NMR Characterisation of Dicyclopentadiene Resins and Polydicyclopentadienes

YEONG-SHOW YANG,[1] ERIC LAFONTAINE,[2] and BRUNO MORTAIGNE*[2]

[1]Cray Valley, Groupe Total, Centre de Recherches de Verneuil, 60550 Verneuil en Hallate, and [2]DGA/Centre de Recherches et d'Etudes d'Arcueil, 16 bis, Avenue Prieur de la Côte d'Or, 94114 Arcueil, France

SYNOPSIS

Dicyclopentadiene (DCPD) thermosetting resin has been characterized by nuclear magnetic resonance (NMR) technique. The main monomer in DCPD resin is found to be in endo isomer form. Solid-state ^{13}C cross polarization/magic angle spinning and ^{13}C high-power decoupling NMR techniques have been applied for characterization of polymer network during curing and after cure. NMR spectra of carbon atoms in rigid phase and in mobile phase have been investigated. The possibility of three structural elements in polymer network was discussed. Solid-state NMR technique was applied to study of poly-DCPD oxidation. © 1996 John Wiley & Sons, Inc.

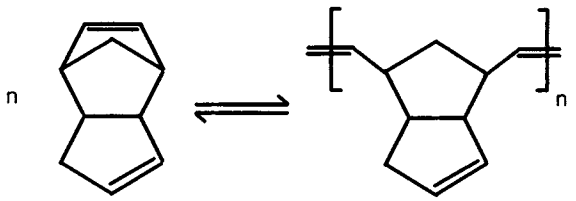
INTRODUCTION

The use of dicyclopentadiene (DCPD) as a comonomer in several polymeric systems such as ethylene–propylene–diene monomers (EPDM) and unsaturated polyesters has been documented.[1] Recently, DCPD resins have been formulated to make tough thermosetting materials via ring opening methathesis polymerization or ROMP reaction.[2-4] Unlike other thermosetting resins such as polyurethanes, epoxies, and unsaturated polyesters, the polymer properties of which are dependent on the prepolymer molecular structures, DCPD resins polymerize to give a homogeneous material the properties of which are essentially intrinsic to DCPD.

The DCPD resins are formulated in two components, A and B. Component A contains DCPD monomer, ethylenic comonomers, cocatalyst, and additives. Component B is ≥99% identical to component A, apart from containing an organometallic catalyst instead of the cocatalyst.

The catalyst for the metathesis polymerization is often a chloride or an ammonium salt of transition metals such as tungsten and molybdenum.[4,5] The cocatalyst is usually an organic metal such diethyl aluminum chloride (DEAC).[4,5] The catalyst and the cocatalyst must be stored separately, otherwise the reaction starts immediately. The additives are used to adjust viscosity (typically 300 mPa) as well as to modify the impact properties of the polymer. The additives used for DCPD resins may include all types of elastomers. Among them, polybutadiene is often used because of low material cost.

The reaction mechanism of the DCPD ROMP reaction has been described elsewhere.[6,7] However, it can be simplified as:



It should be noticed that the cyclic unsaturation of the second cyclopentene ring most probably takes part in the ROMP reaction, too. The two ROMP reactions might occur simultaneously and are highly exothermic due to relief of ring-strain on the bicyclic DCPD molecule.

The second metathesis reaction is not thought to proceed to completion. Nevertheless, it causes a crosslinking phenomenon which results in a three-dimensional network structure. Almost certainly due

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 60, 2419–2435 (1996)
 CCC 0021-8995/96/132419-17

to its highly cyclic structure, poly-dicyclopentadiene (PDCPD) resins present an extraordinary toughness.

The industrial processing of DCPD resins is made by RIM (reaction injection molding) or by RTM (resin transfer molding). The two reactive liquid components are dosed and mixed under pressure in a mixing head whereupon they enter into a closed mold in which the mixture polymerizes. Reaction kinetics of the DCPD RIM process has been studied.[8,9] Moreover, a viscoelastic study has been carried out to correlate the molecular structure of PDCPD with physical behavior.[6,7]

However, a literature review shows that there is a lack of studies on this polymer structure characterization. This work is trying to carry out a characterization study on the PDCPD structure by nuclear magnetic resonance (NMR) technique.

EXPERIMENTAL

Materials and Preparation

A 99.9% purity DCPD sample from Shell was used as received for NMR characterization as raw material reference. It was in crystalline form at room temperature.

Two-component DCPD resin (Telene®) of TELENOR Company was used for cure study and polymer characterization. For liquid NMR characterization, each component DCPD resin was respectively injected in a liquid NMR glass vial (for direct liquid-state NMR analysis); The two-component DCPD resin has been mixed in a static mixer and injected in a glass vial under an inert atmosphere. This formulation has been adjusted to have a gel time around 20 min in order to have enough operating time. The sample was put in a zirconia rotor with a cap and then put in the probe of the solid NMR spectrometer at room temperature. Solid-state ^{13}C-NMR spectra were taken during the reaction, after gelification, in bulk condition.

The resin formulation mentioned above has also been adjusted with a higher amount of catalyst for a shorter gel time, ca. 10 s, and has been molded to make 4 mm-thick plaques by RIM process at 60°C. The cured plaques have been stored outdoors for several weeks at room temperature.

Another DCPD resin without elastomer has been formulated and was cured into 4 mm-thick plaque in quasiadiabatic condition. The plaque was, then, postcured at 100°C for 30 min. After postcure, the reaction was nearly completed. Differential scanning calorimetry (DSC) measurement showed that conversion was higher than 99.9%. A small piece of cured plaque was taken and grounded into powder. The powdered sample was prepared for solid-state NMR measurements.

Instruments

Liquid NMR spectra were registered on a Bruker AM-300 spectrometer operating at 300.13 and 75.4 MHz for ^{1}H and ^{13}C nuclei, respectively. A 2% solution of the samples in $CDCl_3$ were prepared in a 5-mm-o.d. sample tube at 25°C for most of the NMR measurements. Instead, for 2D-INADEQUATE spectra, 30% sample solution in $CDCl_3$ was prepared in a 10 mm sample tube. Chemical shifts are given in ppm from tetra methylsilane (TMS).

One-dimensional ^{1}H-NMR spectra were obtained at 300 MHz using a 10.15 μs pulse width (equal to 90° flip angle) with a 5 s recycle time for 32 scans. ^{13}C spectra were obtained at 75.4 MHz using a 5.15 μs pulse width (equal to 90° flip angle), with a 10 sec recycle delay for 1024 scans, and ^{1}H broad band decoupling.

Connectivity between protons was established by two-dimensional correlated spectroscopy (COSY)[10,11] using a standard pulse sequence D1-90°-D0-90°-FID, in which D1 (recycle delay) = 6 s with a spectral width of 6024 Hz and D0 (evolution delay of shifts and coupling) = 3 μs. The spectra were collected as 16 × 8 K datum points.

^{13}C-^{1}H correlation spectra were accomplished by a standard pulse sequence, with quadrature detection in both dimensions.[12] The spectra widths were F_2 = 8770 Hz and F_1 = ±906 Hz. The fixed delays correspond to an average $^{1}J(^{13}C\text{-}^{1}H)$ coupling of 140 Hz. The spectra were collected as 8K × 1K datum points. A Gaussian multiplication was applied in both dimensions before Fourier transformation.

The ^{13}C-^{13}C correlated spectra were obtained by using a symmetrized 2D-INADEQUATE[13,14] with 120° conversion pulse to give COSY-like symmetry representation. The following manipulation parameters were applied: a ^{13}C 90° pulse of 10 μs; 5 ms of spin-echo period (corresponding to an average value of $^{1}J(^{13}C\text{-}^{13}C)$ = 50 Hz); 9000 Hz of spectra width; 2-s recycle delay; 64 scan accumulation for each of 1024 time increments with 2K datum points. The data were processed with sin-bell weighting multiplication and zero filling at 4096 × 1024 matrix before Fourier transformation.

Solid-state cross polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker MSL-200 spectrometer at 50.32 MHz for

^{13}C.[15,16] The cured samples were crushed into a powder under liquid nitrogen and then were placed in a fused zirconia rotor fitted with Kel-F caps and spun at 6 KHz at the magic angle (54.7°). ^{13}C chemical shifts were referenced to the glycine carbonyl (assigned at 176.03 ppm). The spectra were obtained by using cross-polarisation pulse (hydrogen 90° pulse equalling 4.1 μs), high-power decoupling during acquisition, 0.015 s acquisition time, 5 s recycle delay, 1024 scans, and 1.4 ms mixing time. The mixing time was calculated from the peak intensities obtained at various contact times between 50 μs and 25 ms (see Fig. 1).

Solid-state NMR spectra were also recorded in a high-power decoupling (HPDEC) sequence (classic ^{13}C sequence: 90° pulse with high-power ^{1}H decoupling during acquisition). The HPDEC NMR spectra used almost the same conditions as for the CP/MAS NMR spectra except that the recycle delay was 0.1 s instead of 5 s, and 4096 scans instead of 1024 scans were accumulated for spectra manipulation.

RESULTS AND DISCUSSION

Raw Material Characterization

The raw material characterization was conducted with liquid NMR experiments; samples were dissolved into 2% solution in $CDCl_3$. Figure 2(a) shows ^{1}H-NMR spectrum of pure DCPD sample in $CDCl_3$ solution, while Figure 2(b) shows its corresponding ^{13}C-NMR spectrum. The peaks in the neighborhood of 77 ppm on Figure 3 represent resonance peaks of $CDCl_3$.

The COSY ^{1}H-^{1}H spectrum of pure DCPD sample is shown in Figure 3. Figure 4 shows the ^{13}C-^{1}H chemical shift correlation spectrum of DCPD, while Figure 5 shows the ^{13}C-^{13}C 2D-INADEQUATE spectrum of DCPD.

From the NMR spectra shown in Figures 2–5, one may attribute all of the proton and carbon peaks for the pure DCPD sample used in this study. The peak attributions are shown in Tables I and II for ^{1}H and ^{13}C, respectively.

Tables I and II also show the ^{1}H and ^{13}C peak attributions of an endo-DCPD, made by Laurens et al.[17] The comparison reveals two facts. First, the DCPD sample used in this study is likely an endo-DCPD isomer since all of the experimental peaks agree well with literature results. Furthermore, the ^{13}C-NMR results of this study show satisfactory resolution for the C8 nuclei and the C9 nuclei. Both

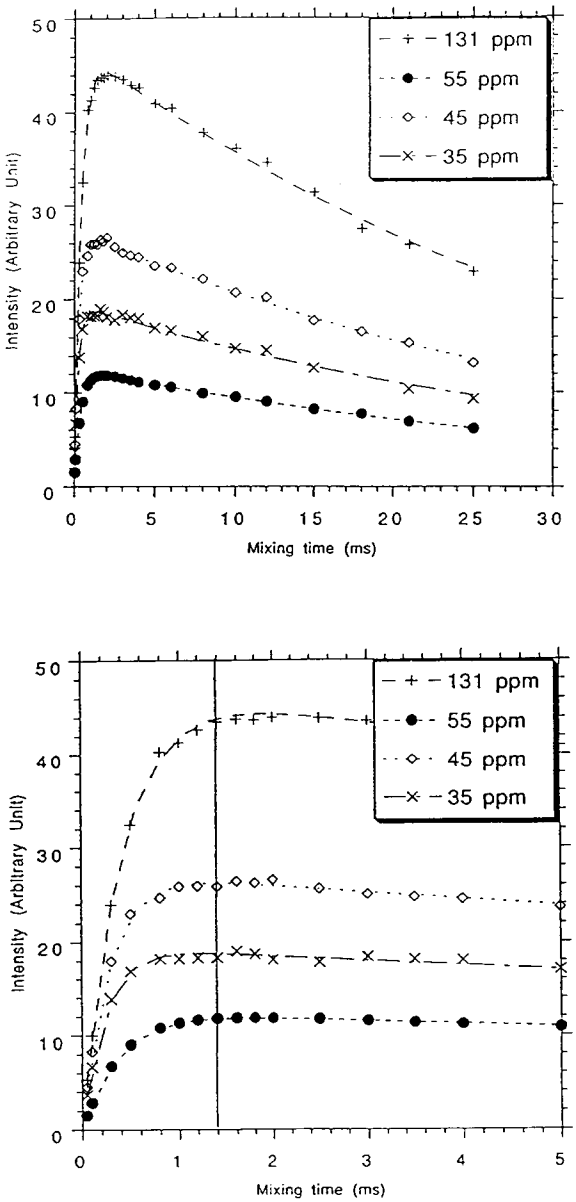


Figure 1 Intensity versus mixing time in solid-state (CR/MAS) NMR spectra for poly-DCPD sample.

are located on the double bond of the 5-ring cycle of DCPD. The proton spectrum also shows satisfactory resolution for the two protons (H8 and H9) which are located on the double bond of the 5-ring cycle of DCPD. However, according to literature results,[18] it was difficult to distinguish C8 from C9, or H8 from H9 in the previous studies.

It is noticed that the resonance peaks of molecules on the 6-ring cyclic double bond are significantly different from those on the 5-ring cyclic double bond either in ^{1}H-NMR or ^{13}C-NMR attribution. This fact may help one to investigate the reactivity dif-

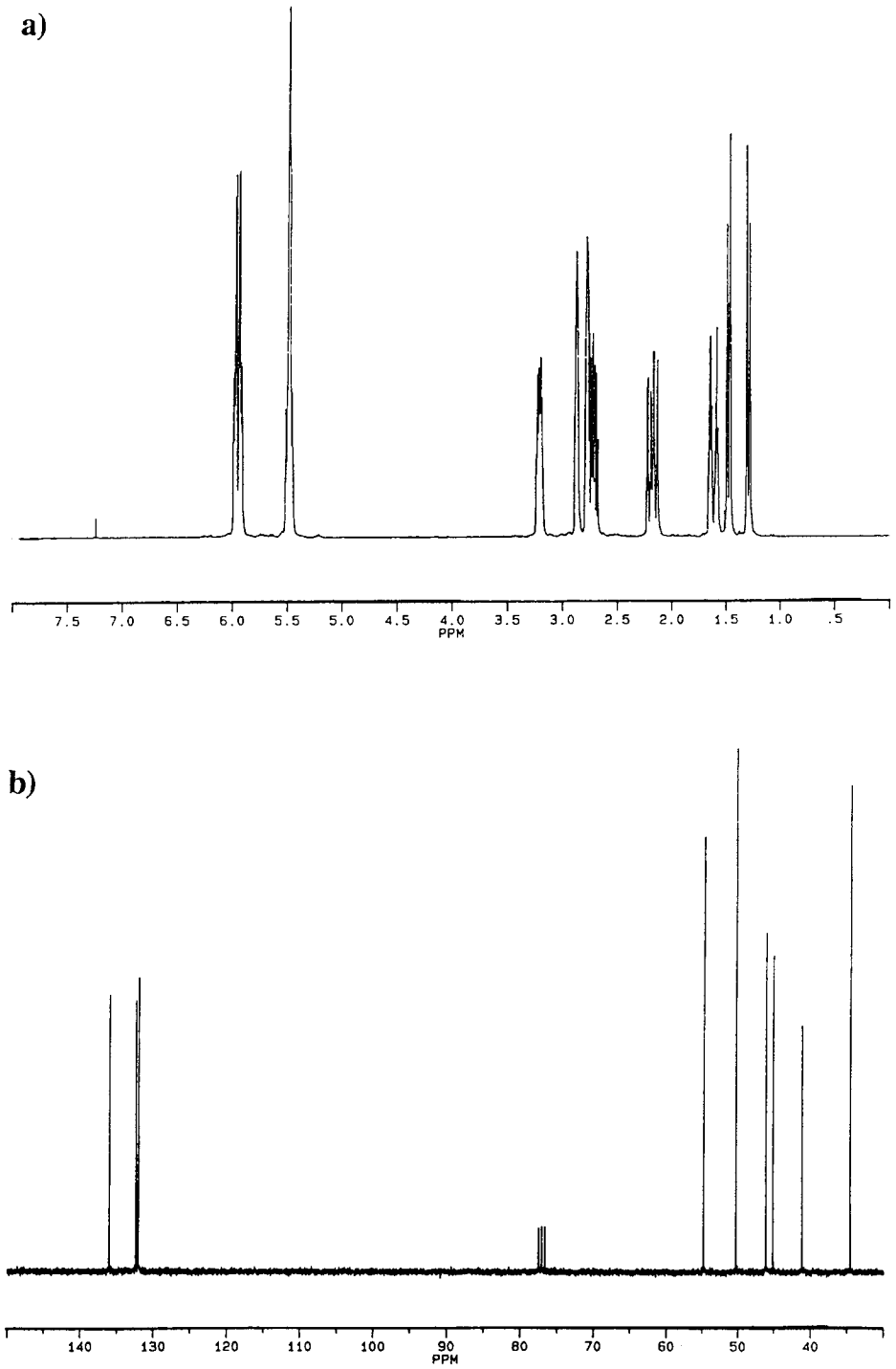


Figure 2 Pure DCPD sample in $CDCl_3$. (a) Liquid-state ^1H NMR spectrum. (b) Liquid-state ^{13}C NMR spectrum.

ference between the 6-ring cyclic double bond and the 5-ring cyclic double bond of DCPD in the polymerization process.

Figure 6(a) shows ^{13}C-NMR spectrum of B component of Telene DCPD resin. It is recalled that the B component of DCPD resin contains DCPD monomer, ethylenic comonomers, organometallic catalyst, and additives. If one compares Table II with Figure 6(a), one can find that all of the peaks of endo-DCPD monomer are present in Figure 6(a). It

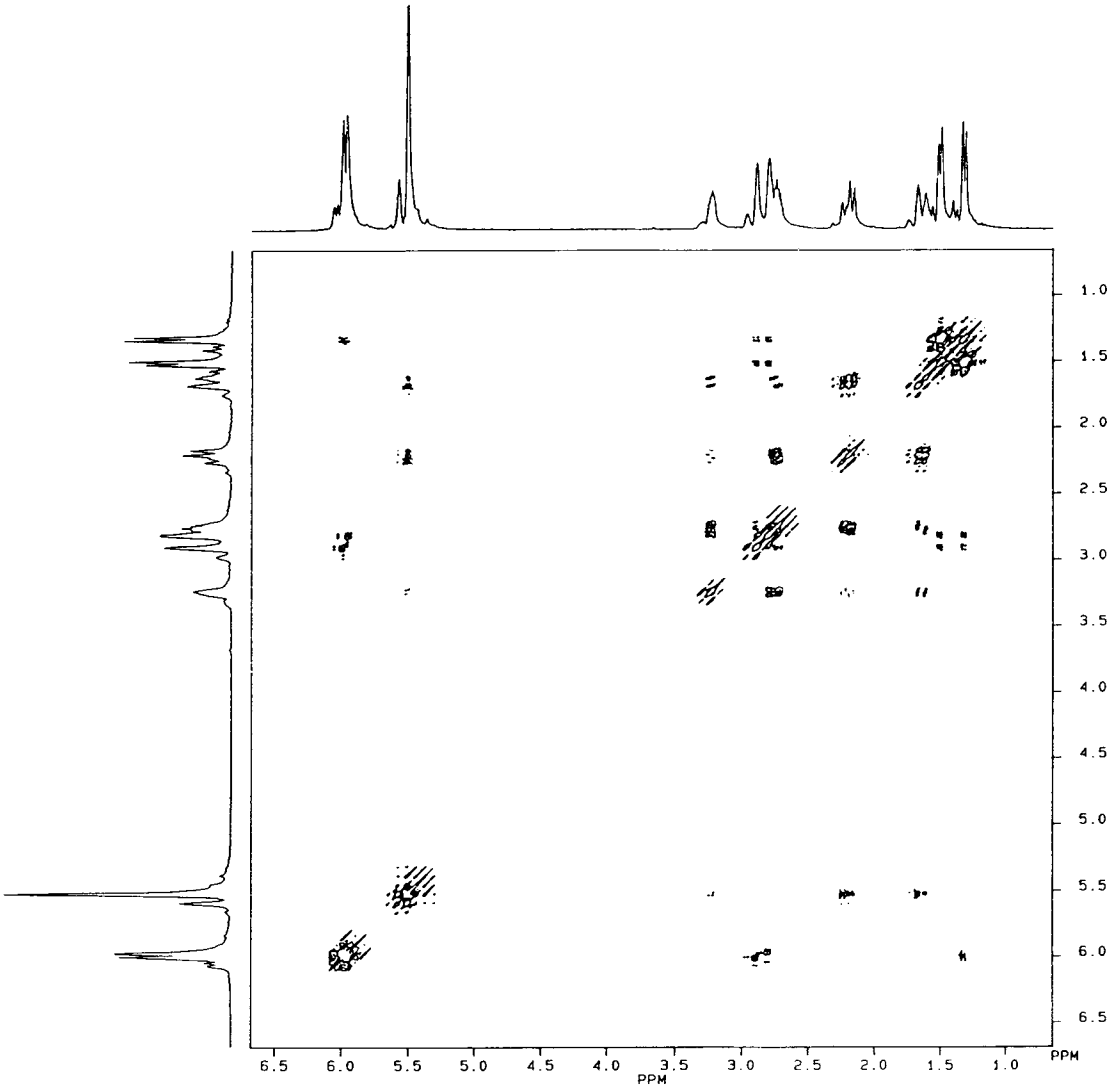


Figure 3 COSY ^{1}H-^{1}H NMR spectrum of pure DCPD sample in $CDCl_3$.

reveals that the DCPD monomer used in DCPD resins is likely an endo-type isomer. Since it usually contains more than 90% of pure DCPD monomer in the resin formulation, it is obvious that all of the significant peaks of DCPD dominate the signal response in the NMR spectrum.

The additives used for DCPD resins may include all types of elastomers. Among them, polybutadiene is often used because of low material cost. A ^{13}C-NMR spectrum of polybutadiene with a 100,000-Da molecular size is shown in Figure 6(b). On Figure 6(a), several important peaks of polybutadiene have been found. Peaks in the range between 128 and 131.5 ppm are the carbons of the double bonds on the linear chain, while peaks at ca. 27 and 33 ppm present the single-bonded carbons of polybutadiene.[18] By the results of Figure 6(a), it is found that the elastomer content is less than 5%. The resonance peaks of side chain double bonds of polybutadiene (at 143 and 114 ppm) are not detected. It may be because the polybutadiene content is relative small in the resin. The peaks in the neighborhood of 77 ppm on Figure 6(a) represent resonance peaks of $CDCl_3$. All of the other peaks may be belong to the ethylenic comonomers and organometallic catalyst.

Curing Study and Polymer Characterization

This part of the study was conducted with a solid NMR spectrometer. Figure 7(a) shows ^{13}C CP/MAS NMR spectrum of DCPD resin in bulk condition 20 min cured after mixing. After 20 min cure, the system just reaches the gel point and is no longer in a pure liquid state. Figure 7(b) shows ^{13}C HPDEC

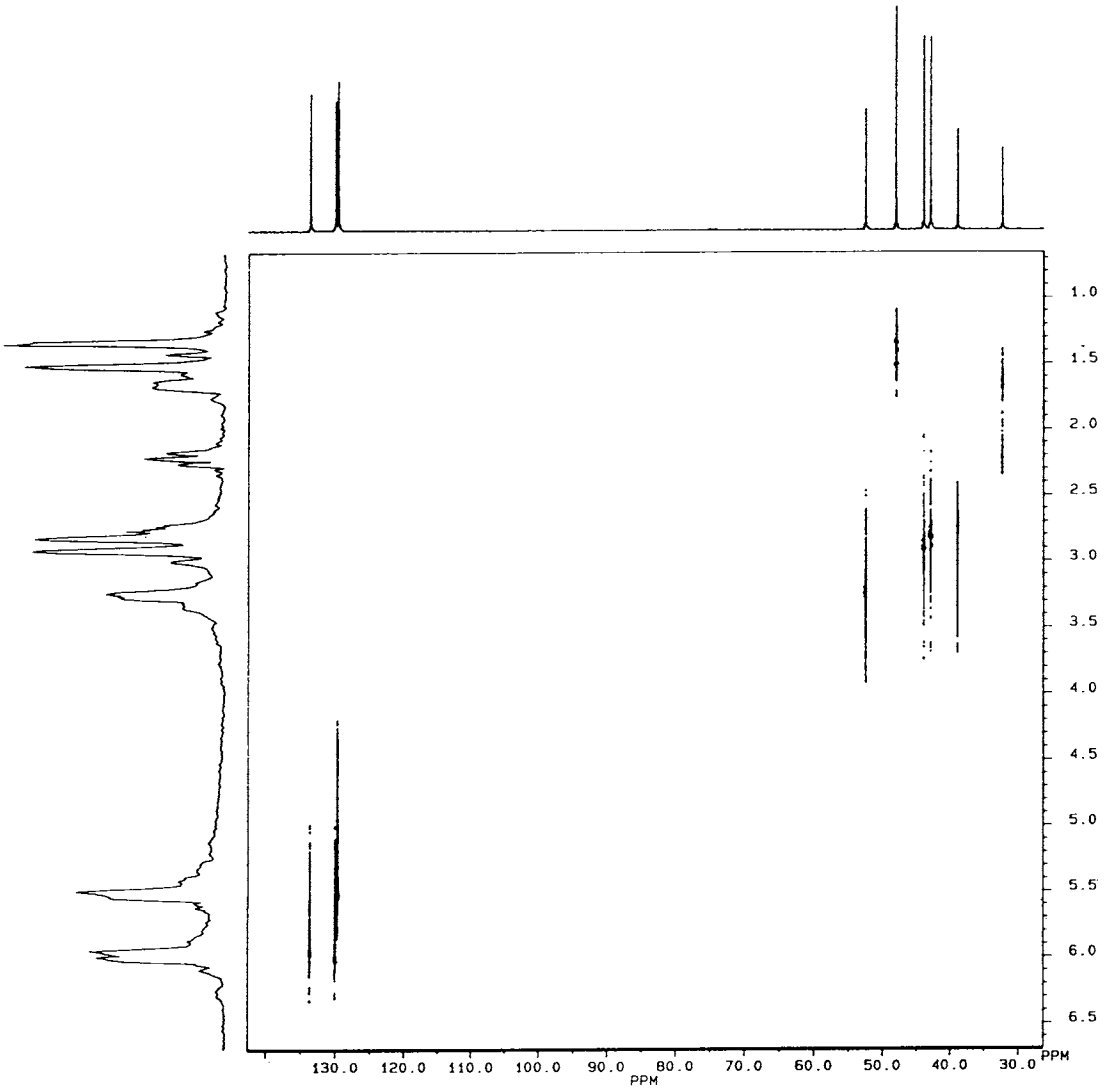


Figure 4 Heteronuclear shift-correlated two-dimensional ^{1}H-^{13}C NMR spectrum of pure DCPD sample in $CDCl_3$.

NMR spectrum of DCPD resin in bulk condition 20 min cured after mixing. The spectrum was measured with 0.1 s of relaxation time.

Normally, the ^{13}C CP/MAS NMR spectrum, with a long relaxation time such as 3 s, shows the resonances of all of the carbon atoms in the system, including both in the gel (or solid) state and in the mobile (or liquid) state. On the other hand, the ^{13}C HPDEC NMR spectrum with a short relaxation time (ca. 0.1 s) only shows the resonances of carbon atoms in the mobile phase.

Figure 8(a) shows ^{13}C CP/MAS NMR spectrum of DCPD resin in bulk condition after 4 h cure at room temperature. Figure 8(b) shows ^{13}C HPDEC NMR spectrum of DCPD resin in bulk condition after 4 h cure at room temperature. The NMR measurement condition for Figure 8 is the same as that for Figure 7.

For comparison, Figure 9(a) and (b) show the ^{13}C CP/MAS and HPDEC NMR spectra, respectively, of the poly-DCPD sample without elastomer. If one compares the ^{13}C CP/MAS NMR spectra shown on Figures 7(a) and 8(a), one finds that the NMR spectra for the fully formulated system right after the gel point and near the end of curing are mostly the same. Moreover, both spectra are highly similar to those of the well-cured system without elastomer as shown on Figure 9(a). This comparison reveals two important facts:

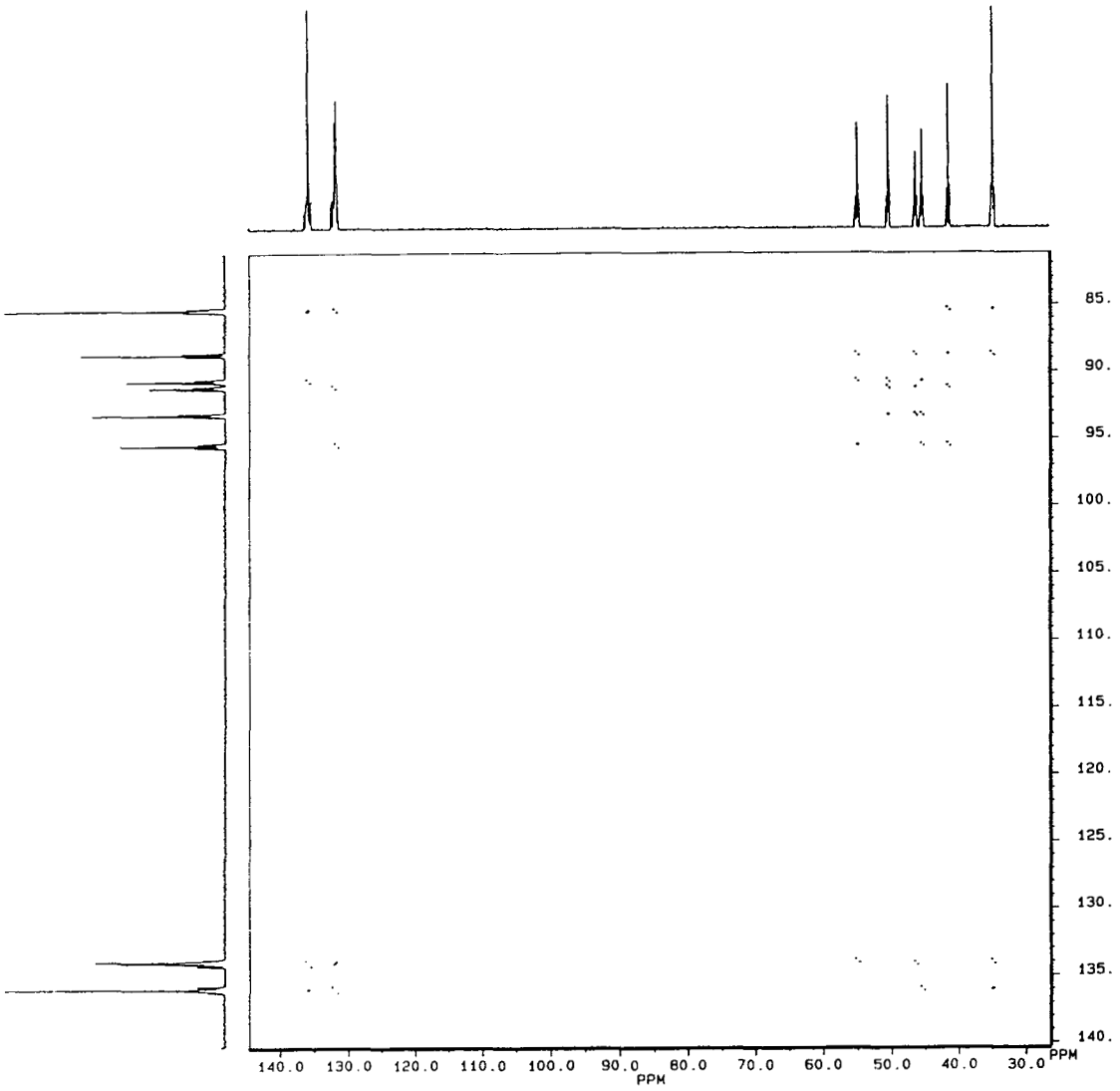


Figure 5 Symmetrized INADEQUATE ^{13}C-^{13}C two-dimensional NMR spectrum of pure DCPD sample in $CDCl_3$.

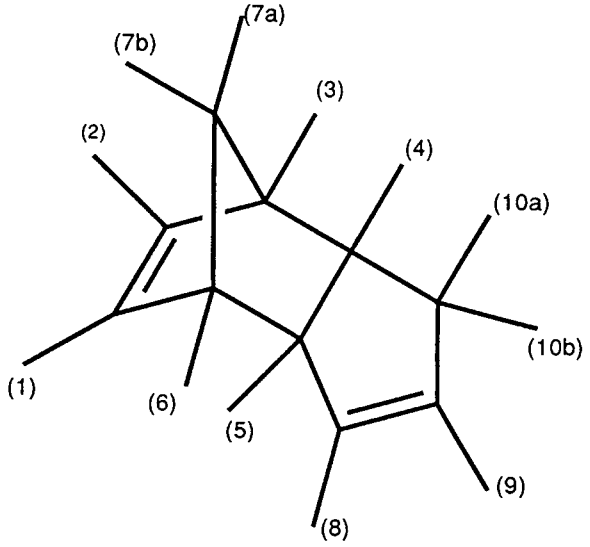
1. no significant influence of the polybutadiene phase on the ^{13}C CP/MAS NMR spectra of curing system; and
2. the curing system shows the same ^{13}C CP/MAS NMR spectra after the gel point until fully cured.

The unseen polybutadiene NMR peaks are believed to be due to its small amount in the system as well as the broader peaks of DCPD and poly-DCPD. Since the ^{13}C CP/MAS NMR spectrum shows the resonances of all of the carbon atoms in the system, the peaks of polybutadiene are certainly much smaller than those of DCPD and poly-DCPD, just like in the uncured system shown on Figure 6 by liquid state NMR investigation. Moreover, the major peaks of DCPD and/or poly-DCPD in the ^{13}C CP/MAS NMR spectra are largely broader. Consequently, the small peaks of polybutadiene are likely immersed in the broader peaks of DCPD and poly-DCPD and are not visible.

The fact of identical ^{13}C CP/MAS NMR spectra on Figures 7(a), 8(a), and 9(a), however, is quite surprising. The polymerization conversion for the case corresponding to Figure 7(a) is around 5%, while that for Figure 8(a) is higher than 80% and that for Figure 9(a) is near 100%. The result of identical ^{13}C CP/MAS NMR spectra may be likely due to the broader peaks in the spectra. Another reason for this similarity may come from the similarity of the polymer molecular structure and the DCPD monomer. The latter possibility is discussed as follows.

Table I ^{1}H Peak Attribution of DCPD

N° H	δ^1H (ppm): This Study	δ^1H (ppm)[17]
1	6.10	5.93
2	6.11	5.99
3	2.90	2.88
4	2.70	2.72
5	3.20	3.21
6	2.80	2.79
7a	1.30	1.30
7b	1.45	1.47
8	5.50	5.50
9	5.60	5.50
10a	1.65	1.62
10b	2.20	2.18



endo-DCPD

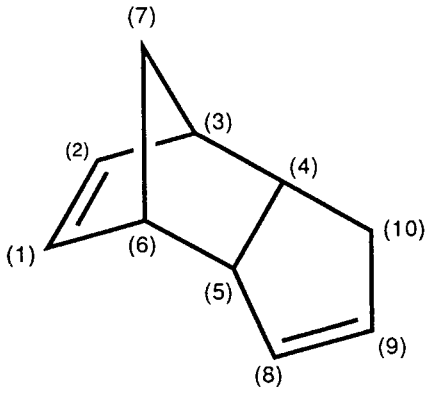
If one considers that the polymer network is purely built up by the DCPD monomer by ignoring the effects of comonomer and additives, there are three major structural elements in the poly-DCPD network structure, shown as Schemes 1, 2, and 3, in which only the form of Scheme 3 results in a cross-linking network. The two others only contribute in polymer chain increments.

It may be reasonable to assume that all of the cyclic carbons in the three types of structural elements have resonance peaks similar to those of their corresponding cyclic carbons, shown in Table II. Also, the aliphatic ethylenic carbons of the structural elements may have resonance peaks similar to those of the ethylenic carbons of polybutadiene on the linear polymer chain. As shown in Scheme 2, the hydrocarbon sequence formed with C9b and C10b between cyclic structure is very similar to the repetitive sequence in linear polybutadiene. In this case, the ^{13}C CP/MAS NMR spectra of the curing system in all of the curing stages are logically identical since the uncured monomer and the polymer have similar resonance peaks. Consequently, they are similar to the fully cured system even though it has no additive. Only signal intensity should increase after polymerization (but they are in the neighborhood of the spectra) and no new resonance peaks are detected.

For a not fully cured system, the ^{13}C CP/MAS NMR spectra such as Figures 7(a) and 8(a) on different cure time are not useful to study the polymer network because of the resonance similarity of the monomer and the polymer. The ^{13}C CP/MAS NMR spectrum of a fully cured system without additive may, however, provide some network information. Based on the same assumption mentioned previously, the peak of C1b on Scheme 2 should have the same resonance as that of C1 of DCPD monomer on Table II, i.e., around 136 ppm. The peak of 136 ppm shown on Figure 9(a) represents less than 2% of the broader peak (maximum point at 131 ppm) which represents all of the double bonds in the polymer structure. Instead, the peak of 136 ppm for the system before cure, as shown on Figure 7, represents around 25% of all of the peaks of carbon atoms on

Table II ^{13}C Peak Attribution of DCPD

N° C	δ^{13}C (ppm): This Study	δ^{13}C (ppm)[17]
1	135.94	136.00
2	132.31	132.41
3	46.22	46.21
4	41.23	41.18
5	54.81	54.80
6	45.20	45.17
7	50.34	50.34
8	131.97	132.06
9	131.92	132.06
10	34.69	34.70



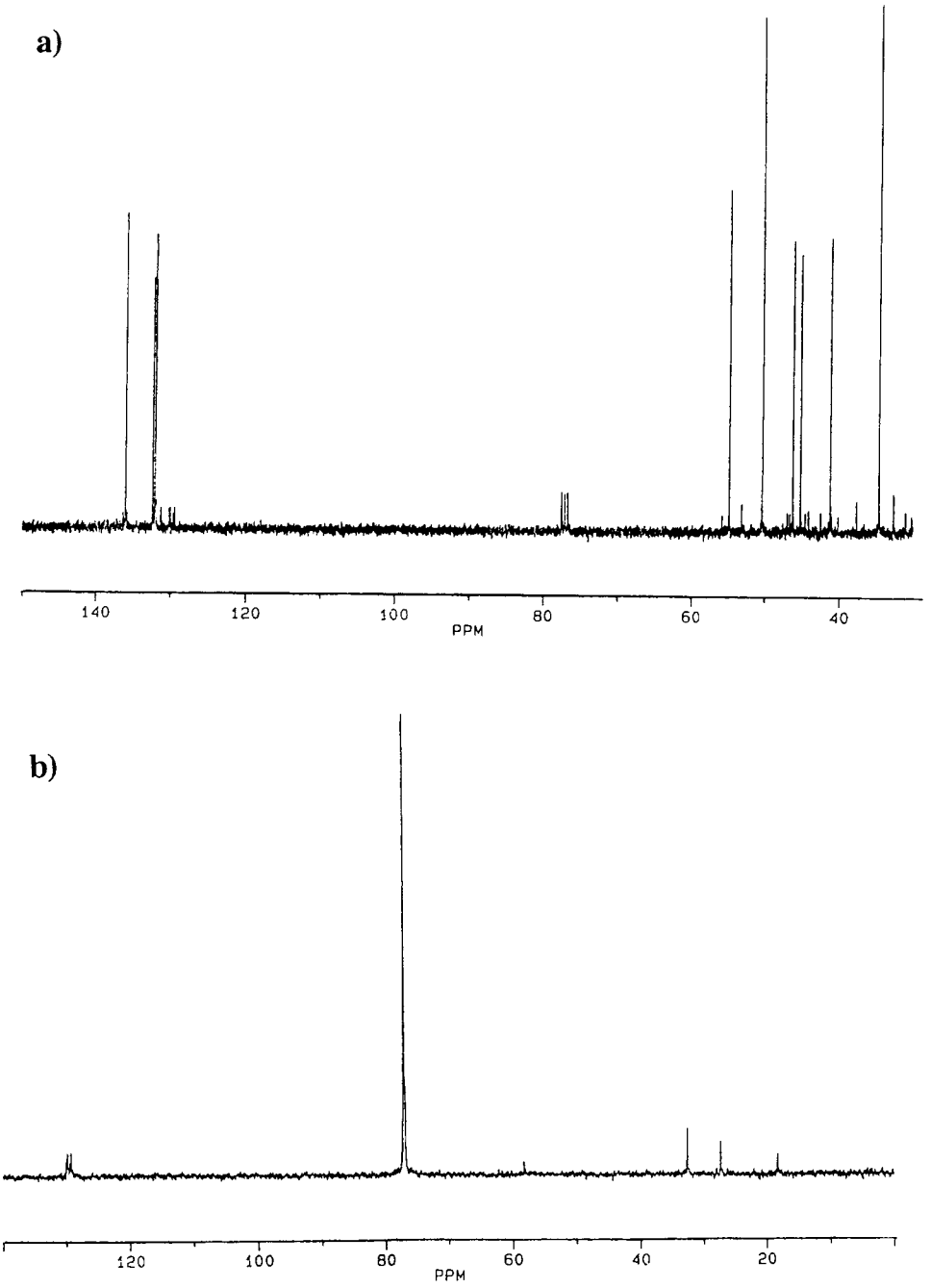


Figure 6 (a) Liquid-state ^{13}C-NMR spectrum of DCPD resin (B component) in $CDCl_3$. (b) Liquid-state ^{13}C-NMR spectrum of polybutadiene in $CDCl_3$.

the double bonds of monomer. This result reveals that the double bond of the six member ring is more reactive for the metathesis reaction than that of the five member ring. Consequently, the structural element shown on Scheme 2 is likely not representative of the polymer network structure. One, however, cannot distinguish the contribution of Scheme 1 (uncrosslinked form) and Scheme 3 (crosslinked form) in the final polymer structure by Figure 9(a). Another technique such as dynamic viscoelasticity study may be helpful for further understanding the network structure of poly-DCPD.

Different from the ^{13}C CP/MAS NMR spectra, the ^{13}C HPDEC NMR spectra show significantly different results. Figures 7(b) and 8(b) show the ^{13}C HPDEC NMR spectra of a fully formulated resin

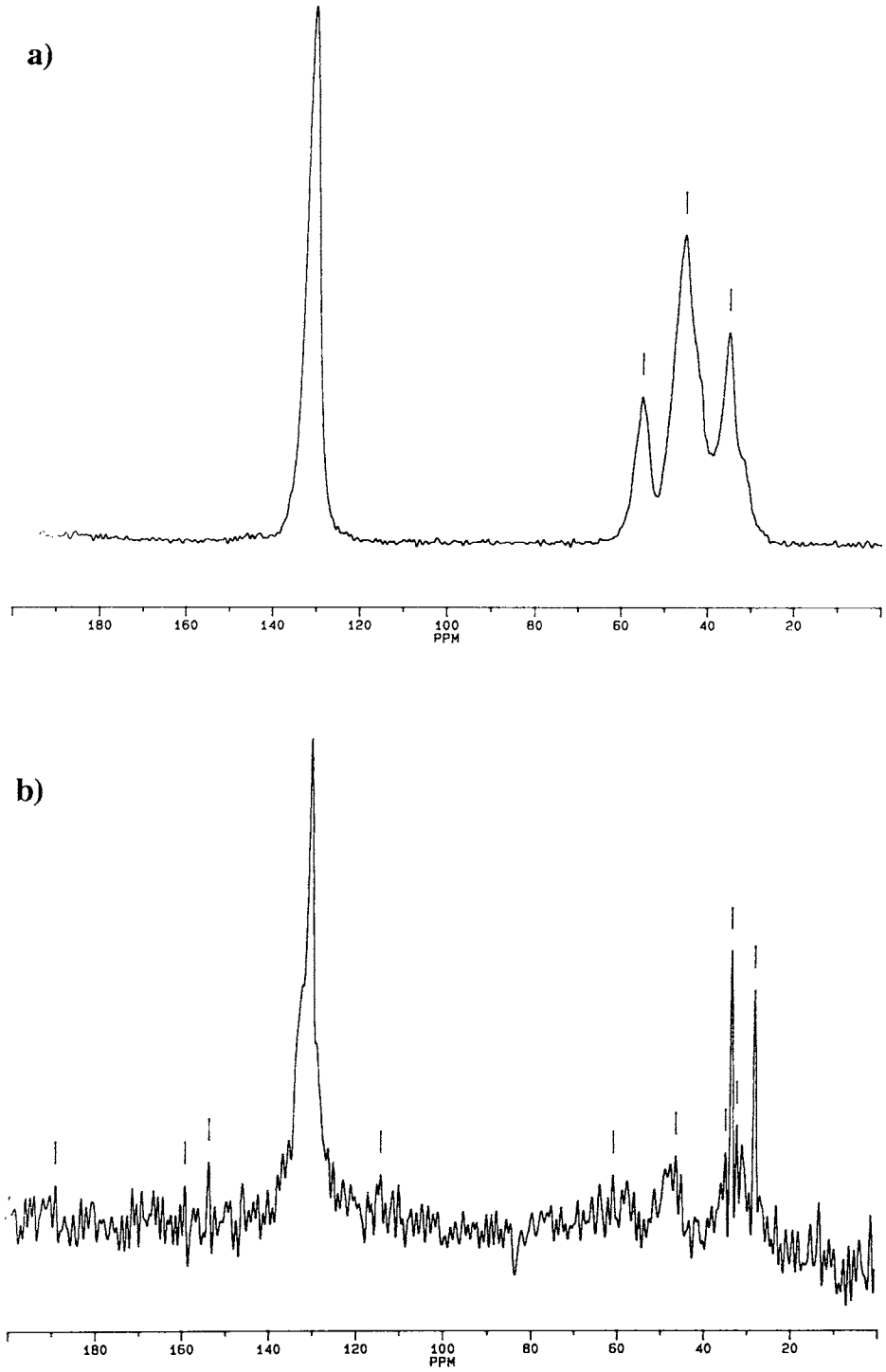


Figure 7 DCPD resin cured in bulk at room temperature, 20 min after mixing, *in situ* NMR measurement. (a) ^{13}C CP/MAS NMR spectrum. (b) ^{13}C HPDEC NMR spectrum, with recycle delay = 0.1 s.

cured at room temperature for 20 min and 4 h, respectively. On both figures, the representative peaks of polybutadiene are significantly found as are the peaks of DCPD or poly-DCPD.

As mentioned before, the ^{13}C HPDEC NMR spectrum with a short relaxation time (ca. 0.1 s) only shows the resonances of carbon atoms in the mobile phase. In fact, the "mobile" phase may in-

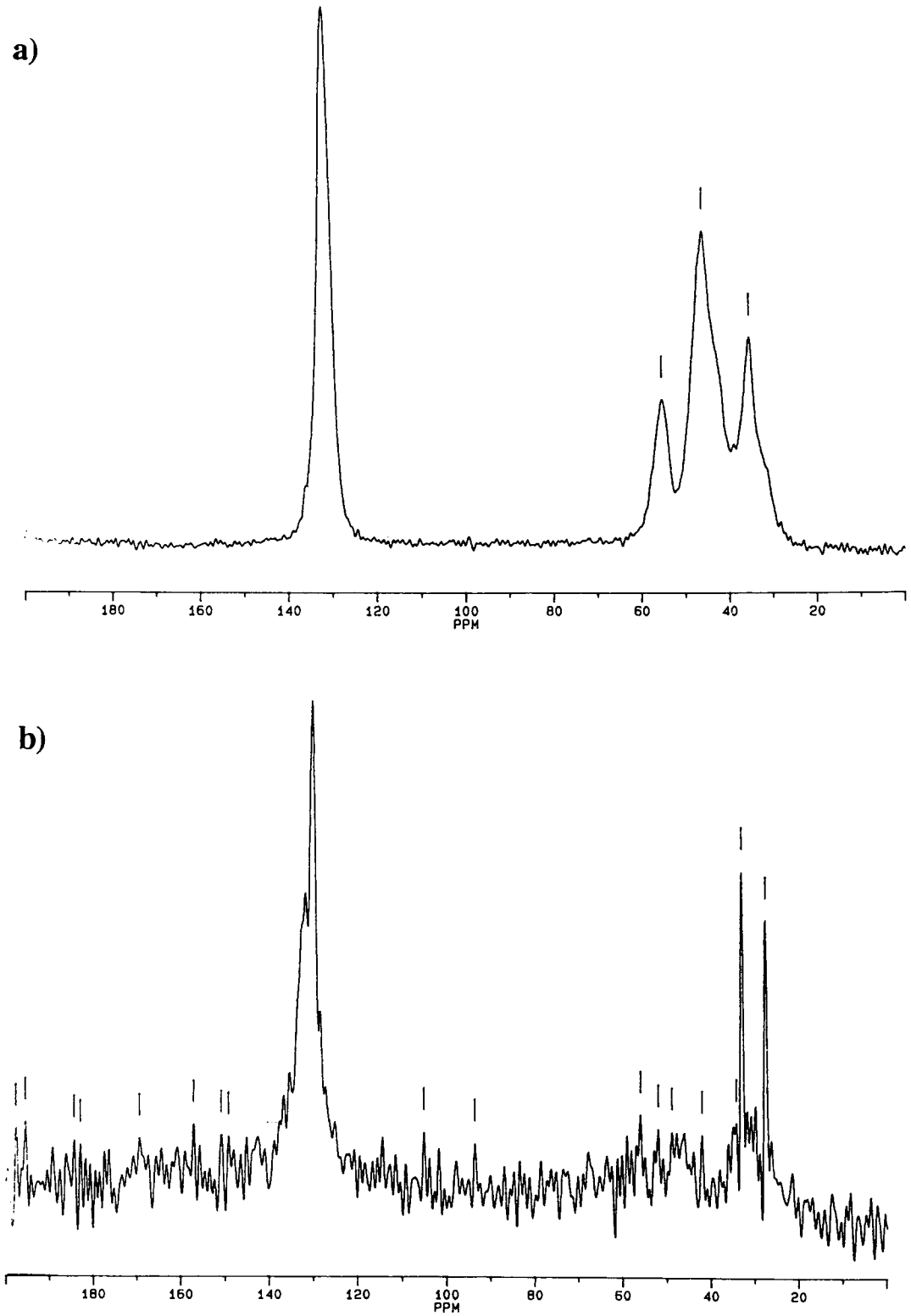


Figure 8 DCPD resin cured in bulk at room temperature, 4 h after mixing, *in situ* NMR measurement. (a) ^{13}C CP/MAS NMR spectrum. (b) ^{13}C HPDEC NMR spectrum, with recycle delay = 0.1 s.

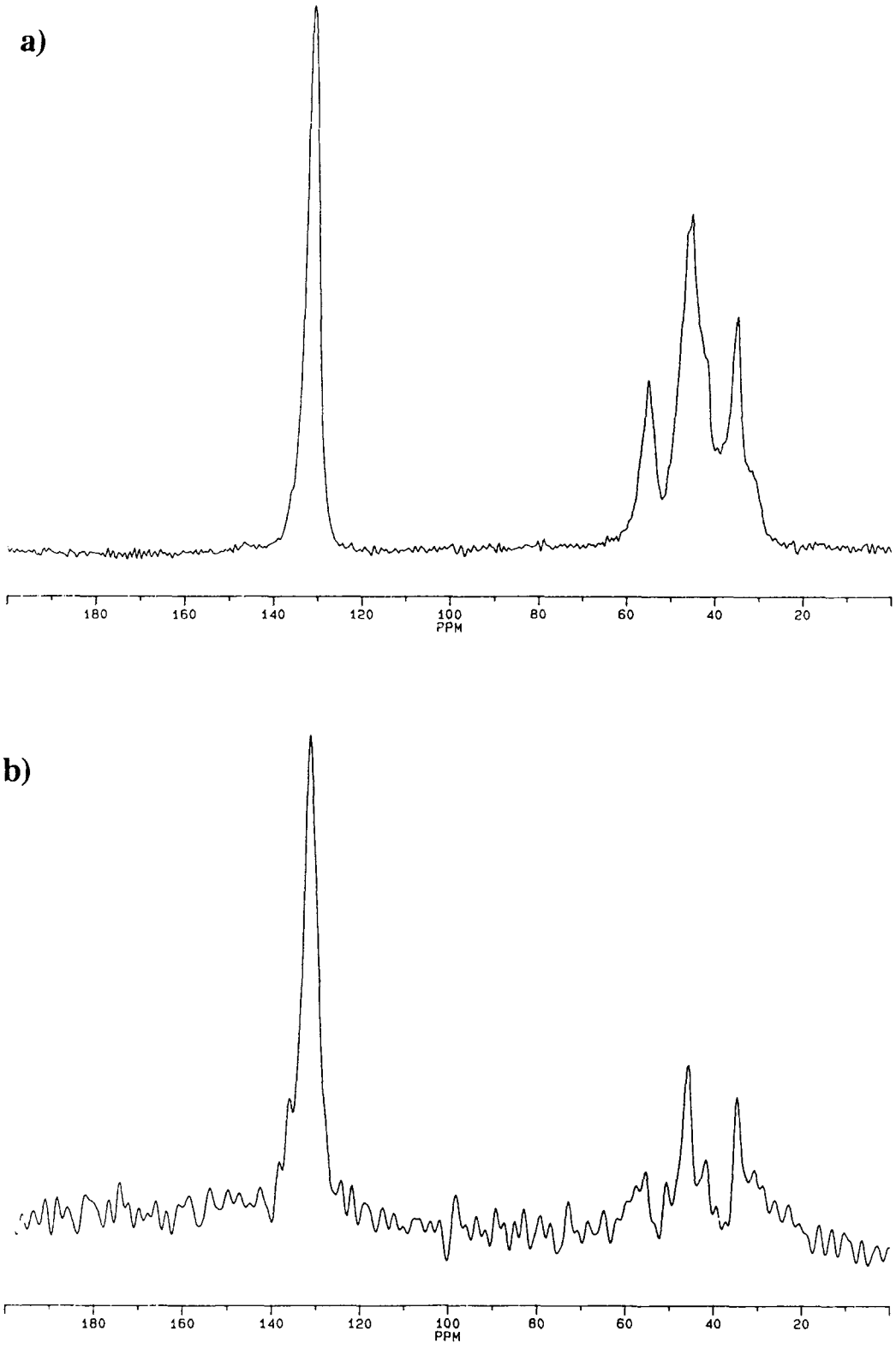
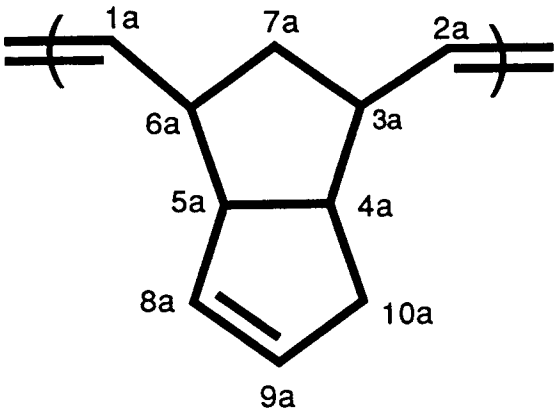
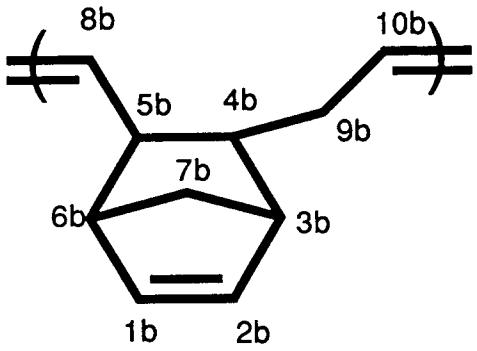


Figure 9 Well-cured DCPD resin without polybutadiene. (a) ^{13}C CP/MAS NMR spectrum. (b) ^{13}C HPDEC NMR spectrum, with recycle delay = 0.1 s.



Scheme 1



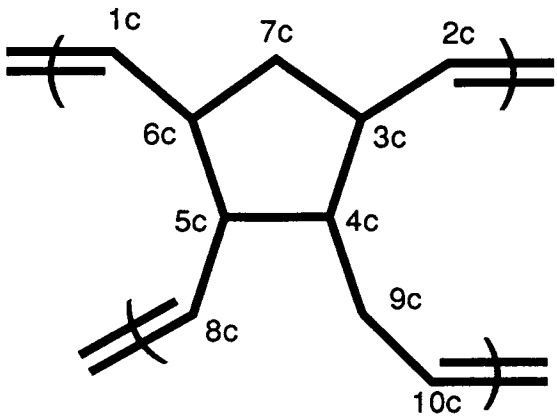
Scheme 2

clude unreacted monomers, short or relatively short molecules which are not grafted on the network, mobile pendant chains grafted on the network, and long polymer chain segments between crosslinking points. The ^{13}C HPDEC NMR spectrum really depends on the relaxation time of the measuring system. Figure 10 shows the ^{13}C HPDEC NMR spectrum of the same system for Figure 7(b) except the relaxation time for Figure 10 is 0.5 s instead of 0.1 s for Figure 7(b). Making a comparison on Figures 7(a), 10, and 7(b), one finds that the decrease of relaxation time results in an increasing significance of polybutadiene's peaks.

On both Figures 10 and 7(b), one finds the major peaks of both DCPD (and/or poly-DCPD) and polybutadiene. The major difference between these two figures is that the peaks of DCPD and/or poly-DCPD are more significant in Figure 10 than in Figure 7(b). It is because, in the condition of longer relaxation time, the poly-DCPD molecular chains either in pendant situation or located between crosslinking points may be more likely detected in Figure 10 than in Figure 7(b). On the other hand, one may say that the peaks of DCPD/poly-DCPD in Figure 7(b) may be attributed to the unreacted DCPD monomers and uncrosslinked, linear poly-DCPD chains.

Similar to Figure 7(b), Figure 8(b) also shows the major peaks of both DCPD (and/or poly-DCPD) and polybutadiene in the "mobile" phase after 4 h curing in bulk condition. Generally speaking, both figures have similar NMR spectra. The conversions of DCPD in both cases, however, are quite different. The reacting system for Figure 7(b) should contain more free, unreacted DCPD monomers than that for Figure 8(b). Therefore, one may conclude that the peaks of DCPD/poly-DCPD in Figure 7(b) should be more attributed to the unreacted DCPD monomers and less to uncrosslinked and linear poly-DCPD chains. By contrast, the peaks of DCPD/poly-DCPD in Figure 8(b) should be more attributed to uncrosslinked and linear poly-DCPD chains and less to the unreacted DCPD monomers.

Different from Figures 7(b) and 8(b), Figure 9(b) shows the resonances of mobile poly-DCPD chains only, not those of polybutadiene and free DCPD monomer, because the system for Figure 9(b) does not contain additive and is well cured. The mobile poly-DCPD chains shown on Figure 9(b) may be more attributed to the uncrosslinked and linear poly-DCPD chains and, perhaps, less to some pendant poly-DCPD chains. Generally speaking, Figure 9(b) is similar to Figure 9(a) except the peaks in Figure 9(b) are less broad than in Figure 9(a). The peak at 136 ppm, corresponding to the six-member cyclic double bonds shown in Scheme 2, is clearly observed in Figure 9(b), although it is still relatively small compared with the whole broader peaks of all types of double bonds. However, this peak is much more significant in Figure 9(b) than in Figure 9(a). This result reveals that the structural element of Scheme 2 does exist in the final polymer structure, while its



Scheme 3

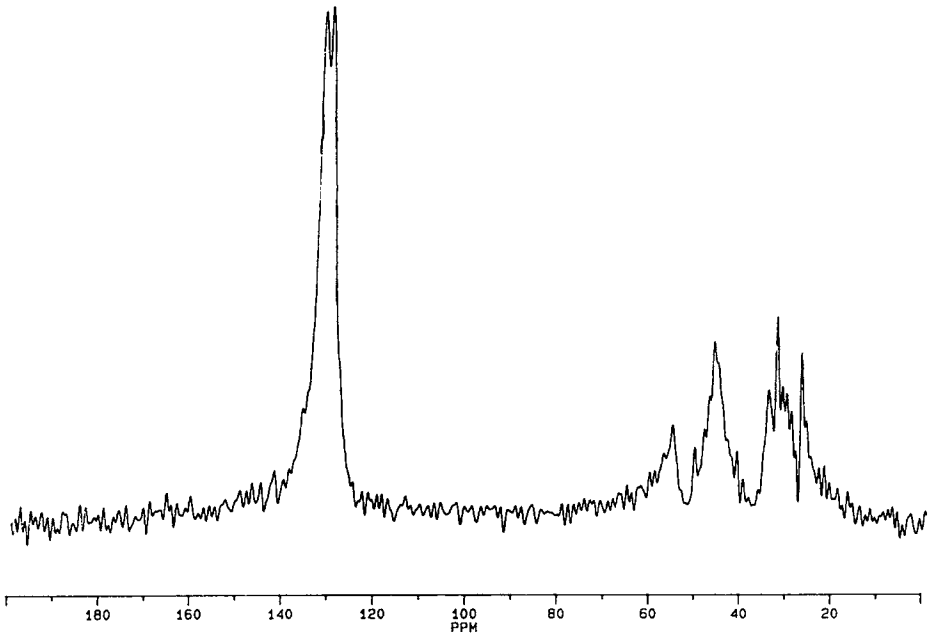


Figure 10 DCPD resin cured in bulk at room temperature, 20 min after mixing. ^{13}C HPDEC NMR spectrum with recycle delay = 0.5 s.

extent in the whole structure is relative unimportant and it is likely present in the uncrosslinked polymer chains and, perhaps, in the pendant polymer chains.

Oxydation Study

As mentioned in the experimental section, a resin formulation similar to that for Figures 7(a) and 8(a) but with a shorter gel time, ca. 10 s, has been prepared to make plaques by RIM process at 60°C. The cured plaques have been stored outdoors for several weeks at room temperature. A sample taken from the surface of one of the RIM plaques was ground into powder under liquid nitrogen. This powder was prepared for solid-state NMR investigation. Figure 11(a) shows the ^{13}C CP/MAS NMR spectrum of the sample taken from the surface of RIM plaque. In fact, Figure 11(a) is quite similar to Figures 7(a), 8(a), and 9(a) in spite of different resin-curing situation and resin formulation. One, however, finds a small but very broad peak in the neighborhood of 80 ppm in Figure 11(a), which has not been found in Figures 7(a), 8(a), or 9(a).

Another sample was taken from the center of the same RIM plaque studied for Figure 11(b). It was also ground into powder under liquid nitrogen for solid-state NMR investigation. The ^{13}C CP/MAS NMR spectrum of this sample is shown in Figure 11(b). Similar to Figures 8, 10, and 12 and different from Figure 11(a), Figure 11(b) does not show a broadening in the neighborhood of 80 ppm. The only difference between the samples for Figures 11(a) and 11(b) is that the former is from the surface and the latter is from the center of the same RIM plaque. This analysis proves that the sample from the surface of the RIM plaque has been oxidized during the outdoor storage.

In order to identify the nature of the broad peak at 80 ppm, another sample taken from the center of RIM plaque was ground under air and the powder was put in an oven at 60°C under air for 7 days. The purpose of this procedure is to prepare a highly oxidized poly-DCPD sample for comparison. The ^{13}C CP/MAS NMR spectrum of this highly oxidized sample is shown in Figure 12. By comparing Figure 12 with Figure 11(b), several significant facts are observed.

First of all, all of the peaks in the range between 25 and 60 ppm, which correspond to the carbon atoms on C—C liaison, in Figure 11(b) have been merged together and become a large and broad peak, centered at 43 ppm, shown in Figure 12. It may mean that the polymer network of the highly oxidized sample is more crosslinked and more dense than the unoxidized sample.

The second point is that a broad peak in the neighborhood of 78 ppm is obviously detected. This peak represents the carbon atoms single bonded to oxygen nuclei which are produced by the oxidation procedure. The third point observed

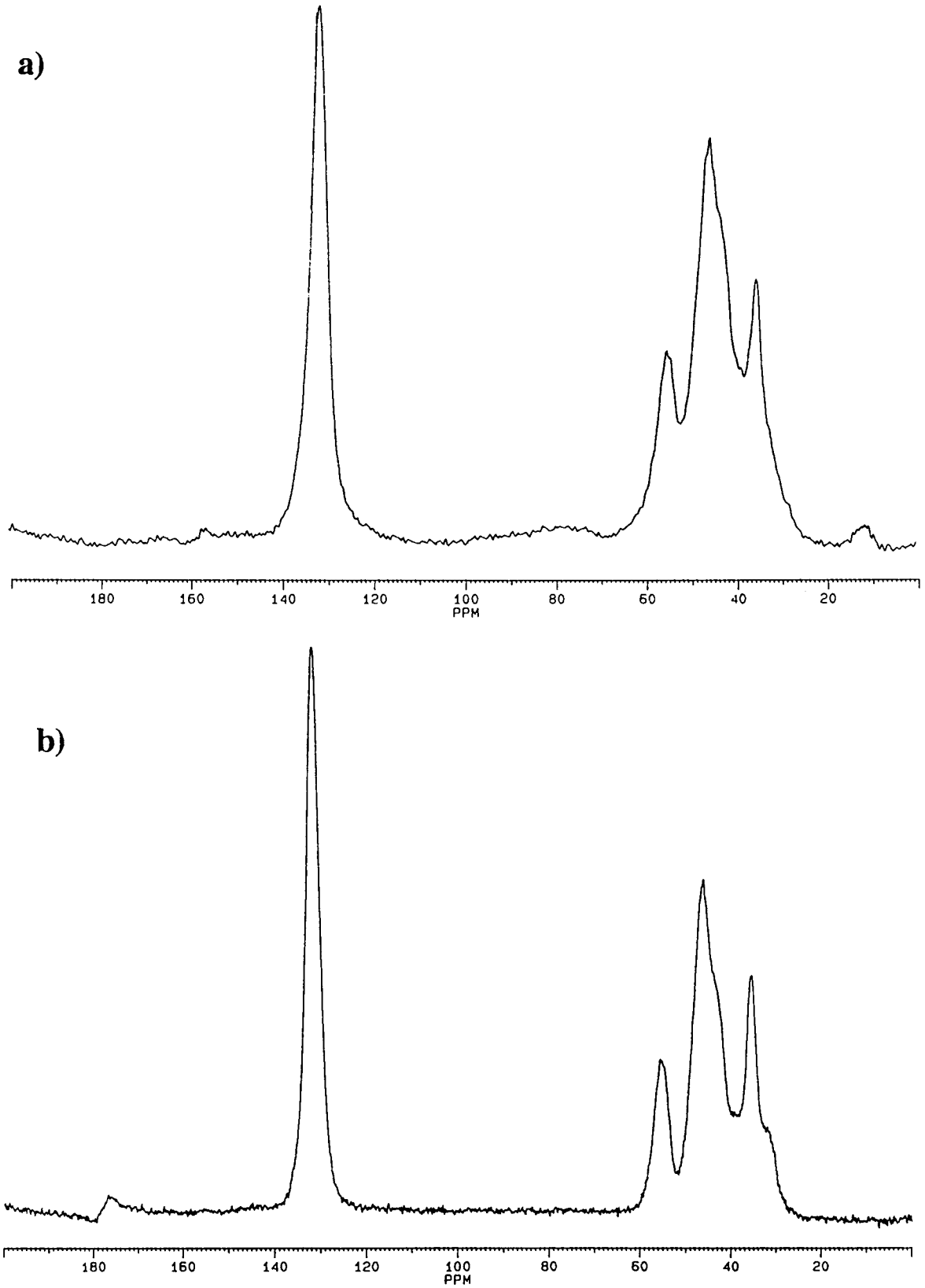


Figure 11 ^{13}C CP/MAS NMR spectrum of RIM-molded poly-DCPD plaque (a) from sample surface and (b) from sample center.

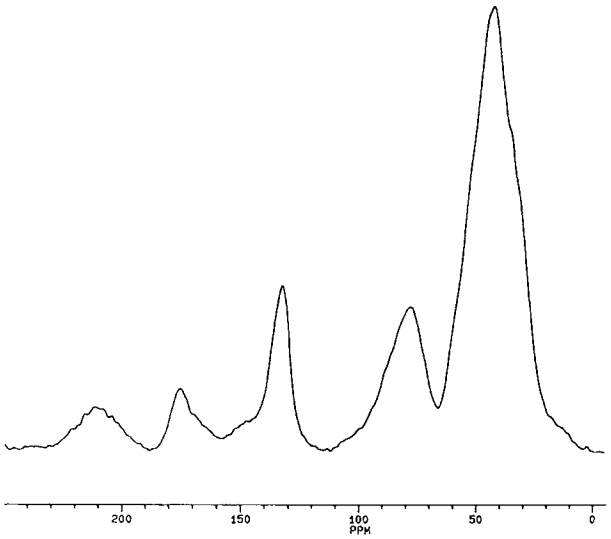


Figure 12 ^{13}C CP/MAS NMR spectrum of highly oxidized poly-DCPD sample.

in Figure 12 is that the peak of 132 ppm, representing carbon atoms in C=C groups, becomes smaller. It reveals that the double-bond content in the oxidized sample becomes less due to consumption by oxidation.

Peaks around 174 ppm are also detected and assigned to carbonyl groups of acid and/or ester chemical functions. In the 210 ppm area, carbonyl groups of cetonic and/or aldehydic functions induced during oxidation of poly-DCPD were identified.

Based on the above discussion, the small broad peak in the neighborhood of 80 ppm, shown in Figure 11(a), can be identified as a carbon atom single bonded to an oxygen nucleus formed on the surface of the RIM plaque by oxidation during outdoor storage. Other evidence for the occurrence of oxidation during outdoor storage is the decrease of the ratio of the C=C peak (132 ppm) to all of the C—C peaks (from 25 to 60 ppm) in Figure 11(a), compared with that in Figure 11(b). The oxidation process certainly results in a decreasing content of double bonds in the polymer network. In fact, the oxidation extent of the sample on the surface of RIM plaque seems not to be very high by comparing Figure 11(a) with 11(b).

The current results of the oxidation study shown above, certainly, are not sufficient yet for network characterization of oxidized poly-DCPD. However, it should be addressed here that this preliminary study may lead to a new route for oxidation kinetics study of poly-DCPD and for network characterization of oxidized poly-DCPD, in the future.

CONCLUSION

The DCPD monomer used for thermosetting DCPD resin is identified, by NMR technique, to be an endo isomer of DCPD. This study shows a relatively better accuracy on the attribution of ^{13}C and ^{1}H peaks of DCPD monomer than literature data.

The study with ^{13}C CP/MAS NMR technique shows that the ^{13}C CP/MAS NMR spectra for the curing DCPD system are similar to each other after the gel point until cured. Since the peaks of polybutadiene additive are not significantly detected, the ^{13}C CP/MAS NMR spectra of a fully formulated system are likely the same as those of a cured system without additive. The very small peak of six-member cyclic double bonds reveals a significantly lower extent of 6-member cyclic double bonds in the network structure.

The study with ^{13}C HPDEC NMR technique, on the other hand, shows the existence of mobile phase, including polybutadiene additive, unreacted DCPD monomers, linear poly-DCPD chains, and/or pendant poly-DCPD chains, in the final polymer matrix. The results show that the relatively small content of 6-member cyclic double bonds is likely present in the linear poly-DCPD chains and/or pendant poly-DCPD chains rather than in the crosslinked network.

By the ^{13}C CP/MAS NMR technique, one may put in evidence that the surface of a cured poly-DCPD plaque may suffer an oxidation process during storage after molding. Due to oxidation, a formation of carbonyl functional groups and a decrease of double bonds content are identified in the ^{13}C CP/MAS NMR spectrum of surface sample. However, the sample in the center of the cured plaque does not show any similar phenomena in the NMR spectra. It may be a steric effect by the sample thickness which limits the diffusion of oxygen into the center of the sample for proceeding oxidation. This new technique may be further explored for oxidation kinetics study of poly-DCPD and for network characterization of oxidized poly-DCPD, in the future.

REFERENCES

1. J. P. Schik, *Proc. Int. AVK Conf.*, Berlin, p. 24 (1991).
2. E. A. Ofstead and N. Calderon, *Makromol. Chem.*, **154**, 21 (1972).
3. A. J. Amass, M. Lotfipour, J. A. Zurimendi, B. J. Tighe, and C. Thompson, *Makromol. Chem.*, **188**, 2121 (1987).

4. BF Goodrich Corp., US patent 4,484,010 (1993).
5. BF Goodrich Corp., European patent application, N° 324, 979 (1988).
6. S. Doughty, G. Recher, and Y. S. Yang, *Kunststoffe German Plastics,* **82**(12), 12 (1992).
7. S. Doughty, G. Recher, and Y. S. Yang, *Kunststoffe German Plastics,* **82**(12), 1191 (1992).
8. L. Matejka, C. Houtman, and C. W. Macosko, *J. Appl. Polym. Sci.,* **30,** 2787 (1985).
9. M. Shmorhum, lecture, *7th Ann. Meeting of Polym. Proc. Soc.,* Hamilton, Ontario, Canada, Apr. 1991.
10. W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.,* **64,** 2229 (1976).
11. K. Nagayama, *J. Magn. Res.,* **40,** 321 (1980).
12. A. Bax and G. Morris, *J. Magn. Res.,* **42,** 501 (1981).
13. D. L. Turner, *J. Magn. Res.,* **49,** 175 (1982).
14. T. H. Mareli and R. Freeman, *J. Magn. Res.,* **48,** 158 (1982).
15. S. R. Hartmann and E. L. Hahn, *Phys. Rev.,* **128,** 2042 (1962).
16. A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.,* **59,** 569 (1973).
17. T. Laurens, D. Nicole, P. Rubini, J. C. Lauer, M. Matlengiewicz, and N. Henzel, *Magn. Res. Chem.,* **29,** 1119-1129 (1991).
18. Q. T. Pham, R. Pétiaud, H. Waton, and M. F. Llauro-Darricades, *Proton and Carbon NMR Spectra of Polymers,* Penton Press, London (1991).

Received November 1, 1995
Accepted November 1, 1995