Study of radical products of mechanically destructed poly(*N*-vinylene carbazole)

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Free radicals generated by mechanical destruction of poly(*N*-vinylene carbazole) have been studied. Two types of chain-end radicals have been found in the system at 100K in accord with the polymer fracture theory. At 273K these radicals started to decay and new, more stable main-chain radicals have been observed. When O_2 was introduced into the system, the chain-end radicals disappeared rapidly giving rise to ROO· radicals, which decayed at 200K generating nitrogen centred cation radicals.

Keywords Poly(*N*-vinyl carbazole); electron spin resonance; free radicals; mechanical destruction; solid state

INTRODUCTION

The main goal of the e.s.r. study of free radicals in polymers is usually to find out radicals obtained by generation and to determine theif structure and stability. Mechanical destruction produces primarily two types of chain-end radicals[1]. The radicals of the form $\cdot CH_2-R$ are not sterically hindered and decay earlier; the other radicals are more stable and decay at higher temperatures. More stable radicals are often formed by isomerization and can be studied by the e.s.r. method[2]. In mechanically destructed polymers the radicals are on the sample surface and thus they are not protected from air oxygen[3,4] they change to peroxy radicals. The change is in many cases complete; the e.s.r. spectrum changes to an assymmetric singlet, or partial, when not all radicals react with O_2[3]. The ROO· radicals usually decay as the temperature is raised to 273 K.

In this paper radicals generated by mechanical destruction of poly(*N*-vinylene carbazole) have been studied. We have investigated radicals in the absence of oxygen and also when oxygen has been introduced into the system at 93 K. The present radicals, their structure and relative stability have been determined by detailed analysis of the e.s.r. spectra.

The structure of radicals is determined by analysis of the e.s.r. spectra. Since the spectra are usually multicomponent, simple methods of analysis do not yield satisfactory results. The analyses have to be done by simultaneous determination of individual component spectra and their representation in the overall spectrum. The programme used for this purpose has been described elsewhere[5]; the programme is based on the minimalization of the least squares functional by the gradient method and the position, height and width of the individual component spectra and the corresponding *hfs* constants are optimized.

EXPERIMENTAL

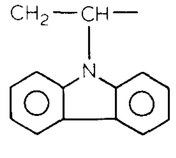
Commercial sample of poly(*N*-vinylene carbazole) was used; produced by BASF, name LUVIKAN, M 170. Molecular weight $\bar{M}_n = 5.10^5$, ($\bar{M}_w/\bar{M}_n = 1.20$), $T_g = 498$ K, m.p. 593 K, density 1.186 g cm^{-3}.

Cylindrical samples, 7 mm in diameter and 7 mm in length were prepared by melting of granules in a matrix at 473 K and at 50 mPa. After 10 min annealing the sample was allowed to cool to room temperature (35 min) at the given pressure.

Mechanical destruction was done in a special ampoule by drilling with a vidium drill 4.10^{-4} m in diameter under vacuum (5.10^{-5} mm Hg). The ampoule was dipped in liquid nitrogen in a dewar vessel during the drilling. The method has been described in detail elsewhere[6].

RESULTS AND DISCUSSION

The structure of the spectrum is the same over the temperature range between 100 and 270 K. The overall spectrum (A) is multicomponent. It consists of the two one-component spectra (B and C) assigned to radicals I and II (*Figure 1*) with the hyperfine coupling constants: I(B): $a_H^\alpha = 2.0$ mT; $a_H^\beta = 0.5$ mT; II(C): $a_H^\alpha = 1.5$ mT; $a_H^{\beta_1} = 1.1$ mT; $a_H^{\beta_2} = 3.3$ mT; $a_N = 0.5$ mT.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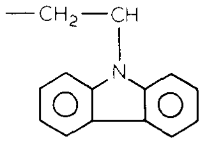
II

They are primary products of main-chain scission. At 153 K, their representation in the overall spectrum is not the same. The number of the type II radicals is 18 fold compared with the type I radicals.

A more marked change of the overall spectrum is seen at 300 K (*Figure 2*). *Figure 2* shows that a new type of radical is formed. The new radical determining the structure of the spectrum at 360 K (*Figure 2*) is the radical III ($a_H^{\beta_1} = 3.8$ mT; $a_H^{\beta_2} = 0.9$ mT; $a_H^{\beta_3} = 4.1$ mT; $a_H^{\beta_4} = 1.3$ mT). We have not observed hyperfine splitting coming from N atom in radical III, though environment for the

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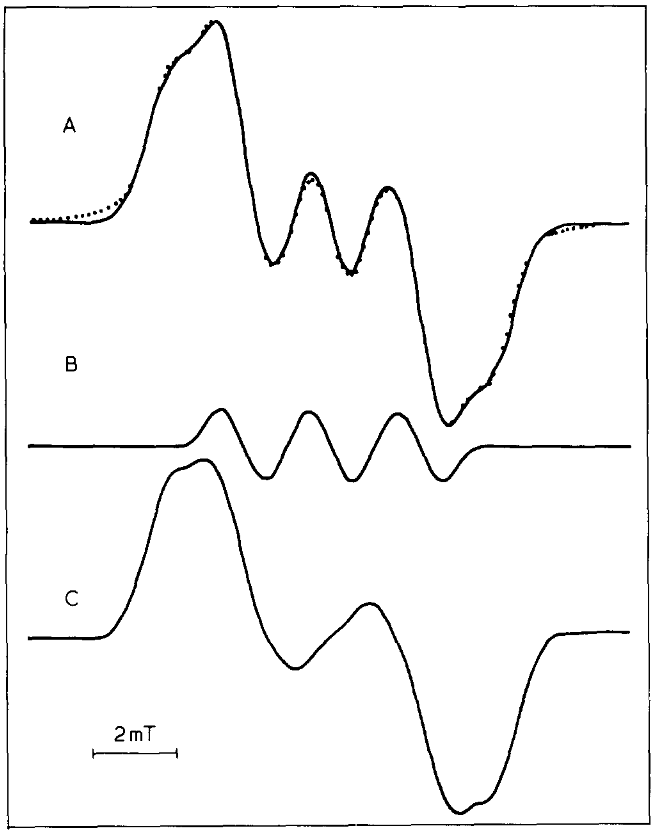


Figure 1 E.s.r. spectra of free radicals trapped in mechanically degraded poly(*N*-vinylene carbazole). Measured at 153 K. A, (· · ·) experimental, (——) theoretical; B, theoretical spectrum corresponding to radical I; C, theoretical spectrum corresponding to radical II

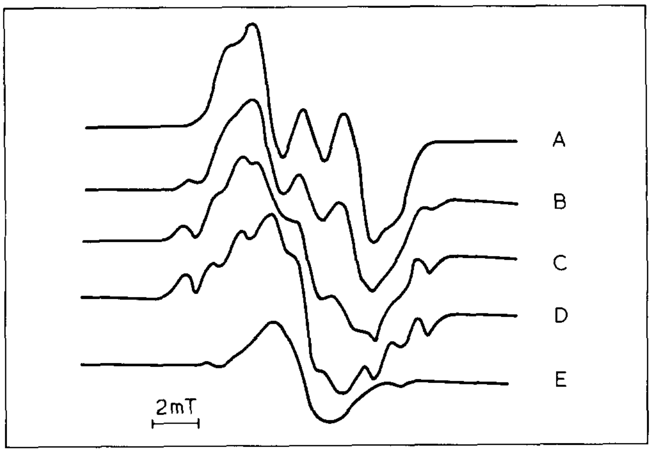
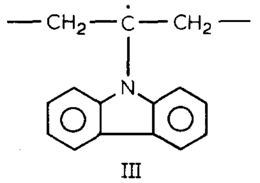


Figure 2 Experimental e.s.r. spectra of free radicals trapped in mechanically degraded poly(*N*-vinylene carbazole). Measured at various temperatures: A, 153 K; B, 300 K; C, 340 K; D, 373 K; E, 408 K

unpaired electron in both radicals II and III is similar. This could be explained by different rotational state of carbazole group in discussed radicals caused by different steric hindrances.



III

The study of the e.s.r. spectra of deuterated polystyrene showed[2] that at 240 K chain-end radicals change to more stable main-chain radicals. A similar situation arises in the case of poly(*N*-vinylene carbazole). At 300 K, main-chain radical III is formed and at the same time the radical II starts to decay rapidly.

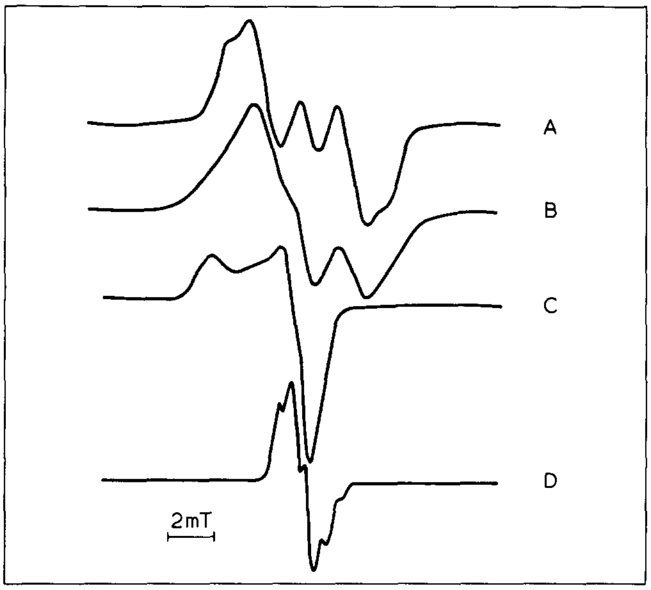
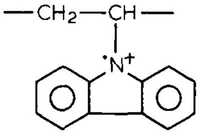


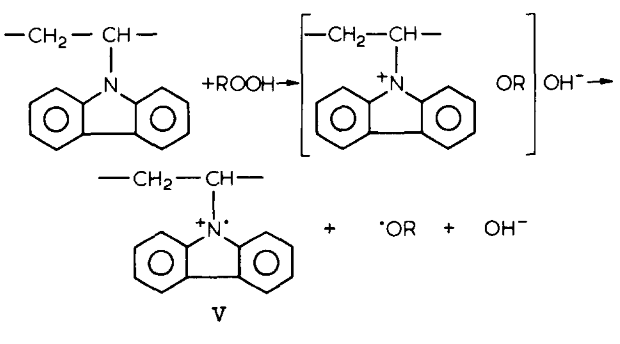
Figure 3 Experimental e.s.r. spectra of free radicals trapped in mechanically degraded poly(*N*-vinylene carbazole) (during measurement at 93 K, air was introduced to the system). Measurements at various temperatures: A, 77 K; B, 83 K; C, 155 K; D, 323 K

If, after mechanical destruction, air is introduced to the system, the shape of the spectrum changes rapidly. The spectrum is asymmetrized. Peroxy radicals are formed by reaction of oxygen with alkyl radicals. At 155 K (*Figure 3*) alkyl radicals vanish. At 200 K, the shape of the spectrum again changes. Although ROO· radicals decay in most of the mechanically destructed polymers and no other types are formed, it is not the case with poly (*N*-vinylene carbazole); at 200 K, a spectrum occurs which has been analyzed in detail elsewhere[7] (*Figures 3* C and D) and corresponds to the radical V.



V

Formation of this radical can be explained by the known mechanism of the reaction of amines with hydroperoxides[8]. In this case we can expect formation of hydroperoxides as one of the products of the reaction of peroxy ROO· radicals with their own or neighbouring polymer chain. Hydroperoxides thus formed are able to react with amine nitrogen of vinyl carbazole leading to radicals V.



The study of free radicals in irradiated poly(*N*-vinylene carbazole)[7] showed that the radical V is relatively stable. This is also supported by the present results according to which the radical V vanishes at the temperature as high as 400 K.

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