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Bleaching of Bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) in Polymer Solution and Polymer Matrix

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Bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) (BDN), a Q-switch dye for neodymium lasers, bleached in polymer matrix such as poly(butyl methacrylate). To elucidate the bleaching mechanism, the effect of water-soluble polymer added to dimethyl sulfoxide (DMSO) solution of BDN on the bleaching rate was investigated. BDN was reduced by a water-soluble polymer such as poly(vinyl alcohol) (PVA), starch, and cyclodextrin (CD) in DMSO. BDN bleached in DMSO solution with PVA and bleaching rate depended on the saponification number of PVA. BDN was also bleached by adding CD to DMSO solution. From the concentration dependence of CD on BDN bleaching rate, it was presumed that the vicinity of Ni of BDN is not included in β- and γ-CD, but is included in α-CD. For avoiding reduction of BDN by CD, 2,4,5-tri-*O*-methoxy-β-cyclodextrin (T-β-CD) was examined. BDN was not reduced by an inclusion complex of BDN with T-β-CD. The storage life of Q-switch with matrices of poly(butyl methacrylate) and polystyrene was determined. The Q-switch with polystyrene matrix having transmittance of 70.0% is expected to have transmittance of 70.4% after strage for 10 years at 25 °C.

The toluene solution of bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) (BDN) in glass cell has been used for a Q-switch of neodymium laser, because BDN has absorption peak at 1060 nm, that is the oscillation wavelength of neodymium laser. A solid state Q-switch is desirable for making it small and its life longer. BDN bleaches so remarkably in vinyl polymers that the solid state Q-switch is impracticable. The bleaching of BDN in solution was studied from various points of view[1–4] and it was found that there are two types of bleaching mechanism of BDN: (1) Oxidative bleaching by attacking of radicals[1–3] and (2) reductive bleaching by coordination of solvent to Ni.[4] The oxidative bleaching could be decreased by removing radicals or by inclusion of BDN with cyclodextrin (CD).[3] The author wishes to elucidate the mechanism of bleaching of BDN in polymer matrix. It seems that reduction of BDN by coordination of oxygen in polymer to Ni of BDN is a cause of the bleaching. In order to confirm this assumption, the correlation between the amount of OH group and the bleaching rate was studied with addition of water-soluble polymers containing plenty oxygen such as poly(vinyl alcohol) (PVA), starch, and CD[3] to a dimethylsulfoxide (DMSO) solution of BDN. The storage time and resistance to oscillation of a solid state Q-switch using polystyrene (PS) matrix will also be reported.

Experimental

Materials. BDN was purchased from Kodak Co. and CD from Tokyo Chemical Co. 2,4,5-Tri-*O*-methoxy-β-cyclodextrin (T-β-CD) was presented by Dr. H. Yamaguchi (Colledge of Technology, Ibaraki University). Low molecular weight PVA samples from Unichika Chemical Co. were used after precipitation three times from methanol solution in toluene. Their saponification number was 81.7 (UMR-20H®), 63.8 (UMR-20M®), and 35.0 (UMR-20L®). Starch 2-hydroxypropyl ether of Matsutani Chemical Co. (Stacodex®) was used as starch which was purified by precipitation three times from toluene–methanol system. Butyl methacrylate (PBMA) polymerized in xylene was purified by precipitation three times from methanol–xylene system. A high impact polystyrene from Denki Kagaku Co. (TPUSH®) was purified by precipitation three times from toluene–methanol system. Benzoin ethyl ether (BEE) was purchased from Nakarai Chemical Co. DMSO and petroleum ether of reagent grade by Nakarai Chemical Co. and toluene of Spectral grade by Wako Junyaku Co. were used.

The inclusion complex of BDN with T-β-CD was prepared by the following procedure: BDN (10 mg) and T-β-CD (100 mg) were dissolved in toluene (100 ml) and the solution was stirred for 10 min at 60 °C. Toluene was evaporated with a rotaryevaporator, and the inclusion complex in residue was dissolved into petroleum ether. The liquid was centrifuged at 1000 g for 10 min to remove excess BDN.

Measurement. UV-visible spectra and IR spectra were measured by Shimadzu MPS-5000 spectrophotometer and Shimadzu 430 infrared spectroscope, respectively. The light source for bleaching experiments was Ushio 500 high-pressure marcury lamp with an output of 150 mW cm^{-2}.

Results and Discussion

The effect of polymer on bleaching rate of BDN in solution. The toluene solution of BDN was not bleached in the experiment for a day. A commercial poly(methyl methacrylate) (PMMA) added to the solution caused bleaching as to decrease the absorption peak at 1100 nm. Because the logarithm optical density (OD) at 1100 nm decreased linearly with time at 25 °C, the bleaching reaction is of the first order BDN. But purified PMMA, which was precipitated three times from methanol–toluene system, showed no bleaching effect. When 1 ml of aqueous potassium iodide solution (10%) was added to 10 ml of a toluene solution of commercial PMMA (10%), and the mixture was shaken vigorously and made to stand for 30 min, the color of water layer changed to yellow. This phenomenon suggests the existence of peroxide in the commercial PMMA. It was also shown that benzoin peroxide bleached BDN.[3] It is likely that the remaining peroxide in the commercial PMMA used for polymerization bleached BDN. A peroxide must be removed from polymer by reprecipitation when the polymer is used for matrix of Q-switch. On the other hand, BDN was bleached reductively in a DMSO solution and the absorption peak at 1100 nm shifted to 1030 nm. The rate constant of bleaching reaction was $5.24\times10^{-4}\,\mathrm{min}^{-1}$ at 25 °C. The author proposed a previous paper,[4] that two DMSO molecules coordinate to BDN and the coordinated DMSO molecules reduce BDN to an anion radical in the similar manner as *N*,*N*-dimethylformamide (DMF), and that the following equation holds:

$$\mathrm{BDN} + 2(\mathrm{DMSO}) \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{BDN(DMSO)_2} \xrightarrow{k_2} \mathrm{BDN}\cdot^{\ominus}. \qquad (1)$$

Equation 2 can be obtained from Eq. 1.

$$\frac{\mathrm{d[BDN]}}{\mathrm{d}t} = -k_2\frac{k_{+1}}{k_2+k_{-1}}[\mathrm{BDN}][\mathrm{DMSO}]^2 \qquad (2)$$

Addition of commercial PVA to DMSO solution of BDN made the bleaching rate of BDN to increase. The mechanism of this reaction is thought that DMSO coordinating to BDN takes up proton from OH of PVA and reduces BDN with this proton. A similar reaction mechanism was preveously reported for α-tocopherol.[4] The mechanism can be expressed by the following equation.

$$\mathrm{BDN} + 2(\mathrm{DMSO}) \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{BDN(DMSO)_2}, \text{ and} \qquad (3)$$

$$\mathrm{BDN(DMSO)_2} + \mathrm{PVA} \xrightarrow{k_2} \mathrm{BDN}\cdot^{\ominus}. \qquad (4)$$

Equation 5 can be derived from Eqs. 3 and 4.

$$\frac{\mathrm{d[BDN]}}{\mathrm{d}t} = -\frac{k_{+1}k_2[\mathrm{PVA}]}{k_{-1}+k_2[\mathrm{PVA}]}[\mathrm{BDN}][\mathrm{DMSO}]^2, \qquad (5)$$

where [PVA] is the concentration of monomer unit of PVA. By changing k_{+1}, k_{-1}, and k_2 purposely, the inclination of the plot between [PVA] and bleaching rate varies. For confirming this relation, the experiments were carried out by using PVA with different sapponification numbers. The effect of UMR-20H, -M, and -L in DMSO solution of BDN on the bleaching rate is shown in Fig. 2. Figure 2 shows that the larger the saponification number is, the larger the apparent bleaching rate constant as well as the smaller the slope of plot become. It appears therefore, that the bleaching rate correlates with the number of OH group.

BDN was also reduced by starch. The effect of hydroxypropyl starch (Stacodex®) on the bleaching rate of BDN in DMSO solution is shown in Fig. 3. The hydroxypropyl starch has the following chemical structure.[6]

Starch-O-$\mathrm{CH_2}$-CH(OH)-$\mathrm{CH_3}$.

The inclination of relationship between the concentration of the starch and the bleaching rate of

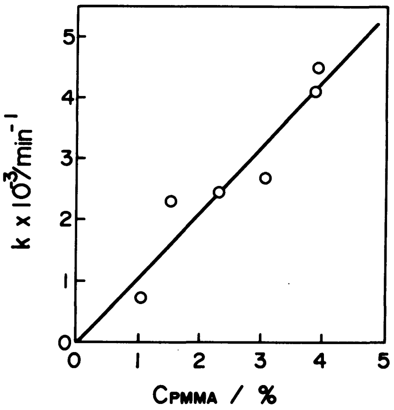

Fig. 1. Dependence of bleaching rate of BDN on the concentration of commercial poly (methyl methacrylate). Concentration od BDN is 5.13×10^{-5} mol dm^{-3}.

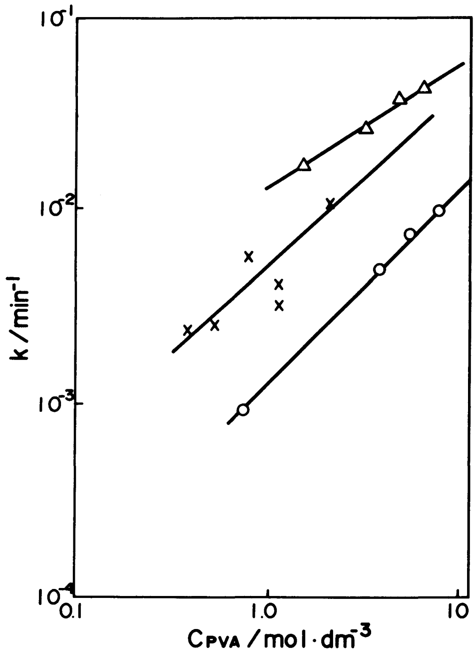

Fig. 2. Dependence of bleaching rate of BDN on the concentration of poly (vinyl alcohol).
—O—: UMR-20L®, —X—: UMR-20M®, —Δ—: UMR-20H®. Concentration of BDN is 5.13×10^{-5} mol dm^{-3}

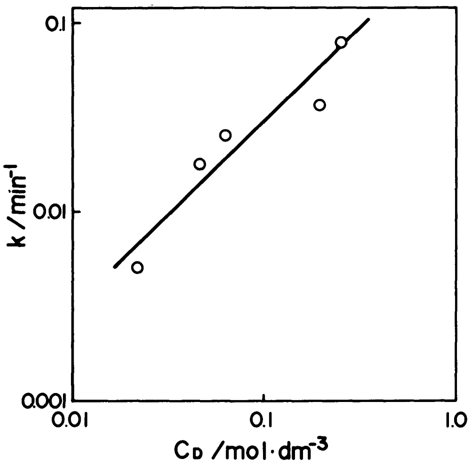

Fig. 3. Dependence of bleaching rate of BDN on the concentration of starch. Concentration of BDN is 5.13×10^{-5} mol dm^{-3}.

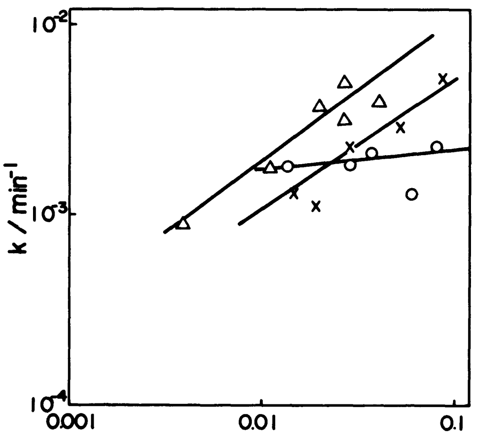

Fig. 4. Dependence of bleaching rate of BDN on the concentration of cyclodextrin.
—O—: α-Cyclodextrin, —X—: β-cyclodextrin, —Δ—: γ-cyclodextrin. Concentration of BDN is 5.13×10^{-5} mol dm^{-3}

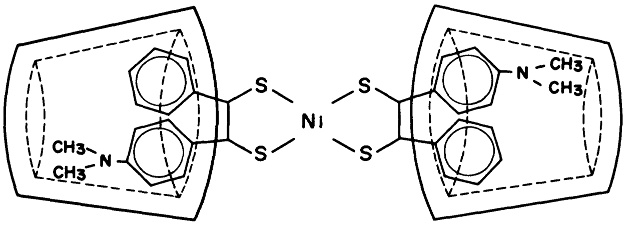

Fig. 5. Assumed structure of the inclusion complex of BDN with β- or γ-cyclodexrin

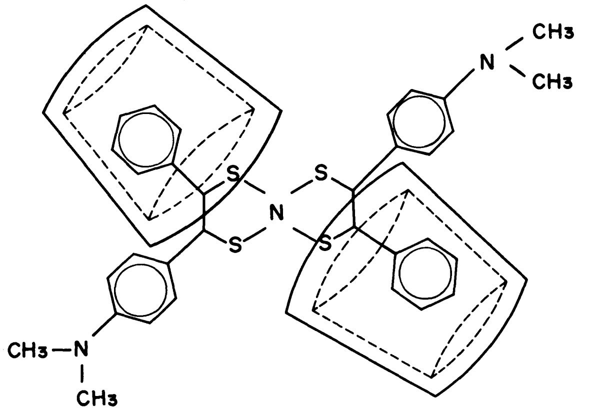

Fig. 6. Assumed structure of the inclusion complex of BDN with α-cyclodextrin.

BDN is unity from Fig. 3. We was recognized in the previous paper[3] that we must reexamine the behavior of BDN in CD. From the following experiment, it was found that BDN is reduced by CD in DMSO solution. The effect of CD on the reduction rate of BDN is shown in Fig. 4 which shows that the bleaching rate of BDN with γ-CD (glucose number, 8) is larger than that with α-CD (glucose number, 6) and β-CD (glucose number, 7). This result will be due to the fact that γ-CD has more OH groups than α-CD and β-CD. The inclination of the plot between concentration of CD and bleaching rate was 0.6—0.7 for β-CD and γ-CD and that was 0.1 for α-CD. Since the CD concentration exceeds that of BDN, it seems that all BDN molecules are included in CD. The fact that BDN was bleached even by β-CD and γ-CD of which have spacious hydrophobic pores indicates that the central Ni of BDN is not included in CD as shown in Fig. 5. Because α-CD has less OH groups than other CD species, it is expected that the slope of plot between concentration of α-CD and bleaching rate must be unity. From the facts that the slope was 0.1, and that α-CD has small hydrophobic pore, a vicinity of Ni of BDN molecule may clog the pore as shown in Fig. 6.

From the above discussion, BDN included in CD seems to be reduced to a product, possibly an anion radical. The material which does not reduce BDN would be considered. T-β-CD with methoxyl instead of OH groups in a toluene solution of BDN did not change the spectrum even after a long time of standing. The optical spectrum of petroleum ether solution of BDN with T-β-CD is shown in Fig. 7. The spectrum differs from that of BDN toluene solution in a point that near-infrared absorption peak at 1100 nm shifts to 960 nm. Because the d–d transition appears at visible region, this compound must not be a reduced product of BDN. A stable inclusion complex was formed, because bleaching rate constant of BDN in petroleum ether with T-β-CD was larger (k=0.151 min^{-1}) than that in toluene solution (k=0.088 min^{-1}), UV light was irradiated after BEE (1%) was added to the solution. IR spectra of BDN included in T-β-CD, BDN, and T-β-CD are compared in Fig. 8. The assignment and absorbance of each peak and the ratios

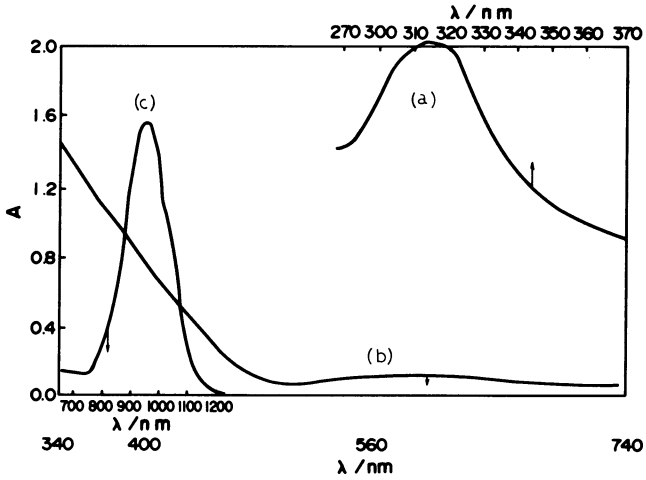

Fig. 7. Optical absorption spectra of inclusion complex of BDN with 2,4,5-tri-*O*-methoxy-β-cyclodextrin. (a) Ultra violet region of spectra, (b) visible region of spectra, (c) near infrared region of spectra. Prepared by the procedure of the Experimental section.

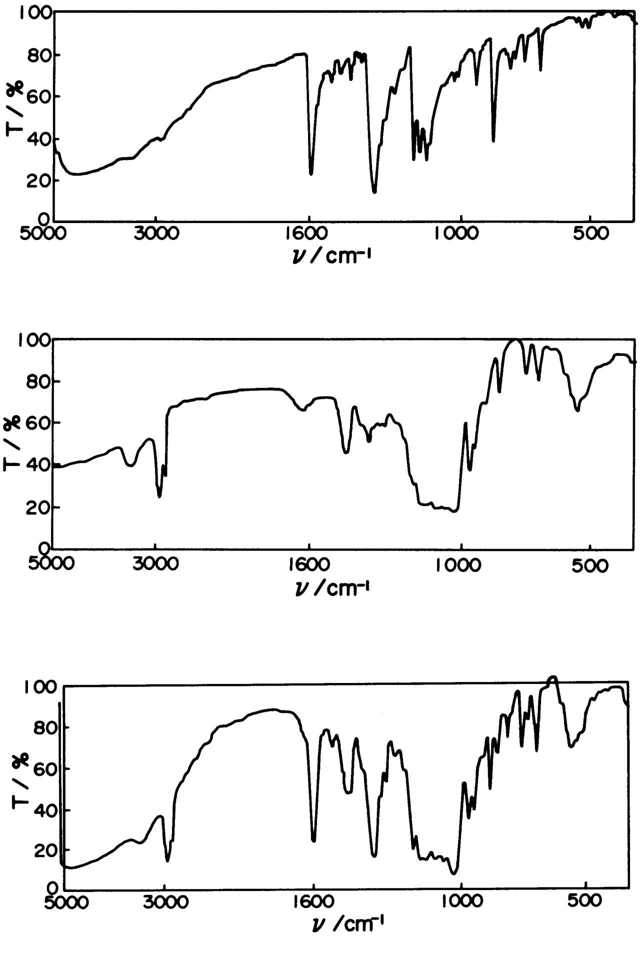

Fig. 8. Infrared spectra of (a) BDN, (b) T-β-CD, (c) inclusion complex of BDN with T-β-CD

Table 1. The Change of Optical Density of Each Infrared Peak of Bis[1-(4-dimethylaminophenyl)-2-phenylethanedithione]nickel(0) by Inclusion to 2,4,5-Trimethoxy-β-cyclodextrin

cm^{-1}	Assignment[9]	BDN		BDN+T-β-CD	
		OD	$OD/OD_{N(CH_3)_2}$	OD	$OD_{N(CH_3)_2}$
1590	$N(CH_3)_2$	0.66	1.0	0.64	1.0
1340	C=C	0.85	1.3	0.80	1.3
875	C–S	0.42	0.64	0.32	0.5

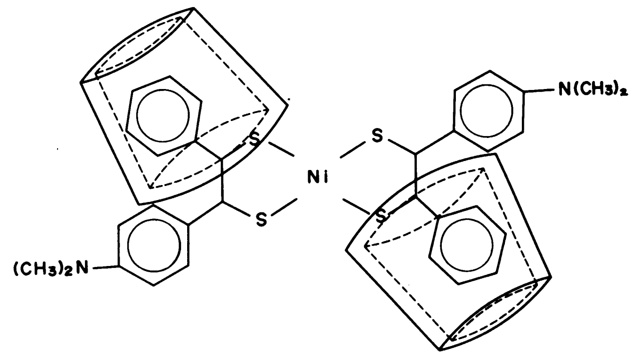

Fig. 9. Assumed structure of the inclusion complex of BDN with T-β-CD.

of optical density for other peaks to that for $\nu(N(CH_3)_2)$ are shown on Table 1. As seen in Table 1, the absorbance of ν(C–S) peak of BDN in T-β-CD decreased by about 20 percent from that of BDN itself. The structure illusteated in Fig. 9 deloneated that $N(CH_3)_2$ group is projected in solvent and benzene ring and C–S are included in CD pores. It will be that BDN is occluded by T-β-CD more shallowly than by α-CD. From this reason, the resistance to attack by radicals of BEE disappears. Storage life of solid state dye Q-switch and resistance to repeating oscillation.

A solid-state dye Q-switch of wich PBMA matrix was prepared. The absorbance was determined with time(days) kept in an electric oven at 69, 83, and 103 °C. Because logarithm absorbance at 1100 nm decreased linearly with the storage time, the rate constant was estimated from tangent of the linear relations. The Arrhenius plot for decay of solid-state dye Q-switch is shown in Fig. 10. Extrapolation of the plot gives the assumed storage life at each temperature (Table 2). The storage time at 30 °C is assumed to be about 2 months. Because PBMA was purified by careful reprecipitation, bleaching of BDN will not occur by residual peroxide, but by reduction with butoxyl group. The Arrhenius plot of bleaching rate of BDN in toluene which contains a small amount of peroxide is also shown in Fig. 10 for comparison.

The author considered that the storage life would be improved by dispersing BDN in a polymer as low-T_g-polystyrene with no N and O atoms, because styrene with lower T_g will decrease damage induced by

Table 2. Estimated Preserved Lifetime of the Q-Switch of Which Dispersion Medium is Buthyl Methacrylate

	Preserved temperature/°C						
	0	10	20	30	40	50	60
k/d^{-1}	3.6×10^{-3}	5.0×10^{-3}	6.7×10^{-3}	8.9×10^{-3}	1.2×10^{-2}	1.5×10^{-2}	1.9×10^{-2}
$T_{70\to75}$/y$^{a)}$	0.34	0.25	0.18	0.14	0.10	0.08	0.06

a) The year for increasing transmittance from 70 to 75%.

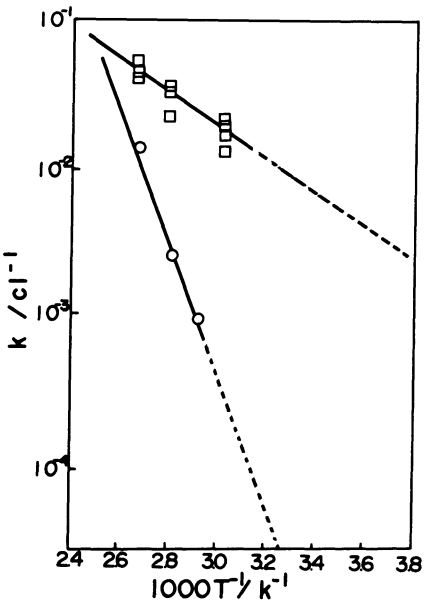

Fig. 10. Arrhenius plot of Q switch which is composed of BDN and poly(n-buthyl methacrylate). —□—: Solid state Q switch of which primary transmittance is 70%, —O—: liquid Q switch of which BDN concentration is 5.13×10^{-5} mol dm^{-3}

Table 3. Estimated Preserved Lifetime of the Q-Switch of Which Dispersion Medium is Polystyrene

	Preserved temperature/°C					
	0	10	20	30	40	50
k/d^{-1}	8.5×10^{-8}	6.6×10^{-7}	2.3×10^{-6}	1.2×10^{-5}	3.2×10^{-5}	1.4×10^{-4}
$T_{70\to75}$/y$^{a)}$	6930	892	256	49	18	4

a) The year for increasing transmittance from 70 to 75%.

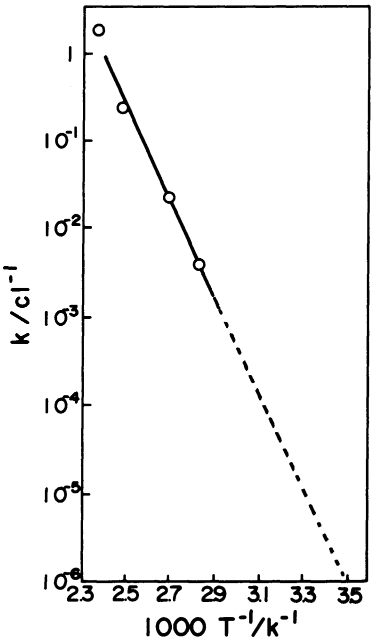

Fig. 11. Arrhenius plot of Q switch which is composed of BDN and polystyrene.

laser.[7,8] A mixed solution of BDN and polystyrene in toluene was coated in 10 μm thickness on a PMMA plate of 1 mm thickness and dried at room temperature. The sample was stored in an oven at 88, 100, and 130 °C. Absorbance at 1100 nm plotted against storage time revealed that logalithm OD decreases linearly with storage time. The Arrhenius plot of bleaching rate constant is shown in Fig. 11. The bleaching rate at each temperature and the storage life assumed by rate constant are given in Table 3. The bleaching rate constant k at 25 °C was estimated from Fig. 11 to be 5×10^{-6}d^{-1}. The result indicated that the transmittance of improved solid-state Q-switch of 70.0% will change to 70.4% after 10 years storage.

The resistance to repeating oscillation of the Q-switch was measured. The Q-switch with BDN dispersed in PBMA withstood against oscilation of 20000 times by 200 J YAG laser for one day, while that dispersed in low-T_g-polystyrene withstood 100 times' oscillation by the similar experiment for 2 hours. The solid Q-switch is believed to be useful for practical use.

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