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Journal of Photochemistry and Photobiology
A: Chemistry 86 (1995) 253–257

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

On the localization of the unpaired electron in a macroradical of a propagating polymer chain during low-temperature, solid-phase polymerization of *p*-diethynylbenzene

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Received 4 November 1993; accepted 2 August 1994

Abstract

An electron spin resonance (ESR) study of the UV- or γ-induced polymerization of *p*-diethynylbenzene (DEB) crystals over a wide temperature range (77–300 K) has revealed that the unpaired electron of the macroradical of the propagating polymer chain (77–230 K) is localized on the terminal monomer link to give a doublet splitting in the ESR spectrum. Delocalization n the polyconjugated system takes place at 230–310 K by addition of the linear macroradical to the double bond of the polymer. In this case, a normal polyene-type radical, observed during the polymerization of acetylenic monomers at elevated emperatures, is formed and shows a singlet splitting with a width of $\Delta H \approx 1$ mT in the ESR spectrum. The encounter of the macroradical with the double bond probably occurs via polymer chain propagation.

Keywords: Unpaired electrons; Polymer chains; Polymerization; *p*-Diethynylbenzene

1. Introduction

Polymerization of acetylenic monomers leads to the formation of polymers with a system of conjugated bonds characterized by a high degree of delocalization of π electrons in the macromolecule. This accounts for the main features of the physical and chemical properties. If such a system has an unpaired electron, its degree of delocalization will depend on the type of orbital which it occupies. Thus, for example, if a free radical of the propagating polymer chain is formed via the opening of a triple bond, the unpaired electron will belong to the P_{xy} orbital in the plane perpendicular to the plane of the conjugated P_z orbital. In this case, a considerable localization of the unpaired electron on the terminal fragment of the macroradical may be expected because of the small overlapping functions. However, a narrow singlet signal with a width of $\Delta H = 1.0$ mT is found in the electron spin resonance (ESR) spectrum, indicating the delocalization of unpaired electrons in the radicals during the polymerization of acetylenic monomers (phenylacetylene, diphenylacetylene, phenoxyacetylene, etc.) [1,2]. It should be noted that, in these experiments, the polymerization was carried out in the liquid phase at elevated temperatures (420–470 K) where, due to intense molecular mobility, the polymer chain propagation may be complicated by reactions of the macroradicals with the double bonds of the polymer formed and by the formation of polyene-type radicals. When studying the low-temperature polymerization of compounds of this type in rigid crystal lattices, the propagation of a linear polymer chain and the addition to a double bond (to give a branched polymer) may be separated in principle. In this work, we report an ESR study of the structure of the macroradical formed during low-temperature, solid-phase polymerization of *p*-diethynylbenzene (DEB).

2. Experimental details

The polymerization of polycrystalline samples of DEB at 77 K was initiated with ^{60}Co irradiation, electrons from a U-12 accelerator ($E = 4.5$ MeV) or UV light from a DRSh-1000 lamp. The ESR spectra were recorded on an ESR-21 spectrometer ($\lambda = 3.2$ cm) at a microwave power of about 10^{-4} W and a temperature of 77 K. The ESR spectra of the samples were obtained in the following manner: the sample, irradiated at 77 K, was heated to a given temperature and kept at this temperature for a specific period of time; the sample was then cooled to 77 K and its ESR spectrum was

Elsevier Science S.A.
SSDI 1010-6030(94)03938-0

recorded. Each point on the kinetic curves in Fig. 4 (see later) was obtained by the same procedure. The experiments show that the concentrations of the radicals obtained coincide when a single sample is used for all points (different temperatures and times) of the curves in Fig. 4 (see later), or when new samples are used for each point of the curves. The polymer yield was determined gravimetrically. For this purpose, samples irradiated at 77 K were dissolved in an acetone–hydroquinone mixture at 210 K; the solvent and unreacted monomer were then evaporated in vacuum at 300 K.

3. Results and discussion

At small irradiation doses ($D < 500$ kGy), the ESR spectrum of DEB shows a triplet with a splitting between the extreme components of $2\Delta H_3 = 11.0$ mT (Fig. 1, spectrum 1). It is well known that such an ESR spectrum is associated with a cyclohexadienyl radical formed on irradiation of benzene and its derivatives [3]. If an H atom is added to a triple bond C≡C, a vinyl-type radical should be formed with a well-resolved hyperfine structure (HFS) due to the non-equivalent protons [4]. Thus, on irradiation of DEB, an H atom may add to the phenyl ring in spite of the presence of triple bonds. Radicals formed on removal of a hydrogen atom from the DEB molecule ($HCCC_6H_4CC^{\cdot}$) contribute to the badly resolved central part of the ESR spectrum.

On heating the sample irradiated with a small dose ($D < 500$ kGy, 77 K) at 150–230 K, the ESR spectrum is transformed into a doublet with a splitting of $\Delta H_2 = 2.6$ mT (Fig. 1, spectrum 2). Calorimetric and optical investigations show that polymerization proceeds in the same temperature range and the polymer yield in the sample dissolved in an acetone–hydroquinone mixture at 210 K is $\Theta = 0.6\%$ ($D = 500$ kGy). Therefore, it is natural to connect the observed transformation of the ESR spectrum with polymerization. DEB polymerization results in the opening of the triple bonds and the formation of a polyconjugated system. Since the P_z electrons of the C≡C bonds take part in the conjugated π system and the orbital of the unpaired electron in the propagating macroradical is in the orthogonal xy plane, the unpaired electron probably does not participate in the conjugation and is localized on a terminal monomer link to give the doublet splitting in the ESR spectrum.

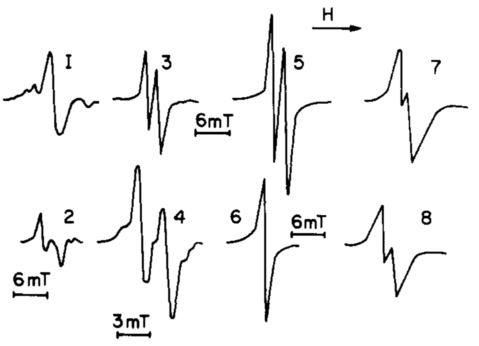
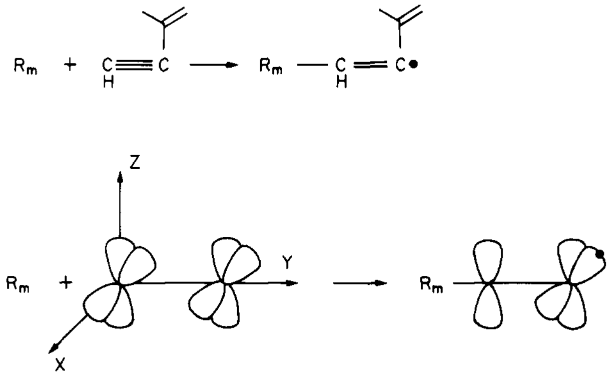


Fig. 1. ESR spectra of DEB irradiated at 77 K (6-deutero-substituted DEB). Dose (kGy): 300 (1, 2); 1000 (3, 4); 4000 (5, 6); UV-irradiated DEB (7, 8). Temperature (K): 77 (1, 3, 5, 6, 7); 150 (2, 4, 8).

We may conclude that the radical with a doublet ESR spectrum, observed during heating of the sample, is the macroradical of the propagating polymer chain formed from the monomer radical in the initiation reaction

$$R_m + M \longrightarrow R_p \tag{1}$$

The chemical and electronic structure of the reagents of reaction (1) can be represented as



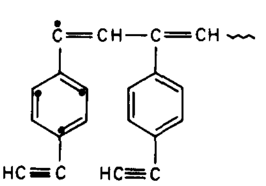
Radical addition to the ethynyl group can occur, in principle, at both α and β positions with respect to the phenyl (Ph) ring. However, in accordance with the classical rule, the most probable attack is at the carbon atom with the most hydrogens attached.

Further growth of R_p

$$R_p + M \xrightarrow{k_p} R_p + P \tag{2}$$

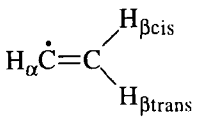
does not change the ESR spectrum, since the R_p radical structure does not depend on the number of links in the macroradical because of the localization of the unpaired electron only on one monomer link (P is a fragment of the polymer chain).

On detailed examination of the ESR spectrum, it appears that each doublet component has a triplet HF substructure with a splitting of $\Delta H = 0.6$ mT (Fig. 1, spectrum 4) pointing to the formation of the radical



(R_{pl})

by C_β atom attack. Part of the spin density is delocalized on the Ph ring. HF splittings for the vinyl radical



are $\Delta H_\alpha = 1.6$ mT, $\Delta H_{\beta trans} = 6.8$ mT and $\Delta H_{\beta cis} = 3.4$ mT [4]. The observed decrease in ΔH_2 compared with the given values of ΔH_β are also connected with partial spin delocalization to the Ph ring. This also indicates that the π electrons of the nearest Ph ring in the R_{p1} radical (probably the π electrons of the other Ph groups also, if they preserve their conformation after addition of subsequent monomer units to R_{p1}) do not take part in the polyconjugation of the chain.

As can be seen in Fig. 1 (spectra 3 and 5), with increased irradiation dose ($D > 500$ kGy), a doublet structure arises even in the ESR spectra of samples which were not heated, i.e. even at 77 K there is a radical reaction of polymer chain initiation and further addition of monomer molecules

$$R_m + M \xrightarrow[\gamma,\beta,UV]{77\ K} R_p + M \longrightarrow R_p + P \qquad (1')$$

It is significant that R_p formation takes place only during irradiation. After irradiation is stopped, the relationship between the intensities of the ESR lines in R_m and R_p does not vary, however long the sample is kept at 77 K.

To confirm the assumption that a doublet ESR spectrum is associated with the localization of the unpaired electron of the propagating macromolecule on a terminal link, we studied DEB molecules which had been deuterated in the ethynyl group. As expected, the doublet splitting for the $DCCPh\dot{C}=CD$ (R_p) radical was absent and the ESR spectrum consisted of one line with a width of $\Delta H = 1.0$ mT. The measured radiation yields and radical concentrations for deuterated and undeuterated DEB are practically the same ($G = 0.05/100$ eV). Thus experiments with selective deuteration of DEB in the $-C{\equiv}CH$ group confirm that the doublet splitting in the ESR spectrum of irradiated DEB is due to the hyperfine interaction of the unpaired electron with a proton from one of the ethynyl groups.

To ensure that the doublet ESR spectrum is associated with the polymerization process and not with individual molecule conversions, the matrix isolation method was used. To this end, samples were prepared by the simultaneous deposition of DEB and Xe on a cooled surface. It is well known that rare gases are sufficiently stable on irradiation and can be used as an 'inert' matrix. Xenon was chosen because it may be readily condensed at 77 K, its molecular weight is close to that of DEB ($M_{DEB} = 126$, $M_{Xe} = 131$) and, consequently, the diffusion coefficients are similar. The dilutions of DEB molecules by Xe were 1:100 and 1:200. The ESR spectrum of irradiated, pure Xe (77 K, $D > 1000$ kGy) was absent, whereas the spectrum of the samples containing DEB consisted mainly of one line with a width of $\Delta H = 1.6$ mT for DEB and $\Delta H = 3.4$ mT for phenylacetylene, indicating monomer radical formation. The doublet spectrum was not observed. The presence of a cyclohexadienyl radical, observed during the irradiation of pure DEB, was not found. Obviously, at this dilution, the hydrogen atoms removed from DEB molecules have disappeared.

It should be noted that, on heating the γ-irradiated DEB samples ($D > 1000$ kGy), ΔH_2 irreversibly increases together with the growth of a triplet HF substructure (Fig. 1; spectra 3 and 5, $\Delta H_2 = 2.1$ mT; spectra 2 and 4, $\Delta H_2 = 2.6$ mT). This may be associated with the fact that, at low temperature, in addition to R_{p1}, a radical of the $HCCPhC=\dot{C}H$ (R_{p2}) type is present at a comparable concentration, formed via ethynyl group attack on a C_α atom, with a characteristic splitting of $\Delta H_{2,\alpha} = 1.6$ mT. At higher temperatures, the fraction of R_{p2} decreases, probably because of the preferential conversion of R_m and R_{p2} into R_{p1} via chain propagation. The low-temperature photolysis of DEB at 77 K leads to an even larger proportion of R_{p2} (Fig. 1, spectra 7 and 8). As can be seen in Fig. 1, the ESR spectrum of photoirradiated DEB at 77 K is a doublet with a width of 1.7 mT. Photoirradiation was carried out by UV light ($\lambda = 230$–340 nm) with stirring of small DEB crystals in liquid nitrogen in order to prevent high local concentrations of the radicals.

Thus at 77 K and low irradiation doses ($D < 500$ kGy), mainly R_m radicals are present in the DEB samples (Fig. 1, spectrum 1), turning into R_{p2} radicals at higher irradiation doses at 77 K (R_{p1}, R_{p2}, Fig. 1, spectra 3 and 5). On heating the samples to 150–230 K, the thermally induced reaction of monomer addition proceeds (R_m, $R_p + M \rightarrow R_p$ (in the main R_{p1})). In accordance with this, the radicals R_p are recorded mainly at 150–230 K and are characterized by the localization of the unpaired electron on the terminal fragment of the macromolecule.

Further heating of the sample at 230–240 K results in a singlet ($\Delta H = 1.0$ mT) in the ESR spectrum, characteristic of an unpaired electron delocalized on a polyconjugated system (Figs. 2 and 3). At 270–300 K, HF interaction disappears completely and the spectrum is represented by a single line, practically identical with the ESR spectrum of ordinary polyconjugated polymers obtained during thermal polymerization of acetylene derivatives in the melt or solution [1–3].

Fig. 4 shows the kinetic curves corresponding to the formation of radicals with a singlet ESR spectrum (R_s), as well as the change in the total concentration of all the radicals in the sample $[R] = [R_m] + [R_p] + [R_s]$ (curve 1). In the range 240–300 K (when R_s is formed), the total concentration (the concentration can be determined with an accuracy of 5%–10%) of the radicals R remains practically unchanged as a function of tem-

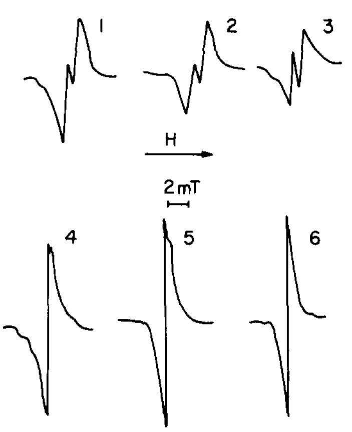


Fig. 2. Change in the ESR spectrum of photoirradiated DEB (λ=230–340 nm, T=77 K) during sample heating. Temperature (K): 95 (1); 128 (2); 253 (3); 261 (4); 263 (5); 288 (6).

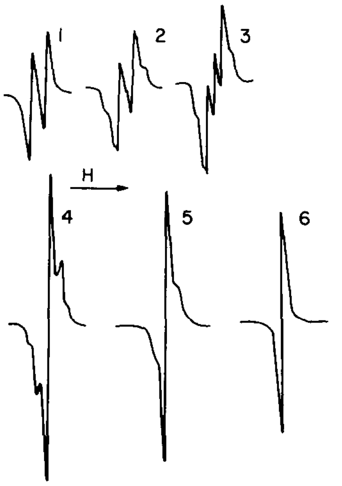


Fig. 3. Change in the ESR spectrum of γ-irradiated DEB (D=1400 kGy, 77 K) during sample heating. Temperature (K): 195 (1); 238 (2–4); 243 (5); 288 (6). Time (min): 5 (2); 25 (3); 120 (4); 240 (5); 300 (6).

perature. This provides evidence for the transition of one type of radical into another, $R_p \rightarrow R_s$ as the reaction $R_m \rightarrow R_p$ is completed below 240 K.

Comparison of the curves in Fig. 5 shows that the rate of R_s formation depends strongly on the initial concentration of the radicals $[R]_0$ which had previously accumulated in the sample, i.e. the conversion $R_p \rightarrow R_s$ is strongly bimolecular in character. Moreover, from Fig. 5, it can be seen that the reaction rate increases with time and the kinetic curves have autocatalytic character, i.e. the product accumulating in the process takes part in the reaction. It is natural to assume that this product is the polymer. An R_p macroradical, when meeting polymer bonds, can be added to the double bonds of the polyene system. As a result, an unpaired electron is formed in the P_z orbital and can be delocalized in the conjugation system

$$R_p + P \xrightarrow{k_s} R_s + P \qquad (3)$$

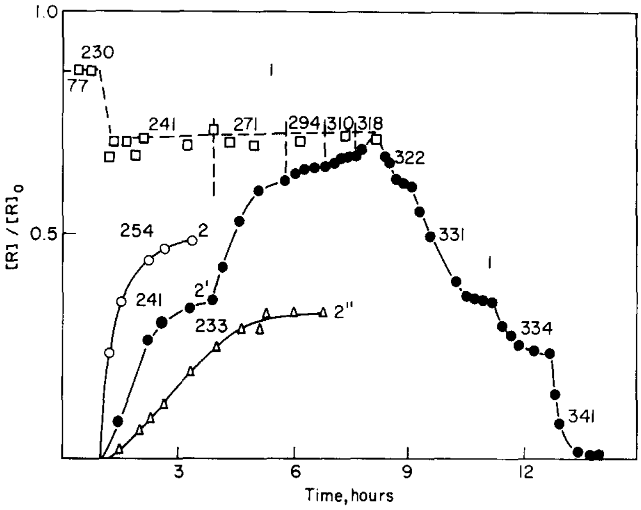


Fig. 4. Change in the total concentration of all radicals in the sample on heating from 77 to 341 K (1). Temperature (K) is given in the graph. Curves 2, 2′ and 2″ are the kinetics of R_s radical formation at various temperatures (D=1400 kGy).

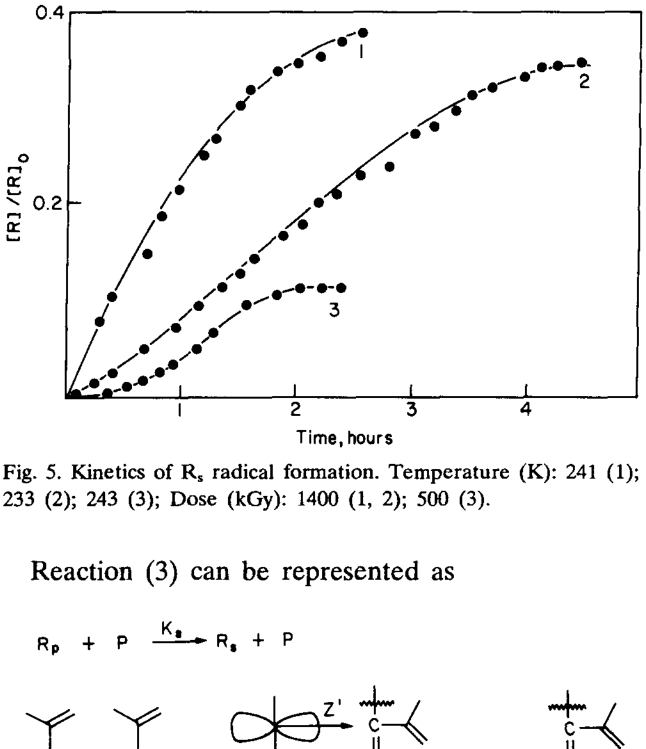
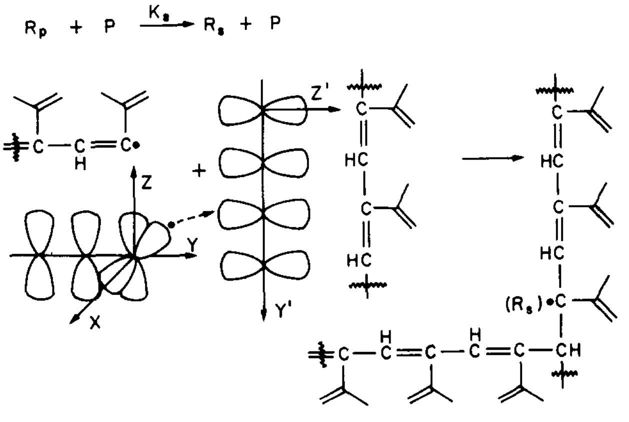


Fig. 5. Kinetics of R_s radical formation. Temperature (K): 241 (1); 233 (2); 243 (3); Dose (kGy): 1400 (1, 2); 500 (3).

Reaction (3) can be represented as



The polymer yields for a dose of 1400 kGy and temperatures of 233 and 295 K are Θ=1.5% and 3% respectively.

On further heating of the sample, when all the R_p radicals have been transformed into R_s, the polymer yield continues to increase and is $\Theta = 5.8\%$ at $D = 1400$ kGy and 340 K. Hence, in addition to reactions (2) and (3), monomer addition to radical R_s occurs

$$R_s + M \xrightarrow{k'_p} R_p + P \qquad (4)$$

which can be neglected at 230–300 K, since the polymer formed under these conditions is readily soluble and thus has a small number of crosslinkages. As can be seen in Fig. 4, the kinetics of radical decay and radical R_s formation are connected in a stepwise manner, characteristic of various bimolecular reactions in the solid phase (stepwise recombination of radicals [5,6], cooling and reviving of polymer chains [7], etc.).

For reaction (3) to proceed, it is necessary for the R_p radical to be transferred and to encounter a double bond of the polymer chain in the reaction volume. However, at temperatures far from the melting point (365 K), there is no molecular mobility to transfer the macroradical or polymer molecule as a whole in the crystal matrix. The radical R_p is probably transferred via monomer molecule addition. The fact that the total concentration of the radicals within a wide temperature interval remains practically unchanged also indicates that R_p transfer is not a result of macroradical molecule motions as a whole. The radicals begin to decay at high temperatures (320–340 K) and the radical decay kinetics depend strongly on the degree of polymer crosslinkage: the higher the initial radical concentration, the more rigid the polymer spatial network and the more stable the captured R_s radicals.

These speculations are in satisfactory agreement with the data obtained by optical and spectroscopic investigations of photoinduced and γ-induced polymerization of DEB monocrystals over a wide temperature range (4.2–300 K). It has been shown that, on UV and γ irradiation of DEB monocrystals within this temperature range, polymerization takes place. Monocrystals retain their form and size. The polymer formed shows the optical dichroism indicative of polymer stereoregularity.

4. Conclusions

These investigations demonstrate that the unpaired electron in the propagating macroradical of acetylenic monomers is localized on the terminal vinyl group to give a doublet splitting on its proton in the ESR spectrum. Delocalization takes place when the linear macroradical encounters the double bonds of the polymer formed. In this case, the unpaired electron enters the conjugated system, forming an ordinary polyene radical with spin delocalization and giving a singlet with a width of $\Delta H = 1$ mT in the ESR spectrum. The encounter of the macroradical with the double bond of the polymer formed probably occurs via polymer chain propagation.

Acknowledgement

This research was supported by Grant No. REL000 from the International Science Foundation.

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