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On the Mechanism of the Protective Action of Aromatic Amines in the Radiolysis of Polymers. Sensitized Formation of Amine Ion-Radicals

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It is known that the addition of certain substances to polymers protects them from chemical transformations occurring under the action of radiation. These substances, which have received the name antirads, as a rule belong to compounds of the aromatic class. Of especially great interest in this respect are aromatic amines, concerning which it is known that they protect both degrading and cross-linking polymers. The mechanism of action of antirads is unclear: it is not even known whether the protective action of antirads is connected with reactions between antirad molecules and radicals arising during the radiolysis of polymers, or whether the protective action is effected at the "pre-radical" stage of radiolysis, i.e., is connected with processes of transfer of excitation energy or of an electron.

In the present work the protective action of aromatic amines on the radiation degradation of polymethyl methacrylate was investigated. Two samples of polymethyl methacrylate were prepared. One sample (I) was obtained by photopolymerization of the monomer (molecular weight $\sim 7 \cdot 10^6$), the other sample (II) by thermal polymerization in the presence of dinitrile of azoisobutyric acid at 60° (molecular weight $\sim 10^6$). In both cases the polymerization was carried out in the absence of air. The polymer was reprecipitated twice with methanol from a benzene solution. The number of ruptures was determined from the number-average molecular weight of the polymer (before and after irradiation). The molecular weight was calculated from the intrinsic viscosity by the formula: $[\eta] = 4.8 \cdot 10^{-5}(1.91M)^{0.80}$, used in work ([1]). Films of polymethyl methacrylate 100μ thick were prepared from a solution of the polymer in methylene chloride; the antirad was introduced into the solution beforehand. The films were brought to constant weight in a high vacuum and irradiated with γ-rays from Co^{60} in vacuum at room temperature or at the temperature of liquid nitrogen. The dose rate was $6.6 \cdot 10^{18}$ eV/l $\cdot$ sec.

The antirad action of β-naphthylamine, phenyl-β-naphthylamine, diphenylamine, and triphenylamine was investigated. In experiments with phenyl-β-naphthylamine the consumption of the amine during radiolysis was studied.

Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

The amine concentration in the film before and after irradiation was determined by dissolving the film in chloroform and spectrophotometrically measuring (at 520 mμ) the dye formed on coupling of the amine with n-nitrobenzenediazonium in alcoholic solution ([2]) (the polymer precipitates in this process).

For investigation of the spectrum of films irradiated at −196° without thawing, the cell compartment of an SF-4 spectrophotometer was modified in such a way that a quartz Dewar with flat windows could be placed in it in the path of the light beam. The film was fastened to a frame inserted into a special holder allowing the frame to be moved vertically inside the Dewar filled with liquid nitrogen. The optical density of the film was measured relative to liquid nitrogen. In these experiments the film was irradiated already fixed on the indicated frame.

In Fig. 1, curves 1 and 2 show the dependence of $1/M$ on dose upon irradiation at room temperature of the pure polymer (curve 1) and of the polymer containing 0.05 mol/l triphenylamine (curve 2). In Fig. 2 is shown the dependence –

dependence of the number of scissions on dose in the presence of various concentrations of phenyl-β-naphthylamine. For both cases, the yield of the number of scissions does not depend on dose. For the pure polymer the yield of the number of scissions G is 1.7, which agrees with the data of other authors ([3,4]). In the presence of amines, the yield of scissions decreases with increasing amine concentration and is 0.65 at a phenyl-β-naphthylamine concentration of 0.2 mole/l. For the other amines investigated, the destruction yield proved to be approximately the same.

Fig. 1. Dependence of $1/M$ (polymer I) on irradiation dose.
1 –irradiation at room temperature, 3 –at −196°, 2 –irradiation in the presence of 0.05 mole/l triphenylamine at room temperature, 4 –at −196°.

Fig. 2. Dependence of $1/M$ (polymer II) on dose in the presence of phenyl-β-naphthylamine.
1 –in the absence of additives (constructed for $G = 1.7$), 2 –0.033, 3 –0.05, 4 –0.18 mole/l.

Analogous curves (3 and 4 in Fig. 1), constructed for polymers irradiated at −196°, differ substantially from the curves obtained at room temperature. The number of scissions, with increasing dose, tends toward a limiting value and is smaller (see also ([4])) than upon irradiation at room temperature: for the pure polymer the initial yield of scissions is $G = 0.8$, and for the polymer containing 0.05 mole/l triphenylamine, $G = 0.4$.

Interesting results were obtained in studying the behavior of amines during

Fig. 3 and Fig. 4 graphs

Figure 2: Fig. 3 and Fig. 4 graphs

the radiolysis of polymers. Determination of the concentration of phenyl-β-naphthylamine after radiolysis at room temperature showed that the consumption of amine at small doses is equal to 1–2 molecules per 100 eV of energy absorbed by the polymer. Films containing amines and irradiated at -196° become colored in different colors depending on the amine present: pink (β-naphthylamine), green (phenyl-β-naphthylamine), blue (diphenylamine, triphenylamine). On heating the films to room temperature, the coloration rapidly and irreversibly disappears. Films containing no amines, at the same irradiation doses, remain colorless in the visible part of the spectrum.

Figure 3 shows the absorption spectra of the colored products obtained at -196° in liquid nitrogen. For a film containing triphenylamine, the absorption spectrum of the radiolysis product, in general appearance and in the position of the maximum, is very similar to the spectrum of the ion-radical $\dot{N}(C_6H_5)_3$, obtained upon illumination of a frozen solution of triphenylamine in an ether–isopentane–ethanol mixture (5 : 5 : 2) ([5]) and upon flash photolysis of triphenylamine in hexane solution at 20° ([6]). Thus, it can be asserted with considerable confidence that the colored products of radiolysis

represent ionized amine molecules. The concentration of ion-radicals increases approximately in proportion to the dose in the dose region up to $1 \cdot 10^{20}$ eV/g and then tends toward a constant value (Fig. 4). The concentration of ion-radicals does not depend on the amine concentration in the range from 0.01 to 0.2 mole/l of triphenylamine. The disappearance of the coloration of the films with increasing temperature is evidently associated with neutralization of the ion-radicals by electrons released from traps as the temperature is raised. The process

Fig. 3. Absorption spectra of polymethyl methacrylate films containing 0.05 mole/l amine, irradiated at -196°.
1 —β-naphthylamine, 2 —triphenylamine, 3 —diphenylamine, 4 —phenyl-β-naphthylamine, 5 —polymethyl methacrylate without additives

Fig. 4. Dependence of the optical density (at the absorption maxima) on dose: 1 —phenyl-β-naphthylamine, 2 —triphenylamine

of neutralization can also explain the attainment of a limiting concentration of ion-radicals. To determine to what extent the formation of ion-radicals is due to the high-molecular nature of the substrate, a solution of diphenylamine (0.005 mole/l) was prepared in a mixture of isopentane with methylcyclohexane. Upon irradiation of such a solution at -196° (in the form of a transparent and colorless glass), a coloration appears with the same absorption spectrum as for a solution of diphenylamine in polymethyl methacrylate. Frozen glass without amine gives no coloration upon irradiation. In this connection it is interesting

to note that frozen glass containing, in addition to the indicated hydrocarbons, ethanol, gives an intense coloration upon irradiation (7). From these data it may be concluded that the appearance of coloration upon irradiation of frozen solutions is not associated with the high-molecular nature of the substrate. It is possible that coloration appears only in those cases where the polymer or hydrocarbon glass contains electron-donor molecules—amines or alcohol. It is interesting that no formation of coloration was observed upon irradiation of polystyrene containing diphenylamine.

The effect of diphenylpicrylhydrazyl (DPPH) on the degradation of polymethyl methacrylate was also investigated. No effect of DPPH (at a concentration of 0.01 mole/l) on the degradation yield upon irradiation of films was observed either at room temperature or at -196°. The consumption of DPPH, determined spectrophotometrically at 520 mμ, upon irradiation at room temperature proved to be equal to 3.5 radicals per 100 eV of energy absorbed by the film.

In discussing the data obtained, two questions are of greatest interest: 1) the mechanism of formation of ion-radicals and 2) whether the formation of ion-radicals is connected with the protective action of amines during radiolysis of polymers, or whether these two processes proceed independently of one another. To discuss these questions it is first necessary to estimate the radiation yield of ion-radical formation, which can be done from spectrophotometric data. Although the extinction coefficients for the ion-radicals we obtained are unknown, nevertheless, following (5), it may be assumed that the extinction coefficients for the ion-radicals of triphenylamine and tritolylamine are close; for the latter compound $\varepsilon = 1.1 \cdot 10^4$ (8). Thus, from the spect-

from the spectrophotometric data (Fig. 4, film thickness 100 μ), we find that at a dose of $1 \cdot 10^{20}$ eV/g the concentration of ion-radicals is $1 \cdot 10^{-3}$ mole/liter, and

$$G^{+}_{N(C_6H_5)_3} = 0.8$$

(per 100 eV of energy absorbed by the entire system). Such a high yield cannot be explained by the direct action of radiation on the amine. Indeed, since the concentration of amine in these experiments was 0.05 mole/liter, the electron fraction of the amine in the film is 0.012, which gives, for the yield of ion-radicals calculated for the direct action of radiation, a value of 67. This is about 5 times greater than the energetically possible value, taking the ionization potential of the amine to be about 7 eV (ionization of triphenylamine occurs under the action of light of 2000 Å ([5])). This calculation shows that the formation of ion-radicals occurs as a result of the fact that the energy absorbed by the substrate is transferred in one form or another to the amine and causes its ionization. Either a mechanism of electron transfer from the amine to a positive polymer ion is possible, or transfer of excitation energy from the polymer to the amine, leading to ionization of the amine.

To answer the second of the questions posed above, it is necessary to compare the radiation yield of ion-radical formation with the protective effect of the amines. The yield of ion-radical formation, 0.8, coincides with the decrease in the yield of breaks in the polymer chain in the presence of triphenylamine, 0.05 mole/liter, at room temperature: $1.7-0.85 = 0.85$. Since it is natural to suppose that the sensitized formation of ion-radicals does not depend on temperature, it follows from this calculation that the protective action of amines is entirely due to energy-transfer processes.

In conclusion let us consider the form of the curve of the dependence of the number of breaks on dose. Suppose that polymer radicals are formed initially without rupture of the main chain, for example, by the mechanism proposed by Slovokhotova and Karpov ([9]). The primary radicals undergo the following transformations:

1) A monomolecular reaction with rupture of the main chain, rate constant

$$k_1 = 10^{13} \exp(-E/RT),$$

where E is equal to the heat of depolymerization plus the activation energy of the direct reaction (~ 6 kcal/mole), i.e., $E \sim 13 + 6 \sim 18$ kcal/mole.

2) A bimolecular reaction of primary radicals (rate constant k_2), in which no rupture of the main chain occurs. Upon irradiation at low temperature, reactions 1) and 2) do not take place and only accumulation of primary radicals proportional to the dose, kD, occurs. Upon heating of the polymer, reactions 1) and 2) proceed at very high concentrations of primary radicals. It is easy to show that under these conditions the dependence of the number of breaks on dose is determined by the following equation:

$$\text{Number of breaks} = \frac{k_1 kD}{k_1 + k_2 kD}.$$

At high doses the number of breaks tends to the constant value k_1/k_2, as was found experimentally (Fig. 1).

Upon irradiation at room temperature, reactions 1) and 2) proceed already during irradiation and lead to a low stationary concentration of primary radicals. Under these conditions the bimolecular reaction practically does not occur, and the number of breaks is equal to kD.

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Note: Figure translations are in progress. See original paper for figures.