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Hydroxylation of Polyisoprene via Addition of Haloacetic Acids to the Double Bond

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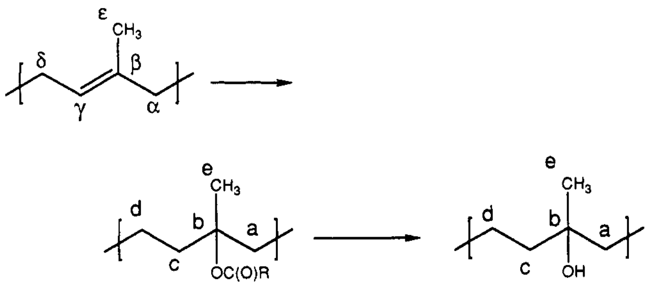
ABSTRACT: Polyisoprene reacts with 1–3 mol equiv of halogenated acetic acids, such as trifluoro-, trichloro-, and dichloroacetic acid, to give carboxy polyalkanes in an inert solvent at 0 °C to room temperature. The reactivities of *trans*- and *cis*-polyisoprene are similar. The resulting polymer is brittle for low molecular weight polymer or tacky for high molecular weight polymer and thermally unstable. It loses weight around 135 °C equivalent to nearly all of the acid added and turns into an unknown polyalkane structure. Saponification of the polyester with $NaOCH_3$ in toluene/methanol mixture gives a *tert*-hydroxyl-containing polyalkane, namely an alternating copolymer of ethylene and α-methylvinyl alcohol. This polymer slowly hardens at room temperature to give a plastic material with a T_g at 45–70 °C. Its tensile mechanical properties exhibit low elongation of break and stiffness. Polybutadiene and chloroprene do not react with acids under these conditions, implying a tertiary carbenium ion as an important intermediate.

Introduction

Polyalkanes containing hydroxyl functional groups cannot usually be obtained by polymerization of an appropriate monomer containing the hydroxyl group, but are made by secondary reactions on various precursor polymers; this limits the family of hydroxyl-containing polyalkanes. Poly(vinyl alcohol) is prepared from several different precursors, such as poly(vinyl acetate), by various chemical modifications.[1] Recently, Chung et al. published a number of different routes for preparation of polymers containing primary hydroxylated polyalkanes, using borane polymer intermediates.[2] Trialkylsilyl ether of poly(vinyl alcohol) and its copolymers are also prepared by aldol group transfer polymerization of silyl vinyl ethers.[3] Whereas these routes involve polymers prepared from monomers already containing contemplated functional groups that could be converted to hydroxyl groups, the addition of oxygen-containing radicals to the polymer backbone also has been pursued. Polydienes are one of the most versatile precursors for such chemical modifications to introduce chemical functionality.[4] For example, hydrochlorination of hevea (*cis*-1,4-polyisoprene) or balata (*trans*-1,4-polyisoprene) has been studied extensively.[5] Whereas hydrochlorination of polybutadiene (PBD) is slow[6a] and requires a catalyst for a facile reaction,[6b] sulfenyl chloride derivatives were found to add smoothly to olefinic double bonds of polyisoprene (PIP)[7] and PBD.[8] Substitution of the chloride group of these polymers with organic anions, such as cyanamide, benzoate, phenoxide, etc., and trichloroacetic acid has been accomplished with a phase transfer catalyst.[9] Carboxylation of PBD double bonds with a mixture of a catalytic amount of sulfuric acid and a saturated aliphatic and aromatic carboxylic acid was also reported.[10] These esters could be saponified by heating in alcoholic KOH solution to give hydroxyl groups. Epoxidation of the double bond[11] followed by nucleophilic ring opening[11c] or photooxidation[12] also gives hydroxylated polymers.

We found that certain halogenated carboxylic acids, such as trifluoro-, trichloro-, and dichloroacetic acid, add to the double bond of PIP to give carboxy-containing polymer, which can be saponified to give polyalkane containing tertiary hydroxyl groups (Scheme I). The addition reaction takes place without catalyst in hydrocarbon or chlorinated solvents. This reaction did not take place with PBD or chloroprene, exhibiting a high selectivity as in the case of hydrochlorination. The high yield of the observed addition product is rather unexpected, since halogenated carboxylic acids and their conjugated anions are known to be poor nucleophiles.[13] We describe in this paper the scope and a possible mechanism of the reaction.

Scheme I



Results and Discussion

Reaction of Halogenated Acetic Acids with Polyisoprene. The addition reaction typically takes place in about 15 wt % solution of PIP in an inert organic solvent with 1–3 equiv of halogenated acid at 0 °C, in the absence of catalyst. The progress of the addition reaction can be monitored by the disappearance of ^1H NMR resonance at 5.1 ppm due to olefinic protons and the appearance of new peaks at 1–2 ppm. In the case of reaction with trichloroacetic acid (TCA), the ^{13}C NMR spectrum shows a new peak at 91.1 ppm due to the acetylated tertiary carbon, the disappearance of PIP olefinic peaks, and the shifting of the methyl peak (C_ϵ) from 23.43 ppm of *cis*-PIP to 22.97 ppm (C_e) and a methylene carbon (C_α) from 32.3 ppm to 38.30 ppm ($C_{a,c}$) (Figure 1a, Table I). When trifluoroacetic acid (TFA) was used, two sets of quartets at 156 (J = 40.8 Hz) and 114.5 ppm (J = 285.6 Hz), due to carbonyl and the methyl carbon of the trifluoroacetyl group, were also found. The IR spectrum of this product also shows the disappearance of double bonds of polyisoprene at 838 and 842 cm^{-1} and the appearance of a sharp strong peak at 1780 cm^{-1} due to the ester carbonyl of trifluoroacetate. Small peaks at 0.8–0.9 ppm and around 2.0 ppm in ^1H

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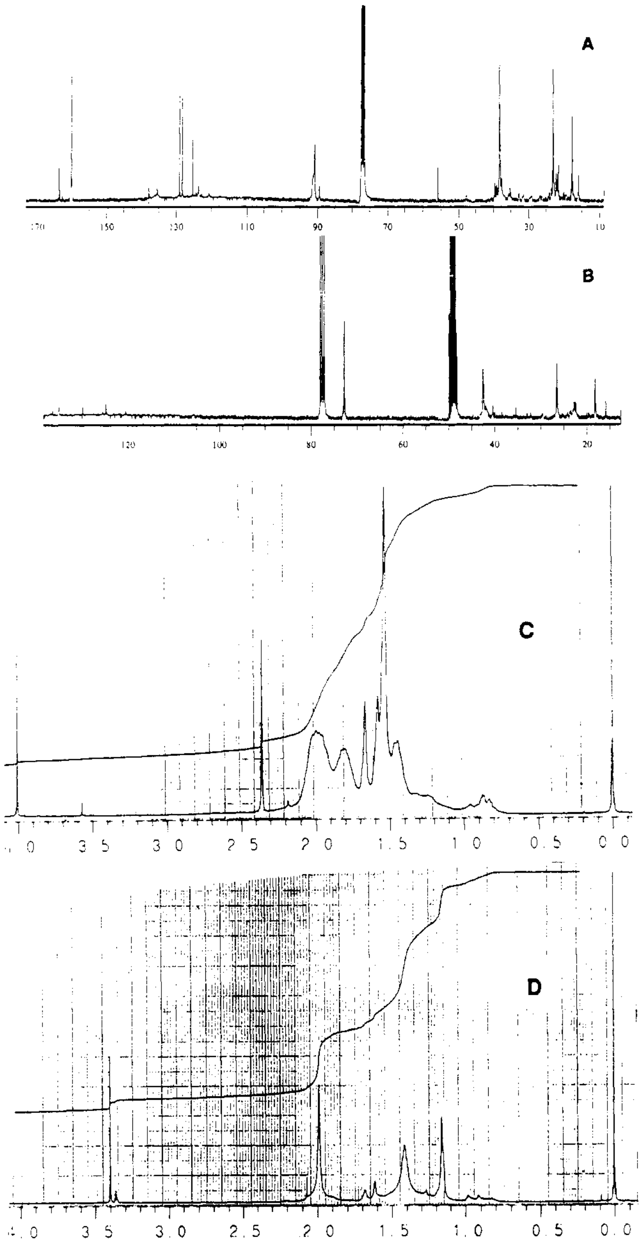


Figure 1. ^{13}C NMR (75.57 MHz) and ^{1}H NMR (300 MHz) spectra of trichloroacetylated polyisoprene (a) and saponified polymer (b) and ^{1}H NMR of the corresponding polymers (c) and (d). In spectra a, the carbons of the CCl_3 group and the carbonyl group are seen at 89.4 ppm (a very weak peak) and 160.1 ppm. Residual toluene is also found (at 17.6 and 125–129 ppm). See Table I for the ^{13}C NMR peak assignments and text for the ^{1}H NMR assignment.

NMR spectra indicate some degree of cyclization to cyclohexene rings.[4b,5c] Most olefinic groups react eventually, but the reaction becomes very slow when about 80% of the olefinic group is reacted.

Trifluoro- (pK_a = 0.52),[14] trichloro- (pK_a = 0.51), and dichloroacetic acid (DCA, pK_a = 1.30) were found to react under these conditions. As the acid pK_a values increase, the addition reaction slows down. Since a linear relationship between pK_a values and nucleophilic reaction rates within a class of acids is observed in many cases,[15] our results indicate a nucleophile reaction mechanism. We propose that the reaction proceeds by the nucleophilic attack of the olefinic group on the acid to give a tertiary carbenium ion, followed by coupling with the carboxylate anion. For reaction to occur, the nucleophilicity of the polymer double bond must be compatible with the electrophilicity of the acid proton, in addition to the nucleophilicity of the carboxylate anion.[13a] Whereas stronger acids reacted readily with the polymer, monochloroacetic acid (pK_a = 2.87) and acetic acid (AcOH, pK_a = 4.75) did not give appreciable amounts of acetoxylation even under more demanding conditions, in contrast to the similar reaction with PBD. Attempts to acetoxylation with acetic acid will be discussed in more detail separately.

Table I
^{13}C NMR Peak Assignment of Polyisoprene and Chemically Modified Polyisoprenes

carbons	PIP	HCl reacted PIP	CCl_3COOH reacted PIP	hydroxylated PIP	partially reacted PIP
α-cis	32.3				32.0, 32.2
α-trans	40.1				40.0, 18.0
β-cis,trans	135.1				135.1
γ-cis,trans	125.2				125.1
δ-cis,trans	26.5				26.7
ϵ-cis	23.4				23.4
ϵ-trans	16.0				15.9
a,c		44.2	38.3	41.6, 42.3	
b		74.3	91.1	72.9	
d		20.2	21.4–22.5	22.5, 23.5	
e		29.8	23.0	26.5	

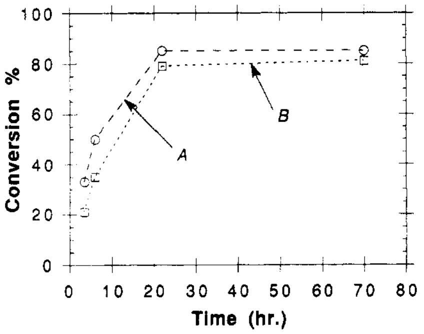


Figure 2. The conversion percentage of the olefinic group to the carboxylated group was determined by the ^{1}H NMR peak intensity ratios of olefinic methyl (1.61 ppm) and the carbinol methyl (1.18 ppm) peaks. Curve A is of the trans isomer and curve B is of polyisoprene prepared by anionic polymerization.

The rates of reaction of *cis*- and *trans*-PIP were really identical, when they were reacted separately (Figure 2). However, the trans segment of anionically polymerized polyisoprene seems to react much slower than the cis segment, evidenced by ^{13}C NMR of partially reacted polymers, which will be discussed later in conjunction with a brief mechanistic study.

The solvents investigated include hexane, toluene, dichloroethane, and dichloromethane. The reaction rate was faster in toluene or chlorinated solvents than in hexane. The solubility of TFA in hexane and toluene below 0 °C is low, resulting in little addition. Since the reaction is second order, concentration also affects the reaction rate. Thus, the reaction can be accelerated by higher concentration of acid or by raising the reaction temperature. When the reaction was carried out at reflux in toluene, rapid disappearance of the double bond could be seen by ^{1}H NMR, but no peak at 93 ppm was found in ^{13}C NMR, implying that mostly cyclization occurred. When comparing two reactions, one in 2 M solution (18 wt %) and another in 0.2 M solution (1.8 wt %), with one to one equivalent of acid to the polymer, the former showed 60% of the olefinic group reacted in 16 h, whereas less than 5% for the latter was reacted (Figure 3). Typically, 1–2 M of the polymer solution was employed for preparative work.

There is no polymer chain degradation during this chemical modification. GPC analysis showed that the

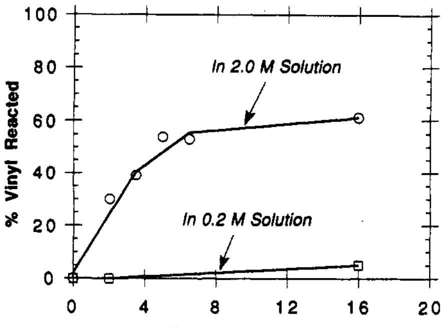


Figure 3. Comparison of the reaction rates in two concentrations shows a tendency of a second order reaction. Reaction conditions: 1 equiv of CF_3COOD was used with polyisoprene prepared by anionic polymerization, in toluene at 0 °C. More conditions can be found in Table II.

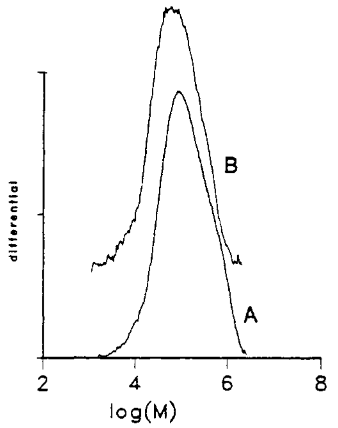


Figure 4. GPC of *trans*-polyisoprene before (A) and after (B) hydroxylation. A: $M_n = 8.1 \times 10^4$, $D = 4.3$. B: $M_n = 8.6 \times 10^4$, $D = 4.6$.

modified polymer has nearly the same polydispersity as the untreated polymer, and a slightly higher molecular weight (Figure 4). The isolated TFA adduct showed deterioration at room temperature during 2 weeks, as evidenced by coloration and evolution of gaseous products, but the adduct with chlorinated acetic acids showed no apparent decomposition over the period of 6 months. This difference in the stability of the adduct must originate from the leaving group activities (nucleofugalities) of the corresponding acetate groups. The trifluoroacetate group was found to have higher nucleofugality than the trichloroacetate group in a hydrocarbon solvent.[16] The resulting polymer is brittle (for low molecular weight polymer) or tacky (for high molecular weight polymer) and thermally unstable. It loses most of the acid around 135 °C and turns into an unknown structure of polyalkane with an IR spectrum reminiscent of that of a copolymer of ethylene and propylene. The physical properties of these carboxylated polymers are poor. However, saponification of the ester gives alternating copolymer of ethylene and α-methylvinyl alcohol.

Saponification. These carboxy PIPs were saponified to give alternating copolymers of poly(ethylene-*alt*-α-methylvinyl alcohol). Saponification can be done in an aqueous system for homopolymer of low molecular weight, but basic methanolysis works well for most cases. For example, when a low molecular weight, brittle polymer of TFA-added PIP (DP = 40) was saponified in a biphasic mixture of 2 N NaOH solution and toluene, a clean cleavage of trifluoroacetate bonds (1780 cm^{-1}) to generate hydroxyl groups (3420 and 1160 cm^{-1}) was obtained. A high molecular weight polymer (from *cis*-PIP of M_n = 39 900; D = 6.9 by GPC) did not undergo saponification under these conditions; however, methanolysis with $NaOCH_3$ in a mixture of toluene and methanol (2:1 in volume) gave clean conversion to the alcohol. In methanolysis, no precipitation of polymer occurred during the course of the reaction. At the end of reaction, the base was neutralized with acetic acid, which caused precipitation of certain polymers depending on the hydroxyl content. Partially reacted polymers can be purified by precipitation into MeOH, but polymers with more than 80% of the olefinic group converted are soluble in MeOH. These polymers were usually purified by filtering off insolubles in a mixture of MeOH and CH_2Cl_2 or THF, followed by evaporation of the solvent, or by precipitation of the polymer into water from a MeOH solution. In most of cases the saponification step can be carried out without isolation of the acetoxylated polymer. At the end of the acetoxylation, excess $NaOCH_3$ solution is added for direct saponification.

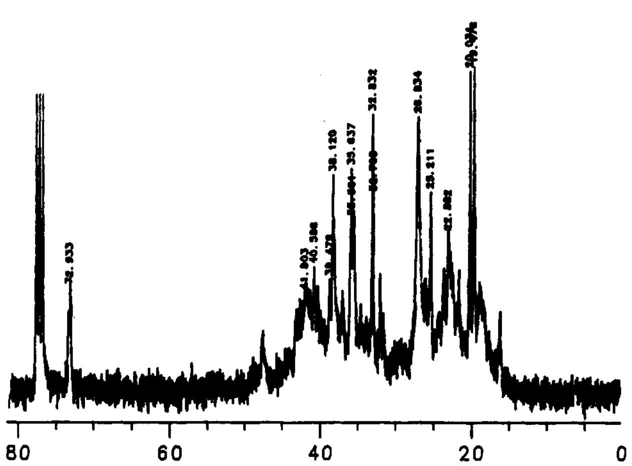


Figure 5. ^{13}C NMR in $CDCl_3$ of polyisoprene which was treated with trifluoroacetic acid at 60 °C, followed by saponification.

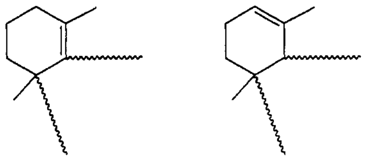
The NMR spectrum of this saponified product shows some differences from the acetoxylated polymer; it resembles that of hydrochlorinated PIP. The comparison of the ^{13}C NMR of the hydroxylated, and hydrochlorinated PIP[4c] is summarized in Table I. The tertiary carbon (C_b) moves to 73 ppm, reflecting change to a hydroxyl group containing carbon. The peaks corresponding to $C_{a,c}$ and C_e appear around 42 and 23 ppm as doublets with almost equal intensities regardless of the starting PIP stereochemistry. We speculate that these doublets reflect the stereochemistry of the resulting product, in which an equal amount of syndiotactic and isotactic isomers exist. These findings further support our proposed mechanism involving a tertiary carbenium ion as an intermediate, with low stereoselectivity. This is different from hydrochlorinated PIP, where a certain degree of stereoselectively is manifested such that *cis*-PIP gives crystalline material but *trans*-PIP gives an amorphous material.[17]

Since the NMR peaks of this compound are much better resolved than that of acetates and can be interpreted unambiguously, most characterization was done on the hydroxy derivative. When the reaction is prematurely terminated for anionically polymerized PIP, the NMR peaks due to the cis isomer are diminished greatly, while those of trans isomer are persistent. This indicates the difference in the reaction rates between these two stereo centers. Among these partially reacted polymers, the C_α peak at 32.2 ppm for cis polymer splits into two peaks at 32.09 and 32.2 ppm. These additional peaks are also found in case of hydrochlorination[4c] and are due to the differences in the isoprene segment environment, depending on whether the neighboring segment is hydroxylated or as

Table II
Reaction with Anionically Polymerized Polyisoprene with CF_3COOD in Toluene

	reaction conditions			% reacted	
sample	reaction time, h	reaction temperature, °C	[polymer]:[acid], mol/L	by vinyl	by methyl
A	2	0	2:2	30	35
B	16	0	2:2	60	60
C	2	0	0.2:0.2	7	0
D	16	0	0.2:0.2	10	5
E	16	ambient	2:6		

yet unreacted. As the addition reaction proceeds to a higher degree, a new peak at 18.0 ppm appears regardless of the stereochemical structure of the polymer or the type of acid used (Figure 1b). DEPT[18] and APT[19] experiments proved that the 18.0 ppm peak is a methylene carbon, but we cannot assign it to any of the carbons in the proposed structure in Scheme I. When the reaction temperature was 60 °C, cyclization seemed to predominate. There were new sets of ^{13}C NMR peaks, such as peaks at 19.5 (CH_2 carbon according to DEPT), 20.0 (CH_3), 32.83 (quaternary C or CH_2), 35.6 (quaternary C or CH_2) ppm, in addition to a small amount of peaks due to the hydroxylated segment (Figure 5). These peaks must be due to cyclohexene derivatives resulting from cyclization.[4b,5c] For the product prepared at 80 °C, no peak at 73 ppm was found, and the peaks responsible for the cyclic compounds were more intense.



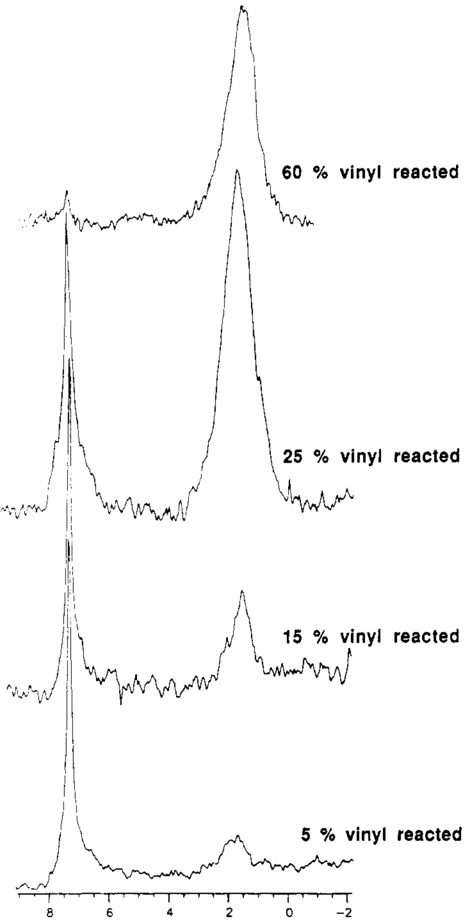


Figure 6. ^2H NMR of polyisoprene in various stages of reaction with CF_3COOD. The labels in the figure correspond to those in Table II.

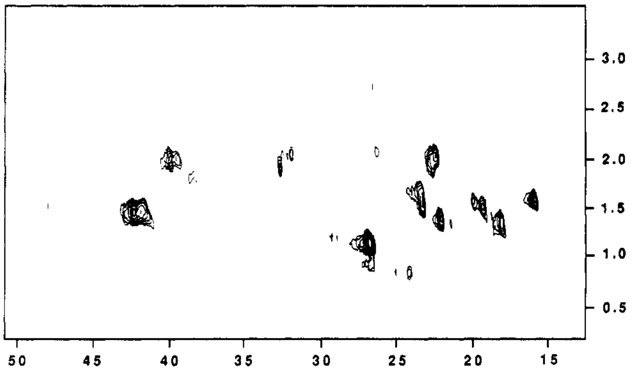


Figure 7. 2D C-H COSY NMR of sample E in Table II. The high concentration (50% in $CDCl_3$) of the sample needed to obtain this spectrum caused poor resolution in certain region of the ^1H NMR spectrum.

Reaction with Deuterated Trifluoroacetic Acid. To obtain more insight into the addition reaction, deuterated TFA was reacted with polyisoprene, and the progress was monitored by ^1H NMR, ^2H NMR, and ^{13}C NMR. We performed three reactions which are summarized in Table II. Two reactions employ an equivalent amount of acid and polymer at 0 °C, one in 2 M (A and B in Table II) and the other in 0.2 M solution (C and D in Table II), and the samples were taken at interval of several hours. The third reaction (E in Table II) was carried out at ambient temperature in the presence of excess acid. The amount of olefinic reacted was determined by ^1H NMR and reported in the table. The ^2H NMR spectra of the first four samples are shown in Figure 6. These spectra show that the olefinic proton undergoes a rapid deuterium exchange before any protonation takes place at the double bonds. As more olefinic group is reacted, more aliphatic carbon shows deuteration, and the intensity of the olefinic deuterium peaks gets smaller. However, in this case the measurement of olefinic peak intensity as the indicator for the degree of reaction was found to be highly erroneous due to excessive deuterium exchange at this position. More reliable data was obtained by comparing the intensity of the methyl peak of hydroxylated PIP (1.18 ppm) and that of PIP (1.61 ppm). Sample D was found to have about 10% of the olefinic group reacted by ^1H NMR, but examination of ^{13}C NMR spectra showed no carbinol carbons. Sample C showed a small amount of addition (ca. 5%), but still all three isomers of PIP, including 3,4-vinyl isomer, were observed in ^{13}C NMR. The deuterium peaks in the alkyl region of this sample in ^2H NMR seem to arise from a 1,3-proton shift of the olefinic protons to the methyl group, as well as by addition of acid to the olefinic group. It seems that under these dilute conditions, the rate of the addition reaction is very slow. Samples A and B show about 60% and 30% of the olefinic group reacted. Of all these samples, only A showed a peak at 18.0 ppm. In sample B, all of the peaks due to the 3,4-isomer disappeared, indicating this isomer might be more reactive than other isomers. Sample E was prepared in such a manner so as to have all possible microstructures, so it was reduced at room temperature to induce some cyclization, and prematurely stopped. A 2D C-H COSY NMR spectrum of this sample was obtained for unambiguous peak assignment (Figure 7). The methyl peaks in the 0.8–0.9-ppm region in ^1H NMR correspond to 23.37, 25.1, and some portion of the peak at 26.8 ppm in ^{13}C NMR. The

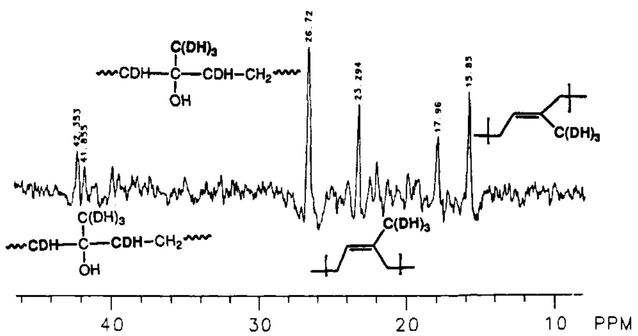
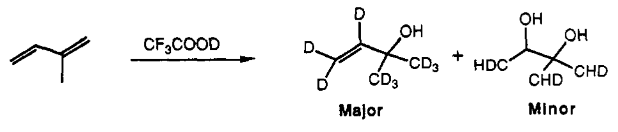


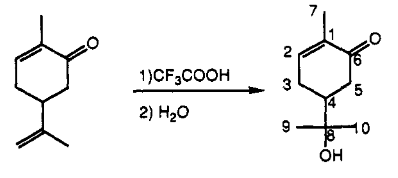
Figure 8. ^{13}C NMR differential spectrum of hydroxylated polyisoprene derived from the reaction with CF_3COOD. See the text for detail.

allylic methyl group in cyclohexene can be identified at 20.0 ppm. It is coupled to the 1.57-ppm peak in ^1H NMR. A peak at around 22 ppm (2.05 ppm in ^1H NMR) could be due to the endocyclic allylic methylene, but peaks around 32–35 ppm were found to have no protons attached.[20]

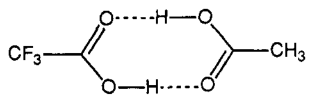
The identification of deuterated carbons would provide a valuable clue to the reaction mechanism. The position of deuteration in the polymer chain was identified by a differential ^{13}C NMR spectrum generated by subtraction of the gate-controlled irradiated spectrum, obtained while both proton and deuterium were irradiated, from the spectrum obtained while only proton was irradiated. Deuterated carbon has a higher intensity in the spectrum of which both are irradiated, due to the nuclear Overhauser effect, and shows positive peaks (Figure 8) after subtraction. All carbon except C_d of the hydroxylated polymer was found to be deuterated, suggesting the tertiary carbenium ion intermediate has a longer life time than the proton exchange rate. Interestingly, the 18.0-ppm peak (1.36 ppm in ^1H NMR) is also deuterated, indicating it might originate from C_δ in PIP. Our best guess for this peak is that it is due to a cyclohexene derivative. One possibility is that the endocyclic olefinic group could have reacted with TFA to give cyclohexanol at the latter stage of the reaction.

Model Reactions. We were interested to see if high chemoselectivity could be achieved in a small molecule. Even though it is well known that addition of trifluoroacetic acid occurs to an electron-rich double bond, such as 2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran, or vinyl ethers, its synthetic utility in chemoselectivity is not much explored. Trifluoroacetic acid was found to add preferentially to the 3,4 double bond of isoprene in toluene at 0 °C when about 1 equiv of acid was employed in a 0.9 M scale reaction. If the acid concentration is high or the reaction temperature is about 0 °C, oligomerization of isoprene predominated. Similarly, a high yield of selective addition of trifluoroacetic acid was achieved at the exo double bond of carvone, while the endocyclic double bond was inert.





Attempted Acetylation with Acetic Acid. Monochloroacetic acid and acetic acid did not show any addition to PIP in refluxing toluene during several days. Since addition of AcOH to PBD in the presence of sulfuric acid is known, we attempted the acetylation with various protonic and Lewis acid catalysts. Weak acid catalysts, such ZnI_2, $NiCl_2$, $Al(CH_3)_3$, and Nafion, did not bring about any acetylation, even with almost stoichiometric amounts of catalyst to acid. With strong acids, such as $AlCl_3$ or $TiCl_4$, cross-linking resulted. Similarly, with sulfuric acid as a catalyst, only a small amount of gel resulted. When TFA was used as a catalyst, no addition of either acid was found. Since AcOH is more nucleophilic than TFA,[13] the AcOH should read preferentially to the long-lived tertiary carbenium ion generated by protonation by TFA. However, in a competition experiment with a mixture of TFA and AcOH, in ratio of 1:2, 1:1, and 2:1, only the former acid was found to react with *trans*-PIP. For comparison, the reaction was carried out under conditions where the reaction rate was slow, at 0.4 M solution with a 1:1 ratio of *trans*-PIP to the mixed acid during 6 h at 0 °C. The degree of reaction estimated by NMR was very low, but IR showed the trifluoroacetate carbonyl at 1780 cm^{-1}, but no signs of acetate at 1730–1750 cm^{-1}. Taking the methyl vibration at 1380 cm^{-1} as an internal standard, the peak intensity of 1780 cm^{-1} of trifluoroacetates shows that there is a linear relation of the amount of trifluoroacetate to the TFA:AcOH ratio. Carboxylic acids in an organic solvent exist as dimers. Since the carbonyl oxygen of AcOH is more nucleophilic, it is possible that these two acids would form a mixed dimer, I, which would have lower acidity than the pure TFA, thus preventing addition of either acid. The extreme case of protonation on the carbonyl group would be formation of a salt II, whose acidity or electrophilicity cannot be speculated upon at this point.



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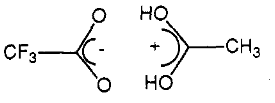

II

Reaction with Other Polydienes. Polybutadiene is missing a weak electron-donating methyl group to stabilize the tertiary carbenium ion resulting from the acid addition. On the other hand the chlorine in chloroprene has a negative inductive effect but positive resonance. Examination of these polymers in the reaction with acid would help to elucidate the reaction mechanism. The addition reaction did not occur to the double bond of PBD or chloroprene with any of the halogenated acetic acids under conditions where polyisoprene reacted. A PBD, which has microstructure of 45% 1,2-vinyl and 55% mixture of 1,4 cis and trans isomers, showed no reaction with TFA at room temperature over several days. Similarly, chloroprene showed no reaction, even in boiling toluene with TFA in the presence of various catalysts. These results also are consistent with a stable carbenium ion mechanism.

Properties of Hydroxylated Polymer. The hydroxylated polymers are relatively stable, exhibiting onset temperature of thermal decomposition in thermal gravimetric analysis at 400 °C. The T_g of the polymer is dependent upon the degree of the reaction. Thus 50% hydroxylated polymer shows a T_g at 45 °C, whereas 85% hydroxylated polymer shows a T_g at 65 °C. Thus, hydroxylated polymer is a glassy plastic material at room temperature. When the polymer derived from *cis*-polyisoprene of M_n = 39 900,

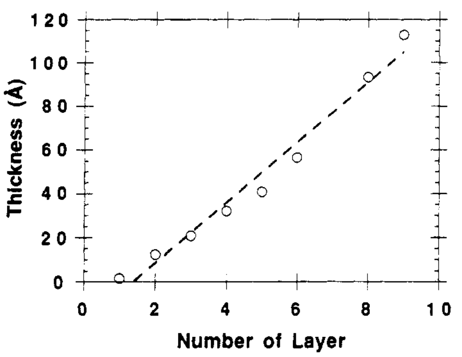

Figure 9. Ellipsometric thickness vs layer number of the Langmuir–Blodgett film of hydroxylated polyisoprene.

D = 6.9 (by GPC with PMMA standard) was pressed at 120 °C, a uniform semitransparent film was obtained. This film slowly hardened at room temperature to give a stiff material with tensile mechanical properties of modulus, 161 ± 14 kpsi; maximum strength, 2376 ± 184 psi; and the elongation at break, 24 ± 13%.

This polymer has a structural resemblance to that of the copolymer of ethylene and vinyl alcohol (EVOH), except for the absence of an α-hydrogen to the hydroxyl group. EVOHs with varying ratios of ethylene and vinyl alcohol are important oxygen barrier packaging materials. Oxygen permeability of hydroxylated polyisoprene was, however, rather high compared to EVOH, probably due to its lack of crystallinity. As expected its moisture barrier properties were better than EVOH.

Langmuir–Blodgett Experiment. The hydroxylated polymer exhibits interesting surface properties. It forms a monolayer structure on a Langmuir–Blodgett film balance. The layer showed no hysteresis up to 20 mN/m, and the area/repeating unit was about 18 Å^2. The transfer of the monolayer to a silicon wafer gave z-type deposition, with average thickness of 8 Å out of 20 layers, as determined by ellipsometer (Figure 9). The sessile drop contact angle of layers beyond the second layer was 42°. These results could be explained by a monolayer structure of closely packed hydroxyl groups on the water/air interface with alkyl groups being tightly folded in air, but with occasional mistakes in the chain alignment to expose the hydroxyl groups to the air side. Regeneration of the polar surface by each deposition could be responsible for rather unusual z-type deposition.

Experimental Section

Polyisoprene was prepared by anionic polymerization with *s*-BuLi as an initiator in hexane at room temperature. Stereochemically pure cis and trans polyisoprene and polybutadiene were purchased from Polyscience Inc. Hexane was dried by refluxing with oligomeric living polystyrene under nitrogen and distilled just prior to use. Anhydrous toluene, sodium methoxide, and a sodium methoxide solution in methanol was purchased from Aldrich and used as received. Halogenated acetic acids are from various commercial sources and used without further purification. All acid addition reactions illustrated were conducted under nitrogen atmosphere unless otherwise mentioned. Oxygen and moisture permeation tests were performed according to standard ASTN methods. Tensile mechanical properties were measured on an Instron mechanical tester (Model 1123) with head speed of 0.1 in./min at ambient temperature; thermal properties were obtained from Du Pont thermal analyzers 9600 with heating rate of 20 °C/min. For the Langmuir–Blodgett experiment, a KSV LB 5000 film balance fitted with a Teflon trough and a platinum Wilhelmy plate was used. Subphase water used for the Langmuir experiment was purified by a NanoPure water purification apparatus (resistivity 17.0 MΩ m), and the samples were spread in $CHCl_3$ in about 0.1 mg/mL concentration. The compression rate was 5.5 cm^2/min. Langmuir–Blodgett vertical film transfer on a silicone wafer surface was carried out at constant surface pressure of 17 mN/m. The rate of vertical immersion of the wafer was ca. 5 mm/min. The wafer was first treated with a 10% HF solution, followed by rinsing with water and CH_2Cl_2. The wafer was argon plasma treated prior to deposition using a March plasma cleaner. It usually has about 15 Å of SiO_2 layer. The thickness of the film was determined by Rodolph ellipsometer, and a sessile drop goniometer was used for the contact angle measurement.

Reaction of Polyisoprene with Trichloroacetic Acid. To 5.00 g of *trans*-PIP (M_n = 81 000, P/D = 4.3, 73.5 mmol of double bond) in 40 mL toluene was added 36.25 g (222 mmole) of trichloroacetic acid at 0 °C, and then the mixture was stirred for 70 h. The polymer was precipitated from 200 mL of methanol, cold pressed into films, and then vacuum dried. The product weighed about 6.3 g. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.8–1.0 (m, CH_3 in cyclics), 1.4 (br), 1.5 (s, CH_3), 1.8 (br), 2.0 (br). ^{13}C NMR (ppm, $CDCl_3$): 21.4, 22.5 (C_d), 23.0 (C_e), 38.3 ($C_{a,c}$), 91.1 (C_b), 160.08 (CO). IR (carbonyl): 1760 cm^{-1}.

Reaction of Polyisoprene with Trifluoroacetic Acid. To 2.0 g (29.5 mmol) of an anionically polymerized PIP (M_n = 17 700, D = 1.05) in 60 mL of anhydrous toluene was added 4.6 mL (60 mmol) of trifluoroacetic acid at 0 °C, and the mixture was sitrred for 24 h. The polymer was precipitated from MeOH and vacuum dried. The product weighed 2.32 g. ^{1}H NMR (ppm, $CDCl_3$): 0.8–1.0 (m, CH_3 in cyclics), 1.4 (br), 1.5 (s, CH3), 1.8 (br), 2.0 (br). ^{13}C NMR (ppm, $CDCl_3$): 23.25 (C_e), 38.03 ($C_{a,c}$), 92.14 (C_b), 114.4 (CF_3, J = 285 Hz), 156.0 (CF_3CO, J = 41 Hz). IR (carbonyl): 1780 cm^{-1}.

Reaction with Dichloroacetic Acid. To 2.0 g (29.5 mmol) of *trans*-PIP in 120 mL of 1,2-dichloroethane was added 7.5 mL (90 mmol) of dichloroacetic acid at 0 °C over a period of 45 min, and then the mixture was stirred for 24 h. The solvent was concentrated under vacuum, and the residue was diluted with chloroform and precipitated from MeOH. ^{1}H NMR spectrum at this point showed complete removal of DCA from the sample. The product weighed 2.25 g after drying. The ^{1}H NMR spectra showed about 13% of the double bond had reacted. IR (carbonyls): 1760 and 1740 cm^{-1}.

Saponification of Trichloroacetoxylated PIP. To 20 mL of toluene solution containing 5.0 g (24.5 mmol) of the previously prepared trichloroacetylated PIP was added 12.4 g (36.8 mmol) of 24% NaOMe solution in MeOH, and the solution was stirred for 16 h at room temperature. To this was added 1.40 mL of acetic acid. The mixture was poured into MeOH. The insoluble particulate was filtered off, and the filtrate was concentrated in vacuo. To the concentrate was added about 100 mL of a mixture of THF and MeOH (5:1), and the insoluble material was filtered off again. The evaporation of the solvent gave 2.0 g of the product. ^{1}H NMR (ppm, $CDCl_3$): 0.8–1.0 (m, CH_3 in cyclics), 1.16 (3 H, s, CH_3), 1.42 (6 H, br), 1.61 (s, CH_3 of PIP), 2.0 (s, OH). ^{13}C NMR (ppm, $CDCl_3$): 22.5, 23.5 (C_d), 26 (C_e) 40.0–42.0 ($C_{a,c}$), 72.9 (C_b). IR (hydroxyl): 3420, 1160 cm^{-1}. T_g (DSC): 68.5 °C. Onset temperature of decomposition (TGA): 415 °C. Anal. Calcd for $C_5H_{10}O$: C, 69.72; H, 11.90; O, 18.57. Found: C, 74.63; H, 11.19; O, 14.18.

A One-Pot Procedure. To 1350 mL of dry toluene was added 102 g (1.5 mol of double bond) of *cis*-polyisoprene, and the mixture was stirred overnight, with occasional heat to dissolve into a homogeneous solution. To this was added 228 g (2.0 mol) of trifluoroacetic acid over a period of 3 h via a syringe at room temperature. The color of the solution turned light purple and then light brown. The mixture was stirred for 16 h. To this was added 300 mL of methanol, which eliminated coloration, followed by 250 g (4.5 mol) of sodium methoxide. The mixture was stirred for 2 h, and then 140 mL of acetic acid and 150 mL of methanol were added. The polymer was found to settle down at this stage. The supernatant was decanted off and the polymer was washed with methanol (twice with 500 mL) and 50% methanol in water (twice with 1 L). The washed polymer was dissolved in the mixture of methanol and methylene chloride (5:95) and then filtered through a sintered glass filter. The polymer was precipitated in 5–8-fold excess methanol in a blender, then pressed into films. After the films were dried in a vacuum oven, 90 g of product was obtained. ^{1}H NMR showed virtually all of the PIP double bond had reacted, but about 30% was identified as the cyclic products. Anal. Calcd for $C_5H_{10}O$: C, 69.72; H, 11.90; O, 18.57. Found: C, 79.09; H, 11.60; O, 8.91. T_g (DSC): 65 °C. The onset temperature of decomposition (TGA): 380 °C. The oxygen permeability on about 3.3-mil-thick film was 34 cm^3 O_2 mil/100 in.^{2} atm day at 30 °C and at 76% room humidity. The water permeability at 37.8 °C at 90% humidity was 0.65 gram mil/100 in.^{2} day. Tensile modulus, 161 ± 14 kpsi; maximum strength, 2376 ± 184 psi; the elongation at break, 24 ± 13%.

Reaction of Isoprene with Deuterated Trifluoroacetic Acid. To 10 mL of deuterated toluene containing 1 mL of isoprene was added 1 mL of trifluoroacetic acid at −78 °C and then the mixture was warmed to 0 °C. The reaction could be followed by ^1H NMR. The reaction was carried out for 16 h, and then 10 mL of D_2O was added. The organic layer was separated and dried with $MgSO_4$. A small fraction of this solution was treated with trimethylsilyl chloride and then subjected to GC/MS analysis, which showed that the major component of the product is fully deuterated 1,1-dimethylallyl alcohol in addition to a small amount of partially deterated 2-methyl-2,3-dihydroxylbutane. High-resolution MS of the major product: calcd as $C_8D_9H_9OSi$ 167.16761, found 167.1692.

Reaction of (*R*)-(−)-Carvone with Trifluoroacetic Acid. To 3.0 g of (*R*)-(−)-carvone in 50 mL of methylene chloride was added 9.2 mL of trifluoroacetic acid and then the mixture was heated under reflux for 2 h. NMR analysis showed complete conversion to trifluoroacetate at this point. ^{13}C NMR (ppm, $CDCl_3$): 15.36 (C_1), 22.72, 22.93, (C_9, C_{10}), 26.64 (C_3), 38.87 (C_4), 44.29 (C_5), 89.24 (C_8), 114.32 (CF_3, quartet, $J = 286.21$ Hz), 135.59 (C_1), 143.42 (C_2), 155.86 (CF_3CO, $J = 41.45$ Hz), 197.99 (C_6).

To the crude reaction mixture of trifluoroacetate was added water, and the organic layer was separated and washed with $NaHCO_3$ solution and water. After drying, 3.04 g of product was obtained. The hydroxylated product was purified by column chromatography, using silica gel and a mixture of ether in hexane as an eluent. ^1H NMR (ppm, $CDCl_3$): 1.20, 1.23 (3 H, exo CH_3), 1.56, 1.61 (6 H, CH_3), 2.2–2.7 (m, 5 H), 6.8 (br, 1 H). ^{13}C NMR (ppm, $CDCl_3$): 15.42 (C_1), 26.94, 27.13, 27.24 (C_8, C_{10}, C_3), 39.57 (C_4), 46.06 (C_5), 71.32 (C_8), 135.07 (C_1), 144.98 (C_2), 200.11 (C_6). MS (*m*/*e*): 150 (40%, $M^+ - OH$), 135 (100%, $M^+ - OH$ and CH_3).

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