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Kinetics investigations for holographic Bragg grating based on polymer dispersed liquid crystal*

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This paper investigates the monomer kinetics of polymer dispersed liquid crystal (PDLC) grating. Fourier transform infrared (FTIR) spectra are used in the studies of photoreaction kinetics. The results indicate that there is a relative stable stage arises after a very short initial stage. Based on FTIR studies, the monomer diffusion equation is deduced and necessary numerical simulations are carried out to analyse the monomer conversion which is an important point to improve phase separation structure of PDLC grating. Some simulation results have a good agreement with experimental data. In addition, the effects induced by monomer diffusion constant D and diffusion–polymerization-ratio rate R are discussed. Results show that monomer conversion can be improved by increasing value of D. Besides, a good equilibrium state ($R = 1$) is more beneficial to the diffusion of monomer which is important in the process of phase separation.

Keywords: polymer dispersed liquid crystal, diffusion kinetics, Bragg grating
PACC: 0520D, 4240E

1. Introduction

A bottle-neck problem of polymer dispersed liquid crystal (PDLC) grating is the high threshold voltage, which restricts its applications in optical communication, integrated optics, optical storage and new flat panel display, etc.[1−4] Sutherland *et al* point out that improving phase separation configuration from the investigation of molecular kinetics is the method to decrease the threshold voltage from root.[5] There have been large amounts of experimental studies about the materials effects on kinetics, such as average functionality,[6] surfactant[7,8] and dilution additive.[9] These investigation are helpful for developing the kinetics studies. However, the theoretical explanations of molecular kinetics behaviour have rarely been investigated at present. It is necessary to make clear the kinetic process of PDLC grating and provide some useful guidance according to theory.

Several years before, we have deduced one-dimensional diffusion equation of PDLC grating, some basic results have been obtained. The photoreaction process of monomers and the diffusion process were considered separately in that deduction.[10] However, it is known to us that the monomer diffusion process is companied with the photoreaction, the reason of the diffusion is the concentration differences of monomer which is induced by the photoreaction of the monomer. The two processes are interacted with each other. So it is unprecise to consider that the two are independent in our previous work. In this paper, the photoreaction process is studied through Fourier transform infrared (FTIR), the reaction rate constant is calculated indirectly by using the FTIR results. And then an improved diffusion equation which combines the photoreaction and diffusion together with the diffusion–polymerization-rate ratio R, is deduced. Numerical results of monomer conversion

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at different exposure time are given, which are very close to the experimental results obtained through gravimetric method. In addition, the decisive factors which affect the photoreaction and diffusion of monomer are discussed through numerical analysis of diffusion equation. According to these results, we discuss some ways to increase the monomer conversion and improve phase separation.

2. Photoreaction and diffusion kinetics

2.1. Photoreaction kinetics and the calculation of photoreaction rate constant

For investigating monomer photoreaction kinetics during exposure, the mixture which contains photosensitive monomer and nematic liquid crystal is injected in the LC cell (cell gap, 10 μm), and radiated with a laser beam ($\lambda = 532\,\mathrm{nm}$, $I = 3.6\,\mathrm{mW/cm^2}$). During this process, FTIR spectrum (Bio-Red 3000) is used to test the infrared absorption band of –C = C– (wavenumber = $1636\,\mathrm{cm^{-1}}$) at the exposure time $t = 0$, 1, 5, 10, 15 and 20 min, respectively. The spectra are given in Fig.1.

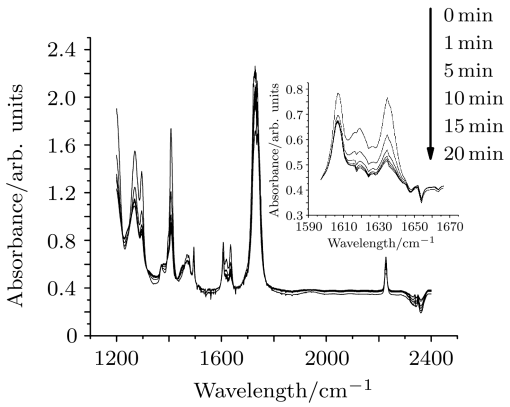


Fig.1. FTIR spectra at 0, 1, 5, 10, 15 and 20 min. The inlet shows the magnified scale at $1636\,\mathrm{cm^{-1}}$ band.

It is evident that the absorbance at $1636\,\mathrm{cm^{-1}}$ band decreases with the exposure time. The absorbance change-rate at 0, 1, 5, 10, 15, 20 min can be calculated through the following equation:

$$A = \left[100 \times \left(1 - \frac{A'_t}{A_0}\right)\right], \tag{1}$$

where A is absorbance change-rate, $A_{t'}$ and A_0 represent the absorbance at time $t = t'$ and $t = 0$, respectively. The results are given in Table 1.

Table 1. Change-rates of absorbance ($1636\,\mathrm{cm^{-1}}$ band) at 0, 1, 5, 10, 15, 20 min.

exposure time/min	0	1	5	10	15	20
A/%	0	39.47	51.41	57.81	60.39	61.78

Then, the curve of change-rate versus time is fitted with the following function:[11]

$$A = K(1 - \mathrm{e}^{-at^2})\left(\frac{t}{t+c}\right), \tag{2}$$

where K, a, and c are fitting parameters.

Combining results listed in Table 1 and Eq.(2), we give the fitted curve in Fig.2, and obtain the fitting parameters simultaneously, where $K = 0.65$, $a = 3175$, and $c = 1.15$.

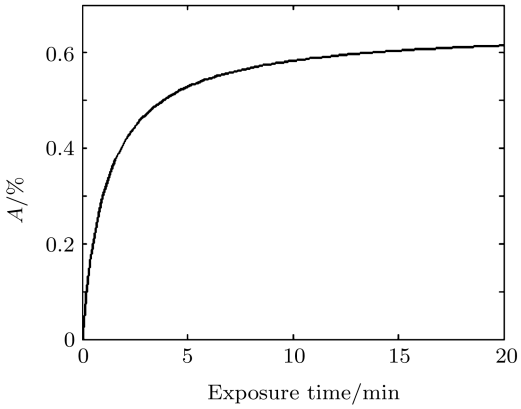


Fig.2. Fitting curve of the change-rate versus the exposure time at $1636\,\mathrm{cm^{-1}}$ band.

According to the fitting results, we can calculate easily the photoreaction rate of monomers under the radiated conditions mentioned above, and express its time dependence as follows:[11]

$$R_\mathrm{p} = K\left[\frac{2at^2\mathrm{e}^{-at^2}}{t+c} + \frac{c(1-\mathrm{e}^{-at^2})}{(t+c)^2}\right]. \tag{3}$$

The dependence of photoreaction rate and time can be calculated through Eq.(3), and result is given in Fig.3. It is shown that the photoreaction rate rises up to $0.8\,\mathrm{s^{-1}}$ quickly at the beginning of the exposure (about 1.2 s after exposure), because the photoinitiator contained in the mixture absorbs the laser energy and products a great number of free radicals which induces the photopolymerization and increases the reaction rate. Because of the consuming of free radicals,

the rate drops down rapidly to a very small value after the mixture is exposed about 2–2.5 min, and decreases continually to $0.0013\,s^{-1}$ when the exposure time reaches 20 min. The reaction rate changes a little from 2.5 min to 20 min. But it changes a lot from the beginning to 2.5 min, however this stage is very short in comparison with the whole exposure process, and our study focuses on the stage from 2.5 min to 20 min, so this short process is neglected in the simulations. For simplifying the deduction of diffusion equation, the average reaction rate at the stage from 2.5 min to 20 min is calculated to substitute the rate in the whole exposure. And its value calculated from Eq.(3) is $0.0036\,s^{-1}$.

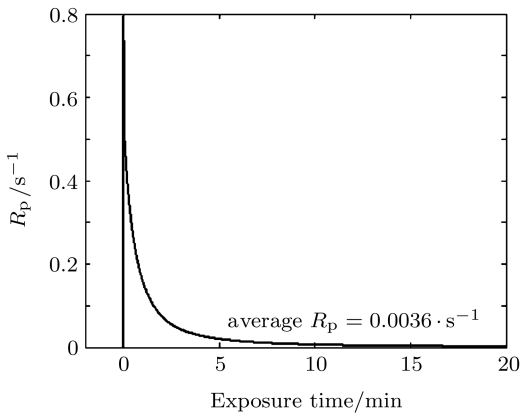


Fig.3. The photoreaction rate curve calculated through Eq.(3). The average rate during the exposure is $0.0036\,s^{-1}$.

For the purpose of diffusion simulations carried out below, it is necessary to calculate the photoreaction rate constant in the exposure. It is well known that the polymerization of monomer relates closely with the amount of free-radical which is determined by the number of photos absorbed by photoinitiator in mixture. In other words, the intensity absorbed by the mixture affects greatly on the reaction rate constant. The absorbed intensity I_{abs} satisfies Lambert–Beer law[12]

$$I_{abs} = I_0[1 - \exp(-2.3\varepsilon[\mathrm{PI}]l)], \tag{4}$$

where I_0 is the intensity of radiation source, ε is the extinction coefficient of the photoinitiator near 532 nm, [PI] represents molar concentration of photoinitiator, and l is thickness of the LC cell. The relationship between reaction rate R_p and rate constant k can be expressed as,[13]

$$R_p = k \cdot [M] \cdot (f_i \times I_{abs})^{\frac{1}{2}}, \tag{5}$$

where $[M]$ is the molar concentration of monomers and f_i is the quantum yield of photoinitiator.

Applying Eqs.(4) and (5), we can calculate the photoreaction rate constant. Assume that the quantum yield $f_i = 0.7$,[5] and $[M]$, [PI] in our mixture are 9.86 mol/L and 3.8×10^{-3} mol/L, respectively. The extinction coefficient of photoinitiator for which Rose Bengal (RB) reported previously, is about $10^4\,(\mathrm{mol \cdot cm})^{-1}$.[14] And $l = 10\,\mu$m, I_0 is $3.6\,\mathrm{mW/cm^2}$. The average photoreaction rate calculated above is $0.0036\,s^{-1}$. Thus, the average reaction constant in the whole process of exposure is $0.0008\,s^{-1}$.

2.2. Diffusion kinetics equation and numerical simulations

The diffusion kinetic equation has been deduced in our previous works. In the deduction of the equation, an assumption has been done, which considers that the polymerization and diffusion of monomers are independent on each other in the whole exposure.[10] Whereas, the polymerization produces the difference of monomer concentration between dark zone and bright zone, such difference promotes the monomer diffusion from high concentration zone to the low. And the diffusion affects the monomer concentration both in dark and bright zones. So the polymerization and diffusion processes are dependent on each other.

Normally, the diffusion of materials induced by difference of concentration is always expressed in the form of Fick diffusion equation,

$$\frac{\partial \phi_M(x,t)}{\partial t} = D\frac{\partial^2 \phi_M(x,t)}{\partial x^2}, \tag{6}$$

where, $\Phi_M(x,t)$ is the concentration of monomer at the position of x and the exposure time t. D represents diffusion constant of monomer.

Considering that the photopolymerization of monomer is companied with the diffusion, we can modify Eq.(6) as,

$$\frac{\partial \phi_M(x,t)}{\partial t} = D\frac{\partial^2 \phi_M(x,t)}{\partial x^2} + \gamma\phi_M(x,t), \tag{7}$$

$$\gamma = -k\left\{2I_0\left(1 + \cos\left(\frac{2\pi}{\Lambda}\right) \cdot x\right) f_i\right.$$

$$\times[1-\exp(-2.3\varepsilon[\mathrm{PI}]l)]\Big\}. \tag{8}$$

The second term, $\gamma\Phi_{\mathrm{M}}(x,t)$, at the right side of Eq.(7) represents the effects caused by photopolymerization. Where, γ is expressed in Eq.(8). I_0 is intensity of radiation, k is polymerization rate constant. [PI], ε and f_{i} represent the molar concentration, the extinction coefficient, and the quantum yield of photoinitiator, respectively. Λ and l are the grating period and cell gap.

Equation (7) is a second order nonhomogeneous partial differential equation. To solve it, some boundary conditions should be set. First, the monomer concentrations at the centres of dark zone and bright zone are considered. At the bright zone centre, the monomer is consumed as the reason of photopolymerization mainly. And at dark centre, it changes because of the diffusion action. Assuming that the monomer concentrations both at dark centre and bright centre have the same form with the Arrhenius equation, we obtain the first boundary condition

$$\phi_{\mathrm{M}}(0,t)=\phi_{\mathrm{M0}}\exp(-at), \quad \text{(Bright zone centre)} \tag{9}$$

$$\phi_{\mathrm{M}}\left(\frac{\Lambda}{2},t\right)=\phi_{\mathrm{M0}}\exp(-bt), \quad \text{(Dark zone centre)} \tag{10}$$

where Φ_{M0} is monomer concentration before exposure, a and b are called the change-rate of polymerization and diffusion, respectively. Define the diffusion–polymerization-rate ratio R,

$$R=\frac{b}{a}. \tag{11}$$

Secondly, before exposure, the mixture is an uniform system. So, monomer concentrations at the arbitrary position are equal each other. So, the other boundary condition is,

$$\phi_{\mathrm{M}}(x,0)=\phi_{\mathrm{M0}}, \quad (0\le x\le \Lambda/2). \tag{12}$$

Combining Eqs.(7) and (8), using boundary conditions (9)–(12), and adopting variable separation approach, we get the Fourier solution of diffusion equation (7) and express it as following:

$$\phi_{\mathrm{M}}(x,t)=\phi_{\mathrm{M0}}\left[\mathrm{e}^{-at}+\frac{2x}{\Lambda}(\mathrm{e}^{-aRt}-\mathrm{e}^{-at})\right]+\sum_{n=1}^{\infty}\left\{\frac{2(1-\cos(n\pi))\phi_{\mathrm{M0}}}{n\pi}\times M\sin\left(\frac{2(n\pi)}{\Lambda}\right)x\right\}, \tag{13}$$

$$M=\left[\frac{\left(\dfrac{2x}{\Lambda}+1\right)(\gamma+a)}{L-a}\right][\mathrm{e}^{-at}-\mathrm{e}^{-Lt}]-\left[\frac{\dfrac{2x}{\Lambda}(\gamma+aR)}{L-aR}\right][\mathrm{e}^{-aRt}-\mathrm{e}^{-Lt}], \tag{14}$$

$$L=\left(\frac{\Lambda}{2n\pi}\right)^2 D-\gamma. \tag{15}$$

At the centre of bright zone, the following expression should be satisfied,[10]

$$\begin{aligned}&\frac{\partial\phi_{\mathrm{M}}(0,t)}{\partial t}=\gamma\phi_{\mathrm{M}}(0,t),\\&\phi_{\mathrm{M}}(0,t)=\phi_{\mathrm{M0}}, \quad (t=0),\\&\phi_{\mathrm{M}}(0,t)=0, \quad (t=\infty).\end{aligned} \tag{16}$$

Thus, we obtain

$$\phi_{\mathrm{M}}(0,t)=\phi_{\mathrm{M0}}\exp(\gamma t). \tag{17}$$

Let $I_0=3.6\,\mathrm{mW/cm^2}$, $k=8\times10^{-4}\,\mathrm{s^{-1}}$, $\Lambda=1\,\mu\mathrm{m}$, $\varepsilon=10^4\,(\mathrm{mol\cdot cm})^{-1}$, $[\mathrm{PI}]=3.8\times10^{-3}\,\mathrm{mol/L}$, $l=10\,\mu\mathrm{m}$, $\Phi_{\mathrm{M0}}=0.7$. Use Eq.(17), calculate the monomer concentration at the position $x=0$ from $t=2.5\,\mathrm{min}$ to $20\,\mathrm{min}$, and record the results once per minute. Then fit the results in the form of Eq.(9), the value of "a" is obtained, $a=0.0075$. Substitute it into Eq.(13), let $R=1$, and assume $D=10^{-11}\,\mathrm{cm^2\cdot s^{-1}}$.[10] The values of other parameters are the same as above, thus, the distribution of monomer at the time $t=3$, 6, 10, 15, 20 min are numerically simulated by computer. In simulation, the summation term is added from $n=1$ to $n=360$ for approximation, restricted by the calculation capability of the computer. Figures 4(a) to 4(e) are the results of simulation. The little fluctuation in these figures is the reason of summation approximation, and some large fluctuations near $x/\Lambda=0.5$ are the reason of the sinusoidal summation which is not convergent at that position. That is a pure mathematical reason. It is evident in Fig.4 that the monomer concentration

decreases as the increasing of the exposure time, and when the time reaches 20 min, the residual monomers in bright zone ($0 \leq x/\Lambda \leq 0.25$) are less than 10%.

To analyse the monomer conversion after exposure at bright zone, average monomer concentrations are calculated by the following equation:

$$\bar{\phi}_{\mathrm{M}} = \frac{4}{\Lambda} \int_0^{0.25} \phi_{\mathrm{M}}(x,t) \mathrm{d}\left(\frac{x}{\Lambda}\right). \tag{18}$$

The results are given in Fig.5. And it is found that the average monomer concentration in bright zone is only 0.06 when the exposure time is 20 min. Define monomer conversion to be $(\phi_{\mathrm{M0}} - \bar{\phi}_{\mathrm{M}})/\phi_{\mathrm{M0}}$. Thus, when $t = 20$ min, the monomer conversion at bright zone reaches 91.4%. Such a result is high enough for a good phase separation, and is helpful for the improving of PDLC grating's electro–optical (E–O) properties.

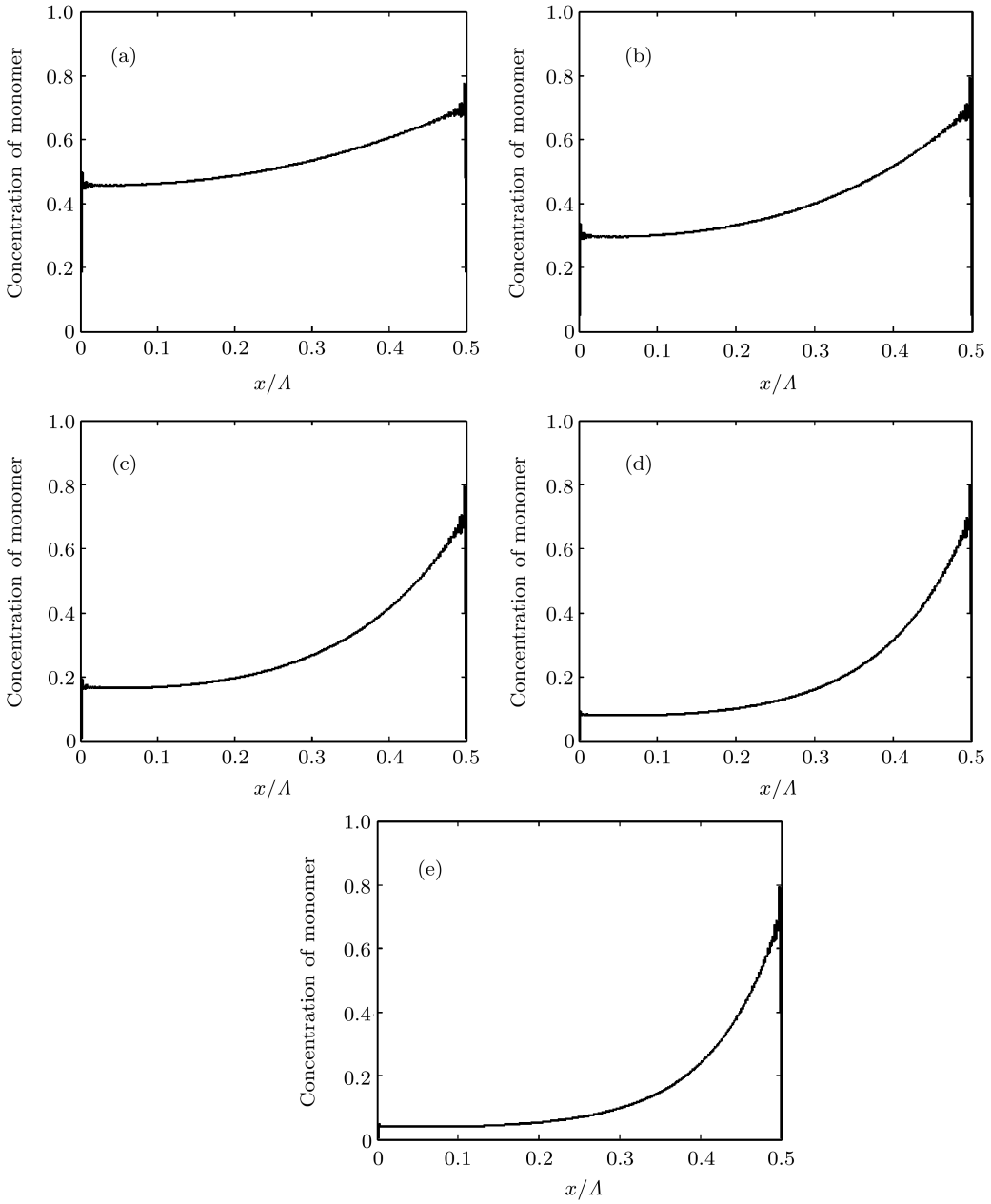


Fig.4. Monomer concentration distribution at the exposure time t is 3 min (a), 6 min (b), 10 min (c), 15 min (d), and 20 min (e).

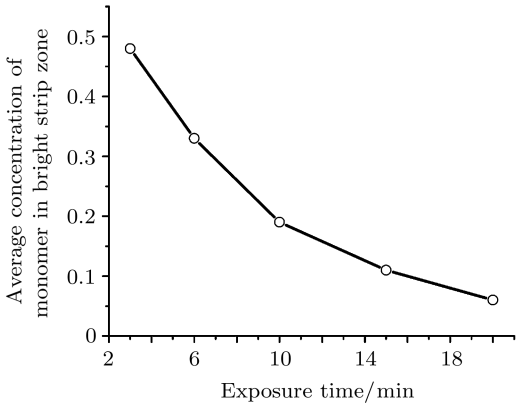


Fig.5. The average monomer concentration in the bright zone.

3. Experiments

In order to express the rationality of the diffusion equation, monomer conversions are measured and compared with our theoretical results. In experiments, we use single beam with 532 nm wavelength to radiate the mixture under the same conditions mentioned in the theory. And then measure the monomer conversion. Because the cross-linked polymer formed in the experiment cannot dissolve in tetrahydrofuran, chloroform or the other normal solutions, so the monomer conversion cannot be tested through gel permeation chromatography (GPC). Thus, chemical gravimetric method is adopted. The steps of gravimetric approach are listed below.

a) Measure the masses of LC cell without mixture (M_0) and the same cell with mixture (M_1). The mixture mass is obtained $M_1 - M_0$. The mixture is mixed through the LC/monomers = 3:7, therefore, the monomer mass before exposure is $0.7(M_1 - M_0)$.

b) Exposing the mixture with the laser for about 20 min. Immerse the polymer film in the alcohol for about 24 h to extract the LC and some residual monomers contained in the polymer, and then blow-drying it with pure nitrogen in the clean bench.

c) Considering a part of monomers which are surrounded by the cross-linked polymer and cannot dissolve in alcohol, we scrunch the film as the powder, then re-immerse it in the pure alcohol for about 24 h.

d) Put the powder in centrifuge and then obtain cross-linked polymer powder.

e) Drying polymer powder under the temperature of 50°C for about 1 h. (The temperature cannot over 150°C for avoiding some thermo-reactions).

f) Then, weigh the mass of the dry powder and obtain the polymer weight (M_2).

g) Finally, the monomer conversion is calculated, $M_2\ /(0.7(M_1 - M_0))$.

From experiments, the monomer mass before exposure is 18.22 mg, and the polymer powder mass tested is 16.12 mg. Thus, the monomer conversion is 16.12/18.22 = 88.4%, which is only 3% discrepancy with theoretical value obtained through diffusion equation. This discrepancy might come from the following points: (1) The small instability of the exposure intensity, which affects the polymerization of monomers; (2) The intensity distribution of a laser beam is of Gaussian form, so intensities of edge and the centre are unequal in fact, whereas it is considered as equal in the theory; (3) There are some unpredictable errors in the measurements.

4. Discussions

Monomer conversion is a very important point in the preparations of PDLC grating. A higher monomer conversion leads to a higher cross-linked density which promotes the phase separation. Applying the diffusion kinetics equation, we discuss the effects which brought by monomer diffusion constant D and diffusion–polymerization-rate ratio R on the monomer conversion. The methods to enhance the monomer conversion are analysed qualitatively.

Supposing that all the other parameters are invariable, we only change the value of monomer diffusion constant. Then the monomer concentration distributions at $t = 20$ min are simulated through Eq.(13). The initial values of parameters in Eq.(13) are the same with above. We find in simulation results (Fig.6) that the monomer concentration decreases as the increasing of monomer diffusion constant. When $D = 10^{-9}\,\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, the concentration is near zero. That is because the monomer diffuses easily in the mixture with large diffusion constant, so more monomers can diffuse from dark zone to bright zone with fewer blocks.

To increase monomer diffusion constant, one effective way is to dilute the mixture with some dilutions, such as n-vinylpyrrolidone (NVP). White *et al* have obtained the Bragg grating with good E–O properties through the adding of NVP.[9] Liu *et al* have also obtained a smooth phase separation inter-

face through di-functional Neopentyl glycol diacrylate (it is another acrylate monomer with good diffusion characteristic).[15] The other way is to increase environment temperature to enhance kinetic property of monomers. The method has also approved by Song *et al.*[16]

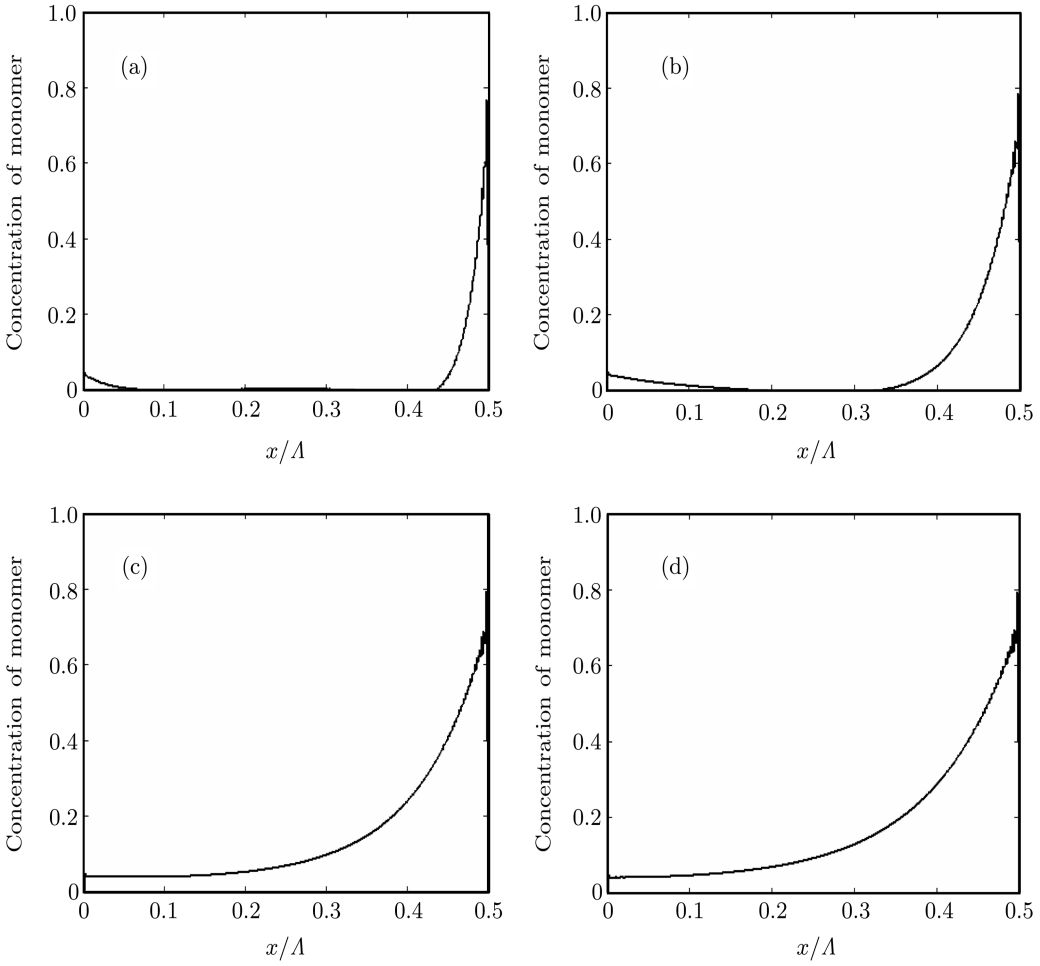


Fig.6. Monomer concentration distribution at $t = 20\,\text{min}$ under the different diffusion constant. $D = 10^{-9}\,\text{cm}^2\cdot\text{s}^{-1}$ (a), $D = 10^{-10}\,\text{cm}^2\cdot\text{s}^{-1}$ (b), $D = 10^{-11}\,\text{cm}^2\cdot\text{s}^{-1}$ (c), and $D = 10^{-12}\,\text{cm}^2\cdot\text{s}^{-1}$ (d).

The diffusion–polymerization-rate ratio R is the parameter which relates monomer diffusion and polymerization together. Assuming that reaction rate constant and diffusion constant are invariable, the simulations with different R values are carried out, and shown in Fig.7. An interesting point that we found in Fig.7: the monomer concentration in the bright zone is higher than that in dark zone when $R = 2$, 3, and 4, and the differences increase with the increase of R. That is because the diffusion is quickly than polymerization in those cases which leads to a great many of monomers accumulated in bright zone and cannot be consumed on time. These are not benefit for the phase separation of PDLC grating and its E–O properties, undoubtedly. When $R = 1$ (shown in Fig.7(a)), there is a good equilibrium constructed between diffusion and polymerization. If the diffusion constant of mixture is small, it should be exposed with a lower intensity beam to realize the equilibrium between diffusion and polymerization. Contrarily, if the diffusion constant is large, thus the high intensity exposure should be adopted. Some ways can be used to modulate the system which reaches equilibrium. Except for the changing of monomer diffusion constant and environment temperature, the concentration of photoinitiator is another aspect. In the case of a large diffusion constant, this concentration increases correspondingly. And the concentration should decrease if the diffusion constant of the mixture is small.

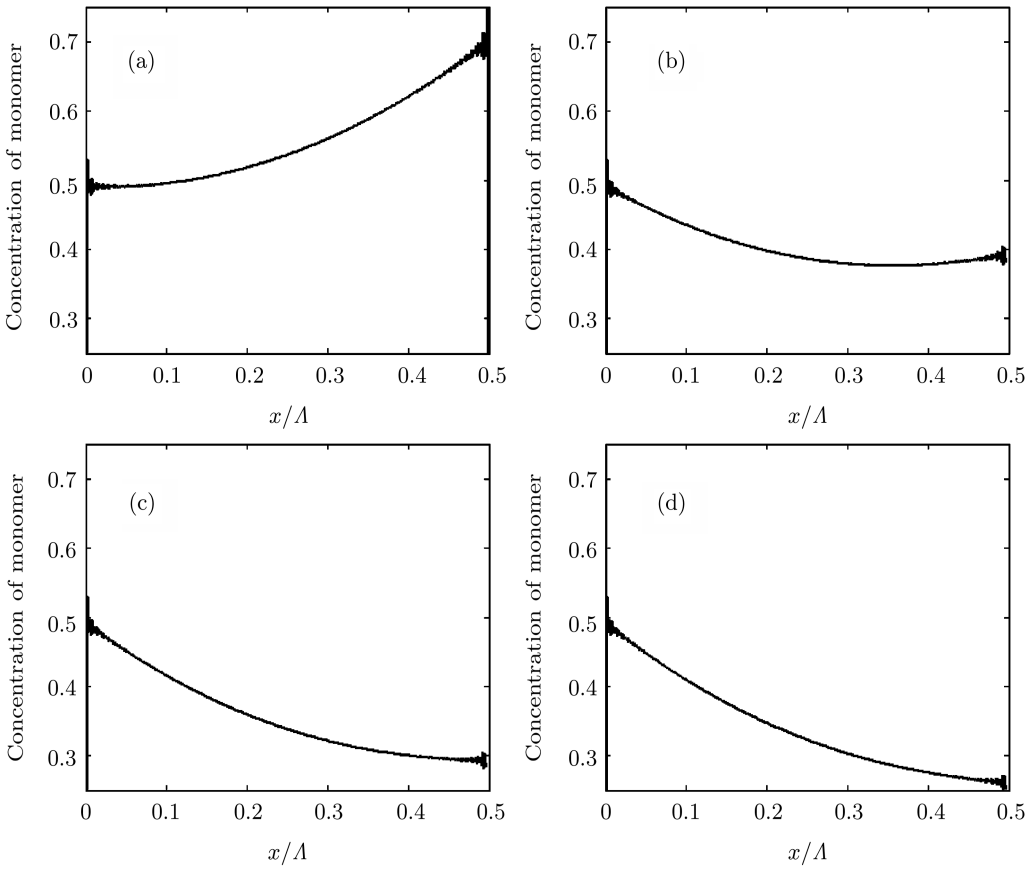


Fig.7. The monomer concentration distribution at $t = 2.5$ min, with different diffusion–polymerization-rate ratios. $R = 1$ (a), $R = 2$ (b), $R = 3$ (c), $R = 4$ (d).

5. Conclusions

We have carried out the kinetic investigation of Bragg grating based on PDLC. FTIR spectrum is used to photoreaction studies. Through the results, it is indicated that the reaction rate rises up in a considerable short time (the total time of rise up and drop down is about 2–2.5 min which is only 1/10 of the whole exposure time), then drops down and stabilizes at a small value. That is to say, there is a relatively stable status after that stage. So, it is meaningful to investigate the kinetics at the stable stage. The photoreaction rate at such stable stage is $0.0036\,\mathrm{s}^{-1}$, and the corresponding rate constant calculated is $0.0008\,\mathrm{s}^{-1}$. Besides, an amendatory diffusion equation is obtained. In this equation, the interaction problem between polymerization and diffusion processes is resolved, and the Fourier solution of the equation is given. Based on diffusion equation solutions, some numerical simulations are carried out from three aspects: 1) monomer concentration affected by exposure time; 2) effects of monomer diffusion constant on concentration; 3) equilibrium between photoreaction and diffusion. It is indicated that the monomer conversion when the exposure time is 20 min is 91.4% from the theory. The result shows the great agreement with experimental data, which is 88.4%. The effects brought by mixture's diffusion constant D and diffusion–polymerization-rate ratio R are also discussed. Simulation shows that a higher monomer conversion can be obtained when D is large ($D = 10^{-9}\,\mathrm{cm}^2/\mathrm{s}$). Such results point out that monomer conversion can be improved by increasing the diffusion constant. In addition, the equilibrium of the diffusion and polymerization is a decisive point. When $R = 1$, the system reaches equilibrium state which is beneficial to the improvement of monomer conversion.

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