Chemical Modification of 1,4-Polybutadienes by Fluorochlorocarbene

Rudolf E. Cais* and Shahabuddin Siddiqui

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received October 3, 1986*

ABSTRACT: Fluorochlorocarbene was prepared by thermolyzing phenyl(fluorodichloromethyl)mercury according to the procedure devised by Seyferth and trapped in situ by the alkene functionality of 1,4-*cis*- and -*trans*-polybutadienes to introduce varying levels of the fluorochlorocyclopropyl moiety. The glass-transition temperatures for fluorochlorocarbene adducts are intermediate between those for the analogous difluorocarbene and dichlorocarbene adducts, and no evidence for crystallinity is found. High-field ^1H, ^{13}C, and ^{19}F NMR spectroscopy was used to characterize the detailed chemical microstructure of these adducts. The addition is stereospecific and preserves the alkene geometry of the parent polybutadiene, although the cyclopropyl rings are disposed in a stereoirregular (*atactic*) fashion with respect to the chain backbone. The reactivity of a double bond is independent of its sequence environment, so that a random distribution of cyclopropanated sites is obtained. The methine ring carbons are always nonequivalent in the trans isomer owing to unequal geminal substitution of the apical carbon, so that adjacent cyclopropyl units exhibit several relative orientations analogous to regiosequence isomers. Syn and anti isomers are not equiprobable for cis rings, and NMR spectroscopy shows that the more hindered *syn*-Cl structure is preferred by a ratio of 1.65:1.

Introduction

The chemical modification of existing polymers can often lead to novel materials with interesting and desirable properties which are inaccessible otherwise by conventional polymerization techniques. The success of this approach to new polymers depends on the specificity of the derivatization reaction; competing side reactions cannot be tolerated if a uniform product is desired. This condition usually requires a parent polymer which undergoes facile chemical conversion so that forcing and harsh reaction conditions with increased probability of undesirable pathways can be avoided.

1,4-Polybutadienes are ideal substrates in many ways in that the reactivity of the double bonds can be exploited in many addition reactions to modify the backbone of the polymer. A variety of such possibilities has been explored by Pinazzi et al.[1] A particularly interesting reaction is the addition of a carbene species to afford an unusual saturated backbone incorporating cyclopropyl moieties. The traditional route to this class of materials has employed base-induced α-elimination to form the carbene in situ,[2] but there are difficulties with this procedure. For example, the parent polydiene can rearrange under the influence of strong base[3] and the heterogeneous reaction environment favors a block sequence structure.[4]

Pinazzi et al.[5] have utilized the Seyferth reaction[6] to generate dihalocarbenes under mild conditions so that they are trapped cleanly by polybutadienes without the above problems. We have followed the same procedure and employed multinuclear NMR spectroscopy to examine the detailed chemical microstructures resulting from the addition of symmetrical dihalocarbenes to 1,4-polybutadienes. Thus both difluorocarbene[7] and dichlorocarbene[8] adducts have been prepared with full retention of the original double bond configuration after exhaustive replacement of the alkene functionalities with cyclopropyl units. High-resolution NMR experiments showed that both monomer and stereosequence isomerism were generated at random during these reactions.

In light of this it seemed interesting to us to consider the implications of asymmetrical carbene substitution, e.g., fluorochloro, which allows syn and anti isomerism. Pinazzi et al. have studied an analogous case with bromochlorocarbene, but they did not consider the detailed chemical microstructures of their products.[5] Our present NMR study shows that cis adducts favor the more hindered *syn*-Cl isomer. Furthermore, addition to 1,4-*trans*-polybutadiene is not regiospecific, and thereby another form of isomerism is introduced. This report details the synthesis of these adducts and their characterization by high-field ^1H, ^{19}F, and ^{13}C NMR. In addition, we compare certain physical properties with those reported for the analogous difluoro and dichloro adducts at various degrees of conversion.

Experimental Section

Materials. 1,4-*trans*-Polybutadiene (*trans*-PBD) was obtained according to a published procedure.[9] 1,4-*cis*-Polybutadiene (*cis*-PBD) was a commercial sample from Aldrich Chemical Co. and was used as received. The isomeric purity of the cis and trans starting materials was checked by ^{13}C NMR and found to be at least 98%. The 1,2 content was vanishingly small.

Dichlorofluoromethane was obtained from SCM Specialty Chemicals and dried by diffusion through a column packed with $P_2O_5/CaCl_2$ (1:4). Methanol was refluxed over $Mg(OMe)_2$ (generated in situ) and distilled prior to use. Tetrahydrofuran (THF, HPLC grade) was passed through a column of basic alumina to remove water and peroxides. Phenyl(fluorodichloromethyl)-mercury ($PhHgCCl_2F$) was obtained in greater than 70% isolated yield by treatment of a THF slurry of phenylmercuric chloride and dichlorofluoromethane with freshly generated sodium methoxide at −40 °C according to Seyferth's published procedure.[10] Benzene (99.9%) was refluxed over calcium hydride for 24 h, distilled, and stored over molecular sieves (4A, 8–12 mesh) in an inert atmosphere. Sodium iodide (Gold Label, 99.999% purity) was purchased from Aldrich Chemical Co. and dried for 24 h at 140 °C in a vacuum oven.

General Procedure for Carbene Addition. A 1% (w/v) polymer solution was prepared by stirring the desired isomer in benzene at room temperature under a nitrogen atmosphere. A 20% molar excess of $PhHgCCl_2F$ (with respect to alkene units in the starting polymer) was then added to the polymer solution along with sodium iodide (2-fold excess with respect to $PhHgCCl_2F$). The mixture was rapidly stirred, heated, and maintained at reflux for 6–8 h. Afterward the mixture was cooled to room temperature and filtered to remove crystals of NaI, NaF, and PhHgI, which had settled out on standing. The filtrate was concentrated to one-fourth its volume in a rotary evaporator at room temperature to precipitate additional PhHgI crystals, which were then removed by centrifugation. The clear polymer solution was then added to an excess volume of methanol containing 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant to precipitate the polymer. The polymer was isolated, washed several times with methanol, and dried for 24 h at room temperature under vacuum. It was then redissolved in chloroform and subjected to final washing and drying after a second reprecipitation in methanol. The extent of reaction was readily determined by 500-MHz ^1H NMR spectroscopy (vide infra).

0024-9297/87/2220-1004$01.50/0

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

NMR Spectroscopy. ^{1}H NMR spectra were recorded at 500 MHz and 25 °C with a JEOL GX-500 spectrometer, using 5% (w/v) copolymer solutions in $CDCl_3$. Tetramethylsilane (Me_4Si) was used as the internal reference standard for all reported chemical shifts. The respective proton resonances were integrated to provide the areas which were compared to determine composition.

Proton-decoupled ^{13}C NMR spectra (50.31 MHz) were acquired at 50 °C on a Varian XL-200 spectrometer, with 15% (w/v) polymer solutions in $CDCl_3$ containing Me_4Si as the internal reference. Integrated intensities of protonated carbons (full NOE) were measured for obtaining sequence probabilities. The ^{13}C DEPT experiment[11] was performed on partially converted samples to identify carbon types (methylene, methine, and quaternary). This experiment was somewhat ambiguous owing to widely different $^1J(^{13}C-^1H)$ values (e.g., methylene vs. cyclopropyl methine carbons), so a 2D ^{13}C hetero J-resolved experiment[12] was done as well.

^{19}F NMR spectra (470.7 MHz) were accumulated on the JEOL GX-500 spectrometer at room temperature with 5–7% (w/v) polymer solutions in $CDCl_3$ containing hexafluorobenzene (HFB) as a secondary chemical shift reference ($\Phi^* = -163$ ppm). About 200 transients were collected with a sweep width of 40 kHz with 64K memory. A delay of 7.5 s between 90° pulses was chosen, and broad-band proton irradiation was used to remove all ^{1}H–^{19}F scalar coupling.

Results and Discussion

Generation of Fluorochlorocarbene. There are two general schemes to produce fluorochlorocarbene. The classic route invokes the base-induced α-elimination of certain mixed halo substrates, e.g., fluorodichloromethane,[13] methyl fluorodichloroacetate,[14] *sym*-tetrachlorodifluoroacetone,[15] etc. The second scheme, due to Seyferth,[10] affords :CFCl in a neutral environment by thermolysis of organometallic precursors. $PhHgCFCl_2$ is one such precursor that generates :CFCl very efficiently in situ at slightly elevated temperatures. We adopt the latter approach here based on the work of Pinazzi et al.[5] and our previous experience with dihalocarbene addition to 1,4-polybutadienes.[7,8]

$PhHgCFCl_2$ was synthesized according to the following published procedure.[10,16]

$$PhHgCl + FCHCl_2 \rightarrow PhHgCFCl_2$$

The organomercurial product was obtained in ~75% yield. Although the generation of :CFCl from this precursor is quite rapid at ~80 °C, thermolysis is at least 5 times faster if sodium iodide is present. Under our conditions the reaction was complete after 4–6 h of vigorous stirring when sodium iodide was included. We found that 1,4-PBD was about 80% efficient in scavenging the carbene, so a slight molar excess of $PhHgCFCl_2$ was required over the stoichiometric amount for a given degree of conversion. In this way a series of polymers having different cyclopropyl:alkene ratios was prepared by utilizing various concentrations of $PhHgCFCl_2$ in the starting mixture. Essentially complete (>99%) conversion could be achieved, thereby affording the structural equivalent of a 1:1 alternating copolymer of ethene with 3-fluoro-3-chlorocyclopropene. These carbene adducts (PBD:CFCl) were amorphous (vide infra), and readily soluble in $CHCl_3$, benzene, toluene, THF, etc.

The ground-state electronic structure of :CFCl is a singlet, like other dihalocarbenes,[17] so that addition to alkenes is expected to be stereospecific. As we shall see this is the case, in that *cis*-PBD gives exclusively cis cyclopropyl rings,

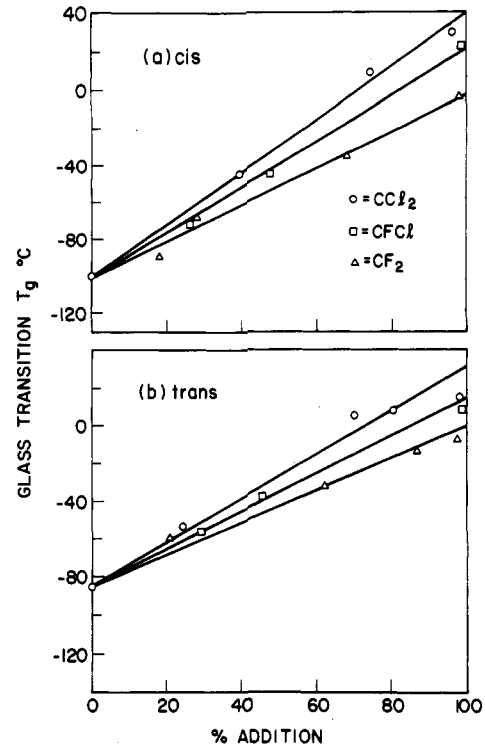


Figure 1. Glass-transition temperatures for *cis*-PBD:CXY (a) and *trans*-PBD:CXY (b) adducts at various extents of reaction, for X = Y = Cl (○), X = Cl, Y = F (□), and X = Y = F (△).

and likewise the trans polymer gives only trans rings. However, adjacent rings form stereoirregular (atactic) diad sequences. Since :CFCl is unsymmetrical we need to consider yet another form of isomerism involving syn and anti structures, so that the adducts have quite complex structural environments overall. These are revealed in detail by the NMR studies described below.

Thermal Properties. The PBD:CFCl adducts (i.e., both cis and trans) are thermally stable up to ~250 °C when all alkene functionality has been converted to cyclopropyl groups. Weight loss sets in at higher temperatures according to TGA analysis, presumably due to hydrogen halide elimination. These materials are not as stable as their difluoroanalogues.[7] The glass-transition temperatures (T_g) increase in a quite linear manner with increasing cyclopropyl content, as was observed for other dihalocarbene adducts of PBD.[7,8] These T_g values are compared in Figure 1, and it is not surprising to find that the values for :CFCl adducts fall between those for $:CF_2$ and $:CCl_2$ adducts at equivalent levels of conversion. Replacement of fluorine by the larger chlorine substituent raises T_g.

The homopolymer *trans*-PBD is highly crystalline and its T_g is very indistinct by thermal analysis. Literature values range from −107[18] to −18 °C,[19] and we observed a weak transition in the DSC trace centered around −85 °C.[7] A linear extrapolation of the copolymer T_g values, which were much more distinct, agrees with this value as shown in Figure 1. Recent work by Wunderlich et al.[20] reveals a similar T_g for 100% *trans*-1,4-PBD.

We find no evidence by DSC of a crystalline melting point for PBD:CFCl adducts, unlike the case for the analogous difluoro compounds.[7] The unsymmetrical dihalo substitution introduces an additional degree of structural irregularity that effectively inhibits the development of any crystallinity.

500-MHz ^{1}H NMR Studies. The 500-MHz ^{1}H NMR spectra of *cis*- and *trans*-PBD:CFCl at intermediate conversions are shown in Figure 2. Olefinic protons are the

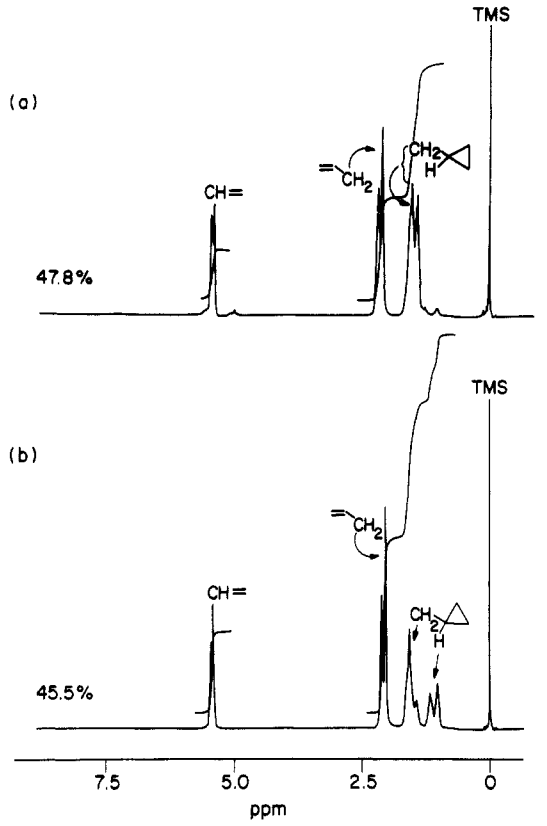


Figure 2. 500-MHz ^1H NMR of *cis*-PBD:CFCl (a) and *trans*-PBD:CFCl (b) having 47.8% and 45.5% conversion, respectively. The reference is tetramethylsilane (Me_4Si).

most deshielded at 5.4 ppm and vanish after complete conversion, along with the more shielded resonances at 2.1 ppm, which correspond to the allylic methylene protons. The degree of conversion (expressed as percent reacted double bonds) can be calculated simply by comparing the integrated intensities of olefinic and aliphatic proton resonances.

The next set of resonances going to higher field arises from the aliphatic methylene protons on the carbon next to the cyclopropyl group. This peak occurs at 1.52–1.66 ppm and fortuitously overlaps the signal from cyclopropyl methine protons in *cis*-PBD:CFCl at 1.42 ppm (Figure 2a). However the cyclopropyl methine proton resonance is well resolved for *trans*-PBD:CFCl at 1.07 and 1.18 ppm (Figure 2b). These two peaks have equal integrated intensities as expected, since they reflect the syn and anti methine protons which must be equiprobable for trans adducts. The proton syn to Cl is more shielded than the proton anti to Cl. The latter proton experiences a larger three-bond coupling with fluorine than the former, and this shows as doublet fine structure with a coupling of ~20 Hz.[21]

These cyclopropyl methine resonances are the most useful in distinguishing cis and trans isomerism by ^1H NMR, and the spectra show that :CFCl addition is completely stereospecific, thereby preserving the double bond configuration in the cyclopropyl ring. This result is in accord with the known behavior of singlet carbenes.[17] ^1H NMR is not sensitive enough to address the question of stereoselectivity involving syn and anti addition to *cis*-PBD, where the relevant methine resonances are obscured as noted above. These proton spectra are most useful for monitoring the degree of conversion and cis–trans isomerism, whereas more detailed microstructural features are best gleaned from ^{13}C and ^{19}F NMR spectra.

General Features of 50.3-MHz ^{13}C NMR Spectra. Figure 3 compares the 50.3-MHz ^{13}C NMR spectra of *cis*- and *trans*-PBD:CFCl at intermediate conversion, where the full manifold of structural variation is displayed. Three distinct chemical shift regions may be distinguished from low to high field, corresponding to olefinic, gem-dihalo, and aliphatic carbons, respectively. Complete conversion to the cyclopropanated polymer is verified by noting the absence of olefinic resonances. Analogous ^{13}C spectral regions were recognized in the spectra from PBD:CF_2 and PBD:CCl_2 adducts.[7,8]

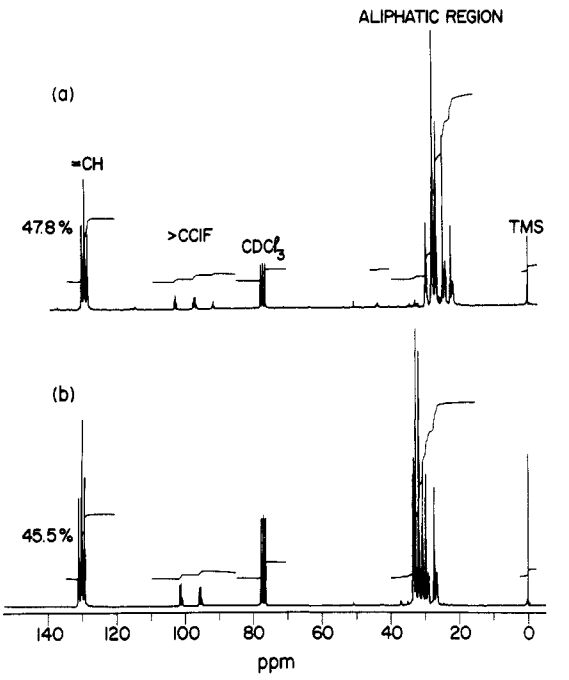


Figure 3. Entire spectral region for the 50.31-MHz ^{13}C NMR spectra of *cis*-PBD:CFCl (a) and *trans*-PBD:CFCl (b) having 47.8% and 45.5% conversion, respectively.

The carbon-type assignments are trivial for the olefinic and gem-dihalo carbons, owing to their large downfield shifts and the unique one-bond fluorine coupling pattern ($^1J(^{13}C-^{19}F) \sim 288$ Hz) for the latter. In the present case the aliphatic resonance region is far more complicated than that observed for the symmetrical dihalo adducts,[7,8] owing to the additional syn and anti isomerism. It is not so easy to edit this region into methine and methylene carbons owing to the multiplicity and proximity of resonances, which make proton-coupled spectra illegible. The DEPT experiment[11] was performed, but the results were questionable owing to the large difference in $^1J(^{13}C-^1H)$ values for acyclic and cyclopropyl carbons (130 vs. 168 Hz, respectively). A two-dimensional $^{13}C-^1H$ J-resolved experiment provided the definitive assignments, and this will be described in a separate publication.[12]

The degree of conversion may be established from these spectra by comparing the integrated intensities of olefinic and cyclopropyl methine carbon resonances. The values so obtained for the series of PBD:CFCl adducts were in good agreement with those derived independently from ^1H NMR spectra (vide supra). The geometry of the cyclopropyl rings is immediately apparent from the >CFCl resonance pattern, which is a doublet for trans rings and a pair of doublets for cis rings. The ^{13}C NMR spectra confirm that there is no scrambling of the double bond geometry upon carbene addition. Additional evidence for this conclusion, along with a detailed consideration of resonance fine structure, is presented below.

Detailed ^{13}C Microstructure of *cis*-PBD:CFCl Adducts. The 50.3-MHz ^{13}C NMR spectra of the *cis*-PBD:CFCl adducts at 26.1%, 47.8%, and 99.0% conver-

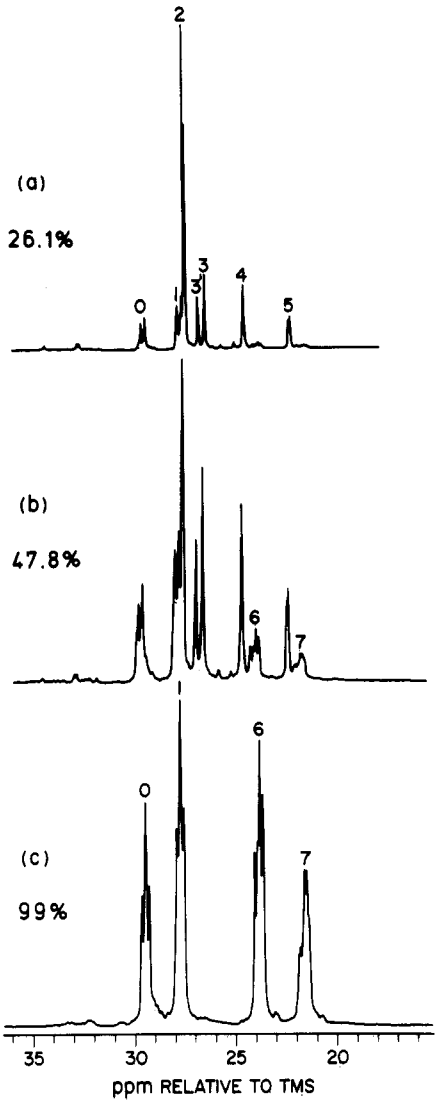


Figure 4. Aliphatic resonance region of 50.31-MHz ^{13}C NMR spectra from *cis*-PBD:CFCl having 26.1% (a), 47.8% (b), and 99% (c) conversion. The carbon numbers are defined in Figure 7 and their chemical shifts are listed in Table I.

Table I
^{13}C Chemical Shifts of Aliphatic Carbons in *cis*-PBD:CFCl Adducts (See Figures 4 and 7)

peak desig	sequence assignt	chem shift, ppm vs. Me_4Si
0	anti CC[a]	29.66, 29.49, 29.30
1	syn CC[a]	27.93, 27.76, 27.58
2	DD	27.48
3′	anti (DC,CD)	26.79
3	syn (DC,CD)	26.47
4	syn (DC,CD)	24.52
5	anti (DC,CD)	22.22
6	syn CC	24.07, 23.91, 23.82, 23.66
7	anti CC	21.89, 21.80, 21.56, 21.49

[a] Heteronuclear ^{13}C–^{19}F coupling is obvious at low conversion. At higher conversions, fine structure from the different diastereoisomers is superimposed to give apparent triplet patterns.

sions are expanded in Figure 4–6, which show the aliphatic, dihalomethylene, and olefinic carbon resonances, respectively. The prolific fine structure observed in each region attests to the structural complexity of these materials. Nevertheless, on the basis of our prior studies,[7,8] the observation of model compounds,[7] and the utilization of 2D NMR,[12] it has been possible to interpret this fine structure in detail. The assignments are summarized in Tables I–III, which include the appropriate ^{13}C chemical shifts.

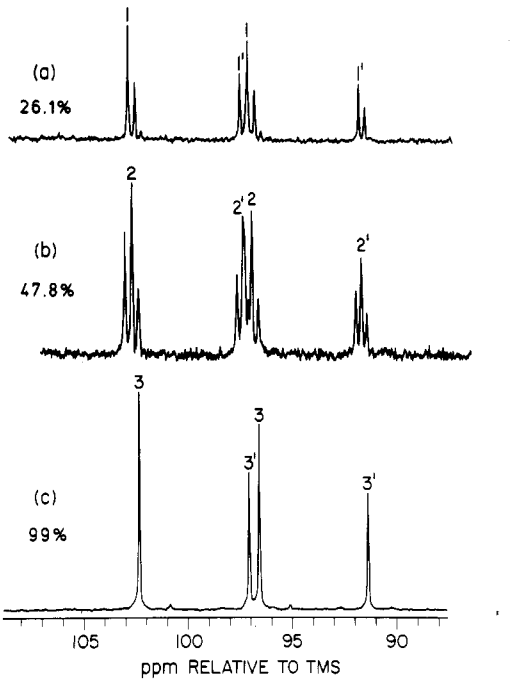


Figure 5. Detailed >CFCl ^{13}C NMR spectra from *cis*-PBD:CFCl having 26.1% (a), 47.8% (b), and 99% (c) conversion. The assignments are given in Table II.

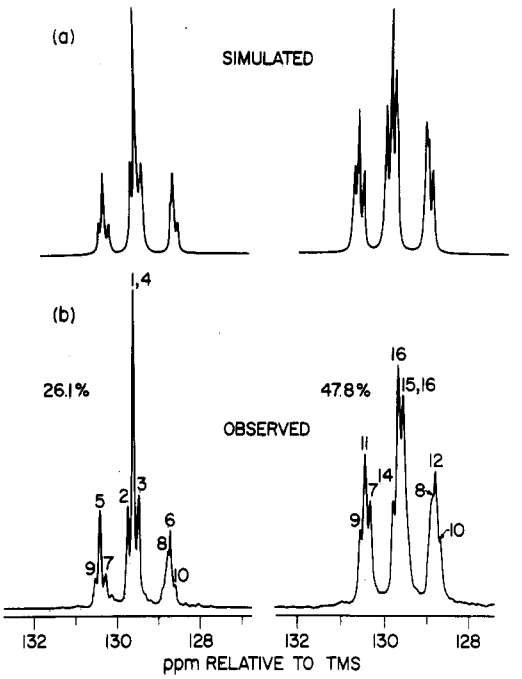


Figure 6. Detailed olefinic ^{13}C NMR spectra from *cis*-PBD:CFCl having 26.1% and 47.8% conversion (b), with corresponding simulated spectra (a). The numbered sequences are assigned in Table III.

Table II
^{13}C Chemical Shifts for the Dihalo (>CClF) Carbon of *cis*-PBD:CFCl (See Figure 5)

peak desig	sequence assignt	chem shift, ppm vs. Me_4Si
1	syn DCD (d, J = 290 Hz)	102.93, 97.16
1′	anti DCD (d, J = 287 Hz)	97.52, 91.82
2	syn DCC (d, J = 290 Hz)	102.62, 96.86
2′	anti DCC (d, J = 287 Hz)	97.27, 91.57
3	syn CCC (d, J = 290 Hz)	102.33, 96.56
3′	anti CCC (d, J = 287 Hz)	97.05, 91.35

Representative structures in Figure 7 illustrate the conventions used for the assignments; the notations C and

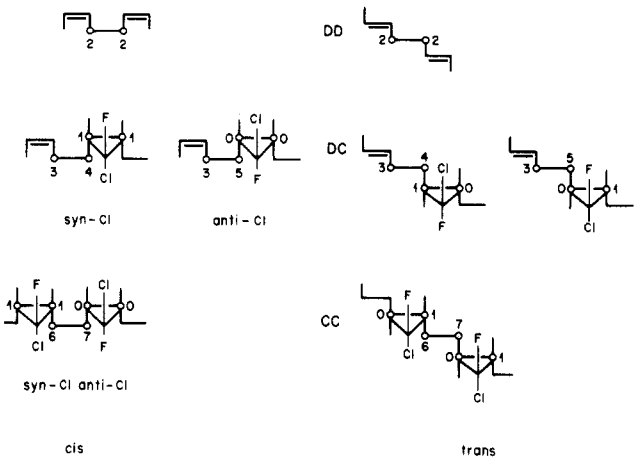
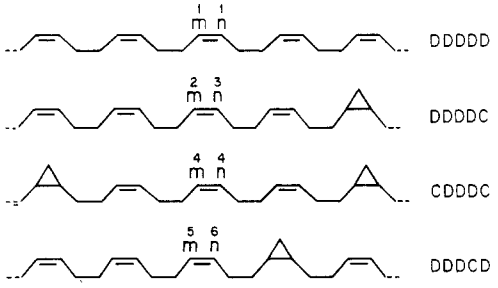


Figure 7. Numbering scheme to identify aliphatic carbons in monomer sequence diads for *cis*-PBD:CFCl and *trans*-PBD:CFCl adducts.

Table III
^{13}C Chemical Shifts for the Olefinic Carbons of *cis*-PBD:CFCl Adducts (See Figure 6)[a]



	peak desig	sequence assignt, ppm vs. Me_4Si
1	DDDDD-m,n	129.63
2	DDDDC-m	129.75
3	DDDDC-n	129.48
4	CDDDC-m,n	129.63
5	DDDCD-m	130.42
6	DDDCD-n	128.72
7	CDDCD-m	130.29
8	CDDCD-n	129.02
9	DDDCC-m	130.53
10	DDDCC-n	128.61
11	CDDCC-m	130.44
12	CDDCC-n	128.77
13	DCDCD-m,n	129.53
14	DCDCC-m	129.77
15	DCDCC-n	129.53
16	CCDCC-m,n	129.64

[a] Some representative sequences are shown above.

D represent reacted ($CH_2\overline{CHCHCH_2}$) and unreacted ($CH_2CH{=}CHCH_2$) polymer units, respectively, and their combination denotes particular monomer sequences. Eight types of aliphatic carbons are differentiated (numbers 0–7), depending on their structural environment, as shown in Figure 7. syn and anti are used designate the position of the larger halogen (Cl) with respect to the alkyl (main-chain) cyclopropyl substituents.

There are two diastereoisomers for the CC monomer sequence in both the cis and trans cases (neglecting the unsymmetrical dihalocarbon), since the cyclopropyl methine carbons are asymmetric centers which can be *R* or *S*. A cis ring must have an *RS* (or the mirror image *SR*) pair, whereas a trans ring must have an *RR* (or *SS*) pair. The two diastereoisomers are *RS–RS* and *RS–SR* for the CC diad in cis adducts, and *RR–RR* and *RR–SS* for the corresponding trans case. The sequences *SR–SR* and *SR–RS* (for cis), and *SS–SS* and *SS–RR* (for trans) are indistinguishable from their corresponding enantiomers above by NMR. We have no means to make absolute tacticity assignments, but as the polymers are perfectly atactic this is of little consequence.

The aliphatic ^{13}C resonances from *cis*-PBD:CFCl (Figure 4) are far more complicated than their counterparts from the symmetrical dihalo adducts,[7,8] owing to the generation of syn and anti isomers by the nonstereoselective addition of :CFCl across the double bond.[22] The isomerism effectively doubles the number of peaks expected from cyclopropyl methine and adjacent methylene carbons on the basis of monomer and stereosequence effects alone.

There is a large chemical shift difference between syn and anti resonances; this is most apparent at complete conversion (Figure 4c) when there is only one type of monomer sequence diad (CC) (i.e., compare the shifts of carbons 6 vs. 7 and 1 vs. 0). The methylene carbon next to the ring is less shielded when the syn halogen is Cl. We have established the syn and anti assignments unambiguously with a two-dimensional heterocorrelated experiment, which will be described in a separate publication.[12] The ratios of peaks 1:0 and 6:7 are 1.67 and 1.64, respectively. These values are consistent with a probability of *syn*-Cl addition in the range 0.62–0.63. This probability is independent of the monomer sequence environment and degree of conversion, as we shall see below. Moss et al.[22] have also found that the more hindered *syn*-Cl isomer is preferred during :CFCl addition to various substituted alkenes, although their *syn*-Cl probability of 0.75 for addition to *cis*-butene is higher than we find for our system.

At intermediate conversion three monomer sequence diads are likely, namely CC, CD, and DD, so the spectra exhibit maximum complexity (Figure 4b). The minor fine structure observed reflects the effect of fluorine coupling and stereosequence (tacticity). At low conversion cyclopropyl rings are isolated, so the 10.3-Hz doublet splitting on methine carbons 0 and 1 (Figure 4a) must reflect $^2J(^{19}F-^{13}C)$ scalar coupling, as no sequence isomerism is likely. At intermediate conversion more fine structure appears which reflects diad tacticity and gives an apparent triplet structure to each of these resonances, which is most prominent at complete conversion (Figure 4c).

Allylic methylene carbons (types 2 and 3) and those next to the ring (types 4–7) exhibit diad monomer sequence sensitivity. Carbon types 3–5 and 6 and 7 are also susceptible to syn and anti isomerism. The appropriate peak ratios (see assignments in Table I) give a probability of *syn*-Cl addition of 0.63 at both 26% and 48% conversion. Methylene resonances from CC diads (carbons 6 and 7) show significant fine structure which is attributed to diad stereosequences, as well as a $^3J(^{13}C-^{19}F)$ coupling of about 3 Hz. These aliphatic carbon assignments are summarized in Table I.

Figure 5 shows the resonance pattern from the quaternary dihalo carbon, which is strongly deshielded with respect to the aliphatic resonances by the electronegative F and Cl substituents. This carbon suffers a large $^1J(^{13}C-^{19}F)$ coupling of 285 Hz and therefore gives a doublet resonance for each unique structural environment. There is a significant difference in chemical shift between the syn and anti isomers of 6 ppm; the *syn*-Cl structure has the more deshielded apical carbon. The *syn*-Cl probability measured from these peaks is 0.64, in good agreement with the values obtained from the aliphatic carbon resonances.

The only sequence effects that influence the >CFCl resonance involve monomer spequence triads (DCD, DCC, and CCC). For example, after complete conversion all

Table IV
^{13}C Chemical Shifts for the Aliphatic Carbons of *trans*-PBD:CFCl Adducts (See Figures 7 and 8)

peak desig	sequence assignt	chem shift, ppm vs. Me_4Si
0	CC[a]	30.65, 30.47
1	CC[a]	33.36, 33.28, 33.14, 33.07, 32.93
2	DD	32.75
3	DC, CD	31.95, 31.59
4	DC, CD	29.76, 29.67
5	DC, CD	27.30, 27.21
6	CC	29.12, 28.95, 28.81, 28.65
7	CC[a]	26.67, 26.43

[a] The fine splittings arise from higher order sequence isomerism (both monomer and stereosequence) and $^{13}C-^{19}F$ scalar coupling, which combine to cause appreciable overlap.

monomer triads are CCC, so the sharp fluorine-coupled syn/anti doublets seen in Figure 5c indicate that there is no sensitivity to the three distinct diastereoisomers for the CCC sequence or the regiosequence isomers that are present (vide infra). The combination of three sequence environments, syn and anti isomers, and heteronuclear coupling produces 12 lines; two overlap in the central region so in practice 11 are resolved (Figure 5b). The assignments are summarized in Table II.

The olefinic carbon resonances for *cis*-PBD:CFCl are shown in Figure 6 at two levels of conversion. The symmetry and strong similarity in resonance patterns at high and low conversions are deceptively simple and mask the fact that the olefinic carbons have the longest range sensitivity to structural isomerism and exhibit 16 lines from monomer sequence pentads. These lines have been assigned according to our prior observations of the symmetrical PBD:CX_2 adducts,[7,8] and the chemical shifts are given in Table III.

Figure 6 also shows the results from computer simulation of the olefinic resonance patterns, using the chemical shift assignments in Table III and assuming a Bernoullian distribution of reacted units (C). The measured line width was 3 Hz, and the only parameter adjusted to fit the observed spectra at both conversions was the fraction of reacted double bonds. The simulations match the observed spectra well, although there are minor intensity deviations that may result from a sensitivity to syn and anti structure in C units flanking the observed D unit.

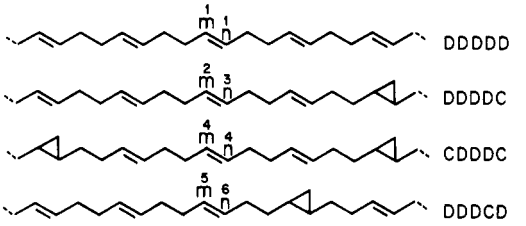
Detailed ^{13}C Microstructure of *trans*-PBD:CFCl Adducts. The aliphatic carbon resonances for *trans*-PBD:CFCl adducts at 29.1%, 45.5%, and 99.0% conversion are expanded in Figure 8, with a summary of the corresponding sequence assignments in Table IV. Carbon types (see Figure 7) were assigned by a 2D heteronuclear *J*-resolved experiment.[12] The eight principal peaks in this region result from a combined sensitivity to syn and anti isomerism and monomer sequence diads, like their counterparts in the cis adducts. However, syn and anti carbons must be equiprobable for the present trans case, and this is verified by the ratios of peaks 0:1, 4:5, and 6:7, which are all unity. The allylic methylene (carbon 3) is also a 1:1 doublet for the same reason. The methylene carbon next to the ring is more shielded when the syn halogen is fluorine (i.e., compare the shifts of carbons 7 vs. 6 and 5 vs. 4), as was the case for *cis*-PBD:CFCl.

Interestingly, the methine carbons are no longer equivalent in a cyclopropyl ring which is trans and can be distinguished as type 0 or 1 depending on whether the attached proton is syn or anti to chlorine, respectively (Figure 7). On the basis of the shifts we observed for the analogous carbons in the difluoro (~28 ppm)[7] and dichloro (~36 ppm)[8] adducts, we assign the upfield cyclopropyl methine resonance to carbon 0 and the downfield resonance to carbon 1. These assignments were confirmed by a 2D heterocorrelated experiment.[12]

Table V
^{13}C Chemical Shifts for the Dihalo (>CClF) Carbon of *trans*-PBD:CFCl Adducts (See Figure 9)

peak desig	sequence assignt	chem shift, ppm vs. Me_4Si
1	DCD (d, J = 289 Hz)	101.63, 95.88
2	DCC (d, J = 289 Hz)	101.13, 95.38
3	CCC (d, J = 289 Hz)	100.79, 95.04

Table VI
^{13}C Chemical Shifts for the Olefinic Carbons of *trans*-PBD:CFCl Adducts (See Figure 10)[a]



peak desig	sequence assignt	chem shift, ppm vs. Me_4Si
1	DDDDD-m,n	130.15
2	DDDDC-m	130.26
3	DDDDC-n	129.97
4	CDDDC-m,n	130.15
5	DDDCD-n	131.02
6	DDDCD-n	129.32
7	CDDCD-m	130.93
8	CDDCD-n	129.53
9	DDDCC-m	131.25
10	DDDCC-n	129.27
11	CDDCC-m	130.97
12	CDDCC-n	129.32
13	DCDCD-m,n	130.15
14	DCDCC-m	130.09
15	DCDCC-n	129.79
16	CCDCC-m,n	130.15

[a] Some representative sequences are shown above.

The above resonances have fine structure due to ^{19}F coupling and stereosequence effects. For example, methylene carbons next to the ring have a small (~3 Hz) $^3J(^{19}F-^{13}C)$ interaction (see resonances 4 and 5) yet show conspicuous multiplicity in the CC sequence (resonances 6 and 7), which must reflect the atactic nature of the polymer. The cyclopropyl methine carbons 0 and 1 are doublets with $^2J(^{19}F-^{13}C)$ values of 12 (carbon 1) and 9.7 Hz (carbon 0). This splitting is best seen at low conversion in the DC (CD) sequence (Figure 8a), where the resonances are not broadened by monomer and stereosequence effects. We do not attempt to assign this fine structure in detail.

The >CFCl carbon resonances of *trans*-PBD:CFCl adducts at 29.1%, 45.5%, and >99% conversion are shown in Figure 9. There are six main peaks due to the three C-centered monomer sequence triads (DCD, DCC, and DCD) and the $^1J(^{19}F-^{13}C)$ doublet coupling of 289 Hz. At complete conversion the only monomer sequence triad is CCC, so the doublet in Figure 9c is readily identified. Similarly the DCD resonance may be identified at low conversion where it gives the most intense doublet (Figure 9a), whereupon the DCC (CCD) assignment follows by default. Syn and anti isomerism is not a factor here as it was for the >CFCl resonance in cis adducts described above, and there is no apparent sensitivity to tacticity. The assignments are summarized in Table V.

The olefinic resonance patterns for *trans*-PBD:CFCl adducts at 29.1% and 45.5% conversion are detailed in Figure 10, where the strong similarity to the patterns for

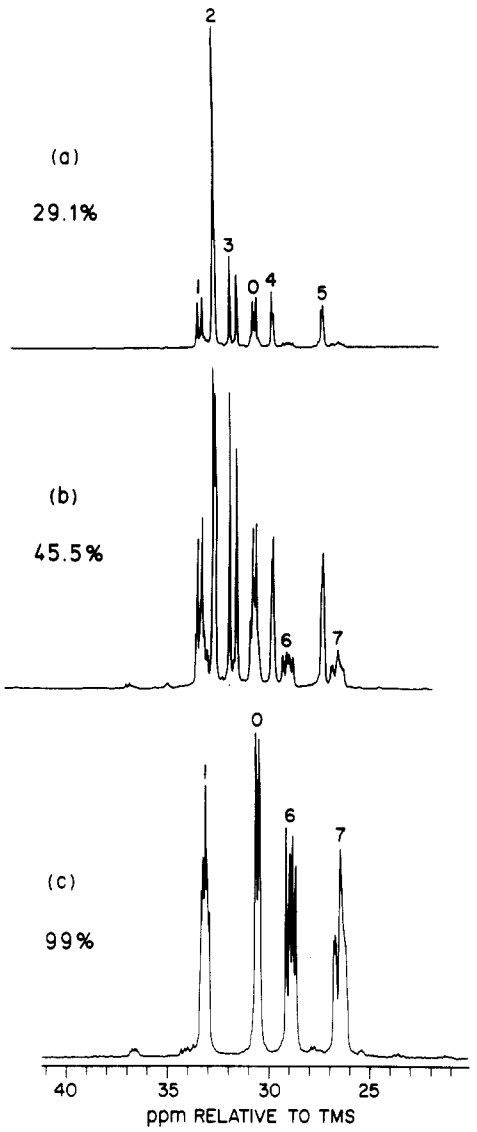


Figure 8. Aliphatic resonance region of 50.31-MHz ^{13}C NMR spectra from *trans*-PBD:CFCl having 29.1% (a), 45.5% (b), and 99% (c) conversion. The numbered peaks are assigned to carbon types in Figure 7 and their chemical shifts are listed in Table IV.

cis adducts (Figure 6) can be noted. There is the same sensitivity to D-centered monomer sequence pentads which creates 16 lines. These were assigned as before and the shifts are given in Table VI. The resonance patterns were computed given these assignments and a measured line width of 4 Hz by assuming a Bernoullian distribution of C and D units. This assumption proved reasonable, based on the adequate simulation obtained in Figure 10.

^{19}F NMR Spectra of *cis*-PBD:CFCl Adducts. The 470.7-MHz ^{19}F NMR spectra of *cis*-PBD:CFCl adducts at low, intermediate, and essentially complete conversions are shown in Figure 11. There are two widely separated groups of signals at −125.8 and −163.7 ppm. These correspond to fluorine in *syn*-Cl and *anti*-Cl structures, respectively. The integrated intensities give a syn probability of 0.63, which is in excellent agreement with the value determined from ^{13}C NMR. The syn:anti ratio is independent of conversion.

These assignments were confirmed by a two-dimensional heterocorrelated NOESY experiment[12] and are consistent with the shielding of fluorine by two methylene carbon γ-substituents in the *anti*-Cl structure compared to the two hydrogen γ-substituents in the *syn*-Cl structure. The geminal fluorines in *cis*-PBD:CF_2 adducts[7] showed a similar large difference in chemical shift according to whether the γ-substituent is carbon or hydrogen, but they also exhibited geminal spin–spin coupling, which is presently not a factor.

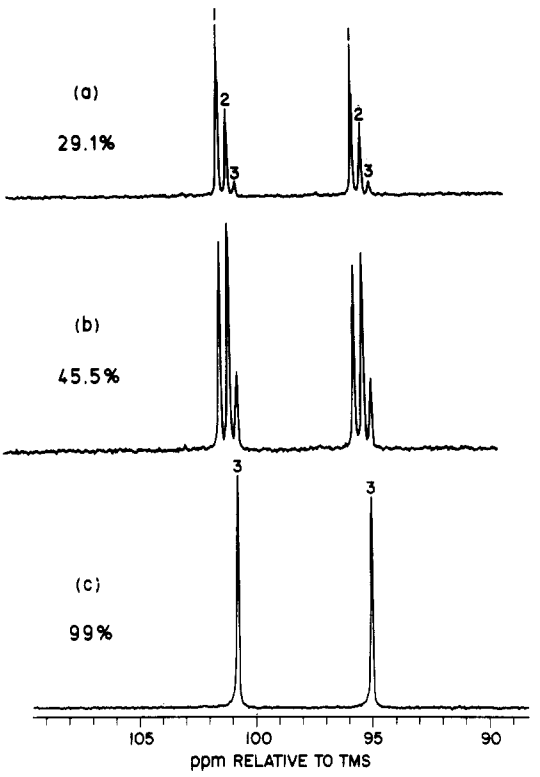


Figure 9. Detailed >CFCl ^{13}C NMR spectra from *trans*-PBD:CFCl at 29.1% (a), 45.5% (b), and 99% (c) conversion. The numbered assignments are given in Table V.

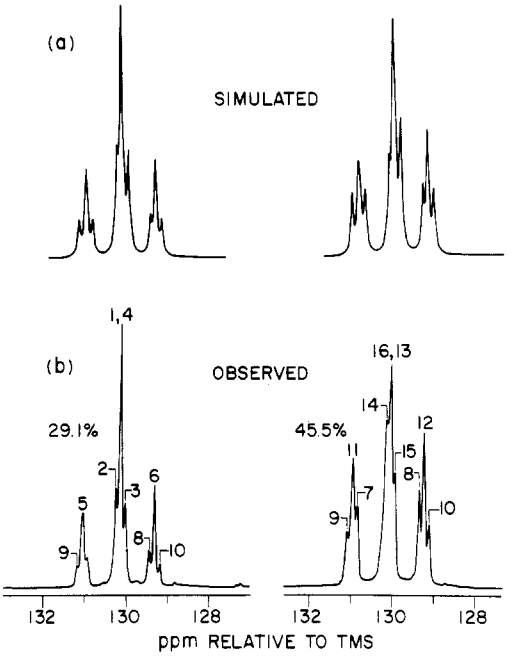


Figure 10. Detailed olefinic ^{13}C NMR spectra from *trans*-PBD:CFCl having 29.1% and 45.5% conversion (b), with corresponding simulated spectra (a). The numbered sequences are assigned in Table VI.

The high-field signal from the anti structure has considerable fine structure, but it is so strongly overlapped that definitive assignments to monomer sequence and stereosequence effects cannot be made. The low-field signal is better resolved and allows the identification of components from the DCD, DCC, and CCC monomer se-

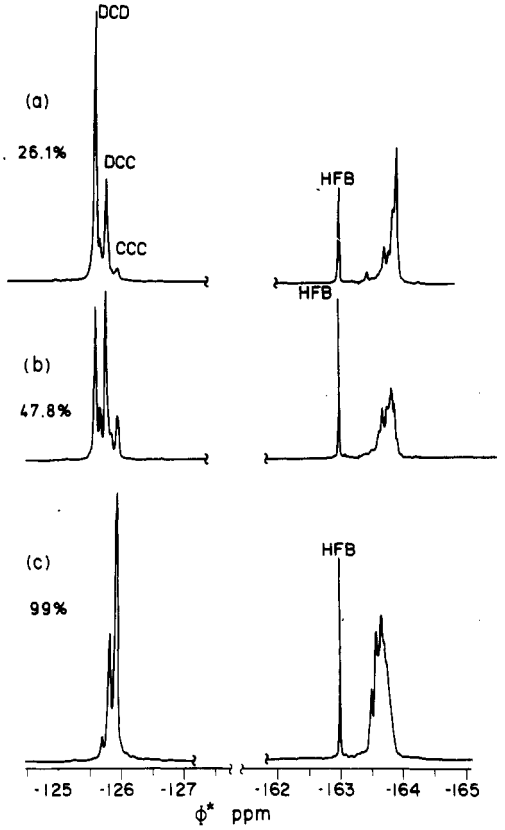


Figure 11. 470.7-MHz ^{19}F NMR spectra from *cis*-PBD:CFCl having 26.1% (a), 47.8% (b), and 99% (c) conversion. The chemical shift reference is hexafluorobenzene (HFB) at −163 ppm. The downfield signals arise from the syn isomer, and the upfield signals arise from the anti isomer.

quence triads, as shown in Figure 11. Interestingly the CCC sequence is further split into three components at complete conversion (spectrum c, Figure 11). We saw that the analogous fluorine in PBD:CF_2 adducts was insensitive to tacticity,[7] so the likely explanation for the present fine structure involves the distribution of syn and anti structures about the central syn structure. There are three possibilities: syn–syn–syn, syn–syn–anti (which is equivalent to anti–syn–syn), and anti–syn–anti. If these follow a Bernoullian distribution, their intensities should be in the ratio 2.8:3.2:1, respectively, given that the probability for syn placement is 0.63. The actual ratio is more like 5:11:1, so that the distribution of syn and anti placements is not Bernoullian. It would appear therefore that there is a neighboring-group effect on stereoselectivity for this case.

^{19}F NMR Spectra of *trans*-PBD:CFCl Adducts. The 470.7-MHz ^{19}F NMR spectra of *trans*-PBD:CFCl adducts at various conversions are shown in Figure 12. The fluorine always has one hydrogen and one carbon γ-substituent in trans rings, so its chemical shift falls in the middle of the widely spaced doublet seen for cis adducts, and there is no syn and anti distinction. Nevertheless the resonance is a complicated multiplet that reflects structural isomerism.

The effects of the three monomer sequence triads DCD, DCC, and CCC can be seen best at low conversion, and their positions are assigned in Figure 12a. The DCD peak is basically a singlet as the D units flanking the central observed C unit have no chiral centers. However stereochemical differences impose fine structure on the resonances as soon as two or more C units are adjacent owing to the various relative configurations of the asymmetric cyclopropyl methine and dihalomethylene carbon centers.

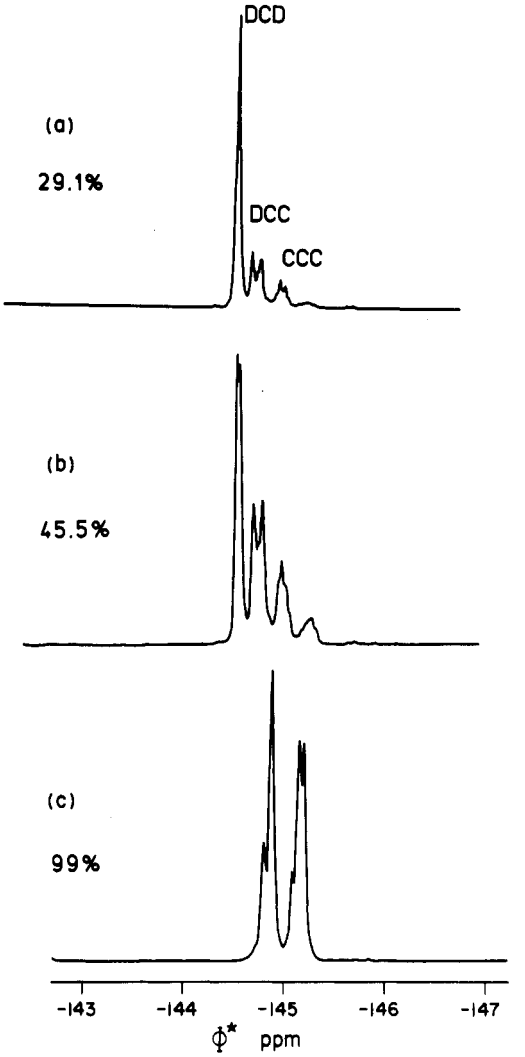


Figure 12. 470.7-MHz ^{19}F NMR spectra from *trans*-PBD:CFCl having 29.1% (a), 45.5% (b), and 99% (c) conversion.

There are three nonequivalent stereoisomers within the CCC triad for the analogous difluorocarbene adduct *trans*-PBD:CF_2,[7,12] where the cyclopropyl methine carbons can be disposed in the following configurational sequences: *RR–RR–RR*, *RR–RR–SS*, and *SS–RR–SS* (these may be likened to the more familiar *isotactic*, *heterotactic*, and *syndiotactic* stereochemical triads in vinyl homopolymers). The methine carbons must have the same configuration for a trans ring, and the sequence *SS–SS–SS*, *SS–SS–RR*, and *RR–SS–RR* cannot be distinguished from their corresponding mirror images above. These three environments resulted in a ~0.5 ppm dispersion of ^{19}F chemical shifts for *trans*-PBD:CF_2, and it is reasonable to expect a similar sensitivity of the ^{19}F resonance from *trans*-PBD:CFCl.

A perfectly *atactic* triad stereosequence would result in a symmetrical 1:2:1 triplet (the geminal ^{19}F coupling manifest in the *heterotactic* triad for *trans*-PBD:CF_2 is not a factor here). The actual ^{19}F spectrum from *trans*-PBD:CFCl at complete conversion has a smaller chemical shift dispersion of about 0.3 ppm and is primarily a doublet, as shown in Figure 12c. No monomer sequence triads other than CCC are present, so that the unsymmetrical substitution of the dihalomethylene carbon must be responsible for the unexpected pattern.

A brief examination of the structures in Figure 7 suggests that the CCC triad in *trans*-PBD:CFCl will have four nonequivalent sequences for methine carbon *types*, namely 01–01–01, 01–01–10, 01–10–01, and 10–01–01. These may

be likened to directional or regiosequence isomers. In addition, each of these will be subject to the various stereoconfigurational possibilities described above so that the central fluorine in the CCC triad will reside in more than just three magnetically nonequivalent environments. Closer inspection of spectrum c in Figure 12 reveals some fine structure and at least five lines, but these are strongly overlapping so that the pattern is not amenable to any ready interpretation beyond the demonstration that *trans*-PBD:CFCl is highly stereoirregular.

Conclusions

Polybutadienes trap fluorochlorochlorocarbene generated according to the Seyferth method very efficiently, and exhaustive reaction of the double bonds may be realized. The glass-transition temperatures of the adducts increase linearly with conversion, and extrapolation of the values for the trans polymer gives a T_g of −85 °C for the starting material. Monomer and stereosequence are not subject to a neighboring-unit effect during the reaction, although it appears there is a bias in the distribution of syn and anti isomers for the cis polymer. The more hindered syn isomer is preferred when :CFCl adds to a cis double bond.

Acknowledgment. We are grateful to Dr. H. M. Gilroy for providing TGA measurements.

References and Notes

(1) Pinazzi, C.; Gueniffey, H.; Levesque, G.; Reyx, D.; Pleurdeau, A. *J. Polym. Sci., Part C* **1969**, *22*, 1161. See also: Pinazzi, C.; Brosse, J. C.; Pleurdeau, A.; Reyx, D. *Appl. Polym. Symp.* **1975**, *26*, 73.
(2) Pinazzi, C.; Levesque, G. *J. Polym. Sci., Part C* **1969**, *16*, 4695. See also: Bradbury, J. H.; Senake Perera, M. C. *Br. Polym. J.* **1986**, *18*, 127.
(3) Dias, A. J.; McCarthy, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*, 162.
(4) Komoroski, R. A.; Horne, S. E., Jr.; Carman, C. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 89. See also: Carman, C. J.; Komoroski, R. A.; Horne, S. E., Jr. *NMR and Macromolecules*; Randall, J. C., Ed.; American Chemical Society: Washington, DC, 1984; *ACS Symp. Ser. No. 247*, Chapter 11, p 167.
(5) Pinazzi, C.; Levesque, G. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264*, 288.
(6) Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65.
(7) Siddiqui, S.; Cais, R. E. *Macromolecules* **1986**, *19*, 595.
(8) Siddiqui, S.; Cais, R. E. *Macromolecules* **1986**, *19*, 998.
(9) Rinehart, R. E.; Smith, H. P. *Macromolecular Syntheses*; Wiley: New York, 1978; Collect Vol. 1, p 125.
(10) Seyferth, D.; Darragh, K. V. *J. Org. Chem.* **1970**, *35*, 1297.
(11) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.
(12) Cais, R. E.; Mirau, P. A.; Siddiqui, S. *Br. Polym. J.*, in press.
(13) Hine, J.; Burske, N. W. *J. Am. Chem. Soc.* **1956**, *78*, 3337.
(14) Hine, J.; Duffey, D. C. *J. Am. Chem. Soc.* **1959**, *81*, 1129.
(15) Moss, R. A.; Gerstl, R. *J. Org. Chem.* **1967**, *32*, 2268.
(16) Seyferth, D.; Murphy, G. J. *J. Organometal. Chem.* **1973**, *49*, 117.
(17) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971.
(18) Stempel, G. H. *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H. Eds.; Wiley-Interscience: New York, 1975, p V-2.
(19) Bovey, F. A.; Winslow, F. H. *Macromolecules: An Introduction to Polymer Science*; Academic: New York, 1970; p 10.
(20) Grebowicz, J.; Aycock, W.; Wunderlich, B. *Polymer* **1986**, *27*, 575.
(21) Williamson, K. L.; Li, Y.-F.; Hall, F. H.; Swager, S. *J. Am. Chem. Soc.* **1966**, *88*, 5678.
(22) Moss, R. A.; Gerstl, R. *Tetrahedron* **1967**, *23*, 2549.

Spin–Lattice Relaxation of Dipolar Energy of Polypropylenes

John M. Ballinger, Larry A. Kasuboski, and Cecil Dybowski*

Department of Chemistry, University of Delaware, Newark, Delaware 19716.
Received August 18, 1986

ABSTRACT: The temperature dependence of the spin–lattice relaxation rate [T_{1D}^{-1}] of the dipolar energy of the protons of polypropylene is reported. Measurements for three samples demonstrate that it is sensitive to motions involved in both the α and β relaxations of polypropylene.

Introduction

Segmental motions of polymers produce efficient relaxation of nuclear spins.[1] Careful measurements of line widths,[2] spin–lattice relaxation times of the Zeeman energy in the laboratory frame, T_1,[3] and in the rotating frame, $T_{1\rho}$,[4] time constants for the decay of spin order,[5] and relaxation under dipole–dipole suppression experiments[6,7] complement other spectroscopic techniques such as light scattering and dielectric dispersion measurements and mechanical relaxation measurements in analyzing the dynamic properties of polymeric materials.[8]

For a spin system subject to anisotropic interactions, magnetic dipole–dipole couplings among spins provide an energy reservoir. Fluctuations of internuclear vectors efficiently return this dipolar reservoir to thermal equilibrium, a process easily monitored with NMR pulse techniques.[9] The exponential time constant, T_{1D}, for this relaxation process measures molecular reorientational dynamics of the system.[9]

For many polymers in bulk, anisotropic motions produce an effective proton dipolar reservoir.[10,11] The heterogeneity of semicrystalline polymers can result in a fractionation of this reservoir. This subdivision of the dipolar reservoir is observed as nonexponential relaxation of the dipolar energy, for example for the protons of the polyethylene. Nonexponential relaxation has also been observed for other magnetic parameters, particularly for the spin-locked magnetization.[12]

Polypropylene is the quintessential polymer for investigation with NMR spectroscopy.[12] This semicrystalline polymer exhibits several thermal transitions that involve quenching of molecular motions. The side-chain methyl group experiences motions that may be different from those of the backbone chain and which may play a major part in relaxing the overall spin system when spin diffusion is effective.[2,4,8,12] Various forms of polypropylene, ranging from the atactic highly amorphous material to the highly crystalline isotactic material, have different mechanical properties.[13] The mechanical relaxation properties can be correlated with the morphology, such as the amount of amorphous material. We report measurements of the relaxation rate of the dipolar energy of the protons of polypropylene as a function of temperature and amorphous content.

Experimental Section

The samples of polypropylene were given to us by Dr. Walter Freeman of Hercules, Inc. They were used as received. NMR

0024-9297/87/2220-1012$01.50/0