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Structural Analysis of the Alternating Copolymer Poly(chloroacrylonitrile-*alt*-cyclohexadiene)

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ABSTRACT: 2-Chloroacrylonitrile and 1,3-cyclohexadiene have been copolymerized by using radical and coordination initiators. Elimination reactions were carried out in the brominated and the virgin copolymer using KF and a phase-transfer catalyst in order to prepare derivatives which facilitated in the characterization of the copolymer. ^{13}C NMR and attached proton test (APT) indicate that the HCl elimination from the virgin copolymer leads to the formation of a highly substituted olefin. FT-IR analyses of the copolymer and its derivatives suggest the formation of essentially 1,4-linkages across the cyclohexene unit. The copolymer microstructure has been characterized by ^{1}H NMR, two-dimensional proton *J*-correlated (COSY), ^{13}C NMR, DEPT, and two-dimensional ^{1}H–^{13}C chemical shift correlated (CSCM) spectroscopic techniques. These studies indicate the presence of 1,4-linkages, while simultaneously suggesting the absence of a significant amount of 1,2-linkages in the copolymer.

Introduction

Regular alternating copolymers are commonly synthesized from monomer pairs that form intermediate donor–acceptor complexes.[1-5] These systems include the diene–dienophile type in which the charge-transfer (CT) complex can also undergo competitive Diels–Alder cycloaddition reactions. Both cyclic and acyclic dienes, such as 1,3-pentadienes, 1,3-cyclohexadienes, furans, isoprene, butadiene, and piperylene, serve as electron donors in conjunction with electron acceptors, which include maleic anhydride, and polar vinyl monomers, such as acrylonitrile, 2-chloroacrylonitrile, and methyl 2-chloroacrylate.[3-7]

Polymerization of these CT complexes can occur spontaneously or can be initiated by numerous species with a substantial increase in polymerization rate. Typical initiators include free radical systems (AIBN, benzoyl peroxide), Lewis acids ($ZnCl_2$, $AlCl_3$), and metal salts (silver triflate).

Among these systems, the use of 1,3-cyclohexadiene (CHD) as the donor monomer is intriguing in that the copolymers formed may be used as a substrate for subsequent elimination or addition reactions. The ability to locate cyclohexene rings along a polymer chain may serve as a method of incorporating isolated phenyl rings in the polymer after aromatization. In this manner, polyphenylenes have been synthesized under severe conditions from unsubstituted cyclohexadienes[8] while more recently the use of the acetate derivative of 5,6-dihydroxy-1,3-cyclohexadiene,[9,10] has yielded high molecular weight polyphenylenes under milder conditions.

The mechanism of polymerization of 1,3-CHD can proceed via either 1,2- or 1,4-additions across the ring. For example in the case of diester substituted CHD's, the relative content of 1,2 versus 1,4 structures has been found to be a function of ester type.[10] In the case of the alternating copolymerization of 1,3-CHD and polar vinyl monomers the mechanism of polymerization through the CHD ring has not been fully elucidated.[11]

In this paper, we describe the structure of the copolymer poly(2-chloroacrylonitrile-*co*-1,3-cyclohexadiene), hereafter labeled poly(CAN/CHD), utilizing TGA, FT-IR, ^{13}C and ^{1}H NMR, 2D ^{13}C^{1}H correlated (CSCM), 2D COSY, ^{13}C-distortionless enhancement by polarization transfer (DEPT), and attached proton test (APT) spectroscopy. Two-dimensional NMR techniques have previously been used in characterizing copolymer microstructure.[12] Derivatives of this copolymer, synthesized via either addition (bromination) or elimination reactions, have been used in structure confirmation.

Experimental Section

Materials and Methods. 1,3-CHD (98% Aldrich Chemical) was distilled over CaH_2. 2-Chloroacrylonitrile (99% Aldrich

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Table I
Copolymerization Results of 2-Chloroacrylonitrile (CAN) and 1,3-Cyclohexadiene (CHD) with Various Initiator Systems

polymer	initiator (mol %)[a]	polymerizatn temp (°C)	polymerizatn time (h)	monomer feed compositn CAN/CHD (mmol)	polymer yield (%)
CC2	BPO (1)	85	72[b]	12.5/21	55
CC3	AIBN (1)	50	72[b]	18.7/31.5	72
CC4	AIBN (0.05)	50	72[b]	18.7/15.8	62
CC5	AgOTf (4.4)	25	96	75/126	58
CC7	AgOTf (4.4)/AIBN (0.5)	0	504	75/126	14
CC8	AgOTf (0.65)/AIBN (0.15)	25	182	75/126	32
CC9	$AlCl_3$ (4.4)	50	240	75/126	25
CC10	$ZnCl_2$ (0.025)	40	24	75/126	n/a
CC11[c]	AIBN (0.025)	60	44	44.5/44.5	93
CAN-1	AIBN (0.05)	50	120	37/0	21
CC12	AIBN (0.5)	0	504	19/32	trace
CC13	AgOTf (4.4)	0	504	25/42	trace

[a] Initiator concentration based on the amount of CAN. [b] Actually needed less than 72 h. [c] Polymerization was carried out in benzene.

Chemical) was purified by passage over a column of neutral alumina prior to polymerization. All the other reagents were used as received. Thermogravimetric analyses were performed on a Du Pont 1090 thermal analyzer under a nitrogen atmosphere. FT-IR transmission spectra of samples were recorded in KBr pellets using a Digilab FTS-40 instrument.

^1H NMR (300 MHz) and DEPT (75.5 MHz) spectra were recorded on an IBM-Bruker instrument. ^{13}C NMR (50.3 MHz) and all other two-dimensional NMR spectroscopic experiments were carried out by using a Nicolet NT-200 spectrometer. The system is equipped with a Nicolet 1280 data processor and a NIC Model 293 A′ programmable pulser. The ^{13}C NMR, ^1H NMR, and CSCM were obtained on ca. 10% polymer solutions in 99.8% chloroform-*d* and 2D-COSY was obtained by using a 4% polymer solution in 100% chloroform-*d*. Chemical shifts are reported referenced to chloroform-*d* (77.00 ppm for ^{13}C and 7.24 ppm for ^1H). All spectra were recorded at 25 °C.

A sweep width of 7.2 kHz was used for the ^{13}C NMR spectra with a digital resolution of 0.04 ppm. A delay time of 0.2 s was used for experiments with nuclear Overhauser enhancement (NOE) and 10 s for experiments without NOE. A total of 20000 transients were obtained for spectra with NOE and 8000 transients without. The same peaks were observed in both cases except the intensities of the peaks in the spectra without NOE quantitatively reflect the number of each type of carbon.

DEPT spectra were obtained to determine the multiplicities of each ^{13}C resonance using the following standard pulse sequence (where RD is relaxation delay):[13]

^1H, RD–90°–τ–180°–τ–θ–τ–decouple;
^{13}C, (RD + τ)–90°–τ–180°–τ–acquire.

The multiplicity of each carbon is determined by varying the proton pulse θ. With $\theta = 135°$, methine and methyl signal intensities are positive and methylene signals are negative. With $\theta = 90°$, only the methine carbon signals are observed. The quaternary carbons have zero intensity for all values of θ.

COSY spectra were obtained to identify protons coupled to the olefinic protons of the cyclohexene unit in the copolymer. The homonuclear COSY was performed by using the standard pulse sequence RD–90°–t_1–90°–acquire.[14] A total of 256 blocks of 1K data points were acquired. A total 128 scans were obtained for each block with a sweep width of 1400 Hz. A 5-s delay was used between scans. The raw FIDs were conditioned by using sinusoidal multiplication prior to the first Fourier transformation. The resulting interferograms were zero-filled to 512 data points and conditioned by double exponential multiplication with an apodization factor of 2 prior to the second Fourier transformation. The spectrum was symmetrized and displayed as a countour plot showing off-diagonal peaks for protons coupled to one another.

Two-dimensional ^{13}C–^1H chemical shift correlated map (CSCM) spectroscopy was performed to correlate ^{13}C signals to the ^1H signal to the corresponding directly attached proton. The following standard pulse sequence[15] was used for the CSCM:

^1H, RD– 90°–(t_1 + Δ_1)–90°–Δ_2–decouple;
^{13}C, RD–$t_1/2$–180°–$t_1/2$ + Δ_1– 90°–Δ_2–acquire.

A total of 128 blocks of 2K data points were acquired with 640 scans for each block and a delay time of 2 s. The delay times, Δ_1 and Δ_2, were set to 3.57 and 1.79 ms, respectively, optimized for $J_{C-H} = 140$ Hz. The sweep width was 6492 Hz for ^{13}C and 1600 Hz for ^1H. The FIDs were processed by using a double-exponential multiplication with an apodization factor of 2 prior to the first Fourier transformation. The resulting interferograms were zero-filled twice to give 512 data points followed by double-exponential multiplication with an apodization factor of 2 prior to the second Fourier transformation. The data was displayed as a contour plot showing responses for the carbons and their directly attached protons.

Table II
Copolymer Composition of Poly(chloroarylonitrile-*co*-cyclohexadiene)

polymer	feed ratio CAN/CHD	CAN/CHD composition		
		^1H NMR	elemental anal.	TGA
CC2	0.60	46/54		
CC3	0.60	45/55	49/51	51/49
CC4	1.18	43/57	52/48	53/47
CC5	0.60	46/54	49/51	51/49
CC7	0.60	44/56		
CC8	0.60			50/50
CC9	0.60	48/52		52/48
CC10	0.60	46/54		

Copolymerization. The bulk copolymerization of 2-CAN and 1,3-CHD has been carried out varying conditions as shown in Table I. In a typical copolymerization, CHD (10.1 g, 126 mmol), CAN (6.7 g, 75 mmol), and the initiator AgOtTf (0.8 g, 3.3 mmol) were charged in a reaction tube under nitrogen atmosphere. The contents were degassed by freeze–thaw cycles and the tube was sealed under vacuum. After reaction at a specified temperature, the polymer was dissolved in chloroform and run through a column of silica to remove the silver salt. The concentrated polymer was precipitated in methanol and dried under vacuum.

Elimination of Poly(CAN/CHD). Potassium fluoride dihydrate (1.12 g, 12 mmol) and TBABr (7.8 g, 24 mmol) were added to a flask containing water (3 mL) and THF (100 mL). The contents were stirred, poly(CAN/CHD) (1 g) in THF was added to the flask, and the contents were stirred at 40 °C for 72 h. After the reaction, the product weas concentrated and precipitated in methanol and dried at 40 °C under vacuum.

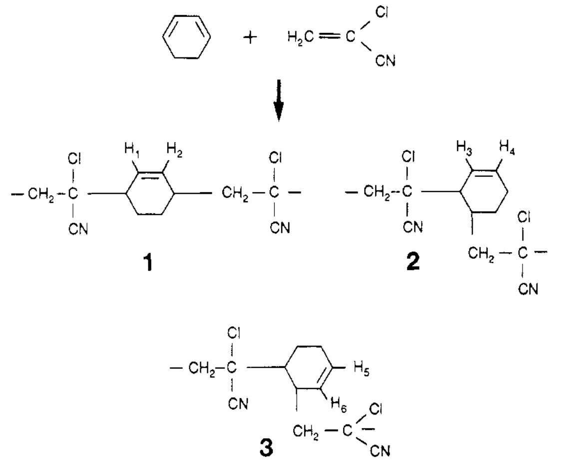
Bromination of Poly(CAN/CHD). The bromination was carried out according to the reported procedure.[11]

Elimination of HCl and HBr from the Brominated Poly(CAN/CHD). Potassium fluoride dihydrate (1.7 g, 18 mmol) and TBABr (11.6 g, 36 mmol) were added to a flask containing water (3 mL) and THF (100 mL). The contents were stirred, and the brominated copolymer (1 g) in THF was added to the reaction flask and stirred for 5 days at 40 °C. The product was concentrated, precipitated in methanol, and dried at 40 °C under vacuum.

Results and Discussion

The copolymerization of 2-CAN and 1,3-CHD has been carried out under conditions of varied monomer feed ratios, type of initiator, and reaction temperature as shown in Table I. The composition of the resultant poly(CAN/CHD) copolymer was determined by thermogravimetric

Scheme I



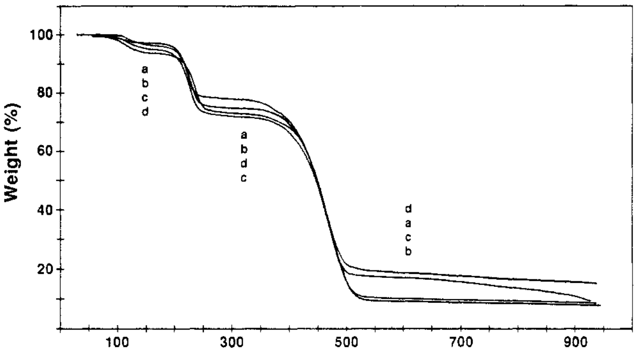


Figure 1. Thermograms of poly(chloroacrylonitrile-*co*-cyclohexadiene): (a) CC7; (b) CC3; (c) CC2; (d) CC5.

analysis (HCl content eliminated), ^1H NMR, and elemental analysis on selected copolymers as shown in Table II. The results indicate that the copolymers contain an equimolar amount of 2-CAN and 1,3-CHD irrespective of reaction conditions as expected for alternating copolymerization. The AIBN-initiated homopolymerization of 1,3-CHD[16] yields no polymer while we find that 2-CAN homopolymerizes at a very slow rate. These observations suggest the alternating tendency of these two monomers. Nagai et al.[7a] showed by UV spectroscopy that 2-CAN and 1,3-CHD form a distinct charge-transfer complex (CTC). Homopolymerization of this CTC will yield the 1:1 alternating copolymer having the possible structural isomers **1**, **2**, and **3** shown in Scheme I.

It should be noted from Table I that AIBN or AgOTf alone as initiator at 0 °C (CC12 and CC13) failed to initiate the copolymerization of CAN and CHD, whereas the combined use of AIBN and AgOTf at 0 °C (CC7) resulted in copolymerization, albeit with low yield. This can be compared with the lowering of the polymerization temperature of vinyl monomers by AIBN and benzoyl peroxide initiators in the presence of Lewis acid[2,17] which is attributed to a reaction between the two components.

Initial ^{13}C NMR spectra of these copolymers show them to be the same, having identical peaks and relative intensities, independent of reaction conditions. This serves as further proof that the CT complex controls the copolymerization and thus a direct comparison of all these materials can be made.

Derivatization of Poly(CAN/CHD). As was seen with ^{13}C NMR, the TGAs of the copolymers are nearly identical. As shown in Figure 1 the initial weight loss below 175 °C can be attributed to the loss of moisture and/or solvent while the step between 190 and 300 °C is due to the elimination of HCl from which the copolymer composition was determined. Chemical and thermal derivatization, leading to either addition or elimination products, was carried out on CC9 to help characterize the copolymers structure.

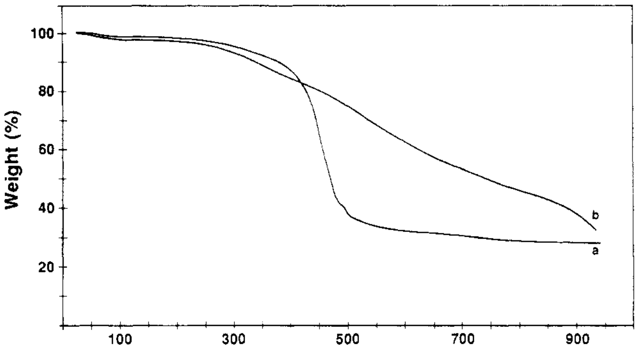
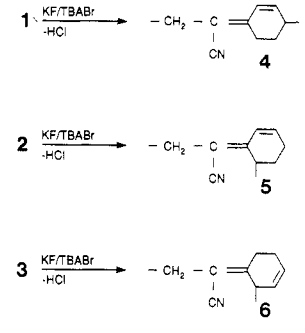


Figure 2. Thermograms of (a) poly(CAN/CHD) after chemical elimination and (b) poly(CAN/CHD) after bromination and subsequent elimination.

Scheme II



In order to obtain a better defined elimination product, we have carried out a base-catalyzed elimination reaction on the poly(CAN/CHD) using a phase-transfer system of potassium fluoride with tetrabutylammonium bromide (KF/TBABr). Though fluoride substitution products may arise from this reaction, we find from FT-IR and ^{13}C NMR studies[18] that the elimination pathway, outlined in Scheme II, occurs almost exclusively. Hydrogen abstraction occurs preferentially from the allylic site yielding the three possible structures **4**, **5**, and **6**. TGA of the polymer after elimination, Figure 2a, showed the HCl elimination to be complete. Elemental analyses also showed no detectable chlorine confirming the completeness of the HCl elimination.

A more highly unsaturated polymer was obtained by brominating the original poly(CAN/CHD) copolymer followed by KF/TBABr elimination. Addition of Br_2 across the double bond of the cyclohexene ring leads to a brominated material that lost 2 mol of HBr and 1 mol of HCl/mol repeat unit upon elimination as shown in Scheme III. HBr elimination occurs much more rapidly than HCl elimination, and thus most of the rings along the polymer chain become cyclohexadiene units conjugated with a double bond as shown by structures **7**, **8**, **9**, and **10**. The elimination of HCl and HBr was complete as shown by TGA in Figure 2b.

FT-IR Spectroscopy. The FT-IR spectra of the poly(CAN/CHD) copolymers were identical, independent of synthetic conditions. The C—H stretch and –C≡N stretch are shown in Figure 3 with the –C≡N stretch for the virgin copolymer at 2237 cm^{-1} (Figure 3a) proving to be quite useful for structural analysis. After KF/TBABr elimination, Figure 3b, the original cyano peak disappears

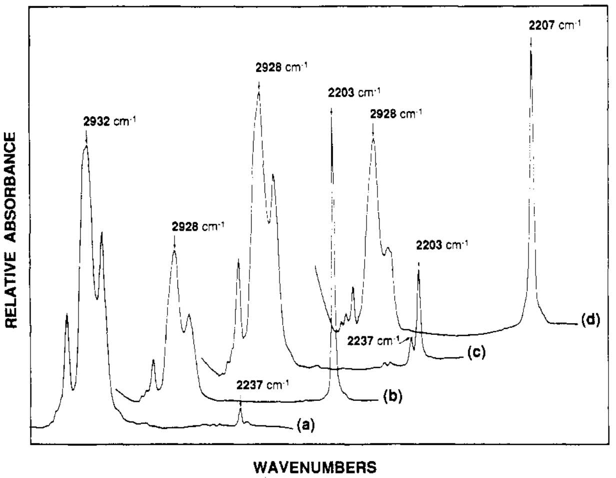
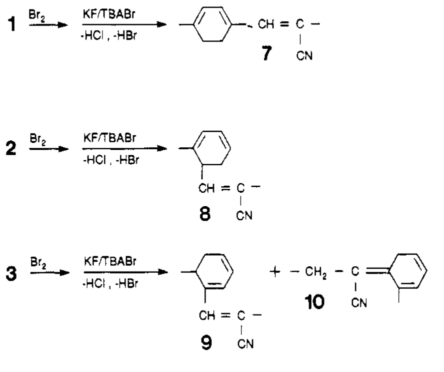


Figure 3. FT-IR spectrum of (a) virgin poly(CAN/CHD), (b) the KF/TBABr elimination product of poly(CAN/CHD), (c) the thermal elimination product of poly(CAN/CHD), and (d) the KF/TBABr elimination product of brominated poly(CAN/CHD).

and is replaced by a new strong peak at 2203 cm^{-1}. The low intensity of the absorbance at 2237 cm^{-1} in the virgin copolymer can be attributed to the presence of the electron-withdrawing chlorine.[19] The increased peak intensity, accompanied with a shifting to lower energy indicates that the reaction with KF resulted in the elimination of HCl creating a conjugated cyano group. It should be noted that the presence of structures **4**, **5**, and **6** shown in Scheme II should give rise to at least two peaks since they are conjugated with either one or two double bonds. It should also be noted[20,21] that the absorption frequency of a cyano group in conjugation with one double bond is not generally lowered as far as 2203 cm^{-1}. These absorptions are more likely to be found at ca. 2220 cm^{-1}, and thus our observed absorption can be attributed to a cyano group conjugated with more than one double bond. (Cyano groups in conjugation with one double bond can have their absorption frequencies lowered to ca. 2200 cm^{-1} when it is also conjugated with an electron-donating group,[22] but this is not the case here.) The presence of only one peak suggests that all cyano groups are in conjugation with the same number of double bonds, and thus, structure **6** is most likely not present in the reaction product and thus structure **3** is not present in the as-made copolymer. The thermal elimination of HCl from poly(CAN/CHD) yields a product that also exhibits a major cyano peak at 2203 cm^{-1} as shown in Figure 3c. This suggests that the two elimination products have similar structures. The small peak at 2237 cm^{-1} indicates that the thermal elimination process is not as effective as the base elimination.

The FT-IR spectrum of brominated poly(CAN/CHD) and subsequently eliminated by KF is shown in Figure 3d. The strong cyano absorption is present at 2207 cm^{-1} indicative of the HCl eliminated and conjugated functional group. The absence of absorption at 2237 cm^{-1} shows the elimination to have proceeded to completion. The brominated copolymer exhibited a new peak at 655 cm^{-1}, due to the C–Br stretch which disappeared after elimination. The bromination reaction did not alter the –C≡N stretch as evidenced by a small peak at 2240 cm^{-1}. After elimination no visible competitive fluorine substitution has occurred as shown by the TGA in Figure 2. The presence of a significant amount of C–F on the polymer would have been shown by an elimination of H–F. The elimination of HX rather than substitution by fluorine during treatment with KF/TBABr has been reported for halogen-containing polymers under similar conditions,[23] in agreement with our results. The above results indicate that the KF/TBABr treatment of the brominated poly(CAN/CHD) does proceed via an elimination process as outlined in Scheme III. Scheme III shows that the cyano group in structure **8** is conjugated with one double bond, whereas structures **7**, **9**, and **10** are conjugated with three double bonds. The formation of structure **9** can be excluded because of the facile abstraction of the tertiary hydrogen from the cyclohexene unit as observed in the virgin copolymer. The presence of a combination of structures **7**, **8**, and **10** in the reaction product would be expected to give rise to more than one peak for the cyano group. The appearance of only one IR peak at 2207 cm^{-1} (regardless of whether the spectrum is taken at a resolution of 8 or 0.5 cm^{-1}) suggests that this peak is due to only one of these possibilities.

Scheme III



As discussed previously, cyano groups conjugated with only one double bond do not generally have absorption frequencies much lower than 2220 cm^{-1}. This serves as initial evidence for the exclusion of structure **8** which extrapolates to the exclusion of structure **2** in the original copolymer. In addition, it can be expected that the absence of either of the 1,2-linkages suggests both should be absent in the virgin copolymer due to their equivalent probability of formation. However, our FT-IR analyses of these poly(CAN/CHD) derivatives separately exclude both 1,2-linkages (structures **2** and **3**) in the copolymer independent of the above conjecture. The exclusion of either of the 1,2-linkages provides strong support, albeit indirect, of the fact that the copolymer under investigation is composed of mainly 1,4-linkages across the cyclohexene unit and that the IR peaks at 2203 (Figure 3b) and 2207 cm^{-1} (Figure 3d) can be assigned to structures **4** and **7** respectively.

A direct comparison of structures **4** and **7** shows the former to be conjugated with two double bonds while the latter is conjugated with three. It is known that the exact position of the cyano group frequency is also dependent on the double-bond substitution pattern.[10] This makes it difficult to compare the effect of extended conjugation lengths on absorption frequencies. There are also indications that substituents on highly conjugated systems, relatively long distances from cyano groups, also affect its frequency of absorption.[24]

The aromatization of the cyclohexene unit in the poly(CAN/CHD) and analysis by IR spectroscopy for the substitution pattern would be more convenient for the identification of (1,2) and (1,4) linkages across the aromatic ring. Nagai et al.[11] aromatized the brominated poly(CAN/CHD) by thermal treatment at 250 °C for 1–2 h. Their IR spectrum of the thermally treated product exhibited peaks at 1600 cm^{-1} characteristic of an aromatic compound and a peak at 825 cm^{-1} characteristic of a para-substituted benzene derivative. From these obser-

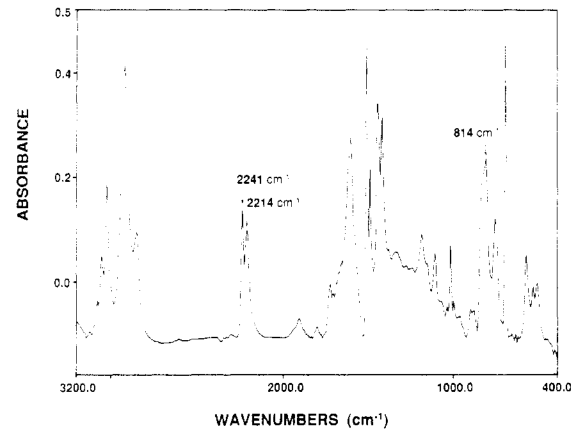
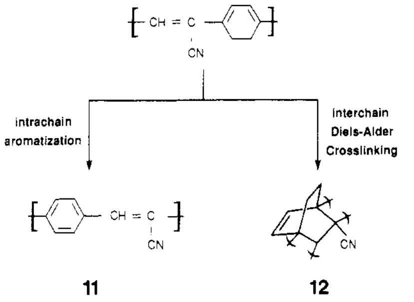


Figure 4. FT-IR spectrum of brominated poly(CAN/CHD) heated at 250 °C for 2 h.

Scheme IV



vations, they concluded that poly(CAN/CHD) contains mainly 1,4-linkages across the cyclohexene unit. However, the IR spectrum showed a significant amount of sp^3 C–H stretching indicating incomplete aromatization. These IR results do indicate that the polymer contains 1,4-linkages but do not rule out the possibility of 1,2-linkages. We also attempted to aromatize the brominated copolymer by heating at 250 °C for 2 h and 300 °C for 12 h. The IR spectrum of the thermally treated polymer is shown in Figure 4, and large proportions of sp^3 C–H stretching can be seen indicating incomplete aromatization. In addition, there is a new peak at 814 cm^{-1} characteristic of 1,4-disubstituted benzene units as observed by Nagai et al.[11] However, there were two cyano peaks at 2241 and 2214 cm^{-1} which were visible even after the polymer was heated at 225 °C for 12 h under vacuum. The peak at 2241 cm^{-1} is relatively stronger than the cyano peak in the virgin copolymer. This peak may be due to the formation of competing Diels–Alder reaction product as shown in Scheme IV. Complications in this structure are also possible due to reactions through the cyano group.

The cyano group in structure **12** has no electron-withdrawing group, such as chlorine in the virgin poly(CAN/CHD), to lower the intensity of the cyano peak, and there is no conjugated double bond to lower the frequency of absorption. In addition, the presence of structure **12** would indicate the origin of the sp^3 C–H stretching, while the complete aromatization of the copolymer should not show any sp^3 C–H stretching. The peak at 2214 cm^{-1} is assigned to a cyano group conjugated with an aromatic ring. It should be noted that the cyano group conjugated with cyclohexadiene in structure 7 shows a peak at 2207 cm^{-1} (Figure 3d). The cyclohexadiene is more electron donating than the aromatic ring in structure **11**. Therefore, the cyano bond in structure 7 is weaker than in structure **11**, and hence the cyano peak of 7 appears at lower energy. This is confirmed by work that shows the position of the cyano peak in substituted benzonitrile is affected by the electron-donating ability of the substituent.[21] More recently Green et al.[24] has reported that the electron-donating ability of a substituent lowered the energy of absorption of a cyano group in a highly conjugated system.

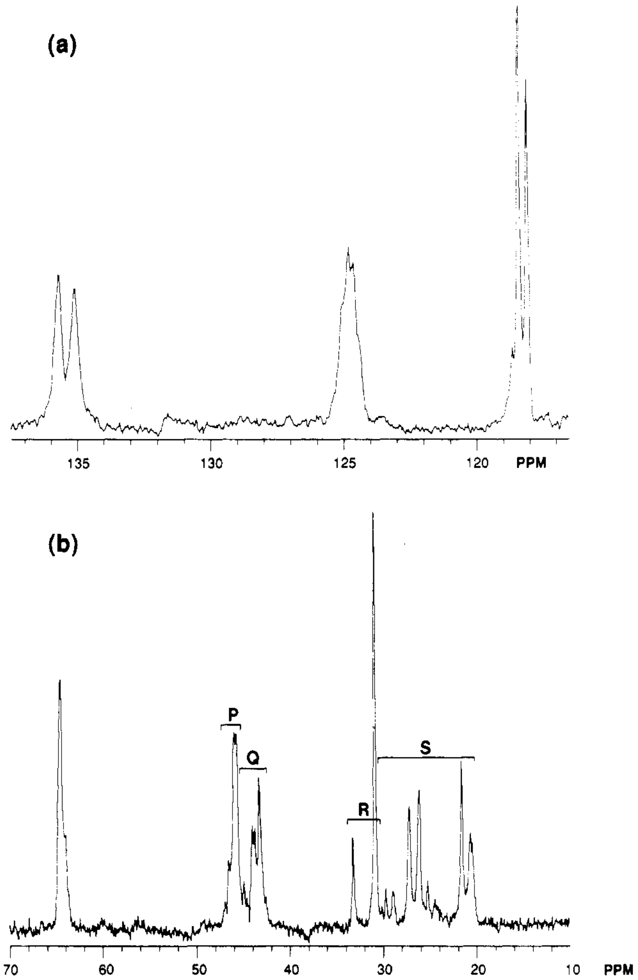


Figure 5. 50.3-MHz ^{13}C NMR spectrum of poly(CAN/CHD): (a) olefinic region; (b) aliphatic region.

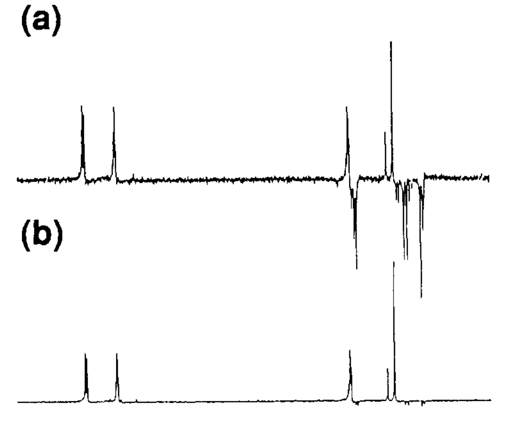


Figure 6. 75.5-MHz DEPT spectra of poly(CAN/CHD), CC5: (a) CH_2, negative; CH, positive; quaternary, zero intensity; (b) CH, positive; others, zero.

^{13}C NMR Spectroscopy. The 50.3-MHz ^{13}C NMR spectrum of poly(CAN/CHD) CC5, is shown in Figure 5 (parts a and b) and was nearly equivalent for all samples. The 75.5-MHz DEPT spectrum is shown in Figure 6 (parts a and b). From the DEPT spectrum, the peaks at 118.6,

Table III
^{13}C NMR Peak Assignments

peak (ppm)[a]	monomer	assignment
135.64, 135.04	CHD	olefinic
124.76, 124.58	CHD	olefinic
118.63, 118.40, 118.08	CAN	cyano carbons
64.47, 63.89, 63.59	CAN	quaternary
46.86, 46.50, 45.93	CHD	methine[b]
44.92, 43.95, 43.67, 43.19, 42.47	CAN	methylene
33.14, 30.80	CHD	methine
29.61–20.36	CHD	methylene

[a] Resolution is ±0.04 ppm. [b] Assignment to CHD methine adjacent to quaternary carbon of CAN unit.

118.4, and 118.1 are assigned to the cyano carbon of the chloroacrylonitrile unit. This assignment is consistent with the values reported for various cyano compounds,[25] vinyl acetate–vinylidene cyanide copolymers,[26] and our results on poly(2-chloroacrylonitrile). The presence of more than one peak for the cyano carbon can be attributed to various stereo sequences in the copolymer main chain.

Also from Figure 6, the peaks at approximately 64.5 ppm are assigned to the quaternary carbon of the CAN unit. The presence of several peaks for this carbon also can be attributed to the various possible stereo sequences in the copolymer main chain. This is the most deshielded carbon in the saturated carbon region of the spectrum due to the presence of adjacent electronegative chlorine and cyano groups. Further analysis of the DEPT spectrum also allows assignment of the peaks at 135.6, 135.0, 124.8, and 124.6 to the olefinic carbon of the cyclohexene unit of the copolymer. The assignments of peaks for the individual olefinic carbons will be discussed later in the discussion of the chemical shift correlation map. Due to their positive intensity in the DEPT spectrum, the peaks labeled P (~45.9 ppm) and R (33.1, 30.8 ppm) in Figure 5b are assigned to the methine carbons of the CHD unit of the copolymer. The peaks labeled P are assigned to the methine carbon adjacent to the quaternary carbon containing chlorine and cyano groups, and the peaks labeled R are assigned to the remaining methine carbon of the cyclohexene unit by chemical shift differences. These assignments were made by comparing the number of bonds separating these methine carbons from the electronegative chlorine and cyano groups. Comparison of these assignments can be made with the assignments made for poly(cyclohexadiene) in which the methine carbons appear in the 39–41 ppm range.[27] These chemical shift differences can be understood by comparing the deshielding effect of the β-cyano and chloro groups for one methine carbon and shielding effect of the same substituents that are in the γ-position for the other methine carbon.[28]

The ^{13}C peaks labeled S (29.6, 28.7, 27.1, 26.0, 25.1, 24.5, 21.5, 20.6, and 20.5 ppm) in Figure 5b are assigned to the methylenic carbons of the CHD unit in the copolymer. The peaks labeled Q are assigned to the methylenic carbon of the CAN unit in the copolymer. This CH_2 carbon is more deshielded than the CH_2 carbon of the CHD unit due to the presence of adjacent electronegative chlorine and cyano groups. It should be noted that the chemical shift of allyllic carbons, as in **2** or **3**, are not influenced very much by adjacent double bonds;[25] therefore, the above assignments made by considering the inductive effect of the cyano and chloro substituents are justified. A list of assignments and chemical shifts for each carbon is given in Table III for reference.

^1H NMR Spectroscopy. The 300-MHz ^1H NMR spectrum of poly(CAN/CHD) is shown in Figure 7. Comparing the ^1H NMR spectra of poly(cyclohexadiene) (PCHD), 3,3′-bicyclohexienyl (BCH),[27] and our poly(CAN/CHD), we note all of the copolymers' peaks are shifted downfield. The individual peaks assignments are made by comparing the ^1H–^{13}C chemical shift correlated (CSCM) and two-dimensional proton J-correlated spectroscopy (2D ^1H COSY) of the poly(CAN/CHD). The CSCM is shown in Figure 8 and the 2D ^1H COSY is shown in Figure 9. The CSCM in Figure 8 indicates that the peak at 2.7 ppm is correlating with the carbon peaks labeled P and R, previously assigned to the methine carbon of the CHD by the DEPT spectrum in Figure 6. Therefore, the broad singlet peak at 2.7 ppm in Figure 7 is assigned to the methine protons of the cyclohexene unit of the poly(CAN/CHD). The proton peak at ~2.1 ppm in Figure 8 is correlating with the carbon peaks labeled Q previously

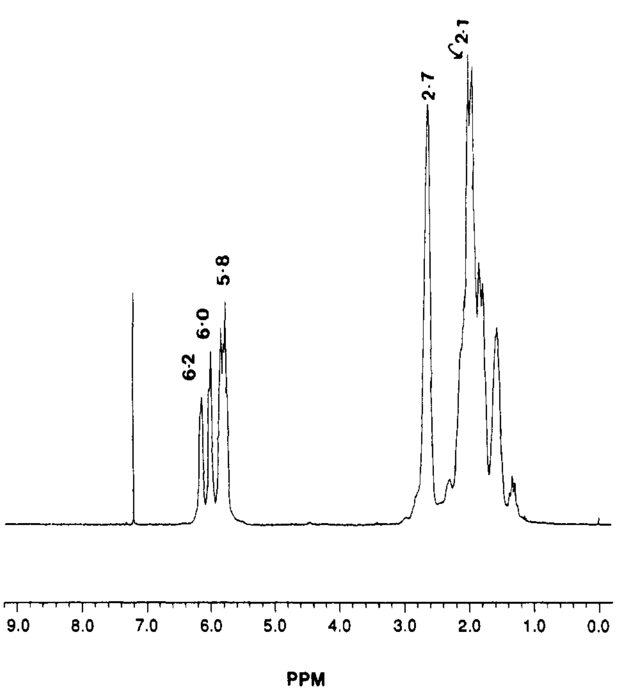


Figure 7. 300-MHz ^1H NMR spectrum of poly(CAN/CHD).

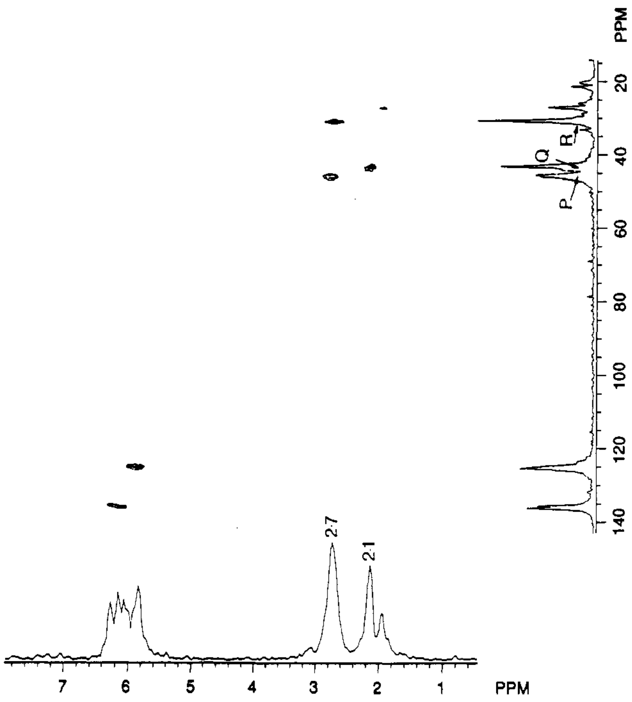


Figure 8. ^1H–^{13}C chemical shift correlation map for poly(CAN/CHD).

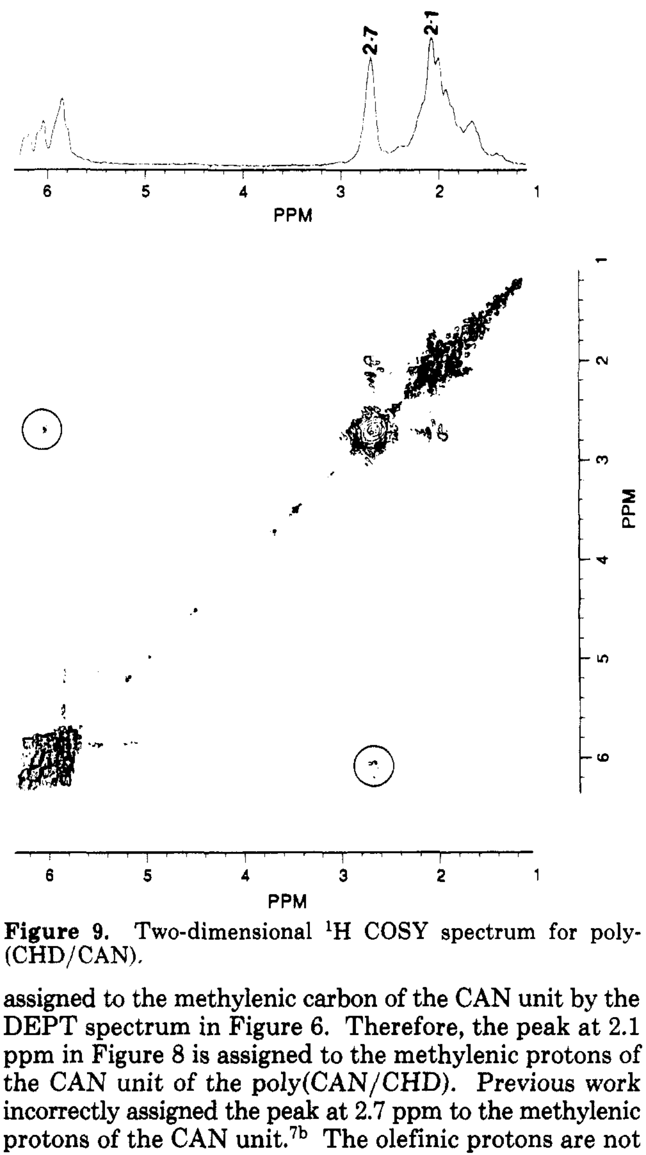


Figure 9. Two-dimensional ^{1}H COSY spectrum for poly(CHD/CAN).

assigned to the methylenic carbon of the CAN unit by the DEPT spectrum in Figure 6. Therefore, the peak at 2.1 ppm in Figure 8 is assigned to the methylenic protons of the CAN unit of the poly(CAN/CHD). Previous work incorrectly assigned the peak at 2.7 ppm to the methylenic protons of the CAN unit.[7b] The olefinic protons are not well-resolved in Figure 8. However, the CSCM clearly indicates that the downfield olefinic protons are correlating with the carbon peaks at ~135 ppm and the high-field olefinic protons are correlating with the carbon peaks at ~125 ppm. These olefinic protons are clearly resolved in the 2D ^{1}H COSY in Figure 9. The COSY spectrum indicates that the olefinic protons are coupled to the protons at 2.7 ppm. We have already assigned the peak at 2.7 ppm to the methine protons of the CHD unit by the CSCM above. A close analysis shows that all three sets of olefinic protons are coupled to these methine protons, while coupling to methylenic protons is not seen. The presence of structures 2 and 3 would show correlations of the olefinic protons, H_3 and H_6, with the methine protons but should also show the correlation of the H_4 and H_5 olefinic protons to methylenic species. This observation is in accord with essentially 1,4-linkages, shown in structure 1.

There are other possible reasons as to why the olefinic–methylenic cross correlations are not observed. Short spin–spin relaxation times for the methylene protons would result in signal loss during the COSY experiment. This problem has been addressed for the case of poly(vinyl chloride).[29] The coupling constants for the olefinic and methylenic protons may also be too small for any significant detection under the conditions of this COSY experiment. Spectra taken at higher resolution (i.e., 300–500 MHz) might show these cross correlations, if they exist. It should be noted that Schilling et al.[30] have been able to detect couplings between protons separated by four bonds, as compared to the three bonds in this case.

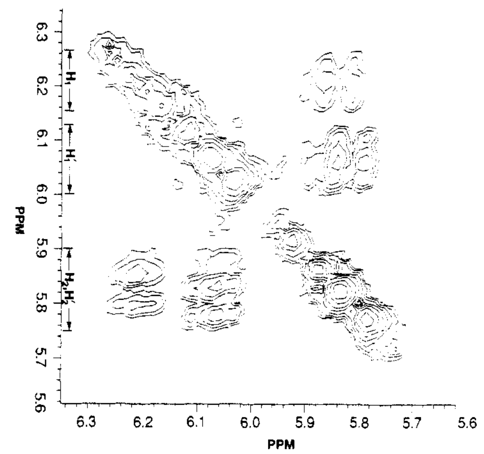


Figure 10. Expanded olefinic region of 2D ^{1}H COSY spectrum of poly(CHD/CAN).

Two-dimensional NMR techniques are definitely powerful tools for the structural elucidation of polymers. In this case, though we are unable to completely rule out the presence of 1,2-linkages across the cyclohexene unit, the combination of our NMR and FT-IR results strongly suggests that their existence in any substantial amount is doubtful.

The expanded 2D ^{1}H COSY for the olefinic protons of poly(CAN/CHD) is shown in Figure 10. There are two strong correlations, H_1, H_2 and H_1', H_2'. The comparison of protons attached to the olefinic carbons in structure 1 indicate that H_1 is more deshielded than H_2 due to its close proximity to the electron-withdrawing chlorine and cyano groups. Since the peak at about 6.2 ppm is coupled to the peak at about 5.8 ppm and the peak at about 6.0 ppm is also coupled to the peak at about 5.8 ppm, the peaks at 6.2 and 6.0 ppm are assigned to the proton H_1 and the peak at 5.8 ppm is assigned to the proton H_2 in structure 1. The integration of the 5.8 ppm peak is equivalent to the sum of the integrals for the 6.0 and 6.2 ppm peaks. The CHD unit in poly(CAN/CHD) contains two chiral centers and hence there are four possible stereoisomers. These four stereoisomers will lead to two pairs of enantiomers. Therefore, the two sets of peaks for H_1 are probably due to these two pairs of enantiomers. It should be noted that two sets of peaks are assigned to the olefinic protons in the crystalline and amorphous regions of poly(cyclohexadiene).[27] Our NMR results indicate this is not the case with poly(CAN/CHD), and differential scanning calorimetry (DSC) also indicates the copolymer is amorphous. Finally, the olefinic carbons in the ^{13}C NMR of poly(CAN/CHD) can be assigned easily. We have shown that the peaks at ~6.2 and 6.0 ppm can be attributed to the proton attached to the C_1-carbon and the peak ~5.8 ppm can be attributed to the proton attached to the C_2-carbon. When the CSCM in Figure 8 are compared, the peaks at 135 ppm are assigned to the carbon attached to H_1 and the peaks at 125 ppm are assigned to the carbon attached to H_2 as shown in structure 1.

Conclusions. The structure of the polymer obtained from the copolymerization of the charge-transfer complex of chloroacrylonitrile and cyclohexadiene has been shown to be a completely alternating copolymer. FT-IR spectral analysis of poly(CAN/CHD) reacted with KF, and the brominated copolymer treated with KF, suggests that the two possible 1,2-linkages are absent. The absence of either of the two types of 1,2-linkages in the cyclohexene unit strongly suggests that the other type of 1,2-linkage is also absent because they should be able to form with equal probability. Therefore, the FT-IR studies seem to show that the CAN/CHD copolymerization results mainly in 1,4-linkages in the cyclohexene unit irrespective of the initiator or temperature of polymerization.

An extensive nuclear magnetic resonance study involving ^{1}H, 2D ^{1}H COSY, ^{13}C NMR, DEPT, and CSCM allowed a complete structural assignment and indicated that the methine protons are allyllic to the double bond in the cyclohexene unit. This is consistent with the copolymer containing essentially 1,4-linkage in the cylcohexene unit, though the absolute exclusion of 1,2-linkages is not possible. The peaks for the various types of carbons in the CAN/CHD copolymer were assigned with use of the DEPT spectrum of the above copolymer.

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The Structure of Poly(D-(−)-β-hydroxybutyrate). A Refinement Based on the Rietveld Method

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ABSTRACT: The crystal structure of optically active microbial poly(D-(−)-β-hydroxybutyrate) has been refined with the Rietveld whole-fitting method applied to powder X-ray diffraction data. This natually occurring polymer gives rise to a very crystalline phase and therefore to very detailed and resolved powder profiles. Reliability of the refinement is discussed in relation to results obtained from previous studies on oriented-fiber diffraction patterns. The conclusion is that well-detailed powder profile data are highly discriminatory toward structural models not very dissimilar from each other. This result is considered an encouraging step toward a more general assessment of the accuracy of structural parameters obtained from best fitting of powder X-ray diffraction profiles.

Introduction

The structure of crystalline polymers can be determined or refined through best-fitting of X-ray powder diffraction profiles.[1,2] This technique, known as the Rietveld whole-fitting method,[3] is the only accessible X-ray diffraction approach when, for some reason, it is impossible to obtain oriented samples.

Some recent successful structure determinations, adopting this method,[1,2] raised the problem of what confidence should be attributed to the structural models one

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