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Photochemical kinetics for holographic grating formation in phenanthrenequinone doped poly (methyl methacrylate) photopolymer*

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The photochemical kinetics of phenanthrenequinone (PQ) doped poly (methyl methacrylate) photopolymer in holographic recording was studied theoretically and experimentally. The diffusion of PQ molecules during holographic recording was negligible because of its small diffusion coefficient at room temperature. A photochemical reaction kinetics model of PQ/PMMA was established. The analytical expressions for the temporal variations of transmittance and diffraction efficiency were derived. By fitting the experimental curves, some parameters related with the polymer components were obtained by the proposed model, which can be used to analyze the photochemical process and will be helpful to the optimization of material preparation.

Keywords: phenanthrenequinone doped poly(methyl methacrylate), photochemical reaction
PACC: 4270, 8140

1. Introduction

As recording medium for holographic storage, phenanthrenequinone (PQ) doped methyl methacrylate (PQ/PMMA) photopolymer has attracted attention for its advantages of negligible shrinkage and controllable thickness up to several millimeters.[1−6] PQ/PMMA is major composed of PQ and PMMA, in which PQ acts as sensitizer and PMMA as matrix. In the process of material synthesis, a spot of methyl methacrylate (MMA) monomers are remained if the monomer polymerization reaction is inadequate. It was proposed that the change of refractive index was contributed by the density modulation of PQ molecules. Veniaminov[7] studied the diffusion of PQ molecules at various environmental temperatures and proposed the photochemical reaction: PQ molecules were excited to PQ radicals and attached to PMMA macromolecules in illuminated zones. Hsiao[8] proposed that new molecules PQ–nMMA formed through reaction between PQ molecules and residual MMA molecules (mainly forming PQ–MMA adduct which consisted of one PQ molecule and one MMA molecule). At this time, the polymerization reaction of MMA was initiated by photoinitiator PQ molecules, which resulted in a small quantity of PMMA oligomers forming.

Diffusion was considered as the main factor of the hologram grating formation in most photopolymers, especially in the free-radical polymerization system.[9−11] Photoinitiator stimulated by coherent light initiates a spatially non-uniform polymerization, which results in the concentration gradients produced. Thus, the diffuse of monomers from the un-illuminated zones to the neighboring illuminated zones leads to the modulation of the spatial index. Zhao[12] proposed a one-dimensional diffusion model based on DuPont's photopolymer. In this model, the variation of reactant concentration is produced by diffusion and the photopolymerization reaction. By assuming a linear dependence of the polymerization rate on light intensity, this model accounted for the low spatial frequency cutoff and reciprocity failure. Sheridan[13] developed a one-dimensional diffusion model by introducing a non-local response in order to explain the high spatial frequency cutoff. Many physical variables in this model need to be determined by means of nonlinear fitting to experimental curves in conjunction with Ko-

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gelnik's coupled-wave theory.

To clarify the mechanism of the grating formation, the understanding of medium response is necessary. In this paper, a kinetic model for photochemical reaction in PQ/PMMA polymer was proposed. The polymerization rate was assumed linearly proportional to monomer concentration following the analysis of Odian[14] and Kwon.[15] Because of the low diffusion coefficient in this polymer, diffusion process of PQ molecules was neglected at room temperature. Based on the PQ radical termination mode, the analytical expressions of transmittance and diffraction efficiency were derived. Some important kinetics parameters, which involved in the proposed model, were obtained by a nonlinear fitting. The fitted kinetics parameters were discussed in detail.

2. Theoretical analysis of medium response

In photopolymers, there are two reasons for the concentration change of each component in the illuminated zones. One reason is the compositions diffusing from the un-illuminated zones to the illuminated zones, the other is the photopolymerization reactions ($F(x,t)$) in the illuminated zones. That is to say

$$\frac{\partial [M](x,t)}{\partial t} = D_i \frac{\partial^2 [M](x,t)}{\partial x^2} + F(x,t), \qquad (1)$$

where $[M](x,t)$ is the concentration of components and D_i is the diffusion coefficient of the i-component.

The refractive index modulation mainly ascribed to the concentration variety of PQ content in PQ/PMMA polymer.[8] We primarily focused on the influence of PQ molecule diffusion on the grating formation, and then gave an estimate for the diffusion distance of molecules. During grating recording process, the concentration gradient of PQ molecules increases between the illuminated and the un-illuminated zones, which results in the increase of the PQ molecules diffusion. And the concentration gradient reaches the maximum value when the photochemical reaction stops. At this time, an estimation of the diffusion coefficient can be obtained using Fick's second law,

$$\frac{\partial [\mathrm{PQ}](x,t)}{\partial t} = D_{\mathrm{PQ}} \frac{\partial^2 [\mathrm{PQ}](x,t)}{\partial x^2}, \qquad (2)$$

where $[\mathrm{PQ}](x,t)$ is the concentration of PQ component and D_{PQ} is the diffusion coefficient of free PQ molecules. This differential equation can be solved by substituting the boundary condition and initial condition. The limit case when the concentration gradient reaches the maximum is considered. Assuming that PQ molecules disappears when the concentration gradient reaches to the maximum, which leads to the $[\mathrm{PQ}](x,0) \approx 0$ in the illuminated zone. And we consider that the concentration is constant $[\mathrm{PQ}]_0$ at the un-illuminated zone ($x = 0$). That is, the boundary condition can be written as $[\mathrm{PQ}](0,t) = [\mathrm{PQ}]_0$. And when $x = L$, a diffusion limit is shown as[16]

$$\left.\frac{\partial [\mathrm{PQ}](x,t)}{\partial x}\right|_{x=L} = 0, \qquad (3)$$

where L is the distance over which the concentration gradient disappears. By substituting these conditions into Eq.(2), the temporal variation of the PQ concentration $[\mathrm{PQ}](x,t)$ and the average diffusion length $\bar{x}$ as the function of the diffusion coefficient and time are written as[16]

$$[\mathrm{PQ}](x,t) = [\mathrm{PQ}]_0 \sum_{k=1}^{\infty} \left[\mathrm{erfc}\left(\frac{2(k-1)L + x}{2\sqrt{D_{\mathrm{PQ}} t}} \right) + \mathrm{erfc}\left(\frac{2kL - x}{2\sqrt{D_{\mathrm{PQ}} t}} \right) \right] \times (-1)^{k-1}, \qquad (4)$$

$$\bar{x} = 2\sqrt{D_{\mathrm{PQ}} t}. \qquad (5)$$

In Eq.(4), $\mathrm{erfc}(x)$ is defined as

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} \mathrm{e}^{-t^2} \mathrm{d}t. \qquad (6)$$

According to Eq.(5), if the grating is formed in 30 minutes, in order to make a diffusing distance of 10^{-2} μm (1% of grating spacing in this study), the diffusion coefficient of PQ molecules must be in the order of 10^{-19} m^2/s. Veniaminov *et al*[17] have obtained the diffusion coefficient by holography methods and have found that it is related to the environmental temperature. The diffusion coefficient is in the order of 10^{-21} m^2/s at 20 °C, and it increases to 10^{-19} m^2/s in the temperature range from 50 °C to 75 °C. Therefore, it is reasonable to ignore the diffusion process of PQ molecules in our experiment environmental (room temperature). According to equation (1) we can get

$$\frac{\partial [\mathrm{PQ}](x,t)}{\partial t} = F(x,t). \qquad (7)$$

It must be pointed out that the diffusion of small nMMA molecules cannot be neglected, especially the residual MMA molecules because it is about two and a half times lighter than PQ molecules. In this case, a small quality of nMMA oligomers (i.e. short PMMA

chain) will be produced by PQ initiation.[8] However, the effect of this process on index modulation can be neglected because the matrix is also PMMA chains. As a result, the index modulation in PQ/PMMA photopolymer mainly depends on the refractive index variety of the PQ component in the illuminated zones.

3. Photochemical reaction kinetics

According to the analyses mentioned above, the principal photoreaction in PQ/PMMA photopolymer is a local response. The photoreaction process involves two main steps named as initiation and termination, as described by Eqs.(8)–(11). When the sample is illuminated by a non-uniform light, PQ molecules in illuminated zones are excited into PQ• radicals. Some PQ• radicals transfer their reactive group to nMMA molecules ($n = 1, 2, \ldots$) and form nMMA• radicals. In this stage, this transfer is related with the diffusion of small nMMA molecules (especial residual MMA molecules) because of the low diffusion coefficient of PQ molecules. The PQ• and nMMA• radicals will be terminated through two possible mechanisms. One termination occurs when two nMMA• radicals are close enough due to the radicals diffusing and rearranging. When the content of short nMMA chains (mainly MMA molecules) is tiny, this termination is negligible because of the high viscosity of long nMMA chains. The other termination in Eq.(11) is the reaction of nMMA• radicals and PQ• radicals. Because the lightest MMA• radicals has the highest diffusion coefficient, PQ-MMA adducts are the main product as shown in Ref.[8].

Initiation:

$$\mathrm{PQ} \xrightarrow{h\nu} \mathrm{PQ}\bullet, \tag{8}$$

$$\mathrm{PQ}\bullet + n\mathrm{MMA} \xrightarrow{k_i} n\mathrm{MMA}\bullet + \mathrm{PQ} \quad (n = 1, 2, \ldots), \tag{9}$$

Termination:

$$m\mathrm{MMA}\bullet + n\mathrm{MMA}\bullet \xrightarrow{k_{tb}} (m+n)\mathrm{MMA} \quad (m, n = 1, 2, \ldots), \tag{10}$$

$$n\mathrm{MMA}\bullet + \mathrm{PQ}\bullet \xrightarrow{k_{tp}} \mathrm{PQ} - n\mathrm{MMA}. \tag{11}$$

In this kinetics model, k_i, k_{tp} and k_{tb} are the reaction rate constants. It has been assumed that k_{tp} and k_{tb} do not depend on the chain length of nMMA. In the case of photochemical formation of free radicals, many initiation mechanisms involve a photochemical electron transfer reaction, thus, the initiation rate R_i can be written as[18]

$$R_i = \Phi' I_a, \tag{12}$$

where Φ' is quantum yield efficiency and I_a is the absorbed light intensity. I_a is related to the concentration of PQ molecules according to the Lamber–Beer's law,

$$I_a(t) = I_0(1 - \mathrm{e}^{-\varepsilon[\mathrm{PQ}](t)d}), \tag{13}$$

where $[\mathrm{PQ}](t)$ is the concentration of PQ molecule as a function of time. d is the thickness of material. I_0 is the incident intensity. ε is the natural molar absorption coefficient.

In the above analysis, we assume that the content of short nMMA chains is small and the reaction in Eq.(10) is negligible. In practice, this assumption can be realized by increasing the polymerization degree of polymer. At the steady state condition, the termination rate is equal to the initiation rate,[19]

$$R_{tp} = R_i = \Phi' I_a. \tag{14}$$

Applying the steady state condition to Eqs.(7), (13) and (14), the concentrations of PQ molecules is described as

$$-\frac{\partial[\mathrm{PQ}]}{\partial t} = R_{tp} = \Phi I_0(1 - \mathrm{e}^{-\varepsilon[\mathrm{PQ}](t)d}). \tag{15}$$

Thus, the temporal variations of PQ component in the illuminated zone is,

$$[\mathrm{PQ}](t) = (\varepsilon d)^{-1} \ln\left[1 + (\mathrm{e}^{\varepsilon d[\mathrm{PQ}]_0} - 1)\mathrm{e}^{-\varepsilon d\Phi' I_0 t}\right]. \tag{16}$$

Introducing Eq.(16) into Eq.(13), the absorbed intensity can be achieved,

$$I_a(t) = \frac{I_0(\mathrm{e}^{\varepsilon d[\mathrm{PQ}]_0} - 1)\exp(-\varepsilon d\Phi' I_0 t)}{1 + (\mathrm{e}^{\varepsilon d[\mathrm{PQ}]_0} - 1)\exp(-\varepsilon d\Phi' I_0 t)}. \tag{17}$$

When a light beam with an intensity of I_0 is incident normally onto the sample, a partial light is absorbed and the remainder is transmitted, i.e. $I_0 = I_a(t) + I_t(t)$. Then the transmittance $T(t)$ defined as $I_t(t)/I_0$ can be expressed as

$$T(t) = \frac{T_{\mathrm{sf}}}{1 + (\mathrm{e}^{\varepsilon d[\mathrm{PQ}]_0} - 1)\exp(-\varepsilon d\Phi' I_0 t)}, \tag{18}$$

where T_{sf} is a parameter which is related to the scattered and the reflected light, as obtained from Fresnel formulae.

According to the Kogelnik's theory,[20] when the effect of dimensional shrinkage can be neglected during exposure as well as diffraction grating is recorded

at symmetrical geometry, the diffraction efficiency $\eta(t)$ is expressed as

$$\eta(t) = T_{\rm sfa}\sin^2\left(\frac{\pi d\Delta n(t)}{\lambda\cos\theta}\right), \tag{19}$$

where λ is the wavelength of the probe beam, θ is the Bragg matched angle at this wavelength, $T_{\rm sfa}$ is a parameter that takes into account the scattering effects. The refractive index modulation $\Delta n(t)$, which depends on the concentration variety of the reactants between the illuminated and the un-illuminated zones, can be described as[21]

$$\Delta n(t) = \frac{\left(n_0^2+2\right)^2}{6n_0}\left(\sum_{i=1}^{k} R_i\left[\Delta M_i\right](t)\right), \tag{20}$$

where n_0 is the mean refractive index of the material, $[\Delta M_i]$ is the concentration variety of the i-component between the illuminated and the un-illuminated zones, and R_i is the molar refraction coefficient.

In PQ/PMMA photopolymer, the photochemical reaction results in the concentration variety of PQ and nMMA molecules in illuminated zones. The concentration variety of nMMA molecules always accompanies with concentration variety of PQ molecules because the product is PQ–nMMA molecules. Then the contribution of nMMA molecules to the index modulation can be combined with the PQ molecules. Thus, a parameter of synthetic molar refraction coefficient $R_{{\rm PQ},n{\rm MMA}}$ is used to characterize the influence of PQ–nMMA on refraction index. This parameter is related to the average molecular chain length of nMMA. The diffraction efficiency as the function of the temporal variation of the components can be written as

$$\eta(t) = T_{\rm sfa}\sin^2\left(\frac{\pi d R_{{\rm PQ},n{\rm MMA}}(n_0^2+2)^2}{6n_0\lambda\cos\theta}\left((\varepsilon d)^{-1}\ln\left(1+(\mathrm{e}^{\varepsilon d[{\rm PQ}]_0}-1)\exp(-\varepsilon d\Phi' I_0 t)\right)-[{\rm PQ}]_0\right)\right). \tag{21}$$

It can be seen from Eqs.(18) and (21) that there are four dominant parameters (ε, Φ', $T_{\rm sf}$ and $R_{{\rm PQ},n{\rm MMA}}$) in this model, where ε, Φ' and $T_{\rm sf}$ are the function of recording wavelength. These parameters may be related with the polymer components nMMA. In order to analyze this relationship, these values can be obtained by fitting the experimental curves of the temporal variation of transmittance and diffraction efficiency.

4. Experiments and discussion

PQ/PMMA samples were prepared using a typical monomer polymerization technique. The PMMA matrix was formed through polymerization reaction of MMA monomers by making use of thermal initiator zaodiisobutyronitrile (AIBN). The polymerization degree and the average molecular chain lengths of polymers were two crucial parameters to determine material components, which could be adjusted by varying the environmental parameters in the polymerization process according to the Arrhenius theory.[15] We prepared three samples with different polymerization temperatures and time. The number-average molecular weight ($\overline{M_n}$), the weight-average molecular weight ($\overline{M_w}$) and the polydispersity (defined by $\overline{M_w}/\overline{M_n}$) are used to describe the polymerization of MMA monomer. These parameters were measured by the Agilent-1100 Gel permeation chromatograph (GPC) and the corresponding values were shown in Table 1. The concentration of the PQ component in these samples was $[{\rm PQ}]_0 = 1.417\times10^{-4}$ mol/cm^3. The mean refractive index of the samples was $n_0 = 1.493$ and the thicknesses were 1.20 mm for all experiments.

Table 1. Molecular weights of polymers from GPC measurements.

sample number	$\overline{M_n}(\times10^5)$	$\overline{M_w}(\times10^5)$	polydispersity
1	2.0171	4.9825	2.4701
2	1.9401	4.3058	2.2194
3	1.1473	2.5832	2.2516

The experimental setup for measuring the transmitted light intensity was shown in Fig.1. Using a spatial filter and two diaphragms, a 532-nm beam from a DPSS laser was expanded and restricted to a spot in a diameter of 1.5 mm. And then the beam incident normally onto the PQ/PMMA sample. We fixed the incident intensity at 3.63 W/cm^2 and the evolution of transmittance intensity was monitored by a power meter. The experimental data of transmittance for the three samples and the fitted curves using Eq.(18) were shown in Fig.2. The parameters of absorption coefficient, quantum yield efficiency and $T_{\rm sf}$ were obtained by fitting the experimental curves.

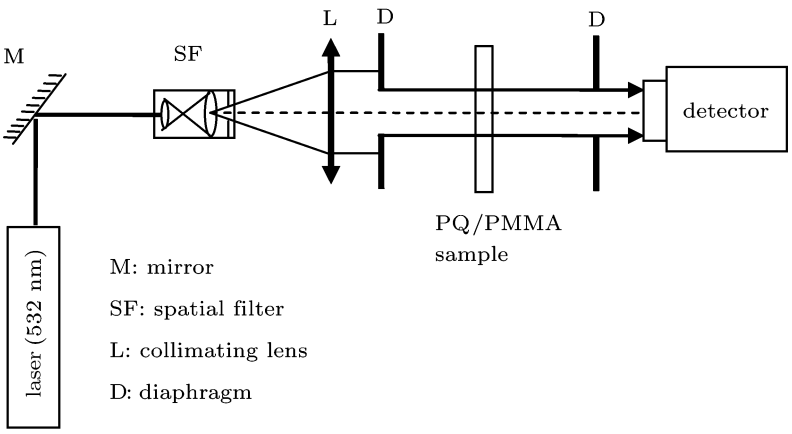


Fig.1. Experimental setup for the transmittance measurement.

Figure 3 shows the two-wave coupling experimental setup. A beam from the same DPSS laser was split into two beams with the equal intensity of 150 mW/cm^2. The holographic grating was recorded in symmetric geometry with the incident angle of $\theta = 18.3°$, corresponding to a spatial frequency of 1170 lines/mm. The diffracted intensity was monitored in real time by a 633-nm beam from a He–Ne laser at the Bragg matched angle. The diffraction efficiency is defined as the ratio of the diffracted light intensity to the incident light intensity. The experimental data are fitted by using Eq.(21) as shown in Fig.4, and the synthetic molar refraction $R_{\mathrm{PQ},n\mathrm{MMA}}$ was obtained.

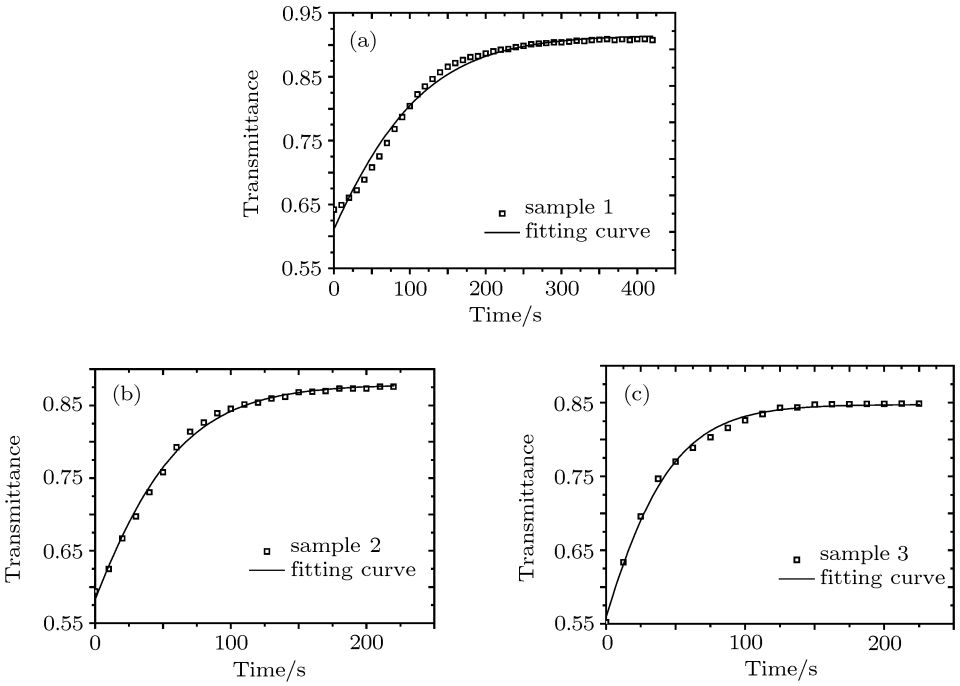


Fig.2. Transmitted intensity as the function of time in (a) sample 1, (b) sample 2 and (c) sample 3. Squared dots show the experimental result; Continuous line shows the fitting result.

It can be seen from Fig.2 and Fig.4 that the theoretical results are consistent with the experimental results. The results for the fitted parameters of the absorption coefficient, quantum yield efficiency, T_{sf} and synthetic molar refraction were shown in Table 2.

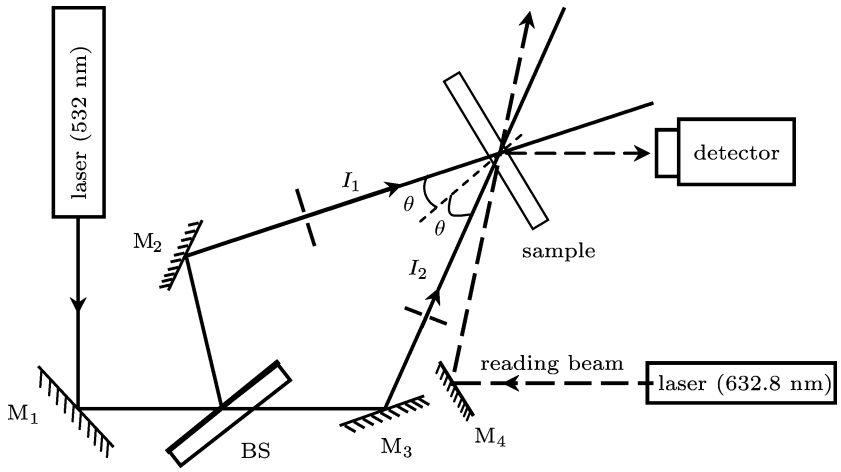


Fig.3. The holographic scheme of two-wave mixing.

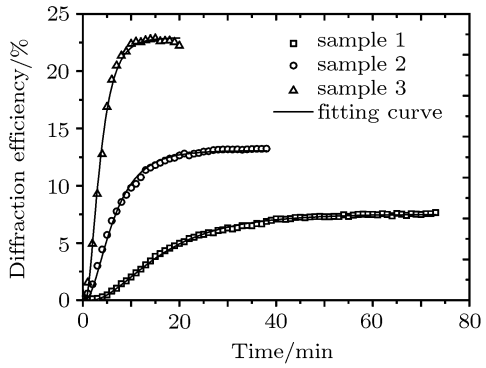


Fig.4. Experimental and fitted diffraction efficiency curves as the function of time.

In Table 2, the average molecular weight decreases with the sample number increases, while the quantum yield efficiency Φ' obviously increase. This result can be explained by the molecules stability. The decrease of the average molecular weight results in the short of average nMMA chain length, which weakens the stability of nMMA molecules and makes the possibility of photochemical reaction increase. As a result, photons of incident light are easily captured and the quantum yield efficiency increases. With the increase of the average molecular weight, the parameter $T_{\rm sf}$, which takes into account the light not transmitted owing to scattering and reflecting, has a little decline. This result implies that the decrease of stability of PMMA matrix will result in the increase of scattering and reflecting. ε represents the absorption of PQ in PMMA matrix and it is similar in the three samples, which is an expected result because the absorption is determined by PQ molecules. It is worthwhile to emphasize that the synthetic molar refraction, which is related to the contribution of molecules chain length to the index modulation, also has no significant change in our samples. This result demonstrates that PQ molecules are major responsible for the index modulation in this medium.

Table 2. The fitted parameters at 532 nm.

sample number	ε ($\times 10^4$ cm^2/mol)	Φ' (mol/Einstein)	$T_{\rm sf}$	$R_{{\rm PQ},n{\rm MMA}}$(cm^3/mol)
1	2.38	0.0156	0.916	25.07
2	2.42	0.0287	0.879	24.65
3	2.42	0.0478	0.840	23.64

5. Conclusions

The photochemical mechanism for the holographic recording in PQ/PMMA polymer was investigated. It has been demonstrated that the diffusion process of PQ molecules during holographic recording is negligible at

room temperature. Analytical expressions for the temporal variation of the transmittance and the diffraction efficiency were achieved. This theory fits the experiment well. By nonlinear fitting, the parameters of the absorption coefficient, quantum yield efficiency, $T_{\rm sf}$ and synthetic molar refraction were obtained. It is found that the average molecular weight mainly affects the quantum yield efficiency. And the study of synthetic molar refraction coefficient demonstrates that the structural transformation of PQ molecules is the main reason for the formation of refractive index modulation in this medium. This model will be beneficial to the optimization of the polymer synthesis and holography application in PQ/PMMA polymer.

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