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MECHANISM OF THE SHIELDING EFFECT OF AROMATIC AMINES DURING RADIOLYSIS OF POLYMERS. SENSITIZED FORMATION OF AMINE-ION RADICALS

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PICATINNY ARSENAL
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MECHANISM OF THE SHIELDING EFFECT OF AROMATIC AMINES DURING RADIOLYSIS OF POLYMERS. SENSITIZED FORMATION OF AMINE ION-RADICALS

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It is known that addition of certain agents to polymers shields them from the chemical conversions which occur under the influence of radiation. These agents, which have been given the name anti-radiation agents, as a rule are members of the aromatic class. Aromatic amines are of particularly great interest in this respect, and it is known that they shield both addition and polycondensation polymers. The mechanism of the effect of anti-radiation agents is not clear; it is not even known whether the screening effect of anti-radiation agents is connected with reactions between the molecules of the agents and the radicals which result from radiolysis of the polymers, or whether the shielding effect is brought about at the "pre-radical" stage of the radiolysis, i.e. is connected with the processes of excitation-energy transfer or an electron transfer.

The shielding effect of aromatic amines on the radiation destruction of polymethylmethacrylate is investigated in the present work. Two samples of polymethylmethacrylate were prepared. One sample (I) was obtained by photopolymerization of the monomer (M.W.$\sim 7 \cdot 10^6$), and the second (II) by thermal polymerization at 60 (M.W.$\sim 10^6$) in the presence of the dinitrile of azoisobutyric acid. In both cases the polymerization was carried out in the absence of air. The polymer was reprecipitated twice from benzene solution with methanol. The number of ruptures was determined from the average molecular weight of the polymer (before and after radiation). The

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molecular weight was calculated from the characteristic viscosity according to the formula:

$$\angle \bar{\eta} 7 = 4.8 \cdot 10^{-5} (1.91 \text{ M})^{0.80},$$

which is used in work [1]. Polymethylmethacrylate films 100 thick were prepared from a solution of the polymer in methylene chloride. An anti-radiation agent had been previously added to the solution. The films were brought to constant weight under high vacuum and then exposed to γ-rays from Co^{60} under vacuum at room temperature or at the temperature of liquid nitrogen. Power of the dose was $6.6 \cdot 10^{18}$ ev/l·sec.

The anti-radiation effect of β-naphthylamine, phenyl-β-naphthylamine, diphenylamine, and triphenylamine was investigated. The consumption of amine during radiolysis was investigated in experiments with phenyl-β-naphthylamine. The concentration of the amine in the film before and after exposure was determined by dissolving the film in chloroform and then spectrophotometric measurements (at $520 m\mu$) of the dye formed by combination with p-nitrobenzoyldiazonium in alcohol solution [2] (the polymer is precipitated out hereby).

In order to investigate the spectrum of films irradiated at -196° without thawing the housing of an SF-4 spectrophotometer was rebuilt in such a way that a quartz Dewar flask with flat windows could be placed in it in the path of the light-ray. The film was fastened onto a frame set up in a special holder which made it possible to shift the frame vertically inside the Dewar flask, which was filled with liquid nitrogen. The optical density of the film was measured relative to the liquid nitrogen. In these experiments the film was irradiated after it was secured to the indicated frame.

Curves 1 and 2 in Figure 1 show the relation 1/M to dose in radiation of a pure polymer (curve 1) and a polymer containing 0.05 mol/l of triphenylamine (curve 2) at room temperature. The relation of number of ruptures does not depend on the dose. For pure polymer the yield of number of ruptures G is 1.7, which is in agreement with the data of a number of workers [3, 4]. In the presence of amines the yield of ruptures is reduced as the amine-concentration is increased and is 0.65 at a phenyl-β-naphthylamine concentration of 0.2 mol/l. The yield of destruction turned out to be approximately the same for other amines investigated.

Analogous curves (3 and 4 in Figure 1) have been constructed for polymers which have been irradiated at a temperature of -196°, and which differ considerably from the curves obtained
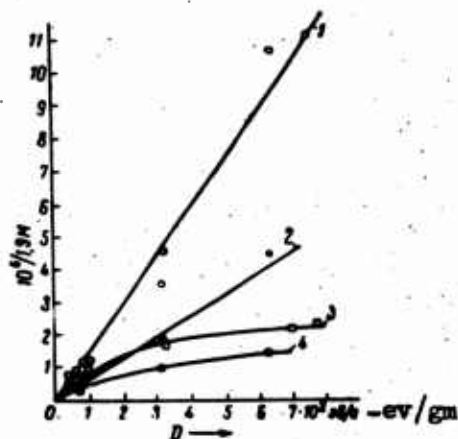
Figure 1. The relation 1/M (polymer I) to radiation-dose. 1 - irradiation at room temperature; 3 - at -196° ; 2 - irradiation in the presence of 0.05 mol/l triphenylamine at room temperature; 4 - at -196° .
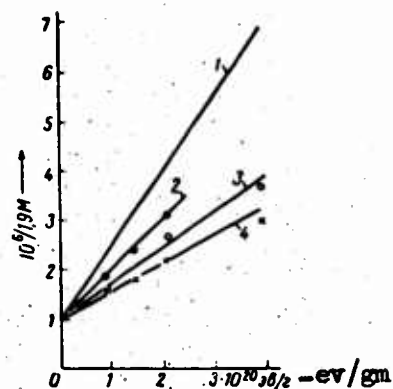
Figure 2. The relation 1/M (Polymer II) to dose in the presence of phenyl-β-naphthylamine. 1 - in the absence of additives (constructed for G = 1.7); 2 - 0.033; 3 - 0.05; 4 - 0.18 mol/l.

at room temperature. When the dose is increased the number of ruptures tends to a limiting value even less (see also [4])than for that of radiation at room temperature; for a pure polymer the initial yield of ruptures G = 0.8; for a polymer containing 0.05 mol/l of triphenylamine G = 0.4.

Interesting results were obtained on investigation of amines during 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 1-2 molecules for 100 ev of energy absorbed by the polymer. Films containing amines and irradiated at a temperature of -196° are tinted in various colors depending on the amine present: rose (β-naphthylamine); green (phenyl-β-naphthylamine; blue (diphenylamine and triphenylamine). When the films are heated to room temperature the color quickly and irreversibly disappears. Films which do not contain amines when given the same doses of radiation remain colorless in the visible region of the spectrum.

Absorption-spectra of colored products obtained at a temperature of -196° in a liquid nitrogen medium are shown in
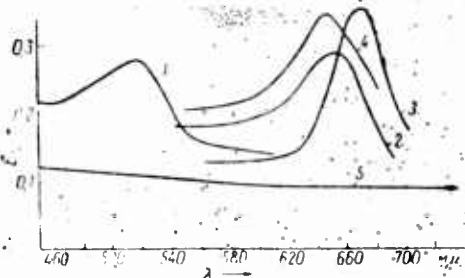
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Figure 3. Absorption spectra for polymethylmethacrylate films containing 0.05 mol/l of amine, irradiated at −196°. 1 − β-naphthyl-amine; 2 − triphenylamine, 3 − diphenylamine; 4 − phenyl-β-naphthylamine; 5 − polymethylmethacrylate without additives.
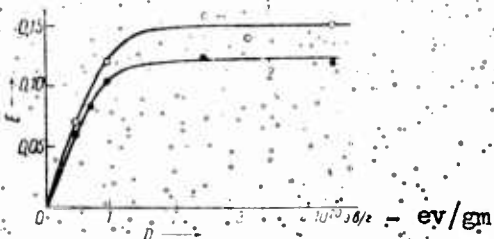
Figure 4. Relation of optical density (at absorption) maximums) to dose: 1 − phenyl-β-naphthylamine; 2 − triphenyl-amine.

Figure 3. For films containing triphenylamine the absorption spectrum of the radiolysis-product in general form and position of maximum is very similar to the spectrum of the $N(C_6H_5)_3$ ion-radical obtained by irradiation by light of a frozen solution of triphenylamine in a mixture of ether-isopentane-ethanol (5:5:2) [5] and by impulse-photolysis of triphenylamine in hexane at 20° [6]. Thus it may be affirmed with great conviction that the colored products of radiolysis are ionized amine mole-cules. The concentration of the ion-radicals increases approx-imately in proportion to the dose in the dose-range up to $1 \cdot 10^{20}$ ev/gm and further tends to a constant magnitude (Figure 4). The concentration of the ion-radicals does not depend on the concentration of the amine in the region from 0.01 to 0.2 mol/l of triphenylamine. The disappearance of coloration in films when the temperature is increased obviously is connected with the neutralization of the ion-radicals by electrons which are freed from traps when the temperature is increased. The attainment of a limiting concentration of ion-radicals can be explained by this neutralization-process as well. In order to explain in what measure the formation of ion-radicals is brought about by the high-molecular nature of the substrate a solution of diphenylamine (0.005 mol/l) in a mixture of isopentane and methylcyclohexane was prepared. When such a solution was

irradiated at -196° (in the form of a transparent and colorless glass) a coloration with the same absorption-spectrum as was also observed for diphenylamine in polymethacrylate appears. Frozen glass without amine gives no coloration when irradiated. In this connection it is interesting to point out that the frozen glass containing ethanol in addition to the hydrocarbons indicated gives an intense coloration when irradiated[7]. From these data the conclusion may be reached that the appearance of coloration during irradiation of frozen solutions is not connected with a high-molecular nature of the substrate. It is possible that this coloration appears only in those cases where the polymer or hydrocarbon glass contains electron-donor molecules such as amines or alcohol. It is interesting that no coloration was observed when polystyrene containing diphenylamine was irradiated.

The effect of diphenylpicrylhydrazyl (DPPH) on the destruction of polymethylmethacrylate was investigated as well. No effect of DPPH (in a concentration of 0.01 mol/l) on the yield of destruction during irradiation of the films either at room temperature or at -196° was observed. The consumption of DPPH, determined by spectrophotometric measurement at $520 m\mu$, under radiation at room temperature turned out to be 3.5 radicals for 100 ev of energy absorbed by the film.

Two problems were of greatest interest when the data obtained were studied: 1) the mechanism of formation of the ion-radicals and 2) is the formation of ion-radicals connected with the shielding effect of amines during radiolysis of polymers or do these two processes take place independent of each other? For discussion of these problems it is necessary first of all to evaluate the radiation yield of formation of ion-radicals, which may be accomplished from the spectrophotometric data. Although the coefficients of extinction for the ion-radicals which we obtained are unknown it may be considered, however, following [5], that the coefficients of extinction for the ion-radicals of triphenylamine and tritolylamine are nearly alike; for the latter compound $\varepsilon = 1.1 \cdot 10^1$ [8]. Thus from spectrophotometric data (Figure 4, film thickness 100 μ) we find that under a dose of $1 \cdot 10^{20}$ ev/gm the concentration of the ion-radicals is $1 \cdot 10^{-3}$ mol/l, and G $\overline{N}(C_6H_5)_3$ = 0.8 (per 100 ev of energy absorbed by the entire system). Such a high yield is impossible to explain by direct action of radiation on the amine. Indeed, since the concentration of the amine in these experiments was 0.05 mol/l, then the electron-portion of amine in the film is 0.012, which gives the magnitude 7 for the yield of ion-radicals on the basis of direct action of radiation. This exceeds by ~5 times the energetically-possible magnitude, considering the ionization-potential of the amine of about 7ev

(the ionization of triphenylamine takes place under the influence of light of 2000Å [5]. This calculation shows that the formation of ion-radicals takes place as a result of the fact that the energy absorbed by the substrate is transferred to the amine in one form or another and causes its ionization. There is a possibility of either a shift of an electron from the amine to the positive polymer ion or a shift of excitation-energy from the polymer to the amine, resulting in ionization of the latter.

In order to answer the second question posed above it is necessary to compare the radiation yield of formation of ion-radicals with the screening effect of amines. The yield of formation of ion-radicals 0.8 coincides with a decrease in yield of ruptures in the polymer chain in the presence of triphenylamine 0.05 mol/l at room temperature: 1.7-0.85 = 0.85. Since it is natural to consider that sensitized formation of ion-radicals does not depend on the temperature, then on this basis it follows that the screening effect of amines is wholly brought about by the processes of energy-transfer.

In conclusion let us examine the form of the curve of the relation of the number of ruptures to dose. Let us suppose that primarily the polymer radicals are formed without rupture of the primary chain, for instance by a mechanism proposed by Slovokhotova and Karpov [9]. The primary radicals undergo the following conversions:
1) A monomolecular reaction with rupture of the primary chain, speed-constant ($k_1 = 10^{13}$ exp (-E/RT), where E is equal to the heat of polymerization + direct reaction activation energy (~ 6 kcal/mole), i.e. $E \approx 13 + 6 \approx 18$ kcal/mole.
2) The bimolecular reaction of primary radicals (speed constant k_2), during which no ruptures of the primary chain take place. During irradiation at low temperatures reactions 1) and 2) do not go and only accumulation of primary radicals proportional to the dose kD occurs. When the polymer is heated, reactions 1) and 2) take place at very high primary radical concentrations. It is easy to show that under these conditions the relation of the number of ruptures to dose is determined by the following equation:

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

At large doses the number of ruptures tends to a constant value k_1/k_2 as also has been found by experiment (Figure 1).

During irradiation at room temperature reactions 1) and 2) take place even on irradiation and result in a low stationary concentration of primary radicals. Under these conditions the

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bimolecular reaction practically does not occur and the number of ruptures is kD.

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