the air/water interface.[13] If amphiphilic polymers, spread at the air/water interface, form monolayers which have oriented structures reflecting their amphiphilic nature, and the monolayers are transferred to solid substrates without disrupting the oriented structures, the LB technique will be a promising method for controlling the supermolecular structure of ultrathin films of amphiphilic polymers.

The transfer of surface films of an amphiphilic polymer by the LB technique was first reported by Tredgold et al.,[3] who used poly(1-octadecene-*co*-maleic anhydride). They

0024-9297/88/2221-2997$01.50/0