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Curing study of dicyclopentadiene resin and effect of elastomer on its polymer network

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Curing of DCPD thermosetting resin has been followed by liquid state and solid state n.m.r. techniques. The liquid state n.m.r. spectra show the peaks corresponding to polybutadiene elastomers and residual DCPD monomers during the curing process. Solid state ^{13}C CP/MAS and ^{13}C HPDEC n.m.r. techniques have also been applied for characterization of polymer matrix during curing for carbon atoms in rigid phase and in mobile phase, respectively. S.e.c. measurements on DCPD resin before and after cure are also carried out to give supplementary information, besides n.m.r. measurements, to investigate the role of polybutadiene in the poly-DCPD network. It is concluded that polybutadiene elastomers could participate in the poly-DCPD network structure in the form of pendant chains or fixed segments in between crosslinking points. A scheme of the final polymer matrix structure is proposed at the end of study.

(Keywords: dicyclopentadiene (DCPD); polydicyclopentadiene (PDCPD); n.m.r)

INTRODUCTION

The use of dicyclopentadiene (DCPD) as a co-monomer in several polymeric systems such as EPDM and unsaturated polyesters has been documented[1]. Recently, DCPD resins have been formulated to make tough thermosetting materials via 'Ring Opening Metathesis Polymerization' or ROMP reaction[2–4]. Unlike other thermosetting resins such as polyurethanes, epoxies, and unsaturated polyesters, whose polymer properties are dependent upon the prepolymer molecular structures, DCPD resins polymerize to give a homogeneous material whose properties are essentially intrinsic to DCPD.

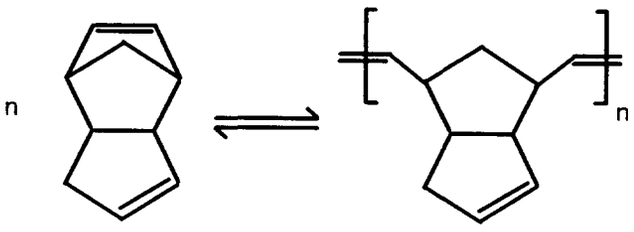
The DCPD resins are formulated in two components, A and B.

Component A comprises DCPD monomer, ethylenic comonomers, co-catalyst, and additives.

Component B is $\geq 99\%$ identical to A apart from containing an organo-metallic catalyst instead of the co-catalyst.

The catalyst of the metathesis polymerization is often chloride or ammonium salt of transition metals such as tungsten and molybdenum[4,5]. The cocatalyst is usually organic metal such diethyl aluminium chloride (DEAC)[4,5]. The catalyst and the co-catalyst must be stored separately, otherwise reaction starts immediately. The additives serve 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, in which polybutadiene is often used for reasons 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 noted that the cyclic unsaturation of the second cyclopentene ring may be most probably undertaken by 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 thought not to proceed to completion. Nevertheless, it causes a cross-linking phenomenon which results in a three-dimensional network structure. Almost certainly due to its highly cyclic structure, poly-dicyclopentadiene (PDCPD) resins present an extraordinary toughness.

The industrial processing of DCPD resins is by RIM (reaction injection moulding) or by RTM (resin transfer

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moulding). The two reactive liquid components are dosed and mixed under pressure in a mixing head whereupon they enter into a closed mould in which the mixture polymerizes. The reaction kinetics of DCPD RIM process has been studied[8,9]. Moreover, a viscoelastic study has been carried out to correlate the molecular structure of PDCPD and its physical behaviour[6,7].

However, a literature review shows that it lacks studies on the polymer structure characterization. A recent study has tried to investigate the network structure of poly-DCPD by solid state n.m.r. technique[9]. It reveals that there is a relatively small amount of six-membered cyclic double bonds remaining in the polymer matrix. This is because the six-membered cyclic double bonds are more reactive than the five-membered cyclic double bonds. The remaining six-member cyclic double bonds are probably present in the linear poly-DCPD chains and/or pendant poly-DCPD chains rather than in the crosslinked network.

This work is to carry out a further characterization study on the PDCPD structure during curing and to investigate the effect of an additive such as polybutadiene on the polymer matrix.

EXPERIMENTAL

Materials and preparation

Two-component DCPD resin (Telene®) supplied by TELENOR company was used for cure study and polymer characterization.

The 2-component DCPD resin has been mixed by a static mixer and been injected in a glass tube (5 mm o.d. sample tube for liquid state n.m.r. analysis) and in a zirconia rotor (for solid state n.m.r. analysis) under an inert atmosphere.

This formulation has been adjusted to have gel time around 20 min in order to have enough operation time. The sample tube—or rotor—was capped and was put in the probe of liquid—or solid—n.m.r. spectrometer at room temperature. Solid state ^{13}C n.m.r. spectra were taken during the reaction, after gel, in bulk condition.

The same 2-component DCPD resin, mixed by a static mixer, was also injected in a 4-mm-thickness glass mould under an inert atmosphere at room temperature to make a flat plaque. This moulding was carried out in a quasi-adiabatic procedure for one day before demoulding.

Instruments

Liquid n.m.r. spectra were recorded on a Bruker AM-300 spectrometer operating at 75.4 MHz for ^{13}C nuclei. Chemical shifts were given in ppm from TMS. ^{13}C spectra were obtained using a 5.15 μs pulse width (equal to 90° flip angle) with a 10 s recycle delay for 1024 scans, and ^{1}H broad band decoupling.

Solid state (CP/MAS) n.m.r. spectra were recorded on a Bruker MSL-200 spectrometer at 50.32 MHz for ^{13}C[10,11].

Two kinds of specimens were prepared. To study the beginning of crosslinking (near gel point) the two components DCPD resin was injected directly under nitrogen in zirconia rotor and we began to record spectra as soon as the sample was in a gel state. To study samples crosslinked for a long time, 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. For all specimens, rotor 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-polarization 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[12].

Solid state n.m.r. spectra were also recorded in a High Power Decoupling (HPDEC) sequence (classical ^{13}C sequence—90°C pulse with high power ^{1}H decoupling during acquisition). The HPDEC n.m.r. spectra used almost the same conditions as for the CP/MAS n.m.r. 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.

Size exclusion chromatography (s.e.c.) was used for molecular weight measurements at room temperature with following column combination: 10^5, 10^4, 10^3 and 500 Å. Tetrahydrofuran (THF) was used as elution solvent at an elution rate of 1.5 ml min^{-1}. All the s.e.c. curves were analysed with a calibration curve obtained from standard samples of monodisperse polystyrene to estimate the molecular weights.

RESULTS AND DISCUSSION

Liquid state ^{13}C n.m.r. spectra of DCPD resin curing in the n.m.r. measurement tube at different reaction times are shown in *Figure 1*. It should be noticed that the sample is in bulk condition without any solvent. The first spectrum (*Figure 1a*) at cure time (t_{cure}) equal to 5 min can be considered as a reference spectrum since the reaction does not really take place yet. The second spectrum (*Figure 1b*) is taken at t_{cure} = 18 min which is before but close to the gel point. As mentioned in the Experimental section, the gel time of this system is around 20 min. Since it is close to the gel point, there, certainly, are immobile macromolecules, and the system viscosity may be relatively high. Consequently, the base line of the spectrum (*Figure 1b*) is very noisy although the scan number has been increased to 151. The third spectrum (*Figure 1c*) is taken at t_{cure} = 75 min, which is beyond the gel point..

There is no doubt that *Figure 1a* represents the resonance of all the carbon atoms in the reaction system because it is in liquid state and the reaction does not take place. The peaks, however, are relatively broad instead of sharp peaks with good signal/noise ratio, usually observed in liquid state ^{13}C n.m.r. spectra. This is because the system is in bulk condition instead of a diluted solution as usual. *Figure 1a* shows all the principal peaks of endo-DCPD monomer[12], in which the peaks in the range between 131 and 136 ppm represent cyclic double bonds of DCPD; while, the peaks at 35, 41, 45, 46, 50 and 55 ppm represent the cyclic C–C bond of DCPD. More precisely, the peak at 136 ppm represents one of the carbon atoms on the six-membered cyclic double bond. It is found from *Figure 1a*, that the ratio of the peak of 136 ppm to all the unsaturation peaks is around 25%. This result agrees with the DCPD molecular structure.

On *Figure 1a*, several important peaks of polybutadiene are also 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[12,13]. By the results of *Figure 1a*, it is found that the elastomer content is less than 5%, which is in accordance with the industrial formulation. The resonance peaks of side chain double bonds of polybutadiene (at 143 ppm and 114 ppm) are not detected. It may be because that the polybutadiene content is relatively small in the resin. All the other peaks may belong to the ethylenic comonomers and organo-metallic catalyst.

When the system approaches the gel point, long chain macromolecules, highly branched macromolecules and crosslinked microgels are probably formed through metathesis reaction of DCPD. This means, during reaction, there are more and more immobile substances occurring in the system. Since the liquid state n.m.r. can only detect highly mobile phase in the system, the immobile substances such as crosslinked macromolecules and microgels may not be detected. Therefore, the mobile phase in the reaction system during curing should normally contain unreacted monomers and mobile additives. *Figure 1b* clearly shows the peaks of polybutadiene because polybutadiene is known to be unreactive in the metathesis reaction of DCPD and it always remains in the mobile phase. It is possible that some of the polybutadiene molecules may be buried in crosslinked particles and lose their mobility. Similar results regarding polubutadiene are found in *Figure 1c* when $t_{cure} = 75$ min.

All the peaks of DCPD are found significantly decreased in *Figures 1b* and *c* by comparing with those in *Figure 1a*. Since the ratio of the peak of 136 ppm to all the unsaturated peaks of DCPD is always around 25% in *Figures 1b* and *c*, it is believed that the detected substance besides polybutadiene should be unreacted DCPD monomer. The fact of decreasing DCPD peaks is understandable because there are less and less residual DCPD monomers in the reaction system during curing. Measuring the residual monomer amount, however, is not the topic in this study and is not feasible by the current technique.

If one takes a rough ratio of unsaturated peaks of polybutadiene to those of DCPD in *Figure 1*, it is found that this ratio starting from a small value in *Figure 1a* through a high value in *Figure 1b* and then down to a medium value in *Figure 1c*. If one considers that polybutadiene is unreactive during metathesis reaction, this ratio should keep increasing with time because of decreasing monomer content. The contrast may be explained by a trapping effect of polybutadiene in the poly-DCPD network. Near the gel point, the polymer network should not be tight and polybutadiene molecules are mobile rather than trapped. Long after the gel point, however, the polymer network can be tight enough to trap a significant part of polybutadiene molecules. If the increase in the amount of trapped polybutadiene molecules is more than the decrease of unreacted monomer, it, then, may result in a decrease in the ratio of polybutadiene to DCPD, as shown in *Figure 1c* vs. *Figure 1b*.

Solid state ^{13}C CP/MAS n.m.r. spectra of DCPD resin curing in the n.m.r. measurement rotor at different reaction time are shown in *Figure 2*. *Figure 2a* represents the spectrum at gel point, i.e. $t_{cure} = 20$ min; while *Figures 2b* and *c* show the spectra at $t_{cure} = 60$ min and 240 min, respectively. All three spectra are very similar to each other. The principal peaks of polybutadiene are not observed in *Figure 2*.

The unseen polybutadiene n.m.r. peaks is believed due to its small amount in the system (less than 5% weight) as well as the broad peaks of DCPD and poly-DCPD. The importance of proton relaxation for ^{13}C n.m.r. studies of solid polymer has been shown by Clemett *et al.* in the case of block copolymer styrene–butadiene–styrene[14]. The relative intensities of peaks are dependent on the

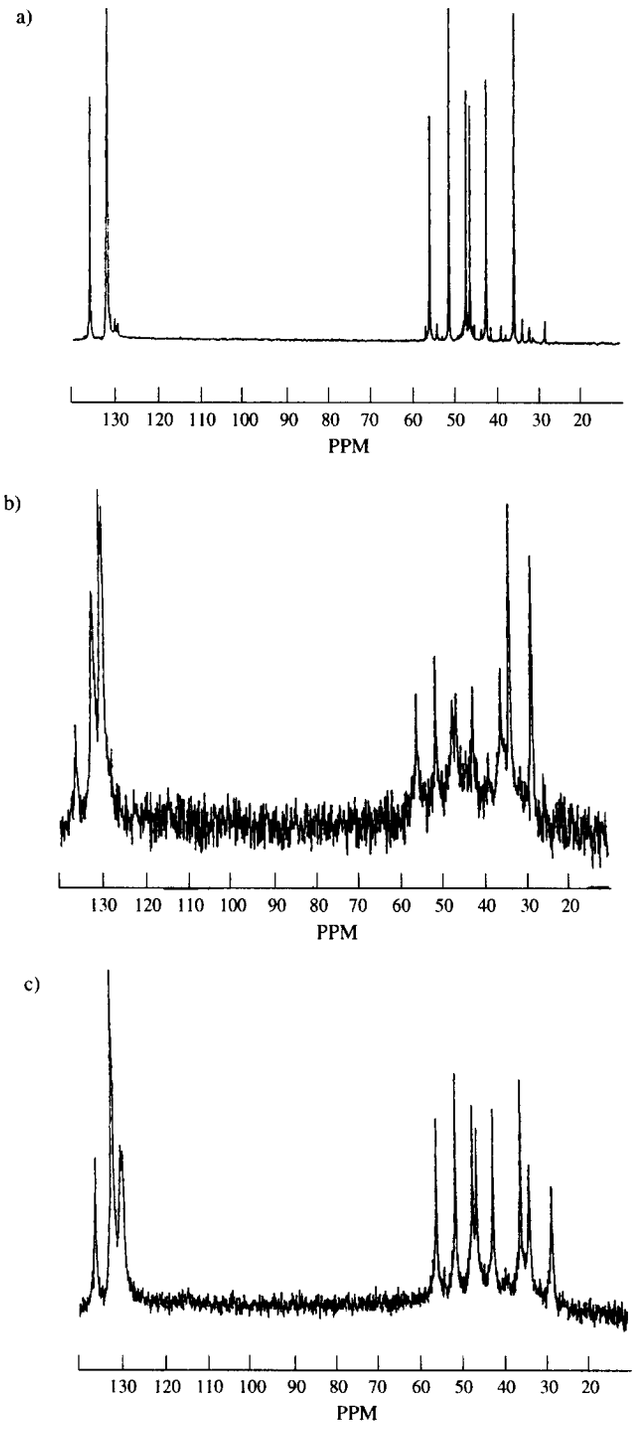

Figure 1 Liquid state ^{13}C n.m.r. spectra of DCPD resin curing: (a) at $t_{cure} = 5$ min; (b) at $t_{cure} = 18$ min; (c) at $t_{cure} = 75$ min

relation between the relaxation times of components and the experimental parameters chosen. Furthermore, CP/MAS under the conditions used (mixing time and recycle delay) favours rigid segment detection.

Since the ^{13}C CP/MAS n.m.r. spectrum shows the resonances of all 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 1a* by liquid state n.m.r. investigation. Moreover, the major peaks of DCPD and/or poly-DCPD in the ^{13}C CP/MAS n.m.r. spectra are largely broad. Consequently, the small peaks of polybutadiene are probably immersed in the broad peaks of DCPD and poly-DCPD and are not visible.

The fact of identical ^{13}C CP/MAS n.m.r. spectra of *Figures 2a, b* and *c* has been discussed in another paper[12]. It is believed due to similarity of carbon atoms on DCPD and poly-DCPD on the n.m.r. spectra. Consequently, the ^{13}C CP/MAS n.m.r. spectra of the curing system in all the curing stages are logically identical since the unreacted monomer and the polymer have similar resonance peaks. It has also been discussed[12] that the double bond of the six-membered ring is more reactive for the metathesis reaction than that of the five-membered

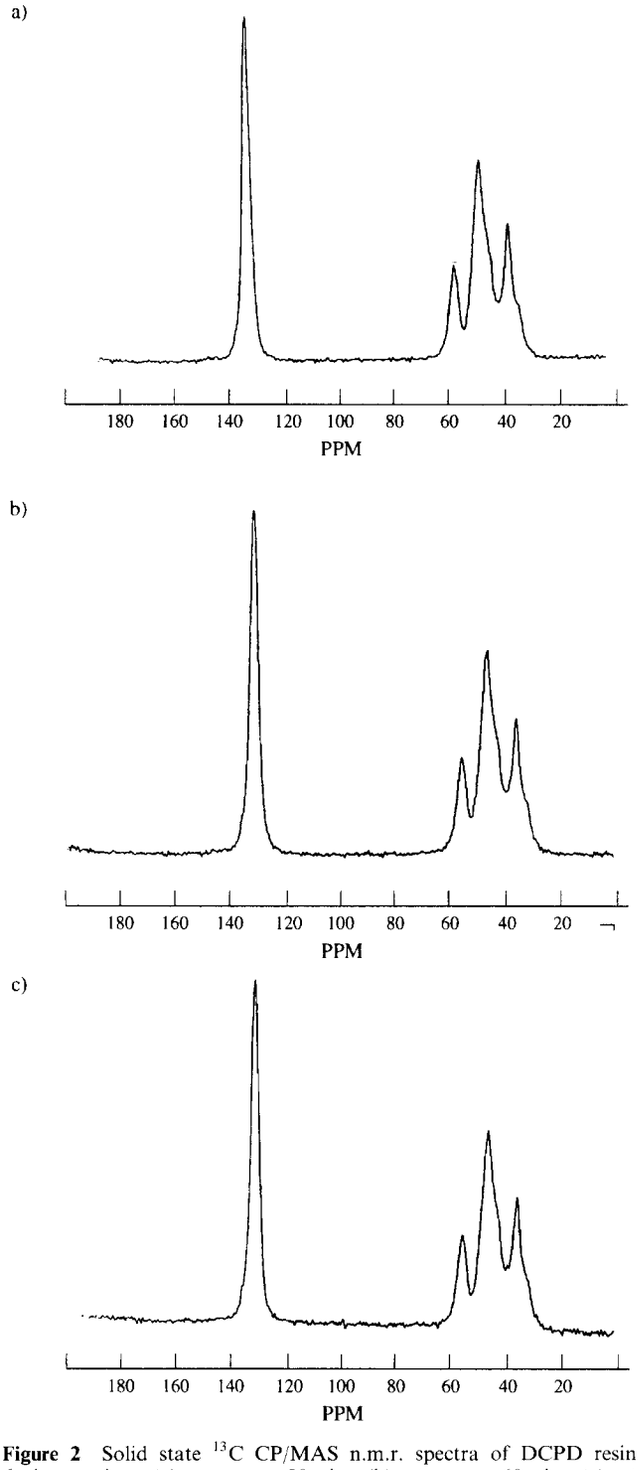

Figure 2 Solid state ^{13}C CP/MAS n.m.r. spectra of DCPD resin during curing: (a) at $t_{cure} = 20$ min; (b) at $t_{cure} = 60$ min; (c) at $t_{cure} = 240$ min

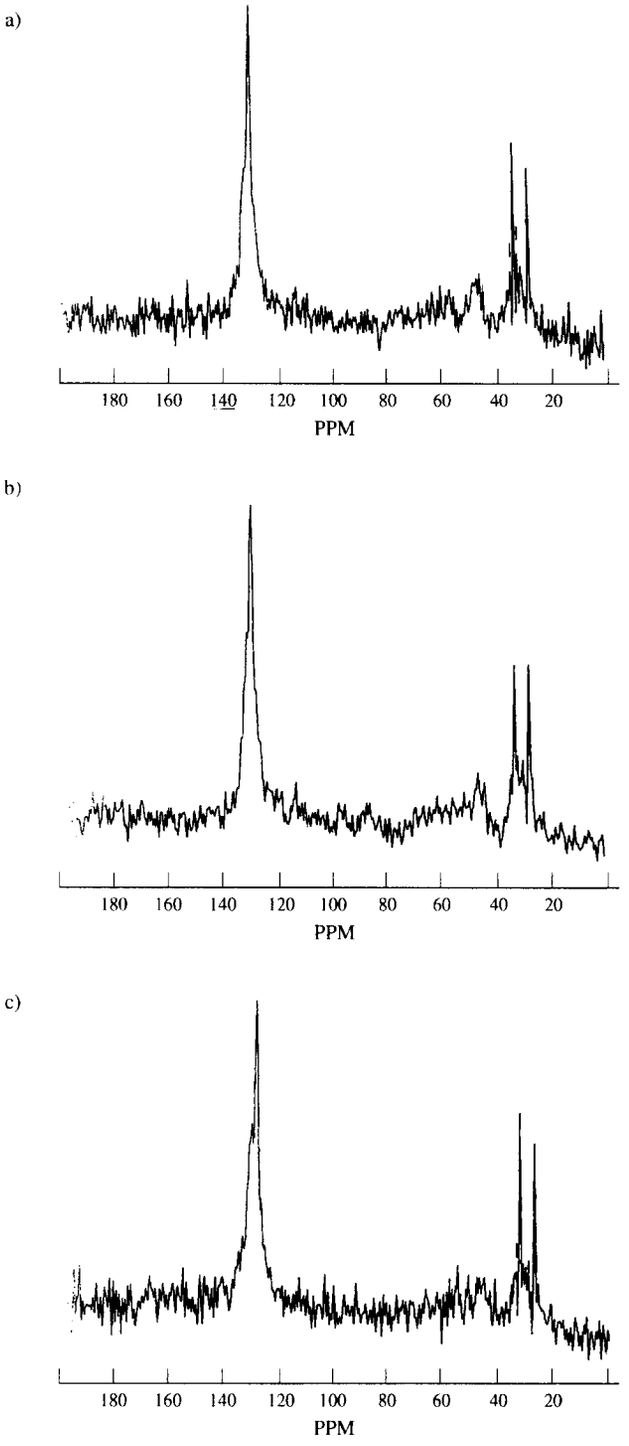

Figure 3 Solid state ^{13}C HPDEC n.m.r. spectra of DCPD resin during curing: (a) at $t_{cure} = 20$ min; (b) at $t_{cure} = 150$ min; (c) at $t_{cure} = 240$ min

ring. It was derived by a fact that the peak of 136 ppm (double bond of the six-membered ring) shown on *Figure 2* represents less than 2% of the broad peak (max. point at 131 ppm) which represents all the double bonds in the polymer structure.

Solid state ^{13}C HPDEC n.m.r. spectra of DCPD resin curing in the n.m.r. measurement tube at different reaction times are shown in *Figure 3*. All the n.m.r. measurements of *Figure 3* are taken with a repetition rate of 0.1 s to detect the resonance of mobile phase only. *Figure 3a* represents the spectrum at gel point, i.e. $t_{cure} = 20$ min; while *Figures 3b* and *c* show the spectra at $t_{cure} = 150$ min and 240 min, respectively. Those spectra are similar to each other. Different from in *Figure 2*, the principal peaks of polybutadiene are clearly observed in *Figure 3*. The peaks of DCPD monomer and/or mobile poly-DCPD become minor, compared to polybutadiene, in *Figure 3*.

The ^{13}C HPDEC n.m.r. spectrum with a short recycle delay (*ca.* 0.1 s) normally shows the resonances of carbon atoms in the soft phase, by saturation of ^{13}C nuclei in rigid phase (recycle delay very short compared with the ^{13}C relaxation time). In fact, the 'mobile' phase may include unreacted monomers, short or relatively short molecules which are not grafted on the network, mobile pendant chains grafting on the network, and long polymer chain segments between crosslinking points. It has been shown that the peaks of DCPD/poly-DCPD in ^{13}C HPDEC n.m.r. spectra can probably be attributed to the unreacted DCPD monomers and uncrosslinked, linear poly-DCPD chains[12].

Similar to *Figure 3*, *Figure 1* also shows the resonances of soft phase. However, the spectra in *Figures 1* and *3* for the same reacting system are not similar to each other in the same spectral reaction region. The difference may be caused by different n.m.r. techniques. The spectra of *Figure 1* are obtained by liquid state n.m.r.; while those of *Figure 3* are obtained by solid state HPDEC n.m.r. Normally, the liquid state n.m.r. shows better resolution of spectra than the solid state n.m.r. That is why the peaks in *Figure 1* are more distinguished than in *Figure 3*. Moreover, the recycle time applied for the liquid state n.m.r. is 0.5 s which is longer than 0.1 s used for the HPDEC n.m.r. Therefore, one finds more significant peaks of DCPD in *Figure 1* than in *Figure 3*. With recycle time of 0.1 s, DCPD ^{13}C were saturated and have low relaxation possibility. The very much more rapid longitudinal relaxation of rubber components in a sample consisting of several components frequently permits the spectrum of the elastomer components to be selectively recorded without special preparation of the samples, by means of 90° ^{13}C pulses[15]. MAS n.m.r. not only detects the rubber but also permits statements concerning the chemical structure of the rubber employed. If the proportion of the soft phase amount to a few percent only, rapid 90° excitation and high power decoupling (HPDEC) are frequently sufficient to suppress the matrix signal. Rubbers are usually measured by direct 90° excitation of the ^{13}C nuclei, since cross polarization is based on dipole–dipole interaction.

It may be concluded that the liquid state n.m.r. may be a useful technique for reaction kinetics study rather than the solid state n.m.r. because of the better resolution and the evidence of presence of DCPD monomer in the liquid state n.m.r. spectra. One, however, needs a reference substance for kinetics study. The kinetics study of DCPD metathesis reaction may be discussed elsewhere.

With liquid state n.m.r. technique, we look for no reacted molecules; with solid state n.m.r.s, using HPDEC sequences, we look for reacted molecules which are as soft phase. Furthermore, solid n.m.r. with HPDEC sequence may be a useful technique for study of polybutadiene polymer in DCPD network.

Parallel to the experiment for n.m.r. measurements shown in *Figures 1*, *2* and *3*, another DCPD resin with the same formulation has been mixed by a static mixer and been injected in a vial under inert atmosphere at room temperature. Small pieces of resin sample from the bulk in the vial have been taken at different reaction time, especially after the gel point. Those samples, then, have been transferred into a test tube with $CHCl_3$ solvent and have rested for 48 h. The gel phases have been removed from the tube and have been washed several times by fresh solvent to remove all the soluble molecules as possible. The gels have been dried under vacuum to remove solvent before n.m.r. measurements.

Figure 4a shows the solid state ^{13}C CP/MAS n.m.r. spectrum of the gel sample taken at 20-min cure time which is just after the gel point, while *Figure 4b* shows the solid state ^{13}C HPDEC n.m.r. spectrum of the same sample. Similarly, *Figures 5a* and *b* show the solid state ^{13}C CP/MAS and HPDEC n.m.r. spectra, respectively, of the gel sample taken at 42-min cure time.

The ^{13}C CP/MAS n.m.r. spectra of the gel samples taken at different reaction time, shown on *Figures 4a* and *5a*, in fact, are very similar to each other. They,

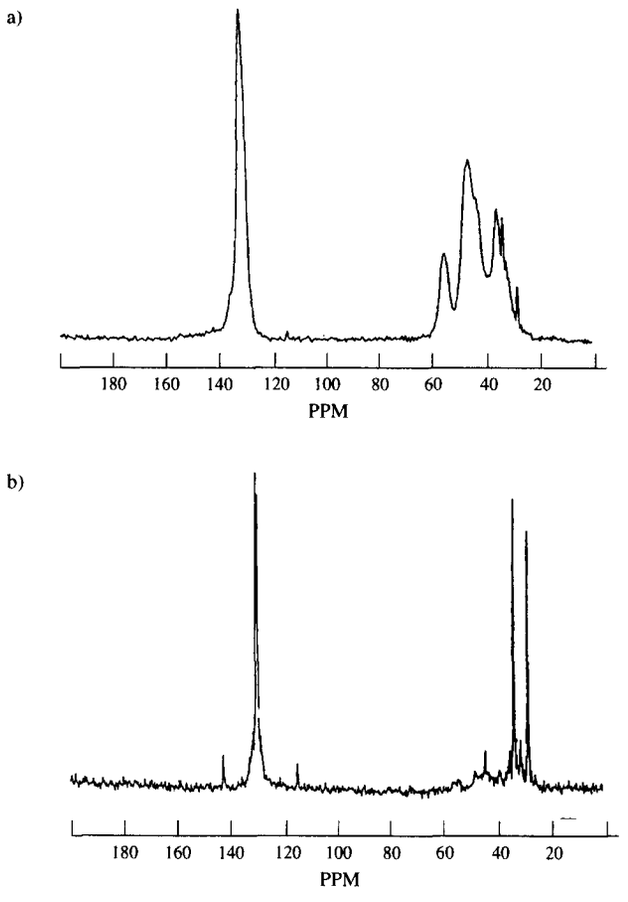

Figure 4 Poly-DCPD gel sample cured at 20 min. The gel sample has been swollen and washed by $CHCl_3$ solvent: (a) solid state ^{13}C CP/MAS n.m.r. spectrum; (b) solid state ^{13}C HPDEC n.m.r. spectrum

furthermore, are also similar to the ^{13}C CP/MAS n.m.r. spectra of the reacting system during curing, shown on *Figure 2*. The only difference is that the peaks of polybutadiene (27 and 33 ppm) are found in *Figure 4a* but not in *Figures 2* and *5a*.

On the other hand, the ^{13}C HPDEC n.m.r. spectrum of the gel sample at $t_{cure} = 20$ min, shown on *Figure 4b*, is somehow different from that of the reacting system at the same time, shown on *Figure 3a*. The peak resolution of *Figure 4b* is much better than that of *Figure 3a*. The peaks of polybutadiene, including the peaks of pendant double bonds at 114 and 142 ppm, are clearly observed in *Figure 4b*. The peaks of DCPD/poly-DCPD are observed in *Figure 4b* but are significantly smaller compared with those of polybutadiene. The ^{13}C HPDEC n.m.r. spectrum of the gel sample at $t_{cure} = 42$ min, shown on *Figure 5b*, however, is similar to those of the reacting system, shown on *Figure 3*.

The results shown above for the gel samples are quite interesting and need to be further discussed. It should be recalled that the gel samples have been treated and washed by solvent. When they were put in $CHCl_3$ solvent after 48 h, the gel at $t_{cure} = 20$ min was greatly swollen, but the gel at $t_{cure} = 42$ min was much less swollen. This is because the gel at $t_{cure} = 20$ min was just after the gel point and the gel structure was loose rather than compact. However, the gel at $t_{cure} = 42$ min had higher conversion and its gel structure became more compact.

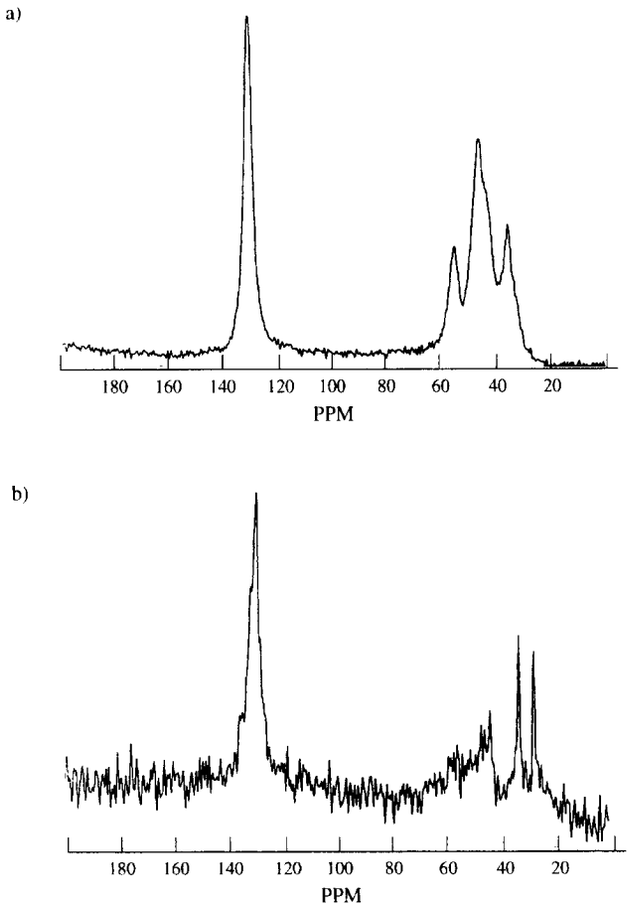

Figure 5 Poly-DCPD gel sample cured at 42 min. The gel sample has been swollen and washed by $CHCl_3$ solvent: (a) solid state ^{13}C CP/MAS n.m.r. spectrum; (b) solid state ^{13}C HPDEC n.m.r. spectrum

Since the gel sample at $t_{cure} = 20$ min has loose structure and is completely swollen and washed by solvent, it is considered that the washed gel no longer contains either DCPD monomer or free polybutadiene molecules. It means all the information observed by n.m.r. is only regarding the polymer network and has no interference from residual monomer and free polybutadiene. With this information, the results of *Figures 4a* and *b* reveal two important observations.

First of all, there are polybutadiene molecules grafting on the poly-DCPD gel network. This is concluded by the observation of polybutadiene peaks in rigid phase (*Figure 4a*) as well as in mobile phase (*Figure 4b*). The observation of polybutadiene peaks in *Figure 4a* but not in *Figure 2* may come from the relative ratio of polybutadiene to the poly-DCPD is higher in *Figure 4a* and its network has been swollen by solvent. Moreover, the observation of polybutadiene peaks in rigid phase may reveal that there are short polybutadiene segments integrated in the compact network structure.

Secondly, grafted polybutadiene segments are more mobile than poly-DCPD segments of the network. This is because one observes mainly poly-DCPD peaks in rigid phase (*Figure 4a*) and mainly polybutadiene peaks in mobile phase (*Figure 4b*). The higher mobility of polybutadiene segments may indicate that the polybutadiene segments in the polymer network are rather on pendant position than between crosslinking points. The polybutadiene found in mobile phase should be long molecular segment rather than short segment in rigid phase.

The observations discussed above are an important indication that polybutadiene molecules participate in the poly-DCPD network. This participation must be done by reacting the double bonds of polybutadiene with those of DCPD through the metathesis reaction. The metathesis reaction on DCPD results in polymer chain length increment or polymer network build-up by adding DCPD molecules on polymer chain. However, the metathesis on polybutadiene causes a rupture of polybutadiene chain which leads to a part of polybutadiene chain linking to poly-DCPD chain and the other part of polybutadiene chain remaining in the linear and uncrosslinked state. The uncrosslinked polybutadiene molecules in the system can be reflected in the HPDEC spectrum as shown in *Figure 3*. They can be washed out such as in the case of *Figures 4a* and *b*. Since the rupture of polybutadiene chain is a static process, the segments of polybutadiene grafting in poly-DCPD chain can be relatively long to be reflected in *Figure 4b* and can also be relatively short as shown in *Figure 4a*. It seems that there are more long segments than short ones in the poly-DCPD network.

The disappearance of polybutadiene peaks in *Figure 5a*, compared with *Figure 4a*, may be due to more poly-DCPD chains in the network than the short polybutadiene segments. The similarity between *Figures 2* and *5a* on CP/MAS spectra may lead to a conclusion that the existence of free polybutadiene molecules in the polymer matrix does not influence the resonance of rigid phase in solid state n.m.r. spectra. The CP/MAS technique detects the resonances of carbon atoms on the network structure only. After the build-up of gel network, the CP/MAS spectra are greatly similar to each other since the polymer structure is quite homogeneous.

As mentioned before, the gel sample at $t_{cure} = 42$ min has denser network structure and is less swollen in solvent than that at $t_{cure} = 20$ min. Although the former is swollen by $CHCl_3$, it is not as swollen as the latter. This means that the free polybutadiene molecules in the former may not be completely washed out. Maybe for this reason, *Figure 5b* shows a HPDEC spectrum similar to *Figure 3*. Since the network is more compact in *Figure 5b* than in *Figure 4b*, one has worse resonance resolution for the former than for the latter.

In order to more understand the role of polybutadiene in the final polymer structure, s.e.c. technology is applied to have complementary information besides n.m.r. technique. The s.e.c. curve of the DCPD resin (B component) is shown on *Figure 6a*. It shows a big peak at 47.5 min of elution time, corresponding to DCPD monomer, and a peak at 25.5 min of elution time, corresponding to polybutadiene elastomer. The measured number and weight average molecular weights of polybutadiene are 255 000 and 630 000, respectively, before curing.

A poly-DCPD plaque of 4 mm thickness has been moulded by injecting the mixed 2-component DCPD resin in a glass mould under inert atmosphere by a quasi-adiabatic procedure for one day. A small piece of the plaque was taken and put in THF solvent for one day to extract mobile molecules. The extraction was analysed by s.e.c.. The s.e.c. curve of the extraction is shown in *Figure 6b*. The results show a peak corresponding to residual DCPD monomer and a very broad but small peak, in the neighbourhood of 33 min of elution time, which may be polybutadiene or linear poly-DCPD. It is very surprising that there is no peak of polybutadiene as shown in *Figure 6a*. The disappearance of polybutadiene peak must be due to non-mobility of polybutadiene in the polymer matrix. It may be because the polybutadiene molecules are totally grafted in the network or they are completely trapped by the dense poly-DCPD network and cannot diffuse out of the matrix into solvent phase. If the reason is the latter, one may help extract the polybutadiene molecules by the grinding method.

A small piece of the same poly-DCPD plaque was ground into powder which was, then, put in THF solvent for one day to extract mobile molecules. The extraction was analysed by s.e.c. The s.e.c. curve of the extraction is shown in *Figure 6c*. The results also show a peak corresponding to residual DCPD monomer as shown in *Figure 6b*. *Figure 6c*, however, shows a significant peak, in the neighbourhood of 29 min, which is the polybutadiene phase extracted from the powder of moulded plaque. The peak of polybutadiene in *Figure 6c* is broader and shows smaller molecular weight than that in *Figure 6a*. The extracted polybutadiene has number and weight average molecular weights of 6420 and 19 370, respectively, which are 30 times less than the original polybutadiene in the formulation before curing.

The results obtained from *Figure 6c* clearly reveal the fact that polybutadiene chains are certainly cut down into shorter molecular chains. The cut of polybutadiene chains must be caused by the metathesis reaction during curing of DCPD resin, as discussed before. Since the remaining polybutadiene chains are 30 times shorter than the original polybutadiene molecules, the metathesis reaction on polybutadiene is certainly not negligible and should play an important role in network structure and also in polymer properties.

If the cut occurred on a free polybutadiene molecule, it would result in one polybutadiene segment grafting on poly-DCPD backbones as pendant chain, and the other segment remaining as a free molecule in the system. The latter segment can be detected by s.e.c. as shown in *Figure 6c*. The grafted and pendant polybutadiene segment, however, is more mobile than the poly-DCPD network and can be detected by the HPDEC n.m.r. as mobile phase as shown in *Figures 4b* and *5b*.

On the other hand, if the cut occurred on a pendant polybutadiene chain of the poly-DCPD network, it may lead to one of two following cases:

(i) two pendant polybutadiene segments on two poly-DCPD back-bones;

(ii) one free polybutadiene segment and a polybutadiene segment fixed in between poly-DCPD crosslinked points.

In both cases, the polybutadiene segments of all types are certainly shorter than before. The pendant segment and the free segments can be measured by HPDEC n.m.r. and s.e.c. as mentioned before. The fixed polybutadiene segments in between crosslinking points may be detected either by HPDEC n.m.r. if the segments are long enough to have relatively high mobility or by CP/MAS n.m.r. if the segments are short. However, the CP/MAS n.m.r. seems not a feasible technique since almost all the polybutadiene peaks are merged in the poly-DCPD peaks as shown in *Figures 2* and *5a*, except in *Figure 4a*. The reason that one observes polybutadiene peaks in *Figure 4a* may be because the gel has been completely swollen by solvent.

With the results shown above, there is no doubt that the polybutadiene molecules will participate in the network formation during curing of DCPD resin. The participation of polybutadiene in the network may be either in pendant chains or in between crosslinking

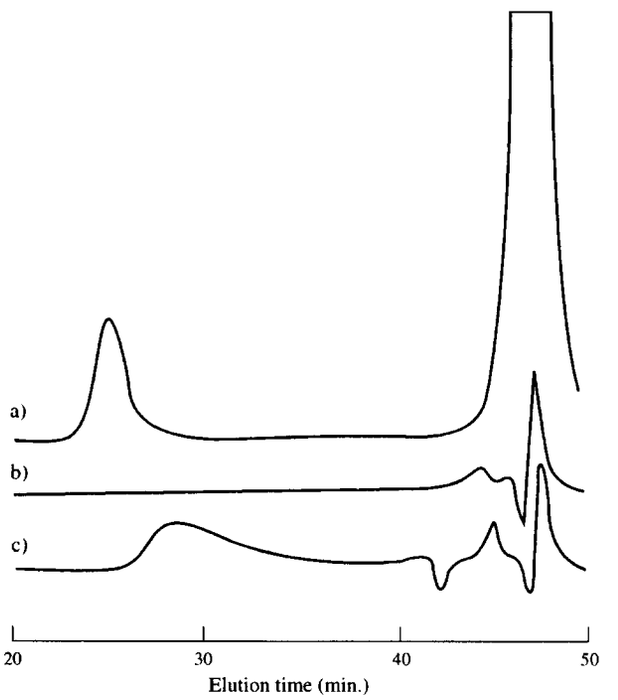

Figure 6 S.e.c. elution curves: (a) DCPD resin before cure; (b) extraction of cured poly-DCPD plaque; and (c) extraction of ground powder of cured poly-DCPD plaque

points. The segments in between crosslinking points can work as molecular spring segments which can absorb impact energy to resist a rupture of polymer network. This is probably the reason that the DCPD resins show an extraordinary impact strength.

Moreover, due to the participation of polybutadiene molecules in the polymer network, the reaction system remains always homogeneous until the end of the cure. This is because the polymer network containing polybutadiene segments shows better miscibility with the free polybutadiene phase in the matrix. Consequently, no phase separation phenomenon occurs during curing. It is, however, not the case in curing processes of the most thermosetting resins such as unsaturated polyester resins[16,17] and polyurethane resins[18,19].

With all the results obtained in this study, a network structure of a DCPD resin cured with polybutadiene elastomer is proposed in *Figure 7*. The neat poly-DCPD network, without elastomer, is mainly composed of three structural elements, shown as (a), (b) and (c) in *Figure 7*. The structural element (b) is the crosslinking point of the network. The content of the structural element (c) is relatively small, compared with (a) and (b). The ratio of the structural element (b) to the element (a) determines the crosslinking density of the network. There may be some residual DCPD monomers, shown as (d) in *Figure 7*, in the matrix, depending on the curing condition.

If one considers the participation of polybutadiene molecules in the network, there are three more structural elements, shown as (e), (f) and (g) in *Figure 7*. The structural element (e) represents the polybutadiene segment in between crosslinking points, and the element (f) shows the pendant polybutadiene segment on the poly-DCPD network. Both are parts of the final polymer network. The element (g) represents a free and unattached polybutadiene segment remaining in the matrix but not on the network.

The conclusion that polybutadiene can participate in the network build-up confirms the results obtained in *Figure 1*. As mentioned, in *Figure 1*, one finds that the ratio of polybutadiene to the residual DCPD monomer increases rapidly and decreases later on during curing by liquid state n.m.r. measurements. In the beginning of the curing, especially before gel point, DCPD is more reactive to metathesis reaction than polybutadiene. The consumption of DCPD is much higher than polybutadiene. Consequently, the ratio increases very fast as shown in *Figure 1b* vs *Figure 1a*. After that, the reaction rate of DCPD monomer becomes less significant, compared with metathesis occurring on the poly-DCPD chains for network build-up or polymer chain condensation. Polybutadiene, however, participates in the network build-up process and its reaction rate becomes more important in this region. Therefore, the ratio of polybutadiene to the residual DCPD monomer decreases as shown in *Figure 1c* vs *Figure 1b*.

Another important fact that has been pointed out in *Figure 1b* is that the residual DCPD monomer content is very much lower than expected at the gel point. Two classical methods, such as d.s.c. technique[20,21] and adiabatic polymerization[8,9] are often used to measure curing kinetics of thermosetting resins. They have been applied to follow the kinetics of metathesis reaction of DCPD resins. Both methods show that the conversion near the gel point is in the neighbourhood of 5% and never exceeds 10%. If one considers that the measured conversion is the conversion of DCPD monomers, the ratio of polybutadiene to the residual DCPD monomer at the gel point should not be as high as shown in *Figure 1b*. A possible explanation for this contrast is that the conversion at the gel point may be underestimated.

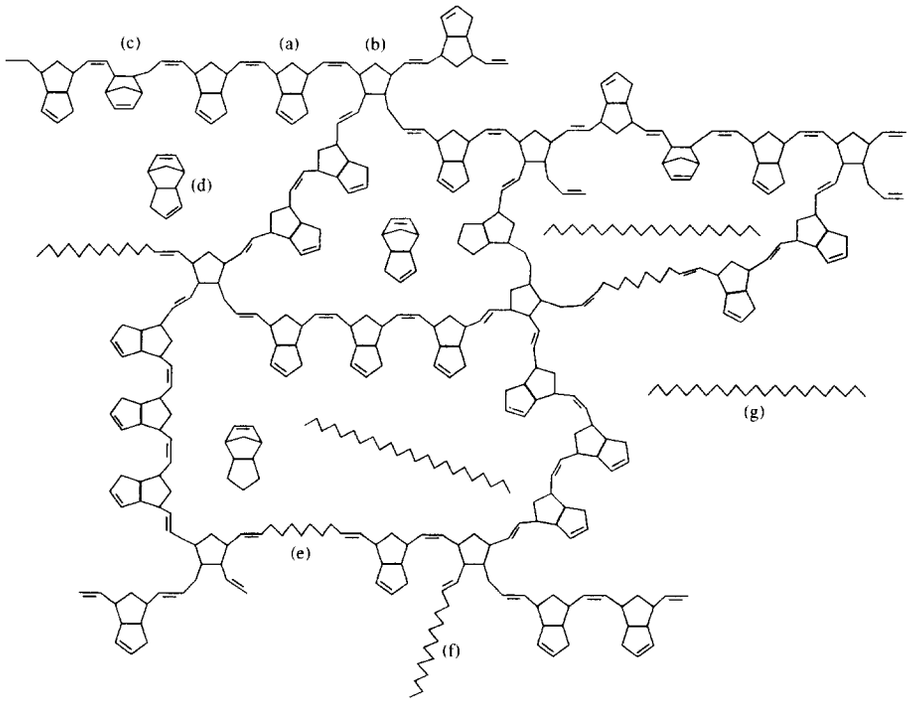

Figure 7 Scheme of proposed structure of poly-DCPD matrix after cure with structural elements: (a) chain units based on bicyclic pentane 2–3 ene molecule; (b) chain units based on cyclic pentane molecule; (c) crosslinking units based on norbornene molecule; (d) residual DCPD monomers; (e) polybutadiene segments fixed in between crosslinking points; (f) pendant polybutadiene segments on the poly-DCPD network; (g) free and unattached polybutadiene segments

It should be noted that the calculation base of the conversion by the two classical methods is the overall heat generated during the curing process. The conversion at gel point is obtained by dividing the heat generated until the gel point by the overall reaction heat. In a classical way, the overall reaction heat for DCPD metathesis reaction is thought of as coming from the opening of the first cyclic double bond of DCPD for chain growth as well as the opening of the second double bond of DCPD for network formation. One, unfortunately, has neglected at least two important reactions.

Looking at the polymer structure proposed in *Figure 7*, one could find there are numerous aliphatic double bonds on the poly-DCPD chains. Those aliphatic double bonds are formed by the ring-opening of DCPD monomers during metathesis reaction. They are, certainly, able to take part in the metathesis reaction as well as the DCPD monomers and to release reaction heat. This reaction could cause a new building of the polymer chains and network, but it would not affect the n.m.r. spectra. Since there are more and more aliphatic double bonds and less and less DCPD monomers in the matrix through the curing process, the reaction heat observed in the latter part of the curing process may come primarily from the metathesis reaction of the aliphatic double bonds.

The second important reaction being neglected is the metathesis reaction on polybutadiene. As discussed before, polybutadiene can also follow metathesis reaction, that results in the rupture of polybutadiene chains to graft polybutadiene segments on the polymer network. This reaction, certainly, will generate reaction heat. It, however, is not included in the classical calculation of reaction heat.

Therefore, it can be concluded that the overall heat measured by the classical methods represents not only the ring-opening reaction of the DCPD monomers but also the clipping reaction of poly-DCPD chains and polybutadiene molecules. The measured overall heat is over-estimated for the ring-opening reaction. Consequently, the conversion at the gel point or another moment, obtained by the classical methods, is under-estimated for monomer conversion, but it is probably correct for overall reaction conversion.

As discussed, the classical methods are not suitable for determination of monomer conversion. The liquid state n.m.r. technique seems to be a better solution for the measurement of monomer conversion because it can detect the residual DCPD monomers as shown in *Figure 1*. It, however, needs an internal reference for following the kinetics of monomer conversion.

CONCLUSION

The results of liquid state n.m.r. spectra of a DCPD resin during metathesis reaction show that the ratio of polybutadiene to the residual DCPD monomer increases rapidly and decreases later on during curing. This is because the DCPD monomers have higher consumption rate in the beginning of the reaction but polybutadiene takes part in the metathesis reaction with poly-DCPD chains at the later stage. The capability of the liquid state n.m.r. technique on measuring the residual DCPD monomers may be further applied to follow the reaction kinetics of DCPD monomer in the future.

The dynamic study with ^{13}C CP/MAS n.m.r. technique on following reaction shows that the ^{13}C CP/MAS n.m.r. spectra for the curing DCPD system are similar to each other after the gel point until cured. The peaks of polybutadiene additive are not significantly detected in the ^{13}C CP/MAS n.m.r. spectra. The very small peak of six-membered cyclic double bonds reveals significantly less six-membered cyclic double bonds in the network structure.

The study with ^{13}C HPDEC n.m.r. technique, on the other hand, shows the existence of mobile phase in the final polymer matrix. Since it is in bulk condition, the mobile phase may include polybutadiene additive, unreacted DCPD monomers, linear poly-DCPD chains and/or pendant poly-DCPD chains. The resolution of the solid state HPDEC n.m.r. spectra is worse than that of liquid state n.m.r. spectra. The results of the solid state HPDEC n.m.r. spectra show that the relative small content of six-member cyclic double bonds are probably present in the linear poly-DCPD chains and/or pendant poly-DCPD chains rather than in the crosslinked network.

It is found that polybutadiene molecules may take part in the metathesis reaction during curing of DCPD resin. This, finally, results in participation of polybutadiene segments on the poly-DCPD network in the form of pendant chains and fixed segments in between crosslinking points. The clipping of polybutadiene chains by metathesis reaction also causes shorter polybutadiene segments remaining unattached in the matrix. The participation of polybutadiene segments in the poly-DCPD network is believed the main reason that poly-DCPD matrix has an extraordinary impact strength and presents a completely homogeneous system until cured.

It should also be noted that the overall metathesis reaction for curing of DCPD resins could include the ring-opening reaction of DCPD monomer and the clipping reaction of poly-DCPD chains and polybutadiene chains. Classical methods for determination of the reaction kinetics by measuring the overall heat generated during curing could be suitable for 'overall' reaction conversion, but not suitable for monomer conversion. An alternative method to follow the monomer conversion is suggested by using the liquid state n.m.r. with an internal reference.

REFERENCES

1 Schik, J. P. *Proc. Int. AVK Conf.*, Berlin, 1991, p. 24
2 Ofstead, E. A. and Calderon, N. *Makromol. Chem.* 1972, **154**, 21
3 Amass, A. J., Lotfipour, M., Zurimendi, J. A., Tighe, B. J. and Thompson, C. *Makromol. Chem.* 1987, **188**, 2121
4 BFGoodrich Corp. *US Patent 4,484,010*, 1993
5 BFGoodrich Corp. *European Patent Application, No. 324,979*, 1988
6 Doughty, S., Recher, G. and Yang, Y. S. *Kunststoffe German Plastics* 1992, **82**, 12
7 Doughty, S., Recher, G. and Yang, Y. S. *Kunststoffe German Plastics* 1992, **82**, 1191
8 Matejka, L., Houtman, C. and Macosko, C. W. *J. Appl. Polym. Sci.* 1985, **30**, 2787
9 Shmorhum, M. Lecture, *7th Ann. Meeting of Polym. Proc. Soc.* Hamilton, Ontario, Canada, Apr. 1991
10 Hartman, S. R. and Hahn, E. L. *Phys. Rev* 1962, **128**, 2042
11 Pines, A., Gibby, M. G. and Waugh, J. S. *J. Chem. Phys* 1973, **59**, 569
12 Yang, Y. S., Lafontaine, E. and Mortaigne B. *J. Appl. Polym. Sci.* 1996, **60**, 2419
13 Pham, Q. T., Pétiaud, R., Waton, H. and Llauro-Darricades, M. F. 'Proton and Carbon NMR Spectra of Polymers', Penton Press, London, 1991, p. 122

14 Clemett, C. J., Smith, E. G., Harris, R. K., Kenwright, A. M. and Packer, K. J. *Polym. Commun.* 1987, **28**, 137
15 Voelkel, R. *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 1468
16 Suspène, L., Fourquier, D. and Yang, Y. S. *Polymer* 1991, **32**, 1593
17 Suspène, L. and Yang, Y. S. 46th Annual Conference of SPI composites, SPI Technical Papers, 7-C, 1991
18 Willkomm, W. R., Chen, Z. S. and Macosko, C. W. *Polym. Eng. Sci.* 1988, **28**, 888
19 Li, C., Goodman, S. L., Albercht, R. M., Cooper, S. *Macromolecules* 1988, **21**, 2367
20 Yang, Y. S., Lee, L. J., Lo, S. K. and Menardi, P. C. *J. Appl. Polym. Sci.* 1989, **37**, 2313
21 Yang, Y. S. and Lee, L. J. *J. Appl. Polym. Sci.* 1988, **36**, 1325