

ACTIVE INTERMEDIATES IN PHOTORADICAL AGING OF POLYMERS*

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Abstract The data referring to the mechanism and efficiency of electronically excited macroradical and radical anion reactions, the important role of photochemical chain reactions in polymers are presented. It was found that by varying photon energy, temperature, photolysis time and competition between thermal and photochemical reactions, it is possible to change the functional composition and molecular weight distribution of polymers.

Keywords Macroradicals, Radical anions, Photochemical reactions, Aging

Free radicals play a major role in the aging of polymeric materials^[1] and are formed either on homolytic scission of the main chain or on homolytic detachment of side group atoms. In general the aging process involves three main stages: initiation – formation of active centers, development of aging – changes in the properties of a material, decay of the active centers of aging.

Radicals and radical ions formed during the aging process of various polymers should possess absorption spectra shifted towards the long-wave regions relative to the starting compounds and large extinction coefficients. Polymers, due to the formation of radicals, become chromophoric, and quantum yields of the reactions often exceed that of the homolytic scission products.

In considering photoradical aging, we will select, among the data available on photoaging of polymers under different conditions, only those that relate directly to photochemical reactions of radicals. Of course, the generation and removal of aging centers can be induced by different types of external action and with different mechanisms.

The condition for the invariance of polymer properties during aging can be written in the form:

$$\delta(M/m)Z \ll 1 \text{ or } \delta M \ll m/Z$$

where δ is the number of defects per chemical bond in the main chain of the polymer; M is the molecular weight of the polymer; m is the molecular weight of a repetition unit; Z is the number of bonds in the main chain per repetition unit.

For most polymers m/Z ranges between 10 and 100, which, at $M \approx 100000$, leads to the properties of a polymeric material:

$$\delta \ll 0.001 \sim 0.0001$$

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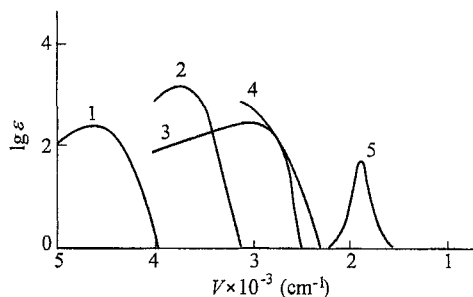


Fig. 1 Absorption spectra of (1) poly(methyl methacrylate) and some of its radicals: (2) $\sim(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\text{C}^*\text{H}(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\sim$, (3) $\sim\text{ROC}^*\text{O}\sim$; (4) $\sim\text{CH}_2\sim(\text{C}^*\text{H}_2\text{OOC})\text{C}(\text{CH}_3)\sim$; (5) $\sim\text{RC}^*\text{O}\sim$.

The situation may change drastically when a polymer is illuminated under conditions when each newly formed defect (macroradical) can give rise to a large number of transformations, thus initiating a nonbranched chain reaction (chain length ν). In this case, the condition for the invariance of the properties of a polymeric material has the form:

$$\delta = \Delta \cdot \nu \ll 0.001 \sim 0.0001$$

where Δ is the number of macroradicals per chemical bond in the main chain of polymer; for $\nu \approx 10 \sim 100$, $\Delta \ll 10^{-4} \sim 10^{-7}$, which is consistent with their steady-state concentration of $10^{15} \sim 10^{12} \text{ cm}^{-3}$.

Photoinduced repeated transformations of macroradicals with the accumulation of products take place in photoradical chain reactions first observed for low- and high-molecular compounds under different conditions.

Characterizing the efficiency of thermal reactions of radicals by their lifetime τ we can obtain the quantitative criterion for the occurrence of such processes

$$\varepsilon_R \Phi I \tau \gg 1$$

For numerous macroradicals responsible for photoradical aging of polymers considered below, the values of ε_R and Φ fall within the ranges $10^{-2} \sim 10 \text{ m}^2 \text{ mol}^{-1}$ and $10^{-1} \sim 10^{-2}$, respectively. Inasmuch as the intensity of solar irradiation at the Earth's surface is $10^{15} \sim 10^{16} \text{ photon}/(\text{s} \cdot \text{cm}^2)$ (depending on the spectral range), the photoradical chain reactions can occur when $\tau \gg 10^3 \sim 10^5 \text{ s}$. Changes in ε_R , Φ and I bring about appropriate change in τ .

Therefore, low amounts of macroradicals can act as defects affecting the properties of polymers on their exposure to light. The demands imposed by the condition for the occurrence of chain photoradical reactions confine the photoradical aging of polymers to the temperature range below their glass transition temperature or melting point (at relatively low initiation rates for the formation of macroradicals).

The formation of radical anions in different polymers takes place as a result of interaction between electrons produced by the influence of functional groups with a positive affinity for electrons. The action of light on radical anions of different types (esters, acids, amides and disulphides) results in their conversion along two major pathways: dissociation and electron ejection. The processes of photoejection of electrons from radical anions (Table 1) decrease their concentration due to electron-hole recombination. The formation of excited states resulting from this process is not affected to any extent by the structure and functional composition of polymers, mainly because of the low probabilities of homolytic decomposition and stabilization of radicals in solids.

Table 1. Quantum yields (Φ) of reactions of electron ejection and dissociation for some radical anions at 77 K

Reaction	$\Phi (\times 10^2)$			
	313 nm	365 nm	405 nm	436 nm
$\sim\text{CH}_2\text{CH}(\text{OC}^*\text{O}^-\text{CH}_3)\text{CH}_2\sim$ $\Rightarrow \text{e}^- +$	—	—	1.0 ± 0.3	0.6 ± 0.2
$\sim\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_2\sim$	3	1.5	—	—
$\Rightarrow \sim\text{CH}_2\text{CHO}^-\text{CH}_2\sim + \text{CH}_3\text{C}^*\text{O}$	2	0.8	—	—
$\Rightarrow \sim\text{CH}_2\text{C}^*\text{HCH}_2\sim + \text{CH}_3\text{COO}^-$				
$\sim\text{CH}_2\text{CH}(\text{C}^*\text{O}^-\text{OH})\text{CH}_2\sim$ $\Rightarrow \text{e}^- + \sim\text{CH}_2\text{CH}(\text{COOH})\text{CH}_2\sim$	—	—	3	2
$\sim\text{CH}_2\text{CH}(\text{C}^*\text{O}^-\text{NH}_2)\text{CH}_2\sim$ $\Rightarrow \text{e}^- + \sim\text{CH}_2\text{CH}(\text{CONH}_2)\text{CH}_2\sim$	—	—	2.5	1.5
$\text{rCH}_2\text{SS}^{*-}\text{CH}_2\text{r} \Rightarrow \text{e}^- + \text{rCH}_2\text{SSCH}_2\text{r}$	—	10	5	2×10^{-2}
$\Rightarrow \text{rCH}_2\text{S}^* + \text{rCH}_2\text{S}^-$	—	1	8×10^{-2}	2×10^{-3}

The reactions of electronically excited radical anions cannot produce any significant molecular mass change (except for aliphatic polyurethanes) and this is indeed confirmed experimentally (Table 2).

Table 2. The influence of photochemical reactions of radical anions on molecular mass change for some polymers

Polymer	Type of reaction	Gel fraction (%)	Molecular mass
Poly(acrylic acid)	γ -Radiolysis at 77 K + Warming to room temperature (only thermal reactions of intermediates)	20.9	$M_w = 2.9 \times 10^5$
	γ -Radiolysis at 77 K + Photolysis of radical anions at 77 K + Warming to room temperature (photochemical and thermal reactions of intermediates)	19.6	$M_w = 2.8 \times 10^5$
Poly(vinyl butyral)	γ -Radiolysis at 77 K + warming to room temperature (only thermal reactions of intermediates)	—	$M_n = 1.6 \times 10^4$
	γ -Radiolysis at 77 K + photolysis of radical anions at 77 K + warming to room temperature (photochemical and thermal reactions of intermediates)	—	$M_n = 1.6 \times 10^4$

Radical cations which may be produced by the action of ionizing radiation on polymers have short lifetimes even in solids at low temperature because thermal reactions (geminate recombination, fragmentation and ion-molecular reactions).

Thus, it is possible say with confidence that the active intermediates playing an important role in photoaging of different polymers are free radicals.

It follows from the data obtained by us that photochemical reactions of macroradicals can affect photoradical aging of polymers in the following manner: (1) destruction of the functional groups of the polymer without affecting its main chain (New functional groups generated in the course of these processes may turn out to be chromophoric and lead to polymer degradation directly during light absorption, or they may possess high reactivity in such chemical reactions as, for instance, oxidation, Table 3); (2) degradation of the main chain of the polymer, greatly affecting the physico-chemical properties of polymers (Table 4); (3) formation of radicals or intermediate products whose reactions lead to polymer crosslinking (Table 5).

Table 3. Dissociation quantum yields for some macroradicals at 77 K

Polymer	Reaction	λ (nm)	$\Phi (\times 10^2)$
Polyethylene	$\sim\text{CH}_2\text{CH}^*\text{CH}_3 \Rightarrow \sim\text{CH}_2\text{CH}=\text{CH}_2 + \text{CH}_3^*$	< 300	0.4
	$\Rightarrow \sim\text{CH}_2\text{CH}^*\text{CH}_3 + \text{C}_2\text{H}_4$		1
	$\sim\text{CH}_2\text{CH}^*\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{CH}=\text{CH}\sim + \text{H}$		20
Polypropylene	$\sim\text{CH}(\text{CH}_3)\text{CH}^*\text{CH}(\text{CH}_3)\sim \Rightarrow \sim\text{CH}(\text{CH}_3)\text{CH}=\text{CH}\sim + \text{CH}_3$	254	2×10^{-2}
Polyisobutylene	$\sim\text{C}(\text{CH}_3)_2\text{CH}^*\text{C}(\text{CH}_3)_2\sim \Rightarrow \sim\text{C}(\text{CH}_3)_2\text{CH}=\text{C}(\text{CH}_3)\sim + \text{CH}_3$	254	1.3×10^{-2}
Poly(acryl amide)	$\sim\text{CH}_2\text{C}^*(\text{CONH}_2)\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{C}(\text{C}=\text{O})\text{CH}_2\sim + \text{NH}_2^*$	313	20
Poly(acrylic acid)	$\sim\text{CH}_2\text{C}^*(\text{COOH})\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{C}(\text{C}=\text{O})\text{CH}_2\sim + \text{OH}^*$	313	10
Poly(vinyl acetate)	$\sim\text{CH}_2\text{C}^*(\text{OCOCH}_3)\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{C}(\text{C}=\text{O})\text{CH}_2\sim + \text{CH}_3\text{C}^*\text{O}$	313	12 ± 0.4
Poly(methyl methacrylate)	$\sim(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\text{CH}^*(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\sim \Rightarrow \sim(\text{CH}_3\text{OOC})\text{C}=\text{CH}$	254	0.4 ± 0.2
	$(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\sim + \text{CH}_3$		
	$\sim(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\text{CH}^*(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\sim \Rightarrow \sim(\text{CH}_3)\text{C}=\text{CH}$		
Poly(vinyl butyral)	$(\text{CH}_3\text{OOC})\text{C}(\text{CH}_3)\sim + \text{CH}_3\text{OC}^*\text{O}$	254	0.1 ± 0.05
	$\sim\text{CH}-\text{CH}_2-\text{CH}\sim \Rightarrow \sim\text{CH}[\text{OC}(\text{C}_3\text{H}_7)=\text{O}]\text{CH}_2\text{C}^*\text{H}\sim$		
	$\text{OC}^*(\text{C}_3\text{H}_7)\text{O}$		4 ± 2

Table 4. Quantum yields of chain scission for some macroradicals at 77 K

Polymer	Reaction	λ (nm)	$\Phi (\times 10^2)$
Polyethylene	$\sim\text{CH}_2\text{CH}^*\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{CH}=\text{CH}_2 + \sim\text{CH}_2\text{C}^*\text{CH}_3$	< 300	0.8
Polyisobutylene	$\sim\text{C}(\text{CH}_3)_2\text{CH}^*\text{C}(\text{CH}_3)_2\sim \Rightarrow \sim\text{CH}=\text{C}(\text{CH}_3)_2\sim + \text{C}^*\text{H}_2\text{C}(\text{CH}_3)_2\sim$	254	10^{-3}
	$\text{RO}_2^* \Rightarrow$ Main chain scission		0.5
Poly(acrylic acid)	$\sim\text{CH}_2\text{C}^*(\text{COOH})\text{CH}_2\sim \Rightarrow \sim\text{CH}_2\text{C}(\text{COOH})=\text{CH}_2 + \text{C}^*\text{H}(\text{COOH})\text{CH}_2\sim$	313	1.5
Polyformaldehyde	$\sim\text{OCH}^*\text{O}\sim \Rightarrow \sim\text{CHO} + \text{C}^*\text{H}_2\text{O}\sim$	313	0.8
Polystyrene	$\text{RO}_2^* \Rightarrow$ Main chain scission	313	3

Table 5. Quantum yields of macroradicals photoconversions, whose lead to polymer crosslinking

Polymer	Intermediates lead to polymer cross-linking	λ (nm)	$\Phi (\times 10^2)$
Poly(acrylic acid)	Ketene	313	10
Poly(acryl amide)	Ketene	313	20
Poly(vinyl butyral)	Macroradicals	254	4

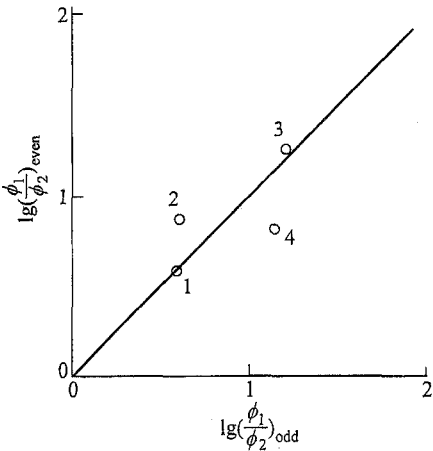


Fig. 2 Calculated and measured dissociation quantum yields for macroradicals in polyethylene (1), poly(acrylic acid) (2), polyisobutylene (3) and poly(methyl methacrylate) (4)

The efficiency of macroradical photoconversions depends on the following factors:

- It should be noted that the data available until now show the efficiency of the dissociation of macroradicals in the polymers to be satisfactorily described by the assumption of free volume representations relating the quantum yield of the process to the dimensions of the product species of radical dissociation V_r and to thermodynamic mean free volume per matrix molecule V :

$$\Phi = \exp(-\alpha V_r/V)$$

The free-volume model can be used to evaluate the dissociation quantum yield for macroradicals in polymers (Fig. 2).

- The quantum yield of photochemical reactions of macroradicals in polymers at 77 K is, as a rule, dependent on the energy of photons within one electronic absorption band and it increases with photon energy. On the other hand, for quantum yields exceeding ≈ 0.1 this dependence disappears (Fig. 3).

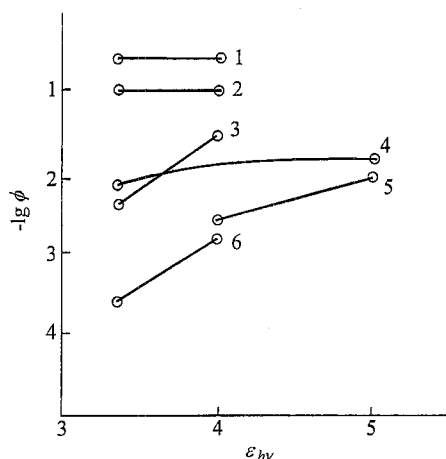


Fig. 3 Quantum yields of radical photodissociation at 77 K versus the energy of exciting photon

- 1) Middle macroradicals in poly(vinyl pyrrolidone)
- 2) Middle macroradicals in poly(vinyl acetate)
- 3) $RS^{\bullet}O_2$ in polypropylene
- 4) Middle macroradicals in poly(vinylene carbonate)
- 5) Macroradicals in poly(vinyl butyral)
- 6) $RS^{\bullet}O_2$ in copolymer of tetrafluoroethylene with hexafluoropropylene

- The influence of the degree of crystallinity on the efficiencies of photoconversions of macroradicals was studied by an example of allyl radicals in polyethylene (Table 6).

Table 6. Quantum yields of main chain scission for polyethylene samples containing allyl radicals in the presence of hydrogen (Φ_1) or without it (Φ_2) and the values of average distance of free valence transference L for reaction $\sim CH_2CH=CHC^{\bullet}HCH_2 \Rightarrow \sim CH_2C^{\bullet}HCH_3 + CH_2=CHCH=CHCH_2$ ~ proceeding without hydrogen

Parameter	Degree of polyethylene crystallinity (%)		
	95	75	40
$\Phi_1 (\times 10^{-2})$	7 ± 1	7 ± 1	10 ± 2
$\Phi_2 (\times 10^{-2})$	2 ± 1	3 ± 1	9 ± 2
L (nm)	—	$0.3 < L < 0.7$	$0.7 < L < 1.9$

These data not only testify to correlation between the values of Φ_2 and L (average distance of free valence transference) and degree of crystallinity but also characterize the scale of transference obtained in polyethylene at 77 K for occurrence of photoreaction.

Our investigation shows that the processes of photoradical aging of polymers can occur in the manner of a

photoradical chain reaction. The most characteristic features of photoradical chain reactions are the following: (1) Anomalously high yields of stable radical transformation products exceeding the stationary concentration of radicals dozens and hundreds of times. The values of chain length for photoradical chain reactions achieved in different polymers studied by us are presented in Table 7, (2) photorecombination of the radicals in a temperature range which rules out their translational mobility in the dark (Fig. 4).

Table 7. The experimentally observed maximum values of chain length (ν) for photoradical chain reactions in some polymers at 77 K

Polymer	ν
Polyacrylamide	≈ 80
Polyacrylic acid	≈ 50
Polystyrene	≈ 25
Polyvinyl alcohol	≈ 100

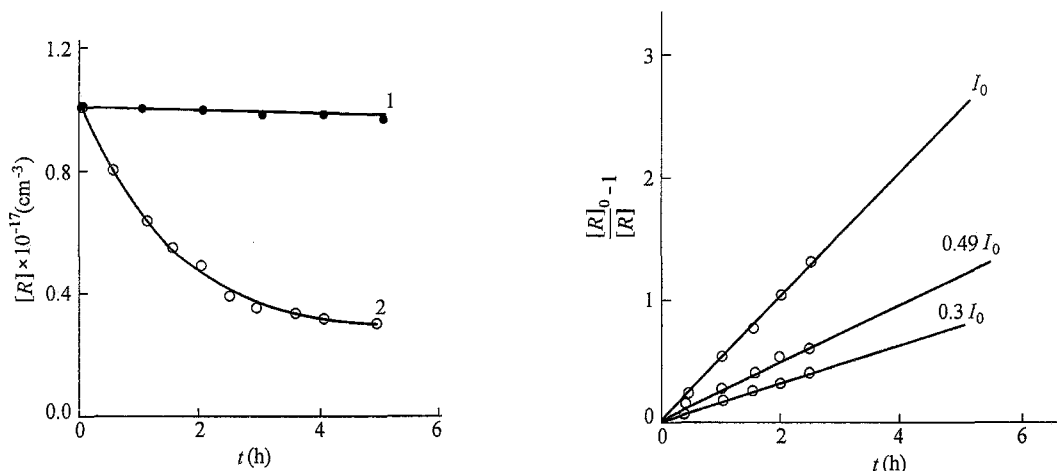


Fig. 4 Kinetic curves for $\sim\text{CH}_2\text{OCONHC}^*\text{HCH}_2\sim$ radicals in 4,6-polyurethane: in the dark at 293 K (1) and upon photoexcitation at $\lambda = 365$ nm (2); linear anamorphoses of the kinetic curves for photorecombination of radicals at varied intensity I of excitation

An intentional change in the properties of a polymeric material can be achieved by making use of the fact that thermal and photochemical reactions of macroradicals can exert different influence on the properties of polymers. For example, the photochemical reactions of alkyl macroradicals R_2 in poly(vinyl butyral) lead to the destruction of the main chain, whereas the thermal reactions of the same radicals result in polymer crosslinking. By carrying out the process at temperatures below 180 K (the range of thermal stability for R_2) and with excitation at $\lambda < 300$ nm, one can perform the polymer degradation, while photoexcitation at longer wavelengths and higher temperatures will lead to polymer crosslinking (Fig. 5).

Therefore, relative contributions from crosslinking and degradation processes to photoradical aging can be regulated by varying the spectral distribution of exciting light and temperature.

When the properties of polymeric material are modified by photochemical reactions of a product formed in a photoradical chain reaction, the contributions from these processes can be controlled by varying such parameters as the wavelength of exciting light (actinic for the intermediate product), exposure time and temperature, or by the addition of agents undergoing thermal chemical reactions with the intermediate product. The statement can be exemplified by the situation encountered in photoradical aging of poly(acrylic acid) and poly(acrylamide) where photochemical reactions of middle macroradicals give rise to ruptures in the main chain and the accumulation of ketene, whereas photochemical reactions of ketene result in polymer crosslinking. As a result, the character of MWD at the early and later stages of photolysis becomes different (Fig. 6).

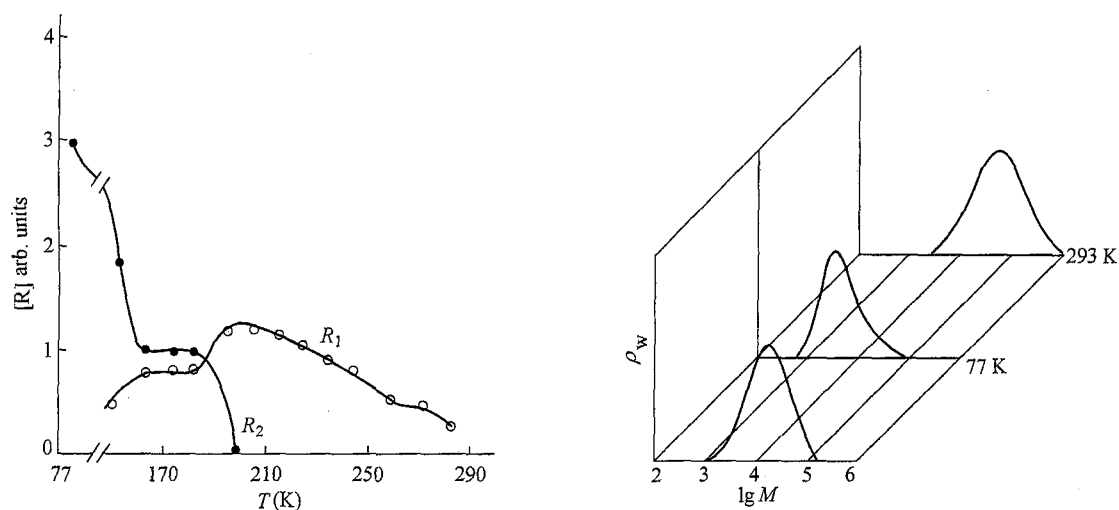


Fig. 5 Temperature dependence of radical concentration in the course of poly(vinyl butyral) heating and the variation of MWD with the temperature of aging (ρ_w is the weight fraction)

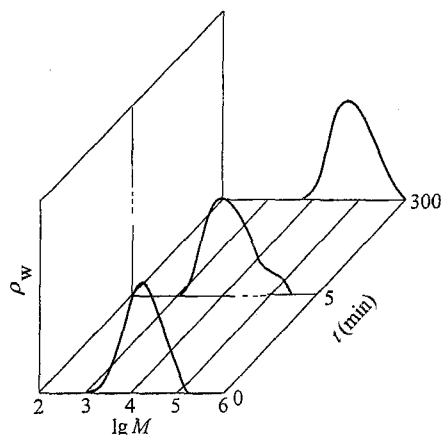


Fig. 6 Variation of MWD in the course of photoradical aging of poly(acryl amide)

The above data show that photoradical chain reactions can be utilized to produce intentional changes in the composition and MWD of polymers. It should be emphasized that these effects are specific for each particular class of polymers. Nevertheless, such phenomena as photostimulated recombination of macroradicals, which can be used for polymer crosslinking are fairly common. In some instances, these phenomena can be used to avoid undesirable heating of a material to temperatures that ensure the required translational mobility of macroradicals, and thus to carry out crosslinking in the crystalline phase (which is hard to perform by other methods) due to photosubstitution or formation of atoms and low-molecular radicals.

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