Transmission in irradiated hydroxyethyl methacrylate copolymer at elevated temperatures

K-P. Lu and Sanboh Lee
Department of Materials Science, National Tsing Hua University, Hsinchu, Taiwan, Republic of China
C.C. Han
Polymer Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Transmission losses were monitored in the ultraviolet-visible spectra of irradiated hydroxyethyl methacrylate (HEMA) copolymer at elevated temperatures. The transmission in irradiated HEMA in the ultraviolet and visible wave length range was almost the same for doses 400 kGy $\leqslant \Phi \leqslant$ 1000 kGy, but was smaller than that of the nonirradiated HEMA copolymer. The reduction in transmission in the irradiated specimens was attributed to the presence of color centers. The concentration of color centers was enhanced by thermal annealing. The transmission data (or absorption data) at 467 nm was found in good agreement with the theoretical model in which the color center production followed a first-order kinetic process. The rate constant satisfies the Arrhenius equation, and the corresponding activation energy is 17.37 kJ/mol and is independent of the dosage. The results were compared with those reported in the literature.

I. INTRODUCTION

The hydroxyethyl methacrylate (HEMA) copolymer is one of the most useful bio-polymers because it exhibits a high-equilibrium water content and is bio-compatible.[1–4] The hydroxyl group and carbonyl group on each repeat unit make the HEMA compatible with water; the hydrophobic α-methyl group and backbone provide hydrolytic stability to the HEMA and impart mechanical strength to the polymer matrix.[5–7] The "structure" of the water in crosslinked HEMA gels, mass transport, and equilibrium swelling have been investigated by many researchers.[8–16]

When polymeric materials are exposed to gamma rays, their properties are altered in different ways. For example, the backbones may undergo scission or crosslinking.[17–22] Scission leads to a reduction in molecular weight, while crosslinking increases the molecular weight. Fujisawa *et al.* observed that the hardness and wearability of ultrahigh molecular weight polyethylene increased with gamma-ray dose.[23] Chou *et al.* observed transmission losses in the ultraviolet-visible (UV-vis) spectrum that increase with increasing gamma-ray dose.[14,15] Todd[24] and David *et al.*[25] investigated the volatile products in the irradiated poly(methyl methacrylate). Ohnishi and Nitta measured the formation rate of free radicals in irradiated poly(methyl methacrylate),[26] and Kusy and Katz determined the fracture surface energy as a function of viscosity average molecular weight in the irradiated poly(methyl methacrylate) (PMMA).[27]

Color centers have drawn attention for several decades. LiF single crystals with color centers may absorb nonlinearly high-power optical radiation and have been used as passive laser switches.[28] These color centers are very stable at room temperature. Lin *et al.* studied transmission in irradiated LiF single crystals at high temperatures as a function of annealing time, but they did not fully explore the evolution in transmission spectra due to complicated variations after short-time annealing.[29] Deng *et al.* analyzed the transmission spectra recovery in irradiated La-doped $PbWO_4$ crystals at room temperature.[30] Wallace *et al.* studied color-center annealing in γ-irradiated polystyrene under vacuum and air atmospheres.[31] Harmon and coworkers reported increases in transmission losses accompanying room-temperature annealing in irradiated polysiloxanes[32] and decreases in transmission losses, which accompany annealing in many other polymer systems.[33–35] Lin and Lee[36] and Lu *et al.*[37] studied transmission recovery in irradiated poly(methyl methacrylate). In the above studies, only polysiloxanes exhibited color center populations that increased with annealing. This paper presents data revealing that the concentration of color centers in irradiated HEMA increases with increasing annealing time and finally reaches a plateau. For the first time, a first-order kinetic model is proposed and is in good agreement with these observations.

II. EXPERIMENTAL

Soft contact lens blanks made of poly(hydroxyethyl methacrylate) (HEMA) copolymer were obtained from the Contact Lens Laboratories Ltd., Montreal, Quebec, Canada. The compositions of HEMA copolymer consist of HEMA, ethylene glycol dimethacrylate (EGDMA), and methacrylic acid (MAA). The blank was 12.8 mm in diameter and 6.0 mm in thickness. They were mounted on a bench lathe and thinned to 1.0 mm. The specimens were ground with 600, 800, and 1200 grit emery papers and then polished with 1.0, 0.3, and 0.05 μm alumina slurries. They were annealed at 40 °C in vacuum for 48 h and then cooled down to room temperature in the furnace. The specimens were placed in glass tubes and then irradiated via a gamma source at a dose rate of 20 kGy/h at room temperature at the Radioisotope Division of National Tsing Hua University. The irradiation doses were 400, 600, 800, and 1000 kGy.

The transmission spectra of the HEMA sample before and after annealing were recorded on a Hitachi (Tokyo, Japan) U-3410 spectrophotometer with a scanning speed of 1200 mm/min in the wavelength range from 250 to 800 nm at 25 °C. The specimen was preheated in a thermostated water bath to the desired temperature and then moved to a thermos cup at the same temperature. The transmission at a wave length of 467 nm was measured periodically. The specimen was kept in the thermos cup at all times except for the transmittance measurement. The process continued until the transmission reached a constant value.

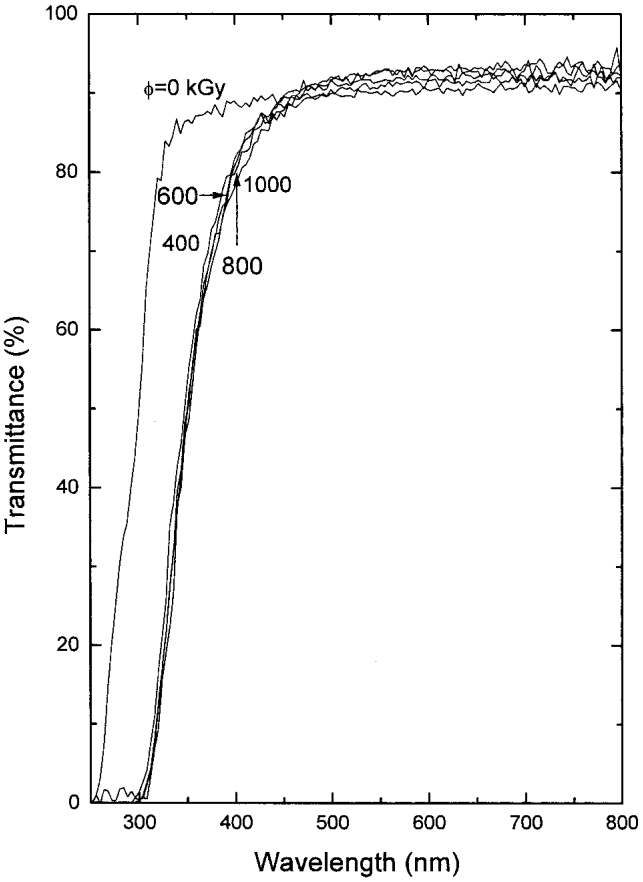

FIG. 1. Transmission in HEMA irradiated with various doses versus UV-vis wave length.

III. RESULTS AND DISCUSSION

The measured transmission values for irradiated HEMA with various doses are plotted against the UV length in Fig. 1. The transmission is almost the same for all doses ($\Phi \geqslant 400$ kGy) and the cut-off wave length shifts to the red as compared to the non-irradiated specimens. Note that the HEMA copolymer contains the hydroxyl group, which is hydrophilic, the methyl group, which supports the hydrolytic stability, and the carboxyl group, which is highly ionizable. The UV-vis spectra of non-irradiated HEMA exposed to various relative humidities do not show a significant difference.

The transmission values for HEMA irradiated with $\Phi = 400$, 600, 800, and 1000 kGy versus annealing time at 80 °C are plotted in Figs. 2(a)–2(d), respectively. During the isothermal annealing, the transmission decreases with increasing time. For a given time interval, the difference in transmission is larger for high doses than for low doses. The cut-off wave length shifts to a longer wave length as the annealing time increases. For a given wave length, the transmission decreases with increasing annealing time for all doses until it remains constant.

The optical absorption A is assumed to be proportional to the concentration n of the color centers by a power law:

$$A = \beta n^p \quad , \tag{1}$$

where β and p are constant. The summation of transmission, reflectance, and absorption is equal to unity. The surface morphology and other defects in irradiated HEMA copolymers do not change during isothermal annealing with the exception of the color centers. In this experiment the specimen surface is flat, and the optical beam is normal to the surface so that the reflectance is independent of the color centers. It is reasonable to assume that the reflectance is zero. Note that even if the reflectance is constant, the following conclusion will not be significantly changed. Thus, we have

$$A = 1 - I \quad , \tag{2}$$

where I is the transmittance. The color center is assumed to follow a first-order annihilation process at a given temperature as

$$dn/dt = -\alpha(n - n_\infty) \quad , \tag{3}$$

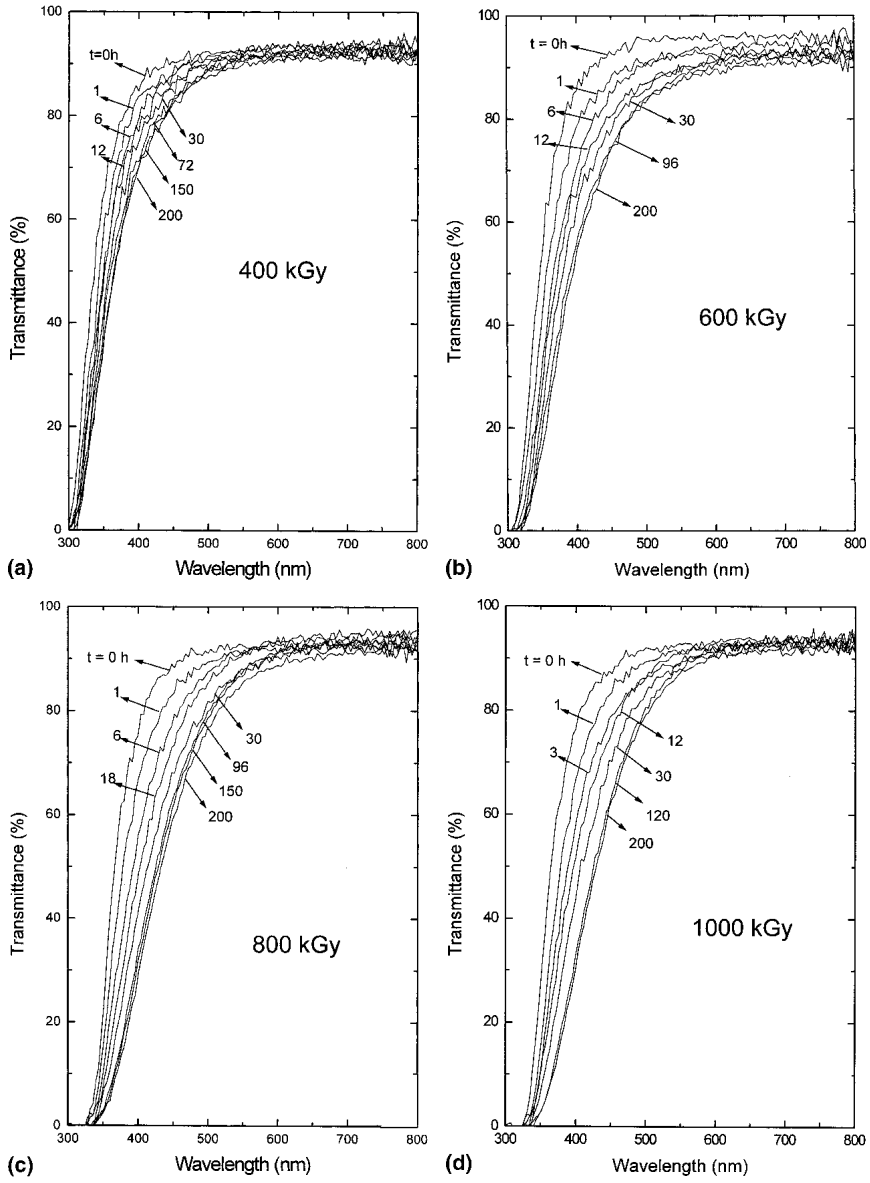

FIG. 2. UV-vis spectra of HEMA irradiated with various doses: (a) 400 kGy, (b) 600 kGy, (c) 800 kGy, and (d) 1000 kGy at different annealing times at 80 °C.

where α is the rate constant and n_∞ is the concentration of color centers at $t = \infty$. Solving Eq. (3), we obtain

$$n = n_\infty\{1 - [1 - (n_0/n_\infty)^{1/p}]\exp(-\alpha t)\}^p \quad , \qquad (4)$$

where n_0 is the concentration of color centers at $t = 0$. Substituting Eq. (1) into Eq. (4) yields

$$A = A_\infty \{1 - [1 - (A_0/A_\infty)^{1/p}]\exp(-\alpha t)\}^p \quad , \qquad (5)$$

where $A_0 = \beta\, n_0^p$ and $A_\infty = \beta\, n_\infty^p$ are the optical absorption at $t = 0$ and $t = \infty$, respectively.

According to Fig. 2, the transmission in irradiated HEMA at a wave length of 467 nm changes pronouncedly with annealing time. Therefore, we may use this wavelength to detect the evolution in transmission. Using the transmission data with Eq. (2), we plot the data of absorption of HEMA irradiated with Φ = 400, 600, 800, and 1000 kGy at wave length 467 nm at different temperatures in Figs. 3(a)–3(d), respectively. The absorption increases monotonically with increasing annealing time until reaching a plateau. The solid lines in Fig. 3 are fitted with Eq. (5) using a least-squares fitting with p being 2 for all doses and temperatures. The corresponding α values are listed in Table I. Note that the transmission (=0.875) as well as the absorption (=0.125) is the same at the initial time of isothermal annealing for all doses. The theoretical curves are in good agreement with the experimental data. In general, the rate constant increases with dose at a given temperature, as shown in Table I. (One exception is $\alpha = 0.0062\ h^{-1}$ at 40 °C and

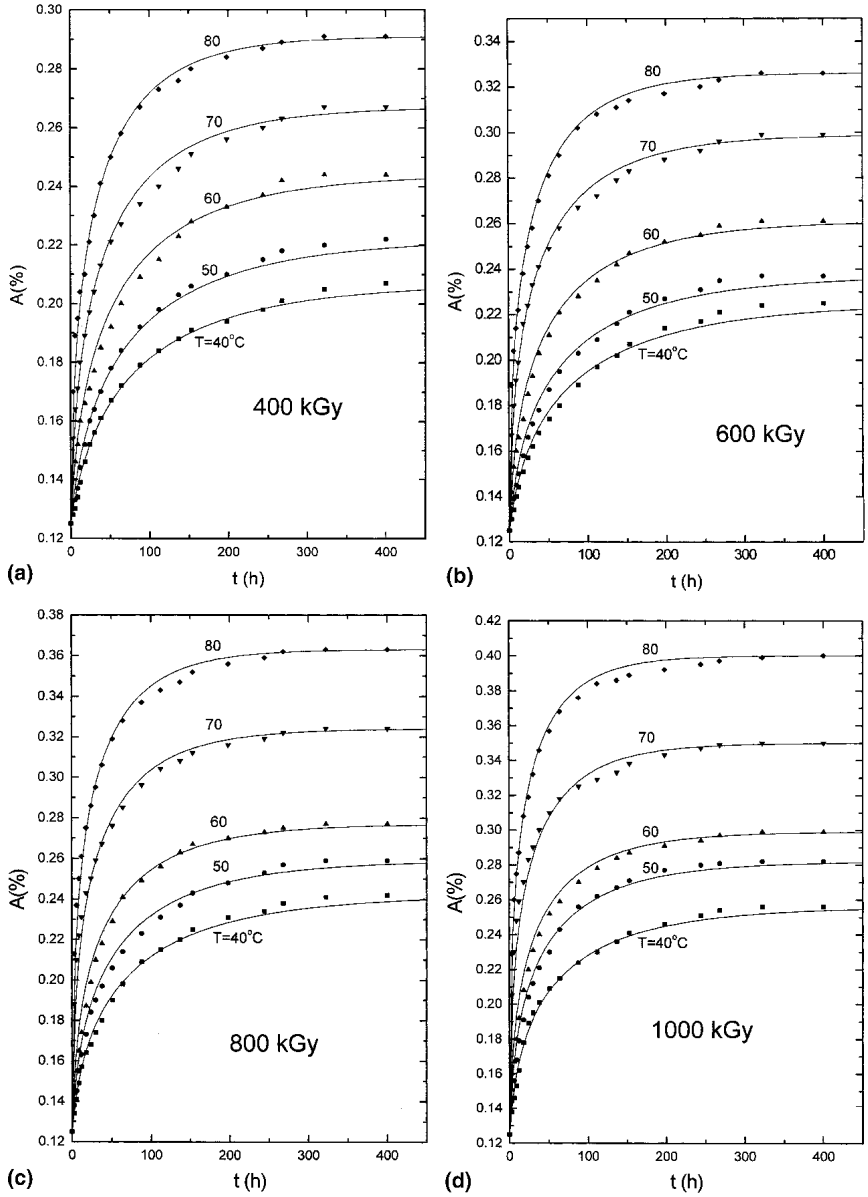

FIG. 3. Absorption of irradiated HEMA at wave length 467 nm as a function of annealing time for samples with various doses (a) 400 kGy, (b) 600 kGy, (c) 800 kGy, and (d) 1000 kGy.

TABLE I. The α value in units of h^{-1} of HEMA.

Temperature (°C)	400 kGy	600 kGy	800 kGy	1000 kGy
40	0.0064	0.0062	0.0068	0.008
50	0.0066	0.0072	0.0083	0.010
60	0.0078	0.0088	0.0104	0.012
70	0.0096	0.0105	0.0127	0.015
80	0.0122	0.0133	0.0149	0.018

600 kGy, which might be due to experimental error.). From Table I, it is seen that the rate constant satisfies the Arrhenius plot as shown in Fig. 4,

$$\alpha = \alpha_0 \exp(-Q/\mathrm{RT}) \quad , \tag{6}$$

where α_0, R, and Q are the pre-exponent factor, gas constant, and activation energy, respectively. T is the absolute temperature in Kelvin. It can be seen from Fig. 4 that all lines are parallel, so the activation energy equals 17.37 kJ/mol for all doses.

The transmission in irradiated HEMA annealed at long times decreases with increasing dose and annealing temperature, as shown in Fig. 5. The experimental data in Fig. 5 can be fitted with the following equation:

$$I = 0.875 - \xi \Phi^B \quad , \tag{7}$$

with the unit of Φ in kGy. According to Fig. 5, the best fit parameters ξ and B were determined and are listed in Table II. The parameter ξ increases with

increasing temperature whereas B is in the range from 0.46 to 0.54, which is greater than 0.39 shown in Eq. (7) for PMMA.

A comparison of transmissions between other polymeric materials and HEMA is made. A recovery of transmission was found in PMMA, but not in HEMA.[37] This implies that the concentration of color centers in PMMA decreases with an increase in annealing time, but the population in HEMA increases. The color-center annealing is a second-order kinetic process for the PMMA and a first-order process for HEMA. The parameter p is equal to 2, regardless of the dose in the case of HEMA and 2, 1.5, 1.2 and 1 corresponding to $\Phi = 400$, 600, 800, and 1000 kGy in PMMA. This implies that the ability of the color center to absorb light is the same for all doses for HEMA but decreases with increasing dose for PMMA. The above comparison is based on the evolution of transmission at wave lengths of 407 nm for PMMA and 467 nm for HEMA. If we choose the same wavelength to compare the two cases, the result would be the same. Wallace *et al.* found permanent and recoverable color centers in polystyrene.[31] Harmon *et al.* also observed these two types of color centers in poly(methylphenylsiloxane) and poly(benzyl methacrylate).[32] Their observations were qualitative. However, Eq. (4) shows quantitatively that the concentration at time infinity n_∞ corresponds the permanent color centers; concentration is exponential decay with time, which corresponds to recoverable color centers.

The transmission in irradiated HEMA is also compared with that of irradiated LiF single crystals. Lin *et al.* found that the transmission in irradiated LiF oscillates at short times and then increases monotonically with increasing time until it remains constant during the isothermal annealing at temperatures 450–520 °C. After irradiation, many kinds of defects such as clusters, and the F, M, R_1, R_2, and H centers are created. Catlow *et al.* found a complicated phenomenon of clusters, which were dissolved into small color centers of F, M, R_1, and R_2 type.[38] The cluster allows UV-vis light to transmit whereas the color centers of F, M, R_1, and R_2 absorb light of different wave lengths. During the short times, the clusters decompose into isolated color centers, which outnumber the annihilation pairs, so the transmission decreases. On the other hand, if the number of color centers created is less than the number of color centers destroyed, the transmission increases. During the long times, all clusters disappear. The color center population for the long times followed a second-order annihilation process. On the other hand, the color center population of irradiated HEMA follows a first-order kinetic process. The color center population of irradiated HEMA is stable at elevated temperatures. The mechanism of color center

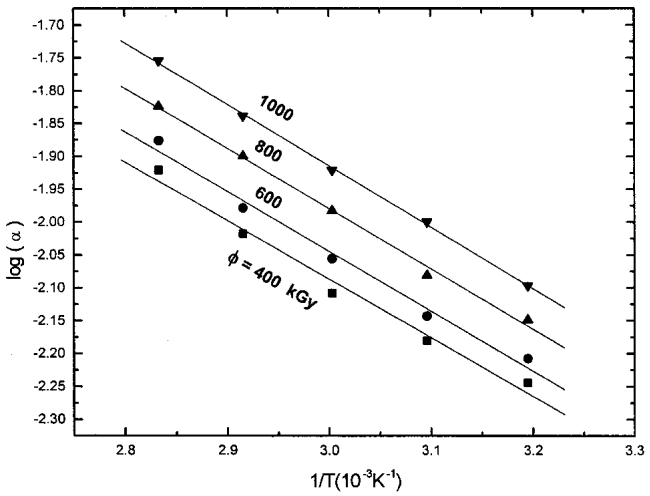

FIG. 4. Arrhenius plot of α in units of h^{-1}.

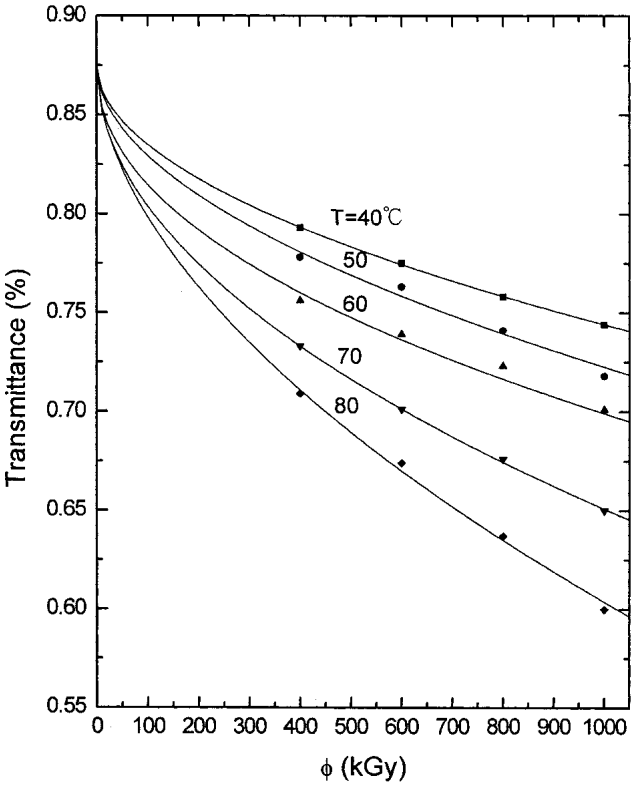

FIG. 5. Transmission in irradiated HEMA at wave length of 467 nm after annealing as a function of doses at various annealing temperatures.

TABLE II. The parameters ξ and B of Eq. (7).

Temperature (°C)	ξ	B
40	0.0038	0.5136
50	0.0041	0.5234
60	0.0071	0.4647
70	0.0072	0.4981
80	0.0061	0.5489

formation in HEMA is unknown, and further investigation is required. Although the LiF single crystals were found useful for Q switching[39] and mode locking[40] in the neodymium lasers because of stable color centers at room temperature, the color centers in irradiated LiF single crystals are unstable at elevated temperatures and cannot be used as laser switches. Thus, the irradiated HEMA is a potential candidate for color center laser applications at elevated temperatures.

IV. CONCLUSION

The transmission in HEMA copolymer at elevated temperatures has been studied in detail. The reduction in transmission in irradiated HEMA arises from the presence of color centers, which can be enhanced by thermal annealing. Assuming that the optical absorption at wave length 467 nm is proportional to the square of concentration of color centers, the measured absorption data are in good agreement with the theoretical model based on a first-order kinetic process of color centers in irradiated HEMA during thermal annealing. The activation energy for kinetic processes in color centers in irradiated HEMA is 17.37 kJ/mol for all doses.

It is seen that the above behavior of irradiated HEMA copolymers is different from that of LiF single crystals. The concentration of color centers is enhanced by thermal annealing for HEMA but reduced for LiF single crystals. In irradiated LiF single crystals, the concentration of color centers oscillates at the early stage and then decreases monotonically with increasing time at high temperature.[26] Because of the instability of color centers at elevated temperatures in LiF, it is not suitable for high-temperature applications of laser switches. The present study indicates that the irradiated HEMA copolymer is a potential candidate for color center lasers both at room temperature and elevated temperatures.

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