

# Mechanism of Radiation Vulcanization of Natural Rubber Latex Sensitized by Monoacrylates

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## SYNOPSIS

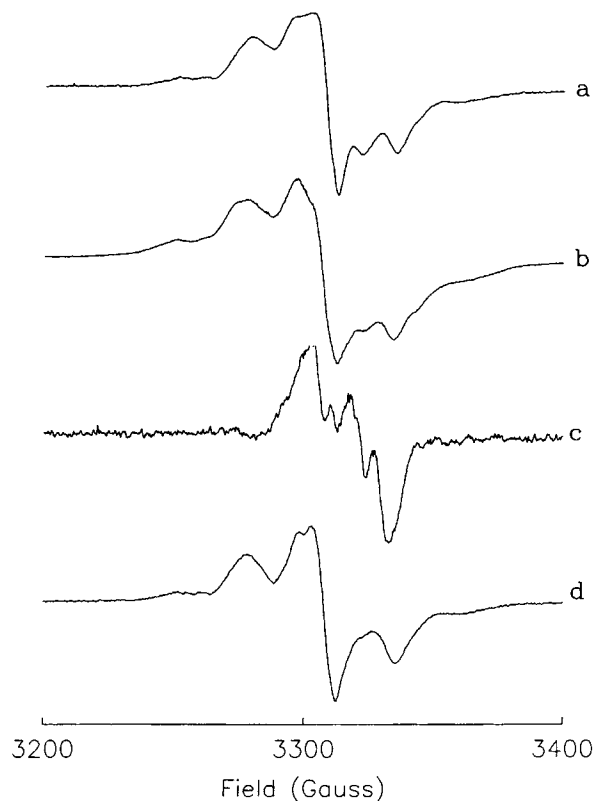
The mechanism of radiation vulcanization of natural rubber with 2-ethyl hexyl acrylate (2EHA) monomer was investigated using electron spin resonance spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The primary radicals formed in the acrylate molecule were found to abstract the allylic hydrogens of the polyisoprene. Crosslinking may occur through the allylic radicals and/or main chain radicals formed on the polyacrylate. Acrylate was found to concentrate in the rigid regions of the cross-linked rubber indicating heterogeneity and a nonuniform distribution of the acrylate in the latex particles. The addition of the acrylate and the irradiation seems to effect the Brownian motion of the latex particles. Both the viscosity and the NMR peak widths are effected by the irradiation. Addition of 5% 2EHA increases the crosslinking by a factor of 3.6. The thermal stability of the rubber first increases with the dose in the presence of acrylate, but drops at higher doses due to peroxide formation. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

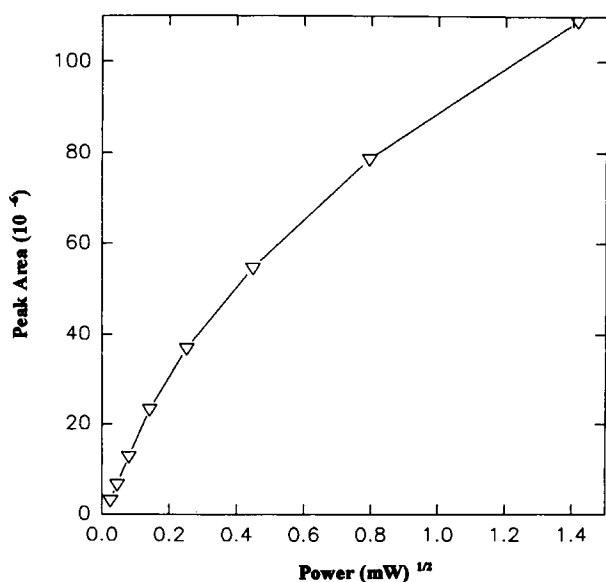
Vulcanization of natural rubber (NR) latex can be performed by ionization radiation, but it requires a dose more than 300 kGy,<sup>1</sup> which is too high a dose to be economical in industrial applications. Halogenated hydrocarbons, such as carbon tetrachloride and chloroform have been used as sensitizers to reduce the dose required for vulcanization.<sup>2-4</sup> The best vulcanized NR latex is produced using a dose below 30 kGy with 5 phr of carbon tetrachloride sensitizer. However, the majority of the carbon tetrachloride remains in the irradiated latex and is released in the working environment.<sup>5</sup> Hence the development of nontoxic sensitizers became a major priority to prevent this pollution of the working environment. Several polyfunctional monomers such as divinyl benzene,<sup>6</sup> diacrylates, and dimethacrylates<sup>5</sup> have been tried as sensitizers.

The effective polyfunctional monomers for vulcanization tend to reduce the stability of the latex, because of their low solubility in NR particles. However, some monofunctional monomers were found to increase the latex stability and to enhance the radiation vulcanization of NR.<sup>7</sup> It was previously believed that polyfunctionality was essential in order to enhance the radiation crosslinking in latex. Makuuchi et al.<sup>7,8</sup> reported studies of the mechanism of radiation sensitized crosslinking of NR latex by monofunctional monomers, such as 2-ethyl hexyl acrylate (2EHA) and *n*-butyl acrylate (*n*BA), with and without carbon tetrachloride. The observation of unsaturation in the polymer led them to propose that a reaction involving radical **I** could result in grafting of the acrylate to the NR, as in reaction (1), which could then polymerize to form crosslinks. In the present study, electron spin resonance (ESR), nuclear magnetic resonance (NMR), and FT-Raman spectroscopy were used to obtain more mechanistic information about this proposal. The physical and thermal oxidative properties of the resultant polymers were also studied.

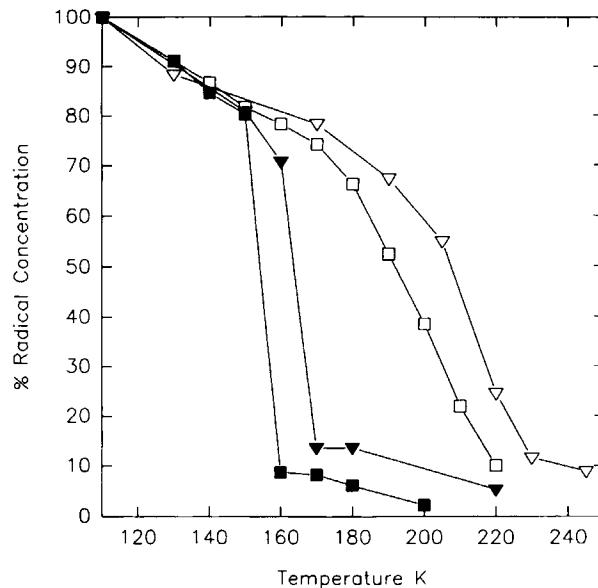
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**Figure 1** ESR spectra of 2EHA irradiated and measured at 77K (a) 40 dB, (b) 20 dB, (c) photobleachable at > 530 nm, (d) remaining after photobleaching.



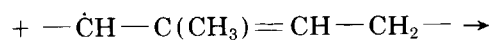
**Figure 2** Power spectrum of irradiated 2EHA at 77 K.



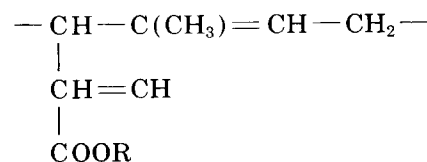
**Figure 3** Change in radical concentration with temperature ( $\nabla$ ) NR, ( $\square$ ) 2EHA/NR (30/70), ( $\blacktriangledown$ ) 2EHA, ( $\blacksquare$ ) 2EHA/ $\text{CCl}_4$  (50 : 5).



I



II



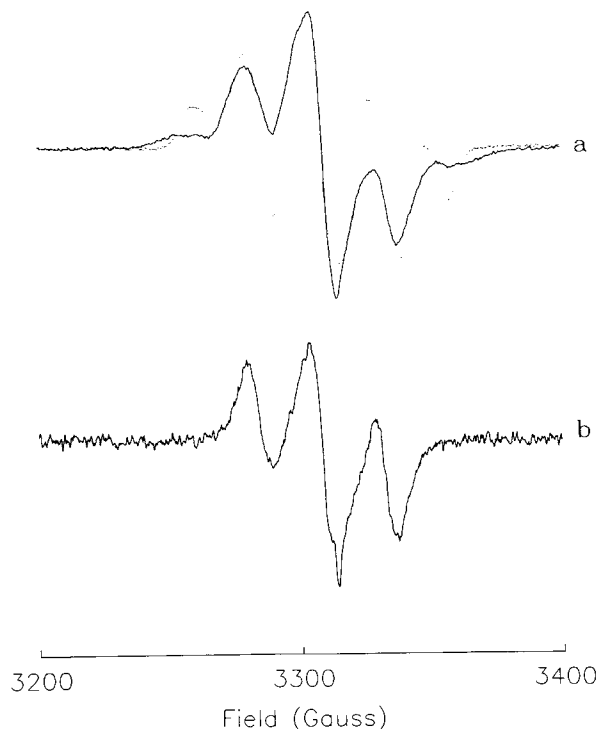
## EXPERIMENTAL

### Materials

NR latex (60% high ammonia) was obtained through Rubber Latex Australia Pty. Ltd. Melbourne. Dry NR, grade SMR-L, was obtained through the Queensland Rubber Co. 2-EHA, 1,6 hexanediol diacrylate (HDDA), and *n*BA were obtained from Aldrich.

### Sample Preparations

For ESR studies, dry NR was packed in ESR tubes and degassed at  $10^{-3}$  Pa for 24 h. A predetermined amount of acrylate and/or carbon tetrachloride was measured into the tube and the sample was freeze thaw degassed several times before sealing under



**Figure 4** ESR spectra of 2EHA irradiated at 77 K and measure at (a) (—) 110 K, (· · ·) 150 K and (b) 220 K.

vacuum. Acrylate samples with or without carbon tetrachloride were freeze thaw degassed and sealed under vacuum.

The acrylate was mixed with dry NR in a Brabender Blender fitted with two counterrotating screws. The blender was operated at room temperature at a speed of 20 rpm. The rubber was introduced into the chamber and mixed for 5 min before the acrylate was added. After adding the acrylate, the mixing continued for further 10 min to achieve a uniform distribution of the acrylate in the rubber. The mixed samples were stored in sealed glass jars until they were irradiated.

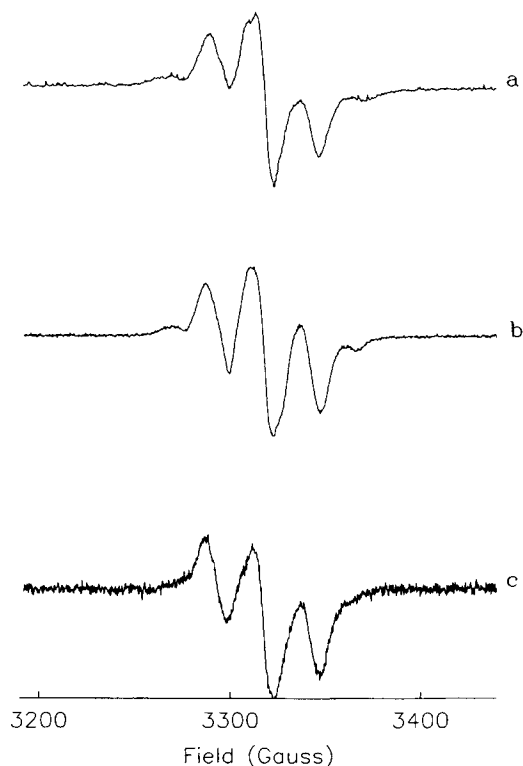
Latex samples were prepared by adding a predetermined amount of acrylate and/or carbon tetrachloride dropwise to the latex while it was stirred vigorously. After the addition, the latex was stirred slowly for another 30 min to obtain uniform distribution of the additives in the latex. The samples were then left in the dark for 24 h before irradiation, to give them sufficient time for the acrylate to dissolve in the rubber particles.

The samples were irradiated (ESR samples at 77K and the other samples at room temperature) using a  $^{60}\text{Co}$  source at a dose rate of 2.5 kGy/h. After irradiation the dry rubber samples were used without further treatment. Rubber films of about 2-

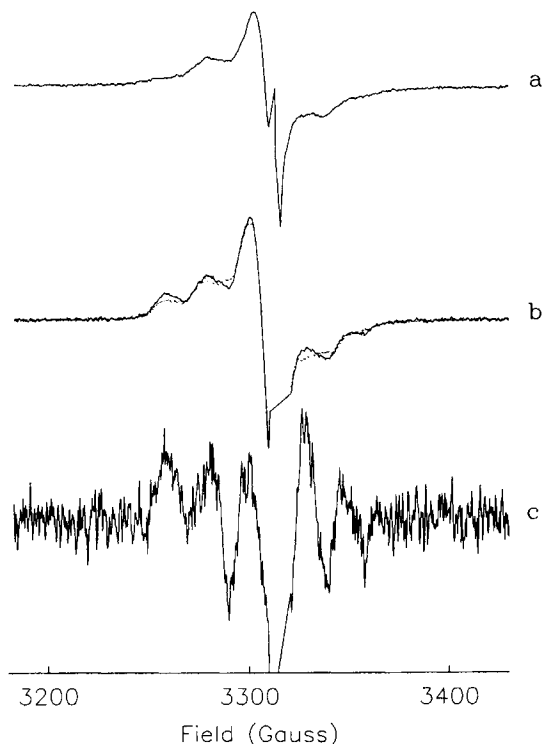
mm thickness were prepared by pouring the latex (unirradiated and irradiated) onto aluminum plates, carefully removing the bubbles on the surface manually and allowing the samples to dry for about 48 h in air. Partially dried sheets were then removed from the plates and dried in a vacuum oven at room temperature.

### ESR Spectroscopy

The ESR spectra were obtained using a Bruker ER 200D X-band spectrometer with a variable temperature unit at a frequency of 9.26 GHz with 332.4-mT field center and 25-mT sweep width. A standard of pitch in KCl (Varian) was used as the reference for absolute radical concentration measurement. The spectra were obtained at 77K and then annealed in progressive steps in order to study the reactions of the radical intermediates. During the annealing, the samples were maintained for 10 min at each temperature and then cooled back to 110K for measurement, in order to obtain quantitative spectra and to avoid the need for Boltzmann corrections. Photobleaching of anion radicals was performed at



**Figure 5** ESR spectra of HDDA irradiated at 77 K and measured at (a) 77 K after photobleaching, (b) 150 K, (c) 260 K.



**Figure 6** ESR spectra of 2EHA : NR (50 : 50) irradiated at 77K and measured at (a) 110 K, (b) (—) 150 K, (· · ·) 160 K, (c) spectrum of the radical disappearing between 150 to 160 K.

77K with an Oriel 1000-W Hg/Xe lamp using either a 495- or a 530-nm cutoff filter.

### NMR Spectroscopy

$^{13}\text{C}$ -NMR spectra of unirradiated and irradiated NR latex with and without sensitizer were obtained using a JEOL GX 400 spectrometer operating at 100 MHz for carbons. The free induction decays (FID) were accumulated using 32,000 data points, with a spectral width of 22 kHz, a  $9.1 \mu\text{s}$  ( $90^\circ$ ) pulse, and a recycling time of 30 s, with gated decoupling. A few drops of  $\text{D}_2\text{O}$  were added to the latex just prior to the NMR measurement for the purpose of locking the instrument.

Solid state  $^{13}\text{C}$ -NMR spectra were obtained with Bruker MSL 200 spectrometer at 50 MHz. The polymers were packed into zirconia rotors and spun at 3 kHz. Spectra were obtained in the solid state from both proton dipolar decoupling (DD) and  $^1\text{H}$ - $^{13}\text{C}$  cross polarization (CP). The DD experiment consisted of a single  $90^\circ$  rf pulse and a recycle time of 5 s with high power proton decoupling during acquisition of data. The CP experiment was performed with 5-ms contact time and 5-s recycle time.

**Table I** Radiation Yields of Radicals at 77K

Natural rubber	1.4
30% 2EHA/natural rubber	1.9
50% 2EHA/natural rubber	2.2
2EHA	3.0
2EHA/ $\text{CCl}_4$	7.1
<i>t</i> -Butyl acrylate	2.6
HDDA	2.7

### Gel Content

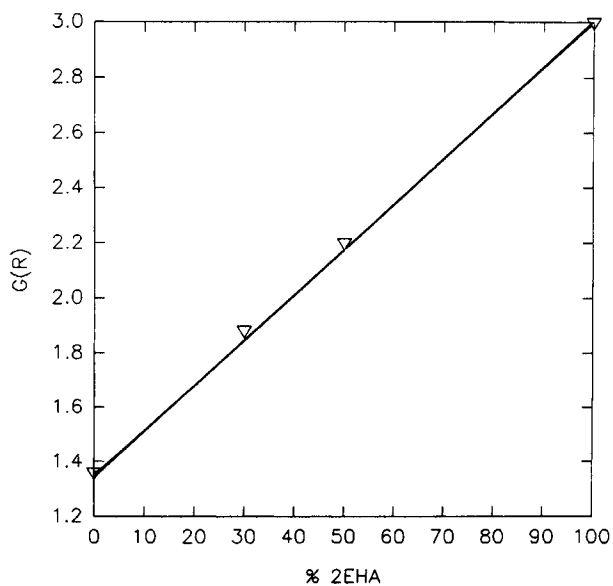
The gel contents of the dried irradiated samples were determined according to the ASTM standard D3616-82. Benzene was used as the solvent and the experiment was conducted at room temperature. The radiation yields of crosslinking and scission were calculated using the Charlesby Pinner equation<sup>9</sup> by plotting  $S + S^{1/2}$  vs. dose, where  $S$  is the soluble fraction.

### Swelling Index

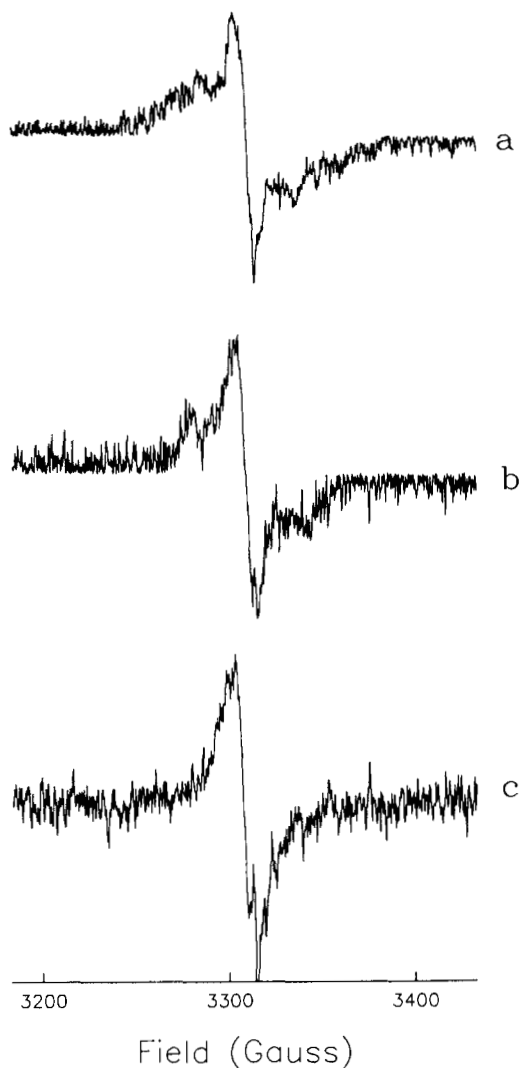
The swelling index was determined according to ASTM standard D3616-82. The network chain density was calculated from the Flory-Rehner equilibrium equation.<sup>10</sup>

### Viscosity

The viscosities of the latex samples were determined according to ASTM standard D1076-88 using a



**Figure 7** Radiation yields of radicals vs. percentage of 2EHA.



**Figure 8** ESR spectra of 30% 2EHA/NR (a) 110–200 K (b) 200–220 K, (c) above 220 K.

Brookfield viscometer operated with spindle 2 at a frequency of 50 rpm. The latex viscosities were determined immediately after irradiation of the samples.

#### Dynamic Mechanical Analyses

Dynamic mechanical analyses (DMA) were carried out using a Perkin–Elmer DMA 7, fitted with a parallel plate probe with a 3-mm diameter tip. A liquid nitrogen furnace temperature control and a scan rate of 5°C/min were used with a frequency of 1 Hz, and a dynamic stress of 600 mN.

#### Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA 7. The samples were

scanned at a rate of 5°C/min from room temperature to 500°C in a dry nitrogen atmosphere.

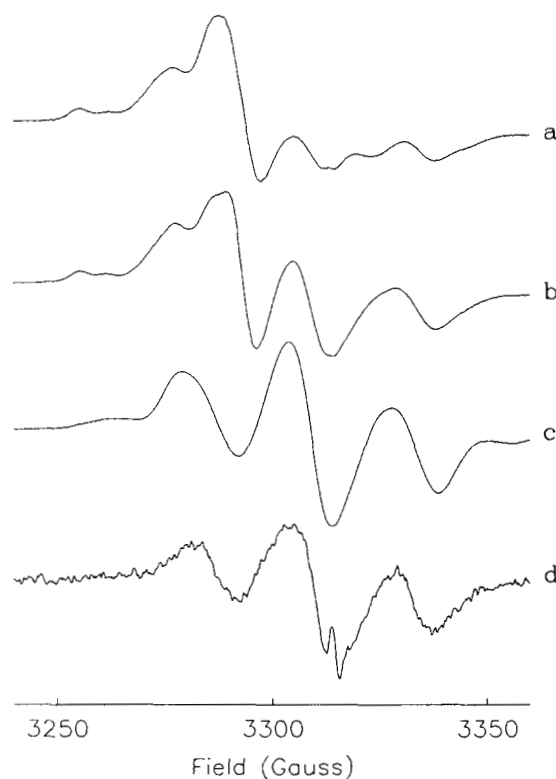
#### Differential Scanning Calorimetry

Samples of equal size were scanned isothermally at 150°C in a Perkin–Elmer DSC7 differential scanning calorimeter. Oxygen was passed through the furnace of the calorimeter as the purging gas at a rate of 25 L/min.

## RESULTS AND DISCUSSION

#### Radical Intermediates

The ESR spectra 2EHA irradiated and measured at 77K are shown in the Figure 1. The broad multiline spectrum changed shape when the power was increased, indicating the presence of more than one radical, and saturation of some of these radicals at higher powers, as shown in Figures 1(a,b). A power plot at 77K is shown in Figure 2. It indicates that saturation begins above a power of 40 dB, hence all the experiments were carried out at 40 dB. The rad-



**Figure 9** ESR spectra of  $\text{CCl}_4$ : 2EHA (50 : 50) irradiated at 77 K and measured at (a) 77 K, (b) 110 K, (c) 130 K, (d) 200 K.

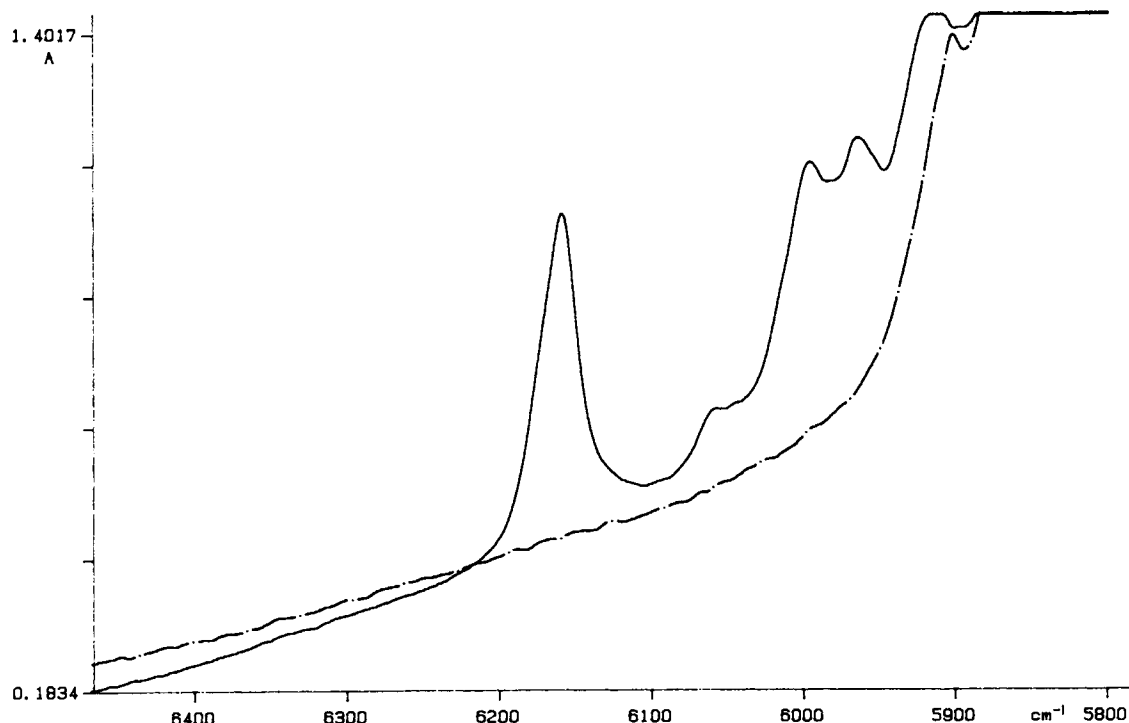


Figure 10 FTIR spectra of 2EHA, (—) unirradiated and (· · ·) irradiated to 1.5 kGy.

icals have a  $g$ -value of 2.003, characteristic of alkyl radicals.<sup>11</sup> Photobleaching of the samples at 77K at a wavelength of 590–900 nm, produced a decrease in the area of the spectrum of approximately 10%. The component of the 77K spectrum lost during photobleaching was predominantly a singlet, as

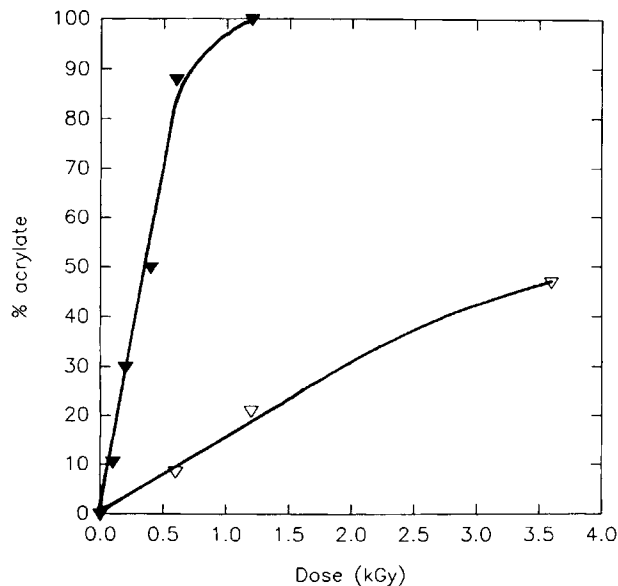
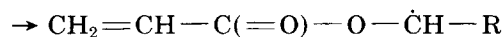
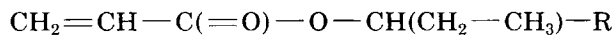
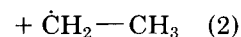


Figure 11 Changes in double bond concentration of 2EHA with dose at (▼) room temperature and (▽) 77 K.

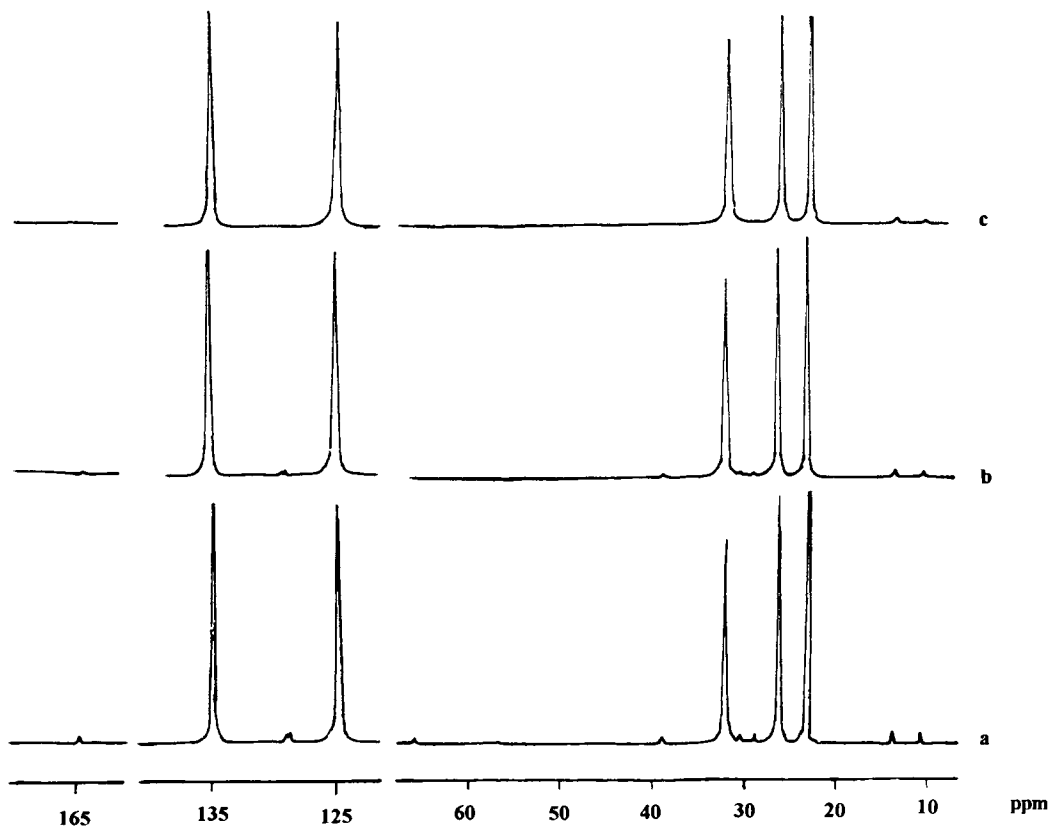
shown in Figure 1(c). The spectrum of the remaining radicals is shown in Figure 1(d). The change in the shape of the spectrum indicated a transition of one radical to another during photobleaching. The addition of an alkyl radical [produced as in reaction (2)] at the carbon atom of the carbonyl group to form an alkoxy radical IV [as in reaction (3)], has been suggested by Hesse et al.<sup>12</sup> This radical gives rise to an asymmetric singlet. These radicals found after  $\gamma$  irradiation were reported by the authors to decompose under the action of light. Previously, Ormerod and Charlesby<sup>13</sup> assigned the strong singlet observed in polyacrylates after  $\gamma$  irradiation to trapped electrons. The spectrum remaining after the photobleaching is shown in Figure 1(d). This spectrum resembles a five-line spectrum with a sharp shoulder on the center peak and a broad shoulder on the peak to the left of the center peak. The total width of the spectrum is 135 G.



III

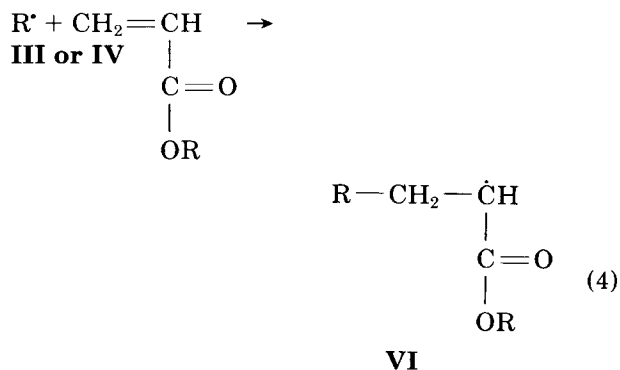
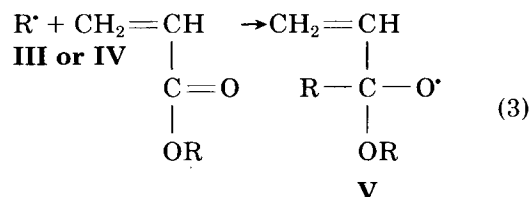


IV



**Figure 12**  $^{13}\text{C}$ -NMR spectra of 5% 2EHA in NR latex after irradiation to (a) 5 kGy, (b) 20 kGy, and (c) 50 kGy.

The photobleached sample was annealed at a higher temperature for 30 min and then cooled to 110K and the spectrum recorded. The drop in the radical concentration with temperature is shown in Figure 3. On annealing, the radical concentration commenced to drop at a lower temperature than in NR, and no radicals were observed above 280K. The change in the spectral shape during heating from 110 to 150K is shown in Figure 4. The total width of the spectrum changed from 135 to 90 G. While the central peak and the two outer regions of the spectrum decreased in intensity, the remainder of the peaks in the spectrum have increased in intensity. This indicates that the primary radicals are rapidly converted into new radical intermediates over this temperature region. The radicals lost on annealing are characterized by a seven-line spectrum. However, it is not possible to make a clear assignment of this spectrum, due to the distortion arising from the increasing intensity in some regions of the spectrum. The change in the total width indicates a conversion of a alkyl-type<sup>14</sup> radical (with a total width of 130 G) to an acrylate-propagating-type<sup>15</sup> radical (radical VI with a total width of 85 G), as shown in reaction (4).



The ESR spectrum of a propagating radical (radical VI) would depend on rotation about the  $\text{C}_\alpha - \text{C}_\beta$  bond, and on the interaction of the unpaired electrons with the  $\text{H}_\alpha$ ,  $\text{H}_{\beta 1}$ , and  $\text{H}_{\beta 2}$  protons. The coupling of the hydrogens with the unpaired electron

**Table II**  $^{13}\text{C}$ -NMR Peak Assignments of 2EHA/NR Latex

Structure	Carbon	Chemical Shift (ppm)
$\begin{array}{c} -\text{C}^3\text{H}_2-\text{C}^1=\text{C}^2\text{H}-\text{C}^4\text{H}_2 \\   \\ \text{C}^5\text{H}_3 \end{array}$	1	135
	2	125
	3	32
	4	26
	5	23
$\begin{array}{c} \text{C}^2\text{H}=\text{C}^1\text{H}_2 \\   \\ \text{C}^3=\text{O} \\   \\ \text{O} \\   \\ \text{C}^4\text{H}_2 \\   \\ \text{C}^5\text{H}-\text{C}^{10}\text{H}_2-\text{C}^{11}\text{H}_3 \\   \\ \text{C}^6\text{H}_2 \\   \\ \text{C}^7\text{H}_2 \\   \\ \text{C}^8\text{H}_2 \\   \\ \text{C}^9\text{H}_3 \end{array}$	1	131
	2	129
	3	166
	4	66
	5	39
	6	31
	7	29
	8	22
	9	14
	10	23
	11	10

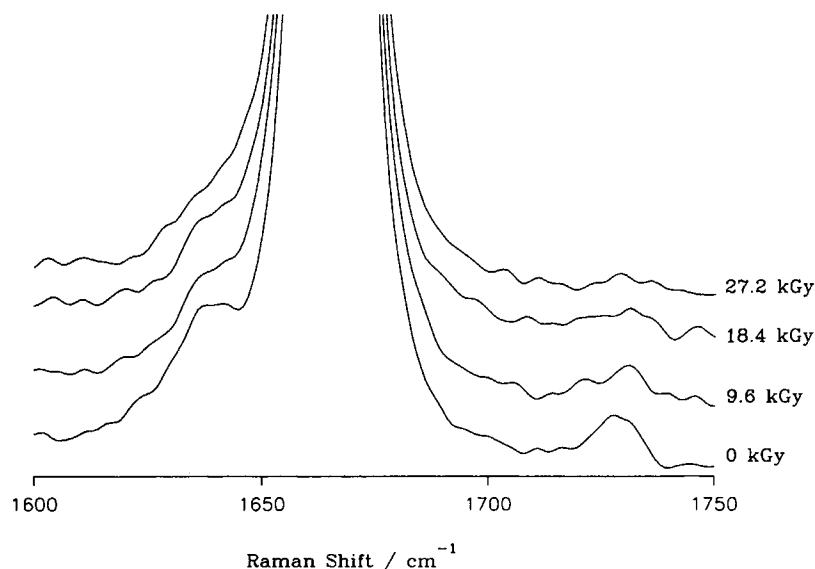
would be particularly dependent on the dehydrat angle of the  $\text{C}\alpha-\text{C}\beta$  bond.<sup>16</sup> Also, because many different chain polymerization reactions may be initiated, the ESR spectra observed could be the summation of the spectra of the several different poly-

**Table III** FT-Raman Peak Assignments of Mixture of 2EHA in NR Latex

Compound	Group	Peak ( $\text{cm}^{-1}$ )
Acrylate	$-\text{C}=\text{O}$	1725
	$-\text{C}=\text{CH}_2$	1640
NR	$-\text{C}=\text{CH}-$	1665

meric macroradicals. Thus the five-line spectrum observed during photosensitized free radical initiated polymerization of methyl, ethyl, and butyl acrylates has been assigned<sup>15</sup> to a combination of a three-line spectrum and a spectrum composed of two three-line components generated by propagating radicals with two different chain-end conformations. The single three-line spectrum has been assigned to a propagating radical in which the coupling of the  $\text{H}\alpha$  and  $\text{H}\beta 1$  with the unpaired electron on  $\text{C}\alpha$  are nearly equivalent. At high temperatures, and in the liquid state, rotation about the  $\text{C}\alpha-\text{C}\beta$  bond produces this spectrum. For the conformation that produces the three-line spectrum, the  $\text{H}\beta 2$  is rotated out of the plane of interaction for the unpaired electron on  $\text{C}\alpha$ . For the second conformation where the couplings of  $\text{H}\alpha$  and  $\text{H}\beta$  are not equal, the  $\text{H}\beta 2$  was rotated into the plane of interaction with the unpaired electron on  $\text{C}\alpha$ , and a spectrum composed of two three-line components is generated.<sup>15</sup>

Above 220K, only a three-line spectrum was observed. This could be the conformation of the prop-



**Figure 13** FT-Raman spectra of 5% 2EHA in NR latex irradiated to (a) 0, (b) 9.6, (c) 18.4, and (d) 27.2 kGy.



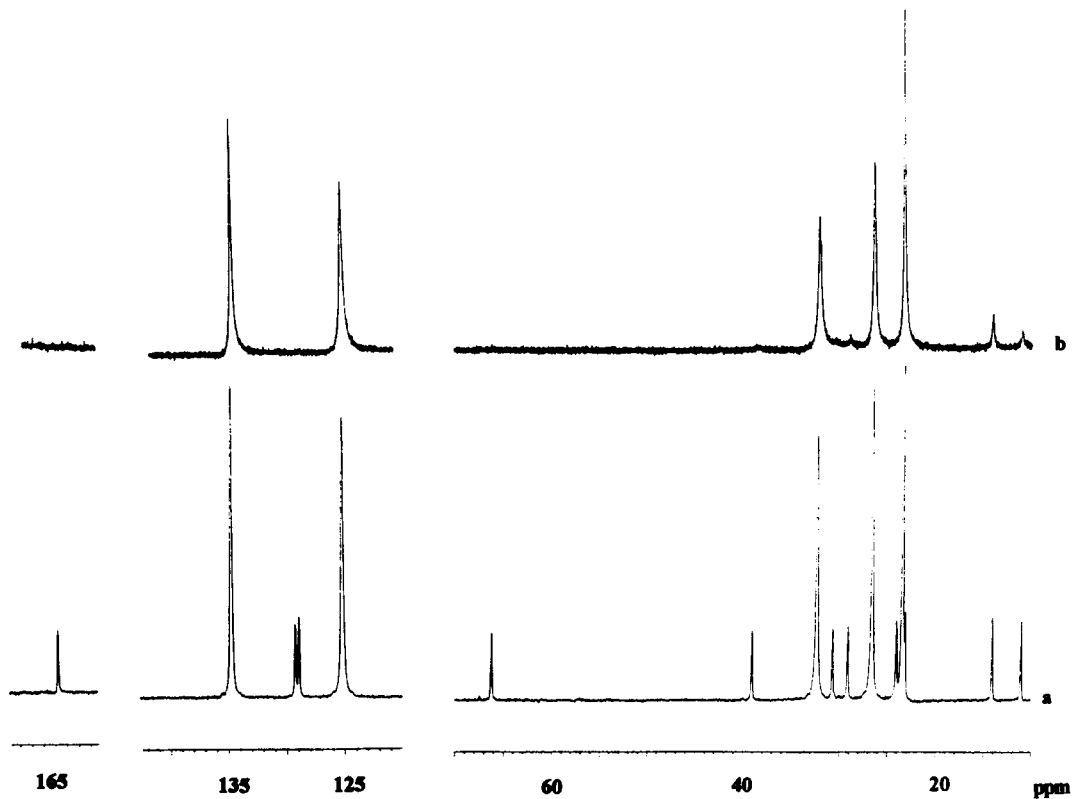


Figure 14  $^{13}\text{C}$ -NMR spectra of 30% 2EHA in NR latex irradiated to (a) 0 and (b) 30 kGy.

agating radical that gave rise to the single three-line spectrum discussed above, or it could be a trapped main chain radical VII that has been observed in

the photopolymerized hexane diol diacrylate.<sup>17</sup> The three-line spectrum observed in the photocured HDDA has been proved to be due to radical VII by

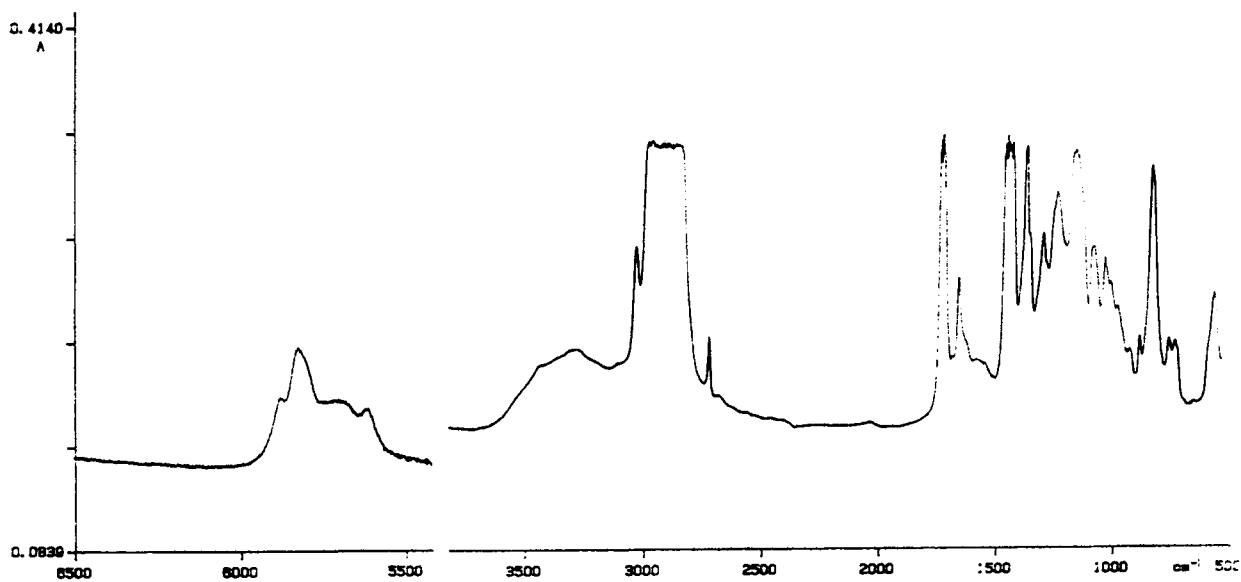
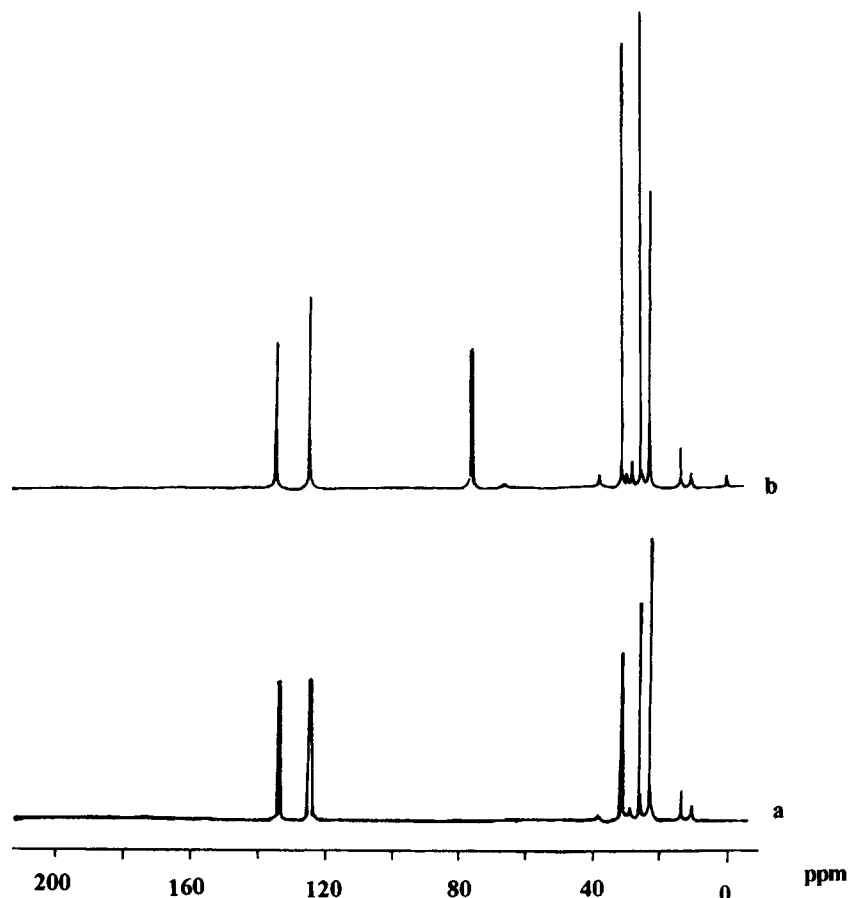
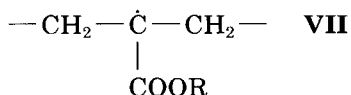


Figure 15 FTIR spectrum of 30% 2EHA in NR latex sample irradiated to 30 kGy, coagulated and dried.



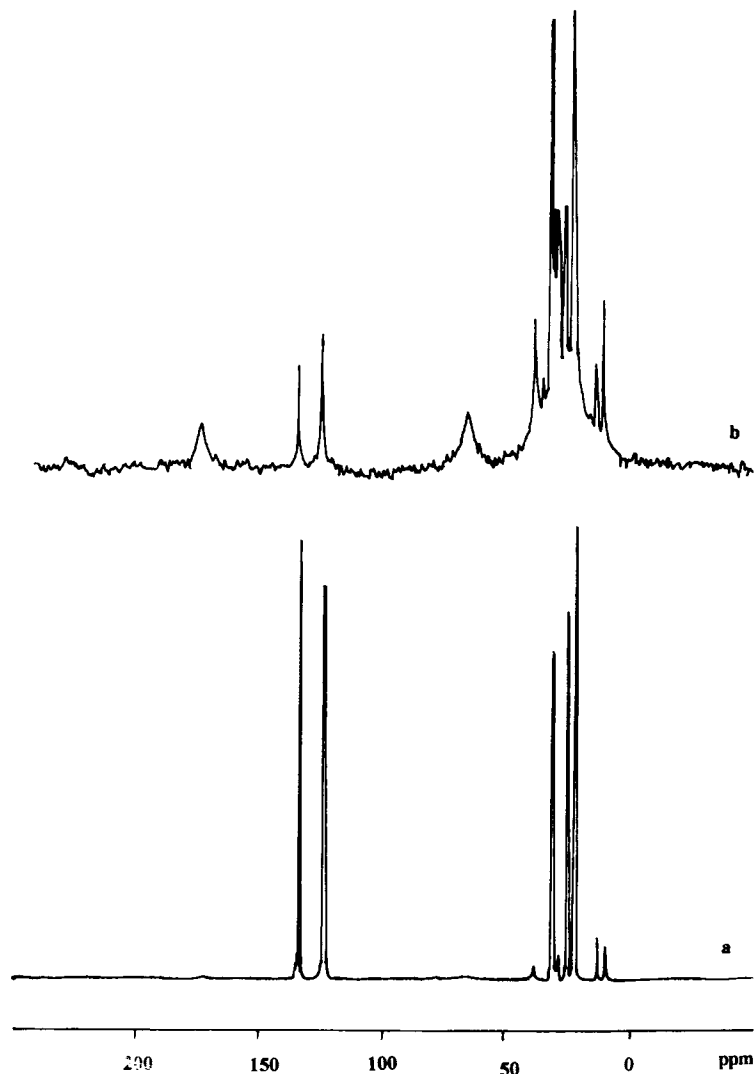
**Figure 16**  $^{13}\text{C}$ -NMR spectra of irradiated latex (30% 2EHA and 30-kGy dose) (a) without and (b) 10%  $\text{CDCl}_3$ . Spectra collected without sample spinning.

using a deuterated HDDA.  $\gamma$  Radiolysis of HDDA gave a similar spectrum to that of 2EHA, as shown in Figure 5. But the three-line spectrum is observed only at 280K. The disappearance of the five-line spectrum during warming indicates that both of the conformations of the propagating radical react at these temperatures. Therefore it is likely that the three-line spectrum in both 2EHA and HDDA at higher temperatures is due to a main chain radical **VII**. 2EHA undergoes gelation during  $\gamma$  radiolysis, and the crosslinking could therefore be through radical **III** and/or radical **VII**.



The ESR spectra of a 50 : 50 mixture of 2EHA : NR are shown in Figure 6. The  $G(\text{R})$  values for NR, 2EHA,  $\text{CCl}_4$ , and mixtures are given in Table I and the plot of  $G(\text{R})$  vs. 2EHA concentration is shown

in Figure 7. These indicate that in the 50 : 50 mixture most of the primary radicals are generated in the 2EHA molecules. As the temperature increases from 110 to 150K the characteristics of the five-line spectrum appears more and more, as observed in 2EHA. However over the temperature range 150–160K, the five-line spectrum starts to reduce in intensity, but other components of the spectrum, as marked in Figure 6(c), increase in intensity. This increase corresponds to the allylic radical observed in polyisoprene with a splitting of 14 G.<sup>18</sup> The difference between the spectra at 150 and 160K is a five-line spectrum, shown in Figure 6(d). This indicates that over this temperature range, the 2EHA propagating radical abstracts an allylic hydrogen from the polyisoprene molecule to produce allyl radicals. These allyl radicals take part in crosslinking.<sup>19</sup> At temperatures above 220K, the spectrum shows features of both the allylic radical and the three-line spectrum of radical **VII**. Crosslinking in 2EHA/NR could occur as a result of radical **III** grafting onto a NR



**Figure 17** Solid-state NMR spectra of coagulated and dried rubber of 30% 2EHA in NR latex irradiated to 30 kGy (a) dipolar decoupling and (b) cross polarization.

molecule with subsequent polymerization of the 2EHA or of radical VII reacting directly with a similar carbon radical or with an allyl radical on the NR molecule. Figure 3 shows that addition of 2EHA reduces the temperature at which the radical concentration starts to decrease. This is as a result of plasticization of rubber by the acrylate, thus reducing the  $T_g$ .

The ESR spectra of irradiated 25% 2EHA/NR measured at 77K indicate the presence of more than one radical, as evident from the change in the peak shape with increasing power. Photobleaching removes a singlet as in pure 2EHA. No five-line spectrum was observed at any temperature during annealing of these samples. Instead, a decrease in the allyl radical concentration over the range from 110

to 180K was visible in the spectra, as shown in Figure 8. Between 200 and 220K, a three-line spectrum with a splitting constant of 24 G disappears, and a singlet was left at 220K. The singlet is the polyenyl radical that has been observed in irradiated polydienes.

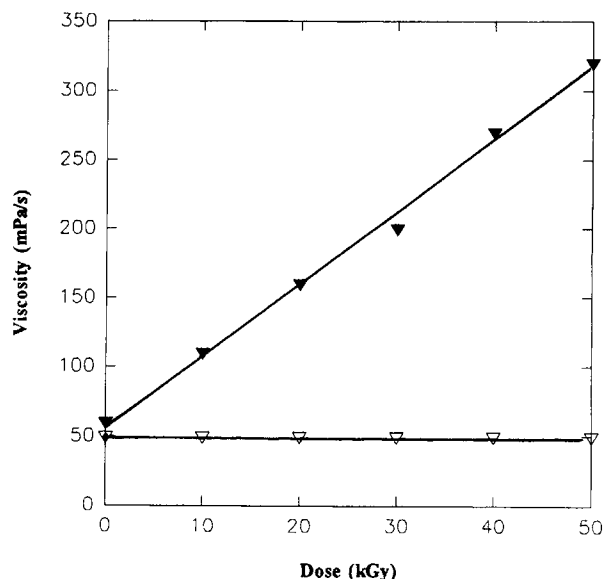
The ESR spectra of a 50 : 50 mixture of 2EHA and  $\text{CCl}_4$  are shown in Figure 9. The  $g$ -value of 2.03 indicates the presence of radicals generated from  $\text{CCl}_4$  in the spectrum at 77K.<sup>20</sup> Irradiation of  $\text{CCl}_4$  produces both  $\text{CCl}_3$  and Cl radicals. Further, the  $G(R)$  of the 50 : 50 mixture of  $\text{CCl}_4$  : 2EHA is more than double that of pure 2EHA. This indicates that the majority of the primary radicals are generated in  $\text{CCl}_4$ , which is more sensitive to radiation. During the annealing from 110 to 130K, less than 10% of the radicals decayed (shown in Fig. 3), but the five-

line propagating radical of 2EHA is visible in the spectra. At higher temperatures, only the three-line spectrum remains. Even if the  $T_g$  of the system has been reduced by the presence of  $\text{CCl}_4$  (indicated by a lower temperature for radical decay, Fig. 3), the three-line spectrum is visible only above 200K (as with pure 2EHA). This further confirms that the three-line spectrum does not arise from a conformation of the propagating radical, but is due to a main chain radical VII. The spectra thus indicate the radicals of  $\text{CCl}_4$  are formed as the primary radicals, and that they react during annealing to form the 2EHA radicals. The addition of  $\text{CCl}_4$  reduces the temperature at which the radicals start to decay.

### Structural Changes During Irradiation

The FTIR spectra of unirradiated and irradiated 2EHA in glass tubes are shown in Figure 10. The percentage decrease in the double bond concentration, as measured by the change in peak at  $6160\text{ cm}^{-1}$ , for room temperature and 77K irradiations are shown in Figure 11. Room temperature irradiations reduce the double bond concentration to zero with a dose of 1.2 kGy. These results were used to calculate the radiation chemical yields for loss of double bonds, which were 43714 and 6848 at room temperature and 77K, respectively. The values are much higher than the values of  $G(\text{R})$  measured for the propagating radicals formed using initiation by irradiation. FTIR spectra could not be observed for the latex samples.

$^{13}\text{C}$ -NMR and FT-Raman spectroscopy were used to monitor the reactions of 2EHA/NR latex.  $^{13}\text{C}$ -NMR spectra of latex containing 5% 2EHA are

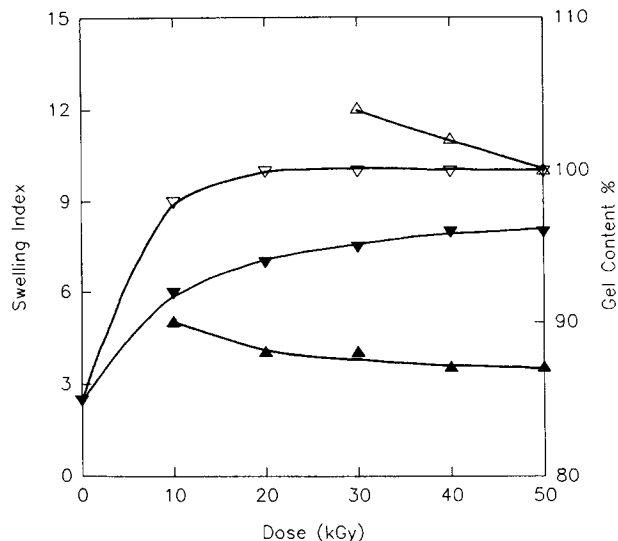


**Figure 18** Changes of viscosity ( $\nabla$ ) with dose ( $\blacktriangledown$ ) without with 5% EHA.

shown in Figure 12, and the peak assignments are shown in Table II. All the peaks in the acrylate decrease in intensity with dose. Line broadening due to reduced mobility near crosslinks have been reported previously; hence the disappearance of the carbonyl peak may be due to line broadening. The FT-Raman spectra of the samples are shown in Figure 13. The peak assignments are shown in Table III. The figure indicates a disappearance of both double bonds and carbonyl peaks, thus a decomposition of acrylate during irradiation. Calculation of the radiation chemical yield for the loss of carbonyl groups,  $G(-\text{C}=\text{O})$ , from the data gives a

**Table IV** Peak Widths (Hz) of Carbon Resonances of Natural Rubber

	C=	=C	—CH <sub>2</sub> —C=	=C—CH <sub>2</sub> —	CH <sub>3</sub>
NR latex	20.6	27.6	20	20	16.6
NR latex/1520 kGy	29.2	33	24	20.7	20.7
NR latex/5% 2EHA	15.2	19.4	18.9	17	15
NR latex/5% 2EHA/5 kGy	11.5	15.4	15.1	13.2	11.3
NR latex/5% 2EHA/10 kGy	12.5	16.1	16.9	14.2	10.8
NR latex/5% 2EHA/20 kGy	12.1	17	16.1	14.5	9.7
NR latex/5% 2EHA/50 kGy	13.2	16.9	16.6	13.3	10.0
NR latex/10% 2EHA	10.4	13.4	13.8	11.1	8.3
NR latex/10% 2EHA/35 kGy	12.9	18.3	19.0	14.3	11.9
NR latex/30% 2EHA	9.6	11.5	11.1	11.1	7.4
NR latex/30% 2EHA/15 kGy	3.6	8.9	17.9	14.3	5.4
NR latex/30% 2EHA/30 kGy	10.7	16.9	19.4	16.1	8.0
NR latex/30% 2EHA/30 kGy/without spinning	32.7	40.4	31.3	25	25
NR latex/30% 2EHA/30 kGy/without spinning/10% $\text{CDCl}_3$	23	26.9	12.5	12.5	18.8



**Figure 19** Variation of swelling index (▲) with and (△) without 5% 2EHA and gel content (▽) with and (▼) without 5% 2EHA.

value of 0.58. This value is slightly lower than the values reported for the radiation chemical yield for formation of carbon dioxide and carbon monoxide in polyethyl acrylate, which is 0.82.<sup>21</sup>

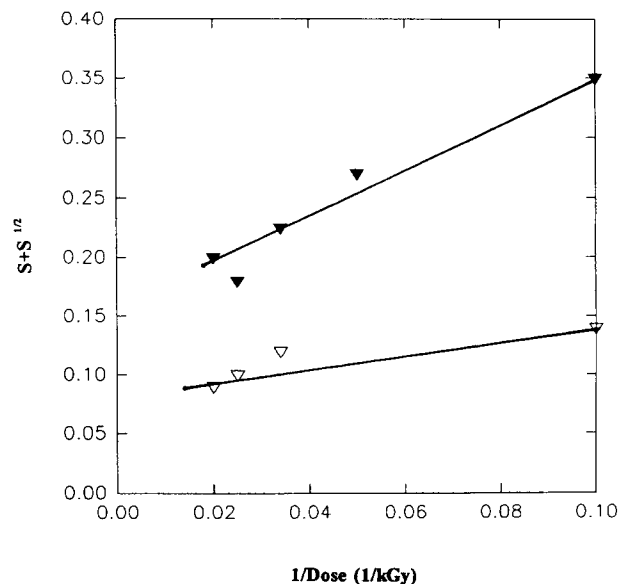
The <sup>13</sup>C-NMR spectra of 30% 2EHA/latex are shown in Figure 14. While the acrylate double bonds, the carbonyl, and the —CH<sub>2</sub>—O— groups (66 ppm) disappeared at a dose of 30 kGy, the rest of the acrylate peaks were reduced in height and broadened. Because the radiation yields calculated from this data are much higher than the 0.82 value, the decomposition of all the acrylates to release carbon dioxide and carbon monoxide cannot be possible. The water in the latex sample, irradiated to 30 kGy, was evaporated on a glass plate and a FTIR spectrum of the dried sample was collected. It is shown in Figure 15. The figure indicates the presence of a very intense C=O peak at 1725 cm<sup>-1</sup> and the total disappearance of the peak at 6160 cm<sup>-1</sup> due to the acrylate double bond. This indicates that, while all the acrylate double bonds have reacted at this dose, the carbonyl groups are still intact. Quantification of the concentrations of the carbonyl groups was not attempted, due to the uncertainty in the film thickness, etc.

After the NMR experiments were complete (about 12 h) for these irradiated latex samples, the rubber particles were found to have been creamed to the top. Thus it was first thought that the disappearance of the acrylate peaks may be due to this creaming of acrylate rich particles to the top of the NMR tube, which would prevent their detection.

**Table V** Swelling Index and Radiation Yields of Crosslinking and Scission

	Dose (kGy)	NR	5% 2EHA/NR
Swelling Index	0	—	—
	10	—	9.2
	20	—	10.2
	30	4.9	10.2
	40	5.4	10.7
	50	5.8	10.7
$G(x)/G(s)$		3.0	5.5
$G(x)*M_{n0}$		2.67e9	9.64e9

Therefore the NMR spectra were collected without spinning the samples. No creaming of the latex was visible after the 12-h period required to collect the spectrum, but the carbonyl and the —CH<sub>2</sub>—O— peaks could still not be detected. Hence line broadening was thought to be the reason for the failure to observe these peaks. About 1 mL of CDCl<sub>3</sub> was then added to the NMR tube, and it was left overnight to swell the latex particles. An NMR spectrum was then collected. Swelling was found to improve the spectrum, as shown in Figure 16. The peak was visible at 66 ppm, which is attributed to the methylene resonance, but still there was no trace of the carbonyl peaks. Solution-state NMR spectra of the latex were therefore not found to be a suitable method for the complete structural analysis of the samples irradiated to doses as low as 30 kGy. The



**Figure 20** Charlesby-Pinner plot (▼) without and (▽) with 5% 2EHA.

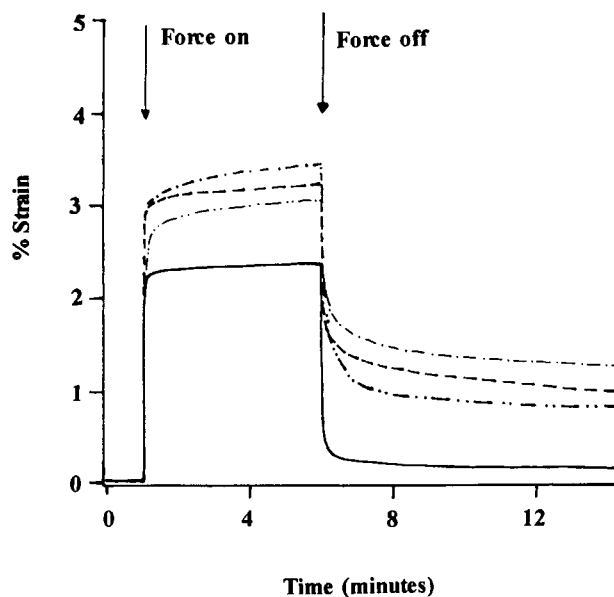
**Table VI** Changes of Tensile Strength, Elongation, and Energy at Break with Radiation Dose

Acrylate (%)	Dose (kGy)	Elongation at Break	Tensile Strength (MPa)	Energy at Break (N/m)
0	0	800	5.0	1.8
0	10	720	5.5	2.2
0	20	650	7.0	2.5
0	30	620	7.0	3.0
0	40	580	6.0	3.2
0	50	560	7.0	3.4
5	0	875	3.0	2.0
5	10	900	9.0	2.7
5	20	950	8.0	4.2
5	30	900	8.0	4.8
5	40	880	8.5	5.2
5	50	1000	8.5	5.1

unsuitability of solution-state spectra to detect crosslinking in rubber irradiated to higher doses (1000 kGy) has been reported previously.<sup>22</sup> However, a small broad peak at 43 ppm was visible in the solution-state spectra. This peak is most likely due to isomerization of the *cis* double bond of the NR molecule.

In a further attempt to observe the acrylate component in the latex samples, the dried sample was analyzed using solid-state NMR. The spectra are shown in Figure 17. Figures 17(a,b) show the single pulse DD spectrum and CP spectrum, respectively. It is known<sup>22,23</sup> that the DD NMR technique is more

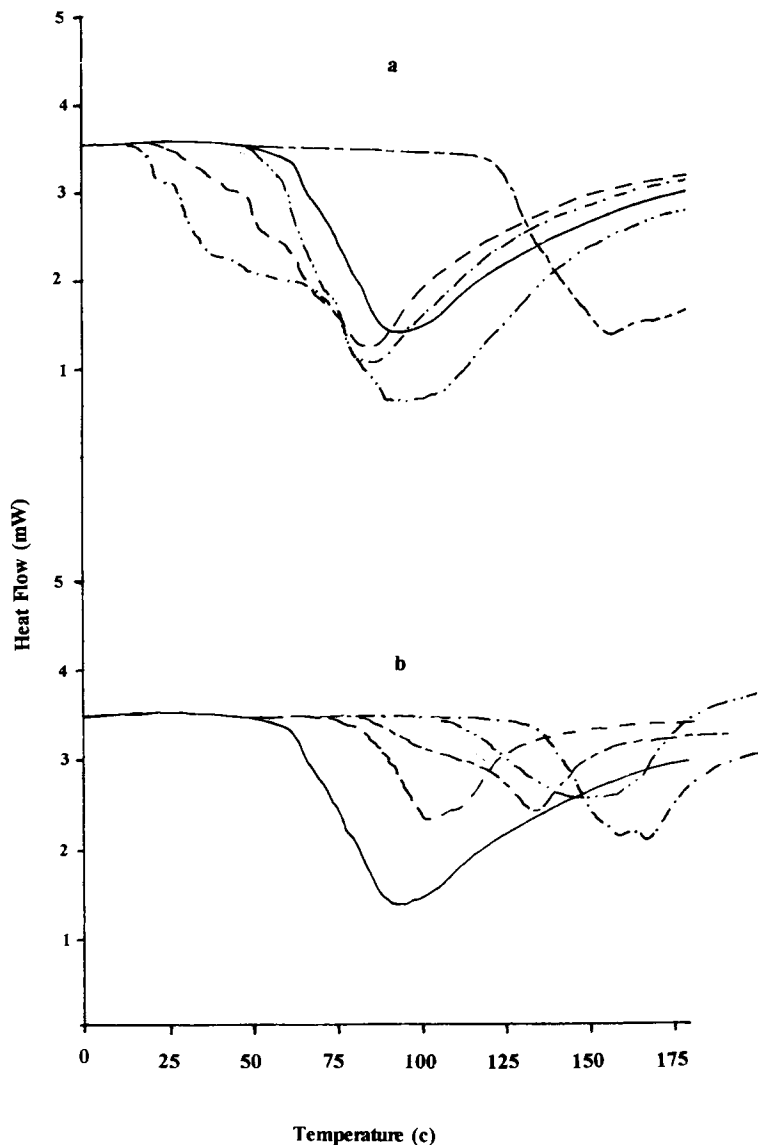
sensitive to the mobile and uncrosslink regions of a polymer than to the more rigid regions, while the CP techniques are more sensitive to the rigid regions. The DD spectrum shows sharp polyisoprene peaks, and peaks due to the pendent methyl and methylene carbons of the 2EHA. Very small peaks at 66 and 173 ppm could also be observed. The CP spectrum, on the other hand, shows peaks corresponding to all the carbons in the 2EHA and polyisoprene. The peaks at 66 and 173 ppm are very broad and the carbonyl peak is shifted to 173 from 166 ppm when the double bond is saturated during polymerization. No double bond peaks at 129 ppm were visible, confirming that all the 2EHA had polymerized. These results clearly indicate that the material is heterogeneous and that the 2EHA is in the rigid regions of the material. Similar heterogeneities have been observed in irradiated polybutadiene,<sup>22</sup> polyisoprene,<sup>24</sup> polychloroprene,<sup>23</sup> and nitrile rubber.<sup>25</sup> This has been explained as being due to crosslink clustering. However, in the present case the fact that all of the acrylate molecules are in the rigid regions indicates that the distribution of the acrylate in the rubber is not uniform. Thus, even if the absorption of 2EHA in the NR sheets was found<sup>7</sup> to be very high, quite a large percentage of the 2EHA also re-



**Figure 21** Creep recovery plots for rubber irradiated with 2EHA for (---) 0, (---) 10, (—) 30 kGy, and (- · - ·) 50 kGy without 2EHA.

**Table VII** Activation Energies for Oxidation

Sample	Dose (kGy)	Acrylate (%)	Activation Energy (kJ/mole)
NR	0	0	100
NR	50	0	136
NR	10	5	125
NR	50	5	135



**Figure 22** Isothermal DSC of rubber irradiated (a) without 2EHA (—) 0, (---) 10, (-·-·) 20, (-·-·-) 30, and (-·-·-) 50 kGy, and (b) with 5% 2EHA (—) 0, (---) 10, (-·-·) 20, (-·-·-) 30, and (-·-·-) 40 kGy.

mains on the surface of the rubber particles in the latex. Therefore the crosslinking, which is sensitized by the acrylate, is higher at the acrylate rich particle surfaces. However, no significant differences in the  $\tan \delta$  curves were found for the samples irradiated to 50 kGy with and without 2EHA.

The peak widths of the  $^{13}\text{C}$ -NMR spectra of irradiated latex samples are given in Table IV. The relatively good peak resolution observed for the latices were believed<sup>26</sup> to result primarily from the effect of Brownian motion. As observed in the table, the addition of 2EHA improves the resolution, indicating a plasticizing effect or a change in the

Brownian motion of the rubber particles. Another significant observation from the table is that the irradiation of latex to a low dose (15 kGy) reduces the peak width. This drop in peak width has to be a result of an increase in the Brownian motion of the latex particles, because very little chain scission occurs in polyisoprene during irradiation. A rhythmic alternating increase and decrease in the electrostatic potential of colloid particles has been observed<sup>27</sup> when a colloidal solution is exposed to very small doses of radiation (NR latex particles are negatively charged at this working pH). An increase of the peak width on further irradiation indicates

restricted molecular motion due to crosslinking and a change in the Brownian motion of the particles. Another possible effect of irradiation on the latex particles is the effect on the proteins surrounding the rubber. The hydrogen bonds, which keep the protein molecules coiled, are destroyed on irradiation, thus the less hydrophilic portions of the molecules come to the surface. This can affect the Brownian motion of the latex particles. Similarly, if the acrylate is on the surface of the particles, the polymerization of the acrylate will change the polarity of the surface, and this could affect the Brownian motion. Spectra collected without spinning the samples gave larger peak widths, as expected. But addition of  $\text{CDCl}_3$  improves the resolution by increasing the molecular motion.

### Viscosity Changes During Irradiation of Latex

The changes in the viscosity of latex with dose are shown in Figure 18. The viscosity was determined directly after the irradiation. The viscosity of NR latex did not change with dose. However, for 5% 2EHA added latex, the viscosity increased with dose, even though the latex did not coagulate. The increase in the viscosity of latex indicates a drop in the stability of latex. This is contrary to the finding of Makuuchi and Tsushima<sup>7</sup> who reported that the viscosity of latex was unchanged in the presence of 2EHA. The method used for mixing chemicals with the latex was similar in both studies. The only difference is that the latex was used as 60% concentration without dilution in the present study compared to 40% in the previous investigation. The drop in the viscosity suggests that the 2EHA molecules do not penetrate the rubber particles, but remain at the interface. During the formation of the polymer, the hydrophilic nature of the particles increases, thus disturbing the colloidal stability of the latex.

### Gel Content and Swelling Index

The gel content and swelling index of rubber irradiated to different doses in the form of latex with and without 2EHA is shown in Figure 19. With 5% 2EHA, a dose of 20 kGy gave a 100% gel. Much lower swelling index values were obtained for samples irradiated in the presence of 2EHA, indicating a higher degree of crosslinking. Swelling data were used to calculate the network chain density and are shown in Table V. The Charlesby–Pinner plots used to calculate the  $G(s)$  and  $G(x)$  values are shown in

Figure 20. Because it was not possible to measure the  $M_{n_0}$  (unirradiated rubber also had a gel content),  $G(x)/G(s)$  values and  $G(x)/M_{n_0}$  values were calculated and are given in the Table V. The addition of 5% 2EHA, shows a 3.6-fold increase in  $G(x)$  but only a 2-fold increase in  $G(s)$ . Hence the addition of 2EHA sensitizes crosslinking more than scission in the NR molecule.

### Tensile and Creep Properties

The elongation at break, energy at break, and tensile strength are tabulated in Table VI. The lower values compared to those published previously probably arise from the difference in postcure treatments in the two studies.<sup>28</sup>

The creep recovery results are shown in Figure 21. The percentage recovery of strain after application of a 100-mN force for 5 min was measured. Total creep deformations depend on three factors: instant deformation due to bond bending and stretching, chain uncoiling, and chain slippage. Thus the higher the crosslink density, the lower is the total deformation, the faster the recovery, and the lower the permanent set. Accordingly, lower deformation, faster recovery, and low set were observed in the samples irradiated to 50 kGy in the presence of 2EHA. The difference between unirradiated samples and samples irradiated to 10 kGy was minimal. The sample irradiated to 50 kGy without 2EHA also showed similar behavior to the unirradiated sample.

### Thermal Degradation

The activation energies for thermal degradation, calculated using DSC temperature scans are given in the Table VII. The results indicate that the crosslinking increases the activation energy.

The isothermal DSC scans were carried out at 150°C and are shown in Figure 22. Results indicate a drop in the induction period with low doses in NR without added 2EHA. This perhaps arises as a result of peroxide formation during irradiation. In the presence of 2EHA, the induction period increases up to 20 kGy, and then begins to drop. The increase in the induction period with dose is reasonable because the apparent rate of degradation decreases with increasing crosslinking. The drop in the induction period at higher doses may be due to the consumption of the sensitizer, thus increasing the peroxide formation and chain scission. The acrylate was found to be consumed totally with a dose of 20–30 kGy as measured by NMR.



## CONCLUSIONS

Alkyl-type radicals, formed as primary radicals during irradiation of 2EHA, initiate polymerization by reacting with the double bonds. A main chain radical is also formed on the poly 2EHA.

In a 50 : 50 mixture of 2EHA/NR, the propagating acrylate radicals abstract allylic hydrogen and form allylic radicals on the rubber molecule. At low 2EHA contents, only main chain acrylic radicals and allylic radicals are observed. The crosslinking can occur by allylic radical clustering reactions with acrylate main chain radical reactions or with radical III located on the 2-ethyl hexyl chain of the acrylate.

2EHA does not distribute uniformly in the rubber particles of the latex, but tends to remain on the surface. Therefore the crosslinking in the rubber is not uniform. Highly crosslinked rigid regions are found in the acrylate-rich areas.

Addition of 5% 2EHA to the latex increases the radiation yield of crosslinking by about 3.6 times.

An increase was found in the resistance to thermal reactions at low doses, but a decrease was observed at higher doses. The sample irradiated to a dose of 30 kGy with 5% 2EHA gave the best balance in properties.

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