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KINETICS AND MECHANISM OF THE DISAPPEARANCE OF RADICALS FORMED DURING THE RADIOLYSIS OF POLYACRILAMIDE

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abstract: An Electron Paramagnetic Resonance (EPR) study of the paramagnetic centers formed by irradiation of polycrystalline polyacrylamide hydrolyzed to different extents was made. In the EPR spectra of the gamma irradiated samples, at room temperature, the presence of three types of paramagnetic centers was observed. The kinetics of the recombination of radicals during thermal annealing has been studied. An adequate decay mechanism is proposed.

key words: polyacrylamide; radiolysis; EPR; gamma irradiation

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Introduction

The irradiation of polymers with ionizing radiations produces chemical transformations, similar to those from organic compounds. C-H, C-C bonds are broken, C=C bonds are formed or disappear, processes which are followed by elimination of gases whose composition depends on polymer structure. The variation of the molecular weight during these reactions is of particular importance. If the irradiation is followed by formation of chemical bonds between the macromolecular chains, an increase of the molecular weight is observed, process, which is named radiochemical cross-linking.

Breaking up of bonds, from the high-molecular chain, leads to the decrease of the mean molecular weight, the process is named radiochemical degradation. The variation of the mean molecular weight produces the modification of physico-chemical and technological properties of polymers. Improved physico-chemical and mechanical properties are obtained in a measure depending on the nature of the polymer, by radiochemical cross-linking while radiochemical degradation produces the contrary effect. The radiochemical behavior of a polymer depends on its structure as follows: in polymers with linear chains of carbon atoms

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cross-linking takes place, while in branched chain polymers a degradation process is proceeding. As practically no polymer with perfectly linear or with integrally branched structure exists, both previously mentioned processes are produced by irradiation. The conditions of irradiation as well as the presence of oxygen play an important role, as it will be seen in this paper. The main intermediate, resulting from the interaction between the ionizing radiation and macromolecules of the polymer is a free macroradical, identified through the EPR technique. The recombination of macro radicals, created through irradiation, results in a bigger macromolecule as well as in a branched network.

Experimental

Polyacrylamide (PAA) of the Medasol type with different degrees of hydrolysis (2400- 0%, 2408-7.5%, 2414-14.5%, 2417-17.5% and 2421-21.5%) produced in Medias [1] through the polymerization of acrylamide, which was synthesized from acrylonitrile, was used. The irradiation of the samples of PAA was carried out with gamma radiations emitted by a source of ^{137}Cs with activity of 5.2 10^{12} Bq which delivered a dose rate of $3.3 \cdot 10^3$ Gy/h [2]. The irradiation dose was determined by means of the Fricke dosimeter. The EPR spectra of the irradiated samples of PAA were recorded on a spectrograph ART 5, that operates in the band X having a high frequency modulation of 100 kHz. For the calculation of the ***g*** factor the ion Mn^{2+} in matrix of calcium carbonate was used.

Results and discussion

The mechanism of radiolysis

ESR spectra like those from Fig. 1 are recorded for the irradiated samples of PAA-Medasol, with doses of the order $10^4 \div 10^5$ Gy, regardless of the degree of hydrolysis, at room temperature as well as at the temperature of liquid nitrogen.

The spectra have a triplet structure (as it may be seen from Fig. 1) in which the ratio of the components has not the same value for all polymers with different degrees of hydrolysis. For all however, the ratio of the intensities of components doesn't corresponds to the one theoretically imposed by the interaction of the odd electron with four or two equivalent protons. The main reasons for this observation are as follows:

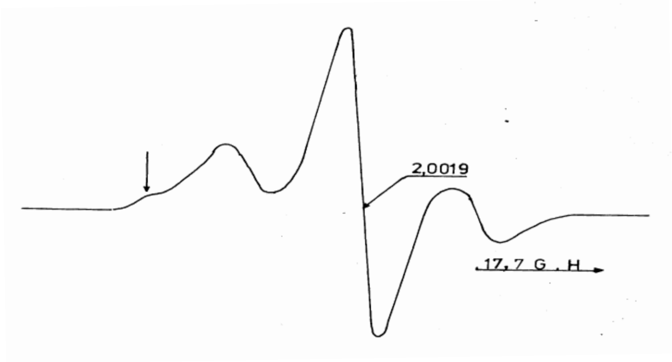
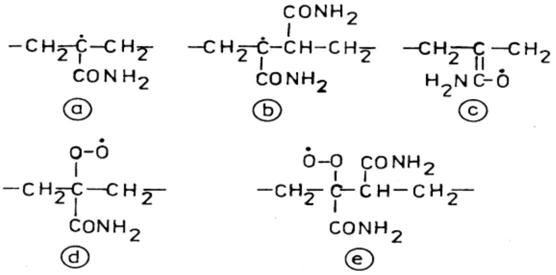


Fig. 1 *The EPR spectrum of a γ irradiated of PAA Medasol.*

a) The spectra of irradiated samples of PAA result from the overlap of spectra belonging to several radical species with different chemical structures. One of them, found in a greater proportion, imposes the general shape of the spectrum registered experimentally.

b) The irradiation of PAA hydrolyzed as well as non-hydrolyzed, was carried out at 77 K and it was found that the triplet structure is maintained, similar with the one obtained through irradiation at room temperature. The difference comes from the lateral components, which are smaller when irradiation is carried out at the temperature of liquid nitrogen. At this temperature the radical trapping is much stronger. This experiment proves that the dipolar magnetic interaction of the paramagnetic centers trapped in the solid matrix of the irradiated polymer is the main factor which contributes to the widening of spectral lines and which differs from a polymer to another. As a consequence, the weakly resolved hyperfine structure of the PAA samples with different degrees of hydrolysis, irradiated at room temperature, is strongly affected by the dipolar interactions of odd electrons of paramagnetic centers. The result of these interactions is the non-uniform widening of the spectral lines, so that those with the smallest intensity are no more observable. This phenomenon is the result of the diminution of the possibility of the motion of the radicals trapped in the amorphous and crystalline zones of the high-molecular network. The studies of EPR spectroscopy, diffuse reflex ion, published in a previous paper [3], as well as information from literature [4], led to the conclusion that paramagnetic centers formed during the radiolysis of PAA are of type a, b, c, from Scheme I, irrespective of their degree of hydrolysis.



Scheme I *The chemical structure of the radicalic species formed during the γ irradiation of PAA*

The macroradicals shown in Scheme I result from the expulsion of the hydrogen atom from the carbon atom bond to the amide group, under the action of radiation, in which the energy of the radiation was cumulated previously. The specificity of this position for the generation of the paramagnetic center is due to the localized energy of excitation, coming from the ionizing radiation, in the neighborhood of that carbon atom, before the expulsion of the hydrogen atom. The homolytic breaking of the C-H bond is more favorable than the heterolytic one because it requires less energy. In macroradical "a" the odd electron interacts with four equivalent protons of the carbon atoms from the β position, which should generate a spectrum with five components. In macroradical "b", the electron interacts with three equivalent protons from the β position that would correspond to a triplet structure. Macroradical "c" with the odd electron on the oxygen atom is formed by a migration process of the radicalic character from the species presented previously.

These paramagnetic centers are formed radiolytically, in different proportions, their spectra overlap and the shape of the experimental spectrum is determined by the one in the largest proportion. As the irradiation of the polymers was done in the presence of air, the paramagnetic species generated radiolytically react with oxygen, forming peroxo radicals, whose structure is shown in Scheme I (I-d). This process is influenced by several factors, the most important of which is the possibility of oxygen diffusion in the irradiated polymer in order to meet radicals of type "a" and "b". It was determinately established [5] that the shape of the spectrum of the radical peroxo is that of a singlet with axial symmetry. In the case of this study the signal of the radical peroxo overlaps over the central component of the signals of primary species. However, the identification of this paramagnetic center was possible by the irradiation of PAA samples with large doses, when the apparition in the left side of a shoulder, marked by an arrow in figure 1, which belongs to this radical was observed.

The accumulation of the paramagnetic centers with the increase of the dose of irradiation (dose rate 3.3 $\cdot 10^4$Gy/h) in the presence of air is exemplified in Fig. 2, for PAA 2400, the others polymers having a similar behavior.

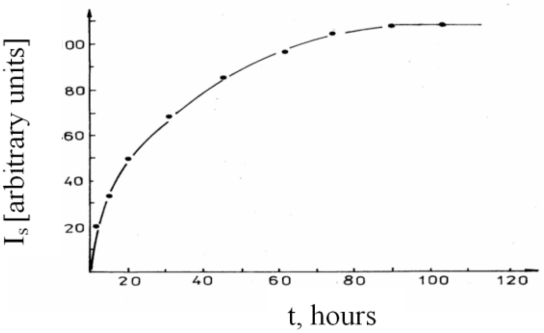


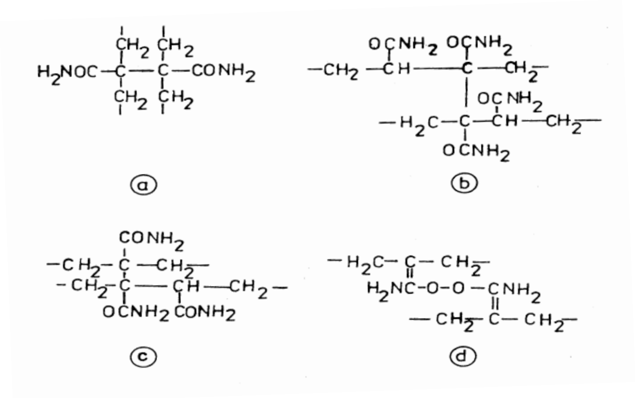
Fig. 2 *The accumulation of the paramagnetic centers in a sample of PAA Medasol 2400 with the irradiation dose.*

It may be seen from Fig. 2 that the intensity of the signal increases with the dose of irradiation, up to about $5 \cdot 10^5$Gy after that a constant level is reached. The behavior observed in Fig. 2 is explained, as follows: the rate of generation of macroradicals increases first linearly with the irradiation time, but reaches a constant value, at a certain moment. This behavior is due to the disappearance of radicals during irradiation, especially at high doses, which proceeds through mechanisms differing from that of radical formation. We mention among these the most important one: the radical - radical recombination, with formation of bonds between macromolecular chains (cross-linking), the reaction of macroradicals with oxygen (experimentally confirmed) and the transformation of radicals in non-paramagnetic species, caused by radiations. The existence of a plateau on the plot representing the accumulation of paramagnetic centers with the irradiation dose indicates that for large doses their rate of formation equals the rate of the process of disappearance.

The disappearance of radicals

The disappearance during irradiation. The extinction of free radicals, during radiolysis of samples of PAA is the process by which the macroradical is deactivated forming stable products. The reactions by which radicals could disappear under the action of radiations are as follows:

a) Recombination. This is the process of pairing of two odd electrons placed on atoms belonging to two different macromolecules. The final result of the process is the duplication of the length of the chain, if the odd electrons are placed on atoms at one end of the macromolecules. A macromolecular network is created, due to the formation of new C-C bonds between the high-molecular chains if the unpaired electrons are disposed on atoms, along the high-molecular chain. The process of recombination, produces the increase of the molecular weight, which is associated with changes in physico-chemical properties such as: the decrease of solubility, the raise of the melting point and the increase in the mechanical resistance of the irradiated polymer. Two radicals of type a, b, c from Scheme I may react between them, generating compounds with the structures showed in Scheme II.



Scheme II *The chemical structures resulting from the process of recombination of macroradicals.*

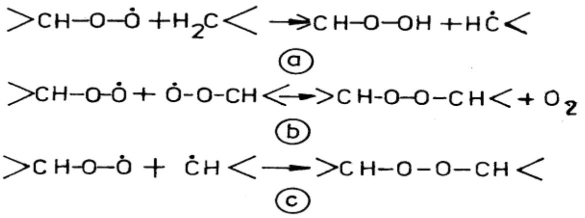
It is important to specify that most of the free radicals, resulting on the irradiation of PAA undergo recombination processes, even during radiolysis although the mobility of high-molecular chains is limited. The striking experimental evidence for that is the curve representing the accumulation of radicals, which reaches a constant value for high irradiation doses.

b) Destruction. It involves break up of some C-C bonds, under the action of radiations and as a result, the polymer is degraded. In the case of the radiolysis of PAA, with heavy rate doses the main effect consists from the diminution of the molecular mass, as a result of the fragmentation of the polymeric chains.

c) Disproportionation. If two macroradicals knock during their thermal motion in the matrix of the polymer, a process of disproportionation takes place, aside from that of recombination. The reaction of disproportionation is produced by a macroradical, which initiates a process of extraction of a hydrogen atom, from another macromolecule close to it. Two macromolecules are formed one of them containing a double bond.

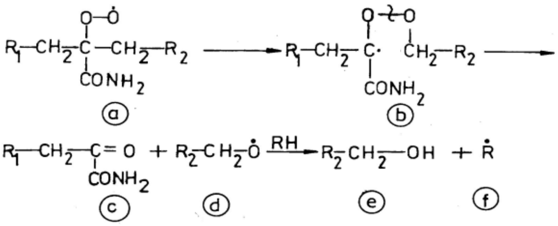
d) The process of transmigration. The radical character, placed on an atom may be transferred on another atom of the same macromolecule, as a result of the increase in mobility of the macromolecule. During this process the conversion of a type of radical into another type is proceeding. The radical I-c appears as a result of the transfer of the radicalic character from the carbon atom to the oxygen atom (Scheme I).

e) The EPR spectra rendered evident a signal of singlet type due to some chain peroxo radicals, formed at the irradiation of PAA in the presence of air [6]. The primary or secondary free radicals react with oxygen forming peroxo radicals of type I-d and I-e. Peroxo radicals have more motion freedom thanks to their chemical structure and consequently a greater reactivity with respect to surrounding polymeric chains, if compared to that of the hydrocarbon radicals. The most probable reactions undertaken by peroxo radicals are showed in scheme III.



Scheme III *Reactions probably initiated by peroxo macroradicals.*

The degradation of the polymer at large doses consists mainly in the decrease of the molecular mass and of the degree of cross-linking, in which an important role is played by the action of oxygen. Depending on the conditions of irradiation, the peroxo radicals undergo different secondary reactions influencing thus the degree of cross-linking of the polymer. The main effect of oxygen is the decrease of the degree of cross-linking which attracts the modification of the physical and chemical properties of the polymer. According to what was stated before, peroxo radicals being less stable than other paramagnetic centers, contribute to the process of degradation of the polymer. Functional groups, such as carbonyl, carboxyl, hydroxyl were detected via spectroscopic methods in the irradiated samples of polymers in the presence of air [7,8]. The way in which the peroxo radicals contribute to the fragmentation of molecule’s chain, in the case of PAA, is showed in scheme IV.



Scheme IV *The degradation of PAA produced by peroxo radicals.*

The peroxo radicals like the radicals on carbon atoms die out during the irradiation of the polymer generating non-paramagnetic species. This explains the decrease of the concentration of radicals during the irradiation with large doses of PAA. Some certain information about the possibility of radiolytic formation of peroxo radicals, aside from the EPR technique was obtained from studies of lioluminiscence [9]. It was established by this method that the way of thermal disappearance of these entities is the one of recombination with formation of tetroxide, as intermediate, which is decomposed then with formation of non-radicalic species : aldehydes, ketones, alcohols.

The thermal disappearance. The reaction isochrones were drawn firstly, in order to establish the thermal resistance of paramagnetic centers formed at the radiolysis of PAA. With this end in view, the irradiated samples of PAA were heated for 5 minutes by-steps of 5^0C, starting from room temperature up to the temperature of full disappearance of radicals. The EPR spectrum of the sample was recorded after each isothermal heating, keeping every time the same conditions. The plots obtained for three polymers are showed in Fig. 3.

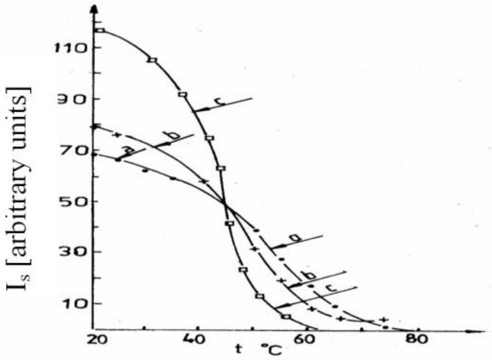


Fig. 3 *The isochrone variation of the intensity of the EPR signal in function of the heating temperature:*
a) PAA 2400 b) PAA 2417 c) PAA 2421.

It is deduced from the shape of the curves that the process of recombination starts at room temperature and ends at about 80^oC. An increase of the thermal stability with the diminution of the degree of hydrolysis is observed as well. The process of thermal disappearance of paramagnetic centers placed on the high-molecular chain is determined by the increase of the mobility of this species produced by temperature. The temperature rise increases the energy of vibration and consequently the amplitude of vibration of the segments of the high-molecular network. When the forces, which maintain the radicals trapped in the network are overcome by the vibration energy, the dislocation of the radicals from the initial positions takes place, followed by their possibility to react in one of the ways described previously.

Kinetic study

The kinetics of the thermal recombination of the radicals formed at the irradiation of the six types of PAA was studied by drawing first the reaction isotherms at some temperatures indicated on the reaction isochrones (Fig. 3). With this end in view, the intensity of the EPR signal was plotted in function of the time of isothermal heating, for each temperature, according to integral kinetic equations with integer and fractional exponents. The chosen value of the reaction order of the recombination of paramagnetic centers was that which corresponds to a straight line, in the above-mentioned graphic plot. The values of the rate constants were calculated from the slopes of the straight lines. The plot of $1/\sqrt{I_s}$ as a function of the time of isothermal heating, for a sample of PAA type Medasol 2417 is shown in Fig. 4.

It may be seen in Fig. 4 that the reaction order 1.5 is the one, which yields a linear dependence. Table 1 contains the values of the rate constants and the reaction orders for two polymers.

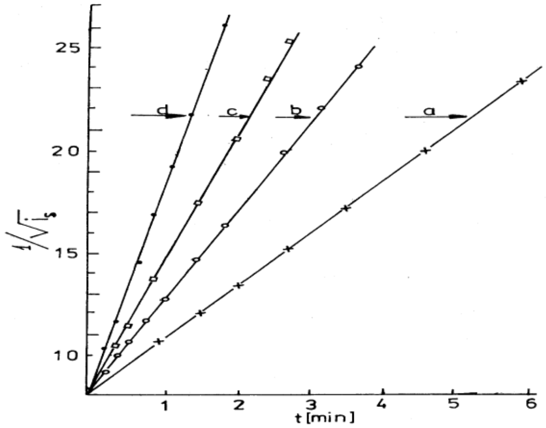


Fig. 4 *Dependence of* $1/\sqrt{I_s}$ *on the time of isothermal heating for PAA 2417:*
a) 65^0C b) 70^0C c) 75^0C d) 80^0C.

The kinetic study showed that the radicals disappear at the heating of the irradiated samples in different ways, but most probably through recombination. This process stands at the background of the cross-linking of the polymer, a process confirmed experimentally [11].

It was established experimentally that the peroxo radicals trapped in amorphous zones of the polymer extract easier the hydrogen atom than the ones from semi-crystalline zones. When this process is produced it is expected that the radicals on carbon produced by extraction of a hydrogen atom from the amorphous region, will also disappear very fast.

Table 1 The rate constants (k), the reaction orders (n) for the process of thermal disappearance of radicals formed during the radiolysis of PAA type Medasol 2421 and 2400.

PAA 2421

t^oC	35	40	45	50	55	60	65	70	75
k	$1.94\cdot10^{-6}$	$6.67\cdot10^{-6}$	$26.1\cdot10^{-6}$	$0.21\cdot10^{-3}$	$0.50\cdot10^{-3}$	$0.86\cdot10^{-3}$	$0.93\cdot10^{-3}$	$1.3\cdot10^{-3}$	$2\cdot10^{-3}$
n	2	2	2	1.5	1.5	1.5	1.5	1.5	1.5

PAA 2400

t^oC	65	70	75	80
k	$5.53\cdot10^{-7}$	$1.24\cdot10^{-4}$	$3.75\cdot10^{-4}$	$16.7\cdot10^{-4}$
n	3	2	1.5	1

Conclusions

Kinetic data rendered evident the influence of the degree of hydrolysis on the reaction order. An increase of the reaction order with the diminution of the degree of hydrolysis was noticed. It may be observed in Table 1 that in the case of PAA 2421 (degree of hydrolysis 21.5 %) the reaction order 1.5 is verified in a temperature range of 30^{0}C (50-80^{0}C) while for PAA 2400 (degree of hydrolysis 0 %) the same reaction order is verified for only 10^{0}C (70-80^{0}C). At the same time a sudden decrease of the reaction order, from three to one is noticed for this polymer. The obedience to reaction orders as high as three or fractional suggests the complexity of the development of the process of thermal disappearance of radicals, more exactly the possibility of simultaneous implication of different mechanisms of disappearance analyzed above. Knowing the kinetic behavior of these radicals is important because depending on the nature of the polymer (in this case PAA) and of the conditions of irradiation, an efficient cross-linking can be achieved through irradiation for practical utilization of the polymer. The present kinetic study gives at least partial information about the mechanism of the thermal disappearance of radicals.

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