Kinetics of *trans-cis* isomerization in azobenzene dimers at an air-water interface

Bharat Kumar[1] and K. A. Suresh[2,*]

[1]*Raman Research Institute, Sadashivanagar, Bangalore 560 080, India*
[2]*Centre for Liquid Crystal Research, P.B. No. 1329, Jalahalli, Bangalore 560 013, India*
(Received 19 March 2009; revised manuscript received 1 July 2009; published 3 August 2009)

We have studied the kinetics of *trans* to *cis* isomerization under the illumination of ultraviolet light, in the Langmuir monolayer of mesogenic azobenzene dimer, bis-[5-(4′-n-dodecyloxy benzoyloxy)-2-(4″-methylphenylazo)phenyl] adipate, at an air-water interface. We find that the *trans* to *cis* isomerization reaction of the molecules in the monolayer shows deviation from the first-order kinetics unlike those reported on Langmuir monolayers of azobenzene molecules. We attribute the deviation from first-order kinetics to the simultaneous photoisomerization of *trans* isomers to form *cis* isomers and the reverse thermal isomerization of *cis* isomers to form *trans* isomers. Our analysis of the rate of change of mole fraction of *trans* isomers to form *cis* isomers indicates a first-order kinetics for *trans* to *cis* photoisomerization reaction and a second-order kinetics for *cis* to *trans* thermal isomerization reaction. This second-order kinetics mechanism is similar to the Lindemann-Hinshelwood mechanism for the unimolecular reactions at low concentration of reactants. The formation of the activated *cis* isomer by collisions is a slow process as compared to the decay of the activated *cis* isomer to *trans* isomer in the liquid expanded phase. This results in the second-order kinetics for the thermal isomerization of *cis* isomers.

I. INTRODUCTION

In azobenzene molecules, molecular conformation can be changed from *trans* to *cis* state or *cis* to *trans* state by isomerization using the techniques such as illumination of ultraviolet (uv) or visible light [1] or applying an electric field [2]. Thin films of such materials which have device applications can be fabricated by different techniques. If the molecules are amphiphilic, they can form stable monolayer at air-water interface which can be transferred onto the solid substrates by Langmuir-Blodgett (LB) technique [3]. From this technique, well-ordered films with desired molecular surface density and thickness can be obtained. Illumination of uv or visible light on the Langmuir monolayers and LB films of azobenzene molecules may result in the *trans-cis* or *cis-trans* molecular switching and can be studied by measuring the surface pressure [4] or electrochemical measurements [5]. This property of reversible molecular switching has been utilized in developing photosensitive devices [6,7] and wetting surfaces [8]. It has also been shown that some azobenzene materials become dichroic and birefringent under the action of light. This effect is called photoinduced optical anisotropy and it provides a means to get light-controlled anisotropy which can be used in photonic applications [9–11]. For many such applications, understanding the kinetics of isomerization reaction in thin films is important. Yim and Fuller showed that the *trans* to *cis* photoisomerization reaction in Langmuir monolayers of azobenzene molecules is a first-order reaction [12]. Liu *et al.* studied the *cis* to *trans* thermal isomerization of azobenzene molecules in the LB film and found that the isomerization follows the first-order kinetics [5]. There are examples of deviation from first-order kinetics in the case of *trans* to *cis* photoisomerization reac-

tion of azobenzene molecules in thin films of polymer [13]. However, no such reaction kinetics have been reported at air-liquid interface.

We report here the kinetics of *trans* to *cis* isomerization of the azobenzene molecules under the illumination of uv light in the liquid expanded phase of the Langmuir monolayer at an air-water interface. The material used to form the monolayer was bis-[5-(4′-n-dodecyloxy benzoyloxy)-2-(4″-methylphenylazo)phenyl] adipate (12D1H). We find that the *trans* to *cis* isomerization shows deviation from the first-order kinetics, unlike those reported for the condensed phase of the azobenzene monolayer [12]. The deviation from the first-order kinetics can be shown as a net result of the simultaneous photoisomerization of *trans* isomers to form *cis* isomers and thermal isomerization of *cis* isomers to form *trans* isomers. We find that the rate equation written by considering a first-order kinetics for *trans* to *cis* photoisomerization reaction and a second-order kinetics for *cis* to *trans* thermal isomerization reaction fits well with the experimentally obtained rate equation. The second-order kinetics mechanism for thermal isomerization reaction of *cis* isomer to form *trans* isomer is similar to the Lindemann-Hinshelwood mechanism for the unimolecular reactions at low concentration of the reactants [14,15].

II. EXPERIMENTAL SECTION

The material 12D1H was synthesized by Kumar *et al.* [16]. It was purified by repeated column chromatography and the purity of the sample was found to be better than 99% by elemental analysis, infrared (IR) and NMR techniques [16]. The surface pressure (π) versus area per molecule (A_m) isotherm was obtained using Nima trough (611M). The trough was enclosed in an aluminum box to prevent air currents and ambient light. Wilhelmy method was used to measure the surface pressure. The stock solution of the 12D1H material
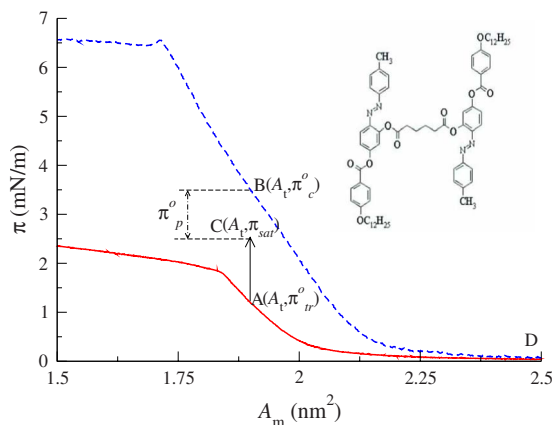
FIG. 1. (Color online) Surface pressure (π) vs area per molecule (A_m) isotherms of the *trans*-12D1H monolayer (continuous line) and *cis*-12D1H monolayer (dashed line). For the kinetic studies of the *trans* to *cis* isomerization, the *trans*-12D1H monolayer was illuminated with uv light (365 nm) at a target area per molecule, A_t [point $A(A_t, \pi_{tr}^{\circ})$]. This results in the increase of surface pressure of the monolayer with time and saturates to a value of π_{sat} [point $C(A_t, \pi_{sat})$]. Molecular structure of 12D1H is shown at top right of the figure.

prepared in the HPLC-grade chloroform was kept in the dark for more than 12 h to ensure that almost all the molecules are in the *trans* state (*trans*-12D1H). Surface manometry was carried out in the dark to get the π-A_m isotherm of the *trans*-12D1H monolayer. To get the π-A_m isotherm of the monolayer with molecules in the *cis* state (*cis*-12D1H), the monolayer was spread and compressed from the gas state under the illumination of the uv light of 365 nm wavelength. The monolayer was compressed at the rate of about 14 (Å^2/molecule)min^{-1}. All the experiments were carried out at the temperature of 24 ± 0.1 °C.

For the *trans* to *cis* isomerization studies in the liquid expanded phase, the monolayer of *trans*-12D1H was compressed to a target area per molecule (A_t) and then illuminated with the uv light of wavelength 365 nm. The process of isomerization changes the surface pressure of the monolayer at this constant A_t. The experiment was repeated for three different values of A_t in the liquid expanded phase of the monolayer. Kinetics of isomerization was studied by measuring π as a function of time (t). Ultraviolet light of wavelength 365 nm was obtained from a high-pressure mercury lamp using an appropriate interference filter (Edmund optics). The intensity of the uv light was measured using a light meter and it was about 1 mW cm^{-2}.

III. RESULTS AND DISCUSSION

A. Surface manometry

Surface pressure (π) versus area per molecule (A_m) isotherms of the monolayers of *trans*-12D1H and *cis*-12D1H are shown in Fig. 1. The *trans*-12D1H monolayer exhibited liquid expanded phase between the A_m of 2.10 and 1.84 nm^2. The monolayer collapsed at a surface pressure of 1.8 mN/m. The *cis*-12D1H monolayer exhibited liquid expanded phase
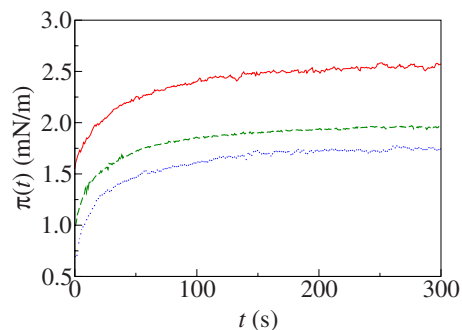

FIG. 2. (Color online) Plot of surface pressure [$\pi(t)$] as a function of time (t) in seconds for three different target area per molecule (A_t): (i) 1.87 nm^2 (continuous line), (ii) 1.92 nm^2 (dashed line), and (iii) 1.96 nm^2 (dotted line) under the illumination of uv light. The corresponding π_{sat} values are (i) 2.67 mN/m, (ii) 2.03 mN/m, and (iii) 1.83 mN/m, respectively.

between the A_m of 2.15 and 1.71 nm^2 before collapsing at a surface pressure of 6.6 mN/m.

B. Kinetics of isomerization reaction

Kinetics of a reaction can be studied by measuring the rate of change of concentration of one or more reactants (or products) [15]. For isomerization reaction studies of the azobenzene molecules in the monolayer at an air-water interface, rate of change of the mole fraction of one of the isomers (*trans*-12D1H or *cis*-12D1H) has to be measured as a function of time. We have obtained the rate of change of mole fraction of *trans*-12D1H molecules in the monolayer from surface pressure measurements. We employed a method similar to the one used to study the kinetics of bulk reactions, where the partial pressures of the reactants or products in the vapor phase are measured [15].

For *trans* to *cis* isomerization studies, the monolayer of *trans*-12D1H in the liquid expanded phase was illuminated with the uv light of wavelength 365 nm at a target area per molecule, A_t (point A in the isotherm in Fig. 1). Photoisomerization of *trans* to *cis* isomer results in the increase of surface pressure with time and saturates to a value of π_{sat}. The increase in the surface pressure is due to the formation of *cis* isomer which has a different molecular conformation and higher dipole moment compared to the *trans* isomer [17]. Figure 2 shows the π-t plot for three different values of A_t. It can be seen that the π_{sat} depends on the value of A_t. The π_{sat} was found to be less than the surface pressure (π_c°) of the *cis*-12D1H monolayer corresponding to the same A_t (point B in the isotherm in Fig. 1). This may be due to the difference in packing of the molecules in the *cis*-12D1H monolayer obtained by two procedures: (1) illuminating the gas phase and compressing it to the liquid expanded phase and (2) illuminating the *trans*-12D1H monolayer already in the liquid expanded phase.

The effective surface pressure of the monolayer at time t after illumination of uv light can be written as the sum of surface pressures due to the individual isomers (*trans* and *cis*) and the surface pressure component arising from the packing of the molecules, i.e.,

$$\pi(t) = \pi_{tr}(t) + \pi_c(t) + \pi_p(t). \tag{1}$$

Here, $\pi(t)$ is the measured (effective) surface pressure of the monolayer at the target area per molecule A_t after time t of illumination of uv light, $\pi_{tr}(t)$ is the surface pressure component due to the *trans* isomer, $\pi_c(t)$ is the surface pressure component due to the *cis* isomer, and $\pi_p(t)$ is the surface pressure component due to the effect of packing of molecules. The term $\pi_p(t)$ is the result of packing differences between the *trans* and *cis* isomers in the monolayer. We assume that this term is proportional to the mole fraction of the *cis* isomers. Considering the surface pressure component due to *trans* isomer to be proportional to the mole fraction of the *trans* isomer and the surface pressure component due to the *cis* isomer to be proportional to the mole fraction of the *cis* isomer in the monolayer, we have from Eq. (1)

$$\pi(t) = \Gamma_{tr}(t) \pi_{tr}^{\circ} + \Gamma_c(t) \pi_c^{\circ} + \pi_p(t).$$

Here, $\Gamma_{tr}(t)$ is the mole fraction of the *trans* isomer at time t, $\Gamma_c(t)$ is the mole fraction of the *cis* isomer at time t, π_{tr}° is the surface pressure of the monolayer of pure *trans* isomer at A_t, and π_c° is the surface pressure of the monolayer of pure *cis* isomer at A_t. $\pi_p(t)$ is assumed to be proportional to the $\Gamma_c(t)$ and hence it can be written as $\Gamma_c(t)\pi_p^{\circ}$, where $\pi_p^{\circ} = \pi_{sat} - \pi_c^{\circ}$. In the present case, π_p° is a negative quantity (Fig. 1). Thus the effective surface pressure of the monolayer turns out to be

$$\pi(t) = \Gamma_{tr}(t) \pi_{tr}^{\circ} + \Gamma_c(t) \pi_c^{\circ} + \Gamma_c(t) \pi_p^{\circ}. \tag{2}$$

Since $\Gamma_{tr}(t) + \Gamma_c(t) = 1$, Eq. (2) yields the following expression:

$$\Gamma_{tr}(t) = \left[\frac{\pi(t) - \pi_{sat}}{\pi_{tr}^{\circ} - \pi_{sat}} \right]. \tag{3}$$

We define the term $\pi_i(t) = \Gamma_i(t)\pi_i^{\circ}$ as "partial surface pressure" of the isomer i ($i = tr$ or c). The partial surface pressure of *trans* isomer at time t is given by $\pi_{tr}(t) = \Gamma_{tr}(t)\pi_{tr}^{\circ}$. Substituting $\Gamma_{tr}(t)$ from Eq. (3), we get the following expression for the partial surface pressure of *trans* isomer:

$$\pi_{tr}(t) = \pi_{tr}^{\circ} \left[\frac{\pi(t) - \pi_{sat}}{\pi_{tr}^{\circ} - \pi_{sat}} \right]. \tag{4}$$

The values of π_{tr}° and π_c° can be obtained from the isotherms of pure *trans*-12D1H and pure *cis*-12D1H monolayers, respectively. Experimentally, we have measured $\pi(t)$ as a function of t for three different values of A_t (Fig. 2). The value of π_p° can be obtained by the relation $\pi_p^{\circ} = \pi_{sat} - \pi_c^{\circ}$, where π_{sat} for a given value of A_t is obtained from Fig. 2. Using these values, we can calculate $\pi_{tr}(t)$ from Eq. (4). The calculated values of $\pi_{tr}(t)$ are plotted as a function of t (Fig. 3).

For a first-order *trans* to *cis* isomerization reaction, $\pi_{tr}(t)$ [which is proportional to $\Gamma_{tr}(t)$], should be an exponential function of time [12]. However, from Fig. 3, we find that the $\pi_{tr}(t)$ data could not be described by an exponential function. On the other hand, the curves can be fitted to an equation of the type
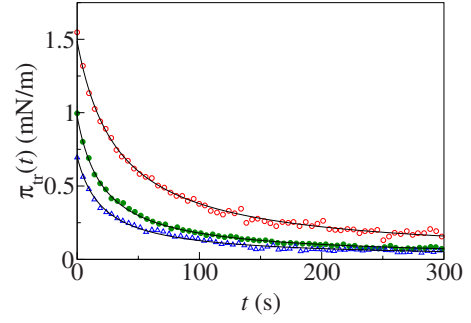

FIG. 3. (Color online) Calculated partial surface pressure of *trans* isomer [$\pi_{tr}(t)$] plotted as a function of time (t) in seconds for three different values of A_t: (i) 1.87 nm^2 (open circles), (ii) 1.92 nm^2 (filled circles), and (iii) 1.96 nm^2 (open triangles). Solid lines are computed using Eq. (5) to fit the data.

$$\pi_{tr}(t) = \frac{a}{1 + bt} + c. \tag{5}$$

Here a, b, and c are the fit parameters. The correlation coefficient for the fit was found to be better than 0.99.

To obtain the rate equation for the *trans* to *cis* isomerization reaction, we differentiate Eq. (5) with respect to time t and express it in terms of $\pi_{tr}(t)$,

$$\frac{d\pi_{tr}(t)}{dt} = -\frac{b}{a}\pi_{tr}^2(t) + \frac{2bc}{a}\pi_{tr}(t) - \frac{bc^2}{a}.$$

Since, $\pi_{tr}(t) = \Gamma_{tr}(t)\pi_{tr}^{\circ}$,

$$\frac{d\Gamma_{tr}(t)}{dt} = -\frac{b\pi_{tr}^{\circ}}{a}\Gamma_{tr}^2(t) + \frac{2bc}{a}\Gamma_{tr}(t) - \frac{bc^2}{a}. \tag{6}$$

C. Kinetic model

Trans to *cis* photoisomerization of azobenzene molecules at air-water interface has been reported to be a first-order reaction [12]. Thermal *cis* to *trans* isomerization in the LB film was also reported to be a first-order reaction [5]. However, in the case of thin film of polymer containing azobenzene, Mita *et al.* reported that *trans* to *cis* photoisomerization deviates from the first-order kinetics [13]. They found that the *trans* to *cis* photoisomerization followed first-order kinetics up to 86% conversion and then deviated from the first-order kinetics. To explain the non-first-order reaction, they proposed a kinetic model considering the influence of free volume distribution in the polymer matrix on the *trans* to *cis* isomerization. Interestingly, in our system, the deviation was observed from the initial stage itself. In our system, since the molecules are in the liquid expanded phase at an air-water interface, the free volume available for the azobenzene moiety is greater than the critical volume required for the isomerization. Hence the isomerization reaction is not restricted by the free volume distribution unlike in the case of the azobenzene molecules trapped in the solid polymer matrix.

In Eq. (6), the $\Gamma_{tr}^2(t)$ term suggests that there is another reaction following second-order kinetics, simultaneously
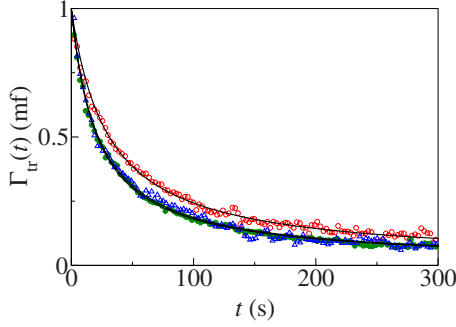
FIG. 4. (Color online) Calculated mole fraction (mf) of *trans* isomer [$\Gamma_{tr}(t)$] plotted as a function of time (t) in seconds for three different values of A_t: (i) 1.87 nm^2 (open circles), (ii) 1.92 nm^2 (filled circles), and (iii) 1.96 nm^2 (open triangles). Solid lines are computed using Eq. (9) to fit the data.

proceeding in the opposite direction to that of the photoisomerization. The reverse reaction may be the thermal isomerization of the metastable *cis* isomer to form the stable *trans* isomer [5].

Under the illumination of uv light on the *trans*-12D1H monolayer, the net rate of the isomerization reaction depends on two processes: (a) photoisomerization of *trans* isomers to form *cis* isomers and (b) thermal isomerization of the *cis* isomers to form *trans* isomers by colliding with other molecules. The rate of change of *trans* isomers is thus given by the following rate equation [14]:

$$\frac{d\Gamma_{tr}(t)}{dt} = -k\Gamma_{tr}(t) + k_{col}\Gamma_c(t)\Gamma_{tr}(t), \qquad (7)$$

where k is the rate constant for photoisomerization reaction of *trans* isomer and k_{col} is the rate constant for the thermal isomerization reaction of the *cis* isomer. Since $\Gamma_c(t) = 1 - \Gamma_{tr}(t)$, we have

$$\frac{d\Gamma_{tr}(t)}{dt} = -k_{col}\Gamma_{tr}^2(t) + (k_{col} - k)\Gamma_{tr}(t). \qquad (8)$$

This equation shows that the rate of change of mole fraction of the *trans* isomer is governed in the initial stages of the isomerization reaction by the first term and in the later stages by the second term. Eventually, the two terms will become equal, resulting in the steady value for $\Gamma_{tr}(t)$. Equation (8) is similar to Eq. (6), except for the constant term which is negligible ($\approx 10^{-6}$). Hence, the above kinetic model of isomerization can explain the experimental result. Solving Eq. (8) for $\Gamma_{tr}(t)$, we get

$$\Gamma_{tr}(t) = \frac{\Gamma_{\circ}\Delta k}{\Delta k + (\Gamma_{\circ}k_{col} - \Delta k)(1 - e^{-\Delta kt})}. \qquad (9)$$

Here, $\Delta k = k_{col} - k$ and $\Gamma_{\circ}$ is the concentration of *trans* isomers at $t = 0$. Since before the illumination of uv light all the molecules are in *trans* state, we have $\Gamma_{\circ} = 1$. Equation (9) is fitted with experimental data and the rate constants are calculated from the fit parameters. Figure 4 shows plot of $\Gamma_{tr}(t)$ as a function of t along with the fitted curves. Table I gives the values of the rate constants calculated for three different A_t.

TABLE I. Values of the rate constants (k and k_{col}) for *trans* to *cis* isomerization at different target area per molecule (A_t).

A_t (nm^2)	π_{tr}° (mN/m)	π_c° (mN/m)	k (s^{-1})	k_{col} (s^{-1})
1.96	0.69	2.70	0.0456	0.0465
1.92	0.99	3.18	0.0474	0.0483
1.87	1.54	3.98	0.0326	0.0335

We have proposed a simple model which takes into account the thermal isomerization of the *cis* isomers to form *trans* isomers. Since, in our system, the monolayer is in the liquid expanded phase, we assume that there is no orientational ordering of the azobenzene moieties of the *cis* isomers.

Studies on the kinetics of *trans* to *cis* photoisomerization reaction in azobenzene containing fatty acid molecules at an air-water interface have reported the rate constant values k to be 9.50×10^{-2} and 3.55×10^{-2} s^{-1} for nearest-neighbor tilt (NN) phase and next-nearest-neighbor tilt (NNN) phase, respectively [12]. The different k values for the two phases show the influence of the molecular packing and structure of the monolayer on the rate of photoisomerization. The k value obtained for our system is of the same order of magnitude (Table I) and somewhat in between that of NN and NNN phases of the fatty acid monolayer.

In the case of monolayer of fatty acids, which is in the condensed phase (NN and NNN phases), the molecules have less degrees of freedom resulting in higher stability of the *cis* molecules. On the other hand, in the 12D1H system, the monolayer is in the liquid expanded phase in which the molecules have more degrees of freedom resulting in higher probability of excitation of the *cis* isomers by collision. This may explain the higher contribution of the thermal isomerization of the *cis* isomers toward the kinetics in the 12D1H system.

In our system, the rate equation shows that the *cis* to *trans* thermal isomerization reaction follows the second-order kinetics. This is similar to the Lindemann-Hinshelwood mechanism for unimolecular reactions [15,18] at low concentration of reactants. Lindemann-Hinshelwood mechanism is a two-step reaction mechanism [18,19]. First, a *cis* isomer with large number of degrees of freedom gets activated by colliding with other molecules. This is a bimolecular event involving two molecules. Then, the activated *cis* molecule decays to form the *trans* isomer. This is a unimolecular event. The overall rate of the reaction is determined by the slower reaction step. Hence, the thermal isomerization of *cis* isomers involves two steps: (a) formation of the activated *cis* isomers and (b) decay of the activated *cis* isomers to form *trans* isomers. In the liquid expanded phase of the 12D1H monolayer, the time scales involved for collision between the molecules are high as compared to the time scales involved in the decay of the activated molecules. Hence, the formation of the activated *cis* isomers will be slow as compared to the decay of the activated molecules. Thus, the formation of the activated *cis* isomers will be the rate-determining step. The activation of the *cis* molecules by collision is a bimolecular event and hence the reaction will have overall second-order

kinetics. In many devices which make use of thin film of azobenzene materials, e.g., the photomechanical devices [1], kinetics of isomerization plays an important role. We have shown that the reverse thermal isomerization of metastable *cis* isomers in the liquid expanded phase can contribute toward the overall reaction rate. These effects have to be considered for making devices with desired applications.

IV. CONCLUSIONS

We have studied the *trans* to *cis* isomerization of mesogenic azobenzene dimer molecule (12D1H) under the illumination of uv light at an air-water interface. We have employed an approach to analyze the experimental results. From our analysis, we find that the *trans* to *cis* isomerization reaction shows deviation from the first-order kinetics. We attribute this deviation to the simultaneous photoisomerization of *trans* isomers to form *cis* isomers and the reverse thermal isomerization of the metastable *cis* isomers to form the stable *trans* isomers. Our analysis indicates a first-order kinetics for *trans* to *cis* photoisomerization reaction and a second-order kinetics for the thermal isomerization reaction of the *cis* isomers to form *trans* isomers. The mechanism of thermal isomerization is similar to the Lindemann-Hinshelwood mechanism for unimolecular reactions at low concentration of reactants. In our system, the thermal isomerization reaction has two steps, i.e., formation of activated *cis* isomers by collision of *cis* isomers with other molecules and then the decay of activated *cis* isomers to form *trans* isomers. The formation of activated *cis* isomers is slow as compared to the decay of the activated *cis* isomers and hence the former step governs the rate of reaction. Since the formation of activated *cis* isomers is a bimolecular event, the thermal isomerization reaction has an overall second-order kinetics.

[1] C. J. Barrett, J.-ichi Mamiya, K. G. Yager, and T. Ikeda, Soft Matter **3**, 1249 (2007).

[2] M. Alemani, M. V. Peters, S. Hecht, K. Rieder, F. Moresco, and L. Grill, J. Am. Chem. Soc. **128**, 14446 (2006).

[3] V. M. Kaganer, H. Mohwald, and P. Dutta, Rev. Mod. Phys. **71**, 779 (1999).

[4] P. Viswanath and K. A. Suresh, Langmuir **20**, 8149 (2004).

[5] Z.-F. Liu, K. Morigaki, T. Enomoto, K. Hashimoto, and A. Fujishima, J. Phys. Chem. **96**, 1875 (1992).

[6] A. Kocer, M. Walko, W. Meijberg, and B. L. Feringa, Science **309**, 755 (2005).

[7] X. Feng, L. Feng, M. Jin, J. Zhai, L. I. Jiang, and D. Zhu, J. Am. Chem. Soc. **126**, 62 (2004).

[8] H. S. Lim, J. T. Han, D. Kwak, M. Jin, and K. Cho, J. Am. Chem. Soc. **128**, 14458 (2006).

[9] A. D. Kiselev, J. Phys.: Condens. Matter **14**, 13417 (2002).

[10] T. G. Pedersen, P. M. Johansen, N. C. R. Holme, and P. S. Ramanujam, J. Opt. Soc. Am. B **15**, 1120 (1998).

[11] O. V. Yaroshchuk, A. D. Kiselev, Y. Zakrevskyy, T. Bidna, J. Kelly, L. C. Chien, and J. Lindau, Phys. Rev. E **68**, 011803 (2003).

[12] K. S. Yim and G. G. Fuller, Phys. Rev. E **67**, 041601 (2003).

[13] I. Mita, K. Horie, and K. Hirao, Macromolecules **22**, 558 (1989).

[14] C. A. Hollingsworth, P. G. Seybold, L. B. Kier, and C.-K. Cheng, Int. J. Chem. Kinet. **36**, 230 (2004).

[15] P. Atkins, *Physical Chemistry* (Oxford University Press, New York, 2006).

[16] B. Kumar, A. K. Prajapati, M. C. Varia, and K. A. Suresh, Langmuir **25**, 839 (2009).

[17] K. Ichimura, S. Oh, and M. Nakagawa, Science **288**, 1624 (2000).

[18] F. A. Lindemann, Trans. Faraday Soc. **17**, 598 (1922).

[19] C. N. Hinshelwood, Proc. R. Soc. London, Ser. A **113**, 230 (1926).