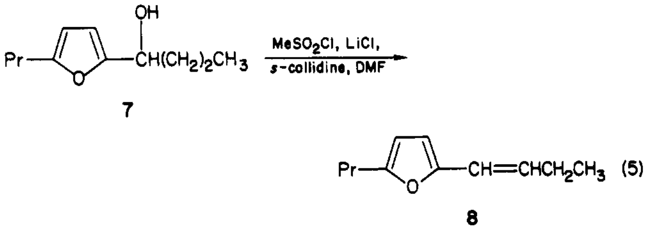
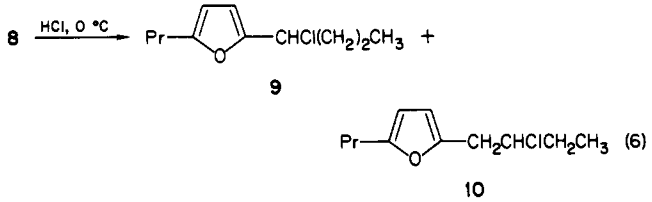
instead, a mixture of *cis*- and *trans*-**8** (largely *trans*-**8**), which was obtained, for example, in 40% yield with the Collington–Meyers reagent[12] (eq 5; DMF = *N*,*N*-dimethylformamide). However, when **8** was allowed to react with HCl in $CDCl_3$ at 0 °C, both **9** and its isomer, **10**, were formed (eq 6), although ^1H NMR measurements showed that **9** was changing irreversibly into **10** under these conditions. Owing to the resonance stabilization of its carbocationoid precursor, **9** presumably was the main product produced initially, and its kinetic instability can, of course, be rationalized on this basis as well.





These findings strongly suggested that the thermal dehydrochlorination rate of **9** would be much faster than that of **10** and that it should be possible to determine the rate for **9** (which could not be isolated in pure form) from mixtures of the two chlorides. Both expectations were fulfilled. At 170 °C in *o*-dichlorobenzene under argon, pure **10** (obtained as the final product from HCl and **8**) had a dehydrochlorination rate constant of only $2.7 \times 10^{-7}\ s^{-1}$. Under identical conditions, the rate of **9** was difficult to measure accurately owing to its great rapidity and to complications stemming, apparently, from the competing rearrangement of **9** into **10**. Nevertheless, replicate runs with chloride mixtures gave constants for **9** within the range of $(6 \pm 3) \times 10^{-3}\ s^{-1}$. Thus, in our experiments, **10** was very stable, while **9** was at least as reactive as the cis chloro ketone, **3b**.

Summarizing the implications of our findings, we conclude that *cis*-**2** structures in PVC would rapidly initiate the growth of polyenes upon heating, owing to the quick conversion of *cis*-**2** into **6**, whose α-chloroalkyl group would dehydrochlorinate with great facility. What obviously remains to be decided is whether the *cis*-**2** concentrations in PVC specimens are high enough to cause major effects on the overall rate of thermolysis. These concentrations should be even less than those of *trans*-**2**, on thermodynamic grounds, and our extensive studies of PVC using ^{13}C NMR spectroscopy[13] have provided no evidence for the occurrence of either structure or structures derived therefrom.[14] However, additional NMR studies might prove to be worthwhile, since our lower detection limits have usually been above the amounts of **2** which, according to Minsker et al.,[1] are present in the polymer.

Acknowledgment. We thank Dr. S. L. Haynie for a gift of *trans*-4-chloro-5-decene.

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Fracture-Induced Free Radicals in Amine-Cured Epoxy Resins

We are using electron paramagnetic resonance (EPR) to investigate the role of macromolecular chain scission in the deformation and failure modes of amine-cured epoxy resins. These are the thermosetting polymers which are widely used as matrix materials in composite structures. In this communication we report on the nature of the free radicals created in epoxy resins as a result of fracture-induced macromolecular chain scissions. Previous EPR studies have shown that free radicals can be generated in polymers as a result of some form of grinding,[1-4] e.g., ball milling or sawing. We have adopted the grinding technique to ensure the chemical stability of the fracture-induced radicals since it is not too difficult to design an apparatus that allows the samples to be ground while maintained at 77 K and kept free of oxygen.

The epoxy system studied was the diglycidyl ether of bisphenol A (DGEBA) cured with stoichiometric amounts of ethylenediamine, ethylenediamine-d_4, and diethylenetriamine. Homopolymerized samples of DGEBA containing ≈4 wt % *N*,*N*-dimethylbenzylamine as an initiator were also investigated.

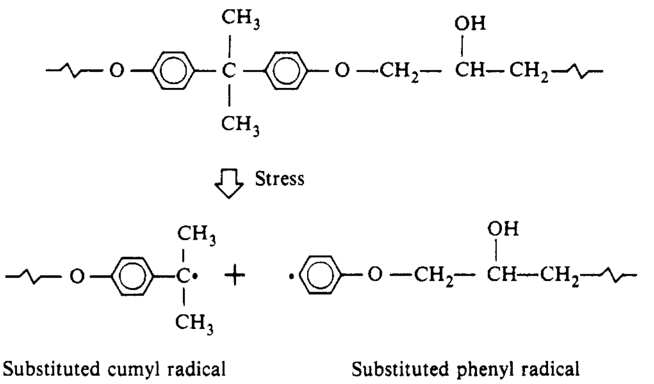

Figure 1. Observed fracture-induced bond scissions.

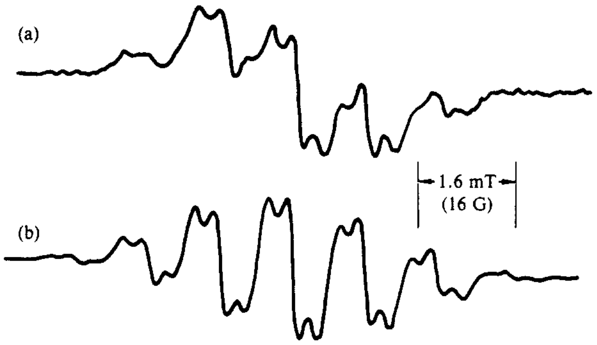

Figure 2. EPR spectrum (a) observed at 300 K from the substituted cumyl macroradical after ball milling of DGEBA epoxy cured with ethylenediamine-d_4 and (b) computer simulated for the substituted cumyl radical.

The cured resins were machined to submillimeter sizes with a cutting tool, either an end mill or a burr, and the shavings were transferred to a Pyrex sample tube containing ten 6-mm-o.d. glass balls. These samples were degassed for ≈ 4 h at high vacuum, <1 mPa, before the sample tube was sealed off. Ball milling was usually carried out with the sample tube in liquid nitrogen for a period of 0.5–1.0 h. All EPR spectra were digitized and stored using a data acquisition system (Varian E-900). The spectra could then be scaled, field-shifted, added, subtracted from one another, or integrated by using available software.

The EPR spectrum of the para-substituted cumyl macroradical shown in Figure 1 was observed in all cured epoxy samples containing DGEBA after ball milling. This radical species is identifiable from the observed seven-line hyperfine pattern associated with the six methyl protons. As shown in Figure 2a, each of the seven lines is further split by two ortho ring protons. Furthermore, as shown in Figure 2b computer spectral simulations for the substituted cumyl radical showed excellent agreement with the experimentally observed spectrum. The best-fit spectrum had the following parameters: $a_{\mathrm{CH_3}} = 1.6$ mT, $a_{\mathrm{H_o}} = 0.45$ mT, and $a_{\mathrm{H_m}} = 0.15$ mT, where $a_{\mathrm{CH_3}}$, $a_{\mathrm{H_o}}$, and $a_{\mathrm{H_m}}$ are the isotropic hyperfine coupling constants for the methyl, ortho, and meta protons, respectively. In Figure 2b the component line shapes were assumed 50% Lorentzian and 50% Gaussian with a full width between points of maximum slope of 0.35 mT.

The EPR spectrum from randomly oriented free radicals usually contains no resolved hyperfine components because of large anisotropic interactions. The hyperfine structure is observable in the spectrum shown in Figure 2 because the methyl protons have a large isotropic splitting (≈ 1.6 mT) and a small anisotropic interaction ($\lesssim 0.35$ mT). The former can be explained by hyperconjugation, whereas the latter is the result of methyl group rotations. The observed line shape and the measured isotropic hyperfine coupling constants are consistent with those previously reported for the cumyl radical.[5]

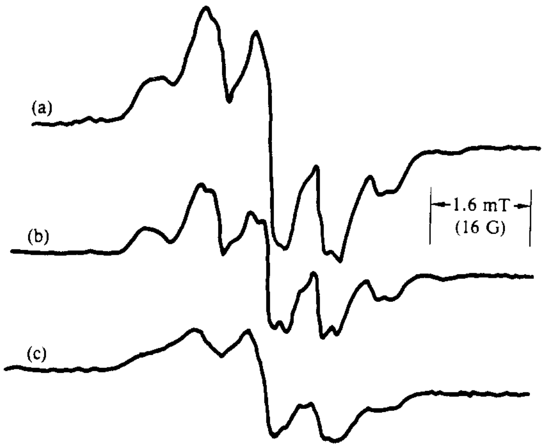

Figure 3. EPR spectrum obtained (a) at 77 K on ball milling a sample of DGEBA epoxy cured with ethylenediamine-d_4 (designated spectrum A), (b) at 77 K after warming the same sample to 300 K for 5 min (designated spectrum B), and (c) by subtracting spectrum B from spectrum A (designated spectrum C).

No free radicals were observed in related low-molecular-weight materials such as 4,4′-isopropylidenediphenol (i.e., bisphenol A) even after 8 h of ball milling at 77 K. This result supports the idea that the substituted cumyl radicals are generated because fracture-induced chain scissions of the type shown in Figure 1 occur in the polymer network.

If the ball-milled sample is retained in the evacuated tube, the seven-line spectrum changes slowly to a single line (line width ≈ 2.2 mT) but is still detectable after 100 h at 300 K. The stability of the substituted cumyl radical can be attributed both to the delocalization of the unpaired electron and to the fact that it is bound to and trapped in the rigid polymer network. The importance of the network rigidity is evident on heating the sample above the glass transition temperature ($T_g \approx 420$ K) whereupon all radicals present decay immediately. When the ball-milled sample is exposed to air, the seven-line spectrum changes almost immediately (within a few minutes) to a single line (line width = 0.95 mT). This irreversible change indicates the formation of a new radical species, and although this may be an oxygen-containing radical the spectrum associated with the large g anisotropy of the peroxy radical[2] was not observed.

Evidence for the formation of the complementary radical (viz., a substituted phenyl radical) involved in the scission process shown in Figure 1 is less certain. When cured samples of the DGEBA epoxy were ball milled and kept at 77 K the spectrum shown in Figure 3a (designated spectrum A) was observed. After the sample was warmed to 300 K for 5 min only the spectrum assigned to the substituted cumyl macroradical, viz., that shown in Figure 2a, remained. The sample was then returned to 77 K and the spectrum shown in Figure 3b (designated spectrum B) was recorded at the previous spectrometer gain setting. The poorly resolved three-line spectrum shown in Figure 3c (designated spectrum C) was obtained by subtracting spectrum B from spectrum A. Thus, spectrum A can be deconvoluted into spectrum B and spectrum C. The latter spectrum may be that of the substituted phenyl radical[6] shown in Figure 1 with only the ortho ring proton splittings being resolved with an isotropic coupling constant ≈ 1.6

mT. However, this assignment is tentative and further measurements are in progress for confirmation.

These results demonstrate that enough main-chain scissions occur in the fracture of amine-cured epoxies so that the resulting radicals are detectable and identifiable by standard EPR techniques. Moreover, since some of these radicals are primary radicals they indicate the molecular failure sites where the chain scissions occur.

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Improved Hole Mobility of Polyacrylate Having a Carbazole Chromophore

Carrier mobility and photogeneration efficiency are essential factors in the performance of photoconductors.[1] Although organic photoconductors have certain advantageous characteristics, they are inferior to inorganic ones in both these properties, particularly carrier mobility.[2] Molecularly doped polymers are widely employed in both research[3-6] and practical uses.[7] In most cases, they exhibit higher carrier mobility than corresponding pendant-type polymers[8,9] except poly(*N*-carbazolylpropylene oxide).[10]

Polyacrylates and polymethacrylates containing adequate chromophores are good candidates for carrier transport materials with high mobility, since their stereoregularity can be controlled by the use of proper catalyst systems.[11] In the previous paper,[12] it was demonstrated that poly(2-*N*-carbazolylethyl methacrylate) has a carrier mobility similar to that of poly(*N*-vinylcarbazole) (PVK) despite its lower chromophore content, and we speculated that this is due to the ease of molecular motion of the carbazole moiety. Since the T_g of poly(2-*N*-carbazolylethyl methacrylate) is 155 °C, side-chain relaxation below the T_g was believed responsible for the enhanced molecular motion. Since this relaxation is known to occur at lower temperatures in polyacrylates,[13] we have measured hole transport characteristics of poly(2-*N*-carbazolylethyl acrylate) and here report that this polymer shows a hole drift mobility one order of magnitude higher than that of the corresponding polymethacrylate.

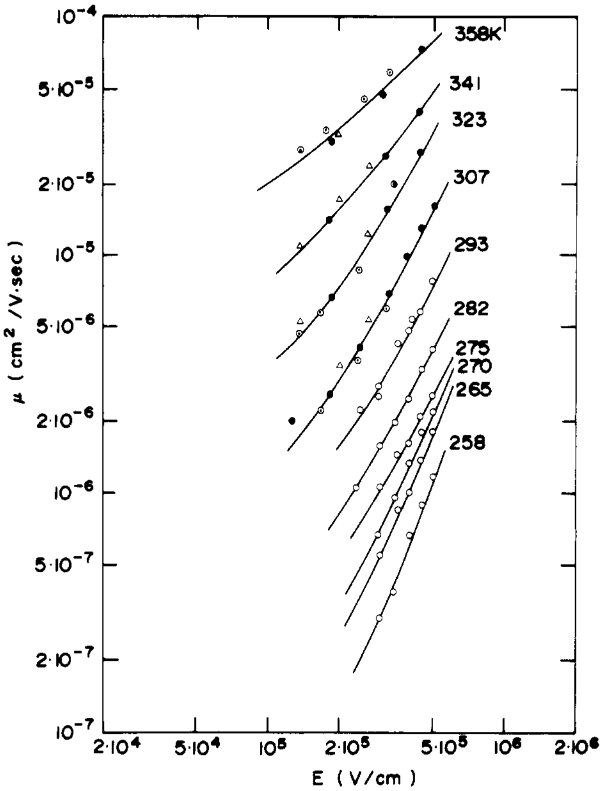

Figure 1. Electric field dependence of hole drift mobilities of poly(2-*N*-carbazolylethyl acrylate) at different temperatures. Thickness of polymer films was 16 (●), 10 (○), 6 (⊙), and 3 μm (△).

The polymer ($\bar{M}_w = 5.6 \times 10^4$) was prepared by polymerization of 2-*N*-carbazolylethyl acrylate[14] in benzene (60 °C for 3 days; yield, 87%) using α,α'-azobis(isobutyronitrile) (0.5 mol %) as an initiator followed by three reprecipitations from methylene chloride solution with methanol. The hole drift mobility was determined by the time-of-flight method[12] using an 8-μs light pulse (435 nm) as incident light on layered samples composed of a thin polymer film deposited on an aluminum substrate from chlorobenzene solution at 40 °C[16] with a thin layer of a-Se deposited on the surface of the film and attached with a translucent top gold electrode. The carrier injection efficiency was measured by the photoinduced discharge method on similar layered samples without a top electrode at 450 nm.[17]

The photocurrent exhibited a very fast initial transient due to the transport of holes in the a-Se layer[18] followed by a well-defined plateau and then a long tail. The transit time was defined as the time at which the plateau and the tail intersected. For a 3-μm specimen, the transient current was dispersive and the transit time was evaluated from the shoulder of the plot of log (photocurrent) vs. log (time). Hole mobility was estimated conventionally from the transit time.

Hole drift mobility measured at various temperatures was strongly dependent on the applied electrical field, as commonly observed in disordered materials (Figure 1). The sample-thickness dependence was not prominent. It is noted that the room-temperature mobilities (at 293 K) are considerably greater than those of the corresponding polymethacrylate and PVK (at 295 K).[8]

For hopping transport among a set of localized sites, the mobility correlates with the average separation between

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