Thus, it can be seen that as $n \to \infty$ the volume of the inscribed oval approaches that of the right prism.

References and Notes

(1) R. J. Rubin and J. Mazur, *J. Chem. Phys.*, **63,** 5362 (1975).
(2) W. Kuhn, *Kolloid-Z.*, **68,** 2 (1934).
(3) C. Hollingsworth, *J. Chem. Phys.*, **16,** 544 (1948).
(4) C. Hollingsworth, *J. Chem. Phys.*, **17,** 97 (1949).
(5) J. J. Weidmann, H. Kuhn, and W. Kuhn, *J. Chim. Phys. Phys.-Chim. Biol.*, **50,** 226 (1953).
(6) R. Koyama, *J. Phys. Soc. Jpn.*, **22,** 973 (1967).
(7) R. Koyama, *J. Phys. Soc. Jpn.*, **24,** 580 (1968).
(8) K. Solč and W. H. Stockmayer, *J. Chem. Phys.*, **54,** 2756 (1971).
(9) K. Solč, *J. Chem. Phys.*, **55,** 335 (1971).
(10) J. Mazur, C. M. Guttman, and F. L. McCrackin, *Macromolecules*, **6,** 872 (1973).
(11) M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, **23,** 356 (1955).
(12) J. Mazur and F. L. McCrackin, *J. Chem. Phys.*, **49,** 648 (1968).
(13) F. L. McCrackin, J. Mazur, and C. M. Guttman, *Macromolecules*, **6,** 859 (1973).
(14) F. L. McCrackin, *J. Chem. Phys.*, **47,** 1980 (1967).
(15) F. L. McCrackin, *J. Res. Natl. Bur. Stand., Sect. B*, **76b,** 193 (1972).
(16) H. E. Daniels, *Proc. Cambridge Philos. Soc.*, **37,** 244 (1941).
(17) H. Kuhn, *Experientia*, **1,** 28 (1945).
(18) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains", Interscience, New York, N.Y., 1963, pp 181 and 183.
(19) In this assumed form of the equation for $\langle R_3(N) \rangle$ we have used the exponent 0.61 which was determined in RMI for the span in a principal lattice direction and which is also consistent with the value obtained by many investigators using Monte Carlo or enumeration–exptrapolation methods. Further, we have arbitrarily assigned the unrestricted random walk value, −0.57, to the constant term in the expression for $\langle R_3(N) \rangle$ because we assume that since the constant term is identical for the average spans of the two kinds of random walks in the case of space-fixed axes that the constant term will also be the same in the asymptotic form for the average *maximum* span of an unrestricted and of a self-avoiding random walk.
(20) M. Abramowitz and I. A. Stegun, Ed., "Handbook of Mathematical Functions", National Bureau of Standards, Washington, D.C., 1964, p 258.
(21) Reference 19, p 256.

Microstructure and Physical Properties of Hydrochlorinated 1,4-Polyisoprene Prepared by Butyllithium in Nonpolar Solvent

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Received August 9, 1976

ABSTRACT: Microstructure of partially as well as completely hydrochlorinated 1,4-polyisoprene prepared by butyllithium in nonpolar solvent has been investigated by means of ^{1}H and ^{13}C NMR spectroscopy. The results show that practically no cyclization occurs in the course of the reaction and that hydrogen chloride adds nearly at random along the polymer chains. The microstructure of the remaining unsaturated units present in the partially hydrochlorinated products is nearly that of polyisoprene indicating equivalent reactivities for the different structural units present in the substrate. The completely hydrochlorinated product is an amorphous material with a T_g 103 K higher than that of the substrate. The variation of T_g is a linear function of the molar percentage of hydrochlorinated units in the polymer.

Hydrochlorination of natural 1,4-polyisoprene such as hevea (*cis*-1,4-polyisoprene) and balata (*trans*-1,4-polyisoprene) has been studied extensively during the last 30 years.[1–5] When in solution, both polymers readily add hydrogen chloride but the reaction is known to produce some amount of cyclized structures along the polymer chain. Nevertheless, hydrochlorinated hevea is a crystallizable material having a syndiotactic type of microstructure; that is, the handedness of the successive quaternary carbon atoms alternates along the polymer chain. In contrast, hydrochlorinated balata does not show any crystallinity. The stereoregularity peculiar to hydrochlorinated hevea has been explained by postulating a chain reaction mechanism specific to cis-1,4 unit sequences.[1,3]

In the present paper we wish to report some results concerning hydrochlorination of highly cis-1,4 well-defined polyisoprene prepared by means of anionic polymerization using butyllithium as initiator and benzene as solvent. This substrate contains 71% of cis-1,4 units, 22% of trans-1,4 units, and only 7% of vinyl units which are essentially of 3,4 structure. Microstructure and physical properties of partially as well as completely hydrochlorinated products have been investigated by means of NMR spectroscopy, x-ray diffraction analysis, and differential scanning calorimetry.

Experimental Section

The polyisoprene sample was prepared in a sealed high-vacuum system using *sec*-butyllithium as initiator and benzene as solvent. Its microstructure determined by ^{1}H NMR spectroscopy is 71% cis, 22% trans, and 7% 3,4. Its number average molecular weight determined by osmometry is 8.6×10^4.

The hydrochlorination reaction was conducted at 298 K on 300 ml of 1% polyisoprene solution in toluene. The solution was first purged with dry nitrogen to remove any molecular oxygen after which dry hydrogen chloride was bubbled through the reaction system at a pressure slightly above the atmospheric pressure. Aliquots of 50 ml were withdrawn from the system at some intervals from 1 to 24 h. The aliquots were purged with nitrogen and washed with distilled water to remove unreacted hydrogen chloride, after which the products were precipitated into methanol. The molar percentage of unsaturated monomer units remaining in the partially hydrochlorinated samples was determined by ^{1}H NMR spectroscopy by using the olefinic resonances near 5 ppm.

The ^{1}H NMR spectra were measured at 100 °C on a Varian HR-220 spectrometer using chlorobenzene as solvent and tetramethylsilane (TMS) as internal reference.

The ^{13}C NMR proton noise-decoupled spectra were measured at room temperature on a Bruker WH-90 spectrometer using deuteriochloroform as solvent and TMS as internal reference. Approximately 5000 pulses with an acquisition time of 0.7 s were used. Flip angle was 30° and spectral sweep width was 6000 Hz.

The glass transition temperatures were measured in duplicate at

Table I
Degree of Hydrochlorination as a Function of Time of Reaction[a] and Number Average Molecular Weight of the Products

Sample	Time of reaction, h	Hydrochlorination, %[b]	$10^{-4}\overline{M}_n$
PI			8.6
PI-HCl-1	1	23	
PI-HCl-2	2	45	
PI-HCl-4	4	74	
PI-HCl-8	8	97	
PI-HCl-24	24	100	14.0

[a] 1% toluene solutions saturated with hydrogen chloride at 298 K and 1 atm. [b] Determined by ^{1}H NMR spectroscopy using the olefinic resonances near 5 ppm.

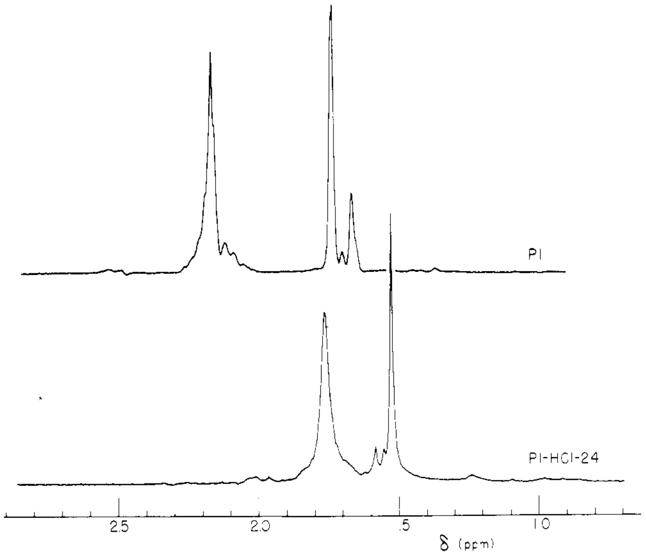


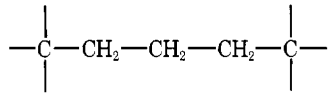
Figure 1. Upfield region of ^{1}H NMR spectra (220 MHz) of polyisoprene (PI) and completely hydrochlorinated polyisoprene (PI-HCl-24).

10 K/min heating rate on a Perkin-Elmer Model DSC-IB calorimeter. The 25-mg samples were previously annealed at 373 K for 15 min and then cooled at a constant rate of 5 K/min to a temperature about 40 K below T_g. The value of T_g was taken as the intersection of the baseline below the transition with the extrapolation of the tangent at the point of inflexion in the DSC heating curve.

Results and Discussion

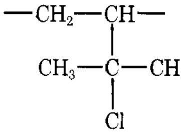
^{1}H NMR Analysis. As shown in Table I, under the experimental conditions mentioned above, e.g., hydrogen chloride pressure of 1 atm and polymer concentration of 1%, nearly quantitative hydrochlorination of the present 1,4-polyisoprene is obtained after 8 h of reaction, at 298 K. Figure 1 shows the upfield region of the 220 MHz ^{1}H NMR spectrum of the product obtained after 24 h of reaction together with that of the substrate. The main features of the spectrum of the hydrochlorinated material are a broad methylene resonance at 1.76 ppm and a sharp methyl resonance at 1.53 ppm. The fact that the methyl resonance appears as a sharp singlet at 1.53 ppm and that no significant resonance is observed in the 0.8–1.5-ppm region of the spectrum indicates that nearly all the methyl groups in the present polymer are attached to carbons bearing a chlorine atom. This confirms the exclusiveness of the Markownikoff's rule for the hydrogen chloride addition and by the same token indicates that no cyclization occurred in the course of the reaction. The later point is based on the absence of any resonance near 0.9 ppm. This contrasts with the earlier observations of Golub and Heller[5] who studied the products of hydrochlorination of hevea (*cis*-1,4-polyisoprene) and balata (*trans*-1,4-polyisoprene) conducted in benzene at temperatures between 313 and 353 K. Their 100-MHz ^{1}H NMR analysis of the products showed the presence of 8 and 17% of cyclized double bonds in fully hydrochlorinated hevea and balata, respectively. A plausible reason for the presence of cyclized structures in their products might well be the higher temperature at which their experiments were conducted, since both hevea and balata are known[6] to undergo cyclization when treated with strong acids at temperatures near 333–353 K.

Turning now to the methylene resonance of the hydrochlorinated material, the main peak observed at 1.76 ppm must represent the methylene groups adjacent to the quaternary carbons in the sequence



$$-\overset{|}{\underset{|}{C}}-CH_2-CH_2-CH_2-\overset{|}{\underset{|}{C}}-$$

On the other hand, it is striking to note that the resonance of the methylene groups in the center of the sequence, which should appear at the higher field region 1.4–1.6 ppm, cannot be resolved in the present spectrum. This is most likely due to the spreading of this resonance produced by vicinal couplings together with the presence of the methyl resonance in that region of the spectrum. Actually, two weak resonances are observed at 1.55 and 1.58 ppm, but these two sharp peaks can be assigned to the two heterosteric methyl groups in the 3,4-hydrochlorinated units formed according to Markownikoff's rule, e.g.,



$$\begin{array}{c} -CH_2-CH- \\ | \\ CH_3-C-CH_3 \\ | \\ Cl \end{array}$$

Golub and Heller[7] have reported that under similar conditions hydrogen chloride reacts with 3,4-polyisoprene to give a product with a predominantly monocyclic structure. According to these authors, such a cyclization would involve the presence of two consecutive 3,4 units, a situation which is not favored in the present polyisoprene which contains only 7% of 3,4 units known to be distributed randomly along the polymer chain.[8]

Information about the relative reactivities of 1,4 and 3,4 units can be obtained from the olefinic resonances of the unreacted units appearing at 5.2 ppm ($>C{=}CH-$) and 4,8 ppm ($>C{=}CH_2$), respectively. Figure 2 depicts that region of the spectrum for the substrate and for the products obtained after 1, 2, and 4 h of reaction. Relative area measurements show that the molar fractions of the 3,4 units are close to 0.07 ± 0.02 for the four samples indicating that, within the experimental error, the rates of reaction of 1,4 and 3,4 units are about identical. Similar information concerning the relative reactivities of cis-1,4 and trans-1,4 units might be in principle obtained from the methyl resonances of the unreacted units appearing at 1.73 and 1.67 ppm, respectively. Unfortunately, the methylene resonances of the saturated units overlap these two methyl resonances in such a way that accurate evaluation of the relative contents of cis-1,4 and trans-1,4 units in the partially hydrochlorinated products is not feasible. This is illustrated in Figure 3 which shows the high-field region of the ^{1}H NMR spectra measured on the products obtained after 1 and 2 h of reaction. Neither of these spectra is a simple summation of the two spectra shown in Figure 1. Actually, spectra in Figure 3 exhibit some additional resonances which may be attributed to the methylene groups in sequences of the type

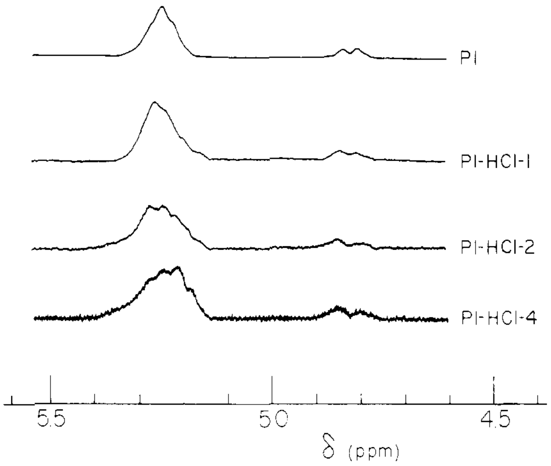


Figure 2. Olefinic ^1H NMR resonances (220 MHz) of polyisoprene (PI) and hydrochlorinated products obtained after 1 (PI-HCl-1), 2 (PI-HCl-2), and 4 (PI-HCl-4) h of reaction, respectively.

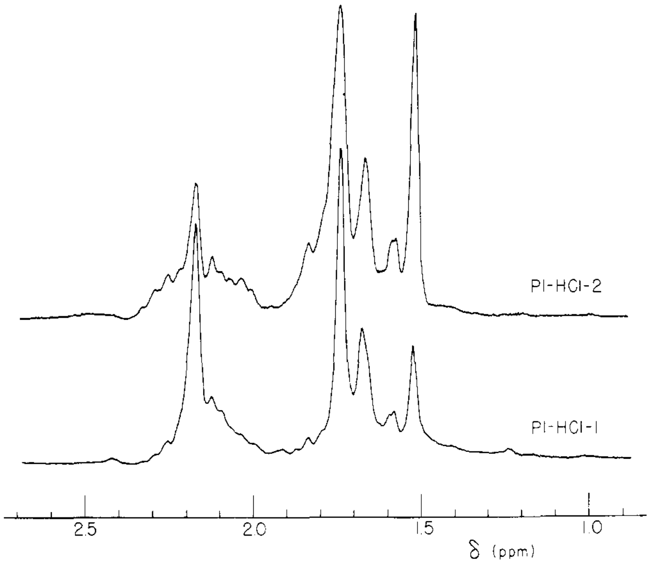
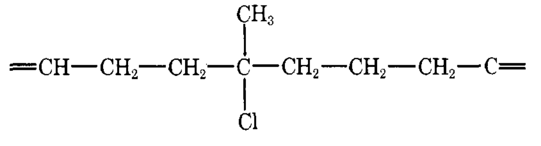


Figure 3. Upfield region of ^1H NMR spectra (220 MHz) of hydrochlorinated products obtained after 1 (PI-HCl-1), and 2 (PI-HCl-2) h of reaction, respectively.



$$=CH—CH_2—CH_2—\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{C}}—CH_2—CH_2—CH_2—C=$$

These new resonances appear all over the region between 1.4 and 2.4 ppm. Interestingly, as the degree of hydrochlorination increases, the resonances corresponding to the methylene groups in the unsaturated units, which appear as a strong peak at 1.78 ppm in the case of the substrate, are progressively replaced by a more complex resonance spread on both sides of the original signal. Assuming that this change reflects the formation of structures such as that depicted above, e.g., AB and BA dyads where A is the unsaturated unit and B the hydrochlorinated unit, one can conclude that hydrogen chloride adds nearly at random along the present 1,4-polyisoprene chains.

^{13}C NMR Analysis. Figure 4 shows the ^{13}C NMR spectrum of the sample obtained after 2 h of reaction together with those of the substrate and the completely hydrochlorinated sample. The values for the chemical shifts of the 1,4 unit resonances observed in Figure 4 are listed in Table II. Also included in Table II are the relative peak areas measured on expanded scale spectra. The nomenclature used here is defined as follows

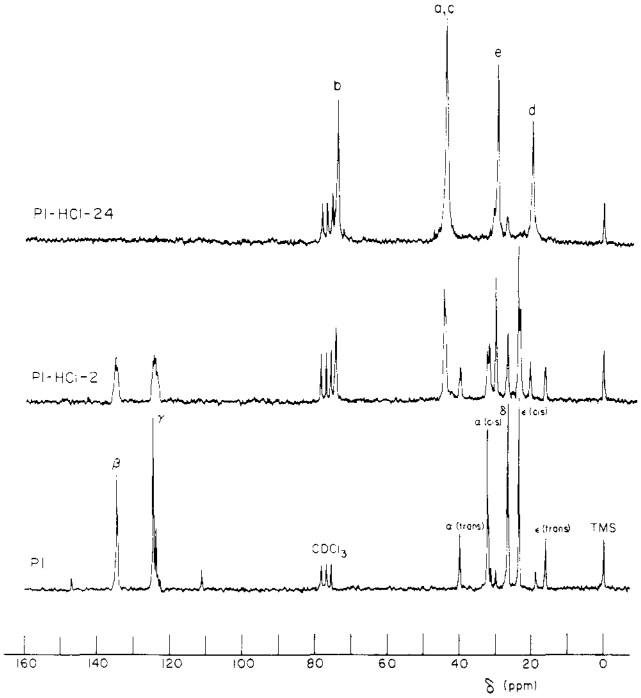
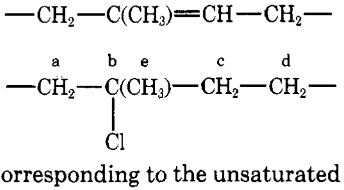


Figure 4. ^{13}C NMR spectra (22.63 MHz) of polyisoprene (PI), 45% hydrochlorinated product (PI-HCl-2), and completely hydrochlorinated product (PI-HCl-24).

Table II
^{13}C Chemical Shifts[a] and Relative Peak Areas[b] for 45% Hydrochlorinated Polyisoprene (PI-HCl-2) Compared to Those of Polyisoprene (PI) and Completely Hydrochlorinated Polyisoprene (PI-HCl-24)

Carbon	PI-HCl-2	PI	PI-HCl-24
α cis	31.6 (40)		
	32.2 (45)	32.3 (79)[c]	
α trans	39.6 (31)	40.1 (26)	
β cis, trans	135.3 (70)	135.1 (69)	
γ cis, trans	124.7 (100)	125.2 (100)	
δ cis, trans	26.5 (60)	26.5 (98)	
ε cis	23.4 (120)	23.4 (75)	
ε trans	16.0 (25)	16.0 (22)	
a,c	44.3 (140)		44.2 (140)[d]
b	74.3 (60)		74.3 (62)
d	20.1 (27)		20.2 (68)
d′	22.9 (42)		
e	29.7 (91)		29.8 (90)

[a] All chemical shifts are given in ppm downfield from TMS. [b] Values given in parentheses; measured on expanded scale spectra. [c] The areas for PI have been normalized by using the C_γ resonance. [d] The areas for PI-HCl-24 have been normalized by using the $C_{a,c}$ resonance.



$$\overset{\alpha}{—CH_2}—\overset{\beta\quad\epsilon}{C(CH_3)}{=}\overset{\gamma}{CH}—\overset{\delta}{CH_2}—$$

$$\overset{a}{—CH_2}—\underset{\displaystyle Cl}{\overset{b\quad e}{C(CH_3)}}—\overset{c}{CH_2}—\overset{d}{CH_2}—$$

Assignments corresponding to the unsaturated 1,4 units were made according to Duch and Grant.[9] There is some evidence[10] suggesting that their original assignments for C_α and C_δ carbons should be inverted but this is not relevant for the purpose of the present analysis. Assignments corresponding to the

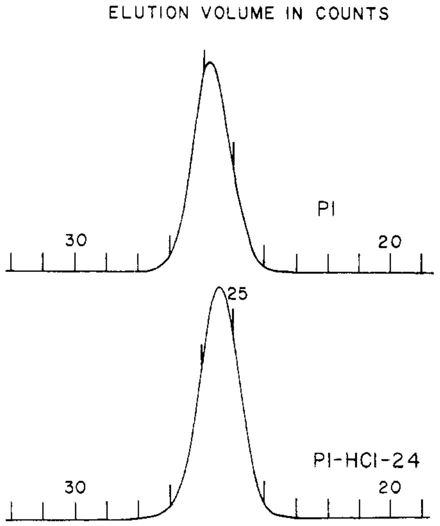


Figure 5. GPC elution curves for the polyisoprene sample (PI) and for the completely hydrochlorinated sample (PI-HCl-24).

saturated 1,4 units have been made by off-resonance proton decoupling experiments. For the sake of simplicity, the 3,4-unit resonances are ignored in the present discussion since they are too weak to be detected in the spectrum of the partially hydrochlorinated product.

Figure 4 and Table II show that all the 1,4-unit resonances observed for both the substrate and the completely hydrochlorinated product are present in the spectrum of the partially hydrochlorinated sample. However, the later exhibits two additional methylene resonance at 22.9 and 31.6 ppm, respectively, with some changes in the relative intensities of the original methylene resonances. For instance, carbon C_d in the saturated unit shows an abnormally weak signal when compared to the other signals corresponding to that unit. A similar behavior is observed for carbon C_δ resonance in the unsaturated unit, while carbon C_α cis resonance is split in a doublet which consists of the original peak at 32.2 ppm and the new peak appearing at 31.6 ppm. The relative intensities of the C_α cis doublet and the C_α trans peak are in good agreement with those measured on the polyisoprene spectrum. This suggests equivalent reactivities for the cis and trans units in the present polymer.

The new methylene resonance appearing at 22.9 ppm can be tentatively assigned to C_d carbons in BA dyads. Actually, these carbons are designated by $C_{d'}$ in Table II. Such an assignment in conjunction with the relative intensities of the 20.1- and 22.9-ppm signals would indicate that about 39% of the saturated B units would be involved in BB dyads. This value is somewhat lower than the value of 45% one should expect for a random distribution of B units in the present polymer which contains 45% of saturated units. On the other hand, assuming identical nuclear Overhauser enhancement factors and identical spin-lattice relaxation time effects for the C_δ resonances in both the spectrum of the partially hydrochlorinated sample and that of the polyisoprene sample, relative intensities given in Table II predict that about 61% of the 1,4-unsaturated units would be involved in AA dyads. This result is somewhat higher than the value of 55% one should expect for a random distribution of A units in the present polymer when ignoring the 3,4 units. The resonance for the $C_{\delta'}$ carbon which should correspond to C_δ carbon involved in AB dyads is not detected in the present spectrum. However, it is likely that this resonance should be superimposed to the methyl C_ϵ cis signal at 23.4 ppm. This is substantiated by the abnormally high intensity measured for the C_ϵ cis resonance when compared to the cis content measured previously from the C_α cis doublet. Unfortunately this point is not clear and, at the present moment, the assignments given above for both the $C_{d'}$ and $C_{\delta'}$ resonances must be considered only on a speculative basis. Nevertheless, the results concerning the relative intensities of C_d and C_δ signals afford the opportunity to establish the relative frequencies of BB and AA dyads in the present polymer. They confirm the previous conclusion that hydrogen chloride adds nearly at random along the present 1,4-polyisoprene chains.

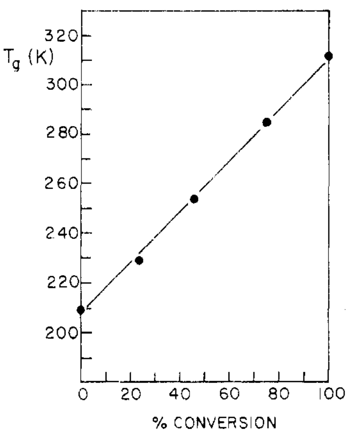


Figure 6. Glass transition temperatures, T_g, measured at 10 K/min as a function of degree of hydrochlorination.

The x-ray powder diffraction pattern of the completely hydrochlorinated sample, measured at room temperature, consists only of a diffuse halo characteristic of a noncrystalline material. From this point of view the present product is more like hydrochlorinated balata (*trans*-1,4-polyisoprene) and contrasts markedly with hydrochlorinated natural rubber (*cis*-1,4-polyisoprene) which is known to give a very well-defined x-ray diffraction pattern. As mentioned previously Bunn and Garner[1] have shown that the main structural feature of hydrochlorinated natural rubber is a stereoregular chain where the successive quaternary carbon atoms have the opposite enantiomorphic configurations. This led these investigators to postulate that hydrogen chloride adds to *cis*-1,4-polyisoprene in such a manner that a chain reaction occurs along the molecular chain. Gordon and Taylor[3] have proposed a mechanism for that chain reaction which involves a *trans*-decalin type of transition state. On the other hand, the same authors suggested that the chain reaction mechanism would be inhibited in the case of *trans*-1,4-polyisoprene, owing to the strong steric hindrance associated with the expected analogous respective *cis*-decalin type of transition state. Consequently, according to these authors the most obvious mechanism for the *trans*-1,4-polyisoprene would be the random addition of hydrogen chloride along the molecular chains. Although the present polyisoprene contains 71% of cis-1,4 units and only 22% of trans-1,4 units, it is likely that cis and trans units are distributed randomly along the chains. This is substantiated by the fact that a bernoullian distribution of cis and trans units has been observed for both 1,4-polybutadiene[11] and 1,4-poly(2,3-dimethyl-1,3-butadiene)[12] prepared with butyllithium in hydrocarbon solvents. If it is such for 1,4-polyisoprene prepared under the same conditions, taking into account the presence of the residual 7 mol % of 3,4 units also randomly distributed along the chains,[8] the number-average length of the cis sequences in the present polymer should be close to 3.5. It is probably this feature of the substrate which is responsible for the absence of crystallinity in the present hydrochlorinated polyisoprene and which also explains the nearly random conversion of the monomer units observed by NMR spectroscopy.

Molecular Weight Changes during Hydrochlorination. The product materials described in Table I were soluble in toluene and in many other solvents including benzene, chloroform, and tetrahydrofuran, but the completely hydrochlorinated product was not soluble in saturated hydrocarbons such as heptane and cyclohexane. As indicated in Table I, number average molecular weight measurements made on both the substrate and the completely hydrochlorinated product show that the reaction did not produce any significant chain alteration in the material. The molecular weight of the hydrochlorinated sample is only 6% higher than the value expected for a quantitative addition of hydrogen chloride. This small discrepancy can be easily explained by the limits of the experimental method. A better confirmation of the absence of any chain degradation during the present hydrochlorination of 1,4-polyisoprene can be obtained from the gel permeation chromatograms shown in Figure 5 where the curve obtained for the completely hydrochlorinated product shows a peak almost identical in both shape and half-width to that obtained for the substrate.

Physical Properties. Figure 6 shows the glass transition temperature of the samples described in Table I plotted as a function of the molar percentage of hydrochlorinated units in the polymer. A linear dependence is observed with a value of T_g for the completely hydrochlorinated polymer 103 K higher than that of the substrate. It is interesting to compare this change of T_g with that produced when saturation is achieved by catalytic hydrogenation of the same substrate. As shown in a previous paper,[13] in the later case T_g is increased by only 4 K indicating that the decrease in chain mobility produced by hydrochlorination of 1,4-polyisoprene is mainly due to the presence of the chlorine atoms along the polymer chains and not to the saturation of the double bonds.

Acknowledgments. The authors thank the Canadian 220-MHz NMR Centre for making the proton NMR measurements and Mr. R. Mayer for making the carbon NMR spectra.

References and Notes

(1) C. W. Bunn and E. V. Garner, *J. Chem. Soc.*, 654 (1942).
(2) H. Staudinger and H. Staudinger, *Rubber Chem. Technol.*, **17**, 15 (1944).
(3) M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **3**, 537 (1953).
(4) J. B. Pande, D. Raghunath, and C. S. Ramakrishnan, *Makromol. Chem.*, **20**, 181 (1956).
(5) M. A. Golub and J. Heller, *J. Polym. Sci., Part B*, **2**, 723 (1964).
(6) N. Grassie, "Chemistry of High Polymer Degradation Processes", Butterworth Scientific Publication, London, 1956, pp 315–319.
(7) M. A. Golub and J. Heller, *J. Polym. Sci., Part B*, **2**, 523 (1964).
(8) Y. Tanaka, H. Sato, A. Ogura, and I. Nagoya, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 73 (1976).
(9) M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).
(10) S. Brownstein, S. Bywater, and D. J. Worsfold, *Macromolecules*, **6**, 715 (1973).
(11) E. R. Santee, V. D. Mochel, and M. Morton, *J. Polym. Sci., Part B*, **11**, 453 (1973).
(12) D. Blondin, J. Regis, and J. Prud'homme, *Macromolecules*, **7**, 187 (1974).
(13) A. Laramee, P. Goursot, and J. Prud'homme, *Makromol. Chem.*, **176**, 3079 (1975).

Possible Characterization of Homopolymer Configuration and Copolymer Sequence Distribution by Comparison of Measured and Calculated Molar Kerr Constants

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ABSTRACT: Molar Kerr constants are calculated for five homopolymers [poly(propylene) (PP), poly(vinyl chloride) (PVC), poly(styrene) (PS), poly(*p*-methylstyrene) (PPMS), and poly(*p*-chlorostyrene) (PPCS)] and three copolymers (PP–PVC, PS–PPCS, and PPMS–PPCS) as functions of their stereoregularities and sequence distributions through adoption of the rotational isomeric state model of polymer chains and the valence optical scheme for addition of bond polarizabilities. Denbigh's values of the necessary bond polarizabilities were used to construct the group polarizability tensors expressed along each of the backbone bonds. Matrix multiplication methods together with Monte Carlo polymer chain generation techniques permitted the calculation of molar Kerr constants for polymers of widely varying stereoregularities and monomer sequence distributions. Only the molar Kerr constants calculated for the polar homopolymers PVC and PPCS exhibit a marked dependence on stereoregularity, while the molar Kerr constants of each of the copolymers are very sensitive to their monomer sequence distribution. On the basis of these preliminary calculations, it appears that the molar Kerr constant may be usefully employed as a sensitive indicator of the conformation, configuration, and/or sequence distribution of polar homo- and copolymers.

Ever increasing emphasis is being placed on the tailoring of polymers to meet specific end use properties. A significant portion of this effort has led to the synthesis of copolymers with useful physical properties markedly different from the properties exhibited by either of the constitutent homopolymers.

A variety of ways exist for the construction of a copolymer from monomer units A and B, e.g., random (–A–B–B–A–B–A–A–B–A–), regularly alternating (–A–B–A–B–A–B–), and block (–A–A–A–A–A–B–B–B–B–B–). The physical properties of the copolymer, especially in the bulk solid state, are critically dependent upon the detailed arrangement of its monomer units or its sequence distribution. Whether or not a copolymer exists in a single homogeneous phase in the bulk solid, for example, is determined by its sequence distribution. Clearly then, it is necessary to develop methods for determining the sequence distributions of copolymers before their effects on copolymer physical properties can be understood and used to produce superior engineering materials.

In some copolymer systems[1–15] high resolution nuclear magnetic resonance (NMR) spectroscopy, which usually employs the C^{13} nucleus as the probe,[6–15] can be used to un-