

# Decay of macroradicals in poly(methyl methacrylate) crosslinked with aliphatic diamines

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Free radicals were generated by gamma-irradiation and mechanical destruction of solid poly(methyl methacrylate) (PMMA) samples crosslinked with aliphatic diamines (1,3-diaminopropane and 1,12-diaminododecane) which have a different number of  $\text{CH}_2$  groups in a molecule. The effects of the method of free radicals generation, crosslinks density and the character of crosslinking agent on kinetic parameters of decay of chain-end PMMA macroradicals have been investigated. For temperatures  $T > 323 \text{ K}$ , the values of apparent activation energy of the decay of chain-end macroradicals rise with an increase of the initial amount of aliphatic amine, and thus with a crosslinks density, up to 0.8 mass % of amine used. 1,12-Diaminododecane yields a crosslinked structure in which apparent activation energies of free radicals decay are higher than those with 1,3-diaminopropane, irrespective of the method of free radicals generation. A similar trend of the increase of apparent activation energy can be observed with an increasing concentration of crosslinking agents for both the mechanical and irradiation method of free radicals generation, the former method giving lower activation energies.

Свободные радикалы были генерированы путем гамма-облучения и механической деструкции образцов твердого полиметилметакрилата (PMMA), сшитого с алифатическими диаминами (1,3-диаминопропаном и 1,12-диаминододеканом), имеющими различное число  $\text{CH}_2$ -групп в молекуле. Обсуждается влияние метода генерирования свободных радикалов, частоты сшивания и природы сшивающего агента на кинетические параметры гибели макрорадикалов PMMA на конце цепи. При температурах  $T > 323 \text{ K}$  значения кажущейся энергии активации гибели макрорадикалов конца цепи увеличиваются с повышением исходного количества алифатического амина, и, таким образом, с возрастанием частоты сшивания, вплоть до 0,8 % по массе используемого амина. С 1,12-диаминододеканом образуется сшитая структура, у которой величина кажущейся энергии активации гибели свободных радикалов выше, чем у структуры, к которой приводит 1,3-диаминопропан, вне зависимости от метода генерирования свободных радикалов. Подобная тенденция возрастания величины кажущейся энергии активации может наблюдаться при увеличении концентрации сшивающих агентов как при механическом, так и при иррадиационном методе

генерирования свободных радикалов, причем первый метод приводит к более низким значениям энергии активации.

Owing to a large amount of different structural units, the different local motions of the main and side chains, macromolecular segments and a macromolecule as a whole may occur in polymers and control the radical activity. New chemical junctions are formed by crosslinking which affect the character of these motions and relaxation processes, which in crosslinked polymers will be different from those in uncrosslinked ones [1].

The most frequent reactions of macroradicals studied in a solid polymer are the reactions of their decay which represent complex reaction mechanisms of both the chemical and physical nature. In the solid polymer, the decay of radical centres is usually controlled by the rate of their nearing. The decay kinetics is thus described by processes which mediate the transport of a free radical site throughout the polymer matrix. As was shown on polymers crosslinked to different conversions [2, 3] or having a different degree of crystallinity [4, 5] and orientation of macromolecules [6], the rate of free valence transport depends on thermodynamic and kinetic flexibility of polymer chains. From a comparison of kinetic parameters of free radicals decay found for different systems, the changes in mechanism of free radical motion can be presumed [7].

In the present paper, the decay of chain-end macroradicals has been studied in PMMA crosslinked with aliphatic diamines, the radicals being generated by gamma-irradiation or mechanical destruction of the polymer. An attempt has been made to evaluate the effects of crosslinking, method of free radical generation and crosslinking agents on the decay characteristics of macroradicals in a modified polymeric structure.

## Experimental

Samples of crosslinked poly(methyl methacrylate) were prepared by reaction of aliphatic diamines with ester groups of methacrylate structural units occurring at temperatures above  $T_g$  (for glass transition) of a polymer. PMMA was prepared by a free radical polymerization of monomer containing dissolved 1,3-diaminopropane (1,3-DAP) and 1,12-diaminododecane (1,12-DAD). The polymerization was carried out at 343 K in glass ampoules sealed under atmosphere of nitrogen. The initiator was 0.1 mass % azobisisobutyronitrile. The bulk of polymer formed after 6 h of reaction was then kept at increased temperature 373 K for 1 h at which the crosslinking was accomplished as aminolysis of ester groups of PMMA. Unreacted diamine was removed by evacuation of samples for 2 h at 323 K and at reduced pressure 20 Pa. Concentration of crosslinks  $\Phi$  and average molar mass  $M_c$  of the chain between two junctions of the network were determined by the method of equilibrium swelling of crosslinked samples in acetone. The respective values were calculated from the Flory—Rehner equation.

DSC measurements of  $T_g$  temperatures of crosslinked samples were carried out on DSC-1B Perkin—Elmer apparatus in atmosphere of nitrogen at linear rate of heating  $16 \text{ K min}^{-1}$ .

Some characterization of crosslinked samples is given in Table 1.

Table 1

Characterization of PMMA samples crosslinked with 1,3-diaminopropane (1,3-DAP) and 1,12-diaminododecane (1,12-DAD)

$w$ (Crosslinking agent) %	$M_v \cdot 10^{-6}$ $\text{g mol}^{-1}$	$\Phi$ $\text{mol dm}^{-3}$	$M_c \cdot 10^{-3}$ $\text{g mol}^{-1}$	$T_g$ K
1,3-DAP				
0	2.176	—	—	373
0.2	2.128	$3.8 \times 10^{-6}$	260	386
0.4	2.034	$8.2 \times 10^{-2}$	2.5	387
0.8	1.987	$4.1 \times 10^{-2}$	3.3	389
1.6	1.732	$2.0 \times 10^{-1}$	1.6	391
6.4	0.719	$7.1 \times 10^{-1}$	0.84	397
1,12-DAD				
0	1.514	—	—	373
0.2	—	$5.6 \times 10^{-4}$	29	384
0.4	1.630	$3.1 \times 10^{-3}$	190	386
0.8	—	$2.7 \times 10^{-4}$	41	386
1.6	1.248	$6.9 \times 10^{-3}$	8.1	388
3.2	—	$1.8 \times 10^{-1}$	3.1	389

$M_v$  viscometrical molar mass.

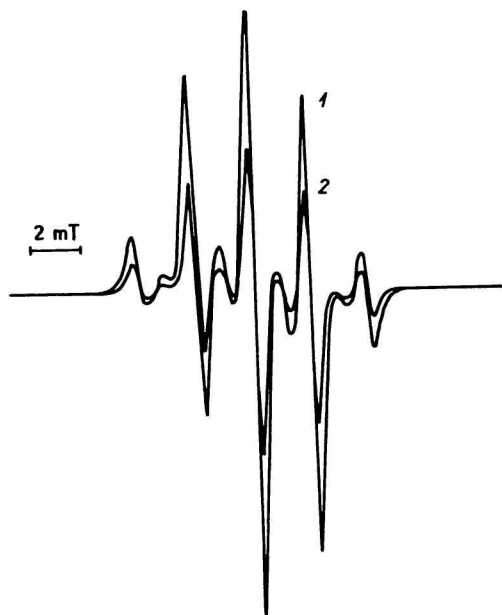
Free radicals in PMMA crosslinked with aliphatic diamines were generated either by gamma-irradiation in vacuum at 195 K, with the irradiation dose 10.5 kGy, or by mechanical destruction of a polymer, drilling it by vidium driller in vacuum at the temperature of liquid nitrogen.

ESR spectra of PMMA macroradicals were measured by means of ESR spectrometer Varian E-4. The study of the decay of free radicals at different temperatures was performed using temperature-controlled equipment Varian E-257 working with gaseous  $\text{N}_2$ . The accuracy of a thermostat was  $\pm 1 \text{ K}$ .

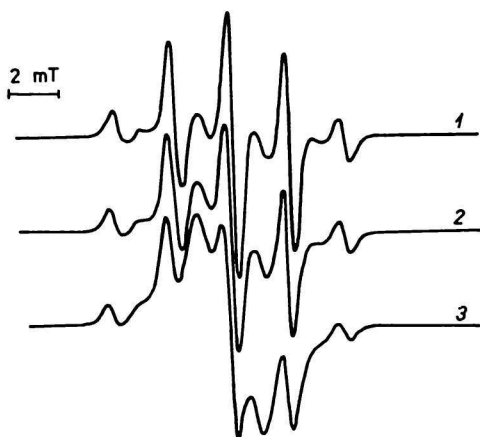
## Results and discussion

Thermal stability of chain-end radicals of uncrosslinked PMMA at 343 K is illustrated by Fig. 1. Radicals were generated by gamma-irradiation with a dose 10.5 kGy. A typical nine-line ESR spectrum has been observed which retained

its shape up to 363 K [8]. In the case of PMMA crosslinked with diamines (content higher than 0.8 mass %) another kind of ESR spectrum, different from the nine-line spectrum, can be observed on increasing the sample temperature through the temperature interval from 303 to 363 K. Fig. 2 shows an example of the gradual development of the spectrum which was obtained by gamma-irradiation of PMMA crosslinked with 1,3-DAP ( $M_c = 8.4 \times 10^2 \text{ g mol}^{-1}$ ) and recorded at temperatures below 363 K. It is obvious that the spectrum of



*Fig. 1.* ESR spectra of free radicals observed in uncrosslinked PMMA, 0 (1) and 7410 (2) seconds following its gamma-irradiation. The spectra were recorded at 343 K.



*Fig. 2.* ESR spectra of free radicals generated by gamma-irradiation of PMMA crosslinked with 6.4 mass % 1,3-diaminopropane. The samples were kept for 390 s and spectra were registered at temperature: 1. 323 K; 2. 343 K; 3. 363 K.

chain-end PMMA radicals changes here to that of more stable radicals, namely to a quartet of allyl radicals, a doublet of chain-centred PMMA radical and a singlet of polyene radical [9], respectively. The qualitatively same result is received when free radicals were generated by mechanical destruction of a cross-linked PMMA. As shown in Fig. 3, increasing temperature brings about a transformation of originally observed radicals into more stable ones similarly as in gamma-irradiation generation.

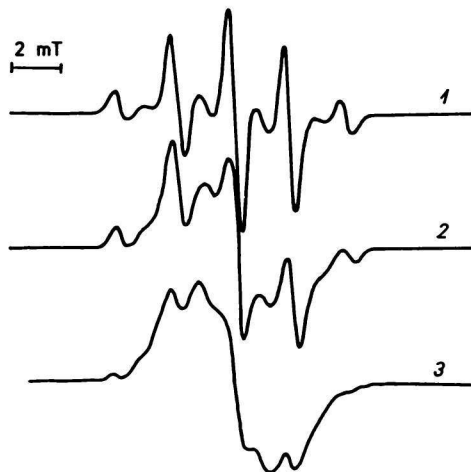


Fig. 3. ESR spectra of free radicals generated by mechanical destruction of PMMA crosslinked with 3.2 mass % 1,12-diaminododecane. The samples were kept for 390 s and spectra were registered at temperature: 1. 333 K; 2. 343 K; 3. 353 K.

Decay of macroradicals in PMMA crosslinked with aliphatic diamines was studied in the temperature interval from 313 to 363 K for gamma-irradiation generation and from 308 to 353 K for mechanical generation. The validity of a kinetic model of the second-order decay is demonstrated in Fig. 4 for the series of decay temperatures and for samples crosslinked with 1,12-diaminododecane ( $M_c = 4.1 \times 10^4 \text{ g mol}^{-1}$ ). The second-order kinetics holds for the decay of macroradicals in all crosslinked PMMA samples and for both methods of radicals generation.

The values of effective activation energies  $E_{ef}$  and pre-exponential factors  $k_{0,ef}$  corresponding to Arrhenius equation were obtained from temperature dependence of rate constants of chain-end macroradicals decay (Table 2). A close connection between mechanism and molecular motions occurring in a given temperature interval may be documented by Fig. 5 where a temperature dependence (through the region 323–353 K) of the rate constants for the decay of chain-end macroradicals in gamma-irradiated PMMA is plotted. At tempera-

Table 2

Effective activation energies  $E_{\text{ef}}$  and pre-exponential factors  $k_{0,\text{ef}}$  for the decay of chain-end macroradicals in PMMA crosslinked with aliphatic diamines 1,3-DAP and 1,12-DAD. Radicals were generated by gamma-irradiation or by mechanical destruction

<u><math>\eta</math>(Crosslinking agent)</u> %	<u><math>E_{\text{ef}}</math></u> kJ mol <sup>-1</sup>	<u><math>k_{0,\text{ef}}</math></u> g spin <sup>-1</sup> s <sup>-1</sup>	<u>Temperature interval</u> K
Gamma-irradiation			
1,3-DAP			
0.2	119	$2.49 \times 10^{-4}$	343—358
0.4	138	0.132	343—358
0.8	149	3.437	343—353
1.6	145	4.621	333—343
6.4	77	$3.53 \times 10^{-10}$	328—343
1,12-DAD			
0	123	$4.09 \times 10^{-4}$	343—363
0.2	116	$1.29 \times 10^{-5}$	343—363
0.4	145	0.867	343—363
0.8	167	$7.88 \times 10^2$	343—358
1.6	132	$3.26 \times 10^{-2}$	333—353
3.2	112	$2.98 \times 10^{-5}$	333—353
Mechanical destruction			
1,3-DAP			
0.2	112	$2.25 \times 10^{-5}$	328—348
0.4	115	$1.12 \times 10^{-4}$	328—348
0.8	123	$3.47 \times 10^{-3}$	328—343
1.6	115	$5.0 \times 10^{-4}$	323—338
6.4	55	$1.55 \times 10^{-13}$	308—323
1,12-DAD			
0	112	$2.26 \times 10^{-5}$	333—353
0.2	114	$5.54 \times 10^{-5}$	333—353
0.4	120	$2.85 \times 10^{-4}$	333—353
0.8	132	$3.55 \times 10^{-2}$	333—353
1.6	109	$1.61 \times 10^{-5}$	333—353
3.2	97	$6.8 \times 10^{-7}$	333—348

tures  $T < 323$  K, only a slight increase of the rate of free radicals decay was observed. Here, for each of the two methods of free radicals generation, effective activation energies do not depend on  $M_c$  practically, for all crosslinked samples. For temperature interval from 303 to 323 K,  $E_{\text{ef}}$  is 20 kJ mol<sup>-1</sup> for gamma-irradiated samples and 45 kJ mol<sup>-1</sup> for mechanically destroyed samples.

In the region of higher temperatures,  $E_{cf}$  increased with a rise of the initial amount of crosslinking agents (Table 2) up to 0.8 mass %, and decreased at higher amounts. This trend is typical for both methods of free radicals generation,  $E_{cf}$  being higher for gamma-irradiated than for mechanically destructed crosslinked samples.

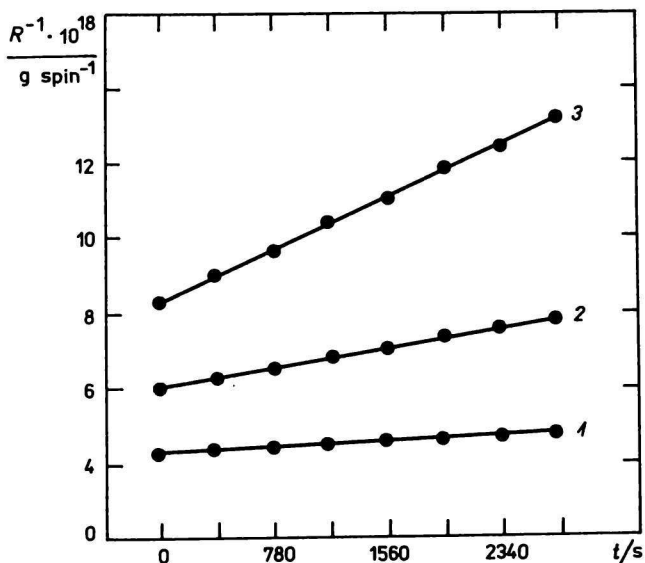


Fig. 4. Time dependence of reciprocal values of concentration of chain-end macroradicals in PMMA crosslinked with 0.8 mass % 1,12-diaminododecane and gamma-irradiated. The spectra were recorded at temperature: 1. 343 K; 2. 353 K; 3. 358 K.

The decay of macroradicals in a solid polymer and thermodynamic transitions are mutually interrelated. The decay reaction of radical centres is usually directly controlled by respective molecular motions of polymer chains which become to prevail in a given temperature interval. Generally, two principle kinds of kinetic motions exist, a motion of main segments of a macromolecule and the motion of pendant groups and branches. Interpretation of kinetic data based on the value of effective activation energy of free radicals decay is assumed to be a complex process involving the migration of a free valence.

Suppose that the effective kinetic parameters characterize the actual decay process of chain-end macroradicals for all samples studied. An increase of  $E_{cf}$  values with an increasing amount of crosslinking agent may be explained through the model of a transition state used in conjunction with a concept of cooperative effect of condensed medium on elementary reactions [10, 11]. The

increasing values of pre-exponential factors  $k_{0,er}$  and activation energies should then be a mirror image of a rising extent of a release of different degrees of freedom in a polymer matrix. Increased demands on the energy necessary for the formation of transition state during the transport of a macroradical in a decay reaction will thus appear. Cooperative effects will be enhanced due to the presence of chemical crosslinks formed from aliphatic diamines in amorphous structure of PMMA.

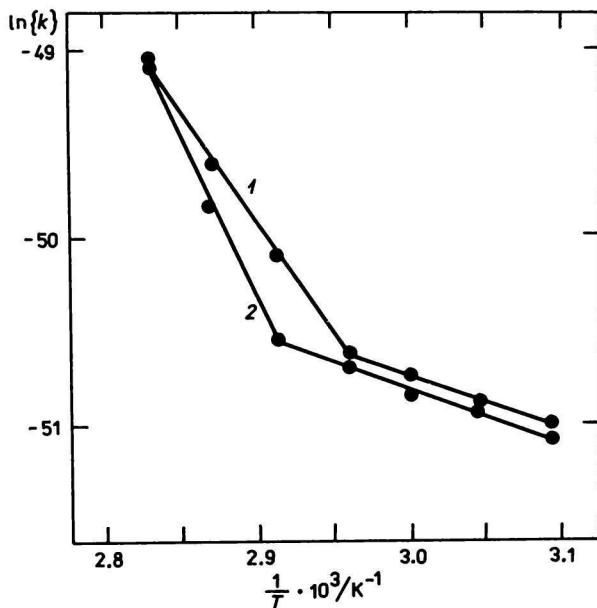


Fig. 5. Arrhenius plot of rate constants for decay of chain-end macroradicals in PMMA crosslinked with 0.2 (1) and 0.8 (2) mass % 1,3-diaminopropane. Free radicals were generated by gamma-irradiation.

Radiolyzed samples gave a higher increase in  $E_{er}$  with initial amount of crosslinking agent than mechanically destructed ones (Table 2). This may be explained by a more pronounced extent of ruptures of macromolecular chains occurring in different places of a polymer network in this latter route of free radicals generation, which reduce the effect of crosslinkages.

The decrease of  $E_{er}$  if higher initial amount of aliphatic diamines than 0.8 mass % were used for crosslinking, which still produce a high density of crosslinks, is likely to be due to a reduction in molar mass of uncrosslinked parent polymer (Table 1), which is a consequence of the method of sample preparation; aliphatic diamines present in the polymerization batch are relative-



ly efficient chain-transfer agents and in higher content will reduce the molar mass of resulting uncrosslinked polymer significantly. Polymer network which is formed at higher temperatures in a subsequent thermally initiated transamination of low molecular mass PMMA represents thus a structure with numerous defects caused by an increased number of loose ends of macromolecular chains [12]. At higher content of aliphatic diamines, a process of an approach of radical sites near occurring in relay-like manner may be implemented to the mechanism as well [13].

In the case of macroradicals decay proceeding through a segmental motion of polymer chains, the effective activation energy of free radical decay is expected to increase gradually with an increasing extent of crosslinking. The decrease of activation energy which was observed for higher contents of crosslinking agent indicates that kinetic parameters found for different degrees of crosslinking represent a complex process including a combination of various effects such as molecular mobility of reactants and chemical migrations interrelated with redistribution of electronic density of reactants. In our preceding papers, in which the effect of crosslinking on the decay of free radicals in polyethylene [14] and poly(vinylidene fluoride) [15] was studied, the effective activation energy was found to increase definitely with an increasing extent of crosslinking. In contrast to this, samples of PMMA crosslinked with relatively high content of ethylene glycol dimethacrylate [7] showed a decrease of activation energy for the decay of chain-end macroradicals within 2—20 mass % of ethylene glycol dimethacrylate. The activation energies observed for the decay of macroradicals in PMMA crosslinked with 1,3-DAP and 1,12-DAD are thus a superposition of several activation energies of multicomponent decay process of chain-end PMMA macroradicals.

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