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Reversible Photodissociation of Hexacarbonyl Tungsten in Cross-Linked Polymers

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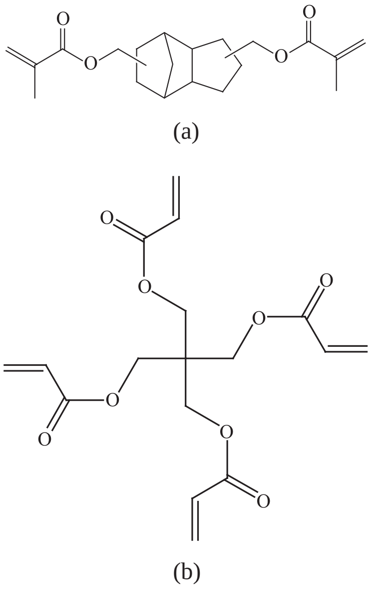
Reversible photochromic reaction of hexacarbonyltungsten(0) caused by the photodissociation of a carbonyl ligand was studied in cross-linked transparent polymers: polymer of bis(hydroxymethyl)tricyclo[5,2,1,$0^{2,6}$]decane dimethacrylate (**A**) and polymer of tetrakis(hydroxymethyl)methane tetrakis(acrylate) (**B**). Rate constants of the photodissociation and recombination reactions were determined from the observed spectral changes. Because the dimensions of the cavities in these polymers, determined by the positron annihilation experiments, were similar to those of the complex $[W(CO)_6]$, the photoactivated complexes could contribute to the coloring of the polymer only when the dissociated CO molecule moved to the neighboring space. In polymer **B**, with a higher density of cross-links between polymer chains, the complex had a higher dissociation rate constant but a lower saturation concentration. These results indicated that the kinetics of the dissociation are controlled by thermal motion of the polymer chains around the gate to the neighboring space. The decay of the complex after recycling of the dissociation–recombination process was much smaller in polymers, especially in polymer **B**, than in DMF solution.

The structures of densely cross-linked polymers can be regarded as randomly arranged cells divided by polymer chains. These cells may be used as the microspaces for reversible chemical reactions. We can easily prepare such reaction systems by polymerizing the monomers in which the reactants are dissolved. Especially if we adopt photopolymerization, the monomer solution can be polymerized at lower temperatures so that the reactants are not lost due to vaporization. In this study, we polymerized the monomers illustrated in Fig. 1 with hexacarbonyltungsten(0).

The hexacarbonyl complexes of the group 6 elements are photochromic.[1–3] The mechanism was analyzed mainly by infrared spectroscopy: photodissociation reactions of colorless hexacarbonyl complexes yield colored pentacarbonyl complexes along with carbon monoxide. If these dissociated species are kept within a small distance, the reaction can be reversible. In this article, we have investigated the behavior of irradiated hexacarbonyltungsten(0), $[W(CO)_6]$, confined in transparent cross-linked polymers.

At the first stage of this study, we expected that the coarseness of the polymer network mainly controlled the kinetics of the dissociation and recombination reactions. However, the analyses of the reaction kinetics showed that such a static model could not explain the results, especially the difference in the dissociation rate constants of the two polymers. Then, we introduced a dynamic model, in which the flexibility of the bulk polymers controlled the movement of carbon monoxide, and could explain the experimental results. In other words, the analysis of the photodissociation kinetics was a new probe to examine the dynamic state of the cross-linked polymers.


(a)

(b)

Fig. 1. Monomers of the cross-linked polymers used in this study. (a) Monomer of **A**: bis(hydroxymethyl)tricyclo[5,2,1,$0^{2,6}$]decane dimethacrylate (DCP). (b) Monomer of **B**: tetrakis(hydroxymethyl)methane tetrakis(acrylate) (A-TMMT).

Experimental

Hexacarbonyl complexes, [W(CO)$_6$] and [Mo(CO)$_6$], were purchased from Sigma-Aldrich. The photocurable monomers bis(hydroxymethyl)tricyclo[5,2,1,0^{2,6}]decane dimethacrylate (DCP) and tetrakis(hydroxymethyl)methane tetrakis(acrylate) (A-TMMT), were purchased from Shin-nakamura Chemical. The photoinitiator 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO) was purchased from BASF.

A solution of [W(CO)$_6$] (1 g) in benzene (2 mL) was added to the mixture of the photocurable monomer (100 g) and the photoinitiator (1 g). The resulting solution was stirred at 50 °C for 10 min. The mixture was poured between two parallel flat glass sheets separated by 1 mm with silicone rubber insulators. Then, it was irradiated with ultraviolet radiation (maximum power 30 mW cm^{-2}, total energy 5.3 J cm^{-2}) from metal-halide mercury arc lamps for four minutes. The polymer containing [W(CO)$_6$] was taken out from the reactor and heated at 170 °C for four hours at a reduced pressure.

The flexural moduli were measured at 25 °C with an intersupport distance of 30 mm on a modulus testing machine (Shimadzu Autograph) according to the procedure described in JIS K7171 and ISO 178. The test pieces had the dimensions of 80 mm × 25 mm × 0.2 mm.

The absorption spectra of the samples were measured with a UV–vis spectrometer (JASCO V-560). Lifetime spectra of positrons in polymerized DCP and A-TMMT were measured in the temperature range between 30 °C and ca. 200 °C in a vacuum with a conventional fast–fast coincidence lifetime spectrometer at University of Tsukuba.[4]

Results and Discussion

Reaction Kinetics. Group 6 metal hexacarbonyls [Cr(CO)$_6$], [Mo(CO)$_6$], and [W(CO)$_6$] that are dissolved in organic solvents are known to change their colors by the irradiation of ultraviolet light.[1–3] The mechanism of the photochromism has been studied mainly with the IR spectroscopy, and it has been revealed that the color change is caused by the dissociation of one of the carbonyl ligands.

$$[\mathrm{M(CO)_6}] \xrightarrow{h\nu} [\mathrm{M(CO)_5}] + \mathrm{CO}. \tag{1}$$

The pentacarbonyl complexes have a 16-electron configuration but with a substantial lifetime. They may combine with carbon monoxide to form colorless hexacarbonyls again or be stabilized by donor molecules to give an 18-electron configuration.

$$[\mathrm{M(CO)_5}] + \mathrm{CO} \rightarrow [\mathrm{M(CO)_6}]. \tag{2}$$

$$[\mathrm{M(CO)_5}] + \mathrm{L} \rightarrow [\mathrm{M(CO)_5(L)}]. \tag{3}$$

Though these reactions were studied in organic solvents, the reactions can occur also in organic polymers. In fact, after we had started our studies, we found a preliminary report that was published half century ago, in which were described similar reactions in a linear polymer, poly(methylmethacrylate) without any quantitative data.[5]

In the first stage of this research, we studied the photochromic reactions of hexacarbonyl molybdenum and tungsten complexes in cross-linked polymers. Both of the complexes became colored upon irradiation with UV light; the color of the polymer containing hexacarbonylmolybdenum(0) changed to gray while the tungsten analogue became yellow. When the colored polymers were left in the dark, their colors faded. Though the polymer containing tungsten complex became colorless, the polymer with molybdenum complex was slightly gray even after several days. In this study, we chose to investigate the photochromic reaction of [W(CO)$_6$] in cross-linked polymers.

We studied two kinds of samples: [W(CO)$_6$] in polymerized DCP (**A**) and the carbonyl in polymerized A-TMMT (**B**) (Fig. 1). The monomer of the former has two methacryloyl groups for polymerization while the latter has four acryloyl groups. Therefore, the number of cross-links per monomer unit is much larger in **B** than in **A**.

When the samples were irradiated with ultraviolet light, they turned yellow, which is a coloring process. Corresponding to the color change, a new absorption peak centered at 423 and 420 nm was observed in the spectra of **A** and **B**, respectively, as illustrated in Fig. 2. This peak was attributed to the pentacarbonyl complex based on IR studies.[1] In each sample, the intensity of the peak increased with the irradiation time as shown in Fig. 3 and was almost saturated after ca. 60 min. Saturation

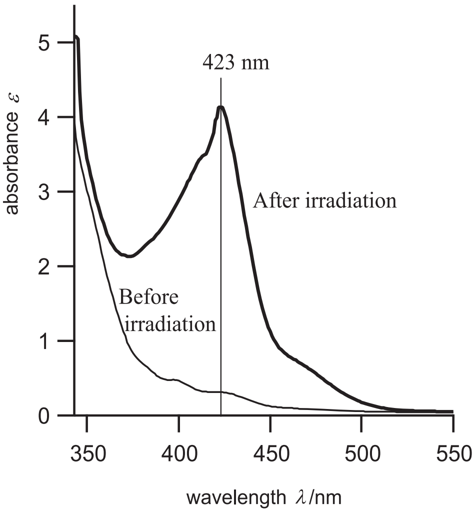


Fig. 2. Absorption spectra of **A** before and after UV-irradiation.

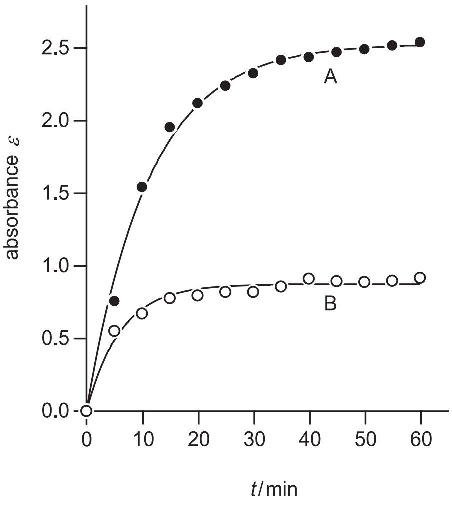


Fig. 3. Time dependences of absorbances at the absorption maxima around 420 nm for **A** and **B** during UV-irradiation.

indicates that the rate of recombination becomes equal to the dissociation rate, and the kinetics can be expressed as Eq. 4.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{d}(C - x) - k_\mathrm{r}x. \tag{4}$$

Here, x is the concentration of the colored pentacarbonyl complex, C is the total concentration of the complex, and k_d and k_r are the rate constants of the dissociation reaction and the recombination reaction, respectively. This equation gives the solution as Eq. 5.

$$x(t) = A\{1 - \exp(-\alpha t)\}, \tag{5}$$

where A is equal to $k_\mathrm{d}C/(k_\mathrm{d} + k_\mathrm{r})$ and α equal to $k_\mathrm{d} + k_\mathrm{r}$. The absolute concentration of the generated pentacarbonyl complex cannot be determined because we cannot obtain a sample consisting only of the dissociated species. Since the observed absorbance is proportional to the concentration of the complexes, in the following analysis, we will use the absorbance as the concentration $x(t)$ of the pentacarbonyl complexes expressed in an arbitrary unit. The observed absorbance data, which is equal to the concentration $x(t)$ in this unit, could be fit to an exponential curve (Eq. 5) as shown in Fig. 3.

When the colored samples are kept away from strong light, they gradually lose their color (decoloring process), indicating a recombination reaction between the pentacarbonyl complexes and the carbonyl ligands. The time dependences of the absorbances of the samples are shown in Fig. 4. Though the samples were kept in the dark at 25 °C, they were inevitably exposed to the light of the UV–vis spectrometer during the absorbance measurements, which takes about 2 min for each measurement. Therefore, the photodissociation reaction in some degree is unavoidable, and both the recombination reaction and the photodissociation reaction proceed during the measurements. Since the exact kinetic treatment of the process with the intermittent irradiation was difficult, we assumed that the irradiation during the UV–vis measurements is equivalent to the weak continuous irradiation through the whole measurement. Then, the kinetics are similar to Eq. 4. The rate constant k_d' of the dissociation reaction is different from k_d in Eq. 4 because the length of exposure time, and the strength of the irradiated light is much lower than in coloring process.

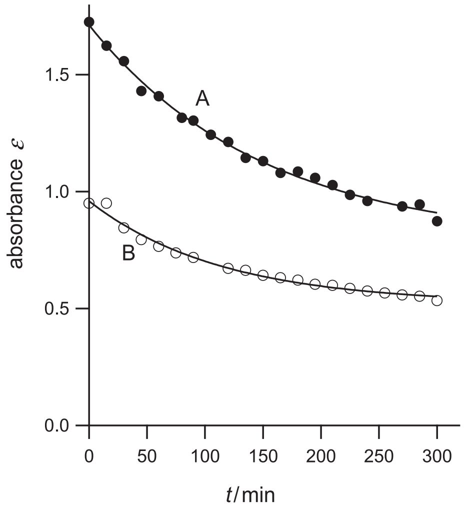


Fig. 4. Time dependences of absorbances at the absorption maxima around 420 nm for **A** and **B** during the decoloring process at 25 °C after UV-irradiation.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{d}'(C - x) - k_\mathrm{r}x. \tag{6}$$

The solution of Eq. 6 is Eq. 7 and different from Eq. 5 because the initial concentration of the pentacarbonyl complex is close to saturation.

$$x(t) = B - r\exp(-\beta t). \tag{7}$$

Here, B is equal to $k_\mathrm{d}'C/(k_\mathrm{d}' + k_\mathrm{r})$ and β equal to $k_\mathrm{d}' + k_\mathrm{r}$. The observed data could be fit to Eq. 4, as shown in Fig. 4. We derived the values of the parameters k_r, k_d, k_d', and C from the fitting parameters A, B, α, and β as follows.

$$k_\mathrm{r} = \frac{\alpha\beta(A - B)}{\alpha A - \beta B}. \tag{8}$$

$$k_\mathrm{d} = \frac{\alpha A(\alpha - \beta)}{\alpha A - \beta B}. \tag{9}$$

$$k_\mathrm{d}' = \frac{\beta B(\alpha - \beta)}{\alpha A - \beta B}. \tag{10}$$

$$C = \frac{\alpha A - \beta B}{\alpha - \beta}. \tag{11}$$

However, simple estimations of their errors gave very large values, and stricter error analyses were required. The equations that described the dependence of the variances of k_r, k_d, k_d', and C on the variances of A, B, α, and β were derived. The equations were complex, and the mathematical software package Maple[6] was used for the derivation of the equation and numerical calculations. The variances of A, B, α, and β were obtained using the curve-fitting procedures carried out with the graphic software IGOR.[7] Numerical results are shown in Table 1.

The rate constants of the recombination reaction are of the order $k_\mathrm{r}(\mathbf{A}) > k_\mathrm{r}(\mathbf{B})$. This order can be ascribed to the difference in the polymer structure. Polymer **B** contains more oxygen atoms in the polymer and has polar sites where the pentacarbonyl complex can be stabilized. Therefore, the rate constant of the recombination reaction is smaller for polymer **B**.

The analyses have shown that k_d for polymer **B** is larger than that of polymer **A**. k_d determines the rate of the dissociation reaction during the coloring process. k_d' also follows a similar trend, $k_\mathrm{d}'(\mathbf{B}) > k_\mathrm{d}'(\mathbf{A})$ though they are much smaller than the corresponding constants during the coloring process (k_d), reflecting the difference in the exposure time and the power of the light in two processes.

Table 1. Curve-Fitting and Kinetic Parameters of the Photodissociation and Recombination Reactions of [W(CO)$_6$] with Estimated Errors in Parentheses[a)]

Curve-fitting parameters			Kinetic parameters		
	Sample **A**	Sample **B**		Sample **A**	Sample **B**
A	2.53(3)	0.875(14)	k_d	0.084(4)	0.158(15)
α	0.089(4)	0.162(15)	k'_d	0.00196(15)	0.0051(5)
B	0.78(3)	0.521(14)	k_r	0.0047(4)	0.0037(4)
β	0.0067(5)	0.0088(8)	C	2.67(3)	0.895(15)

a) Definitions of the parameters are in the text.

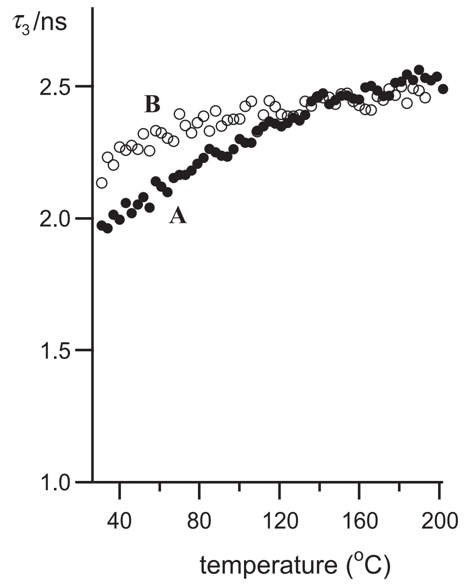


Fig. 5. Temperature dependences of the lifetimes of ortho-positronium τ_3 in **A** and **B**. The lifetime is longer if the positronium is in a larger free space.

Gate Model. All of the carbonyl complexes in polymers **A** and **B** are considered to be activated with a similar probability after irradiation. However, the analysis of the kinetic data has shown that the total concentration of the carbonyl complex that can contribute to the coloring of the polymer is higher in **A** than in **B**. This result indicates that some of the carbonyl complexes in the polymers do not dissociate after they are photoactivated. From positron annihilation experiments (Fig. 5), the average size of the free volume where the positron can move around in both of the polymers is 0.3–0.5 nm^3, corresponding to a diameter of 0.7–0.8 nm. Therefore, the carbonyl complexes in polymer **A** and **B** are confined in cages of similar dimensions. The diameter of the sphere circumscribed about the [W(CO)$_6$] complex, which is equal to the distance between the farthest oxygen atoms, is 0.64 nm. Using the van der Waals radius for oxygen atoms gives the size of the complex approximately equal to or a little larger than that of the average cage. Therefore, only when the dissociated carbon monoxide molecule can go to the neighboring cage, the colored species can be observed. In other words, only the complexes those are in the cages with a gate sufficiently large to allow the dissociated carbon monoxide molecule to leave become colored after irradiation. These are active species, and the complexes in the cages without any gates to the neighboring cage are dead species in the coloring experiments. The ratio of the active species is directly related to the parameter C determined by the analysis of the kinetics, and the value of C in **A** is larger than that in **B**. Therefore, the ratio of the cages with large enough gates is higher in **A** than in **B**. This seems reasonable because the polymer **A** has less cross-links than **B**.

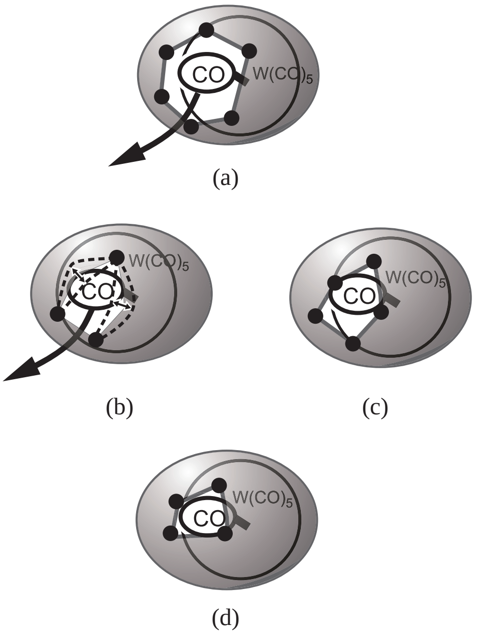


Fig. 6. Schematic picture of the photodissociation processes of the [W(CO)$_6$] complex in different environments. (a) A cage has a large gate to the neighboring cage. The CO molecule can move to the neighboring cage. (b) The size of the gate is intermediate, and the polymer chains are flexible. The CO molecule can move to the neighboring cage by chance. (c) The size of the gate is intermediate, and the polymer chains are rigid. The CO molecule cannot move to the neighboring cage. (d) The gate to the neighboring cage is too small. The CO molecule cannot move to the neighboring cage.

On the other hand, k_d is smaller in **A** than in **B**. This means that the probability in which the carbon monoxide dissociated from the active species can successfully escape to the neighboring cage is lower in **A** than in **B**. Because the carbonyl complex fit in the cage, the gate to the neighboring cage must be just in front of the dissociated carbon monoxide molecule so that the molecule can escape through the gate. Therefore, the probability of successful escape of the molecule is correlated to the area of the gate or the total area of the gates if the cage has more than one gate that is large enough. However, the assumption that the area of the gate is smaller in **A** than in **B** apparently contradicts with the above discussion. The analysis of parameter C indicates that the cages in **A** have larger gates while the analysis of k_d yielded the opposite conclusion. This contradiction cannot be resolved so far as static structures of the polymers are considered.

The polymer chains in **A** and **B** cannot be very rigid since many configurations are possible between the branching points, and the size of each gate varies due to the thermal motion of the chains. If the chains become more flexible and vibrate with larger amplitudes, the complexes in the cage even with smaller gates can escape by chance to the neighboring cage. The gate illustrated in Fig. 6b is open for the carbon monoxide at some instances and close at others. The complexes in these cages have a low probability for substantial dissociation and contribute to the lowering of k_d. If the system contains them in a high ratio, k_d becomes small. On the other hand, if the polymer chains are very rigid, the dissociated carbon monoxide can never pass smaller gates, and only the complexes in the cages with larger gates can escape to the neighboring cage. In this case, the dissociation rate of each active complex is fixed to the upper limit determined by the area of cages because the gate is always open. This dynamic model (Fig. 6) fits the experimental results well. If we assume that the polymer chains in **A** are more flexible and moving in larger amplitudes than those in **B**, the smaller k_d is explained.

The assumption that polymer **A** has chains with higher flexibility is supported by the flexibility of the bulk polymer. The flexural moduli of polymers **A** and **B** are 4.0 and 5.2 GPa, respectively, which shows the polymer **A** is more flexible in bulk. The flexural modulus does not directly indicate the flexibility of the polymer chains; however, it shows the freedom of the motion of polymer chains and reflects the flexibility of the chains. Secondly, the coefficients of thermal expansion of polymers **A** and **B** are 64 and 42 ppm K^{-1}, respectively. The coefficient of thermal expansion indicates the contribution of the anharmonic term of vibration and generally indicates the amplitude of the vibration. The larger value for **A** suggests that the polymer chains in **A** are vibrating greater than in **B**.

In summary, the apparent contradiction in the observed kinetic parameters C and k_d for polymers **A** and **B** can be resolved only with the assumption that the thermal motion of the polymer **A** is larger than that of **B**. This assumption is supported well by the results of other experiments. Before analyzing the results, we expected that the degree of the coarseness of the polymer network, which is the static structure of the polymer, would control the kinetics of the dissociation reaction. However, the analyses of the experimental results revealed that the dynamic nature of the polymer has a strong influence on the kinetics of the photodissociation reaction.

Activation Energy. The smaller rate constant of the recombination reaction in **B** indicates that dissociated ligands are more stabilized in **B**, and this can be related to the structural feature of A-TMMT containing many oxygen atoms. The oxygen atoms make polar sites in the polymer that provide stable positions for the pentacarbonyl complexes and/or carbon monoxide molecules.

At higher temperatures, decoloration is much faster as shown in Fig. 7. The analyses of the change in absorbance at higher temperatures gave an apparent rate constant k, which is the sum of the rate constants of the dissociation reaction and the recombination reaction ($k = k_d{}' + k_r$) as discussed above for the data at 25 °C. The Arrhenius plots of k are convexed curves both for **A** and **B**, as shown in Fig. 8. k_r should obey the Arrhenius equation $k_r = A\exp(-E/T)$ over a small temperature range. However, $k_d{}'$ may not increase as much as expected from the Arrhenius equation because the speed of photodissociation is limited by the intensity of the irradiation light. In fact, k cannot be fitted either with the assumption that $k_d{}'$ also obeys the Arrhenius equation or with the assumption that it is temperature independent. Though quantitative analysis is not possible, the larger increase of k in **A** with increasing temperature is consistent with the above discussion that the polymer chains are more flexible in **A** and have larger thermal motion at higher temperatures.

Reversibility of Photochromic Reaction. One of the most important properties required for a photochromic material is the ability to withstand the cycles of coloring and decoloring. Samples **A** and **B** were heated at 100 °C for ten minutes to become substantially colorless and then irradiated with UV for 60 min. After irradiation, the absorbance of the polymer was measured, and the process was repeated. Similar measurements for the complexes dissolved in the monomers were tried, but the monomers gelled during the cycling. Therefore, the absorbance of the solution of 1 wt % [W(CO)$_6$] in DMF was measured. The absorbance of the DMF solution in each cycle decreases exponentially as shown in Fig. 9. However, the decreases in the absorbances of samples **A** and **B** are much slower. Especially, the small decay in the absorbance of **B** is notable: after seven cycles of irradiation, the absorbance of **B** was 92% of the value after the first irradiation. The good reversibility of **B** indicates that the rigid cross-links of the polymer prevent the dissociated ligands from diffusing to distant sites.

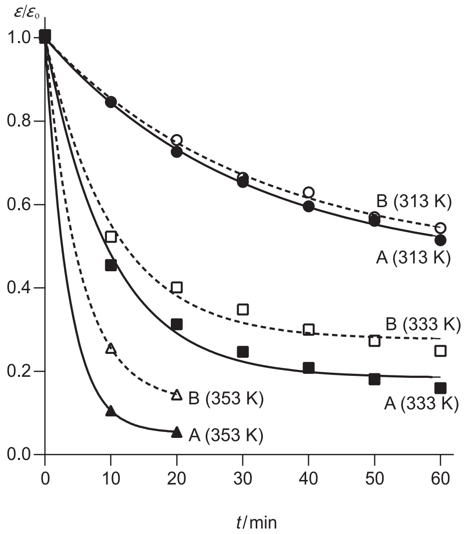


Fig. 7. Time dependences of the relative absorbances at the absorption maxima around 420 nm versus time for **A** and **B** kept in the decoloring process at several temperatures after UV-irradiation. The relative absorbance is defined as $\mathcal{E}/\mathcal{E}_0$ where $\mathcal{E}$ and $\mathcal{E}_0$ are the absorbances at time t and zero, respectively.

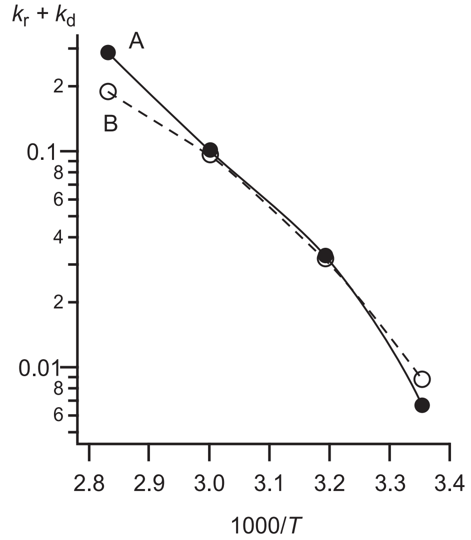


Fig. 8. The Arrhenius plot of the decoloring process for **A** and **B**.

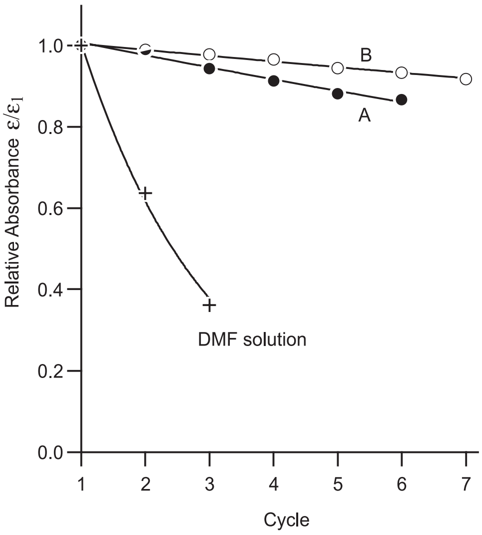


Fig. 9. Plots of relative absorbances at the absorption maxima around 420 nm after UV-irradiation versus number of cycles. The relative absorbance is defined as $\mathcal{E}/\mathcal{E}_1$ where $\mathcal{E}_1$ and $\mathcal{E}$ are the absorbances after the first irradiation and after n cycles of irradiation, respectively.

Conclusion

The kinetic analyses of the photodissociation reaction of the hexacarbonyl tungsten complex have shown that the difference in the kinetic behavior is related to the flexibility of the polymer chains. If the polymer chains are rigid, movement of small molecules is controlled only by the sizes of the openings in the polymer network. However, if the chains are flexible, movement of the dissociated small molecules depends also on the thermal vibrations of the polymer chains. In other words, the microspaces in the cross-linked polymers can be used as the reaction space surrounded by the chains with adjustable flexibility.

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