

polyisoprenyllithium species due to the low reaction order ($\sim 1/4$). Thus at 90% depletion of the original tetramers via complex formation of the type indicated above, the rate of the normal process is still roughly half that in the absence of complexing agent. Since the rate of isoprene polymerization in the absence of diamines is relatively high, effective competition occurs with solvated species until nearly all are in this form. On the other hand, the lithium-based polymerization of butadiene in hydrocarbon solvents is considerably slower than observed with isoprene.¹⁹ In this case although the unsolvated aggregates still persist, they compete less effectively with solvated species of presumably approximately the same reactivity as in isoprene polymerization. The result is that the microstructure change of polybutadiene becomes effective at very low values of R with both diamines.

At values of $R \sim 3$, Figure 5 shows that DIPIP is somewhat more efficient than TMEDA at stimulation of vinyl unsaturation (88% vs. 80%), but still less so than in butadiene polymerization. It is possible that these observations are related to the mixture of 1,4 and 4,1 active chain ends present. If the former resemble solvated butadienyl anion pairs, they will be unassociated, in the trans configuration and give very highly 1,2 polymer.

The 4,1 chain ends, however, according to the model compounds studied will be only partly dissociated to the trans form at this point. Appreciable amounts of cis dimers will remain. Evidence has been presented that the cis active centers are somewhat less vinyl stereospecific.⁵ TMEDA solvation will produce a greater fraction of cis active centers for the 4,1 active centers will be entirely cis⁶ and if butadiene active centers are again taken as models for 1,4 active chain ends, these will be about 60% cis.¹⁸

The order of vinyl unsaturation expected would be DIPIP:butadiene > DIPIP:isoprene > TMEDA:isoprene, as observed.

References and Notes

- (1) Langer, A. W. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1966**, 7 (1), 132.
- (2) Dumas, S.; Marti, V.; Sledz, J.; Schuë, F. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, 16, 81.
- (3) Halasa, A. F.; Schulz, D. N.; Tate, D. P.; Mochel, V. *Adv. Organomet. Chem.* **1980**, 18, 55.
- (4) Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, 19, 1357.
- (5) Worsfold, D. J.; Bywater, S.; Schuë, F.; Sledz, J.; Marti-Collet, V. *Makromol. Chem., Rapid Commun.* **1982**, 3, 239.
- (6) Collet-Marti, V.; Dumas, S.; Sledz, J.; Schuë, F. *Macromolecules* **1982**, 15, 251.
- (7) Bywater, S.; Black, P.; Worsfold, D. J.; Schuë, F. *Macromolecules* **1985**, 18, 335.
- (8) Schuë, F.; Worsfold, D. J.; Bywater, S. *Macromolecules* **1970**, 3, 509.
- (9) Bywater, S.; Worsfold, D. J. *J. Organomet. Chem.* **1978**, 159, 229.
- (10) Assioma, F.; Marchal, J. C. R. *Seances Acad. Sci., Ser. C* **1968**, C266, 195, 369, 1563.
- (11) Brownstein, S.; Bywater, S.; Worsfold, D. J. *Macromolecules* **1973**, 6, 715.
- (12) Lachance, P.; Worsfold, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, 11, 2295.
- (13) Roovers, J. E. L.; Bywater, S. *Polymer* **1973**, 14, 594.
- (14) Dumas, S.; Sledz, J.; Schuë, F.; Raynal, S.; Bywater, S.; Worsfold, D. J. *Polymer* **1983**, 24, 1291.
- (15) Garton, A.; Chaplin, R. P.; Bywater, S. *Eur. Polym. J.* **1976**, 12, 697.
- (16) Garton, A.; Bywater, S. *Macromolecules* **1975**, 8, 694.
- (17) Bywater, S.; MacKerron, D. H.; Worsfold, D. J.; Schuë, F. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, 23, 1997.
- (18) Unpublished.
- (19) Bywater, S. *Comprehensive Chemical Kinetics*; Elsevier: New York, 1975; Vol. 15, Chapter 1.

Hydrochlorination of *trans*-1,4-Polyisoprene Lamellas

Frances Tischler[†] and Arthur E. Woodward*

Chemistry Department, The City University of New York, City College,
New York, New York 10031. Received February 12, 1986

ABSTRACT: Lamellas of synthetic *trans*-1,4-polyisoprene in the α form, prepared by precipitation from amyl acetate solution, were reacted in suspension using an excess of HCl at -7 to -10 °C for various times. The resulting copolymers were quantitatively analyzed by 50.32-MHz carbon-13 NMR spectroscopy using assignments made with the aid of solution-hydrochlorinated samples; the average number of monomer units in the reacted ($\langle B \rangle$) and unreacted ($\langle A \rangle$) blocks was obtained. When the reaction is carried out in acetone using lamellas grown at crystallization temperatures (T_c) of 20 and 30 °C, $\langle B \rangle$ remains constant after 1–2 days of reaction and has a value of 4.8 ± 0.3 ; the average value of $\langle A \rangle$ increases with T_c . The fraction hydrochlorinated in acetone is approximately half the noncrystalline fraction calculated from density measurements. Hydrochlorinated lamellas, dissolved in CDCl_3 , in 4-methyl-2-pentanone, or in heptane and precipitated by solvent evaporation or by cooling, were found by X-ray diffraction to be noncrystalline. When hydrochlorination was carried out in amyl acetate suspension, the results obtained suggest that penetration of the crystal core occurs, particularly at T_c 's of 10 and 20 °C. Wide-angle X-ray diffraction studies show the presence of some completely hydrochlorinated material in the products.

Introduction

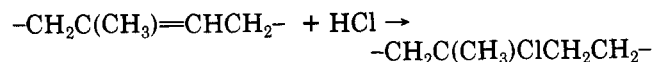
The crystallization of *trans*-1,4-polyisoprene (TPI) from solution leads to overgrown lamellas or lamellar structures in the α or β forms, depending on the conditions used.^{1–5} The epoxidation of *trans*-1,4-polydiene lamellas^{3,6–10} and lamellar structures^{4,11} in suspension, particularly in con-

junction with carbon-13 solution NMR,^{9,10} has been used to examine, in a quantitative fashion, the nature of the surfaces. The selective reaction of the double bonds at the lamellar surfaces leads to a segmented block copolymer in which the reacted blocks correspond to the original chain folds, noncrystallizing chain ends, and any exposed lateral surfaces. If complete reaction occurs at the lamellar surfaces only, and if the noncrystallizing chain ends and lateral areas are small, carbon-13 NMR analysis of the

[†] Allied Fellowship recipient, 1982.

product leads to the determination of (i) the fold length, (ii) the crystalline stem length, and (iii) the degree of crystallinity.

The hydrochlorination of TPI and *cis*-1,4-polyisoprene in solution has been investigated with carbon-13 NMR, and the reactions are reported to proceed by Markovnikov addition,¹² as follows:



In the work to be described below, hydrochlorination of TPI lamellas in suspension is carried out. The product is dissolved and characterized by carbon-13 NMR spectroscopy. From these measurements, the reacted surface fraction and the average number of monomer units in the TPI and in the hydrochlorinated TPI sections of the segmented block copolymer produced are calculated. The carbon-13 NMR assignments were made with the aid of analysis on solution hydrochlorinated products and by epoxidation studies carried out earlier.¹⁰ Following its development, this method was then used to investigate the dependence of the block lengths and the fraction reacted on the crystallization temperature of α -TPI lamellas. It was found in the course of this work, and the parallel studies of TPI lamellar epoxidation,¹³ that the liquid used to carry out the chemical modification reaction must be carefully chosen to avoid penetration of the reactant into the crystalline core. Some experiments concerning the solubility and phase separation of the block copolymers prepared are also described.

Experimental Section

Samples. Unfractionated synthetic TPI (Polysciences, Inc.) was used as received; this was found² to have $M_n = 3.5 \times 10^4$ and $M_w/M_n = 4.8$ from GPC, and a *trans*-1,4 content of 99%.

The method of crystallization involving precooling² (self-seeding) was employed. In this method a mixture containing 0.07% (w/v) TPI in amyl acetate was heated to 100 °C for 1 h, and the solution was filtered, cooled to 0 °C, bringing about precipitation, heated slowly to a temperature at which the precipitate completely dissolved, and crystallized in a constant-temperature bath at either 10, 20, or 30 °C.

Hydrochlorinations. The suspension of TPI lamellas was filtered, washed with amyl acetate, refiltered, and resuspended in either amyl acetate or acetone at concentrations of approximately 1% (w/v). The system was cooled to the reaction temperature (−7 to −10 °C), evacuated, and filled with gaseous HCl until equilibrated; the [HCl]/[double bond] ratio was estimated to be 30/1. Various reaction times ranging from 1 h to 40 days were used. Following reaction, the product was precipitated with methanol at the reaction temperature, washed with methanol, and dried.

Complete hydrochlorination was carried out in amyl acetate suspension at 20 °C and in chloroform solution at 20 °C. Partial hydrochlorinations to various degrees were also carried out in chloroform solution at 25 °C by controlling the reaction time.

Carbon-13 NMR Measurements. The 50.32-MHz carbon-13 spectra were recorded with an IBM WP-200SY NMR spectrometer on 10% polymer solutions in DCCl_3 with Me_4Si as reference. A sweep width of 8333.3 Hz in 32K of memory with a 90° sampling pulse and a 20-s delay time were used. Gated broad-band as well as interrupted broad-band proton decoupling was applied, where the former gives NOE and the latter does not. The number of scans collected in the gated and in the interrupted experiments were 800–1000 and 2400–3000, respectively. T_1 measurements were carried out on a 26% hydrochlorinated block copolymer, prepared in this work, using a nonselective inversion-recovery sequence. A threefold decrease in T_1 for the methylene carbon atoms in hydrochlorinated sections vs. TPI sections was observed. In an earlier study,¹⁰ T_1 's of 0.66 and 0.68 s for methylene carbon-1 and methylene carbon-4, respectively, and 1.31 s for the CH carbon atom were found. All quantitative measurements were made by computer integration.

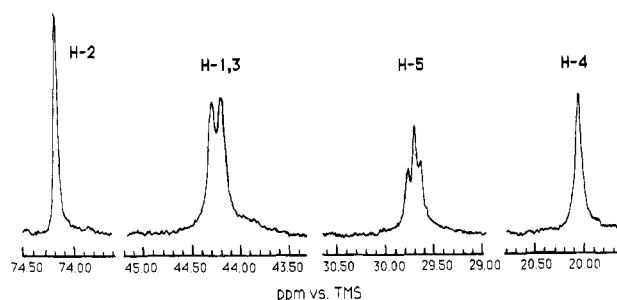


Figure 1. Carbon-13 NMR spectral regions at 50.32 MHz (in CDCl_3) of *trans*-1,4-polyisoprene completely hydrochlorinated in amyl acetate suspension at 20 °C.

Density, DSC, and X-ray Diffraction Measurements.

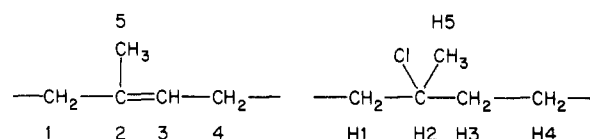
Densities were obtained with an ethanol-water gradient column at 25 °C. The weight fraction of the noncrystalline component, $1 - W_c$, was calculated by assuming a two-phase system with an amorphous density¹⁴ of 0.905 g cm^{-3} and a crystalline density¹⁵ of 1.05 g cm^{-3} . DSC measurements were made with a Du Pont 1090 using an indium standard and 1–3-mg samples. Wide-angle X-ray diffraction photographs were obtained with a 57.3-mm-diameter cylindrical camera.

Dissolution Temperature. A mixture of dry polymer and solvent (1–10% w/v) is heated until the polymer dissolves, and the solution is cooled to 0 °C, causing precipitation, and then heated slowly to the dissolution temperature, T_d .

Morphology. Morphological investigation of preparations in suspension was carried out with a Zeiss microscope with interference contrast optics. Samples dried and shadowed with Au/Pd were viewed with a Philips EM 300 electron microscope.

Results

Carbon-13 NMR Spectra of Hydrochlorinated *trans*-1,4-Polyisoprene. The repeat units of interest in these systems are numbered as follows:



Complete hydrochlorination of *trans*-1,4-polyisoprene, carried out either in amyl acetate suspension or in chloroform solution, leads to four regions of absorption, as expected.¹² However, as can be seen in Figure 1, the methyl carbon (H-5) displays an approximate 1:2:1 triplet and the two equivalent methylene carbons in β positions to the chlorine (H-1 and H-3) display a 1:1 doublet while the other two carbon atoms (H-2 and H-4) give singlets. Partial hydrochlorination carried out in chloroform solution or in amyl acetate or acetone suspension leads to additional resonances in all parts of the spectra, as can be seen in Figures 2 and 3; the assignments and structural formulas corresponding to these figures are given in Table I, where I denotes an isoprene unit, H a hydrochlorinated isoprene unit, and bold lettering the resonance site. At a level of 19% hydrochlorination in solution (spectrum not shown) the resonance found for carbon-4 in the hydrochlorinated chain is very small, the doublet identified with hydrochlorinated carbons-1 and -3 is absent, and only a singlet is found in the H-5 region, all showing, as expected, that mainly isolated H units along with sequences of I units are present. This leads to the identification of separate **IIH**, **IIH**, **III** resonances for the olefinic carbon atoms (2 and 3), (I or H) **HI** for the hydrochlorinated carbon atom (H-2) and (H or I) **HI** and (H or I) **IH** for all others. At 34% hydrochlorination in solution, the four resonances for each of the olefinic carbons are approximately of equal amount and the **IHH-4** resonance is very small. At 70%

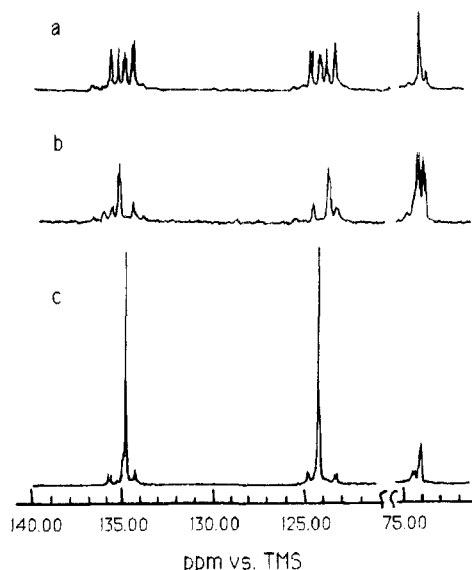


Figure 2. Olefinic and chlorinated carbon region of the 50.32-MHz ^{13}C spectrum of (a) 34% solution hydrochlorinated TPI, (b) 70% solution hydrochlorinated TPI, and (c) 28% suspension hydrochlorinated TPI lamellas.

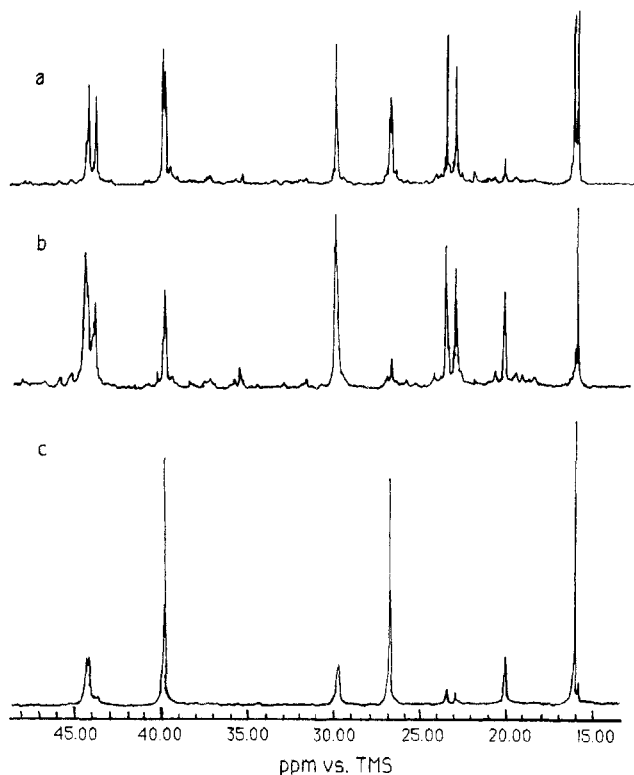


Figure 3. Alkyl carbon region of the 50.3-MHz ^{13}C spectrum of (a) 34% solution hydrochlorinated TPI, (b) 70% solution hydrochlorinated TPI, and (c) 28% suspension hydrochlorinated TPI lamellas.

hydrochlorination in solution, the HHH resonance is strongest in the olefinic region, the III resonances for the olefinic carbons are absent, and the IHH or HHI resonances for all carbons are prominent. For the hydrochlorination carried out in acetone suspension at -7 to -10 °C the HHH sequences in the olefinic region are absent, the IHH and HHI junctions are small in number, and the principal resonances are due to sequences of I only and of H only, as expected for a segmented block copolymer.

Hydrochlorination Levels and Block Lengths. The resonances for the methylene carbon atom 4 show the

Table I
Carbon-13 NMR Frequencies and Assignments for Partially and Completely Hydrochlorinated *trans*-1,4-Polyisoprene

	chem shift, ppm				
	soln reactn, %			suspension reactn, %	
	19	34	70	28	100
IHH-2	135.70	135.66	135.65	135.78	
HHH-2	135.30	135.27	135.29		
III-2	134.92	134.92		134.90	
HII-2	134.45	134.46	134.49	134.37	
HII-3	124.70	124.70	124.60	124.81	
III-3	124.24	124.17		124.25	
HHH-3	123.82	123.85	123.78		
IHH-3	123.35	123.37	123.33	123.29	
IHI-2	74.74	74.70	74.66		
IHH-2	74.74	74.70	74.66	74.65	
HHI-2	74.38	74.33	74.27	74.22	
HHH-2	74.38	74.33	74.27	74.22	74.19
HHH-1, HHH-3		44.29	44.21(sh)	44.25	44.31
(r, m)		44.10	44.09	44.13	44.21
HHI-1, IHH-3	43.98	43.99	43.97	44.00	
IHI-3	43.98	43.98	43.97		
IHH-1, HHI-3	43.55	43.56	43.64	43.69	
IHI-1	43.55	43.56	43.64		
III-1, IHH-1	39.75	39.70	39.63	39.74	
HII-1	39.58	39.59	39.54	39.60	
HHH-5		29.78	29.77	29.77	29.78
(rr, mm)				29.69	29.70
mr, rm)				29.61 (sh)	29.64
IHI-5	29.78	29.78	29.76		
IHH-5, HHI-5	29.78	29.78	29.76	29.77	
III-4, HII-4	26.72	26.72	26.54	26.73	
HHH-4	23.42	23.42	23.41		
IHH-4	23.42	23.42	23.41	23.43	
IHI-4	22.91	22.90	22.87		
HHI-4	22.91	22.90	22.87	22.91	
IHH-4	20.04	20.04	20.03	20.03	
HHH-4		20.04	20.03	20.03	20.07
III-5, IHH-5	16.03	16.02	15.96	16.03	
HHH-5	15.83	15.82	15.83		
HII-5	15.83	15.82	15.83	15.80	

greatest separation, have short T_1 values (see above), and yield the same block lengths within experimental error with and without NOE. Therefore, the resonances due to these carbons were used to calculate the fraction of TPI units hydrochlorinated for all samples. The hydrochlorination of overgrown lamellas, prepared by the precooling method in suspension at low temperatures to completion, should yield segmented block copolymers, made up of unreacted A sections and reacted B sections. If the fold length varies or if there are significant amounts of unreacted chain ends or lateral surfaces, B should be represented by an average, $\langle B \rangle$. If reaction at the surface is not complete and uniform or if the crystallite thickness is irregular, then A should also be given as an average, $\langle A \rangle$. $\langle A \rangle$ and $\langle B \rangle$ can be calculated from resonance areas with the equations $\langle A \rangle = (I_4 + J_4)/J_4$ and $\langle B \rangle = (H_4 + J_4)/J_4$, where I_4 is the area under the resonance for methylene carbon atom 4 at 26.72 ppm (III-4 or HII-4), H_4 is the area under the resonance for this carbon atom at 20.03 ppm (IHH-4 and HHH-4), and J_4 is the average of the areas under the resonances for this carbon atom in HHI-4 and IHH-4 units at 22.91 and 23.43 ppm, respectively. For spectra obtained without NOE but with proton decoupling, $\langle A \rangle$ can also be obtained from the resonance areas for the carbon-3 diene units: $\langle A \rangle = \{[III - 3] + [HII - 3] + [IHH - 3]\}/[IHH - 3]$, where the brackets represent relative amounts for the resonance given therein.

Hydrochlorinations were carried out at -7 to -10 °C on amyl acetate and on acetone suspensions of overgrown α -TPI lamellas grown by the precooling technique from

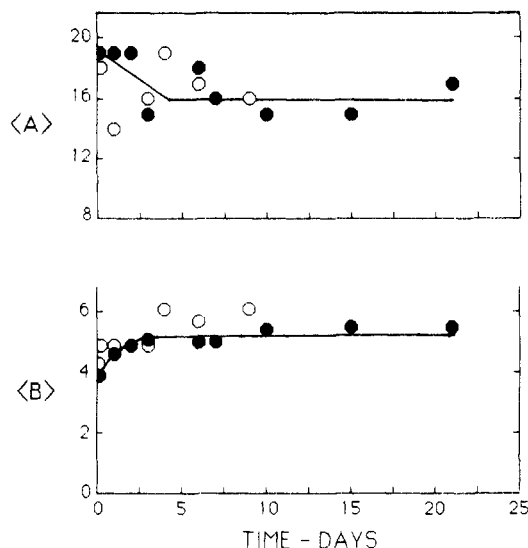


Figure 4. Average block lengths, $\langle A \rangle$ (unreacted) and $\langle B \rangle$ (reacted), vs. time for *trans*-1,4-polyisoprene lamellas crystallized at 30 °C and hydrochlorinated at -10 °C in a suspension of amyl acetate (O) and acetone (●).

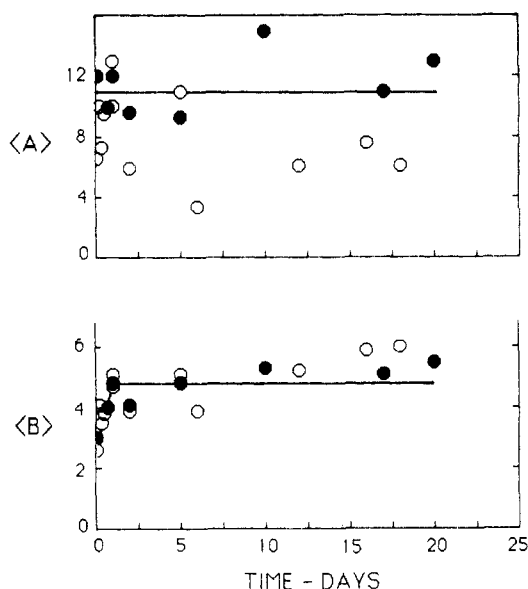


Figure 5. Average block lengths, $\langle A \rangle$ (unreacted) and $\langle B \rangle$ (reacted), vs. time for *trans*-1,4-polyisoprene lamellas crystallized at 20 °C and hydrochlorinated at -7 °C in a suspension of amyl acetate (O) and acetone (●).

amyl acetate using crystallization temperatures of 10, 20, and 30 °C. Carbon-13 NMR measurements with and without NOE were used; when both methods were used with the same sample, agreement within 6% for $\langle A \rangle$ and 4% for $\langle B \rangle$ occurred. $\langle A \rangle$ values were generally obtained with the C-4 resonance areas; in the cases where both C-4 and C-3 resonance areas were obtained agreement within 10% between the two was found and an average value was used. The values of $\langle A \rangle$ and $\langle B \rangle$ for various preparations studied vs. time are given in Figures 4 and 5; the lines on these figures were defined by the results for hydrochlorination in acetate suspension only. It can be seen that the $\langle A \rangle$ and $\langle B \rangle$ vs. time plots depends on the hydrochlorination medium and on the crystallization temperature. When acetone is the hydrochlorination medium, the values of $\langle A \rangle$, $\langle B \rangle$, and F_h become constant after about 1–2 days. For lamellas crystallized at 30 °C the $\langle B \rangle$ values obtained with amyl acetate as the reaction medium are larger than those with acetone, while the $\langle A \rangle$ values

Table II
Noncrystalline Fraction and Parameters Obtained by Hydrochlorination of *trans*-1,4-Polyisoprene Lamellas^a

T_c , °C	$1 - W_c^b$	$(F_h)_f^c$	U^d	$\langle A \rangle_f^e$	L_s^f , nm
10	0.55	0.32 ± 0.05	4.5 ± 0.5	10 ± 2	4.3 ± 0.9
20	0.50	0.29 ± 0.01	4.8 ± 0.5	11 ± 2	5.0 ± 0.9
30	0.44	0.25 ± 0.01	5.2 ± 0.2	16 ± 1	7.0 ± 0.5

^a Grown from 0.07% (w/v) amyl acetate solution at crystallization temperature T_c after precipitation at 0 °C and redissolution at 34 °C using unfractionated polymer, hydrochlorinated in acetone at -7 to -10 °C. ^b Noncrystalline fraction from density measurements. ^c Fraction available for hydrochlorination. ^d Average number of monomer units per fold. ^e Average number of monomer units in crystalline traverse. ^f Average crystallite thickness along chain direction.

(Figure 5) are approximately the same (up to 9 days of reaction). For 20 °C preparations, $\langle A \rangle$ falls below that found when acetone is used; $\langle B \rangle$ shows a relatively slow increase with time up to 10 days and a much larger rate of increase at longer reaction times up to 40 days. Only part of this is shown in Figure 5. Resonances in the olefinic region, attributed to HIH, were also observed in many of these preparations. The hydrochlorination fraction, F_h , found for the 20 °C preparations reacted in amyl acetate, increased after 6 days of reaction to values exceeding 0.50, i.e., values about 60–70% larger than those for similar preparations reacted in acetone. For all 20 and 30 °C preparations, the level of hydrochlorination, F_h , changes with time in the same way that $\langle B \rangle$ does. For samples prepared at 10 °C, hydrochlorination in amyl acetate at -7 °C leads to 74% reaction after 12 days and 100% after 20 days, as compared to hydrochlorination in acetone, which showed $29 \pm 1\%$ reaction from 2 to 8 days and $41 \pm 1\%$ reaction after a 13- to 18-day time period. Over the 2–18-day period, $\langle B \rangle$ was 4.5 ± 0.5 , but $\langle A \rangle$ decreased from 11 ± 2 from 2–8 days to 8 after 13–18 days.

With the assumption that the lamellar surface regions have completely reacted, the constant values [$\langle A \rangle_f$, $\langle B \rangle_f$, and $(F_h)_f$] obtained for $\langle A \rangle$, $\langle B \rangle$, and the hydrochlorination level, F_h , when acetone is used as the hydrochlorination liquid, can be taken as the number of monomer units in the crystalline stem, the average number of monomer units per fold, U , and the surface fraction, respectively. Letting $U = \langle B \rangle_f$ assumes that the number of units in noncrystallizing chain ends and on lateral surfaces as compared to those in the folds is small. The crystalline stem length, L_s , the crystallite thickness along the chain direction, can be calculated from the final value of $\langle A \rangle$ by multiplication by the chain repeat distance, which is 0.439 nm for α -TPI.¹⁵ Values of $(F_h)_f$, $\langle A \rangle_f$, U , L_s , and $1 - W_c$, where $1 - W_c$ is the noncrystalline fraction obtained from density measurements, are given for each preparation in Table II. For all preparations, $(F_h)_f$ is less than $1 - W_c$ by as much as 50%. The U values for preparations crystallized at 10, 20, and 30 °C agree within experimental error, giving a mean value of 4.8. It is also seen that L_s increases with increasing crystallization temperature.

Properties of Hydrochlorinated TPI. Completely hydrochlorinated TPI (~10% (w/v)) was insoluble in heptane and dissolves in amyl acetate at 70–80 °C and in 4-methyl-2-pentanone at 35 °C. When reprecipitated at 25 °C from 4-methyl-2-pentanone this material gave an X-ray diffraction pattern previously reported for rubber hydrochloride¹⁶ and a DSC endotherm at 116 °C. The TPI-hydrochlorinated TPI segmented block copolymers, prepared in acetone at 20 and 30 °C, were recovered from suspension, dried, and subjected to X-ray diffraction, which showed the α -TPI pattern. These block copolymers dissolved in amyl acetate (~10% (w/v)) at 35 °C but

remained in solution at 25 °C, dissolved in heptane over a wide range of temperature, 35–80 °C, and dissolved in 4-methyl-2-pentanone at 32 °C. Upon dissolution in 4-methyl-2-pentanone followed by reprecipitation at 0 °C, the block copolymer gave a diffuse halo X-ray pattern. When X-ray measurements were made on lamellas hydrochlorinated in amyl acetate, both the TPI and hydrochlorinated TPI patterns were apparently present; reprecipitation of these products from 4-methyl-2-pentanone was carried out and X-ray diffraction on the residue yielded the hydrochlorinated TPI pattern having relatively diffuse rings. Suspension-hydrochlorinated TPI recovered at moderate times, dissolved and reprecipitated from 4-methyl-2-pentanone or CDCl_3 , gave no melting endotherm in the 25–150 °C region. Dissolution temperatures as measured for TPI are amyl acetate, 34 °C; heptane, 39 °C; 4-methyl-2-pentanone, 49 °C.

Discussion

The splittings of the carbon-13 NMR resonances for completely hydrochlorinated TPI show that both possible stereoisomers are present in equal amounts, and therefore attack from either side is equally possible. However, the chirality effect clearly depends on the chain conformation since the resonance for the different carbon atoms are either not split at all (substituted C-2 and C-4), split into a doublet, or into a triplet. The 1:1 doublet splitting for the equivalent C-1 and C-3 methylene carbons shows that they are only sensitive to the chirality of the $\text{C}(\text{CH}_3)\text{Cl}$ in the closest connecting unit. The methyl carbon is affected by the chirality of the nearest groups in both directions.¹⁷ For completely epoxidized TPI, both CH_2 carbons and the C-2 quaternary carbon yield doublet splittings while the C-3 oxirane and the methyl carbons yield quartets.¹⁸ Comparison of the carbon-13 NMR spectra of partially hydrochlorinated and partially epoxidized TPI¹⁰ in the olefinic region shows a similarity in the appearance of satellite peaks due to HII and IHH sequences on either side of the unreacted sequences. However, these are not symmetrically placed in the present work due to the asymmetry of the substitution; also, resonances for HIIH are clearly present at low amounts of hydrochlorination while for epoxidation the equivalent resonances can only be observed for high degrees of reaction in the absence of the IIII resonance.

The reaction of HCl with the double bonds in the TPI lamellar structures clearly depends on the suspension liquid used. In acetone, which is essentially a nonsolvent for both TPI and hydrochlorinated TPI, the constancy of $\langle A \rangle$ and $\langle B \rangle$ with time after an initial short period for crystallizations at 20 and 30 °C shows that little penetration of the crystal core occurs. In amyl acetate, which dissolves hydrochlorinated TPI at a lower temperature than it does TPI, the low $\langle A \rangle$ values, the large F_h 's, and the presence of HIIH sequences observed suggest that penetration is occurring when this liquid is used. (The presence of HIIH sequences would lower both $\langle A \rangle$ and $\langle B \rangle$.) Following the initial stages of the reaction the lamellas should consist of a block copolymer core with the unreacted sections inside surrounded by completely hydrochlorinated chains. If due to favorable solvent-polymer contacts the lateral chains loosen or separate from the lamellas, reaction of the unreacted lateral layers exposed will occur, leading to a smaller block copolymer core with unreacted sections of the same length as before. This type of mechanism has been previously suggested to explain results for the chlorination of polyethylene.¹⁹ In the present case a mixture of block copolymer and highly hydrochlorinated chains could lead to the mixed X-ray

patterns observed. In the present work it is seen that as the crystallization temperature decreases from 30 to 10 °C, and therefore the degree of supercooling increases, the lamellas become more susceptible to penetration and reaction. The decrease in crystalline size along the chain direction and the presence of large concentrations of defects with decreasing crystallization temperature would account for this observed change.

The values of F_h , U , and $\langle A \rangle_f$ found with the hydrochlorination method for lamellas crystallized at 20 °C can be compared with those obtained with a different chemical reaction; values for the fraction reacted, $\langle B \rangle_f$ and $\langle A \rangle_f$ of 0.30 ± 0.02 , 5.4 ± 0.8 , and 12 ± 1 , respectively, which agree within experimental error with those in this work, have been obtained by carbon-13 NMR analysis^{10,13} of suspension-epoxidized TPI. These epoxidations were carried out in 2-ethoxyethanol at 0 °C with seven unfractionated synthetic TPI samples crystallized at 20 °C from 0.1% amyl acetate by the precooling method. In an earlier study, epoxidation was carried out in amyl acetate for 20 days using a fractionated TPI sample ($M_n = 2.9 \times 10^5$) crystallized at 20 °C and values for $\langle B \rangle$ of 7.4 ± 0.5 and for $\langle A \rangle$ of 11 were found.¹⁰ The high $\langle B \rangle$ value is due to the choice of amyl acetate as the epoxidation medium, which apparently leads to a mixture of completely epoxidized chains plus the block copolymer.¹³ This effect of the reaction medium is also observed with hydrochlorination as discussed above. The large discrepancy between the noncrystalline fraction ($1 - W_c$) as obtained by density measurements on dried mats and the fraction available for hydrochlorination, F_h , for all preparations, obtained for the same structures in suspension, can be explained qualitatively as due to one or more of the following: (i) an increase in the noncrystalline component due to lamellar collapse and rearrangements upon drying, (ii) a failure of the two-component model employed in the density method, or (iii) the presence of a significant fraction of noncrystalline material not available for chemical reaction. Evidence for (i)²⁰ and (ii)^{21,22} has been advanced for polyethylene lamellas. However the crystallinity derived from solid-state carbon-13 NMR spectra of *trans*-1,4-polybutadiene lamellas agrees with that from density measurements,²³ which would eliminate (ii). Comparison of the solid-state carbon-13 NMR spectrum taken after epoxidation with that taken before suggests that the noncrystalline component reacts completely,²³ eliminating explanation (iii).

The number of monomer units per fold of 4.8 found for TPI lamellas in this study falls within the range previously (3.0, 5.0, and 5.6) found for *trans*-1,4-polybutadiene using the carbon-13 NMR method without a chain-end correction.⁹ Using molecular models the number of monomer units necessary for a tight [110] adjacent reentry fold is three for α -TPI.³ Therefore, the value above suggests considerable adjacent reentry with some fold looseness or occasional nonadjacent reentry.

The carbon-13 NMR results conclusively show that for completely hydrochlorinated TPI an atactic product is produced. However, this product does exhibit an X-ray pattern and a melting endotherm and therefore does crystallize to some extent. This may be due to the roughly equal sizes of a methyl and a chloro substituent, leading to their accommodation in the same unit cell.

Acknowledgment 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. We thank A. Elkayam for the TPI epoxidation

results and F. C. Schilling of AT&T Bell Laboratories for helpful discussions.

References and Notes

- (1) Keller, A.; Martuscelli, E. *Makromol. Chem.* **1972**, *151*, 189.
- (2) Anandakumaran, K.; Kuo, C.; Mukherji, S.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1669.
- (3) Anandakumaran, K.; Herman, W.; Woodward, A. E. *Macromolecules* **1983**, *16*, 563.
- (4) Kuo, C.; Woodward, A. E. *Macromolecules* **1984**, *17*, 1034.
- (5) Xu, J.; Woodward, A. E. *Macromolecules*, in press.
- (6) Stellman, J. M.; Woodward, A. E. *J. Polym. Sci., Part B* **1969**, *7*, 755; *J. Polym. Sci., Part A-2* **1971**, *9*, 59.
- (7) Wichacheewa, P.; Woodward, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1849.
- (8) Tseng, S.; Herman, W.; Woodward, A. E.; Newman, B. A. *Macromolecules* **1982**, *15*, 338.
- (9) Schilling, F. C.; Bovey, F. A.; Tseng, S.; Woodward, A. E. *Macromolecules*, **1983**, *16*, 808; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*(1), 235.
- (10) Schilling, F. C.; Bovey, F. A.; Anandakumaran, K.; Woodward, A. E. *Macromolecules* **1985**, *18*, 2688.
- (11) Tseng, S.; Woodward, A. E. *Macromolecules* **1982**, *15*, 343.
- (12) Tran, A.; Prud'homme, J. *Macromolecules* **1977**, *10*, 149.
- (13) Elkayam, A.; Xu, J.; Woodward, A. E., submitted for publication.
- (14) Cooper, W.; Vaughan, G. *Polymer* **1963**, *4*, 329.
- (15) Takahashi, Y.; Sato, T.; Tadokoro, H.; Tanaka, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 233.
- (16) Bunn, C. W.; Garner, E. V. *J. Chem. Soc.* **1942**, 654.
- (17) In considering a sequence of three hydrochlorinated TPI units the four diastereoisomers are as follows: *RRR*, *SRR*, *RRS*, and *SRS*, with the *R* and *S* representing the chirality of carbon-2. The resulting intensities are 1:2:1 because *SRR* and *RRS* are not distinguishable. Exchange of *R* and *S* yields four additional sequences that under the conditions employed are indistinguishable from the four shown.
- (18) Zemel, I.; Woodward, A. E., unpublished results.
- (19) Chang, B. H.; Siegmund, A.; Hiltner, A. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 255.
- (20) Fanconi, B.; Sarazin, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(2), 173.
- (21) Harrison, I. R.; Runt, J. *J. Macromol. Sci., Phys.* **1980**, *B17*, 83.
- (22) Harrison, I. R.; Juska, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *17*, 491.
- (23) Schilling, F. C.; Bovey, F. A.; Tonelli, A. E.; Tseng, S.; Woodward, A. E. *Macromolecules* **1984**, *17*, 728.

Absolute Tacticity Assignments of Poly(vinyl chloride) via the Two-Dimensional NMR Spin-Lock RELAY Experiment

Molly W. Crowther, Nikolaus M. Szeverenyi,[†] and George C. Levy*

Department of Chemistry, Syracuse University, Syracuse, New York 13210.
Received December 10, 1985

ABSTRACT: A method is demonstrated for the unambiguous assignment of configurational sequences in the carbon-13 NMR spectrum of a homo vinyl polymer. This is achieved by elucidating the connectivity of carbons belonging to even- and odd-ad sequences along the polymer chain. A two-dimensional spin-lock RELAY experiment, involving magnetization pathways $^1\text{H}-^b\text{H}-^b\text{C}$ and $^b\text{H}-^a\text{H}-^a\text{C}$, allows identification of neighboring carbons by recognition of shared protons. This approach has the distinct advantage of observing carbon while preserving the proton shift information which can aid in the identification of sequences by the equivalence or nonequivalence of the methylene protons. The method is demonstrated for poly(vinyl chloride) (PVC), whose tacticity has been well studied. The present report reevaluates carbon chemical shift assignments for PVC dissolved in 1,2,4-trichlorobenzene. By this approach, sequence assignments are made by direct experimental evidence, for both carbon and proton chemical shifts, and without dependence on propagation statistics.

Introduction

Tacticity, or the relative configuration of pseudoasymmetric centers in a vinyl polymer chain, may influence the physical and mechanical properties of a polymer. NMR is particularly useful in studying tacticity because chemical shift is sensitive to configurational sequences and intensities can be utilized to elucidate the propagation mechanism.^{1,2} Carbon-13 NMR is advantageous because of the simplicity of proton-decoupled spectra and the large chemical shift range that allows long configurational sequences to be observed. Increased magnetic field strengths can be used to evaluate even longer configurational sequences which afford a more detailed description of tacticity but complicate spectral assignments. Another complication is the tendency of random propagation to produce sequence probabilities that are alike, limiting the use of peak intensities for the assignment to configurational sequences. An experimental method that would simply assignments and that is independent of the propagation statistics is desirable.

Recently, two-dimensional NMR has been used to make stereosequence assignments.³⁻¹⁰ Bruch et al. have assigned fluorine NMR spectra on the basis of fluorine connectivities (through four-bond scalar coupling) of overlapping configurational sequences.⁶ Likewise, Gippert and Brown have made proton chemical shift assignments based on proton connectivities and the necessary compositional relationships of triad and tetrad configurational sequences.⁷ In this report, carbon chemical shift assignments are made on the basis of connectivities between the methine and methylene carbons of a homo vinyl polymer that belong to odd- and even-ad sequences, respectively.

Outline of Method. In the first step of our approach, a $^1\text{H}-^{13}\text{C}$ shift-correlated spectrum is obtained. In this experiment, an INEPT-type magnetization transfer occurs from a proton to a scalar-coupled carbon.¹¹⁻¹³ The amount of magnetization transferred depends upon the precession frequency of the attached proton and the length of the evolution period. The resultant carbon signal is modulated in amplitude, reflecting the proton chemical shift. Possible configurational sequence assignments for the carbon chemical shifts of the methylene can be reduced by the classification of sequences on the basis of correlation to one or two proton shifts. A single carbon shift correlated

[†]State University of New York, Upstate Medical Center, Department of Radiology, Syracuse, NY 13210.