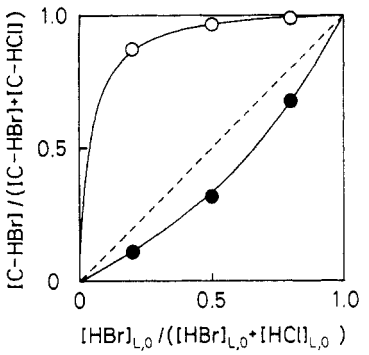


Figure 6. Relationship between the fraction of C–HBr in the membrane and the feed fraction: (●) membrane 1; (○) membrane 2. Experimental and calculated values are summarized in Table III.

trial and error, we fitted eq 9 to the data. The solid lines in Figure 6 were calculated by assuming values $\alpha = K'/K = {}^2/_1$ for membrane 1 and ${}^1/_{25}$ for membrane 2. In other words, in membrane 1, the salt formation constant between the carrier and HCl was 2 times greater than that between the carrier and HBr. In the membrane 2 system, the salt formation constant between the carrier and HBr was 25 times greater than between the carrier and HCl. The different membrane polarities may be the reason for the drastic difference in salt formation constants even though membrane 1 and 2 contained the same fixed carrier. Membrane 1 formed a more stable complex with hydrophilic Cl^- than with hydrophobic Br^-. In contrast, membrane 2 formed a more stable complex with Br^- than Cl^-. In conclusion, the membrane polarity not only determined the transport mechanism but also played an important role in controlling affinity between carriers and substrates (halogen ions).

Conclusions

Membrane 1 (highly polar) transported halogen ions not only by an antiport mechanism with OH^- transfer but also by a symport mechanism with H^+ transfer. Membrane 2 (low polarity) transported halogen ions only by a symport mechanism. Membrane 1 selectively transported Cl^-, while the membrane 2 transported Br^-. The values $K'/K = {}^2/_1$ for membrane 1 and ${}^1/_{25}$ for membrane 2 were determined.

Acknowledgment. We are deeply grateful to Associate Professor Takeo Shimidzu (Division of Molecular Engineering, Graduate School of Engineering, Kyoto University) for his kindly providing the indicator, 1-octadecyl-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran].

Registry No. 1, 32236-74-1; 2, 26222-40-2; bromide ion, 24959-67-9; chloride ion, 16887-00-6.

References and Notes

(1) Ogata, N.; Sanui, K.; Tanaka, H.; Fujimura, H.; Kawachi, Y. *Kobunshi Ronbunshu* **1981**, *38*, 583.
(2) Imashiro, Y.; Yokoi, H.; Yoshikawa, M.; Sanui, K.; Ogata, N. *Nippon Kagaku Kaishi* **1983**, 875.
(3) Yoshikawa, M.; Ogata, H.; Sanui, K.; Ogata, N. *Polym. J. (Tokyo)* **1983**, *15*, 609.
(4) Yoshikawa, M.; Imashiro, Y.; Sanui, K.; Ogata, N.; *J. Membr. Sci.* **1984**, *20*, 189.
(5) Fajans, K.; Hassel, K. *Z. Elektrochem. Angew. Phys. Chem.* **1923**, *29*, 495. Fajans, K.; Steiner, W. *Z. Phys. Chem., Steochiom. Verwandtschaftse.* **1927**, *125*, 309.
(6) Clark, F. E. *Anal. Chem.* **1950**, *22*, 553.
(7) Winkler, L. W. *Z. Anal. Chem.* **1914**, *53*, 359. Treadwell, F. P.; Hall, W. T. "Analytical Chemistry"; 9th ed.; Wiley: New York, 1942; vol II; p 648.
(8) Shimidzu, T.; Yoshikawa, M. *Polym. J. (Tokyo)* **1983**, *15*, 135.
(9) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1.
(10) Lamb, J. D.; Christensen, J. J.; Izatt, S. R.; Bedke, K.; Astin, M. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3399.

Dichlorocarbene Adducts of 1,4-Polybutadienes. Improved Synthesis and Characterization by High-Field NMR

Shahabuddin Siddiqui and Rudolf E. Cais*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 21, 1985*

ABSTRACT: An efficient method for obtaining the dichlorocarbene adducts of 1,4-polybutadienes is described. The procedure involves mild, nonbasic, and homogeneous reaction conditions to generate dichlorocarbene from the organomercury precursor phenyl(bromodichloromethyl)mercury (Seyferth reagent) in the presence of polybutadienes. This methodology represents a significant improvement over treatment of chloroform with strong base in that strictly neutral conditions are employed; no block structure results and high degrees of conversion can be achieved readily. Complete double bond conversion provides the structural equivalent of 1:1 poly(dichlorocyclopropene-*co*-ethylene). We use high-field NMR to characterize the chemical microstructures of the adducts from both *cis*- and *trans*-1,4-polybutadienes at varying extents of cyclopropanation and verify that carbene addition is stereospecific. Proton NMR (500 MHz) is used to measure the degree of conversion and establish the geometry of the cyclopropyl ring. Carbon-13 NMR (125.7 MHz) is used to probe more detailed microstructural features involving monomer and stereosequence effects. Monomer sequence pentads are observed for olefinic carbons in partially converted materials, whereas the gem-dichloro carbons are less sensitive and reveal triad monomer sequences. These quaternary carbons also reveal triad stereochemical sequences in the trans adducts. The copolymers are almost perfectly random (Bernoullian) in both monomer and stereosequence distribution.

Introduction

Recently we described the synthesis and characterization of a series of novel cyclopropanated fluoropolymers obtained by the addition of difluorocarbene to *cis*- and *trans*-1,4-polybutadienes.[1] The carbon-13 NMR assignments of these copolymers, particularly for the cyclopropyl ring carbons, were complicated by the presence of significant ^{13}C–^{19}F scalar couplings, which obscured the fine

0024-9297/86/2219-0998$01.50/0

structure from sequence effects. Thus certain resonance patterns could not be interpreted with complete confidence, so we chose to observe the analogous dichlorocarbene adducts as models to assign these ambiguous features.

The synthesis of the dichlorocarbene adducts of 1,4-polybutadienes (*cis*-PBD:CCl_2 and *trans*-PBD:CCl_2) using the procedure of Komoroski et al.[2] did not prove to be straightforward and efficient in our hands. For example, we could not realize essentially complete double bond conversion (>97%) by this method. The adducts were noticeably colored as well, even at low levels of conversion, probably due to conjugation arising from the reported base-catalyzed isomerization.[3] Moreover, a block sequence structure and two-phase morphology result from the solid alkali metal hydroxide/chloroform system.[2] Thus an improved method for the synthesis of *cis*-PBD:CCl_2 and *trans*-PBD:CCl_2 seemed appropriate.

Pinazzi et al.[4,5] have investigated this system in some detail and found that the generation of dichlorocarbene by base-induced α-elimination was inferior to the thermolysis of phenyl(trihalomethyl)mercury compounds. We therefore adopt the latter procedure here for the synthesis of a series of dichlorocarbene adducts of 1,4-polybutadienes since it utilizes mild, neutral, and homogeneous conditions. Furthermore, this method allows the preparation of purely random adducts having virtually any desired monomer composition (up to >98% double bond conversion). Block monomer sequences are avoided in the resulting copolymers on account of the homogeneous and nonbasic nature of the reaction environment.

The cyclopropanated materials maintain the geometrical configuration of the precursor polymers as expected from the synchronous addition of a singlet carbene across a double bond, which is known to be stereospecific.[6] Proton NMR spectroscopy (500 MHz) confirms this fact and allows a simple determination of the degree of conversion. Furthermore, high-resolution carbon-13 NMR spectroscopy is employed to reveal details of chemical microstructure that were not considered by Pinazzi et al.[4,5] and that were not apparent in the more recent work of Komoroski et al.[2]

Experimental Section

Materials. 1,4-*trans*-Polybutadiene (*trans*-PBD) was synthesized by an emulsion technique utilizing a rhodium-based catalyst,[7] 1,4-*cis*-Polybutadiene (*cis*-PBD) was used as obtained from Aldrich. The isomeric purity of the cis and trans form was better than 98% in both cases, according to an analysis of the starting polymers by carbon-13 NMR. The 1,2 content was vanishingly small. Phenyl(bromodichloromethyl)mercury ($PhHgCBrCl_2$) was obtained in ca. 25% yield according to the procedure of Seyferth et al.[8,9] Repeated attempts to raise the yield to 75% as reported in the literature[9] were not successful. Benzene (99.9%, Aldrich) was refluxed over calcium hydride for 24 h and then distilled and stored over molecular sieves in a nitrogen atmosphere. *tert*-Butyl alcohol was dried by refluxing over activated calcium oxide for 24 h and collected by distillation prior to use for the preparation of $PhHgCBrCl_2$.

General Procedure for Carbene Addition. $PhHgCBrCl_2$ (10–20% molar excess with respect to double bonds in the polymer) was added to the polymer solution in benzene (1% (w/v) at room temperature. The mixture was vigorously stirred and heated under a nitrogen atmosphere. The $PhHgCBrCl_2$ dissolved at about 50 °C and the reaction mixture became completely homogeneous, after which the solution was heated to reflux for 8–12 h. The progress of the reaction could be followed by the disappearance of $PhHgCBrCl_2$ by TLC and also by the precipitation of PhHgBr from solution.

Upon completion of the reaction, the mixture was allowed to cool to room temperature and filtered to remove PhHgBr. More PhHgBr appeared upon concentration of the filtrate under vacuum, and it was separated by centrifugation. The polymer was precipitated into a large volume of methanol containing 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant, collected, washed several times with methanol, and dried under vacuum at ca. 25 °C for 24 h. The polymer was then purified by dissolution in a small volume of chloroform and reprecipitation in methanol. The conversion of double bonds was estimated by integration of the appropriate resonances in the proton NMR spectrum (vide infra).

Analytical Methods. Thermal measurements (DSC and TGA) were performed performed on a Du Pont 1090 thermal analyzer that was equipped with a DSC cell base and a Du Pont 951 thermal gravimetric analysis attachment.

NMR Measurements. The 500-MHz proton NMR spectra of polymer samples were acquired at room temperature on a JEOL GX-500 spectrometer. Typically, a 7–10% (w/v) polymer solution in $CDCl_3$ was used with tetramethylsilane (Me_4Si) as an internal reference standard. The 125.7-MHz carbon-13 NMR spectra were recorded on a JEOL GX-500 instrument, from $CDCl_3$ solutions containing at least 15% (w/v) polymer and Me_4Si as an internal reference. About 10 000 transients were accumulated by using a sweep width of 25 kHz in 64K memory. Pulse repetition times were 5–10 s between 90° pulses (30.0-μs duration), and broad-band proton decoupling was used.

Results and Discussion

Generation of Dichlorocarbene. Dihalocarbenes are generated very conveniently under strongly basic conditions from readily available materials.[6] Of concern, however, is the susceptibility of the carbenophile to the basic conditions employed in these reactions. In such cases, the use of phenyl(trihalomethyl)mercury compounds (Seyferth reagent) as dihalocarbene precursors is preferred, as evident from the work of Pinazzi and Levesque.[5] These reagents release the hypovalent species ($:CX_2$) in a neutral medium under mild thermal treatment.[10] Admittedly most of these reagents are not commercially available and require synthesis involving organomercurial intermediates. Nevertheless, when at hand these organomercury precursors provide very clean and quantitative gem-dihalo cyclopropanation of olefins.

Our attempts to repeat the more traditional literature procedure involving a two-phase basic medium[2] were not successful when forced to high degrees of conversion. We became cognizant of the base sensitivity of 1,4-PBD from the recent study by Dias and McCarthy,[3] which revealed the formation of conjugated double bonds (sequence length ca. 10) along the chain. The extent of blockiness apparently depends on the strength of base employed and not on temperature. Thus, we discarded the option of generating the carbene by base-induced α-elimination of halocarbons in the presence of 1,4-PBD.[4]

cis- and *trans*-1,4-PBD have been shown to trap difluorocarbene very efficiently and thereby afford a series of copolymers having varied compositions with a random monomer sequence distribution.[1] The success of this reaction rested on the choice of carbene precursor, i.e., the organomercurial $PhHgCF_3$, which evolved $:CF_2$ cleanly in a neutral environment. We explore the scope of this procedure here by preparing the dichloro analogues and examining the polymer sequence structure in detail.

Phenyl(bromodichloromethyl)mercury ($PhHgCBrCl_2$) was prepared as the dichlorocarbene precursor by the one-pot synthesis method of Seyferth[9]

$$PhHgCl + BrCHCl_2 \xrightarrow[THF,\ -25\ °C]{t\text{-BuOK}/t\text{-BuOH}} PhHgCBrCl_2$$

This reagent releases dichlorocarbene quantitatively when heated to ca. 80 °C in benzene, and adducts are formed in high yield if an olefinic trap like PBD is present. The

Table I
Glass Transition and Crystalline Melting Temperatures of Dichlorocarbene Adducts of 1,4-Polybutadienes

% conversion[a]	T_g, °C	T_m, °C
	cis-PBD:CCl_2	
0	−99.5	−9.3
40.0	−44.8	
75.0	+8.8	
97.0	+28.9	
	trans-PBD:CCl_2	
0	−85.0	119.0
24.4	−53.4	8.0
70.6	+5.5	
81.0	+7.4	
98.1	+15.2	

[a] Percent conversions determined from ^{13}C and ^1H NMR.

reaction conditions are mild, nonbasic, and homogeneous in contrast to the ubiquitous generation of dichlorocarbene from $CHCl_3$ and strong base in a two-phase system. As the reaction progresses, PhHgBr separates out of solution; however, the polymer product always remains soluble. This homogeneous reaction environment favors the generation of a random monomer sequence distribution and the achievement of high conversion. The reaction is efficient and is essentially complete in 8–12 h.

Using the present method, we were able to synthesize a series of PBD:CCl_2 adducts having different monomer compositions by varying the molar ratio of the precursor to double bonds in the chain. The geometry of the cyclopropyl ring maintains the double bond configuration of the precursor polymer; this result is expected from the ground-state singlet electronic structure of :CCl_2.[11] However, the stereochemical configurations of the materials are random (vide infra).

TGA analysis of *cis*-PBD:CCl_2 and *trans*-PBD:CCl_2 after essentially complete reaction, which gives structural equivalents to alternating 1:1 poly(dichlorocyclopropene-*co*-ethylene) copolymers, shows that these materials are thermally stable up to 350 °C. The excellent stability has been noted by Pinazzi and Levesque.[4] The glass transition temperatures (T_g) of the adducts obey a linear dependence on composition, as expected of random copolymers.[12] Table I shows that the T_g values increase with conversion but never excede room temperature, in contrast to the values reported by Komoroski et al., which approach 60 °C.[2] A possible cause of higher T_g values is cross-linking. We find no evidence for crystallinity in these materials, unlike the case for the analogous difluoro adducts.[1]

Proton NMR of *cis*- and *trans*-PBD:CCl_2 Adducts. Figure 1 shows the 500-MHz proton NMR spectra of the :CCl_2 adducts from each isomer of 1,4-PBD, which are very similar in appearance to those from the corresponding difluoro isomer[1] and do not reveal any sequence fine structure. The cyclopropyl methine proton and methylene protons next to the ring give overlapping signals for the cis adducts but have well-resolved resonances for the trans adducts (see Figure 1). This observation was used to verify that the geometry about the double bond was not scrambled during :CCl_2 addition. Olefinic and allylic proton resonances signify unreacted double bonds and are separated from the rest of the resonances in both isomeric adducts. Therefore proton NMR is a simple method to measure the degree of conversion, as was the case for the analogous difluoro adducts,[1] by comparing the integrated intensities from olefinic and aliphatic resonances.

Carbon-13 NMR Spectra of *cis*- and *trans*-PBD:CCl_2 Adducts. The 125.7-MHz carbon-13 NMR spectra of *cis*- and *trans*-PBD:CCl_2 adducts with partial conversion

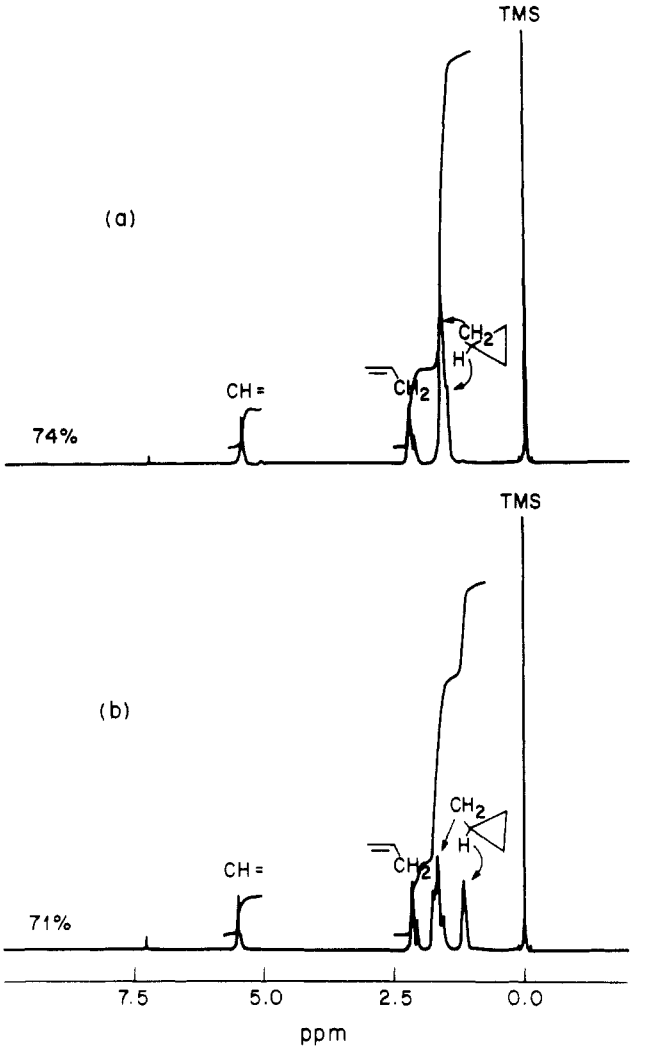


Figure 1. 500-MHz Proton NMR spectra of (a) *cis*-PBD:CCl_2, and (b) *trans*-PBD:CCl_2 adducts with the indicated percent conversions, observed in $CDCl_3$ at room temperature.

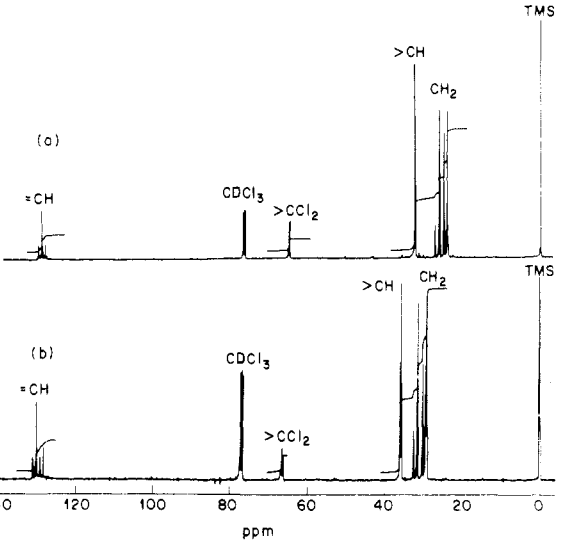


Figure 2. 125.7-MHz Carbon-13 NMR spectra of (a) *cis*-PBD:CCl_2, and (b) *trans*-PBD:CCl_2 adducts at partial conversions, observed in $CDCl_3$ at 50 °C.

are shown in Figure 2. Three spectral regions may be distinguished for each isomer, corresponding to aliphatic, *gem*-dichloromethylene, and olefinic carbons from high to low field, respectively. The protonated and >CCl_2 carbons

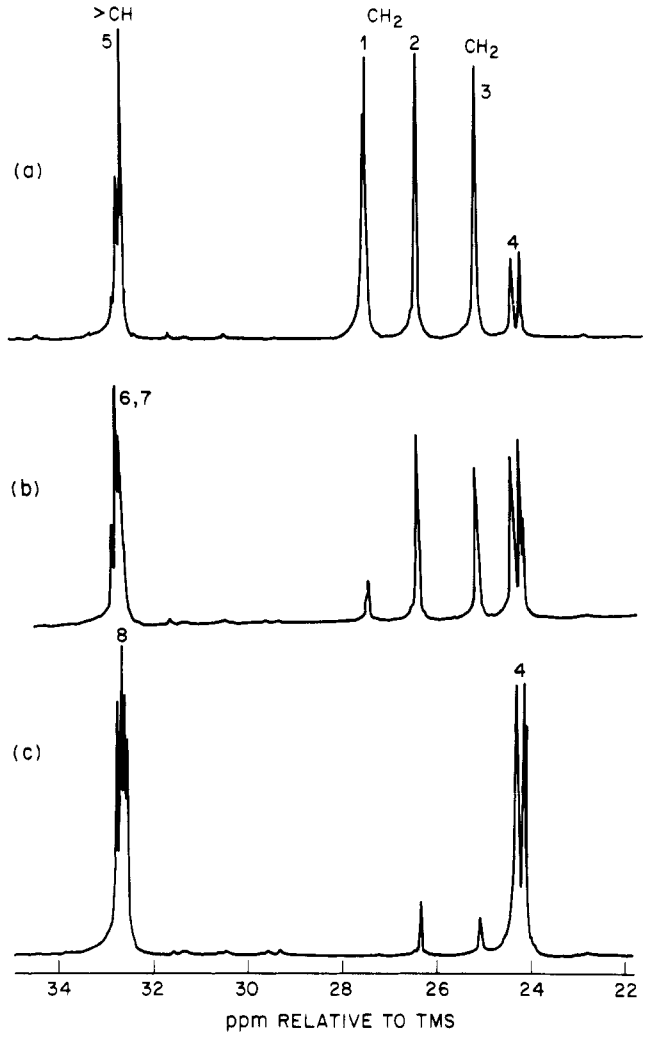


Figure 3. Aliphatic carbon resonances in the 125.7-MHz carbon-13 NMR spectra of *cis*-PBD:CCl_2 adducts at (a) 40.0%, (b) 75.0%, and (c) 97.0% double bond conversion, observed in $CDCl_3$ at 50 °C.

of each isomer have been assigned by Komorski et al.,[2] and these assignments were confirmed in the present work.

The carbon-13 resonances for cyclopropyl methine carbons and methylene carbons next to the ring always appear upfield in cis adducts from the corresponding carbons in the trans materials. This fact gives a clear distinction of cis from trans, and the spectra of the adducts clearly prove that :CCl_2 addition preserves the geometrical isomerism of the starting polymers. Additionally the integrated peak intensities of protonated carbons were used to measure the extent of double bond conversion, and these values were in excellent agreement with the numbers derived from proton NMR spectra (vide supra) and are summarized in Table I.

Detailed Carbon-13 Microstructure of *cis*-PBD:CCl_2 Adducts. The carbon-13 NMR spectra at 40.0%, 75.0%, and 97.0% conversions are shown in Figures 3–5 and illustrate the salient microstructural details of *cis*-PBD:CCl_2 adducts. The corresponding assignments and structural formulas are summarized in Tables II–IV, where the notations C and D are used to represent reacted ($CH_2\overline{CH—CH}CHCH_2$) and unreacted ($CH_2CH{=}CHCH_2$) polymer repeat units, respectively.

Figure 3 shows in detail the aliphatic carbon resonance region of cis adducts, which has fine structure from sequence effects. Methylene carbons that are allylic or next to the cyclopropyl ring exhibit monomer sequence diad

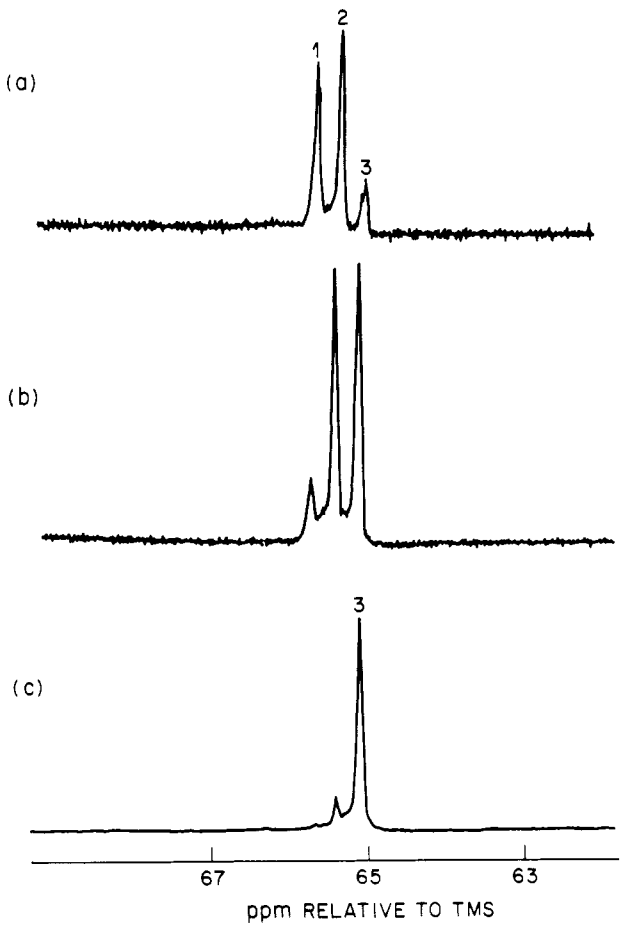


Figure 4. 125.7-MHz Carbon-13 NMR spectra of the dichloromethylene carbon (>CCl_2) in *cis*-PBD:CCl_2 adducts at (a) 40.0%, (b) 75.0%, and (c) 97.0% double bond conversion, observed in $CDCl_3$ at 50 °C.

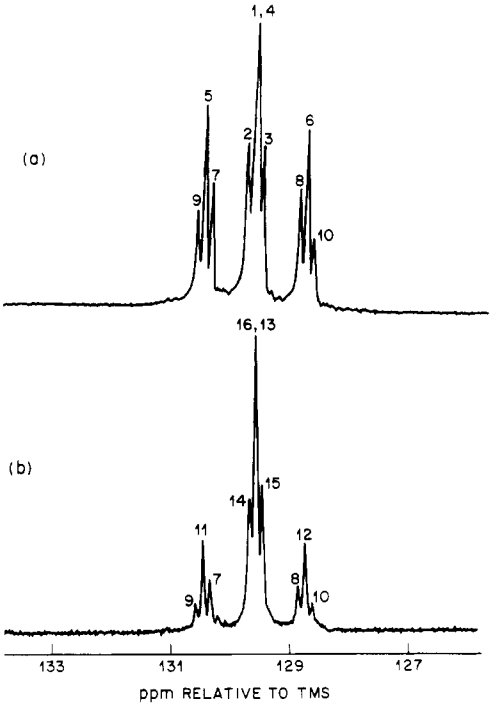
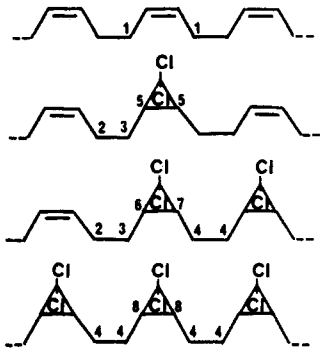


Figure 5. Olefinic carbon resonances in the 125.7-MHz carbon-13 NMR spectra of *cis*-PBD:CCl_2 adducts at (a) 40.0%, and (b) 75.0% double bond conversion, observed in $CDCl_3$ at 50 °C.

effects, whereas the cyclopropyl methine carbon clearly combines monomer sequence triad and tacticity splittings, as assigned in Table II.

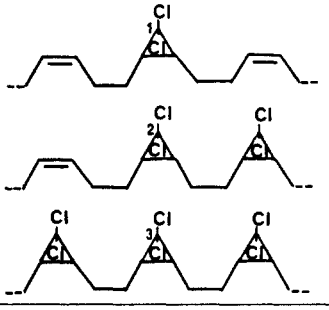
Table II
^{13}C Chemical Shifts of Aliphatic Carbons of *cis*-PBD:CCl_2 Adducts (See Figure 3)[a]



peak desig	sequence assignt	chem shift vs. Me_4Si, ppm
1	DD	27.47[b]
		27.43
2	DC, CD	26.35
3	DC, CD	25.11
4	CC	24.33[b]
	(*m* and *r*)	24.31
		24.16[b]
		24.10
5	DCD	32.58
6	DCC (*m* and *r*)	32.78
7	CCD (*m'* and *r'*)	32.68
		32.61
		32.58
8	CCC	32.77
	(*rr'*,*rm'*,*mm'*,*mr'*)	32.69
		32.63
		32.56

[a] Structural formulas for sequence determinations are shown. [b] Fine structures may arise from higher order monomer sequencing.

Table III
^{13}C Chemical Shifts of Dichloromethylene (>CCl_2) Carbon in *cis*-PBD:CCl_2 (See Figure 4)[a]



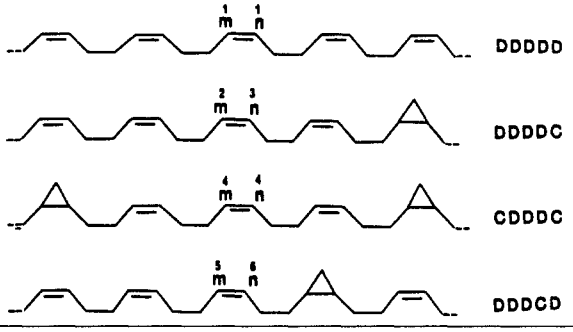
peak desig	sequence assignt	chem shift vs. Me_4Si, ppm
1	DCD	65.71
2	DCC	65.40
3	CCC	65.09

[a] Structural formulas for sequence determinations are shown.

For example, at 97% conversion virtually all monomer sequence triads are CCC, so that any significant resonance multiplicity must represent stereochemical isomerism. Thus we are able to deduce that triad tacticity influences both the cyclopropyl methine carbon and methylene carbons adjacent to the ring. Since the methine ring carbons are not centrosymmetric, the CCC triad stereochemical environment generates four nonequivalent environments accounting for the quartet fine structure. At lower conversions we note the superposition of these tacticity effects on monomer sequence fine structure (Table II).

The gem-dichloro carbon-13 spectral region for cis adducts is shown in Figure 4. These carbons are sensitive to monomer sequence triads but not tacticity. Thus the evolution of DCD, DCC and CCC triads is reflected by the relative change in peak intensities in spectra a and b at 40% and 75% conversions, respectively. Finally, at 97% conversion the sequence CCC yields a singlet carbon resonance, as expected when there is no stereochemical sensitivity. The chemical shifts corresponding to different monomer sequences are compiled in Table III for the quaternary carbon.

Table IV
^{13}C Chemical Shifts of Olefinic Carbons in *cis*-PBD:CCl_2 Copolymers (See Figure 5)[a]



peak assignt	carbon-type sequence	chem shift vs. Me_4Si, ppm
1	DDDDD-*m*,*n*	129.63
2	DDDDC-*m*	129.77
3	DDDDC-*n*	129.50
4	CDDDC-*m*,*n*	129.63
5	DDDCD-*m*	130.48
6	DDDCD-*n*	128.74
7	CDDCD-*m*	130.35
8	CDDCD-*n*	128.87
9	DDDCC-*m*	130.60
10	DDDCC-*n*	128.63
11	CDDCC-*m*	130.46
12	CDDCC-*n*	128.75
13	DCDCD-*m*,*n*	129.58
14	DCDCC-*m*	129.67
15	DCDCC-*n*	129.47
16	CCDCC-*m*,*n*	129.58

[a] Structural formulas for some representative sequences are shown.

The olefinic carbon-13 resonances are the most sensitive to structural environment and are split according to monomer sequence pentads. There are 16 possible lines that have been observed and assigned (see Figure 5 and Table IV). The resonance patterns show a deceptive similarity at low and high conversions, which results from nearly equal upfield and downfield shift contributions within directionally nonequivalent carbon sequences (e.g., DDDDC and CDDDD). A similar effect was noted for the analogous difluorocarbene adducts[1] and for partially epoxidized 1,4-polydienes.[13,14]

For example, we note here that two cyclopropyl groups in a CC diad next to the central double bond cause a drastic spread in chemical shift compared to the presence of an isolated C unit (e.g., compare DDDCC vs. DDDCD, Table IV), whereas when the two rings are disposed about the double bond (i.e., DCDCD), they produce minimal shift perturbation. The overly simplistic pattern is a consequence of the fortuitous overlap of certain peaks (e.g., 2 and 4, 5 and 11, 6 and 12, etc.).

These assignments are supported by computer simulation of the olefinic carbon resonance patterns, which fits Lorentzian lines to the given chemical shifts (Table IV) assuming a constant line width (3 Hz) and a random

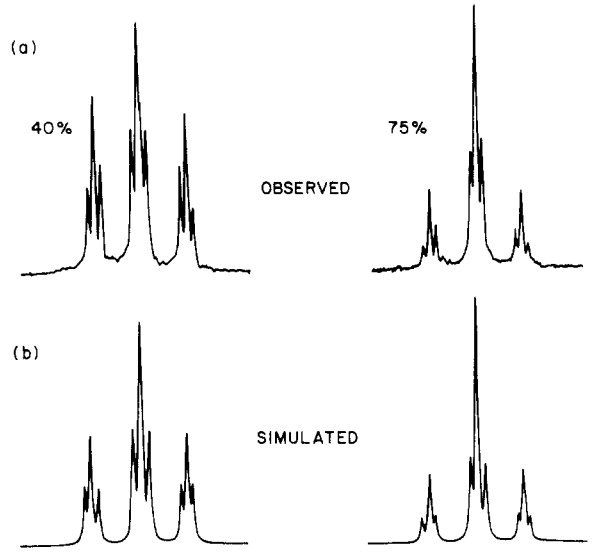
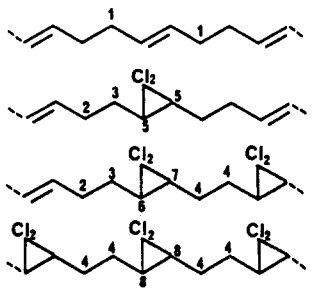


Figure 6. Computer simulations of the olefinic carbon-13 NMR resonances for *cis*-PBD:CCl_2 adducts at the partial conversions shown. The upper spectra are those observed in $CDCl_3$ at 50 °C. The bottom spectra are computer simulations for the corresponding conversions and were generated by using the appropriate chemical shifts (Table IV) and line widths (3 Hz). The sequence probabilities were generated according to Bernoullian statistics.

Table V
^{13}C Chemical Shifts of Aliphatic Carbons of *trans*-PBD:CCl_2 Adducts (See Figure 7)[a]



peak desig	sequence assignt	chem shift vs. Me_4Si, ppm
1	DD	32.71[b]
		32.60
2	DC, CD	31.53
3	DC, CD	30.34
4	CC	29.43[b]
	(*m* and *r*)	29.24
5	DCD	35.90
6	DCC (*m* and *r*)	36.04[b]
7	CCD (*m'* and *r'*)	35.94
		35.85
		35.70
8	CCC	35.91
	(*mr'*,*rr'*,*mm'*,*rm'*)	35.78
		35.77
		35.65

[a] Structural formulas for sequence determinations are shown. [b] Fine structures may arise from higher order sequence effects.

distribution of reacted units. The observed and simulated spectra agree closely at various levels of conversion, as shown in Figure 6.

Detailed Microstructure of *trans*-PBD:CCl_2 Adducts. The carbon-13 NMR spectra of *trans*-PBD:CCl_2 adducts at 24.4%, 70.6%, and 98.1% conversion reveal several significant microstructural details. These spectra are shown in Figures 7–9, and the corresponding sequence assignments are given in Tables V–VII. The carbons in the trans adducts exhibit similar sensitivity to their

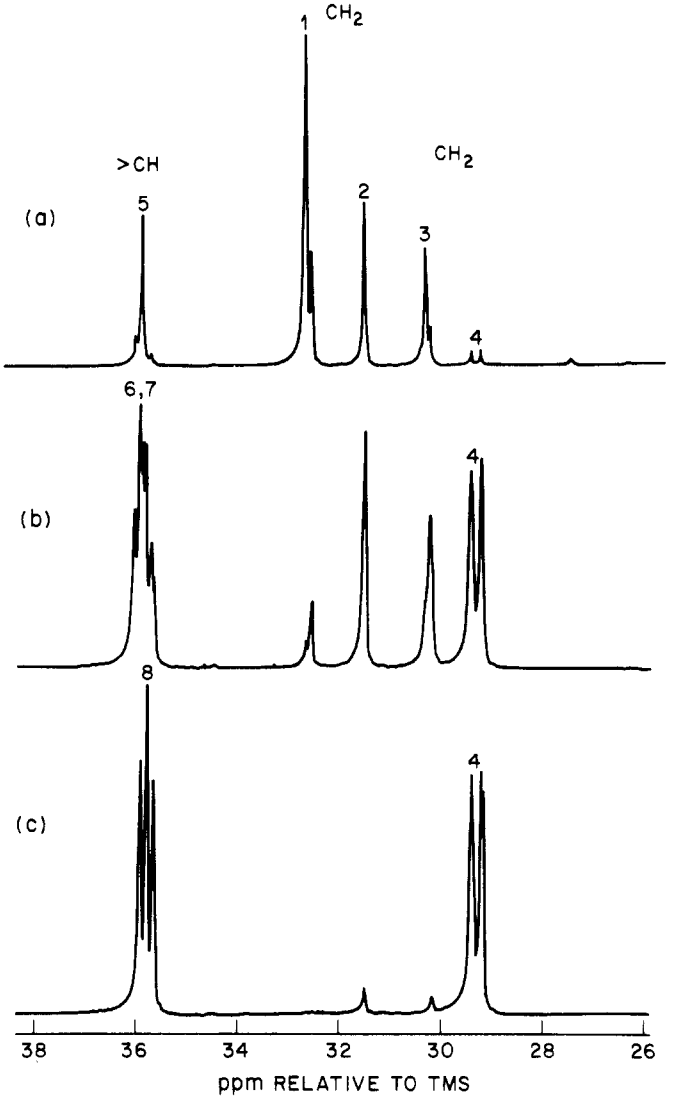
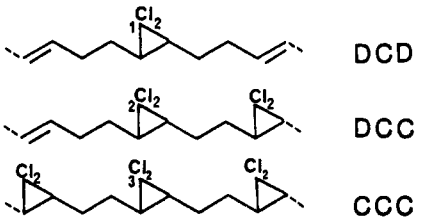


Figure 7. Aliphatic carbon resonances in the 125.7-MHz carbon-13 NMR spectra of *trans*-PBD:CCl_2 adducts at (a) 24.4%, (b) 70.6% and (c) 98.1% double bond conversion, observed in $CDCl_3$ at 50 °C.

Table VI
^{13}C Chemical Shifts of Dichloromethylene (>CCl_2) Carbons of *trans*-PBD:CCl_2 Adducts (See Figure 8)[a]



peak desig	sequence assignt	chem shift vs. Me_4Si, ppm
1	DCD	67.11[b]
		67.06
2	DCC	66.71[b]
	(*m* and *r*)	66.63
3	CCC	66.37
	(*mm*,*rm*, and *rr*)	66.25
		66.13

[a] Structures for sequence determinations are shown. [b] Fine structures may be assigned to the presence of higher order sequence isomers.

structural environment to their counterparts in the cis isomers discussed above. The quaternary >CCl_2 carbon

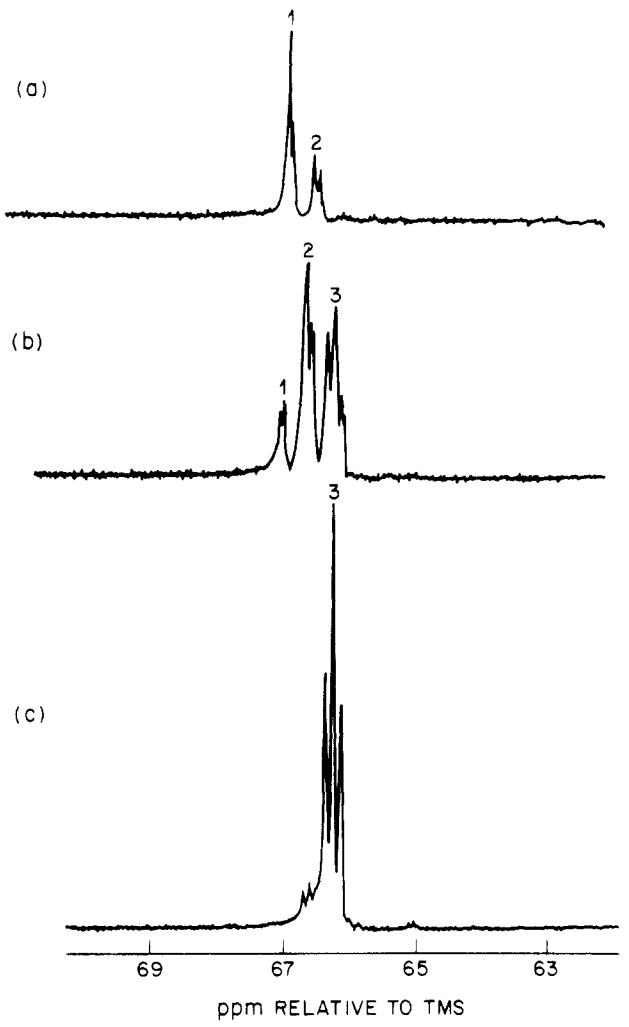


Figure 8. 125.7-MHz Carbon-13 NMR spectra of the dichloromethylene carbon (>CCl_2) in *trans*-PBD:CCl_2 adducts at (a) 24.4%, (b) 70.6%, and (c) 98.1% conversion, observed in $CDCl_3$ at 50 °C.

is the only exception, in that its resonance is sensitive to stereochemical effects that did not perturb the corresponding resonance in cis adducts.

The aliphatic carbon resonances at various levels of conversion are shown in Figure 7. The methylene carbons are sensitive to diad monomer sequences, whereas the cyclopropyl methine carbon exhibits monomer sequence triad splittings. Diad tacticity produces well-resolved *m* and *r* components for the methylene carbon next to the ring (in fact, triad components are just resolved). The cyclopropyl methine resonance has three components at 98.1% conversion, which derive from the four nonequivalent triad stereochemical environments in the CCC monomer sequence (*mm'*, *mr'*, *rm'*, and *rr'*), with fortuitous overlap of the central two lines. The chemical shifts corresponding to these various structural isomers are tabulated in Table V.

The dichloromethylene carbon-13 resonances from *trans*-PBD:CCl_2 adducts are shown in Figure 8, and the corresponding chemical shifts are summarized in Table VI. Both monomer and stereosequence triads have to be considered to explain the observed multiplicity of the >CCl_2 resonance in trans adducts. This is rather surprising since this carbon remained insensitive to tacticity effects at any level of conversion in both *cis*- and *trans*-PBD:CF_2 adducts, as well as *cis*-PBD:CCl_2 adducts. The stereochemical triad effect becomes obvious at 98% conversion, where the monomer sequence triads are almost exclusively

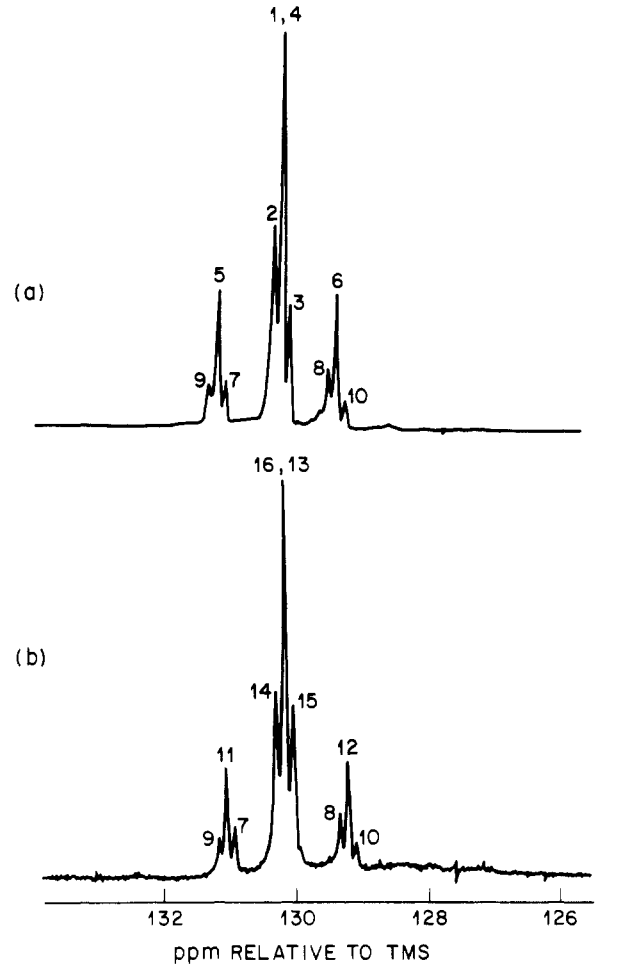


Figure 9. Olefinic carbon region of the 125.7-MHz carbon-13 NMR spectra of *trans*-PBD:CCl_2 adducts at (a) 24.4%, and (b) 70.6% double bond conversion, observed in $CDCl_3$ at 50 °C.

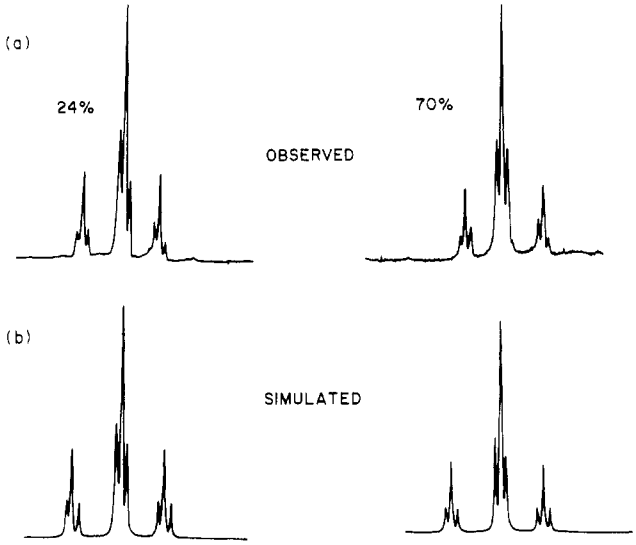
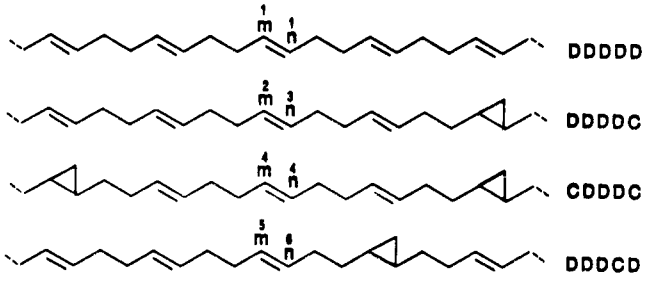


Figure 10. Computer simulation of the olefinic carbon-13 NMR resonances for *trans*-PBD:CCl_2 adducts at partial conversions. The upper spectra are those observed in $CDCl_3$ at 50 °C. The lower spectra are computer simulations for the corresponding conversions and were generated by using the appropriate chemical shifts (Table VII) and line widths (3 Hz). The sequence probabilities conform to Bernoullian statistics.

CCC and the iso, hetero, and syndio components can be observed. The components generate three lines for the centrosymmetric >CCl_2 carbon, in contrast to the four distinct triad environments for the methine and methylene

Table VII
^{13}C Chemical Shifts of Olefinic Carbons of *trans*-PBD:CCl_2 Adducts (See Figure 9)[a]



peak desig	carbon-type sequence	chem shift vs. Me_4Si, ppm
1	DDDDD-*m,n*	130.07
2	DDDDC-*m*	130.20
3	DDDDC-*n*	129.94
4	CDDDC-*m,n*	130.07
5	DDDCD-*m*	131.04
6	DDDCD-*n*	129.23
7	CDDCD-*m*	130.93
8	CDDCD-*n*	129.35
9	DDDCC-*m*	131.18
10	DDDCC-*n*	129.10
11	CDDCC-*m*	131.06
12	CDDCC-*n*	129.23
13	DCDCD-*m,n*	130.18
14	DCDCC-*m*	130.31
15	DCDCC-*n*	130.06
16	CCDCC-*m,n*	130.18

[a] Structural formulas of some representative sequences are shown.

carbons discussed above. At intermediate conversions (e.g. 70%), we observe a more complex spectral pattern for the $>CCl_2$ carbon owing to the superposition of monomer and stereosequence triads.

The olefinic carbon resonances are sensitive to monomer sequence pentads, as expected by analogy with the difluorocarbene case.[1] The spectra are shown in Figure 9 at two levels of conversion. The 16 distinct monomer sequence pentads were assigned as described previously, and the results are summarized in Table VII. These assignments allow a good match by computer simulation, as shown in Figure 10, where we find that Bernoullian statistics are appropriate for the trans isomers as well.

Conclusions

The significance of the generation of dichlorocarbene in the presence a base-sensitive carbenophile like 1,4-polybutadiene under neutral, homogeneous reaction conditions is emphasized here. The present synthetic methodology allows facile double bond conversion to at least >97%, thereby providing structural equivalents of 1:1 poly(dichlorocyclopropene-*co*-ethylene), with a strictly alternating monomer sequence distribution. The partially converted materials are free from blockiness along the chain, in contrast to the structures resulting from preparation under strongly basic heterogeneous conditions.[2]

High-field carbon-13 NMR analysis provides information on the chemical microstructure of PBD:CCl_2 adducts that was not considered by Pinazzi et al.[4,5] The present assignments are more detailed and extensive than those reported recently by Komoroski et al.[2] In particular, the carbon-13 NMR assignments for the *trans*-PBD:CCl_2 adducts are reported here for the first time. We find that :CCl_2 addition to polybutadienes is random in both monomer and stereosequence, due to the homogeneous nature of the reactions described here and the absence of any neighboring-unit effects on reactivity.

Our next paper in this series dealing with halocarbene adducts of 1,4-PBD will describe the products from :CFCl addition. This system is interesting because the carbene is unsymmetrical, so that addition can show stereoselectivity in the case of *cis*-PBD.

Acknowledgment. We are grateful to Dr. T. N. Bowmer for DSC measurements, to L. Johnson for TGA analyses, and to J. M. Kometani for valuable assistance during this study. We would also like to thank Dr. D. Seyferth for drawing our attention to the works by Pinazzi.

References and Notes

(1) Siddiqui, S.; Cais, R. E. *Macromolecules*, in press.
(2) Komoroski, R. A.; Horne, S. E., Jr.; Carman, C. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 89. See also: Huvard, G. S.; Nicholas, P. P.; Horne, S. E., Jr.; *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2005.
(3) Dias, A. J.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 162.
(4) Pinazzi, C.; Levesque, G. *J. Polym. Sci., Part C* **1969**, *16*, 4695.
(5) Pinazzi, C.; Levesque, G. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264*, 288.
(6) Kirmse, W. *Carbene Chemistry*; 2nd. ed.; Academic: New York, **1971**.
(7) Rinehart, R. E.; Smith, H. P. In *Macromolecular Syntheses*; Moore, J. A., Ed.; Wiley: New York, **1978**; Coll. Vol. 1, p 125.
(8) Seyferth, D.; Burltich, J. M. *J. Organometal. Chem.* **1965**, *4*, 127.
(9) Seyferth, D.; Lambert, R. L., Jr. *J. Organometal. Chem.* **1969**, *16*, 21.
(10) Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65.
(11) Gilchrist, T. L.; Rees, C. W. *Carbenes, Nitrenes and Arynes*; Appleton-Century-Crofts: New York, 1969; pp 3, 57.
(12) Havlicek, I.; Coseglia, N.; Migliaresi, C. *Polym. Bull. (Berlin)* **1985**, *14*, 455.
(13) Schilling, F. C.; Bovey, F. A.; Tseng, S.; Woodward, A. E. *Macromolecules*, **1983**, *16*, 808.
(14) Schilling, F. C.; Bovey, F. A.; Anandakumaran, K.; Woodward, A. E. *Macromolecules* **1985**, *18*, 2688.