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Polymerization kinetics of 10,12-pentacosadiynoic acid monolayer and possible acceleration effect of visible light

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Abstract

The molecular area change of 10,12-pentacosadiynoic acid (PDA) monolayer was recorded and large molecular area expansion was observed during UV-polymerization. The expansion speed experienced a quick increase to maximum and then a steady decrease to zero and finally the area change was converted into a slow contraction. The rate of molecular area change depended on the reaction temperature. Turning off the UV-light during the experiments resulted in area contraction. The contraction speed was described with a kinetic equation, which suggested an accompanied area relaxation during the polymerization. A model for the reaction kinetics (both based on the polymerization and the area relaxation) was proposed and well corresponded to the experimental data. By using this model, the 'activation area' was calculated to be 0.127 nm^2 which was little dependence of the reaction temperature. The positive activation area during the monolayer polymerization indicated that there was an increase in area when the activated complex was formed. The rate constant decreased upon elevated surface pressure. The possible effect of visible-light on the monolayer UV-polymerization was investigated in detail by periodically switching on and off the visible light while keeping the UV-light on. An acceleration phenomenon of the visible light on the monolayer UV-polymerization was observed. The acceleration effect was illustrated by the polymerization mechanism and the electronic state of the polymerization intermediates.
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Keywords: 10,12-Pentacosadiynoic acid; Langmuir monolayer; Polymerization kinetics

1. Introduction

In comparison to the polymerization in three-dimensional state, the monolayer polymerization in two-dimensional state exhibits its special characteristics. For instance, some monomers, which cannot be polymerized in three-dimensional state, however, can be polymerized in two-dimensional state [1]. Some polymerization reactions with induction period in three-dimensional state may happen immediately without any induction period in two-dimensional state [2,3]. It is able to produce a new generation of polymers by means of polymerization in two-dimensional state. Due to high-developed electronic techniques and great progress in computer science, the study of polymerization reaction by Langmuir–Blodgett (LB) technique has been directed to a microscopic and quantitative measurement [1,2]. The monolayer polymerization is monitored in a molecular scale during the polymerization. The Langmuir balance is a two-dimensional polymerization reactor (area–dilatometer under a constant surface pressure indeed) which is capable of monitoring polymerization in two-dimensional state on molecular level in detail. Nowadays, the LB technique is used to study polymerization process of reactivated amphiphilic monomers in two-dimensional state and to design a new generation of superstructures.

The linear diacetylene, $R_1–C{\equiv}C–C{\equiv}C–R_2$, and its derivatives play an important role in film forming monomers because of their reactivity in solid state, the absence of protruding 'bulges' and their ability to substitute by a length of alkyl chain without interfering with the molecular packing [3]. Moreover, the diacetylenes exhibit characteristic electronic [4,5] and optic [5,6] properties. Extensive attention had been paid to the polymerization of the diacetylene monolayer [7–10] and multi-layer [10–12]. We have previously shown that the polymerization of the PDA monolayer upon UV-light was surface pressure and temperature dependent [3]; the apparent activation energy

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was estimated and the relationship between the activation energy and the applied surface pressure was discussed therein.

The polymerization kinetics of diacetylene has been studied extensively [13,14]. It is known as a multi-step process where an activated center is produced first followed by a quick formation of the polymer chains. This process is described as a first order rate equation [15]. Some diacetylene monomers in crystals polymerize with acceleration-self phenomena [16,17], whereas monolayer and LB films do not [18]. Therefore, it is of a great importance to study polymerization kinetics in two-dimensional state.

The polymerization kinetics of diacetylene monolayer differs from the two current kinetic models proposed for polymerization [19,20] in two-dimensional state. Hofmann and Peltonen [21] also shown the reaction kinetics of the diacetylenic UV-triggered photo-polymerization by the in situ absorption measurements and determined that the rate constant for a first order consecutive reaction (monolayer to blue polymer to red polymer). This was in agreement with the results from Lio et al. [22], where the nature of the spectral shift was analyzed by a slight rearrangement in the packing of the polymer crystal. In the present study, we described the polymerization kinetics of diacetylene monolayer by a more direct method of LB technique. The concept of area relaxation is introduced and a new kinetic model is proposed to elucidate the mean area change during the experiment. The model described the change of molecular area during the two-dimensional polymerization and calculated the rate constant and activated area of polymerization reaction. The simulated curves corresponded to the experiment data obtained here. Furthermore, evidence is accumulating on the possible effect of visible light on diacetylene monolayer polymerization. In this paper, we investigated the acceleration effect of visible light on the UV-polymerization of diacetylene monolayer and proposed a probable mechanism to interpret the experimental facts.

2. Experimental section

2.1. Materials

The monomer 10,12-pentacosadiynoic acid (PDA), light-gray microcrystals, $CH_3-(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8-COOH$, was purchased from ABCR GmbH (Karlsruhe, Germany) and purified with chloroform for recrystallization before used. The PDA was dissolved in A.R. grade chloroform and the concentration of PDA solutions used here is 0.5 mg/ml. The PDA solution was protected against exposure to natural light and stored in a refrigerator. Subphase solutions were prepared with $CdCl_2$ (A.R. grade) and double distilled water (prepared by SYZ-A type Quartz sub-boiling distiller, pH 5.8) with the concentration of 4×10^{-4} M.

2.2. Langmuir film balance

A homemade computer-controlled film balance was used to carry out all the experiments. The surface pressure was measured with Wilhelmy Pt-plate that was carefully pre-wetted and zeroed in a clean subphase prior to measurement. A special program was designed to perform the kinetic experiment of polymerization, i.e. recording the barrier speed as a function of time and the change of the mean molecular area during UV-irradiation at a constant surface pressure. The Langmuir trough (40×15 cm^2) was placed in a dust-free and nitrogen-full box, and protected against natural UV-light with opaque plastic sheets. The box was temperature controllable (± 0.2 °C). A 20 W low-pressure Hg lamp with $\lambda = 254$ nm hung 12 cm above the monolayer and was used for UV-irradiation. A 300 W Xe lamp (filtrated with a 420 nm filter) was used as visible light lamp-house.

2.3. Experimental procedure

A computer was used to record the change of surface pressure versus mean molecular area. The PDA monolayer polymerization was performed in situ on the Langmuir trough under a constant surface pressure. A known amount of PDA chloroform solution was spread onto the subphase. After 20 min for solvent evaporation, the PDA monolayer was then compressed (9 mm/min) to a designed surface pressure that was kept constant throughout the polymerization by moving the barrier forwards and backwards. After several minutes of stabilization period to regulate the surface pressure, the UV-irradiation polymerization was started by switching on the UV-lamp and both mean molecular area and average barrier speed were recorded as a function of time. The time switching on the UV-lamp was taken as zero polymerization time. The visible light lamp-house switching on and off periodically under UV-irradiation was used to study its effect on the UV-polymerization of PDA monolayer.

2.4. Spectra measurements

A Shimadzu UV-240 UV–visible spectroscopy and a Hitachi 850 Fluorescence Spectrophotometer are used, respectively, to measure the UV–visible absorption spectra and photo-induced emission spectra of the LB films. The wavelength of excitation light for emission spectra measurement is 380 nm.

3. Results and discussion

3.1. Polymerization of PDA monolayer upon UV-irradiation

The indication of polymerization of diacetylene PDA monolayer came from the following facts: (1) The barrier

speed increased to a maximum when irradiating the monolayer with UV-light and dropped down immediately when the UV-light was turned off; (2) After polymerization, by sweeping the surface carefully, a very small amount of red solid residue could be collected; (3) The color of PDA monolayer changed from colorless to red after irradiation, which was a powerful proof of the polymerization of the PDA monolayer. UV–visible absorption and photo-induced emission spectra of the polymers (collected by sweeping the surface carefully after polymerization) are shown in Fig. 1. The wavelength of excitation light for emission spectra measurement was 380 nm. There were two absorption peaks, one at 480 and the other at 528 nm, which were similar to the absorption founded in the corresponding polymerized monolayer at 503 and 540 nm [7]. The absorption was slightly shifted toward the shorter wavelength region because the polymer monolayer was under different stress state [2324]. Moreover, the fluorescence maximums were observed at 620 nm, indicating that the conjugated polymer had been formed because no fluorescence of PDA monomer was detected at this region.

The polymerization kinetic curve, i.e. the barrier speed and mean molecular area change of PDA monolayer under the 10 mN/m constant surface pressure are shown as a function of UV-irradiation time in Fig. 2. Immediately after exposure to the UV-lamp, the barrier moved backwards rapidly and the mean molecular area expanded. The barrier reached a maximum expansion speed of 23.5 mm/min at 1.75 min and then slowly moved backward. The area expansion speed reduced to zero at 7.5 min, then the mean molecular area of the monolayer started to contract. The barrier speed reached to a plateau at 4.5 mm/min and remained constant. The value of barrier speed represented the change of the mean molecular area, i.e. some physical or chemical reaction had happened within the monolayer. During the first 7.5 min expansion, the mean molecule area increased from 0.268 to 0.373 nm^2 (39%). After 7.5 min, the mean molecule area began to contract. Therefore, the polymerization of PDA monolayer in two-dimensional state is neither a pure area expansion process nor pure area contraction process, but a complicated process with rapid expansion and slow contraction.

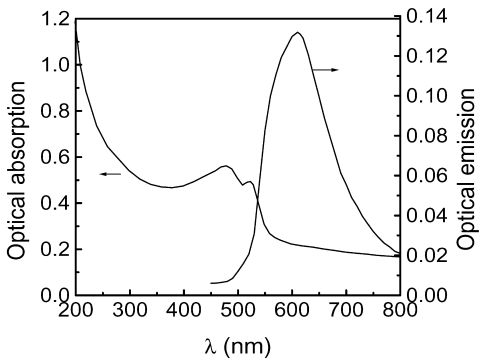

Fig. 1. UV-visible spectra of the polydiacetylene.

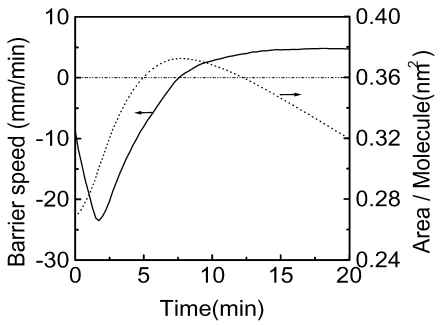

Fig. 2. Barrier speed and mean molecular area vs. time during the polymerization of PDA monolayer under the surface pressure of 10 mN/m and at 20 °C.

The expansion processes during polymerization was not simply due to formation of the shape of polydiacetylene chain, but also due to the significant angle changes in the chain links of the conjugated polymer. As shown in Fig. 2, we calculated the mean molecular area of the ordered PDA monomer to be 0.256 nm^2, and the distance between the unpolymerized monomers was 0.506 nm. Enkelmann [25] had shown that the distance between the chain links of the conjugated polymer after polymerization was 0.49 nm. Thus, a decrease in the mean molecule area during the polymerization is needed. In our case, the mean molecular area increased from 0.268 to 0.373 nm^2 during the first time period of 7.5 min. Since the distance between the polymer chain links could not be changed, the expansion should be ascribed to deviation of the chain links from the vertical state. After 7.5 min, the mean molecular area of PDA monolayer began to contract. In order to understand the fact of the contraction change, the UV-light was switched off while recording the change of barrier speed during the experiments. For the first minute of UV-irradiation, the barrier moved backwards quickly, i.e. the mean molecular area expanded rapidly. The UV-light was switched off after 1 min of irradiation, and the barrier changed its moving direction from backwards to forward immediately, i.e. the mean molecular area from expansion to contraction. The barrier speed reduced to zero in 2 min (Fig. 3). Apparently, the polymerization reaction should be terminated immediately after the UV-lamp has been switched off due to the short life of the radicals. Therefore the following contraction is an independent process of the polymerization in two-dimensional state. It is proposed that the rapid change of area occupied by every repeat unit of the chain (the area was expanding here) can be compensated by the rearrangement of repeat unit in the chain. We named this process as an area relaxation which obeys the exponent attenuation law. The change of the mean molecular area of PDA monolayer during the polymerization consists of two parts, i.e. the change of area arising from polymerization directly and the following accompanied area relaxation.

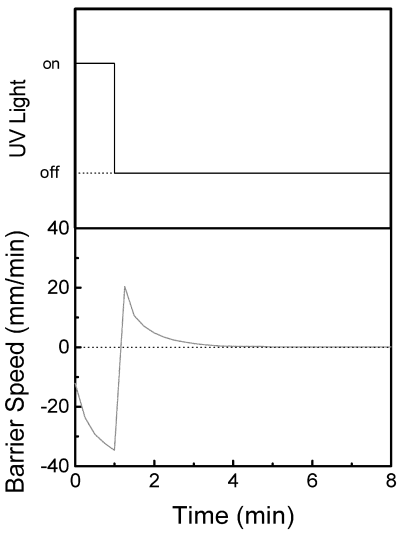

Fig. 3. Barrier speed vs. time during the polymerization of PDA monolayer. The UV-light was switched off after one minute's irradiation under the surface pressure of 5 mN/m and at 20 °C.

3.2. Kinetic model of polymerization in the two-dimensional state

Two polymerization kinetics theories are available in two-dimensional state [13,14]. However, they are not suitable for treating with the simple area change and do not explain the experimental facts presented here. Therefore, it is necessary to create a new model to describe the polymerization kinetics of the PDA monolayer in two-dimensional state.

Supposing that the number of PDA molecules before polymerization is N_0, the number of the remaining PDA molecules at time t during polymerization is N_t, the transient change of area arising from connecting one PDA molecule onto the polymer chain is α_1, thus the change of area arising from polymerization at time t is $\alpha_1(N_0 - N_t)$. If the area relaxation obeys the exponent attenuation law, the area should be $\alpha_2 \exp(-K_2\tau)$ (where α_2 is the change of area caused by one polymerized PDA molecule during long time τ and K_2 the relaxation rate constant). The change of area arising from relaxation after polymerization during the time τ is $\alpha_2\,[1 - \exp(-K_2\tau)]$, thus the total change of area due to relaxation is

$$\int_0^t \alpha_2\left(-\frac{\mathrm{d}N_\tau}{\mathrm{d}\tau}\right)(1 - \mathrm{e}^{-K_2(t-\tau)})\mathrm{d}\tau \tag{1}$$

If A_0 and A_t are the total areas of monolayer before polymerization and at time t during polymerization, the total change of area of monolayer at time t is

$$A_t - A_0 = \alpha_1(N_t - N_0) - \int_0^t \alpha_2\left(-\frac{\mathrm{d}N_\tau}{\mathrm{d}\tau}\right)(1 - \mathrm{e}^{-K_2(t-\tau)})\,\mathrm{d}\tau \tag{2}$$

where the difference is accepted due to the change of area arising from relaxation and the change of area arising from polymerization are opposite, and in fact it depends on the positive or negative value of the parameter α_2. The negative sign is taken for convenience.

If both sides of the Eq. of (2) are divided by N_0, we obtained the following:

$$a_t - a_0 = \alpha_1(1 - \xi_t) + \int_0^t \alpha_2 \frac{\mathrm{d}\xi_\tau}{\mathrm{d}\tau}(1 - \mathrm{e}^{-K_2(t-\tau)})\mathrm{d}\tau \tag{3}$$

where $\xi_t = N_t/N_0$ is the percent of un-reacted PDA monomer molecules at time t, a_0 and a_t the mean molecule area before polymerization and at time t during polymerization, respectively, and can be obtained from the experimental data directly.

In general, the polymerization kinetics of diacetylene can be described as a first order rate equation [13]:

$$\xi_t = \mathrm{e}^{-K_1 t} \tag{4}$$

where K_1 is a polymerization rate constant, thus

$$a_t - a_0 = \alpha_1(1 - \mathrm{e}^{-K_1 t}) - \int_0^t \alpha_2 K_1\, \mathrm{e}^{-K_1\tau}(1 - \mathrm{e}^{-K_2(t-\tau)})\,\mathrm{d}\tau \tag{5}$$

After calculating the convolution integral and simplifying, the following model was obtained

$$a_t = (\alpha_1 - \alpha_2) - \left(\alpha_1 - \alpha_2 + \frac{\alpha_2 K_1}{K_1 - K_2}\right)\mathrm{e}^{-K_1 t} + \frac{\alpha_2 K_1}{K_1 - K_2}\mathrm{e}^{-K_2 t} + a_0 \tag{6}$$

where α_1 and α_2, K_1 and K_2 are constants and can be determined by the fitting of Eq. (6) and actual change of area. a_t is the change of area recorded from the experiment. As a limiting case $a_{t=0} = a_0$ when $t = 0$ and $a_{t=\infty} = (\alpha_1 - \alpha_2 + a_0)$ when $t \to \infty$, i.e. the final area occupied by molecules.

The polymerization kinetic curve of PDA monolayer at 25 °C under a constant surface pressure of 5 mN/m (the dot symbol) and its fitting curve (line) with the Eq. (6) are both shown in Fig. 4. The results were in agreement with the fitting curves during the 20 min polymerization, indicating that the kinetic model proposed here successfully described the mean molecular area change of PDA monolayer during polymerization.

3.3. Calculation of 'activation area'

Whalley [26] had used 'activation volume' to expatiate the reaction mechanism and hypothesized that activation volume was a more pivotal criterion for understanding the reaction mechanism. In this paper we calculated the 'activation area' during the polymerization and studied the polymerization reaction mechanism. The advantages of two-dimensional polymerization at air/water interface

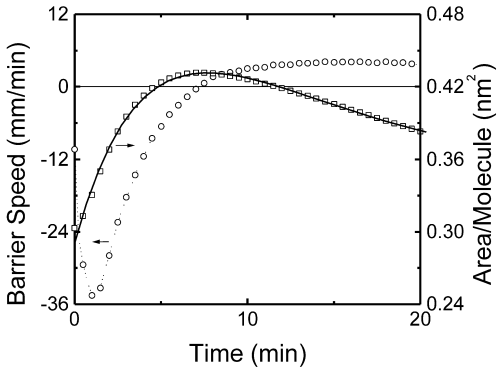

Fig. 4. Barrier speed and mean molecular area vs. time during the polymerization of PDA monolayer under the surface pressure of 5 mN/m and at 25 °C. The fitted mean molecular area curve is also given ($\alpha_1 = 0.3516$, $\alpha_2 = 0.3788$).

included easy calculation of the activation area and pressure changes in two-dimensional state.

The relationship between activation area ΔA and rate constant K_1 is [17]:

$$\ln K_1 = K_0 - \frac{\Delta A \pi}{RT} \tag{7}$$

where π is the surface pressure. The influence of surface pressure on polymerization rate depends on the sign of ΔA. If ΔA is negative, the area decreases during formation of reaction intermediate complex, thus the polymerization will be accelerated when increasing the surface pressure on the contrary, if the ΔA is positive, the area increases during formation of reaction intermediate complex and the polymerization will be decelerated when increasing the surface pressure.

In order to understand the effect of the activation area ΔA and the surface pressure on polymerization rate, a series of polymerization experiments at 10 and 20 °C under different surface pressures were carried out. The polymerization rate curves at 10 °C under four constant surface pressures of 5, 10, 20 and 30 mN/m are shown in Fig. 5. The polymerization in the range of 5–30 mN/m had the character of quick expansion first and slow contraction later. The degree of expansion varied under different surface pressures. Relative

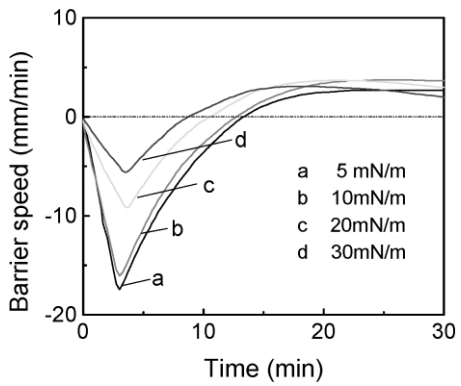

Fig. 5. Barrier speed vs. time during the polymerization of PDA monolayer under various surface pressures and at 10 °C.

area expansion under lower surface pressure was more obvious and the transition from expansion into contraction appeared a little later.

The polymerization reaction rate K_1 of PDA monolayer in two-dimensional state at 10 and 20 °C under five different surface pressures were calculated based on above kinetic model and the values were listed in Table 1. The change of the area relaxation rate constant K_2 with surface pressure was not obvious, but it increased with elevated temperature (see Table 2).

Plots of logarithm of polymerization rate constant, $\ln K_1$, against the surface pressure π are shown in Fig. 6. The activation area ΔA of PDA monolayer in two-dimensional state polymerization can be estimated from the slope of the curves. $\ln K_1$ correlated linearly with π at both temperatures. The reaction rate diminished upon elevated surface pressure, indicating that the area increased in the process of formation of intermediate complex, and corresponded to our experimental results. The slopes of the linear line were −0.0326 (at 10 °C) and −0.0298 (at 20 °C), respectively, and the calculated activation area ΔA was 0.127 nm^2 (at 10 °C) and 0.121 nm^2 (at 20 °C). The positive activation area here indicated that there was an increase in area when the activated complex was formed, and augmented surface pressure should decrease the rate constant. The activation area is independent on the surface pressure and temperature because the temperature did not affect the change of area during the formation of intermediate complex.

3.4. UV-irradiation polymerization together with visible light irradiation

The PDA monolayer was able to be polymerized under UV-irradiation alone (mentioned in Section 3.1) whereas the visible light could not [27]. However, we found that the visible light was able to accelerate the photo-polymerization of the PDA monolayer when the UV-and visible-light were used simultaneously. Since the visible light is not able to initiate the polymerization reaction, the visible light must have some effects on the propagation of the polymer chain.

To our knowledge, the possible effect of visible light on polymerization of diacetylene monolayer has not been reported so far. In order to reveal the effect of the visible light on the UV-polymerization of PDA monolayer, an experiment was designed. The visible light was switched on

Table 1
The polymerization reaction rate K_1 at 10 and 20 °C under different surface pressures

Temperature (°C)	Surface pressure (mN/m)				
	5	10	15	20	30
10	0.0708	0.0579	[a]	0.0411	0.0313
20	0.137	0.116	0.102	0.087	[a]

[a] The polymerization experiments were not done.

Table 2
The polymerization reaction rate K_2 at different temperatures

Surface pressure (mN/m)	Temperature (°C)			
	10	15	20	25
10	0.0569	0.0869	0.122	0.149

and off periodically while the UV-irradiation was kept on all the time. To increase the relative light intensity of the visible light, the Hg lamp hung 20 cm above the monolayer in the experiments. The acceleration of polymerization reaction was observed in the period of time with the visible light on. The correct results could be obtained by this procedure because the comparison was made between two series of time points in one experiment, and any factors that might have effect on the reaction were eliminated except the visible light.

The rate of area expansion per minute in the alternative periods with and without visible light was measured and shown in Fig. 7. The outer envelope of every bar was similar with the polymerization kinetic curve and the value increased from a certain initiate one to a maximum, i.e. the polymerization speed reached to a maximum, then decreased slowly down to zero. The only difference between the normal kinetic curve and the envelope was the time period of expansion process extended from 7.5 min as in Fig. 2 to 12 min as shown here. In Fig. 7, the solid bars represented the rate of area expansion without any visible light irradiation and the diagonal bars express the rate of area expansion together with visible light irradiation. All bars consisted of group steps with regular odd–even jump corresponding to the UV-irradiation with and without visible light irradiation. The jumps of rate of area expansion from the diagonal bars to the solid bars were always larger than that from the solid bars to the diagonal bars, indicating that the area expansion with visible light irradiation was larger, i.e. the visible light irradiation indeed accelerated the polymerization reaction.

The solid line in Fig. 7 was an envelope obtained from connecting every top center of the bars without any visible

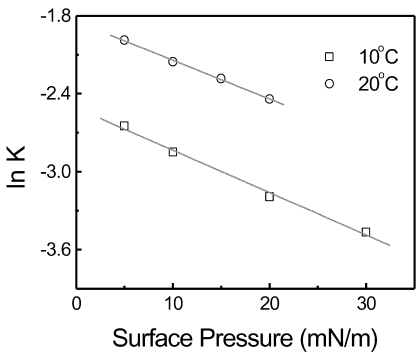

Fig. 6. ln K_1 vs. surface pressure for monolayer polymerization at 10, 20 °C. A linear regression method was used to draw a straight line from experimental data.

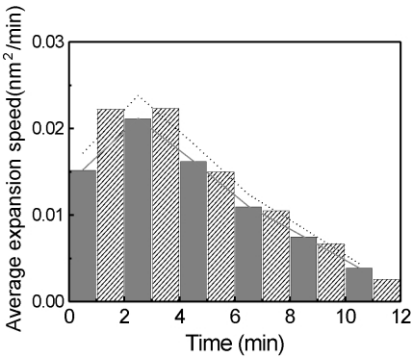

Fig. 7. Average expansion speed vs. time during periodic visible-irradiation on the UV-polymerization of PDA monolayer at the surface pressure of 10 mN/m and at 20 °C.

light irradiation, which represented the change of polymerization reaction rate. The dashed line was the line with another 1/8 added onto every point of the solid line and was almost in concordant with the envelope obtained from diagonal bars together with visible light irradiation. Therefore we conclude that the visible light irradiation accelerates the polymerization reaction up to 1/8. The effect of the acceleration was more obvious in the region of high rate. It has been reported that [23], the photo-initiation of polymerization reaction depends on the exciting of monomer and the wave length should be less than its absorption peak position of 310 nm. After formation of dimer there are two ways to propagate the chain. One is the energy transfer from an excited monomer to polymer chain. The light is in the UV-region and the process is a competition between chain initiation with propagation. The other is excitation of the polydiacetylene chain directly. The essential exciting energy decreases with increasing of the polydiacetylene chain length. It is well known that when the numbers of repeat unit are more than 5, the excitation wave length is about 550 nm for polydiacetylene crystal [27]. The wavelength of the visible light used here was lower than 550 nm and this might be the reason of possible acceleration effect of visible light on the polymerization of PDA monolayer.

4. Conclusion

UV-irradiation polymerization of PDA monolayer is a process with a first quick area expansion and a final slow area contraction. Immediately after switching off the UV-light, the area expansion disappeared and changed to contraction. The area expansion was ascribed to the significant angle changes of the chain links of the conjugated polymer and the area contraction was referred to the relaxation process of the polydiacetylene monolayer which was caused by a slight rearrangement in the packing of the polymer crystal. The total change of area was a combination result of polymerization expansion and relaxation contraction. A new polymerization kinetic

model in two-dimensional state has been proposed based on two factors and well described the experimental results. The activation area of polymerization was determined and was almost independent on the temperature. The activation areas were $0.127\,nm^2$ (at 10 °C) and $0.121\,nm^2$ (at 20 °C), respectively. The positive activation area indicated an increase in area when the activated complex was formed. The rate constant decreased upon elevated surface pressure.

The visible light irradiation was only able to excite chain propagation and accelerated the UV-irradiation polymerization, but was not capable of initiate polymerization of the PDA monolayer. Therefore it is possible to provide us a method to accelerate the UV-irradiation polymerization in two-dimensional state.

Acknowledgements

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