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Chemical Characterization of CTBN and its Epoxy Adduct

Kansas City Division

R. E. Smith

KCP-613-4222

Published January 1990

Topical Report

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CHEMICAL CHARACTERIZATION OF CTBN AND ITS EPOXY ADDUCT

R. E. Smith

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Topical Report
R. E. Smith, Project Leader

Project Team:
E. N. Fuller

Technical Communications
Kansas City Division

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CHEMICAL CHARACTERIZATION OF CTBN AND ITS EPOXY ADDUCT

KCP-613-4222, Topical Report, Published January 1990

Prepared by R. E. Smith

This report describes the analysis of carboxyl-terminated butadiene (CTB), carboxyl-terminated butadiene/acrylonitrile (CTBN), and a CTBN adduct prepared by reaction with Epon 828. Data from gel permeation chromatography, nuclear magnetic resonance spectroscopy, high performance liquid chromatography, and ion chromatography are presented and discussed. Quantitative methods based on carbon-13 and proton NMR for analyzing CTBN are described. Proton NMR was found to be useful in identifying lots that have an abnormal amount of CTBN protons. One such lot exhibited a phase separation of a polybutadiene impurity. Carbon-13 NMR was found to be capable of determining nitrile content directly. Carbon-13 NMR had a relative standard deviation of 8.3% and a proton NMR of 3.9%. Proton NMR was found to be useful in identifying lots that have 5% more CTBN protons than other lots.

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SUMMARY

Methods have been developed for analyzing a carboxyl-terminated butadiene/acrylonitrile (CTBN), Hycar 1300 X8, from B. F. Goodrich, Akron, OH, and the CTBN-epoxy adduct, KCD 20102. For comparison, carboxyl-terminated butadiene (CTB), Hycar 2000 X162, from B. F. Goodrich was analyzed also. The molecular weight distribution was measured by gel permeation chromatography (GPC) using a Waters model 150C gel permeation chromatograph equipped with three microstyrogel columns in tandem, with 1000, 500, and 100 angstrom pore size and refractive index detection. High performance liquid chromatography (HPLC) was performed on a Dionex model 4000 liquid chromatograph equipped with a Hewlett-Packard 1040A diode array detector (DAD) and an octadecyl silica (ODS) column using tetrahydrofuran/water (4:1 v/v) and a DAD. Ionic chloride and sulfate levels were measured by dissolving the polymers in room temperature toluene and extracting with deionized water. Then, the aqueous extract was analyzed by ion chromatography (IC) using the Dionex model 4000 liquid chromatograph.

To determine structural composition, nuclear magnetic resonance (NMR) spectral analysis was performed using a General Electric GN300 NMR spectrometer. Proton NMR was used to quantitate the relative amount of hydrogen as CTBN, and carbon-13 NMR was used to measure nitrile content. These methods are capable of distinguishing incoming lots of CTBN that have a polybutadiene contaminant that is insoluble in the polymer matrix. The relative standard deviation was 3.9% for the proton NMR method and 8.3% for the carbon-13 NMR method. Presently, there is no method (other than carbon-13 NMR) for quantitating nitrile content. These methods are capable of distinguishing incoming lots of CTBN that have a polybutadiene contaminant that is insoluble in the polymer matrix.

DISCUSSION

SCOPE AND PURPOSE

The project objective is to develop methods for analyzing high performance polymers. The specific objective of this report is to develop methods to analyze CTBN and the CTBN-epoxy adduct BKC 20102 produced in the polymer facility at Allied-Signal Inc., Kansas City Division (KCD).

PRIOR WORK

A CTBN-modified epoxy has been used at KCD since 1977,[1] when it was shown that its thermal and electrical properties were equivalent to an unmodified system. The modified epoxy is tougher and only crazes when the unmodified epoxy cracks under high stress or impact loading.

ACTIVITY

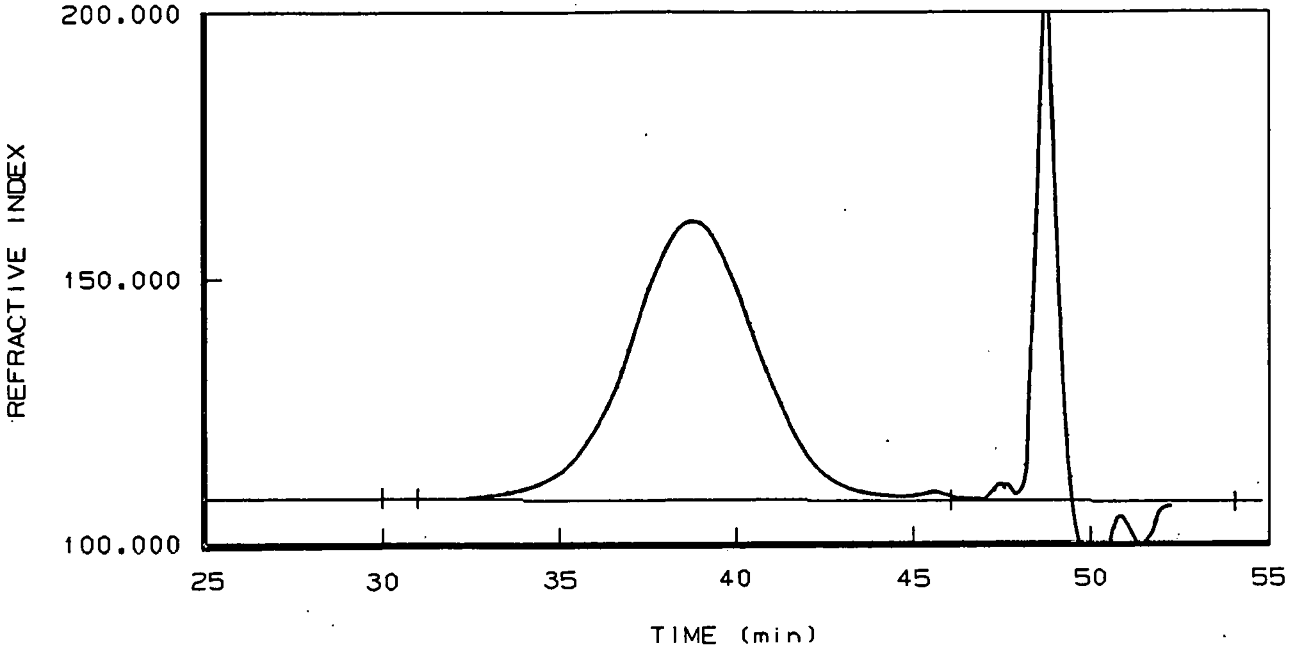
Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a liquid chromatographic method for measuring the molecular size of polymers. The sample is dissolved in room temperature tetrahydrofuran (THF) and is separated on a three-column set. The columns are packed with a porous poly(styrene/divinylbenzene). Small molecules fit easily into the pores and are retained on the column. Larger polymers do not fit into the pores and are not retained. Therefore, the highest molecular weight fractions are eluted first, and the lowest last. The data are used to calculate weight average, number average, and Z-average molecular weights.[2,3] A GPC chromatogram of CTBN (Hycar 1300 X8) is shown in Figure 1. A peak appears at about 37 min, caused by the CTBN. The integral of this peak is shown in the lower part of Figure 1, together with a plot of the cumulative percent of material detected as a function of the logarithm of the molecular weight. These data are used to calculate the molecular weights. When CTBN is reacted with Epon 828, the adduct has an increased molecular weight and produces a different chromatogram (Figure 2). This adduct has a higher average molecular weight as evidenced by the fact that the peak elutes sooner (24 min) than the CTBN. Data for different lots of CTBN are presented in Table 1. A number of physical properties of a polymer depend on its molecular weight and molecular weight distribution, or dispersity. Therefore, the GPC data are useful in establishing a basis to compare future lots of CTBN and adduct.

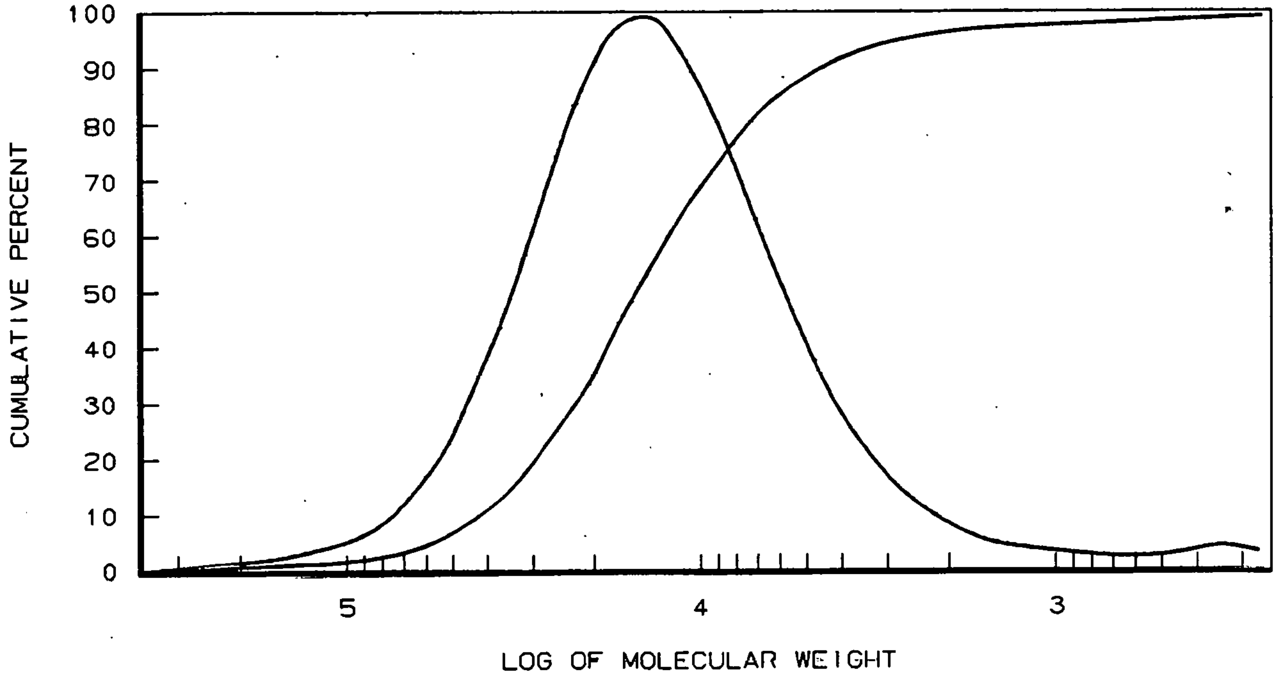
High Performance Liquid Chromatography

CTBN and CTB (Hycar 2000 X162) were dissolved in 80-percent THF and analyzed by high performance liquid chromatography (HPLC). They were separated on an ODS column and detected using a diode array detector (DAD) which can monitor up to six ultraviolet (UV) wavelengths simultaneously. As shown in Figure 3, CTB produces one major peak when the DAD monitors 253 nm. The minor peak at 4 min becomes a major peak, though, when the DAD monitors 220 nm. Thus, components of CTB have different molar absorptivities at specific wavelengths.

Typically, higher molecular weight polymers have a stronger absorbance at lower wavelengths and may be disproportionally represented in chromatograms such as the one in Figure 4. Likewise, CTBN has multiple components that can be identified when the DAD is set at 220 nm, as shown in Figure 5. The HPLC data can be used to characterize incoming lots of CTBN.

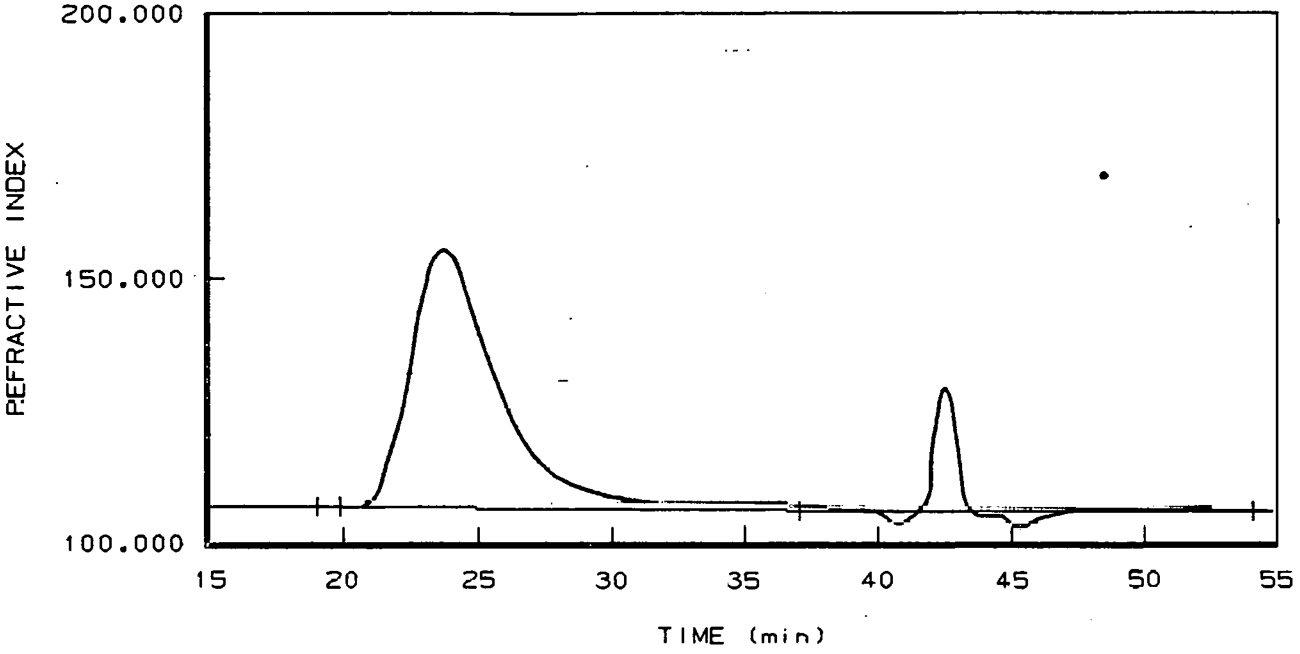


a. CHROMATOGRAM

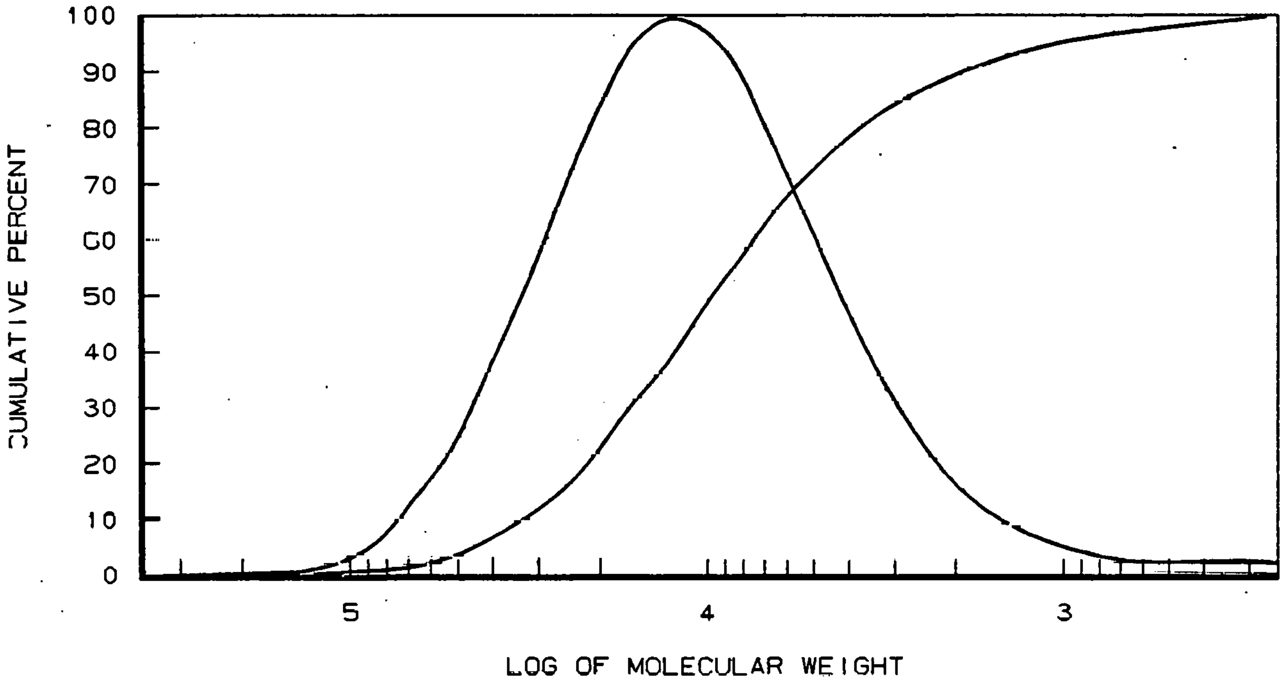


b. MOLECULAR WEIGHT

Figure 1. GPC of CTBN 1300 X8



a. CHROMATOGRAM



b. MOLECULAR WEIGHT

Figure 2. GPC of Epon 828-CTBN Adduct

Table 1. GPC Data on CTBN

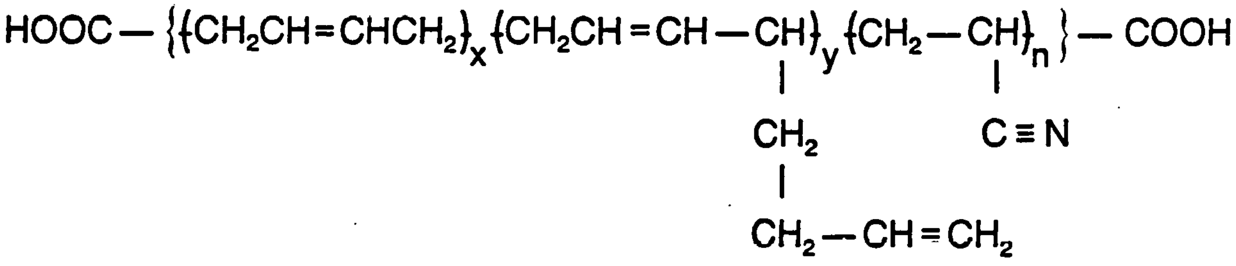
Lot Number	Weight Average Molecular Weight	Number Average Molecular Weight	Polydispersity
361212	5175	2176	2.38
360808	5195	2110	2.46
370403	5242	2110	2.48

Ion Chromatography

To determine ionizable chloride, ion chromatography (IC) was used. The samples were dissolved in toluene and extracted with water. Ionic chloride and sulfate go into the aqueous phase and can be quantitated using IC methods. Values obtained for different lots of epoxy and adduct are given in Table 2.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) can be used to confirm the structural identity of CTBN and its adduct with Epon 828; NMR can also be used for quantitative analysis. The proton spectrum of CTBN is shown in Figure 6, where peak assignments are in accordance with the following structure:



$$\mathrm{HOOC-\{(CH_2CH{=}CHCH_2)_x(CH_2CH{=}CH-\underset{\substack{|\\ CH_2\\ |\\ CH_2-CH{=}CH_2}}{CH})_y(CH_2-\underset{\substack{|\\ C\equiv N}}{CH})_n\}-COOH}$$

The alkyl groups (CH_2 and CH) produce the peaks from 1.3 to 2.6 ppm, and the alkene groups (-CH=CH-) produce the peaks from 4.9 to 5.2 ppm. The proton spectrum of CTB is quite similar, as shown in Figure 7. Both are quite distinct from the proton NMR

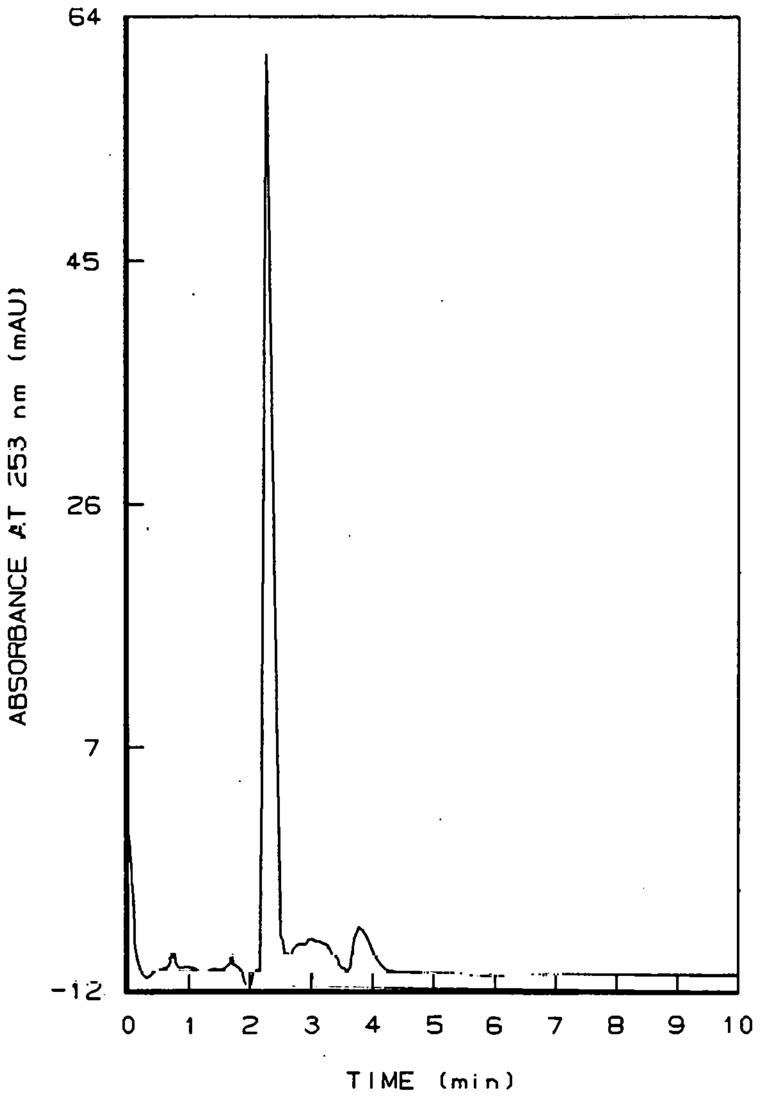
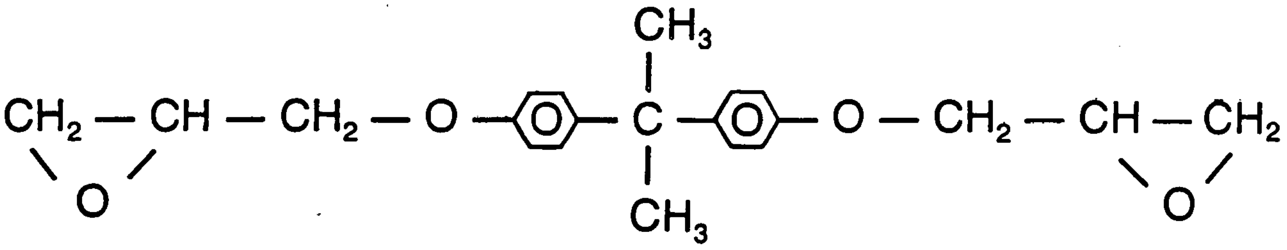


Figure 3. HPLC of CTB--Absorbance at 253 nm

spectrum of Epon 828, which is primarily the diglycidyl ether of bisphenol A (DGEBA):



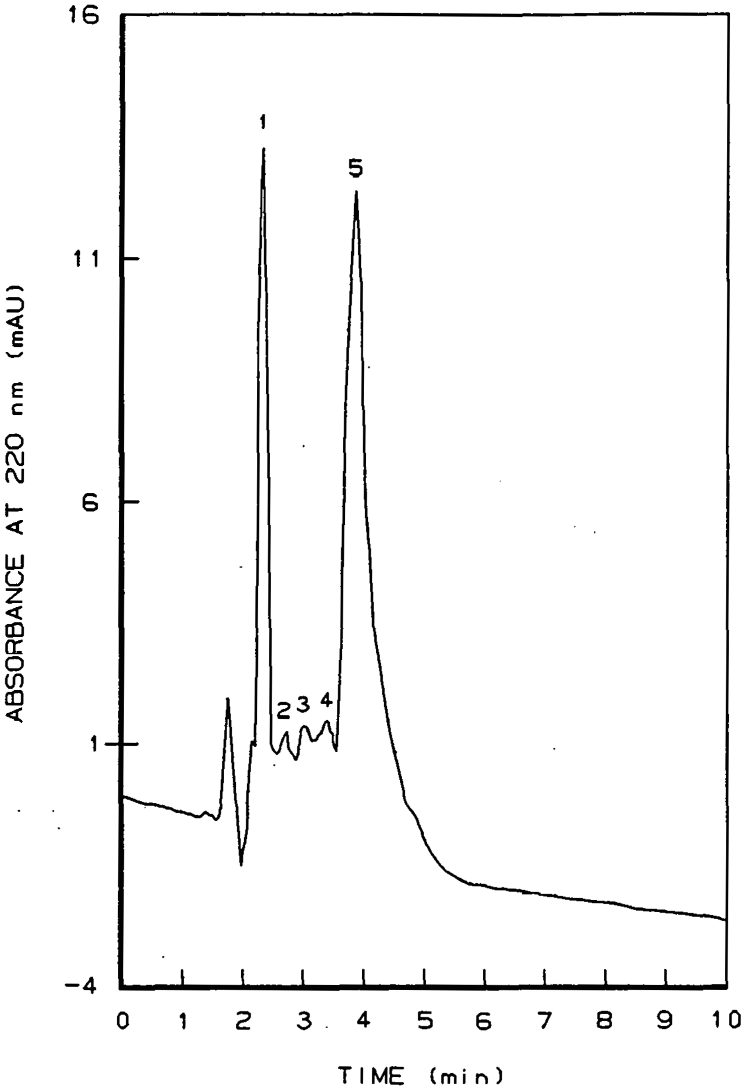


Figure 4. HPLC of CTB--Absorbance at 220 nm

Its spectrum is also shown in Figure 7. The phenyl protons produce the peaks near 7 ppm. The glycidyl ether protons produce the five sets of peaks from 2.6 to 4.2 ppm. The dimethyl protons produce the peak at 1.6 ppm. The CTBN-Epon 828 adduct produces a proton spectrum that contains peaks from each component, as shown in Figure 8. The relative size of the CTBN alkyl protons can be used to quantitate the amount of CTBN in the adduct. The results of the analysis of eight different adducts are shown in Table 3.

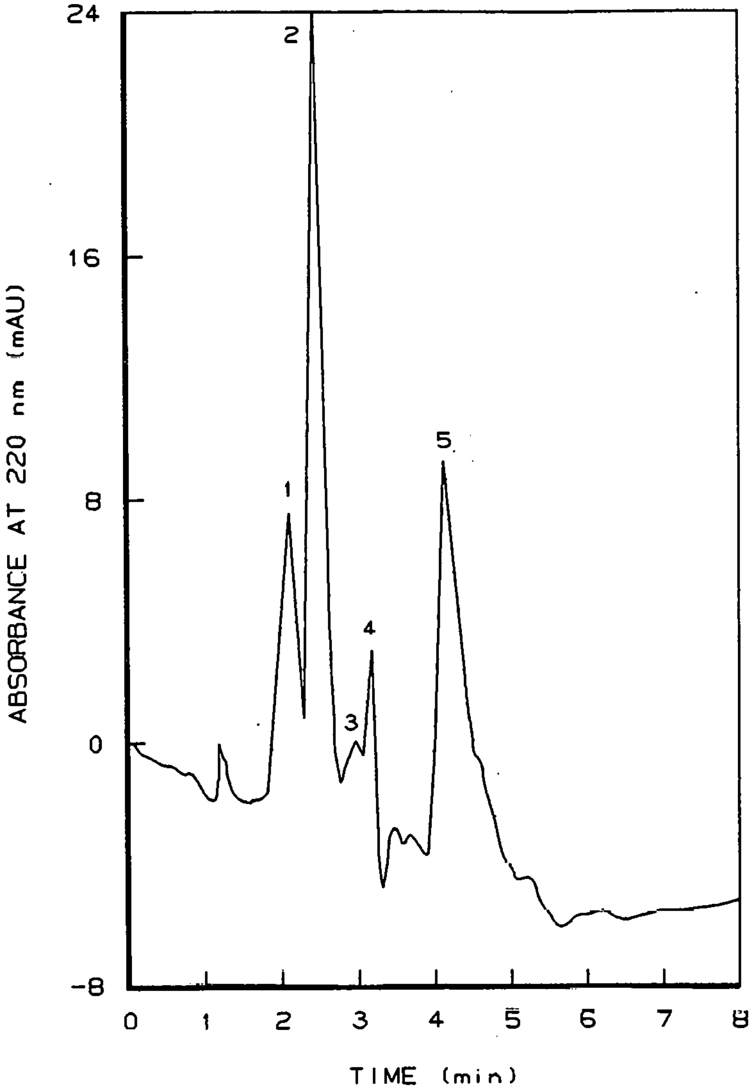


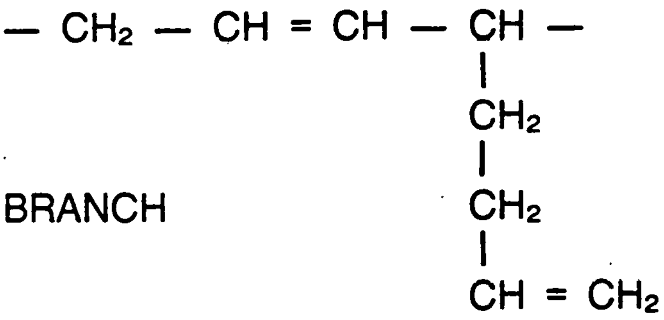
Figure 5. HPLC of CTBN 1300 X8

The relative standard deviation of five replicates is 3.9%. Sample 14 exhibited a phase separation, indicating the presence of an insoluble contaminant. The abnormal percent of alkyl protons observed in this sample confirms its unusual composition and the ability of proton NMR to screen samples for quality assurance.

Table 2. Ions in Epoxy and Adduct

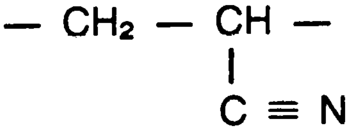
Lot Number	Cl^- (ppm)	SO_4^{2-} (ppm)
Epoxy		
860506	72	2.9
811208	16	0.74
861029	65	1.2
CTBN		
340623	153	11
360808	165	16
361212	144	25

To measure the nitrile content, carbon, hydrogen, and nitrogen analyses were performed. Unfortunately, only total nitrogen can be determined, so trapped nitrogen gas can cause appreciable interferences. To directly observe the nitrile group, carbon-13 NMR was used. As shown in Figure 9, the methylene and methine carbons in CTBN produce a set of peaks from 22 to 45 ppm. There are so many peaks in this region because the chemical environments of the methylene and methine carbons are slightly different. A methylene carbon adjacent to a -COOH would produce a different peak from a methylene several carbons away from a -COOH. Similarly, a methylene located in a block of $-CH_2-CH=CH-CH_2-$ will produce a different peak from a methylene in a $-CH_2-CH=CH-CH_2-$ adjacent to an acrylonitrile group. Likewise, a methylene located in a branch or an acrylonitrile (see below)



$$-CH_2-CH=CH-\underset{\underset{\underset{CH=CH_2}{|}}{\underset{CH_2}{|}}}{\underset{CH_2}{\underset{|}{CH}}}-$$

BRANCH



$$-CH_2-\underset{C\equiv N}{\underset{|}{CH}}-$$

ACRYLONITRILE

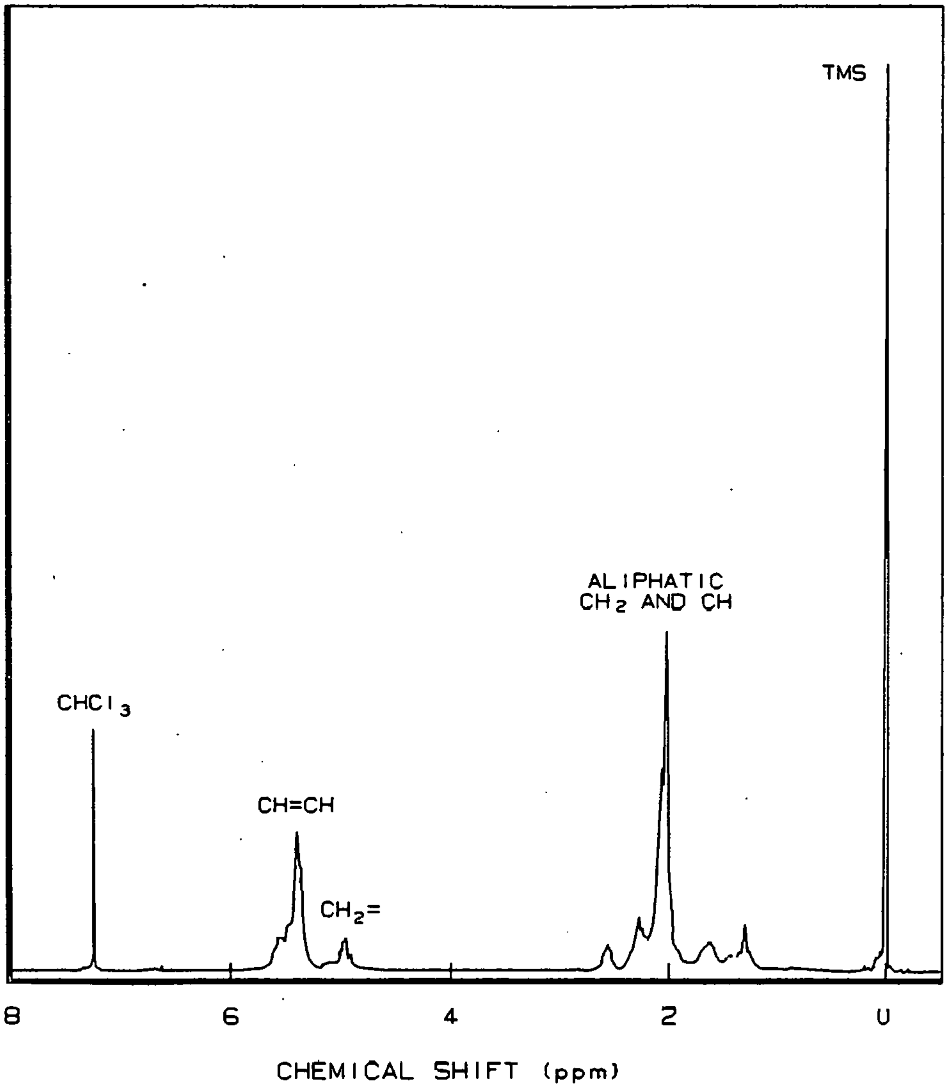


Figure 6. Proton NMR of CTBN 1300 X8

will produce a different peak than a methylene in a straight chain (that is, -CH_2-CH=CH-CH_2). For the same reason, there are several peaks produced by the -CH=CH-carbons located in slightly different environments. The nitrile and -COOH groups, though, produce distinct peaks (as labeled in Figure 9) whose areas are easily integrated, enabling quantitative analysis. Likewise, the -CH= groups in butadiene branches produce a distinct peak.

The carbon-13 spectrum of CTB is almost the same as that for CTBN, except that there is no nitrile peak (Figure 10). Thus,

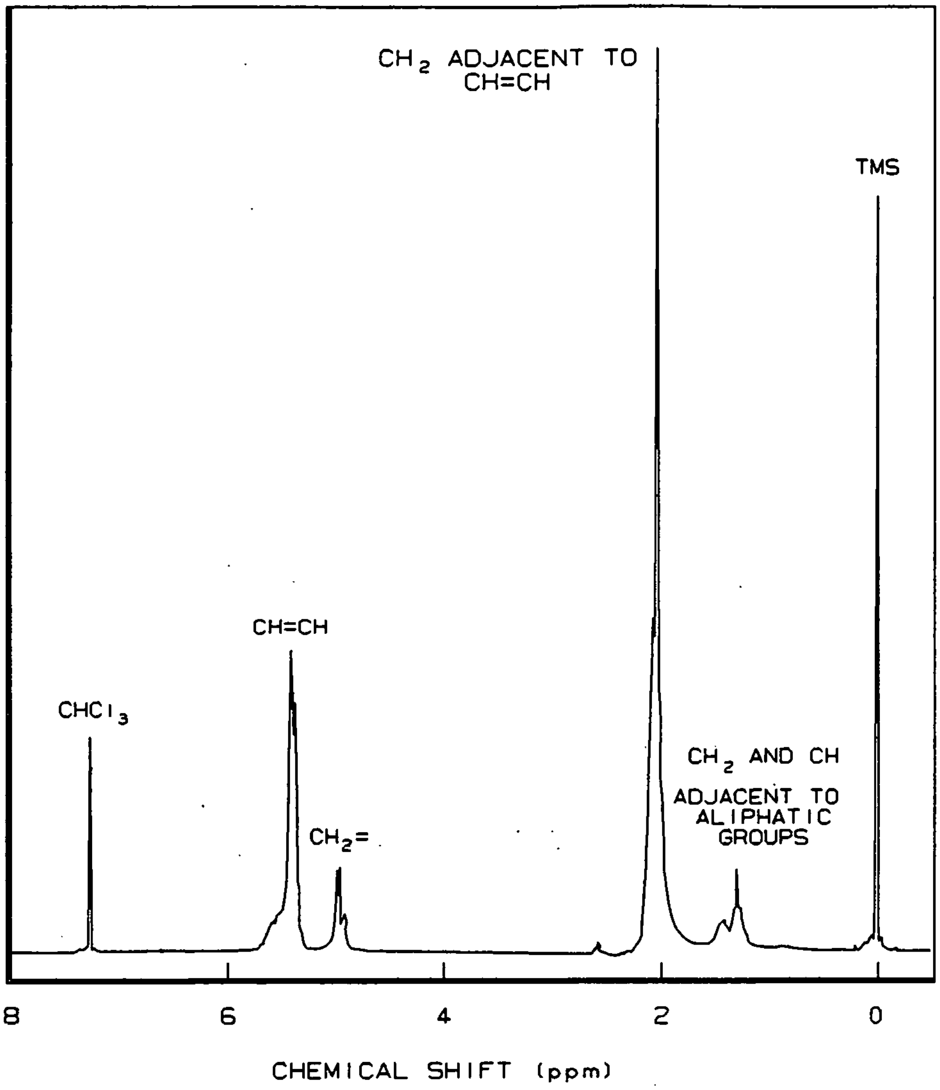


Figure 7. Proton NMR of CTB in $CDCl_3$

when analyzing CTBN/Epon 828 adducts, the relative size of the nitrile peak is directly related to the amount of CTBN in the adduct.

The carbon-13 spectrum of the adduct displays the peaks caused by DGEBA prominantly (Figure 11). To ensure production of an acceptable adduct, it may be useful to analyze the raw material, that is, the CTBN. To do this, standards containing increasing amounts of CTB mixed with CTBN were prepared by Materials

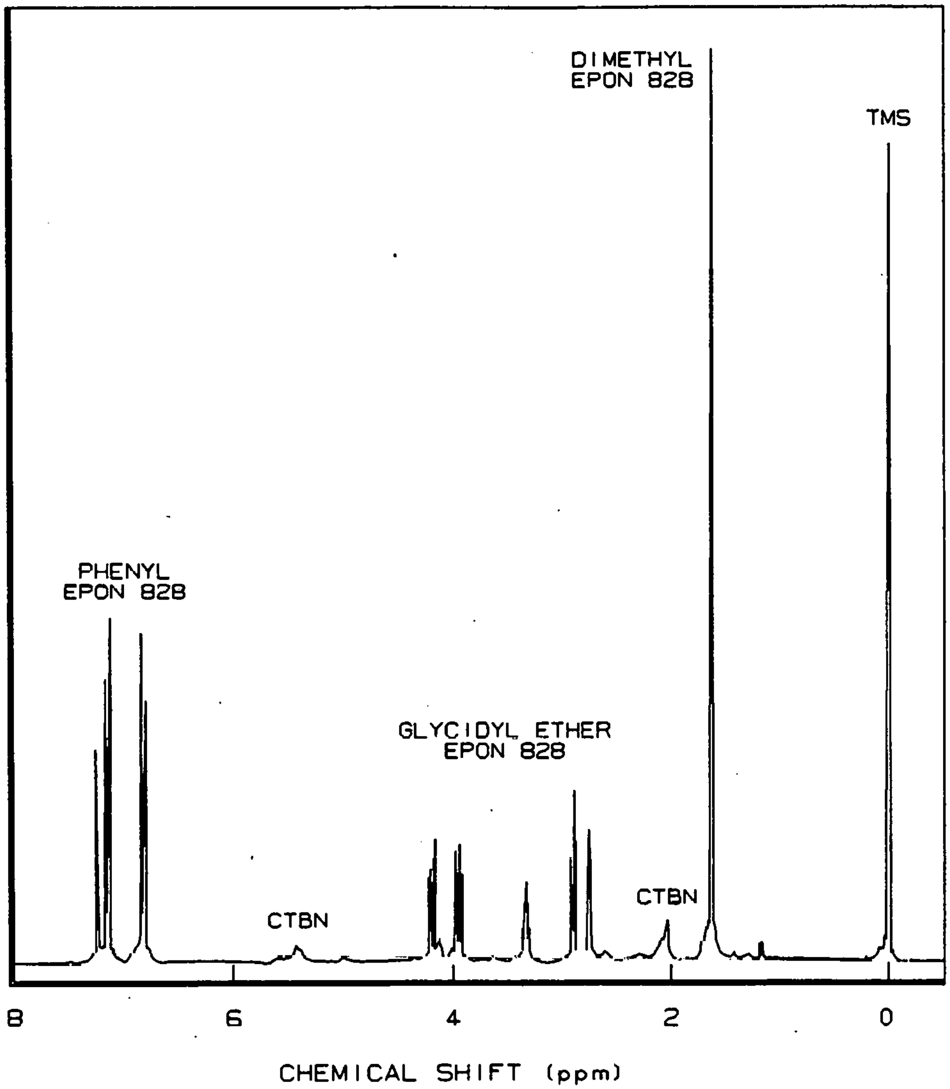


Figure 8. Proton NMR of Epon 828-CTBN Adduct in $CDCl_3$

Engineering. These standards were analyzed by carbon-13 NMR; the results are summarized in Table 4. The relative standard deviation of five replicate measurements was 8.3%. These standards will be useful in any analyses of future lots of CTBN.

The methods used for the proton and carbon-13 NMR analyses were written and are summarized in the appendix of this report. They are available for use if needed.

Table 3. Proton NMR Analysis Showing Hydrogen in Samples of CTBN/Epon 828

Sample Number	Hydrogen (percent)
8	13.7
9	13.2
10	13.4
11	12.7
12	12.5
13	13.2
14	18.5
15	13.5

ACCOMPLISHMENTS

Two polymers, CTB and CTBN, and the adduct of CTBN with epoxy have been analyzed by several methods. The molecular weight distribution was measured by GPC. HPLC was used to separate the major components from minor constituents. Ion chromatography was used to determine ionic chloride and sulfate. Proton NMR was used to quantitate the percent of hydrogens in the epoxy-CTBN adduct caused by the CTBN. Carbon-13 NMR was used to analyze CTBN and CTB for nitrile content. The relative standard deviation was 3.9% for the proton NMR method and 8.3% for the carbon-13 NMR method. Both NMR methods provide information not available by any other technique.

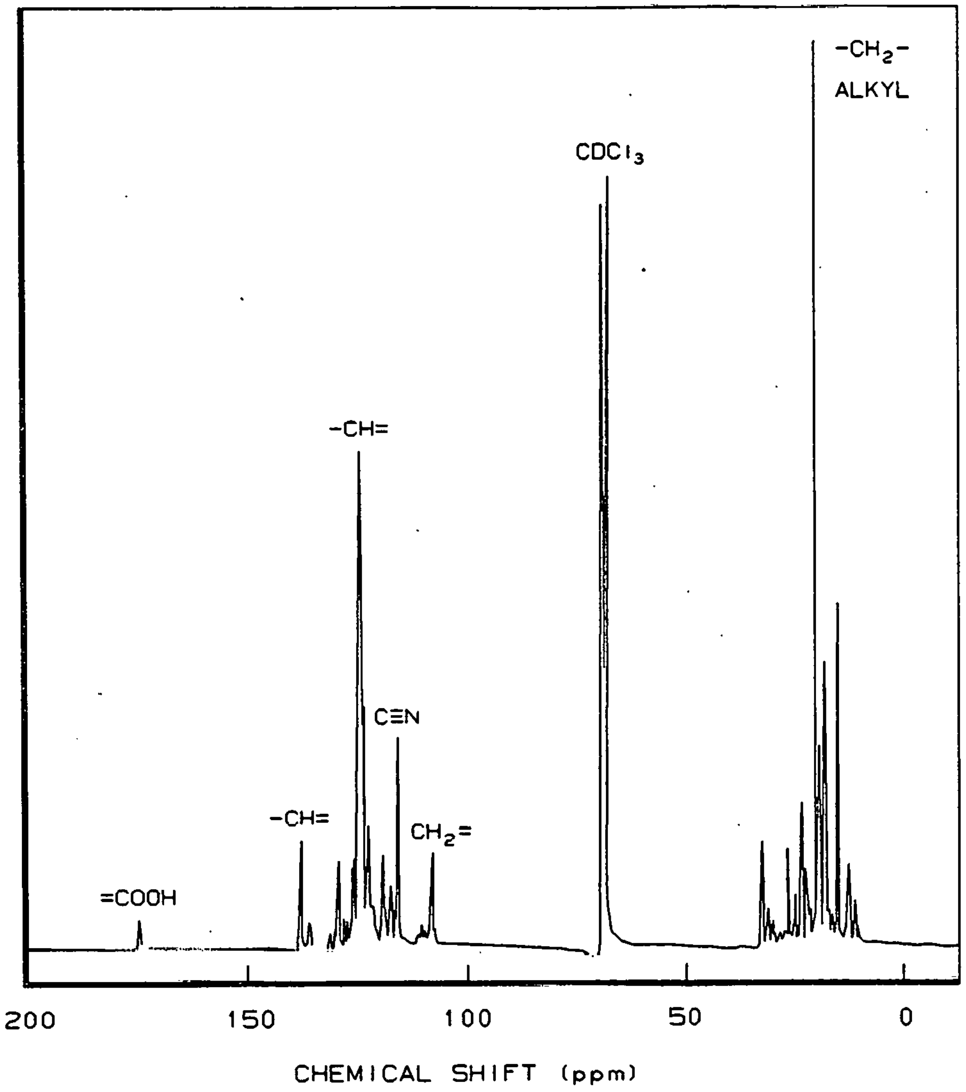


Figure 9. Carbon-13 NMR of CTBN 1300 X8 in $CDCl_3$

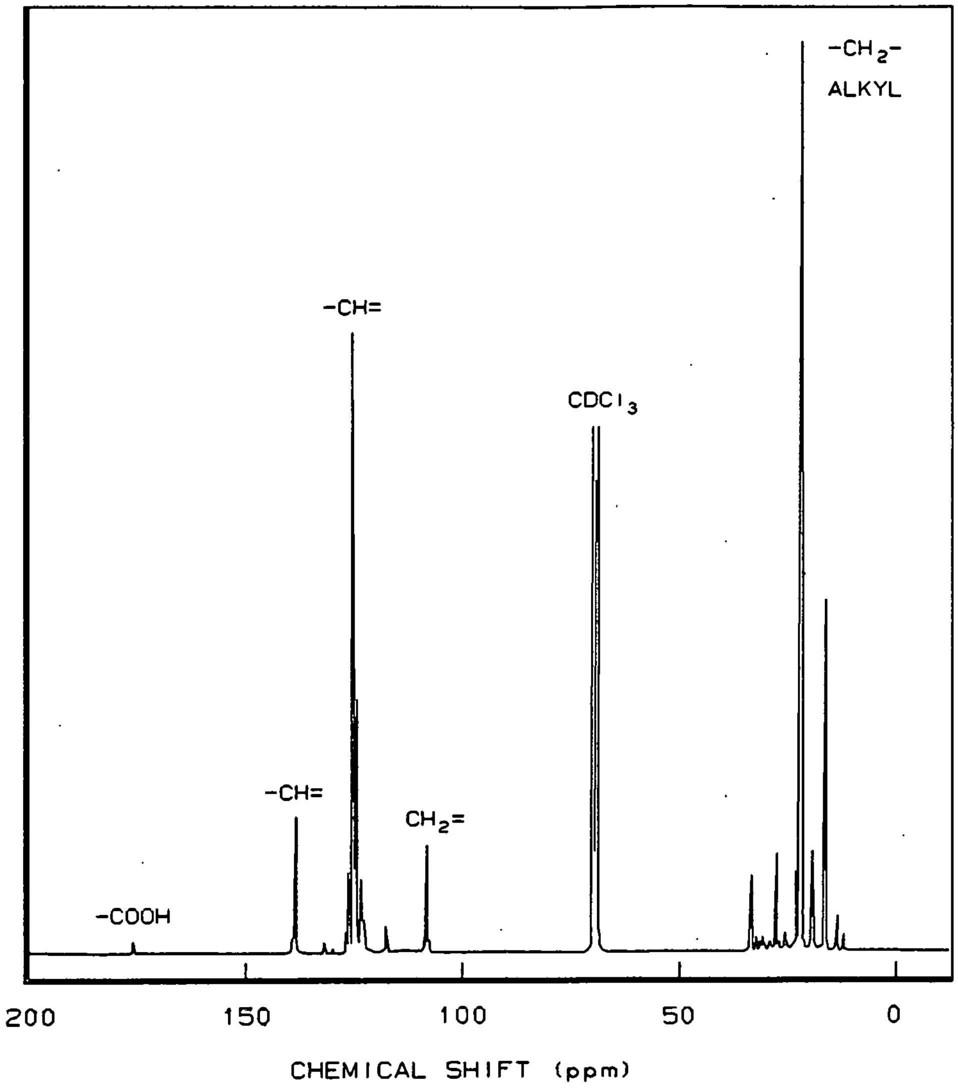


Figure 10. Carbon-13 NMR of CTB in $CDCl_3$

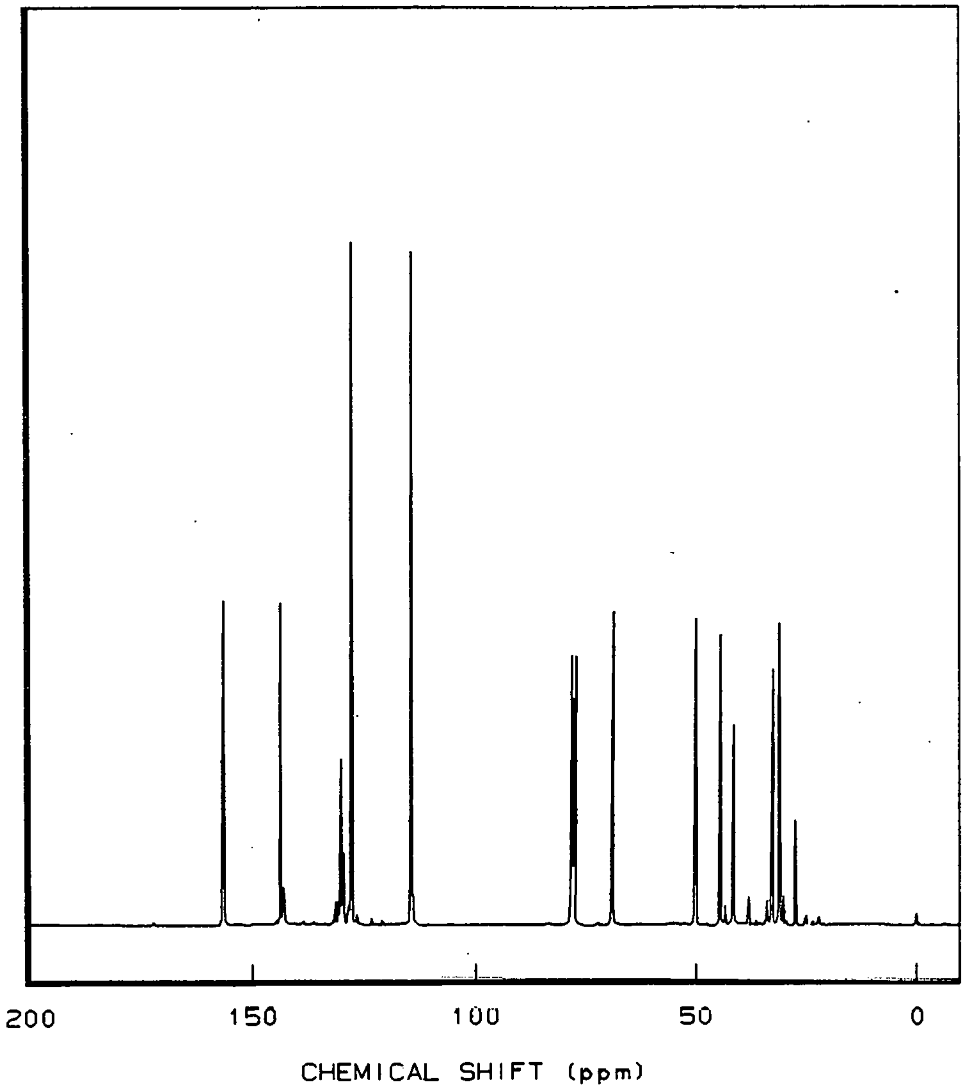


Figure 11. Carbon-13 NMR of Epon 828-CTBN Adduct in $CDCl_3$

Table 4. Carbon-13 NMR Analysis Showing Carbon in Samples of CTB and CTBN

Sample Number	Carbon Content (percent)		
	C≡N	COOH	CH_2=CH-
CTB	0.0	0.68	18.4
CTBN	4.29	0.60	15.8
4	4.21	0.61	16.0
5	4.03	0.59	16.1
6	3.70	0.65	16.2
7	3.60	0.63	16.4

REFERENCES

[1] J. M. Walker, W. E. Richardson, and C. H. Smith, "CTBN-Modified Epoxy Encapsulant". Modern Plastics, Volume 54, Number 68, 1977.

[2] B. Vollmert, Polymer Chemistry. New York: Springer-Verlag, 1973, pp. 426-427.

[3] W. W. Yan, J. J. Kirkland, and D. D. Bly, Modern Size-Exclusion Liquid Chromatography. New York: John Wiley and Sons, 1979.

Appendix A

EXPERIMENTAL METHODS

NMR. All spectra were recorded using a GN300 spectrometer from General Electric (Fremont, CA). For proton NMR, the spectrometer frequency was 300.100 MHz. A 90-degree pulse width (10 microseconds) and an 8-second pulse delay were used. A sweep width of ±2000 Hz was used. For carbon-13 NMR, the spectrometer frequency was 75.12345 MHz. A 30-degree pulse width and a 0.5-second pulse delay were used. Broad-band proton decoupling was employed. The sweep width was ±10,000 Hz.

Ion Chromatography. Chromatograms of aqueous extracts of the polymer dissolved in toluene were obtained using a Dionex (Sunnyvale, CA) model 4000 ion chromatograph equipped with an anion micromembrane suppressor (AMMS), a conductivity detector, and an AS4A separator column. The eluent was 3 mM $NaHCO_3$ plus 2.4 mM Na_2CO_3.