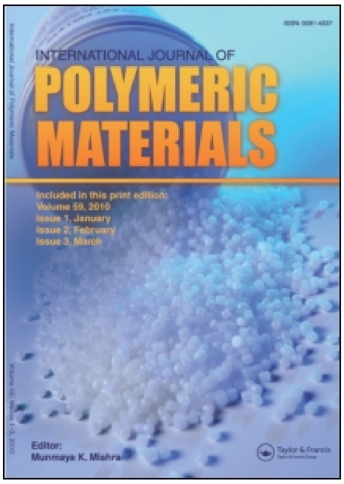

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Radiation Stability of Polymers. New Chain Reactions

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New chain cross-linking, scission and oxidizing reactions in irradiated polymers have been reviewed. The chain photoradical cross-linking and scission reactions proceed under the action of the visible and UV-light in macroradical-containing polymers. Radiation cross-linking mechanism shall be transformed to a chain one if the polymer is subjected to high pressure. Under certain conditions the radiation-chemical oxidizing reactions of macroradical-containing polymers and reactions of electron donor additives in polymer matrix became chain. The mechanisms of the new chain reactions and their significance for radiation stability operation are discussed.

KEY WORDS Polymers, stability, radiation, chain reactions

RESULTS AND DISCUSSION

Ionizing radiation markedly effects the properties of polymeric materials in the conditions of space environments, nuclear and thermonuclear power systems, accelerator units, installations for the conversion and storage of nuclear fuels and so on.[1] Ionizing radiation is also widely used in high technologies, particularly in micro electronics,[2] in membrane technology,[3] and in the manufacturing and modification of new polymeric and composite materials.[4] The radiation stability of polymeric materials is part of the general problem of aging and stabilization of materials. There are a considerable number of works devoted to this problem. Information about radiation stability has been generalized recently in Handbooks[5,6] and a book.[7] Several fundamental conclusions have been made. The radiation stability of polymers depends on many external and internal factors, which one would classify into three groups.[8]

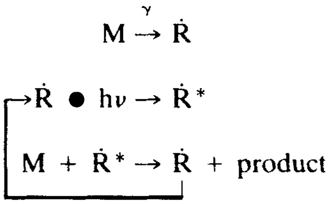
The first group includes intrinsic factors of the polymers. They are such fundamental physical chemical properties as elemental composition, chemical and electronic structure of macromolecules and additives, phase state, amount and structure of the defects and so on. The second group covers the conditions of operation, which are determined by radiation in the environment and radiation loading on the materials: type and energetic spectrum of the radiation, absorbed dose and dose rate, the dynamics of the action of the radiation (permanent or pulse). The third group includes temperature, environment, pressure, mechanical loads, light, electrical and magnetic fields and so on.

From the point of view of control of radiation stability, it is significant to know the most efficient methods or additives, which influence the kinetics and mechanism of ionizing radiation induced chemical reactions. Essential chemical transformations in polymers take place as chain reactions. Therefore, it is important to know the transition conditions under which a chemical reaction proceeds through a chain mechanism.

In this report we shall present investigations of radiation induced chemical conversion in polymers under the combined action of ionizing radiation and such factors as high pressure or light. Under certain conditions high pressure or light change the mechanism of a chemical reaction into a chain reaction. We will also consider new redox chain reactions, which are interesting in connection with the problem of polymer radiation stability. We will formulate some transition criteria under which a conventional radiation induced chemical reaction occurs via a chain route.

PHOTORADICAL CHAIN REACTIONS IN POLYMERS

The change of a polymer's properties depends significantly on the photochemical reactions of macroradicals produced due to absorbtion of ionizing radiation energy. Under the action of light the macroradicals can dissociate or participate in substitution and isomerization reactions. The alternation of photochemical and dark reactions of active radicals can produce peculiar chain reactions known as photoradical chain reactions.[9,10] In this process a photochemical stage is considered to be a propagating stage. The photoradical chain reaction can be schematically represented as follows



$$M \xrightarrow{\gamma} \dot{R}$$

$$\dot{R} \bullet h\nu \rightarrow \dot{R}^*$$

$$M + \dot{R}^* \rightarrow \dot{R} + \text{product}$$

In this report we consider photochemical reactions of macroradicals in polyethylene (PE).[11] In the radiolysis of PE with a yield of 5.8 at 77 K, alkyl macroradicals of the type $\sim CH_2\dot{C}HCH_2\sim$ are formed. PE alkyl macroradicals under UV illumination ($\lambda < 250$ nm) at 77 K produce molecular hydrogen, methane, ethane, ethylene, *trans*-vinylene double bonds and intermolecular cross-links. Their number increases with the illumination time (Table I). Under UV illumination in PE free of alkyl macroradicals, molecular hydrogen and *trans*-vinylene double bonds decrease ca. 15–20-fold. Thus, the formation of the main products is a result of photochemical reactions of alkyl macroradicals.

As photoradical chain reactions occur in the vicinity of the initial radical, the

TABLE I

Products of UV-irradiation of polyethylene containing alkyl radicals[11]

Time of illumination at 77K, min	Concentration, 10^{17}cm^{-3}					gel %
	trans-vinylene double bonds	vinyl-double bonds	hydrogen	methane	ethylene	
0	50	30	60	1	1.5	16
15	80	50	120	13	1.5	24
30	150	90	240	18	1.5	26
70	180	95	320	26	1.9	27
150	320	110	500	32	3.3	31
700	480	140	790	41	11	69

size of the reaction region will be determined by the average value of free valence migration and average chain length $\nu_{\text{av.}}$. If free valence migration has an accidental isotropic character, L is determined as follows

$$L = \mathrm{I}\left(\sum \nu_{\text{av.}}\right)^{0.5}$$

The products of the photoradical chain reactions will be concentrated in these regions, i.e., distributed nonhomogeneously within the polymer bulk. Under UV irradiation of PE for 250 min four *trans*-vinylene double bonds, two intermolecular cross-links and 0.5 vinyl double bond are formed close to the initial alkyl macroradical within a distance of 3.5 nm. These values exceed the average concentration of the same products by ca. 5–10-fold.

Comparison of the data on the cross-linking and destruction, obtained by various methods, favours a nonuniform spatial distribution of the photoradical chain reaction products. An analysis of gel-fraction dependence on the time of UV irradiation by the Charlesby-Pinner equation shows the ratio of quantum yields of destruction and cross-linking is 1.4. From the ESR data this ratio is calculated to be 0.1. Such a great difference in the estimates is likely connected with a highly nonhomogeneous spatial distribution of intermolecular cross-links formed during the course of the photoradical chain reactions. When measuring gel-fraction, we cannot determine the number of cross-links in one micro region, but only the number of the regions where cross-linking takes place.

CHAIN REACTION RADIATION CROSS-LINKING OF POLYMERS AT HIGH PRESSURE

The effect of high pressure on radiation scission and cross-linking of polymers has been studied in elastomers,[12] PE,[13] polyvinyl chloride (PVC), polystyrene (PS) and

TABLE II

Pressure effect on the radiation-chemical yields of cross-linking in elastomers at 295 K[12]

Elastomers	Cross-linking yield	
	0.1 MPa	2 GPa
Polybutadiene	5.3	90
Polynitril-butadiene	20	150
Polystyrene-butadiene	4.3	33
Natural rubber	3.3	15
Polyethylene-polypropylene	0.9	32
Polydimethylsiloxane	18.5	12

TABLE III

Pressure effect on the radiation-chemical yield of cross-linking and kinetic chain length in elastomers at 295 K[15]

Pressure, MPa	Polyisoprene SKI-3		Polynitril-butadiene SKN-40	
	G	ν	G	ν
0.1	1.6	6	40	45
700	17	68	180	210
2000	6.4	25	126	140

polyacrylamide (PAA).[14] The character of radiation cross-linking at high pressure is determined by the chemical structure of the polymer and the values for pressure and temperature.

For elastomers containing unsaturated bonds (polybutadiene, polynitril-butadiene, polystyrene-butadiene and natural rubber), the radiation induced chemical yield of cross-linking increases 5–20 times at a pressure of 2 GPa (Table II). A significant increase in the cross-linking yield for unsaturated rubbers derives from chain cross-linking which proceeds with the participation of double bonds and macroradicals. The kinetic length of the cross-linking chain ν depends on the rate constant ratio between the addition-to-double-bond reaction and that of chain termination (macroradical recombination) as well as on the value of pressure.

From Table III it is seen that the cross-linking yields and kinetic chain lengths are an extreme function of the pressure. Due to the chain mechanism the cross-linking yield at high pressure depends on the dose rate as follows

$$G_c \sim (G_R/D)^{0.5}$$

where G_R is the yield of macroradicals, and D is the dose rate.[13]

Figure 1 presents the dose dependence of the gel-fraction in PE at different irradiation conditions.[13] At 300 K and $P = 0.5$ GPa the cross-linking yield decreases 1.4 times as compared with atmospheric pressure, while the scission yield is two times less than at high pressure.

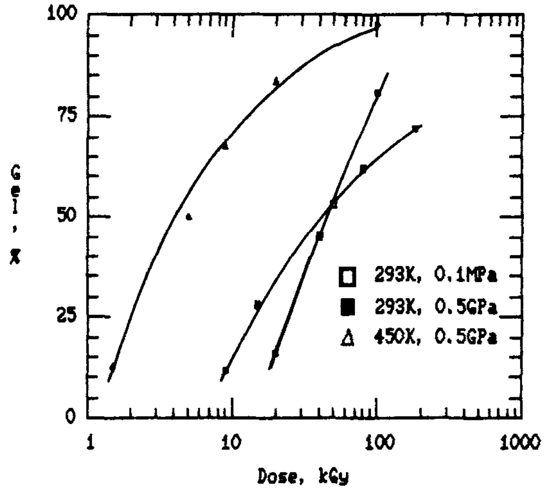


FIGURE 1 Dependence of paramagnetic center concentrations in γ-irradiated PVC films (1), concentration of paramagnetic centers (2) and the amine cation-radicals (3) in γ-irradiated PVC + 0.5 mol/l amine + 0.5 mol/l bromoethane.[18]

TABLE IV

Concentration in vinylidene groups (885 cm^{-1}) in γ-irradiated polyethylene[13]

Sample	Concentration, 10^{18} cm^{-3}
Initial	4
Normal conditions, 70 kGy	2
P=0.5 GPa, 450 K, 7 kGy	0.5

The mechanism of radiation induced gel-formation in PE changes drastically when the temperature exceeds the melting point of the polymer, i.e., higher than 450 K. At 0.5 GPa a gel-dose is shifted to a lower region and equals 1 kGy, i.e., it decreases by a factor of 10 as compared with normal conditions. The cross-linking yield increases by 15–30 times which indicates that PE cross-linking at high pressure and elevated temperature proceeds via a chain route.

The concentration of vinylidene groups in PE irradiated at high pressure are given in Table IV. The decay of the vinylidene groups at high pressure and 450 K is seen to proceed at higher rates compared to normal conditions. The correlation between the rates of cross-linking and double bond decay indicates a decisive role of double bonds in PE cross-linking at high pressure. Such a cross-linking mechanism is confirmed by a series of experiments with polymethylene. In this polymer the cross-linking yield does not depend on the pressure, because the quantity of vinylidene groups is small (less than 10^{17} cm^{-3}).

When chain cross-linking of PE results from macroradical reactions with double bond impurities, the radiation yield of the cross-links is a function of the dose rate

$$G_c(P) = G_0 + k(G_R/D)^{0.5}$$

where G_0 is the radiation yield of the cross-links at normal pressure, and k is the proportionality factor as a function of double bond concentration.[13] The effect of the dose rate is proved by the data in Table V. With decreasing dose rate, gel-content is seen to increase. This effect is not observed under normal conditions.

After irradiation a certain quantity of macroradicals in PE can be stabilized and initiate cross-linking by a chain route if the polymer is compressed. It follows from Table VI, that a significant increase in gel-fraction is observed in irradiated polymer under high pressure. The concentration of stabilized macroradicals measured by the ESR method and additional post-irradiation cross-links have been used to determine the kinetic length of the cross-linking chain. For variations in the macroradical concentration within a range of 3×10^{17}–2×10^{18} cm^{-3}, the kinetic chain length changes from 15 to 4.

Since macroradicals initiate cross-linking, the chain process at high pressure can proceed without any preirradiation. Thus, in aerosol filled PE the gel-content becomes as high as 50% after the samples undergo rolling and 30 min compression at 0.5 GPa and 450 K.[15] Cross-linking is initiated by macroradicals arising due to heat degradation of the roll-produced hydroperoxides.

In unsaturated polymers the cross-links can be distributed nonhomogeneously throughout the bulk. In the majority of cases the cross-links tend to localize in the vicinity of primary macroradicals. The size of such localizations (clusters) L can be estimated on the basis of the kinetic chain length ν and the distance of free valence shift for each elementary cross-linking event. According to estimates L equals 2–5 nm.[15]

TABLE V

Gel-fraction content in polyethylene γ-irradiated at 450 K and 0.5 GPa as a function of dose rate (dose 3.5 kGy)[11]

Dose rate, arb.units	Gel-fraction, %
1	53
0.22	62
0.05	72

TABLE VI

Pressure effect on postradiation cross-linking of polyethylene at 420 K[15]

Dose, kGy	Gel-fraction, %	
	0.1 MPa	500 MPa
7	0	27
12	3	42
38	39	58

CHAIN RADIATION-CHEMICAL OXIDATION REACTIONS IN POLYMERS

Polymeric materials usually contain some impurities and various additives which are known to influence radiation effects in polymers and also undergo radiation changes themselves. The investigations in this field are of special interest for the radiation protection of polymers and the development of film chemical dosimeters.

The role of macroradicals in the radiation-chemical chain reactions in polymers is of particular interest. In the present report the importance of macroradical-additive interaction has been studied. Examples of the oxidation of the aromatic amine- *N,N,N'N'*- tetramethyl-diamine-diphenylmethane (TMDM) in the presence of CBr_4 in polyvinyl chloride and the poly-*N*-vinylcarbazole in the presence of such electron-acceptor additives as CHI_3, CBr_4 and I_2 are considered.

CHAIN OXIDATION OF AROMATIC AMINE IN POLYVINYL CHLORIDE[16–18]

At 77 K the cation-radical amine ($\dot{A}^+$) and an oxidized amine (A^+) (Mihler dye) are stabilized in the γ-irradiated composition PVC-TMDM. Figure 2 shows the temperature dependence of paramagnetic center concentrations and the radiation-chemical yield of A^+. From 77 to 200 K the concentration of paramagnetic centers decreases slowly. Radiation yields incease twofolds. At temperatures higher than 200 K the concentration of paramagnetic centers decreases quickly. At temperatures higher than 250 K the polyenyl radicals are stable, but the concentration of A^+ increases 15–50-folds. Such a considerable rise in A^+ concentration confirms the chain mechanism of post radiation oxidation of the amine. Thus, as follows from the investigation of the temperature dependence of the oxidation rate, the

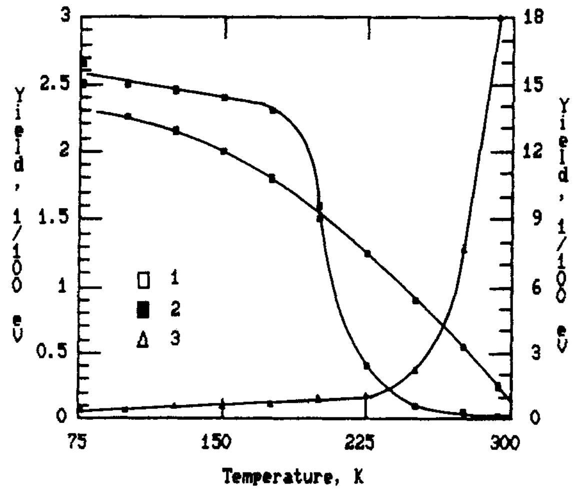


FIGURE 2 Gel-fraction vs dose in PE γ-irradiated: 1—at 0.1 MPa and 293 K; 2—at 0.5 GPa and 293 K; 3—at 0.5 GPa and 450 K.[13]

reaction of amine oxidation transforms into a chain process only when the polyenyl radicals appear in the bulk.

One may suggest that the radiation induced chemical oxidation of an aromatic amine in PVC proceeds as follows

$$\dot{R} \xrightarrow{-\mathrm{HCl}} \dot{R}_p$$

$$\dot{R}_p + A \longrightarrow RH + \dot{A}$$

$$CBr_4 + \dot{A} \longrightarrow CBr_4 \cdots \dot{A} \longrightarrow A^+ \cdots Br^- + \dot{C}Br_3$$

$$RH + \dot{C}Br_3 \longrightarrow \dot{R} + CBr_3H$$

$$\dot{R} + \dot{R} \longrightarrow R\text{—}R$$

As is seen from the scheme of the chain radiation induced chemical oxidation, polyenyl macroradicals play a decisive role during the chain initiation stage. The amine molecules are acceptors of free radicals. They react with polyenyl radicals and form amine radicals $\dot{A}$ which have a lower ionization potential. The radical $\dot{A}$ and the molecule CBr_4 are well known to form a charge transfer complex. This complex dissociates with the formation of the radical $\dot{C}Br_3$ and an anion-cation pair. Thus, the stage of the chain propagation is controlled by the low-molecular weight radicals.

CHAIN OXIDATION OF POLY-*N*-VINYLCARBAZOLE[19,20]

Iodine, iodoform, tetrabromomethane and poly-*N*-vinylcarbazole are well known to form weak charge transfer complexes which dissociate under ionizing radiation forming the carbazolyl macroradical. At temperatures 250 K and higher the carbazolyl radical plays a decisive role in the chain reaction. The reaction of the carbazolyl macroradicals with iodine results in the formation of atomic iodine which participates in a one-electron oxidation of the polymer

$$P\text{—}N\text{—}VC + I \rightarrow P\text{—}\overset{+}{\dot{N}}\text{—}VC \cdots I^-$$

This cation-radical reacts with the carbazolyl group of the neighboring macromolecule

$$P\text{—}N\text{—}VC + P\text{—}\overset{+}{\dot{N}}\text{——}VC \cdots I^- \rightarrow (P\text{—}N\text{—}V\dot{C})_2^+ \cdots \bar{I}$$

The next stage is a one—electron oxidation of dicarbazolyl radical by the molecular iodine

$$(\mathrm{P{-}}\mathit{N}\mathrm{{-}V\dot{C}})_2^+ \cdots \bar{\mathrm{I}} + \mathrm{I}_2 \rightarrow (\mathrm{P{-}}\mathit{N}\mathrm{{-}VC}_2^{2+}) \cdots \bar{2}\mathrm{I} + \mathrm{I}$$

CONCLUSION

The results presented show that in polymeric materials the main reactions (crosslinking, destruction, oxidation) can be transformed into chain reactions. Such transformations can be induced not only by traditional thermal methods, but also by other ones including polymer compression at high pressure, illumination of polymers by UV and visible light and incorporation of electron acceptor additives into the polymeric materials.

Such transformations may be attributed to the following physical and chemical factors. The change in the radiation-chemical process route is most probably a result of the decreasing potential barriers in the course of macroradical intermolecular reactions. For example, at high pressure the intermolecular distances decrease by 5% (PE, 0.5 GPa) which corresponds to the potential barrier decreasing by 10% and the substitution rection rate increasing 10 fold. Under the action of light, the reactivity of the macroradical increases due to a transition to an excited electronic state. Special additives incorporated into the polymeric matrix interact with the stabilized macroradicals and create carriers of free valence.

So, one should consider these chain reactions in polymeric materials when predicting the radiation stability of materials, in particular under the combined action of various physical and chemical factors. In addition, the production of polymeric materials highly sensitive to ionizing radiation and light can be based on these chain reactions.

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