Improved Durability of Norbornadiene Derivatives Using Antioxidized Reagent

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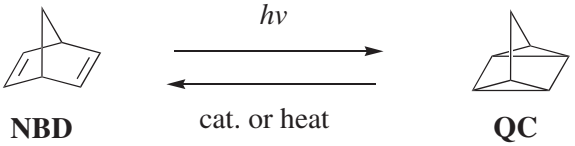
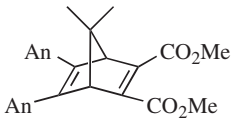
It was found that improvement in durability of NBDs against degradation during repeated cycles of photoisomerization of NBDs to QCs and thermal reversion of QCs to NBDs could be achieved by an antioxidized reagent. Hindered amine derivative was the most effective.

Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system,[1] because photoenergy can be stored as strain energy (about 20 kcal/mol) in a QC molecule. Recently, this photochemical reaction has also been investigated as an optical wave-guide utilizing photoinduced refractive index changes[2] or as a photochromic system potentially applicable to data storage.[3e]



Scheme 1.

Taking these unique characteristics of NBD into account, many NBD derivatives[3] and photoresponsive polymers containing NBD moieties have been synthesized.[4] However, the durability of NBDs that have so far been reported was still not sufficient.[3e,h,i,4f,g]



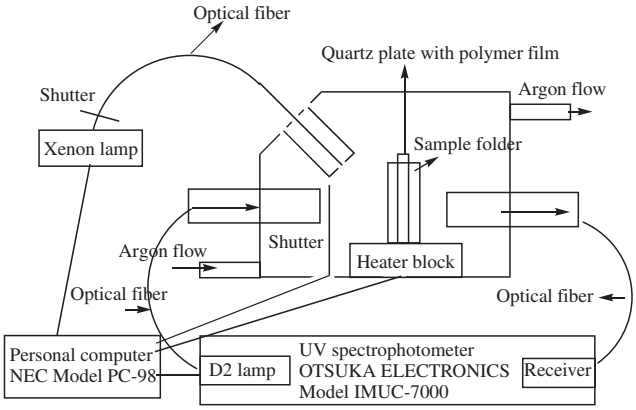
An=*p*-$CH_3OC_6H_5$-

1

Scheme 2. Donor-acceptor NBD derivative **1**.

To improve the durability of NBDs, this time we examined the ability of antioxidized reagents. The examination was carried out under an argon atmosphere by the apparatus, as shown in Figure 1, using the NBDs **1** (Scheme 2)-doped PMMA film on the quartz plate as the samples containing the antioxidized reagent or not containing it.

Initially, the PMMA film was irradiated with a 500-W Xenon lamp until the absorbance of the maximum absorption of the NBDs disappeared. Then, the irradiated film containing the corresponding QCs was heated on a hot plate until the absorbance of the NBDs was reversed. The durability was evaluated from the differences in the absorbance values between the NBDs and QCs at maximum absorption of the NBDs on the first and *n*th cycles of reactions.[5]



Spectrophotometer, heater, and shutter were controlled automatically by personal computer.

Figure 1. Apparatus for the examination of durability of NBDs.

At first, we examined the effect of oxygen for the durability of NBDs. As shown in Figure 2,[5] it was found that NBDs-containing PMMA film that was prepared without oxygen[6] was far more durable than that prepared under air.[7] It was already reported that during the photosensitized isomerization of NBD the oxygen dissolved in the reaction solution accelerated the formation of by-product polymers produced from NBD.[8] Therefore, from this result it is apparent that oxygen contained in the PMMA film promotes the polymerization of NBDs and QCs during the photoisomerization and thermal reversion.

Then, next, we examined the effect of the presence of an antioxidized reagent,[9] shown in Scheme 3, to improve the durability of NBDs. These sample films were also prepared under an argon atmosphere without oxygen. As shown in Figure 3,[5] hindered amine derivative **2**[10] was the most effective for the durability of NBDs in this study. The loss in extinction of NBDs was not detected after 1000 cycles. On the other hand, Ni complex **3**[11] and 2,6-di-*t*-butyl-4-methylphenol **4**[8] markedly decreased the extinction of NBDs over 600 and 300 cycles, respectively. It seems that the organometallic compound is not only effective as an antioxidized reagent but also induces the side reaction by metal catalysis under many reaction cycles, and an oxidized compound produced from phenol derivative **4** by oxygen induces the side reaction of NBDs or QCs.

From all these results, it was found that improvement in durability of NBDs against degradation during repeated cycles of photoisomerization of NBDs to QCs and thermal reversion of QCs to NBDs could be achieved by an antioxidized reagent. Hindered amine derivative was the most effective.

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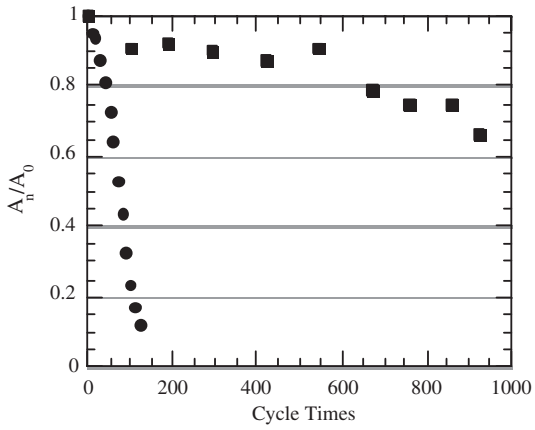


Figure 2. The effect of oxygen on the durability of NBDs **1**; (●) prepared under air; (■) prepared without oxygen.

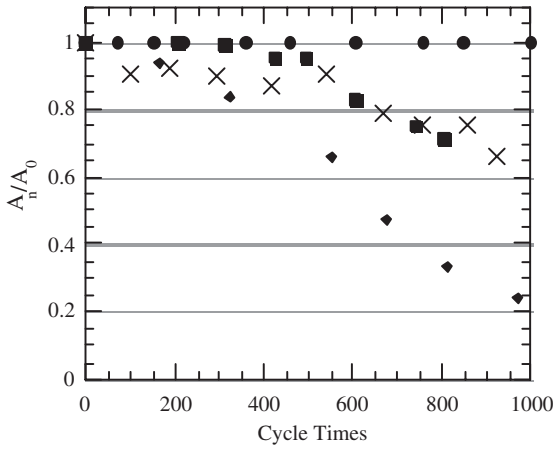
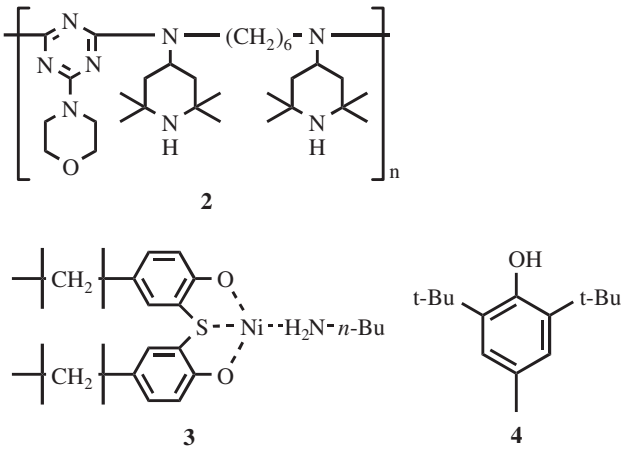


Figure 3. The effect of the antioxidized reagent for the durability of NBDs **1**; (X) in the absence of antioxidized reagent; (●) in the presence of **2**; (■) in the presence of **3**; (◆) in the presence of **4**.



Scheme 3. Antioxidized reagents.

References and Notes

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5 A_0 and A_n are the differences in the absorbance values between NBDs and QCs at λ_{max} of the NBDs on the 1st- and *n*th-cycles of reactions, respectively.

6 NBDs doped PMMA film was prepared under an argon atmosphere from which all oxygen was removed by passage through a column with BASF R-11 copper pellets activated with H_2 prior to use. A solution of NBDs (10 mg) and PMMA (250 mg) in chloroform (2 mL) was degassed by three consecutive freeze-pump-thaw cycles and cast on a quartz plate. Then, the quartz plate-cast film was dried in vacuo at 80 °C for 15 h.

7 NBDs doped PMMA film was prepared under air.

8 H. Taoda, K. Hayakawa, and K. Kawase, *J. Chem. Eng. Jpn.*, **20**, 335 (1987). They reported that the formation of a by-product, polymers obtained from NBD during irradiation, was suppressed by the addition of phenolic radical scavengers.

9 0.5 wt % for NBDs of antioxidized reagent was contained in PMMA film. The wavelength of the maximum absorption of the NBDs was 365 nm in PMMA film. The λ_{max} of **2**, **3**, and **4** was 235, 301, and 282, respectively, and A_{edge} of these compounds was 333, 440, and 305, respectively. Absorbance of **3** and **1** at 365 nm was 0.052 and 0.293, respectively, in 0.1 mM CH_2Cl_2 solution. Then it was considered that the effect of the absorption of the antioxidized reagent was negligible in this study.

10 T. Okuhira, *Polyfile*, **25**, 26 (1988). CYASORB UV-3346 purchased from Cytec Industries Inc., USA. Average M_w is 1600.

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