Dark Reactions of Free Radicals Trapped in Densely Crosslinked Polymer Networks After Photopolymerization

Juraj Pavlinec,[1] Norbert Moszner[2]

[1]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 36, Bratislava, Slovak Republic
[2]IVOCLAR, A.G., Bendererstrasse 2, FL-9494, Schaan, Liechtenstein

ABSTRACT: Difunctional methacrylate monomers containing stiff or flexible spacers were combined with a vinylcyclopropane derivate in a copolymerization to form densely crosslinked networks. The high rate of visible light photoinitiation at 20–22°C was used for starting the polymerization. By switching off the light after 40 s, the long-lived free radicals, trapped in the polymer network, retain radical processes, however, at substantially retarded rates. The postcuring development of the network structure in the investigated samples lasting at least 12 weeks was proved by the increasing density of the crosslinks, by the increasing amount of the gel fraction, and by the decreasing of the residual unsaturation. The relaxation spectra from dynamic mechanical thermal analyses (DMTA) show curves with two evident maxima. The first one belonged the glass transition (T_g) of original network and increases in the postcuring period. The second one belonged to the final structure to which the crosslinked polymer approaches slowly during aging. The final state develops fast during a DMTA thermal scan to 200°C. All procedures proceeded in the dark, but in the presence of air oxygen. The chemiluminescence (CL) response of the postcured samples proved the accumulation of hydroperoxides. The oxidation chain reaction took place in the postcuring time and competed with the building up of additional crosslinks. The majority of postcuring changes were observed during the first 3 weeks of aging. Nine weeks later, the long-lived radicals were still present in the network and maintained the sensibility of the crosslinked polymer to free-radical reactions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 579–588, 2003

Key words: photopolymerization; crosslinking; ageing; mechanical properties; luminescence

INTRODUCTION

Network formation by chain crosslinking (co)polymerization is a complex process which points out numerous diversities from a simple free-radical vinyl polymerization.[1,2] The investigation of the kinetic features of synthesis of densely crosslinked dimethacrylates[3–8] points out the reduced effective reactivity of pendant double bonds and monomer due to increasing steric hindrances. The residual unsaturation is observed as a common phenomenon.[9,10] Reactive microgel particles, multifunctional polymer chains with pendant double bonds, and inter- and intramolecular cyclization affected considerably the structure of the synthesized networks, at least on the submicron level.[1,3,11,12]

The increased density of chemical crosslinks and physical entanglements lead to the restricted mobility of the molecules, even polymer chain segments. The consequence of this phenomenon, observed during free-radical crosslinking polymerization, is radical trapping. This is exceedingly manifested in networks prepared by fast crosslinking polymerizations initi-

ated by light.[13] The lifetime of free radicals depends on the crosslink density of the network and on the surrounding environment and is in minutes, months, or even more.[11,14–17] Nevertheless, the free radicals, highly reactive species, trapped in a polymer network can influence the long-term chemical and physical durability of crosslinked polymer.[1,9,14,18–20] The accessibility of frozen free radicals is strongly influenced by the viscosity and architecture of the surrounding polymer matrix. At low conversions, the trapped free radicals accelerate the rate of polymerization.[7] In photoinitiated crosslinking polymerization, after switching off the light, long-lived free radicals intiate postpolymerization reactions,[11,16,21] which can increase not only the extent of polymerization, but initiate also the degradation of the network.

In various types of polymer networks, the intensity of postcuring reactions depends on the chemical composition, structure, and conditions of the crosslinking polymerization.[21–25] However, available knowledge of postcuring effects is still inadequate to generally predict the final network properties in such complicated systems as the crosslinking polymerization of multifunctional monomers.

This report presents the results of our study of postcuring changes of polymer networks prepared by visible light-initiated crosslinking copolymerization.

Difunctional methacrylate monomers with various spacers between double bonds were combined with the vinylcyclopropane monomer. The changes of the nonreacted double bonds and the crosslinking density are compared with the dynamic mechanical properties and chemiluminescence (CL) response of polymer networks aged in air and in the dark.

EXPERIMENTAL

Polymer networks

The densely crosslinked polymer samples assigned to the postcuring investigation were prepared from the bifunctional monomers shown in Scheme 1. The composition of the polymerization batches are presented in Table I. The initiator for visible light (VL)-induced polymerization of A, B, and C monomer mixtures consists of three components: camphorquinone (CC), 0.3 wt %; ethyl-4-(dimethylamino)-benzoate (EMBO), 0.6 wt %; and 2,4,6-trimethylbenzoyl–diphenylphosphinoxide (Lucirin® TPO), 0.4 wt %. A HELILUX GT® IVOCLAR halogen lamp served as a source of VL. The intensity of 300 mW/cm^2 for 40 s was used for the initiation of the polymerization at 20–22°C. Furthermore, the nitroxyl free-radical TEMPO was added to the polymerization batches as a component which provides reduced sensibility to daylight without retardation of the successive VL polymerization.[26]

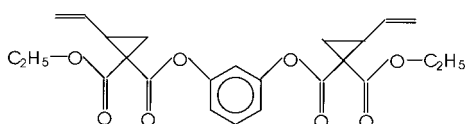The crosslinked polymer bars were prepared in glass molds with elastic gaskets and resilient clamps.

1. **Bis-GMA** Bis-glycolmethacrylate adduct of diphenylolpropan
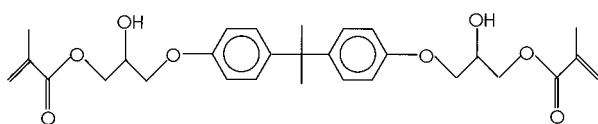
2. **UDMA** Bis-hydroxyethylmethacrylate adduct to 2,2,4-trimethyl hexametyl
diisocyanate
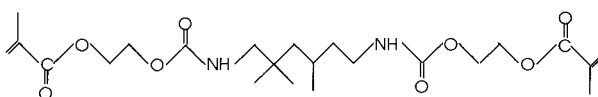
3. **BVCP** 1,3-Bis [(1-ethoxycarbonyl-2-vinylcyclopropane-1-yl) carboxy] benzene

Scheme 1

TABLE I
Composition of Polymerization Batches Used in Preparation of Polymer Network Samples A, B, C, and D Used to Study Postcuring Effects

Component (wt %)	A	B	C	D
Bis-GMA	47	42	42	—
UDMA	52	47	37	79
BVCP	—	10	20	20
TEMPO	0.015	0.015	0.015	—

The size and shape of the polymerization molds were adjusted to the geometry of the light-conducting arm of the lamp.

The testing bars, 2 × 4.5 × 8 mm, for dynamic mechanical thermal analysis (DMTA) were cut from cured polymer discs 8–9 mm in diameter, 2 mm thick. For CL measurements, 0.4-mm-thick discs were prepared.

Thirty-six disc samples were prepared from the same batch at once, in a dark room under red light only. The polymer samples were stored in brown glass bottles in air, at 20–22°C (room temperature), and were taken for analyses in selected intervals.

The preparation of the polymer network D differed from samples A, B, and C. The molds with size 2 × 7 × 30 mm and other sources of VL was used (SPECTRAMAT®, IVOCLAR, 800 mW/cm^2). The time of polymerization was 60 s. The photoinitiator system consisted of only two components: CC, 0.3 wt %, and EMBO, 0.4 wt %.

The residual unsaturation was determined by IR spectroscopy (FTIR, Nicolet Impact 400 spectrometer). The KBr technique, a standard baseline evaluation of spectra and absorbance of peaks in that region at 1637 cm^{-1}, was used.

The average molecular weight between crosslinks, Mc, which is directly related to the degree of swelling, was calculated from results of sol–gel analysis in toluene using a formula for a perfect tetrafunctional network[27]:

$$\frac{1}{Mc} = -\frac{\ln(1 - v_p) + v_p + \chi\, v_p^2}{\rho\, V_s\, (v_p^{1/3} - 2\, v_p/f)} \quad \text{(mol/g)} \quad (1)$$

The Flory–Huggins interaction parameter $\chi = 0.36$ was calculated from solubility parameters of the polymer and solvent. V_s is the molar volume of a solvent; ρ, the density of the crosslinked polymer; and v_p, the volume of polymer network in a swollen gel.

Four to six discs of crosslinked polymer samples in two sets were used for swelling in toluene and determination of the gel content at the end of each aging period. Equilibrium swelling in the dark was attained at 20–22°C after 5 days with twice-exchanged fresh toluene. Hydroquinone, 0.1 g/dm^3, was added to tol-

uene to stop free-radical reactions during swelling. The gels were completely dried at 200°C.

The mechanical properties of the polymer networks were estimated by DMTA. The DMTA spectra were recorded using an apparatus from Rheometric Scientific, Mk-III, software V5.40 (UK). The single-cantilever bending mode was used with a heating rate of 2°C/min at a frequency of 3 Hz in the temperature interval from −50 to 200°C.

The CL was measured by using a LUMIPOL 2® apparatus that was constructed at the Polymer Institute, Slovak Academy of Sciences. The level of discrimination was 2 counts/s at 40°C. The network sample was heated in the measuring chamber of the CL apparatus at the rate of 2.5°C/min under a nitrogen atmosphere. The dependence of the emitting light intensity on the temperature was registered and evaluated by a computer.

RESULTS AND DISCUSSION

Crosslink density

In densely crosslinked networks, the high level of free radicals at the end of photoinitiated polymerization is retained for a long time. The fate of these long-lived radicals depends on further handling of the just prepared network. It should also be remembered that the analyzed polymer samples were not protected against the oxygen in the air. So, the participation of oxygen in postcuring reactions cannot be excluded.

An increase of the insoluble portion and a decrease of the molecular weight Mc of the polymer chain between crosslinks in dependence on the prolonged time of aging confirm in the investigated polymers A, B, and C the significant postcuring reactions (Table II). The trapped radicals partly recombine, forming additional crosslinks, and partly proceed with addition of the soluble portion of the sample to network. These reactions continue slowly, but, nevertheless, to a considerable extent. In network A, the postcuring crosslinking lasts 42 days. The Mc values of 113 and 108 g/mol determined in the beginning of aging were changed to 57 and 61 g/mol, respectively, after 42 days of the postcuring period. The same posteffects with comparable intensity were observed in networks B and C, where the vinylcyclopropane monomer BVCP was also included in the mixture of Bis-GMA and UDMA monomers. Again, a substantial increase both in the crosslink density and the content of the insoluble fraction is realized in the first 21-day period. In the following 3 weeks, the forming of new crosslinks continued, however, with diminished intensity (Table II).

Based on the Mc values, the chains in network C with 20 wt % of the vinylcyclopropane monomer seem to be loosely bound compared to either sample B,

TABLE II
Effect of Time of Aging of the Samples Under Air Atmosphere at Room Temperature in the Dark on the Postcuring Changes of the Gel Content, *Mc*, and Residual Unsaturation C=C in Polymer Networks A, B, and C

Sample	Days after curing	Gel content (wt %)	Mc (g/mol)	Residual C=C[a] (%)
A	0	88.7	113	14.5
		89.8	108	
	21	94.1	65	12.8
		93.7	67	
	42	94.4	57	11.0
		94.0	61	
	84	94.4	56	10.8
		93.8	59	
B	0	87.8	110	15.4
		88.0	111	
	21	91.6	73	10.8
		91.9	77	
	42	93.1	63	9.7
		92.2	66	
	84	93.8	58	7.9
		92.8	60	
C	0	84.9	130	14.3
		84.7	135	
	21	90.0	86	11.2
		90.6	90	
	42	90.7	79	9.6
		90.3	80	
	84	91.0	71	8.8
		91.4	70	

A VL intensity of 300 mW/cm^2 was used for initiation of the crosslinking polymerization during 40 s at 20–22°C.
[a] An average of six determinations.

containing 10 wt % of BVCP, or sample A, consisting only of Bis-GMA and UDMA. The Mc values of 130 and 135 g/mol of network C at the beginning of the dark reactions are higher than those of the Mc's of samples A and B. Afterward, the Mc gradually decreased to 71 and 70 g/mol after 84 days, with a tendency to additional lowering. In samples A and B, there is not a remarkable decrease of Mc between 42 and 84 days of aging (Table II). The accessible free radicals recombine in a shorter time, up to 42 days, in spite of the higher crosslink densities of A and B. The longer activity of the postcuring radical recombination in sample C, and partly in B, is probably connected with the vinylene double bonds in the polymer chains that originated during the BVCP monomer free-radical polymerization.[28] Therefore, the reactions of the vinylene groups quite reasonably explain the continuing of the postcuring processes in C for a longer time compared with the more densely crosslinked networks A and B.

It is worth mentioning that the calculated values of Mc are substantially lower than are the molecular

weights of the monomers. The *Mc* values should be considered as an elastically effective *Mc* between the crosslinks of the network that includes also physical entanglements.

Residual unsaturation

The residual unsaturation in the fully cured densely crosslinked polymers was mentioned already in the early studies of the kinetics of crosslinking copolymerizations.[2,9,16] Even postcured networks contain double bonds inaccessible to reactants present in the crosslinked polymer.

The term "fully cured polymer" without the given details of treatment is insufficient for an exact appreciation of the accessible maximum extent of the crosslinked polymerization. The rates of elementary reactions of the polymerization become progressively diffusion-controlled and decrease by many orders of magnitude during vitrification of the polymerized monomer. Thereby, all factors that stimulate the mobility of molecules, for example, elevated temperature and increasing length of the spacer between double bonds,[13,16,23,29] favor the extent of the reaction. In addition, the time factor also affects the extent of the reactions in postcuring peroxide, namely, in the fast photopolymerized systems.[30]

The FTIR analyses of polymer networks (Table II) indicate that the consumption of double bonds after 40 s of VL curing attained the upper extent of conversions known for fast photopolymerized multifunctional monomers.[13] Consumption of these, about 15% of the residual double bonds, continues in the dark postcuring period at a substantially reduced rate. The residual unstaturation decreases in each sample. The highest reduction was observed for the three-component sample B. Approximately half of the double bonds remaining in the network after VL curing reacted during 84 days of the postcuring period, which represents 7.5% of the total double-bond content in the polymerization batch. In network A, the two-component sample without the BVCP monomer, the postcuring decrease of the unsaturation was 3.7%. These differences probably reflect differences in the rigidity of the corresponding networks. Sample B, from this point of view, looks like the most flexible network (Table II). It is apparent that a moderate concentration of the vinylcyclopropane monomer added to the mixture of methacrylates affects the development of the network architecture, with a positive effect on the reduction of the residual unsaturation. On the other hand, although network C contains 20 wt % of the vinylcyclopropane monomer and shows a looser crosslinking, a smaller reduction of residual double bonds of 5.5% was determined. This can be explained by the polymerization mechanisms of the vinylcyclopropane group.[28] Each reacted vinyl double bond opens a cyclopropane ring and creates a vinylene double bond in the polymer chain. So, the total residual unsaturation decreases to a smaller extent as the larger portion of the vinylcyclopropane groups is polymerized. Similarly, as in the previous section, the occurrence of vinylene groups was considered as the base for prolonged postcuring processes in networks B and C over network A.

It can be concluded that during storage of the networks A, B, and C in the postcuring period the residual vinyl unsaturation decreases. It is difficult to decide to what extent is the decrease of unsaturation connected to reaction diffusion of frozen free radicals on the recombination distance or to the grafting a soluble portion to the network. Nevertheless, lowering the residual unsaturation makes the polymer networks more stable against aging.

Dynamic mechanical testing

Dynamic mechanical spectra are of great importance for the study of material characteristics,[25,31–34] especially the damping tan δ, which is sensitive to all kinds of transitions in polymer systems. Sets of the spectra of the storage modulus E' and the loss factor tan δ recorded in various intervals in postphotopolymerization periods do not differ substantially for polymer networks A, B, and C, although some important tendencies in the development of the polymer structures during aging can be estimated from the sets of the tan δ curves as well as from the material quantities E' and tan δ found for each network. The shapes of the relaxation curves for sample B are shown in Figure 1 as an example. The coordinates of important points for the spectra of all the networks are summarized in Table III.

The tested polymer networks are characterized by two relaxation regions. The position of these transition areas on the temperature axis is defined by the maxima on the tan δ curves. The first maximum on the temperature axis corresponds to the glass transition temperature T_{gI}, which represents the polymer network formed at the end of the photopolymerization. The second glass transition T_{gII} at a higher temperature appears as a response to the new structure which resulted in the sample from the original network, either slowly at temperatures below T_{gI} or fast by increasing the temperature over T_{gI}.[16,17] The repeated DMTA measurements proved that T_{gII} corresponds to the polymer network developed during the first DMTA scan. However, in the samples aged under ambient conditions, the T_g of the final network will occur somewhere between one of the photocured samples and one of the additional thermal-treated samples. It depends on the temperature schedule and when and how fast the postcuring process was accelerated by the increasing of the temperature. Just after photocuring
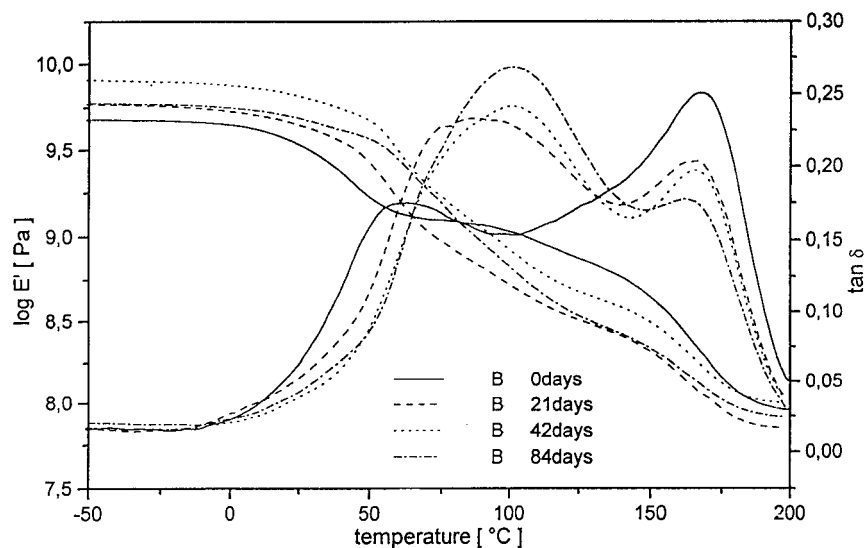
Figure 1 Effect of time of aging of network B under an air atmosphere at room temperature in the dark on the spectra of the storage modulus E' and on the spectra of the loss factor tan δ.

and at temperatures closely above T_{gI}, the recombination in termination and addition of residual nonreacted double bonds exceed the other reactions of the long-lived radicals, namely, over the addition of oxygen from air.

TABLE III
Storage Modulus E', Maxima of Loss Factor tan δ, and Their Positions on the Temperature Axis (T_g) for Polymer Networks A, B, C, and D in Dependence on Time of Aging under Air Atmosphere at Room Temperature in the Dark

Sample	log E' (Pa)		max. tan δ		T_g (°C)	
	T_{gI}	200°C	I	II	I	II
A						
0	9.12	8.06	0.2136	0.2493	59	175
21	8.98	7.90	0.2303	0.2043	79	172
42	8.90	7.81	0.2516	0.1895	88	179
84	8.84	7.91	0.2422	0.1695	90	169
B						
0	9.13	7.96	0.1753	0.2508	62	167
21	8.85	7.85	0.2335	0.2036	87	165
42	8.93	8.00	0.2420	0.1971	100	165
84	8.82	7.92	0.2682	0.1775	101	162
C						
0	9.09	7.98	0.1606	0.2317	79	166
21	8.90	8.12	0.2619	0.1873	92	157
42	8.65	7.80	0.2641	0.1663	96	161
84	8.64	7.87	0.3350	0.1207	103	164
D						
0	8.82	7.77	0.310	0.360	60	122
7	8.43	7.53	0.350	0.325	75	109
14	8.27	7.45	0.395	—	77	—
21	8.20	7.41	0.413	—	80	—
47	7.80	7.08	0.650	—	80	—

The analysis of the DMTA spectra of stored crosslinked polymers A, B, and C indicates that the glass transition temperature T_{gI} increases considerably in the first 6 weeks of aging in air at room temperature (Table III). On the other hand, at the same time, only a slight decrease of T_{gII} was observed. This means that T_{gI} and T_{gII} converged to the T_g of the final polymer with a more homogeneous network structure. After 12 weeks, the T_{gI} for sample A increased from 59 to 90°C (+31°C), and for sample B, from 62 to 101°C (+39°C), and for sample C, the difference is 24°C (from 79 to 103°C).

The damping intensity evaluated by the magnitudes of the tan δ maxima provide additional information of the dynamic mechanical behavior of the aged samples. A prolonged duration of the postcuring intervals influences also the performance of the crosslinked polymers. The DMTA spectra of tan δ show two maxima at different temperatures (Table III). The values of the damping intensity at higher temperature, tan $δ_{II}$, decreases during the postcuring period depending on the storage time. The development of a more rigid network with a higher ability to store and release mechanical energy can be expected. Decreased values of tan δ indicate the improved homogeneity of the crosslinked material and point out the high response to recovery of the energy used in the deformation of the polymer material.

On the other hand, the maximum of tan δ at lower temperatures increases with the extension of the postcuring interval. This likely means that, during aging, the internal friction in samples A, B, and C increases and more of the absorbed energy is dissipated during the cyclic deformation. In linear polymers, this is usually related to a higher mobility and more imperfec-
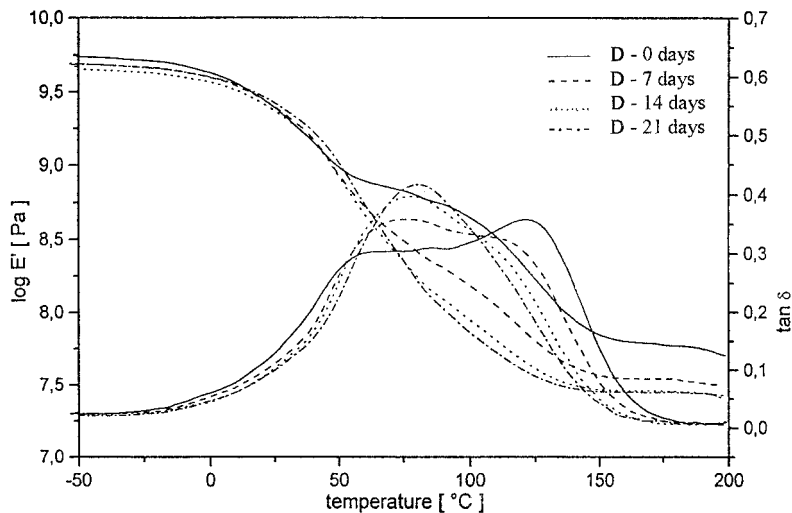
Figure 2 Effect of time of aging of network D under an air atmosphere at room temperature in the dark on the spectra of the storage modulus E' and on the spectra of the loss factor tan δ.

tions of chains and network segments. The tan δ maxima not only increase in magnitude, but also are shifted to higher temperatures (Table III). This displacement indicates the increasing of T_g simultaneously with the damping. In this case, higher toughness can be expected for these samples as a function of the duration of the postcuring period.

The great variability in the development of the network structure during photopolymerization in dependence on the structure and composition of the monomers influences also the course of the postinitiation reactions. Polymer D serves as a good example. The batch for this network differs from sample C in leaving out the monomer Bis-GDM, the nitroxyl free-radical TEMPO, and LUCIRIN TPO in the composed photoinitiator (Table I).

The bimodal shape of the tan δ spectra at the end of photopolymerization of sample D changes after 14 days to a broad peak located within the lower-temperature transition region T_{gI} (Fig. 2). The transition region T_{gII} disappeared. With the aging of sample D, after 47 days, the tan δ spectrum is characterized only by one sharp peak at a lower temperature (80°C). The shape of the spectrum shows a more homogeneous structure of the aged network, however, with a decreased glass transition temperature. In the second DMTA run, the maximum tan δ lies at a slightly higher temperature (96°C), but the second high-temperature T_{gII} at 122°C is not present (Fig. 3).

Based on the hypothesis that development of crosslinks in the postcuring period starts by trapped free radicals, in crosslinked polymer D stored in air,
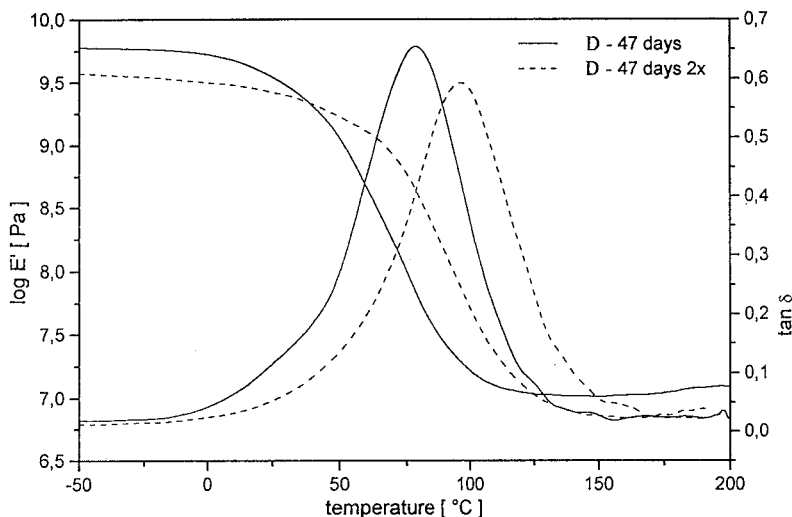

Figure 3 DMTA of network D after aging for 47 days under an air atmosphere at room temperature in the dark. The spectrum of the storage modulus E' and the spectrum of the loss factor tan δ from the first temperature scan are compared with the spectra registered in the repeated measurement of the already-analyzed sample.
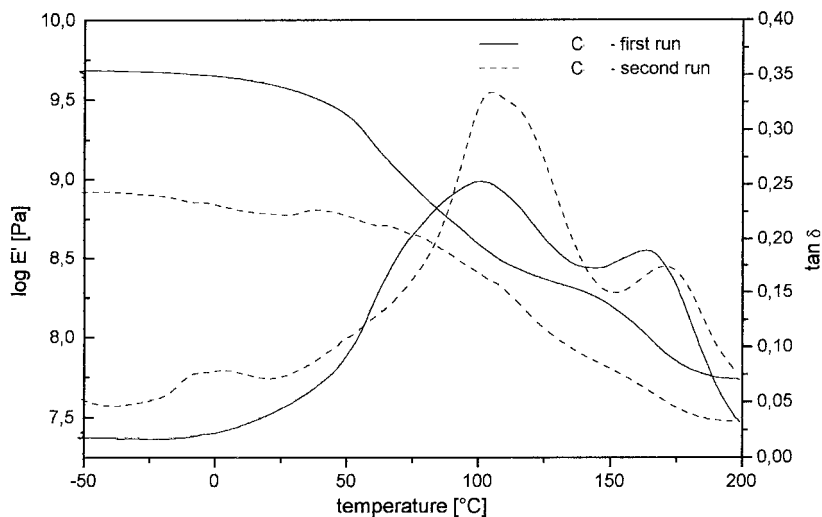
Figure 4 Comparison of the relaxation spectrum tan δ and E' of the 21-day-aged network C with that registered in repeated DMTA on the already-measured sample.

the reactive centers responsible for additional crosslinking are more easily deactivated than in networks A, B, and C. Contrary to this observation, networks A, B, and C all show bimodal tan δ curves, even after 84 days, and T_{gI} shifts to a substantially higher temperature (Table III). Moreover, the second DMTA run of the 21-day-aged samples shows a very similar tan δ spectrum with two transition regions (Fig. 4). Heating this sample to 200°C during the first temperature scan did not cause the transformation of the network structure to the polymer with only one T_g transition region at the higher temperature, as was observed immediately after photopolymerization. This observation indicates that higher temperature does not influence markedly the mobility of the network segments and transport of free radicals to a recombination distance in aged samples A, B, and C.

The reaction diffusion persists as the main mechanism in the postcuring increase of the crosslink density in the samples.

Oxygen from air plays an important role in the postcuring development of the network by reaction with frozen free radicals.[16,24,25] This can be deduced also from DMTA measurements of network D prepared by a combined procedure of photopolymerization and additional thermal curing. The curing temperature of 60°C did not influence markedly E' and tan δ. However, thermal postcuring at 120°C, which is the temperature very close to the upper transition T_{gII}, confirms that the postcuring reactions are fast (Fig. 5). The photocured sample D, already after 15 min of thermocuring, shows only one sharp relaxation peak on the spectrum of tan δ. A weak shoulder remains at the position of the previous low-temperature T_{gI}.
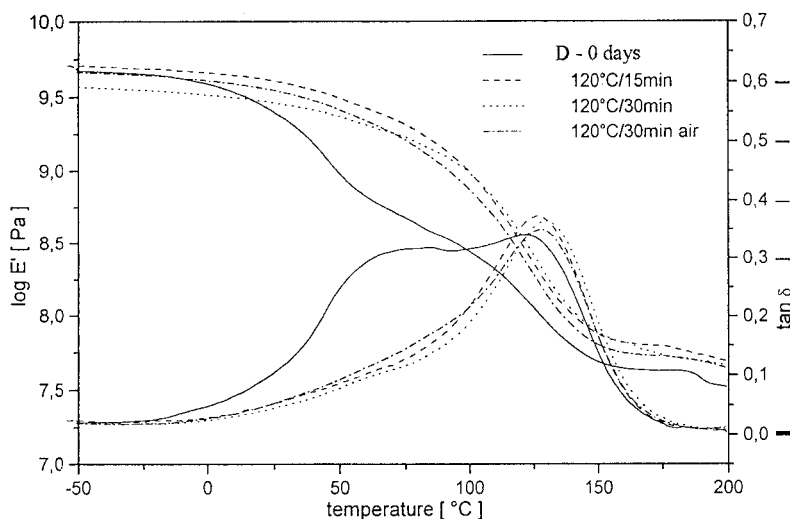

Figure 5 Influence of additional thermal curing at 120°C instantly after photopolymerization of sample D on the spectrum of the storage modulus E' and the spectrum of the loss factor tan δ.
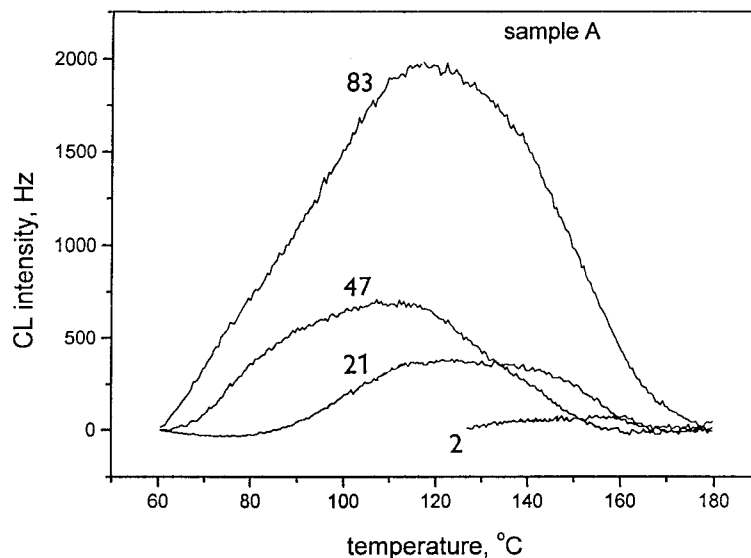
Figure 6   Effect of time of aging of network A under an air atmosphere at room temperature in the dark on the CL response.

These results agree with the assumption that, in the glassy state, a diffusion of small oxygen molecules to trapped free radicals exceed the mobility of the polymer segments and diffusion of the reactants with larger molecules. After aging the samples in air at room temperature for a sufficiently long period, the precursors of crosslinks are deactivated by a reaction with oxygen. The additional curing above the T_g temperature does not result in increased crosslink density and T_g.

Thermally cured samples in molds and those in air did not differ in the course of tan δ. This result points out again that, after releasing the frozen segmental and molecular motions immediately after photopolymerization, the free-radical recombination is accelerated much more compared with the competitive reaction with oxygen.

CL response of stored networks

CL is an extremely sensitive method for the detection of oxidation in polymers, which has been useful in the determination of traces of hydroperoxides. The oxidized polymers emit CL when they are heated in an inert atmosphere to temperatures high enough to decompose peroxides[35–37]:

$$R_1R_2CHOOH \rightarrow R_1R_2CHO\cdot$$

$$+ \cdot OH \rightarrow R_1R_2CO^* + H_2O \quad (2)$$
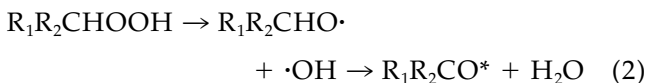
The main reason for the investigation of networks A, B, and C on the CL response is to demonstrate a significant linkage between the frozen free radicals in a photocured network and their conversion to oxidized structures, presumably to hydroperoxides. In dependence on the time of storage, the CL measurements show a continuous increase of light emission in all polymer networks. Figure 6 exemplifies the CL records for the aged network A. The integrals of the curves are proportional to the concentration of the emitting compound. Calculated concentrations of peroxides indicate their high accumulation in the crosslinked polymers (Table IV).

The low intensity of CL at the beginning of the aging of the samples (Fig. 6, curve 2) can be explained by the CL response of decomposition of the intrachain peroxides originated by copolymerization with oxygen.[38] These show the low intensity of CL with the maximum between 145 and 160°C. The CL curves for longer-aged networks showed the maximum intensity at 100–120°C, which we believe belongs to the decomposition of polymeric hydroperoxides. The analogical CL response was observed also in samples B and C.

The shape of the dependencies in Figure 7 shows for networks A and B two stages for peroxide accumulation. The first stage of oxidation is initiated by trapped free radicals. The end of this stage occurs between 21 and 47 days after photopolymerization.

The following increase of peroxide concentration in a polymer network is probably connected with an autoaccelerated oxidation initiated by hydroperoxides accumulated in the first stage of the reaction. At the beginning, higher levels of peroxides were accumulated in polymers B and C compared to sample A, which consists of UDMA and Bis-GMA only. On the other hand, the oxidation autoaccelerates in the second stage at the same postcuring time of 47 days in networks A and B, while in network C, it outlasts the first stage to the end of investigation. There is good reason to anticipate accelerated oxidation after prolonged aging also for sample C.

TABLE IV
Accumulation of Hydroperoxides in Stored Polymer Networks A, B, and C in Postcuring Period

Polymer network					
A		B		C	
Time[a] (days)	—O—O— (mol/kg)	Time[a] (days)	—O—O— (mol/kg)	Time[a] (days)	—O—O— (mol/kg)
2	0.001	1	0.004	0	0.006
21	0.008	20	0.020	19	0.020
47	0.012	46	0.024	45	0.032
83	0.051	83	0.076	83	0.037

Polymer samples were stored under air atmosphere at room temperature in the dark. The presented data were calculated from CL intensity curves recorded during the temperature scan of 2.5°C/min in nitrogen, up to 200°C.

[a] Postcuring time.

The postcuring processes in the densely crosslinked networks A, B, and C show that the accumulation of peroxides is accompanied by the building up of the new crosslinks and the consumption of the residual double bonds. The existing results, however, do not answer to what extent the oxidation chain in the decay of free radicals should be suppressed to prevent harm to the mechanical properties of the network. Nevertheless, the comparison with aging of a similar type of network D, whose polymerization batch did not contain TEMPO, points out the importance of nitroxyl radicals in the preservation of the active centers for additional crosslinking during the dark period in samples A, B, and C. By a comparison of DMTA and CL analysis of densely crosslinked polymers A, B, C, and D, we tried to contribute to the elucidation of the often controversial description of oxygen effects on postcuring reactions in polymer networks.[16,39,40]

CONCLUSIONS

The swelling experiments show the high density of crosslinks in the polymer networks A, B, C, and D, which were prepared by fast photoinitiated free-radical polymerization. The high rate of initiation caused an early vitrification of the system and the postcuring reactions were observed after switching off the light.

Samples A, B, C, and D were prepared from liquid monomers, below the glass transition temperature of the resulting polymer networks. So, the translation and segmental diffusion of reacting moieties were considerably slowed at the observed extent of the reaction. The interruption of VL initiation in crosslinked polymers, however, did not stop the free-radical reactions completely. An increase of the network density revealed bimolecular termination. An increase of the gel content is evidence of the addition of a residual monomer to the network. A decrease of the concentration of nonreacted double bonds detected by FTIR supports a continuation of the polymerization (Table II).

The reaction diffusion prevails in the transport of free radicals to the recombination distance. Oxygen accelerates this reaction; nevertheless, hydroperoxide groups are formed.

The CL response of crosslinked polymers A, B, and C stored at room temperature in air in the dark shows the accumulation of hydroperoxides during aging (Table IV). With respect to the parallel reactions, addition of the remaining monomer and building up of new crosslinks, the fraction of radicals consumed by the initiation of hydroperoxidation depends, probably, on the ratio of the rates of oxygen diffusion to the rates of other reactions.
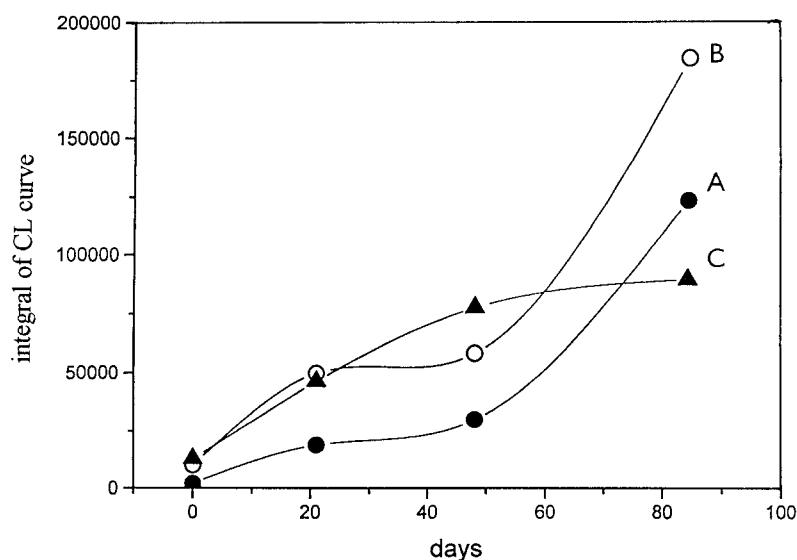

Figure 7 Concentration of accumulated hydroperoxides (au) in networks A, B, and C in dependence on the time of aging in an air atmosphere at room temperature in the dark.

The DMTA relaxation spectra point out a progressive development of the network structure in a stored crosslinked polymer. The increasing degree of crosslinking in samples A, B, and C is reflected in the shifting of the first damping maximum (T_g) to higher temperatures. The position of the second peak remains almost unchanged at the end of 12 weeks of aging (Table III). From this fact, however, it cannot be concluded that oxygen does not influence the final properties of the network. The high levels of accumulated hydroperoxides, reflected in the CL response, provide good evidence of the consumption of part of the trapped free radicals in the reactions with oxygen. The hydroperoxide presence in the crosslinked polymer represents a serious danger for both photo- and thermal stability during handling. The direct affect of oxygen on the deterioration of the dynamic mechanical properties of networks A, B, and C was not observed. On the other hand, the free radicals trapped in copolymer D appeared to be more active in competitive reactions with oxygen which retard additional crosslinking.

References

1. Dušek, K. Coll Czech Chem Commun 1993, 58, 2245.
2. Dušek, K. In Developments in Polymerization; Haward, R. N., Ed.; Applied Science: Barking, 1982; Vol. 2, p 143.
3. Tobita, H.; Hamielec, A. E. Polymer 1992, 33, 3647.
4. Bowman, C. N.; Peppas, N. A. Macromolecules 1991, 24, 1914.
5. Anseth, K. S.; Kline, L. M.; Walker, T. A.; Anderson, K. J.; Bowman, C. N. Macromolecules 1995, 28, 2491.
6. Anseth, K. S.; Wang, C. M.; Bowman, C. N. Polymer 1994, 35, 3243.
7. Bowman, C. N.; Peppas, N. A. J Appl Polym Sci 1994, 42, 2013.
8. Andrzejewska, E.; Lindén, L.-A.; Rabek, J. F. Polym Int 1997, 42, 179.
9. Radiation Curing, Science and Technology; Pappas, S. P., Ed.; Plenum: New York, London, 1992; pp 1–20.
10. Cook, W. D. Polymer 1997, 33, 600.
11. Anseth, K. S.; Anderson, K. J.; Bowman, C. N. Macromol Chem Phys 1996, 197, 833.
12. Okay, O.; Kurtz, M.; Lutz, K.; Funke, W. Macromolecules 1995, 28, 2728.
13. Decker, C. Prog Polym Sci 1996, 21, 593.
14. Kloosterboer, J. G.; Lijten, G. F. C. M.; Grieclanus, F. J. A. M. Polym Prepr 1986, 27, 269.
15. Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. Macromolecules 1990, 23, 1144.
16. Kloosterboer, J. G. Advances in Polymer Science 84; Springer-Verlag: Berlin, Heidelberg, 1988.
17. Burtscher, P. Dent Mater 1993, 9, 218.
18. Antonucci, J. M.; Toth, E. E. J Dent Res 1983, 62, 121.
19. Anseth, K. S.; Bowman, Ch. N.; Peppas, N. A. J Polym Sci Polym Chem 1994, 32, 139.
20. Anseth, K. S.; Decker, C.; Bowman, C. N. Macromolecules 1995, 28, 4040.
21. Bosch, P.; Serrano, J.; Mateo, J. L.; Guzman, J.; Calle, P.; Sieiro, C. J Polym Sci A Polym Chem 1995, 36, 2785.
22. Lecamp, L.; Youssef, B.; Bunel, C.; Lebaudy, P. Polymer 1995, 40, 6313.
23. Kurdikal, D. L.; Peppas, N. A. Polymer 1995, 35, 1004.
24. Decker, C.; Moussa, K. J Appl Polym Sci 1987, 34, 1603.
25. Anseth, K. S.; Bowman, C. N.; Peppas, N. A. Polym Bull 1993, 31, 229.
26. Moszner, N.; Rheinberger, V. U.S. Patent 5 847 025, 1998.
27. Flory, P. J. Principles of Polymer Chemistry; Cornell University: Ithaca, NY, 1953.
28. Sanda, F.; Takata, T.; Endo, T. Macromolecules 1993, 26, 1818.
29. Pavlinec, J.; Moszner, N. J Appl Polym Sci 1997, 65, 165.
30. Decker, C.; Elzaouk, B.; Decker, D. J Macromol Sci Pure Appl Chem A 1996, 33, 173.
31. Murayama, T. Dynamic Mechanical Analysis of Polymeric Material; Elsevier: Amsterdam, Oxford, New York, 1978.
32. Wilson, T. W.; Turner, D. T. J Dent Res 1987, 66, 1032.
33. Xiao, H.; Jiang, M.; Yu, T. Polymer 1994, 35, 5529.
34. Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N. J Polym Sci B Polym Phys 1997, 35, 2297.
35. Chemiluminescence—Principles and Applications in Biology and Medicine; Cambell, A., Ed.; Ellis Horwood: Chichester, UK, 1988.
36. Matisová-Rychlá, L.; Rychlý, J. Polym Degrad Stab 2000, 67, 515.
37. Matisová-Rychlá, L.; Rychlý, J. In Polymer Durability; Clough, R. L.; Billingham, N. C.; Gillen, K. T., Eds.; Advances in Chemistry Series 249; American Chemical Society: Washington, DC, 1996; pp 175–194.
38. Schulz, G. V.; Henrici, G. Macromol Chem 1956, 18–19, 437.
39. Bresler, S. E.; Kazbekov, E. N. Adv Polym Sci 1964, 3, 688.
40. Pavlinec, J.; Moszner, N.; Plaček, J. Macromol Chem Phys 2001, 202, 2387.