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Characterization of a Carboxyl-Terminated Butadiene–Acrylonitrile Copolymer by Two-Dimensional Nuclear Magnetic Resonance

Treliant Fang

AT&T Bell Laboratories, Engineering Research Center, P.O. Box 900, Princeton, New Jersey 08540.

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ABSTRACT: A detailed NMR spectroscopic study was made on a carboxyl-terminated butadiene–acrylonitrile copolymer. Characterization of this polymer was done by using the DEPT technique to classify carbon types, and further structure unraveling was aided by H–H COSY and C–H COSY, as well as COLOC. Quantitative measurements of nitrile concentration in the copolymer can be made with a very long relaxation delay (60 s). End groups originating from 4,4′-azobis(4-cyanopentanoic acid) initiator as well as a Diels–Alder adduct of acrylonitrile and butadiene, 3-cyclohexene-1-carbonitrile, were also detected.

Introduction

Carboxyl-terminated butadiene–acrylonitrile (CTBN) type rubbers constitute an important class of telechelic polymers widely used in toughening thermoset resins.[1] Incorporation of CTBN polymer into epoxy resin of Bisphenol A diglycidyl ether type produces modified resins for encapsulating electronic circuitry.[2] Despite its extensive applications in industry, little knowledge regarding the structure of this polymer is found in the literature. Microstructures of the related butadiene–acrylonitrile copolymer and polybutadiene, on the other hand, are well-characterized. The structural information may be readily available from the literature to facilitate characterization of this vaguely studied telechelic polymer.

^{1}H and ^{13}C NMR spectroscopies have been used for structure determinations of polybutadiene,[3] polyacrylonitrile,[4] butadiene–acrylonitrile copolymers,[5] and butadiene–acrylonitrile–methacrylic acid terpolymer.[6] The peak assignments of previous studies were made entirely on spectral data obtained from more or less isomerically pure polymers, each containing a relatively high concentration of the expected isomeric units, in conjunction with the calculated peak positions using empirical additivity rules[7] derived from structurally similar small molecules. Since there are heavily overlapped peaks in the ^{1}H NMR spectrum, ^{13}C NMR spectroscopy is usually the method of choice.

Although ^{13}C NMR spectroscopy is good in terms of a wider range of chemical shifts and thus less possibility of overlapping peaks, problems associated with questionable assignments occasionally arise from steric-sensitive environments in the carbon skeleton.[8] Furthermore, the nuclear Overhauser effect (NOE) of different carbon types is usually not equal,[9] and the wide spin–lattice relaxation time (T_1) range makes quantitative measurements of carbon signals difficult. Quantitative detection of carbon signals is necessary if peak assignments are made on a statistical basis.[3f] The major goal of this study is to reduce uncertainty in peak assignments by using two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy.

The fast-evolving 2D NMR techniques have been applied extensively to structure determinations of small molecules as well as biological macromolecules such as nucleic acids and peptides. The application of this powerful tool on structure elucidation of synthetic polymers is, however, at its developing stage. Most of the 2D NMR studies on vinyl polymers were done by Bovey and his colleagues at AT&T Bell Laboratories.[10] In this paper the results of the long-range 2D heteronuclear chemical shift correlation (COLOC) as well as other 2D methods applied to the study of the CTBN polymer are discussed.

Experimental Section

Materials. Carboxyl-terminated butadiene–acrylonitrile (CTBN) of different acrylonitrile contents (25%, 18%, and 10%) were supplied by the B. F. Goodrich Co. Acrylonitrile–butadiene copolymer with 37–39% of acrylonitrile content and 4,4′-azobis(4-cyanopentanoic acid) were obtained from Aldrich Chemicals. All polymer samples were prepared in deuteriochloroform in 5-mm tubes with concentrations of 10% (v/w) for ^{1}H NMR and 25% for ^{13}C NMR measurements. The purified CTBN sample used in some experiments was purified by precipitating the polymer from an ethyl acetate solution by adding methanol. The procedure was repeated twice, and the purified polymer was stripped of solvent under vacuum.

NMR Methods. An inverse-gated decoupling technique[11] using WALTZ[12] broad-band decoupling sequences was applied to obtain quantitative carbon spectra. The distortionless enhancement by polarization transfer (DEPT) technique was performed to observe the multiplicity of each protonated ^{13}C NMR peak.[13] Homonuclear two-dimensional correlated spectroscopy (COSY-45) was performed by using the standard two-pulse sequence RD-90°-t_1-45°-FID, except that the second pulse applied was a 45° proton pulse[14] to reduce diagonal peak intensities. Homonuclear 2D J-resolved spectroscopy was performed using the spin–echo pulse sequence RD-90°-$t_1/2$-180°-$t_1/2$-FID.[15] Two-dimensional ^{13}C–^{1}H correlated spectroscopy (C–H COSY)[16] was performed by using composite 180° ($90°_x$-$240°_y$-$90°_x$) carbon pulses. The proton-decoupled C–H COSY experiment was performed by using the Bax–Rutar sequence.[17] The long-range two-dimensional heteronuclear chemical shift correlation experiments were performed by using the Kessler–Griesinger pulse sequence (COLOC).[18]

NMR Measurements. All spectra were obtained on a Bruker AC-250 spectrometer, operating at 250 MHz for ^{1}H NMR and 62.9 MHz for ^{13}C NMR. An Aspect 3000 computer and a QNP four-nuclei probe operating at room temperature were used. Chemical shifts were referenced to the $CDCl_3$ triplet centered at δ 77.00 for ^{13}C NMR and the δ 7.26 residual $CHCl_3$ peak for ^{1}H NMR. Typical 90° pulses were 5.0 μs for ^{13}C NMR and 11.0 μs for ^{1}H NMR. The short and strong ^{13}C pulse is required to ensure a homogeneous excitation leading to quantitative measurements in the inverse-gated decoupling experiments.[19] The ^{13}C DEPT spectra were recorded by using 32K data points over two separate spectral regions: from 15 to 63 ppm and from 105 to 170 ppm. The digital resolutions for these two regions were 0.183 and 0.244 Hz/pt, respectively. Resolution enhancement functions (GB = 0.1, LB = −0.2) were introduced prior to Fourier transformation. A total of 3000 scans were averaged with a recycle time of 6.5 s. The inverse-gated decoupling spectra were recorded by using 32K data points over a spectral width of 16 130 Hz, with the relaxation delay set at 60 s, and a total of 1600 scans accumulated. Similar conditions were applied on a sample doped with 1% chromium acetylacetonate, and a relaxation delay of 10 s was used to test the effectiveness of carbon quantitation.

The 2D COSY-45 spectrum was obtained with a 10% CTBN solution in deuteriochloroform. A total of 16 scans (plus two dummy scans[20]) of 128 t_1 increments were accumulated with a relaxation delay of 2 s. The initial matrix size was 2000 Hz (2K) and 1000 Hz (128w) in F_2 and F_1, respectively. A sine-bell apodization function without phase shift was applied in both dimensions before Fourier transformation. Symmetrization after FT afforded a digital resolution of 1.95 Hz/pt in both dimensions.

The 2D J-resolved spectrum was obtained with a 10% CTBN solution. A total of 24 scans (plus two dummy scans) of 128 t_1 increments were recorded using an relaxation delay of 2 s. The initial size was 2000 Hz (2K) and 62.5 Hz (128w) in F_2 and F_1, respectively. A sine-bell function without phase shift was applied before Fourier transformation. The transformed spectrum was tilted[21] and symmetrized to afford digital resolutions of 0.24 Hz/pt in both dimensions.

The 2D C–H COSY and proton-decoupled C–H COSY spectrum was obtained with a 25% CTBN solution. Aproximate value of the spin–spin relaxation time of the sample was estimated from the FID.[22] This value was then used to set the ^{1}H sweep width, which also determines the t_1(max). A total of 256 scans were accumulated over 128 t_1 increments with a relaxation delay of 4 s. The initial matrix size was 10 000 Hz (2K) and 2000 Hz (128w) in F_2 and F_1, respectively. A sine-bell apodization function without phase shift was applied in both dimensions prior to Fourier transformation. The delay times Δ_1 and Δ_2 were set at 4 and 2 ms, respectively. The digital resolutions after zero-filling in F_1 were 9.77 Hz/pt in F_2 and 7.81 Hz/pt in F_1. The total acquisition time was 19 h for the proton-decoupled experiment.

The COLOC spectrum was obtained with a 25% CTBN solution. Two experiments with different sets of Δ_3 and Δ_4 values were used with the hope of detecting different correlation patterns contributing from different values of $^3J_{C-H}$. In the first experiment, a total of 196 scans (with two dummy scans) were accumulated over 128 t_1 increments with a relaxation delay of 8 s. The initial matrix size was 11 904 Hz (2K) and 2000 Hz (128w) in F_2 and F_1, respectively. A square sine-bell function with $\pi/4$ phase shift was used as the filtering window in both dimensions during Fourier transformation. The delay times Δ_3 and Δ_4 were set at 62 and 31 ms, respectively. The digital resolutions after zero-filling in F_1 were 11.63 Hz/pt in F_2 and 7.81 Hz/pt in F_1. The total acquisition time was 58 h.

In the second experiment, the delay times Δ_3 and Δ_4 were set at 45 and 22 ms, respectively. The experiment was accumulated over 128 t_1 increments, with 120 scans including two dummy scans in each increment, and the relaxation delay was 3 s. The total acquisition time was 14 h.

Results and Discussion

^{1}H NMR Results. Figure 1 shows the ^{1}H NMR spectrum of a CTBN X13 (25% acrylonitrile) sample. The spectrum features a combination of signals of polybutadiene (δ 5.42, 5.35, 5.08, 4.99, 2.04, and 1.43) and butadiene–acrylonitrile copolymer (δ 5.54, 5.49, 5.40, 2.57, 2.32, 2.28, 2.08, and 1.65). Assignments of most of these peaks have been reported,[3a,3e,5a,5b] and a summary of the literature results is listed in Table I. In addition to these known peaks, unassigned peaks were also found in the ^{1}H NMR spectrum, e.g., the peak located at δ 5.08. A broad peak at δ 2.82 and a cluster of peaks centered at δ 1.31, visible in the crude CTBN spectra, were subsequently removed after purifying the polymer by precipitation from an ethyl acetate solution with methanol. The chemical nature of these "removable" peaks will be discussed further in the carbon spectra section.

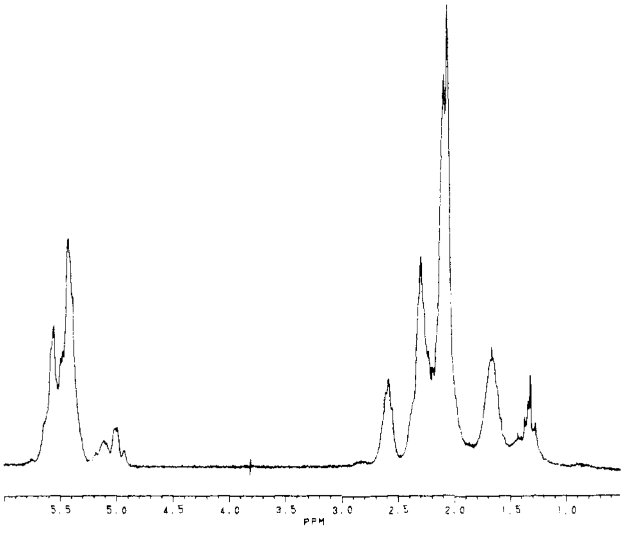


Figure 1. ^{1}H NMR spectrum of CTBN X13 rubber in deuteriochloroform.

Table I
Previous ^{1}H NMR Assignments of Polybutadiene and Butadiene–Acrylonitrile Copolymer

chemical shift	sequence	H type	chemical shift	sequence	H type
5.54	BABAB	=CH–	5.49	ABBAA	=CH–
5.42	*trans*-1,4-BB	=CH–	5.40	ABBAB	=CH–
5.35	*cis*-1,4-BB	=CH–	4.99	1,2-BB	=CH_2
2.57	BAB	CH	2.32	AB	CH_2
2.28	AB	CH_2	2.08	ABB	CH_2
2.04	BB	CH_2	1.65	AB	CH_2
1.43	1,5-BB	CH_2			

Before a detailed discussion can be made, the following nomenclature was adapted: A refers to an acrylonitrile unit, B refers to a butadiene unit; AB refers to acrylonitrile–butadiene diad with the methylene carbon of A pointing to the *left*; V refers to the vinyl-containing group as that in the 1,2-polybutadiene, with the methylene carbon β to the vinyl pointing to the *left*; C refers to a cis double bond in the polybutadiene, and T refers to a trans double bond in the polybutadiene; BB refers to a butadiene diad without specifying its isomeric configuration; a primed unit refers to a reversed methylene connection; i.e., the methylene is pointing to the *right*, as BA′V refers to the following triad:

$$\text{-CH}_2\text{CH=CHCH}_2\text{CH(CN)}\mathit{CH}_2\text{CH}_2\text{CH(CH=CH}_2\text{)-}$$

A boldfaced unit with a structural subunit specified in parentheses refers to the specific group responsible for the absorption in the spectrum; i.e., **AB**(CH) indicates the methine of the acrylonitrile in an AB diad.

Figure 2 shows the COSY-45 spectrum of CTBN X13. In this spectrum, the 1D peaks are projected along the diagonal, and the cross-peaks that are J-coupled to each other appear outside the diagonal as symmetric pairs. Cross-peaks are reported by their respective coordinates in the F_2 and F_1 dimensions. In the low-field region, cross-peaks similar to those of the vinyl group in 1,2-polybutadiene [δ 4.96 (B**V**(CH_2)) and 5.60 (B**V**(CH))] are readily identified (cross-peak 1). The rest of the vinyl peaks of the CTBN are therefore assigned to the 1,2-butadiene–acrylonitrile (VA) diad, which shows a cross-peak at δ 5.08 (**V**A(CH_2)) and 5.38 (**V**A(CH), cross-peak 2). In the high-field region, the cross-peaks are far more complicated. The allylic protons are identified by their coupling with the olefinic protons. Four groups of the cross-peaks appear in the upper left and the lower right of the

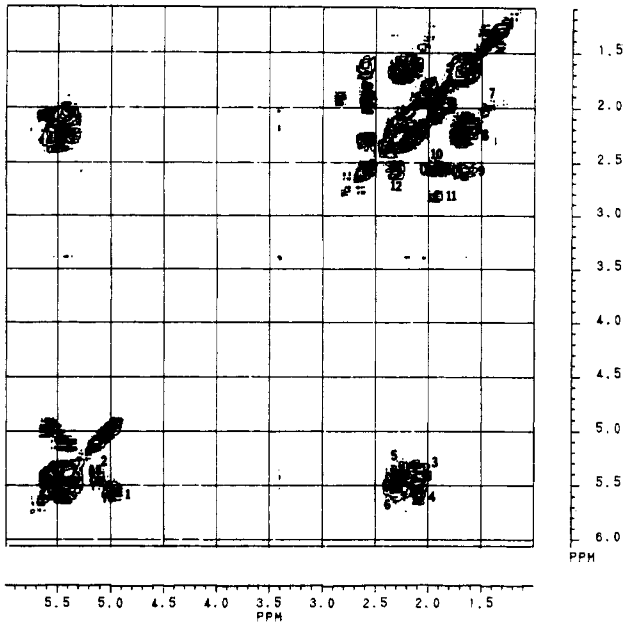


Figure 2. H–H COSY-45 spectrum of the CTBN X13 spectrum. See text for the labels.

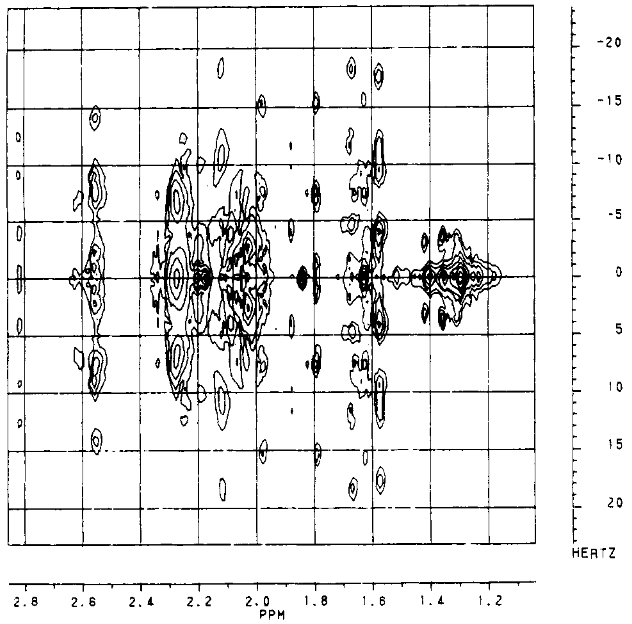


Figure 3. Part of the H–H J-resolved spectrum of CTBN X13.

2D spectrum. The assignments are made as follows. The first high-field cross-peak (cross-peak 3) is assigned to the 1,4-butadiene–butadiene diad [δ 2.04 (BB(CH$_2$)) and 5.40 (BB(CH))], and the cross-peak below (cross-peak 4) is assigned to the 1,4- and 1,2-polybutadiene (BV) diad [(δ 2.07 (BV(CH$_2$) and 5.60 (BV(CH))]. This assignment was made based on the knowledge of chemical shifts of different polybutadiene isomers assigned by the 1D experiments as well as their corresponding cross-peaks found in the olefinic region. The third cross-peak (cross-peak 5) located to the left of the first one is assigned to the BAB triad [δ 2.28 (**B**AB(CH$_2$)) and 5.37 (**B**AB(CH))]. Similar assignment is made on the cross-peak below [cross-peak 6, δ 2.32 (BA**B**(CH$_2$)) and 5.54 (BA**B**(CH))].

In the aliphatic region, six groups of cross-peaks were resolved in the 2D spectrum. The assignments of these peaks were made in a similar manner by their interproton connectivity. The weak cross-peak (cross-peak 7) that appears at δ 1.45 (BV(CH$_2$)) and 2.07 (BV(CH)) is recognized readily by the relative high-field peak of the methylene β to the double bonds. The bulky cross-peak 8 reflects the complexity of the coupling patterns existing between the allylic protons and the methylene protons of acrylonitrile unit (BAB). The methylene and methine cross-peak of the BAB triad was found as cross-peak 9 at δ 1.62 (BAB(CH$_2$)) and 2.56 (BAB(CH)). The allylic–methine cross-peak of the AB diad was assigned as cross-peak 12.

The cross-peaks left unassigned in the COSY-45 spectrum are now classified into two categories: those that can be eliminated by purification of the polymer and those that persist after purification. Cross-peaks in the first category are found at the following positions: δ 1.45 and 1.30; 1.93 and 2.89 (cross-peak 11); 2.35 and 2.89; 2.35 and 5.55. These peaks are considered to be impurities in the CTBN polymer and the chemical nature of these impurities are discussed in ^{13}C NMR Results. Peaks in the second category (δ 1.8–2.0 and 2.55, cross-peak 10) exhibit complicated coupling patterns as indicated in the J-resolved 2D spectra (Figure 3). These are not allylic peaks, since no cross-peak with the olefinic protons was found. The six possible nonallylic methylene containing sequences present in the CTBN polymer are the following: BA, BV, VA, VV, AA, and those methylenes of the end groups. The first two have been ruled out, since they are in contradiction to previous assignments and the signal intensities of the AA sequence would be too weak to account for the cross-peaks in this region due to the low monomer reactivity ratio of acrylonitrile.[5a,5b] The VV sequence is excluded by its characteristic high-field methylene peak (δ ~1.4). This leaves only two possible sources for cross-peak 10: VA and/or the end groups. The direct evidence of the nature of these methylene groups comes from detailed analysis of the 2D J-resolved spectrum. The three cross-sections at δ 1.79, 1.98, and 2.55 share an identical coupling constant of 7.57 Hz, in agreement with the ABX$_2$ methylenes in the 4-cyanopentanoic acid termini.[23]

^{13}C NMR Results. Figure 4 shows the inverse-gated decoupling ^{13}C NMR spectrum of CTBN X13. Quantitative nitrile carbon integration at δ 121.64 and 121.51 can be obtained only when sufficient relaxation delay time (60 s) is used. The remaining carbon signals can be acquired quantitatively by applying a delay time of 10 s.[24] The acrylonitrile content of the copolymer was obtained by the following equations:

$$B = (T - N)/2$$

$$\%\ \mathrm{A} = N/(B + N)$$

where B is the number proportion to moles of butadiene in the copolymer, T is the integral of the olefin and nitrile carbons, and N is the integral of the nitrile carbon.

The acrylonitrile content measured by this method is about 10% lower than the elemental analysis (23% of acrylonitrile rather than 25% reported). Similarly obtained is the carboxyl content of 2.1% (2.4% reported). The reproducibility of these measurements is usually quite good (~5%), if proper care is taken to ensure flat integral base lines.

A complete assignment of the complicated carbon spectrum seems unlikely at first glance. More than 100 resolved lines were found in the spectrum. The assignment started with spectral editing of carbon peaks using DEPT technique. The delay in the DEPT sequence was chosen in such a way that methylene carbons appear as positive peaks and both methyl and methine carbons appear as negative peaks. Figures 5 and 6 show the DEPT spectra of the aliphatic as well as the olefinic part of the copolymer. Note that a resolution enhancement function has

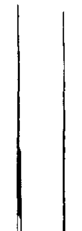


Figure 4. Inverse-gated decoupling ^{13}C NMR spectrum of CTBN X13.

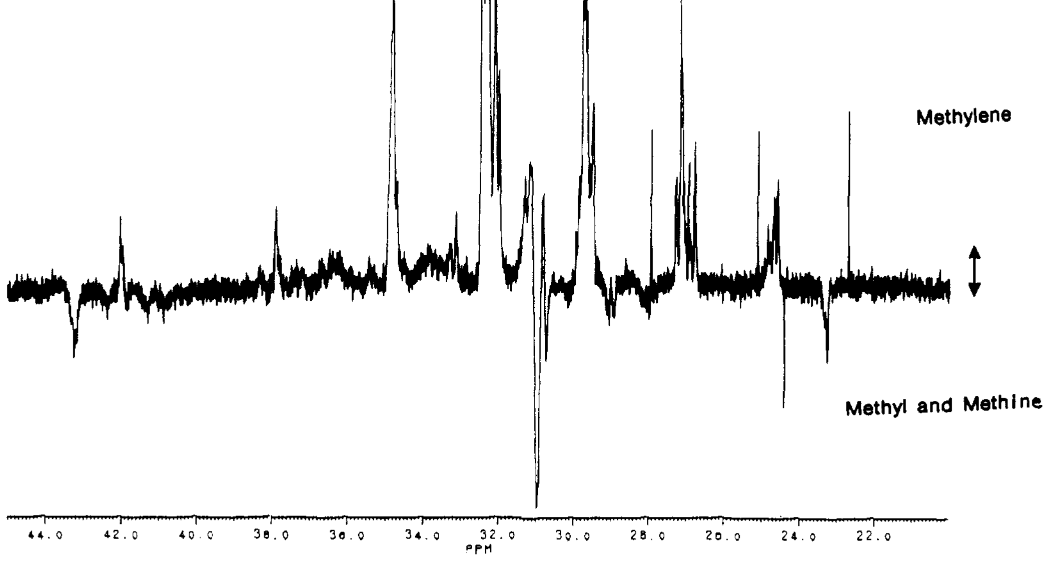


Figure 5. High-field region of the DEPT spectrum of CTBN X13. Methylene carbons appear as positive peaks, and methine and methyl carbons appear as negative peaks. Resolution enhancement was performed by using GB = 0.1 and LB = −0.2 prior to FT.

been applied to the spectra so that peaks belonging to small molecules can be identified by their relatively sharp lines. Six sharp lines were found, and their chemical shifts (δ 126.81, 123.11, 27.94, 25.10, 24.41, and 22.78) match

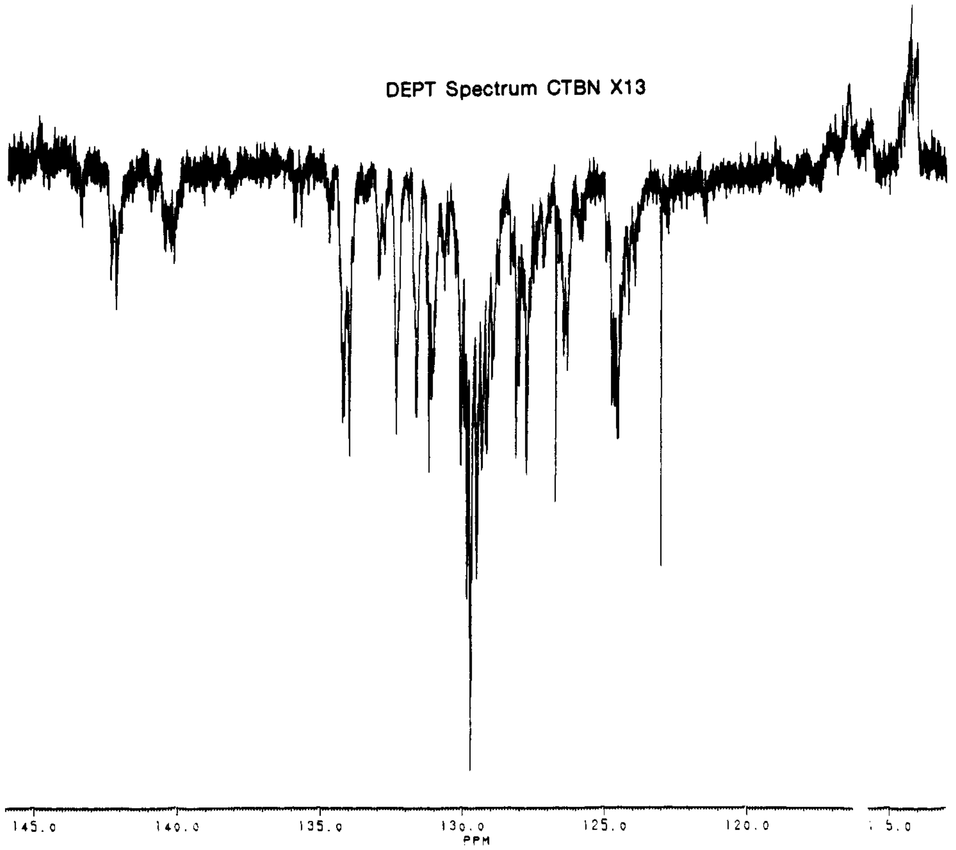
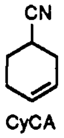


Figure 6. Low-field region of the DEPT spectrum of CTBN X13. Olefinic methylene carbons appear as positive peaks, and olefinic methine carbons are exhibited as negative peaks. Resolution enhancement was performed by using GB = 0.1 and LB = –0.2 prior to FT.

those of 3-cyclohexene-1-carbonitrile (CyCA).



CyCA

Three out of the total of 11 negative peaks in the high-field region of the DEPT spectrum are readily assigned due to their known chemical shifts. The peak at δ 43.31 belongs to VT(CH),[3b] the peak at δ 31.05 belongs to AT(CH),[5d] and the peak at δ 23.28 belongs to $I(CH_3)$ (I refers to the 4-cyanopentanoic acid end group).

$$I = -C(Me)(CN)CH_2CH_2COOH$$

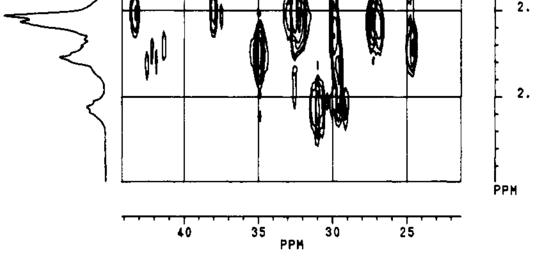
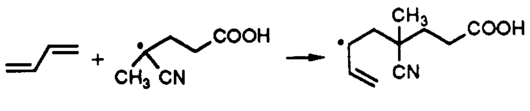


Figure 7. Proton-decoupled C–H COSY spectrum of a purified CTBN X13. Only the high-field region is shown. The respective 1D spectra were plotted along the two projections.

The remaining eight negative peaks are all methine carbons and their assignments are made by the positions of cross-peaks in the C–H COSY spectrum (Figure 7) as well as the expected chemical shifts calculated by a known method.[25] The assignments of these carbon peaks are listed in Table II. Three methylene peaks in the aliphatic region are worth further discussion. The peak at δ 42.03 exhibits the same chemical shift as that for $VVV(CH_2)$.[3c] The low vinyl concentration (14%) in the CTBN polymer, however, completely eliminates this possibility. The cross-peak in the C–H COSY spectrum shows a diffused proton contour centering at δ 2.22, indicative of coupling between the carbon in question and the two diastereotopic methylene protons. In the COLOC spectrum (Figure 8) a cross-peak with the methyl protons of the 4-cyanopentanoic acid end group was found. Calculations were made on several combinations of monomers, and the end group finally pointed the structure of this peak to TV′I (CH_2). The relatively high concentration of this triad in the CTBN polymer is rationalized by the stability of secondary allyl radicals.[26] Apparently the following allyl radical forming initiation step is preferentially weighted over other initiation steps:



The second methylene peak of interest is located at δ 29.54. This previously unreported peak is one of the two methylene carbons of the *cis*-2-butene next to an acry-

Table II
Assignments of ^{13}C NMR Peaks of the CTBN X13 Copolymer

chemical shift (δ)	sequence	carbon type	chemical shift (δ)	sequence	carbon type
176.40	I	COOH	143.46	VV	-CH=
142.45	VC	-CH=	142.28	VT	-CH=
140.56	VA	-CH=	140.36	VA′	-CH=
140.24	TV′I	-CH=	134.31	TTA	-CH=
134.07	TTAT	-CH=	133.06	TV′I	-CH=
133.01	TV′A	-CH=	132.41	ATA	-CH=
131.73	TTTA	-CH=	131.27	ATTA	-CH=
131.17	A′TTA	-CH=	130.15	VTT	-CH=
129.93	CTT	-CH=	129.80	TTT	-CH=
129.59	TTV	-CH=	129.40	TVT	-CH=
129.22	TCT	-CH=	129.05	TCV	-CH=
128.20	TTTA	-CH=	127.85	ATTA	-CH=
126.81	CyCA	-CH=	126.53	ATA	-CH=
126.40	ATAT	-CH=	124.85	TTA	-CH=
124.75	TTAT	-CH=	124.66	TTA	-CH=
124.25	ATV′	-CH=	124.02	ATV′	-CH=
123.11	CyCA, I	-CH=, CN	122.20	CyCA	CN
122.05	AC	CN	121.64	TAT	CN
121.51	AT	CN	120.26	AA	CN
117.15	AV	$=CH_2$	116.44	TV′I	$=CH_2$
115.71	AV′	$=CH_2$	114.31	VT	$=CH_2$
114.09	VC	$=CH_2$	43.31	TVT	CH
42.44	TV′I	CH, e or t[a]	41.28	TV′I	CH, e or t[a]
42.03	TV′I	CH_2	41.88	VA	CH, e or t[a]
41.03	VA	CH, e or t[a]	40.43	TVI	CH
38.40	AVT	CH_2	37.96	VT	CH_2
37.20	TV′I	CH_2	36.34	TA′I	CH_2
36.09	I	C	35.45	TVV	CH_2
34.86	TA′	CH_2	34.70	AAT	CH_2
33.86	TV	CH_2	33.21	I	CH_2
33.11	I	CH_2	32.49	TTT, VC	CH_2
32.36	TTA	CH_2	32.14	TTTA	CH_2
32.05	TTAA	CH_2	31.34	AT	CH_2
31.21	TAT	CH_2	31.05	TAT + AT	CH
30.85	A′VT	CH_2	30.77	A′VT	CH
30.11	I	CH_2	29.95	TV	CH_2
29.78	TA	CH_2	29.54	AC	CH_2
29.41	CI	CH_2	29.10	VAT	CH, e or t[a]
28.10	A′I	CH, e or t[a]	27.94	CyCA	CH_2
27.28	CC	CH_2	27.16	CT	CH_2
26.94	CCA	CH_2	26.78	CC	CH_2
25.10	CyCA	CH_2	24.95	CI	CH_2
24.85	CVA	CH_2	24.66	CV	CH_2
24.60	CA	CH_2	24.41	CyCA	CH
23.28	TV′I	CH_3	22.78	CyCA	CH_2
22.15	TVI	CH_3			

[a] Erythro or threo defined by a Newman projection of this carbon and the other nearest asymmetric center.

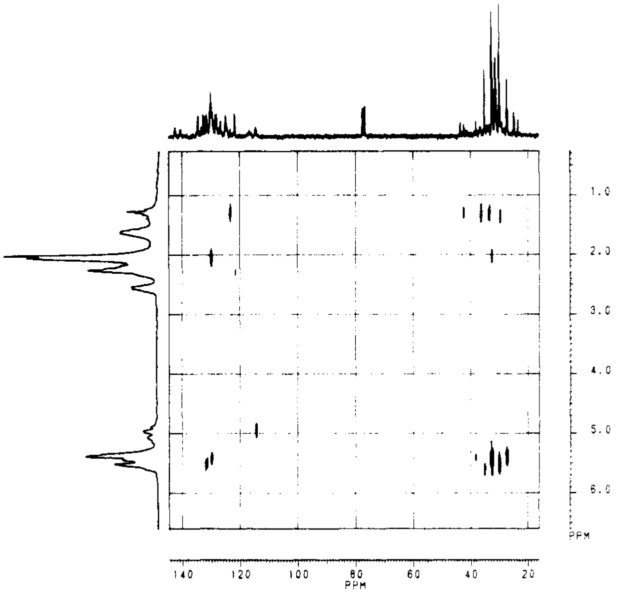


Figure 8. COLOC spectrum of CTBN X13. The delay Δ_3 was set at 62 ms. The respective 1D spectra were plotted along the two projections.

lonitrile unit ($AC(CH_2)$). Similarly found was the peak at δ 24.60, corresponding to the other methylene carbon of the *cis*-2-butene ($CA(CH_2)$).[5d] The integration of the acrylonitrile peaks between δ 30 and 32 (mainly methine and methylene carbons of AB and ABA) is smaller than 2-fold of the area of the CN peaks at δ 121.51 (AT) and 121.64 (TAT), indicating that hidden peaks of acrylonitrile origin are spreading outside this expected chemical shifts region. A quick check in the DEPT spectrum readily picks up some other peaks of acrylonitrile origin: those peaks are located at δ 29.10 and 28.10. These peaks appear as multiplets and are assigned to the diastereomers (erythro and threo, as defined by this asymmetric carbon and the other nearest asymmetric carbon) of VAT and A′I, respectively. The missing methylene carbons of the acrylonitrile unit, however, can not be located with certainty due to severe overlapping with other methylene carbon peaks.

The quaternary carbon and the nitriles of CTBN were located by checking the missing peaks between the DEPT and the broad-band decoupled spectra. The nitrile carbon of the 4-cyanopentanoic acid end group is overlapping with one of the olefinic carbons in 3-cyclohexene-1-carbonitrile (CyCA) at δ 123.11. The CN carbon of CyCA was found at δ 122.20. The quaternary carbon of the end group was found at δ 36.09 as multiplets. Most of these assignments were confirmed by COLOC experiments (vide infra).

In spite of rigorous efforts to locate the two methylene carbons of the 4-cyanopentanoic acid end group from available NMR data, little progress was made because of the ambiguous carbon assignment of the initiator 4,4′-azobis(4-cyanopentanoic acid) (ACPA)[27] and the complexity of the proton coupling patterns. The carbon next to a quaternary center is subject to severe steric interactions, which make validity of empirical additivity rules questionable.[24] Assignment of carbon signals without referring to calculated values can still be made through the C–H COSY spectrum if a resolved proton spectrum is available. The fact for ACPA is that no complete assignment can be made using 1D and C–H COSY data: both methylene carbons exhibit diffused cross-peaks with a proton at δ 2.4. A COLOC experiment was therefore performed on a deuterioacetone solution of the model compound ACPA, and the methylene carbon (δ 34.33) exhibiting a cross-peak with methyl is assigned to C-3. The other methylene carbon (δ 30.11), which does not give any long-range cross-peak, is assigned to C-2. Having the chemical shifts of the methylene carbons of the model compound in mind, the C-3 carbon of the end group was located at δ 33.11. This signal also shows a diffused cross-peak with protons between δ 1.6 and 2.2 in the C–H COSY spectrum.

C–H COSY Results. The spin–spin relaxation time for CTBN was found to be 30 ms, and a very short t_1 increment (0.125 ms) was applied for sensitivity considerations,[22] since resolution in the F_1 dimension is not a concern. The result of a short t_1 increment is surprising: cross-peaks of some weak methine signals (less than 0.5% of total carbons) were readily detected with a total acquisition time of less than 4 h. Experiments per-

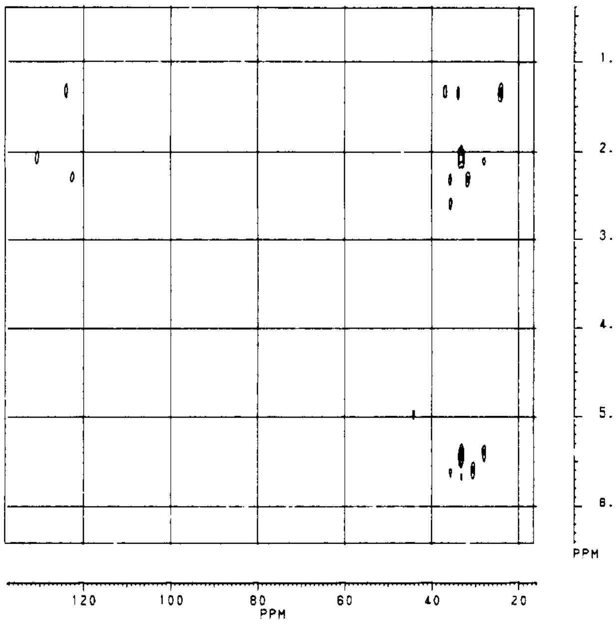


Figure 9. COLOC spectrum of CTBN X13. The delay Δ_3 was set at 45 ms.

formed on other synthetic polymers also confirm the advantage of using a relatively short t_1 increment, and the results of cross-peak intensities vs t_1 duration will be published elsewhere. In addition to the strong cross-peaks found in the expected olefinic and aliphatic regions, some weaker diagnostic cross-peaks were also found in the C–H COSY spectrum.

The dramatic separation of the overlapped methine and methylene peaks of acrylonitrile origin (δ 31) in the 2D spectrum demonstrates the capability of this technique. In the low-field region the spectral resolution is, however, not high enough to separate the cis and trans olefinic carbons. The detection of cis double bonds has to rely on the presence of high-field shifted allylic carbons next to it and a COLOC experiment to confirm this connectivity (vide infra). The four pairs of vinyl cross-peaks found in the high field (δ 114 to 116) and the low field (δ 140 to 142) clearly define the chemical shifts of these vinyl protons, which are unresolvable in the ^{1}H NMR spectra. The methylenes of the 4-cyanopentanoic acid end group are not clearly located. The diffused cross-peak at δ ~33 is assigned to C-3 of the end group by its correlation with the expected proton chemical shift between δ 1.6 and 2.2. The C-2 cross-peak is, however, not obvious to locate due to its proximity to a congested spectral band in the ^{13}C NMR spectrum, in addition to the complicated proton coupling patterns. To increase the cross-peak intensity, a proton-decoupled C–H COSY experiment was performed to eliminate the coupling from protons β to C-2.[17] Results from this experiment were encouraging. Sharper cross-peaks were obtained even with half the number of scans used by the normal C–H COSY experiment (Figure 7). The C-2 cross-peak was observed and located at δ 30.11 and 2.55.

COLOC Results. As a final check on the peak assignments, two COLOC experiments were performed on the CTBN polymer. The first spectrum (Figure 8) was acquired using a long relaxation delay (8 s) to obtain a stronger cross-peak on the quaternary carbon (δ 36.09) of the end group. The delay of Δ_3 was set at 62 ms, corresponding to the detection of a $^3J_{CH}$ of 8.1 Hz. The second spectrum (Figure 9) was acquired using a shorter relaxation delay (3 s) and a shorter Δ_3 (45 ms, $^3J_{CH}$ of 11.1 Hz). The major difference between these two spectra is the presence of cross-peaks at δ 42.03 and 1.29 (TV′I(CH$_2$, CH$_3$)) and δ 29.41 and 1.32 (CI(CH$_2$, CH$_3$)) in the first spectrum and the cross-peak at δ 43.31 and 4.98 (VT(CH, =CH$_2$)) in the second, in addition to the residual one-bond C–H cross-peaks. Careful examination of the cross-sections of the cross-peaks in the first spectrum also shows an additional cross-peak at δ 29.41, 5.35 (CI(CH$_2$, -CH=)). The detection of cis olefinic cross-peaks in the first spectrum is rationalized by selective detection of the smaller coupling constant $^3J_{CH}$[28] between the allylic protons and the proton across the cis double bond. No cross-peak relating to the C-2 peak in the end group was found by COLOC experiments. This can be attributed to the modulation effects from homonuclear H–H couplings. It is reported that the cross-peak intensity is governed, among other factors, by the term $\cos \pi\Delta_3 J_{HH}$, where J_{HH} is the homonuclear coupling constant of the remote proton.[29] It is apparent that if the value of J_{HH} is close to that of $1/2\Delta_3$, no signal would be detected. The value of J_{HH} in C-2 of the end group was found to be ~8 Hz,[23] and therefore the C-4, C-2H cross-peak is not expected to appear in the first COLOC experiment. The assignments of all cross-peaks found in COLOC experiments are listed in Table III, and part of the structural sequences are shown in Figure 10.

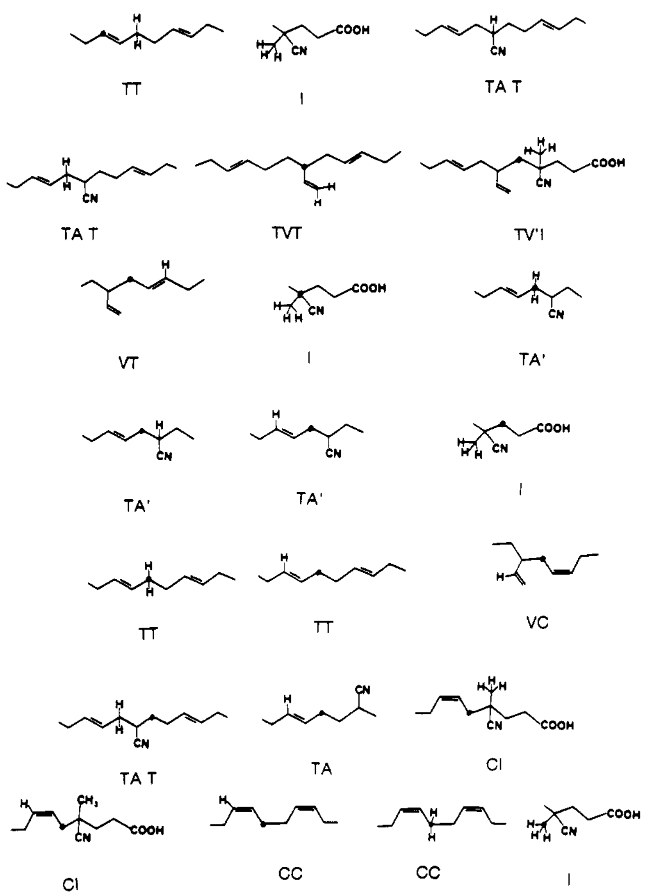


Figure 10. Part of the structural units of CTBN X13 observed by COLOC experiments. The coupled nuclei are shown as dark dots and labeled hydrogens. Nitrile carbons are not labeled.

Conclusions

The structure of a CTBN copolymer was assigned by using 1D as well as 2D NMR techniques. Sharp spectral lines of small molecules can be identified readily from polymer peaks by using resolution enhancement. The Diels–Alder adduct of acrylonitrile and butadiene was found as an impurity in the CTBN polymer. The end

Table III
Cross-Peaks Found by the COLOC Experiments

sequence[a]	cross-peak (^{13}C, ^{1}H)	coupling type	sequence	cross-peak (^{13}C, ^{1}H)	coupling type
TTTA	131.73, 5.51	$^{1}J_{CH}$	VTT	130.15, 5.41	$^{1}J_{CH}$
TTT	129.80, 5.41	$^{1}J_{CH}$	VT	114.31, 5.01	$^{1}J_{CH}$
TT	129.85, 2.07	$^{3}J_{CH}$	I	123.11, 1.32	$^{3}J_{CH}$
TAT	121.64, 2.57	$^{2}J_{CH}$	TAT	121.64, 2.29	$^{3}J_{CH}$
TVT	43.31, 4.98	$^{3}J_{CH}$	TV′I	42.03, 1.29	$^{3}J_{CH}$
VT	37.96, 5.39	$^{3}J_{CH}$	TA′I	36.09, 1.32	$^{2}J_{CH}$
TA′	34.86, 2.32	$^{1}J_{CH}$	TA′	34.86, 2.57	$^{2}J_{CH}$
TA′	34.86, 5.57	$^{3}J_{CH}$	I	33.21, 1.35	$^{3}J_{CH}$
TTT	32.49, 2.04	$^{1}J_{CH}$	TTT	32.49, 5.42	$^{3}J_{CH}$
VC	32.49, 5.67	$^{3}J_{CH}$	TAT	31.05, 2.32	$^{3}J_{CH}$
TA	29.78, 5.57	$^{3}J_{CH}$	CI	29.41, 1.32	$^{3}J_{CH}$
CI	29.41, 5.35	$^{3}J_{CH}$	CC	27.28, 2.04	$^{1}J_{CH}$
CC	27.28, 5.38	$^{3}J_{CH}$	TV′I	23.28, 1.35	$^{1}J_{CH}$

[a] For structures of the sequences, see Figure 10.

group of 4-cyanopentanoic acid was also found in the polymer and is attributed to the initiator used in the polymerization reaction. The relatively high concentration of 1,2-butene end-group linkage is explained by the stability of secondary allyl radicals, which is generated by the attack of initiator on butadiene. The structure of this linkage was observed in the DEPT spectrum and confirmed by both C–H COSY and COLOC experiments. Block polybutadiene units were found in the CTBN polymer, but no block polyacrylonitrile unit was detected. The advantage of spreading a congested 1D spectrum into two dimensions is demonstrated by a complete separation of the methylene and methine groups of an acrylonitrile unit in the CTBN polymer. The results of this study further confirm previous 1D NMR assignments on some of the polymer sequences.

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