

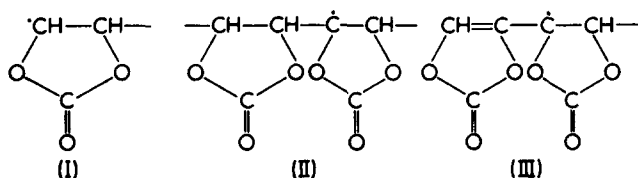
Structure and reactivity of free radicals trapped in mechanically degraded poly(vinylene carbonate)

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(Received 27 May 1977)

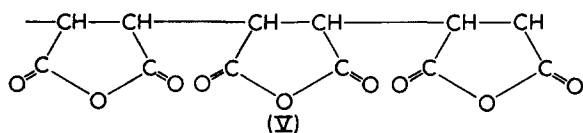
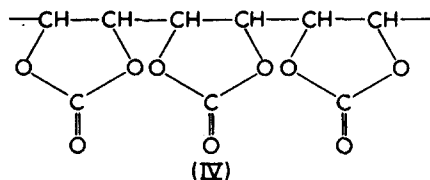
Poly(vinylene carbonate) has been mechanically degraded. The structure and the reactivity of polymer radicals have been studied over the temperature range between -70° and 150° C. At -70° C the following radicals are present:



The hyperfine splitting constants are: (I), $a_H = 1.96$ mT and $a_H = 3.34$ mT; (II), $a_H^1 = 3.2$ mT; (III), $a_H = 1.25$ mT and $a_H = 1.75$ mT. At $+70^{\circ}$ C, new radicals occur and the total spectrum becomes asymmetrical.

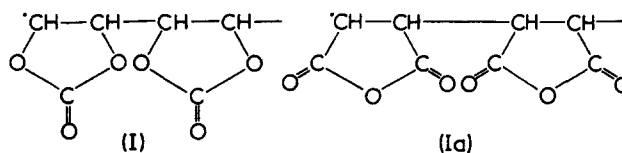
INTRODUCTION

From the viewpoint of the e.s.r. spectroscopy, poly(vinylene carbonate) (IV) has the structure similar to poly(maleic anhydride) (V).



Although the e.s.r. spectra of free radicals of the mechanically degraded poly(maleic anhydride) have not yet been investigated, the radicals trapped in the mechanically degraded copolymer maleic anhydride–methyl methacrylate (MA–MMA) with various amounts of maleic anhydride were studied in detail¹. During mechanical degradation, formation of the primary free radicals is expected mainly by bond scission in the main chain joining monomeric units leading to similar types of radicals [(I) and (Ia)] for poly(vinylene carbonate) and poly(maleic anhydride). However, it does not necessarily follow that hyperfine splitting constants are the same in these radicals since spin density and position

of the β -proton can be different in I and Ia.



Apart from this, it was shown¹ that during alkyl radical decay in mechanically degraded copolymer MA–MMA, allyl and polyene radicals are formed, and in amounts varying with the percentage content of maleic anhydride in the copolymer. Most radicals were formed in a copolymer with 12% of maleic anhydride; in the copolymer containing 2% of maleic anhydride the amount of the radicals was not measurable. It seems that it is maleic anhydride which is responsible for the formation of these radicals. Double bond formation was thought to arise¹ as a result of decomposition of the maleic anhydride ring. The present paper presents a study of radicals formed during mechanical degradation of poly(vinylene carbonate).

EXPERIMENTAL

Vinylene carbonate was prepared by the dehydrochlorination of chloroethylene carbonate in the presence of triethylamine, following the method described by Newman and Addor^{2,3} (b.p., 73° – 74° C/4.3 kPa; m.p. = 22° C; $n_D^{25} = 1.4190$; $d_4^{25} = 1.3541$ g/cm³).

Polyvinylene carbonate was prepared by polymerization of vinylene carbonate in the presence of 0.2 wt % AIBN at 70° C in a sealed ampoule in nitrogen⁴. The limiting viscosity

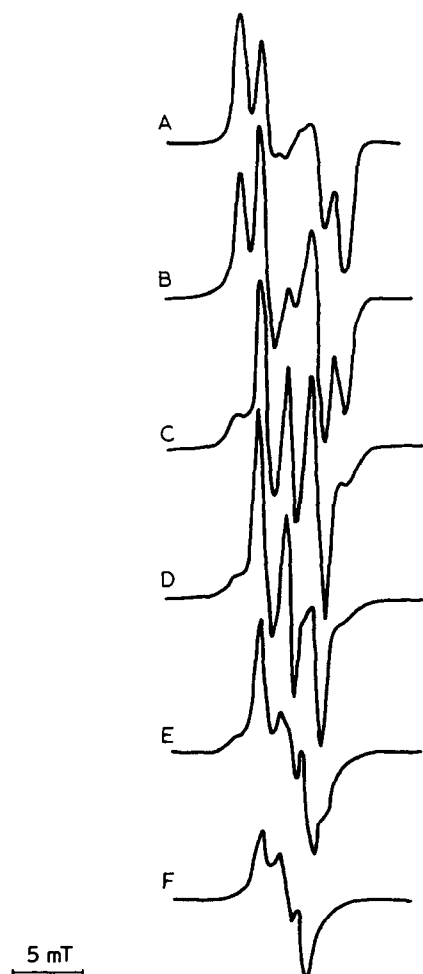


Figure 1 Experimental e.s.r. spectra of radicals trapped after mechanical degradation of poly(vinylene carbonate) at -196°C and measured at: A, -70°C ; B, -15°C ; C, 30°C ; D, 70°C ; E, 120°C ; F, 150°C .

number, determined in dimethylformamide at 25°C in an Ubbelohde viscometer, was $[\eta] = 1.09$ ($c = \text{g}/100 \text{ cm}^3$)⁵. The number-average molecular weight determined by an automatic Hewlett-Packard membrane osmometer in DMF at 30°C was $\bar{M}_n = 3.6 \times 10^5$.

A cylindrical sample was mechanically degraded by a special vidium drill in vacuum in an ampoule dipped into liquid nitrogen as previously described⁶. The e.s.r. spectra were measured on an X-band e.s.r. spectrometer (Zeiss, Jena) over the temperature range -70° to $+150^{\circ}\text{C}$.

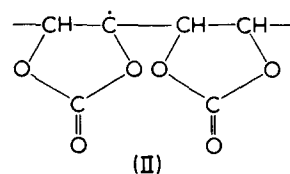
RESULTS AND DISCUSSION

Analysis of the e.s.r. spectrum of the mechanically degraded poly(vinylene carbonate) measured at -70°C (Figure 1) showed the presence of several types of radicals.

It is known that mechanical degradation produces primarily scission radicals⁷; therefore in the e.s.r. spectrum (Figure 1) the presence of these radicals was expected. Since the main chain of poly(vinylene carbonate) consists only of tertiary carbons equally substituted, the main chain scission can lead to the formation of only one type of end radical (I), the presence of which has been confirmed (Figure 1).

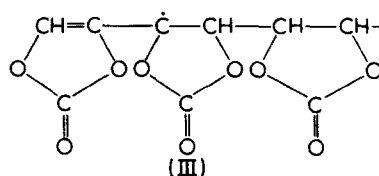
The alkyl radical (II) also present in the spectrum in

Figure 1 was probably formed by transfer reaction between radical (I) and the polymer.



Both the chain scission and the transfer reaction may give rise to only one radical type, viz. (I) and (II) respectively since it is considered that degradation of the carbonate cycles is improbable

The structure of the spectrum at -70°C and changes occurring during the heating process show that apart from these two types of radicals another one is also present in the system. However, since it cannot be the alkyl radical it is assumed that the allyl radical (III) was formed by transfer reaction of alkyl radicals to a polymer that might initially have had double bonds at chain ends.



The hyperfine splitting constants of the radical (III) should differ from those of (I) only in the fact that the spin density is lower in (III). Figure 2 shows component spectra belonging to radicals (I), (II) and (III) and their sum which gives the experimental spectrum observed at -70°C . The component spectra were constructed on the assumption that

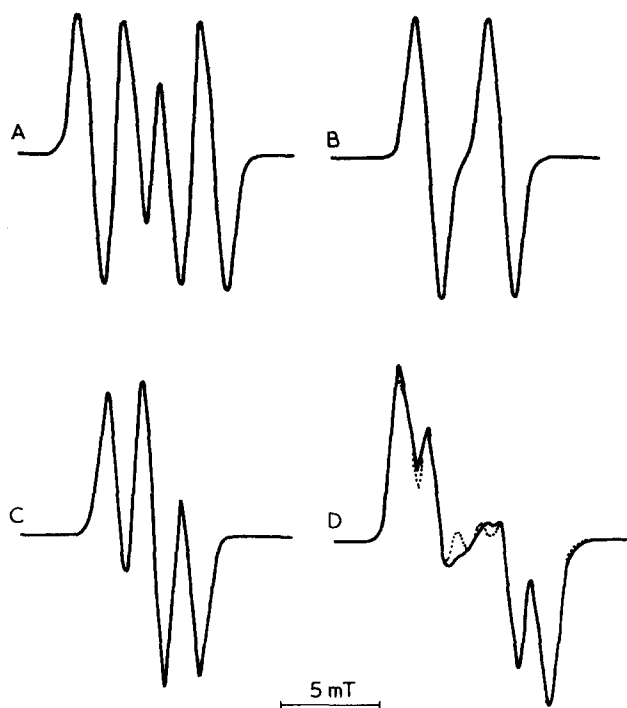


Figure 2 Component spectra of radicals: A, (I); B, (II); C, (III). Used for simulating the experimental spectra trapped in the mechanically degraded poly(vinylene carbonate). D, the total e.s.r. spectrum;, the theoretical spectrum; —, the experimental spectrum

Table 1 Hyperfine splitting constants of radicals (I), (II) and (III)

Radical	a_H^α (mT)	a_H^β (mT)	$\Delta H_{1/2}$ at -70°C (mT)
(I)	1.96	3.34	1.16
(II)		3.2	1.16
(III)	1.25	1.75	1.16

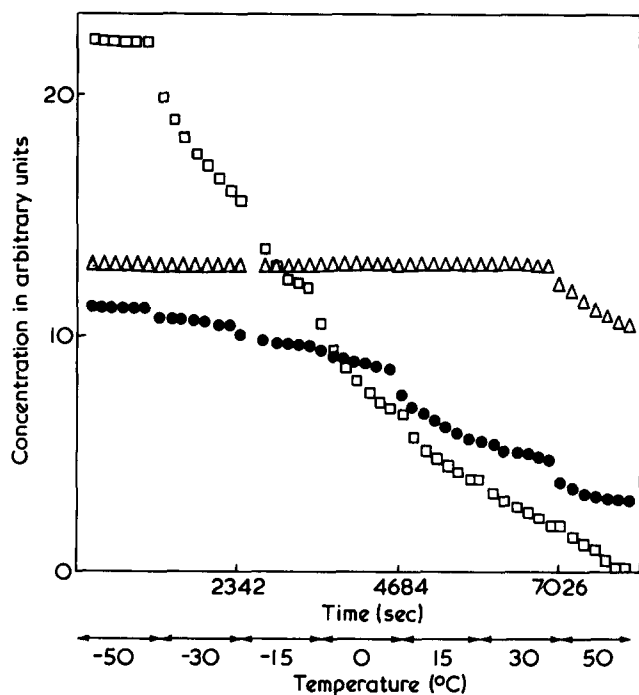


Figure 3 Time and temperature dependences of the concentration of free radicals: □, radical (I); ●, radical (II); △, radical (III)

the shape of the line is Gaussian; Table 1 contains hyperfine splitting constants and linewidths.

The different rate constants for radical decay cause considerable changes in the shape of the total spectrum during their decay (Figure 1) and this enables the individual types of radicals to be identified. For comparison purposes, the e.s.r. spectra of radicals trapped on γ -irradiation of poly(vinylene carbonate) were also measured. The analysis

of the spectrum (-70°C) shows that it consists of the same component spectra of radicals as in the degraded polymer, but in a different ratio. Moreover, a singlet spectrum corresponding to an oxy-radical occurs and the total spectrum becomes asymmetrical.

Figure 3 presents stepwise decay of the individual radicals. As is evident from Figures 1 and 3, the resulting radical is still stable at -50°C (at these temperatures the total spectrum changes only slightly). From -30°C , its concentration rapidly decreases and this radical exerts practically no effect on the total spectrum at $+70^\circ\text{C}$. The concentration of alkyl radical (II) decreases over this temperature interval but not so much as that of the radical (I). In contrast, radical (III) is stable. It begins to decay at $+50^\circ\text{C}$ and this supports our assumption that it is an allyl radical. At 70°C the total spectrum changes markedly (Figure 1). It becomes asymmetrical and a new type of the radical is formed, the spectrum of which has a different g factor. Although we did not succeed in identifying this radical, it is probable that it will be a radical stabilized by one or more double bonds because it is more stable than the radicals (I), (II) and (III). In addition, it follows from the asymmetry of the total spectrum that it should be an oxygen centred radical formed by decomposition of the carbonate ring.

Figure 3 shows that the radicals (I) and (II) decay stepwise, a property that has been observed by many authors^{8,9}. It results from the fact that at a given temperature only a certain fraction of radicals is involved in the reaction. According to Lebedev and Burshtein⁹, who studied chemical reactions in molecular solids on the basis of the 'free volume model', stepwise decay occurs always when the main source of the change of E is the variation of the local properties.

REFERENCES

- 1 Tiño, J., Plaček, J. and Pavlinec, J. *Eur. Polym. J.* 1974, **10**, 291
- 2 Newman, M. S. and Addor, R. W. *J. Am. Chem. Soc.* 1953, **75**, 1263
- 3 Newman, M. S. and Addor, R. W. *J. Am. Chem. Soc.* 1955, **77**, 3789
- 4 Smets, G. and Hayashi, K. *J. Polym. Sci.* 1958, **29**, 257
- 5 Schulz, R. C. and Vollkommer, N. *Makromol. Chem.* 1968, **116**, 288
- 6 Lázár, M. and Szöcs, F. *J. Polym. Sci. (C)* 1967, **16**, 461
- 7 Sohma, J., Kawashima, T., Shimada, S., Kashiwabara, H. and Sagakuchi, Nobel Symp. 22: 'ESR Applications to Polymer Research', (Eds P. O. Kínell, B. Rándy and V. Runnström-Reiro), Wiley, New York, 1973, p 225
- 8 Lebedev, Y. S. and Burshtein, A. I. *Chem. Phys.* 1976, **12**, 259
- 9 Tiño, J., Plaček, J. and Szöcs, F. *Eur. Polym. J.* 1975, **11**, 609