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Molecular Fracture in Poly(chloroprene)

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ABSTRACT: Electron spin resonance spectra are reported from free-radical formation in poly(chloroprene), uniaxially deformed below T_g. Radicals formed following tensile testing are assigned to the allylic species produced by main-chain fractures $-CH_2C(Cl){=}CH\dot{C}H_2$ and $-CH_2CH{=}C(Cl)\dot{C}H_2$. In the presence of oxygen as the test environment the allyl radicals react to produce a peroxy radical species. Similar ESR spectra were produced by UV irradiation. The effect of zinc oxide acting as cross-linking agent did not complicate the ESR spectra, although spectra from dicumyl peroxide cross-linked poly(chloroprene) were assigned to oxidative radical products. The decay of the allyl radicals with temperature is studied.

The electron spin resonance (ESR) spectrum of free radicals produced in uniaxially deformed poly(chloroprene) has not been published previously. Radicals produced by photolysis of poly(chloroprene) have been reported.[1] The ESR spectrum was a broad singlet and no identification of the radical specimens was given. Radicals have recently been detected in ultraviolet irradiated poly(chloroprene)[2,3] (CR) although the assignment was tentative since only a broad first derivative ESR spectrum was obtained and even the second derivative spectrum showed only traces of hyperfine structure. Assignment was not conclusive for interpretation without support of ESR spectra of allylic radicals from other polydienes.[4,5] A peroxy radical species was observed during uniaxial deformation of poly(chloroprene).[6,7] This communication reports radicals produced by tensile deformation of cross-linked poly(chloroprene) using both zinc oxide and dicumyl peroxide as the cross-linking agents. Further, no ESR study of the oxidation of poly(chloroprene) has been published although it has been reported that poly(chloroprene) is more resistant to oxidation than other dienes such as polybutadiene (BR) and polyisoprene (IR).[8] An ESR study of oxidation of BR and IR has already been reported.[9,10] Radicals formed during uniaxial deformation of BR and IR at temperatures below their respective T_g's were tentatively assigned to allyl radicals possibly formed by homolytic cleavage of the weakest bond in the main chain (i.e., midway between the α- methylene bonds), and this would suggest that allyl radicals may be formed during low-temperature deformation of CR.[10]

Experimental Section

The poly(chloroprenes) used in this study were not purified. The structural units in the Neoprene W (DuPont Ltd.) used for ESR studies consisted of approximately 85% trans-1,4, 10% cis-1,4, 1.5% 1,2, and 1.0% of 3,4 addition. Neoprene W was used for the ESR studies, since unlike Neoprene WX and Neoprene G it contained no stabilizer, sulfur, vulcanization disulfide, or other compounds capable of decomposing and producing a vulcanization accelerator and hence complicating the resulting ESR spectrum. For example, Neoprene WX gave on deformation only a broad singlet ESR spectrum with no trace of hyperfine structure. The "G" type of Neoprene gave only a singlet-like spectrum which was possibly the result of inclusion of stabilizers. Samples were also irradiated in evacuated spectrosil tubes with a Phillips UV lamp.

The experimental details of the tensile testing and ESR equipment have been described more fully elsewhere.[9] The specimen was extended at room temperature prior to the low-temperature deformation, since it has been shown that the use of pretest deformation in the rubber-like state induces ductility in the elastomers at low temperature.[9] The resulting morphologies which are obtained in poly(chloroprene) by preorienting the sample prior to cooling and deforming the sample have been described by Andrews and Reeve.[11,12] The specimens were then stretched in liquid nitrogen.

A range of mechanical behavior was observed during low-temperature deformation of poly(chloroprene), and the behavior was dependent on the rate of strain, the degree of cooling, the cross-link density, and the degree of pretest deformation. The modes of deformation observed were crazing, shear yielding, and a region of ductile behavior at high pretest deformation, in which

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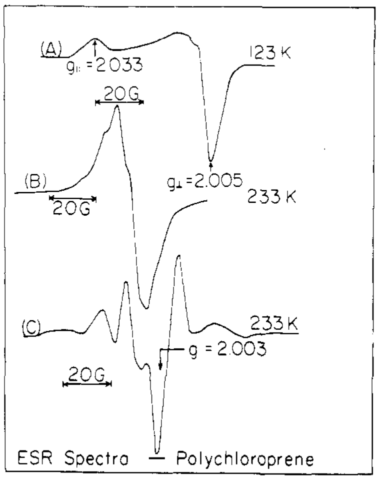


Figure 1. First derivative ESR spectra of zinc oxide cross-linked poly(chloroprene) stretched in liquid nitrogen recorded as the specimen was warmed to (a) 123 K (b) and 233 K. (c) The corresponding second derivative ESR spectrum of (b).

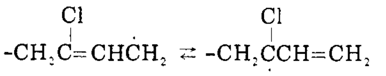
the specimens draw without local yielding. Radical formation was detected in poly(chloroprene) during all the ductile modes of deformation observed below T_g.

Results and Discussion

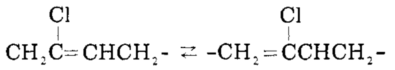
ESR Spectra for Poly(chloroprene). Figure 1 shows the spectrum obtained by tensile testing zinc oxide cross-linked poly(chloroprene) (Neoprene W, DuPont Co.) at 77 K in liquid nitrogen.

The spectrum obtained at 123 K and shown in Figure 1A is an asymmetric signal indicating a peroxy radical with $g_{\parallel} = 2.033$ and $g_{\perp} = 2.005$. Figure 1B shows that as the specimen is warmed to near T_g (=233 K) a broad singlet is detected of overall width 60 G. Figure 1C also shows the second derivative ESR spectrum, which can be a more sensitive technique for illustrating hyperfine structure, recorded at 233 K and corresponding to the first derivative spectrum shown in Figure 1B. A possible five lines are observed with hyperfine splitting of about 12 G. A line is central at the free electron g value, indicating an odd number of lines in the spectrum.

It is possible that the primary radical products produced by the molecular fracture will be the allyl radicals:


$$-CH_2\overset{\overset{Cl}{|}}{C}=CH\dot{C}H_2 \rightleftarrows -CH_2\overset{\overset{Cl}{|}}{\dot{C}}CH=CH_2$$

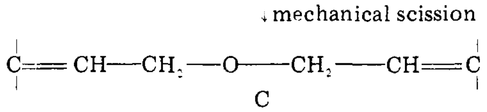
A


$$CH_2\overset{\overset{Cl}{|}}{C}=CHCH_2- \rightleftarrows -CH_2=\overset{\overset{Cl}{|}}{C}CHCH_2-$$

B

The numbers of hyperfine lines expected from such allyl radicals are 5 and 6,[2,3] the β protons being only considered to act as a source of line broadening. This also assumes that the chlorine nuclei with nuclear spin $I = {}^3/_2$ do not further split the lines. If this were possible then the number of expected lines would be $(2 \times 4 \times {}^1/_2 + 1)(2 \times 1 \times {}^3/_2 + 1) = 20$. For nuclei with spin $I > {}^1/_2$, they possess electron quadrupole moments. The chlorine atom is considered a source of line broadening in the resulting ESR spectrum.

The resulting ESR spectrum produced by deforming zinc oxide cross-linked poly(chloroprene) in oxygen-free nitrogen was very similar to that obtained by deforming the polymer which had been cross-linked above T_g and is similar to that given in Figures 1B and C. It appears that *uniaxial deformation of poly(chloroprene) does not fracture* the chemical cross-links produced by zinc oxide. According to Murray and Thompson[13] the nature of the cross-links which form in Neoprene W with no organic accelerator is not known. A possible reaction produces the following structure[13]


$$\overset{|}{\underset{|}{C}}{=}CH{-}CH_2{-}\overset{\downarrow \text{ mechanical scission}}{O}{-}CH_2{-}CH{=}\overset{|}{\underset{|}{C}}$$

C

and molecular fracture at the site indicated in C would give rise to an oxy radical which, in the absence of oxygen, would give rise to a singlet centered at $g = 2.003$.[14] The possibility of the ESR spectra shown in Figure 1 resulting from the superposition of an allyl radical with an even number of lines and a singlet was checked by a power saturation study. However, selected power saturation of the singlet or allyl species was not observed and the ESR spectrum shown in Figure 1C is attributed to an allyl radical species.

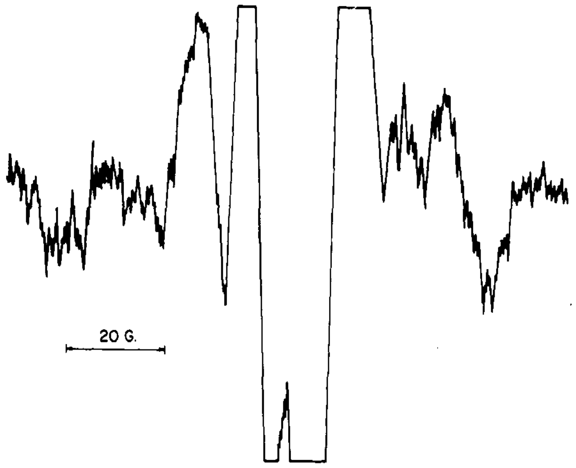


Figure 2. Second derivative ESR spectrum obtained by UV irradiation of zinc oxide cross-linked poly(chloroprene) at 77 K in partial vacuum.

Figure 2 illustrates the second-derivative ESR spectrum obtained by the UV irradiation of the zinc oxide cross-linked poly(chloroprene) at 77 K in partial vacuum. The spectrum appears to be similar to the spectrum for the mechanically stretched sample recorded at T_g (233 K), as shown in Figure 1C. The spectrum for the UV irradiatd sample is again basically a singlet superimposed on some poorly resolved hyperfine splitting. The overall width of the spectrum is 60 G and a possible five lines are observed. Since the spectra for the mechanically produced radical species and the radicals obtained by UV irradiation are similar, the radicals produced by UV irradiation are tentatively assigned to the allyl radicals A and B as given above. It is interesting to compare and contrast in detail the spectra obtained by stretching in liquid nitrogen *(containing oxygen) and then warming to* 233 K. Comparison of the two methods demonstrates that, during the mechanical tests in liquid nitrogen, the peroxy radical species is formed by reaction of the primary radicals with oxygen, i.e.,

$$\dot{R} + O_2 \rightarrow \dot{R}O_2 \qquad (1)$$

Polychloroprene deformed below T_g in an oxygen free nitrogen environment resulted in an ESR spectrum similar to Figure 1B, and the peroxy radical spectrum was not detected.

It is usual for poly(chloroprene) to be cross-linked with *zinc oxide. To complete a set of spectra with the me-*

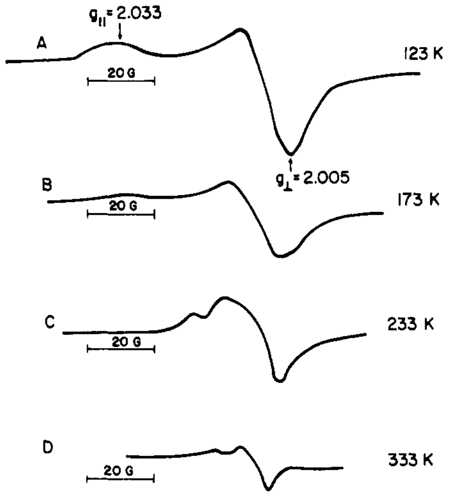


Figure 3. First derivative ESR spectra of dicumyl peroxide cross-linked poly(chloroprene) stretched in liquid nitrogen recorded as the specimen was warmed from 123 to 333 K.

chanically degraded dicumyl peroxide cross-linked BR and IR,[9,10] further tests were conducted using dicumyl peroxide cross-linked PCl. Figure 3 shows the first derivative ESR spectrum of dicumyl peroxide cross-linked poly(chloroprene). The sample was pre-extended by 200% at room temperature and stretched at 77 K in liquid nitrogen at 10^{-3} s^{-1}. The spectra were recorded at the temperatures indicated in Figure 3 as the specimen was warmed to room temperature. The spectra are again consistent with the decay of the peroxy species detected in the low-temperature spectrum at 123 K, decaying to a radical species having overall width of 60 G at 233 K, centered near the free spin value. The radical(s) generated mechanically in dicumyl peroxide cross-linked poly(chloroprene) exists even at 333 K, approximately 100 K above the T_g of the polymer. At 333 K the asymmetric spectrum is still detected and a possible further splitting is observed at the center of the spectrum. These findings are similar to the spectra obtained using the zinc oxide cross-linked poly(chloroprene). The low-temperature spectra must reflect the complex nature of the peroxide cross-linking of poly(chloroprene), and the radicals are most likely attributable to fracture of oxidative cross-links of dicumyl peroxide cross-linked poly(chloroprene), since the thermodynamic strength of the RO–OR bond is considerably lower than main-chain fracture producing resonance stabilized allyl radicals.[10]

Radical Decay in Poly(chloroprene). In order to investigate the stability of the peroxy radicals with respect to the allyl radicals, the samples were warmed from 77 K to above T_g. Figure 4 shows the decay curves for the radicals produced by tensile testing the zinc oxide cross-linked poly(chloroprene) in liquid nitrogen. The decay curve was obtained by plotting against T the radical concentration produced by warming the sample to the temperature T for 5 min and then cooling it to 123 K, the temperature at which the spectra were recorded. The full line in Figure 4 indicates the total radical concentration, and the dotted line gives the estimated relative intensity of the peroxy content of the composite allyl and peroxy radical spectrum as determined by the peroxy peak height at $g_{\parallel}$ = 2.033. The latter curve is similar to that obtained using the integrated areas of the peaks at $g_{\parallel}$ = 2.033. As the peroxy content of the spectra decreases to a concentration below the sensitivity of the spectrometer (~10^{14} spins), the allyl radical species is detected. The peroxy species had completely decayed at a temperature approximately 40 K below T_g, showing that the peroxy radical is less stable than the resonance-stabilized allyl radical and the peroxy radical species decays to yield an allyl species according to

$$\dot{R}O_2 + PH \rightarrow ROOH + \dot{P} \qquad (2)$$

where $\dot{P}$ is an allyl radical on a polymer chain.[15]

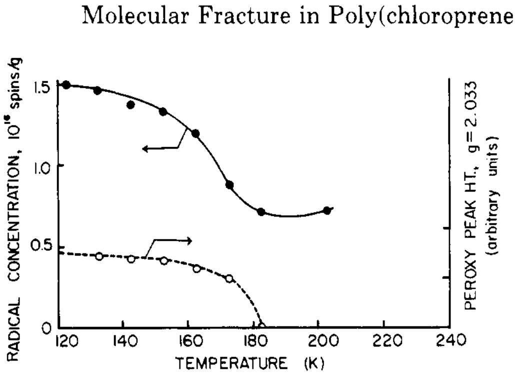


Figure 4. Variation of total radical concentration and peroxy peak height at $g_{\parallel}$ = 2.033 with temperature of zinc oxide cross-linked poly(chloroprene) deformed at 77 K in liquid nitrogen.

Further decay reactions are, of course, possible and these have been discussed elsewhere.[10] The allyl radicals decay near and above T_g to radical products, giving a spectrum containing a weak singlet of overall width 60 G, with a superimposed hyperfine structure and possibly arising from polyenyl radicals. Radicals of this nature have been detected in ultraviolet irradiated poly(chloroprene) and poly(vinyl chloride) specimens.[2,16] Further heating to above T_g causes a rapid decrease in the radical concentration, although the residual signal is still detected even at room temperature. After the samples had been immediately warmed to room temperature, the poly(chloroprene) had highly swollen bands containing environmental gas which gradually escaped over a period of 24 h. Andrews and Reed[12] have also reported gas evolution from deformed natural rubber specimens.[12] The samples also had yellow striations perpendicular to the direction of the tensile test after the specimens had been warmed to room temperature for several days. It is possible that the polyenyl radicals which are formed during the warming process are produced in the highly localized craze bands. The decay of the mechanoradical concentration in poly(chloroprene) with temperature, shown in Figure 4, may be compared with the corresponding data for polybutadiene and polyisoprene.[10] In poly(chloroprene) polyenyl radicals are observed above T_g whereas in BR and IR the radical concentrations were below the sensitivity of the spectrometer, and no residual signal was observed above T_g. Although zinc oxide is diamagnetic it may produce complications in the decay of the radicals. The anomalous radical decay reported for mechanoradical decay in BR and IR was not observed for CR, although the tensile tested CR specimen was held at constant strain during warming above T_g, and the anomalous decay was considerably reduced by this procedure for BR and IR. Unrestrained BR and IR specimens used for radical concentration measurements gave anomalous radical increases near T_g attributable to the formation of radicals resulting from mechanically stored energy release and relaxation of specimen on warming to T_g.[10] Sohma and Sakaguchi[17] have also recently observed anomalous decay curves for mechanoradicals in polypropylene, similar to those reported by Mead, Porter, and Reed.[10] Sohma and Sakaguchi[17] further observed the effect of the excess electric charge on the anomaly by using electron scavengers which produced no anomalous radical decay. Zinc oxide used in the cross-linking agent in CR may also possibly act as an electron scavenger.

In conclusion, the ESR spectra from poly(chloroprene) uniaxially deformed at 77 K in an oxygen environment are composite spectra arising from two radical species. An allyl radical species results from main-chain rupture midway between the α-methylene groups, and a peroxy radical species is formed by reaction of the oxygen in the environment with the allyl radical species. The stability of these allyl radicals with respect to oxygen and temperature is apparently similar to the allyl radicals formed in polybutadiene and polyisopropene. At liquid nitrogen temperature all the radicals were stable. The peroxy radical species is unstable as T_g is approached and decays to give a resonance-stabilized allylic species, which is stable until the temperature of the sample is slightly above T_g. Above T_g a broad singlet is observed and is attributed to a polyenyl radical species.

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Entanglement Networks of 1,2-Polybutadiene Cross-Linked in States of Strain. 8. Trapping of Entanglements in Relaxed and Unrelaxed Configurations

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ABSTRACT: A sample of 1,2-polybutadiene (T_g = −10 °C) is strained in uniaxial extension to a stretch ratio λ_0 at 0 °C, allowed to relax at constant strain for time t_R, cooled to −10 °C, and cross-linked by γ irradiation, thereby trapping a proportion of the entanglements originally present. The network strands contributed by the trapped entanglements are partly in strained configurations (ν_N mol/cm^3) and partly in relaxed (randomized) configurations (ν_{NR} mol/cm^3). Upon release and warming, the sample seeks a state of ease with stretch ratio λ_s in which the forces associated with the trapped unrelaxed entanglements balance the forces associated with the trapped relaxed entanglements and the cross-links. The strand densities ν_N, ν_{NR}, and ν_X (density of network strands contributed by cross-links) can be calculated from measurements of λ_0, λ_s, and the equilibrium tensile stress at λ_0, for various values of t_R and various degrees of cross-linking by different irradiation doses. Based on a two-network model, the stress at any subsequent strain λ is accurately given by the sum $\sigma_N + \sigma_Y$, where σ_N is the stress contributed by a network of trapped unrelaxed entanglements with $\lambda = 1$ as a reference state and σ_Y is the stress contributed by a network of cross-links and trapped relaxed entanglements with $\lambda = \lambda_0$ as a reference state. With increasing t_R at constant dose, ν_X is constant, ν_N decreases, and ν_{NR} is zero until a critical value of t_R is reached and then increases. The trapping probabilities $T_{e,u}$ and $T_{e,r}$ for unrelaxed and relaxed entanglements, respectively, are estimated and compared with the Langley theory. At low values of t_R, $T_{e,u}$ agrees with the Langley theory and $T_{e,r}$ is zero. Beyond a critical value of t_R, $T_{e,u}$ increases and $T_{e,r}$ becomes finite and increases but remains lower than the average value predicted by the Langley theory. The behavior is consistent with the terminal mechanism of relaxation in the tube theory of Doi and Edwards in which the unrelaxed entanglements correspond to topological restraints near the center of the tube contour, and the relaxed entanglements correspond to constraints on the ends of the molecule which have found new tube paths by reptation.

The cross-linking of 1,2-polybutadiene strained in simple extension has been described in previous papers of this series.[1-5] When a strained sample with stretch ratio λ_0 is cross-linked with γ irradiation near the glass transition temperature (T_g), the resulting cross-link network traps the entanglements originally present; after release and warming, the sample seeks a state of ease with stretch ratio λ_s in which the forces associated with the cross-links and the trapped entanglements act in opposite directions. From λ_0 and λ_s, together with stress–strain measurements in extension from the state of ease, or simply from the equilibrium stress at λ_0, the concentration of trapped entanglement strands ν_N can be calculated on the basis of a dual network model and compared with the entanglement strand density estimated from transient measurements on the uncross-linked polymer. To obtain consistent results, especially for stress–strain relations in large extensions of the dual network from its state of ease, it is necessary to attribute deviations from neo-Hookean elasticity to the trapped entanglement network, as de-

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