

SHORT COMMUNICATIONS

Synthesis of New Photoresponsive Polyamides Containing Norbornadiene Residues in the Main Chain

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Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) has been of interest^{1,2} from the view point of solar energy conversion and storage, because this reaction can convert solar energy into thermal energy through the strain energy in the molecule of QC. However, this solar energy conversion and storage system has so far been investigated mostly with relation to low molecular weight NBD derivatives.

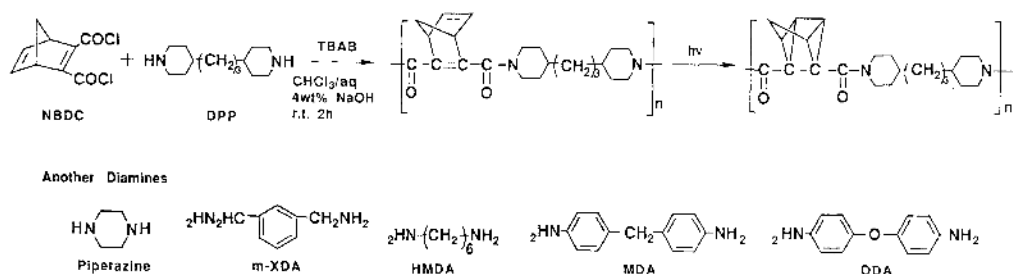
Recently, we reported synthesis of polymers containing pendant NBD moieties by the substitution reaction³⁻⁵ of poly(chloromethylstyrene) with NBD derivatives and by the selective cationic polymerization⁶ of 2-(3-phenyl-2,5-norbornadiene-2-carboxyloxy)ethyl vinyl ether. However, there is no report on the synthesis of any polymer containing

NBD residue in the main chain so far.

This communication reports on the synthesis of some new photoresponsive polyamides containing NBD residue in the main chain by the condensation reaction of 2,5-norbornadiene-2,3-dicarboxylic acid chloride (NBDC) with certain diamines.

NBDC (bp 85 -87°C/0.45 mmHg) was synthesized in 71% yield by the reaction of 2,5-norbornadiene-2,3-dicarboxylic acid with oxalyl chloride.

A typical procedure for the synthesis of polyamide was as follows: 0.631 g (3 mmol) of 1,3-di(4-piperidyl)propane (DPP) and 9.67 mg (0.3 mmol) of tetrabutylammonium bromide were dissolved in 6 ml of 4 wt% aqueous sodium hydroxide solution. To the solution was added 0.651 g (3 mmol) of NBDC dissolved in



Scheme 1.

6 ml of chloroform with vigorous stirring, continuing at room temperature for 2 h. Thereafter, the organic layer was concentrated and poured into diethyl ether. The resulting polymer was reprecipitated from methanol into water, from chloroform into diethyl ether, and dried *in vacuo* at 50°C. The yield of polyamide (P-1) was 0.98 g (92%). Reduced viscosity was 0.09 dl g⁻¹, measured at 0.5 g dl⁻¹ in DMF at 30°C. The IR spectrum of P-1 showed a strong and broad absorption peak at 1615 (C=O and C=C). The UV spectrum (film) showed absorption maximum at $\lambda = 250$ nm. ¹H NMR spectrum (CDCl₃) showed proton signals at $\delta = 0.50$ –3.75 (CH₂, CH, and OH, m, 28H) and 6.50–6.80 ppm (CH=CH, m, 2H).

This result means that polyamide with NBD residue in the main chain was synthesized in high yield by the condensation reaction of NBDC with DPP using TBAB as a phase transfer catalyst. However, the molecular weight of the resulting polymer is rather disappointingly low.

The reactions of NBDC with other secondary and primary diamines such as piperazine, *m*-xylylenediamine (*m*-XDA), hexamethylenediamine (HMDA), 4,4'-methylenedianiline (MDA), and 4,4'-oxydianiline (ODA) were also carried out to give the corresponding polyamides P-2, P-3, P-4, P-5, and P-6, respectively. The reaction conditions and results are summarized in Table I. These results suggest that although the molecular weights are not very high as with P-1, some polyamides with different NBD residues in the main chain were obtained under the same reaction conditions. The UV spectra of the resulting polyamides in dichloromethane solution are summarized in Figure 1.

The polymer solution (0.01 mmol/0.5 ml) in tetrahydrofuran (THF) was cast onto the inside wall of a quartz cell and dried. The cell was photo-irradiated through a thermal-ray cutting filter (Toshiba HA-50) and a UV filter (Toshiba UV-25, except P-1) by a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D)

Table I. Conditions and results for synthesis of polyamides^a

Polym. No.	Diamine	Yield	η_{red}^b	i_{max}^c
		%	dl g ⁻¹	nm
P-1	DPP	92	0.09	250
P-2	Piperazine	81	0.13 ^d	260
P-3	<i>m</i> -XDA	77	0.09	252
P-4	HMDA	79	0.10	250
P-5	MDA	53	0.11	242, 326
P-6	ODA	65	0.11	247, 335

^a Reaction was performed with 3 mmol of each monomer (concn. 0.5 mol l⁻¹) using 10 mol% of TBAB as a phase transfer catalyst in 4 wt% aqueous NaOH solution at room temperature for 2 h.

^b Measured at 0.5 g dl⁻¹ in DMF at 30°C.

^c Measured at film state.

^d Measured at 0.5 g dl⁻¹ in *m*-cresol at 30°C.

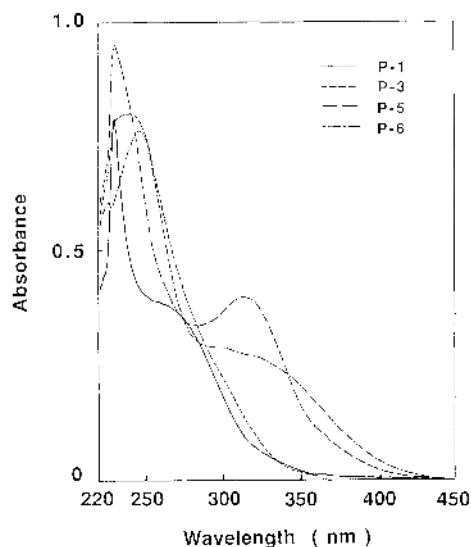


Figure 1. UV spectra of polyamides with NBD residues (1.0×10^{-4} mol l⁻¹) in dichloromethane solution.

at a distance of 30 cm. As shown in Figure 2, the absorption maximum at 326 nm of P-5 film decreased gradually (recorded on a UV-VIS spectrophotometer, Shimadzu Model UV-240), indicating that the NBD moiety was isomerized to the corresponding QC group upon photo-irradiation. The presence of two isosbestic points at 248 and 291 nm in the

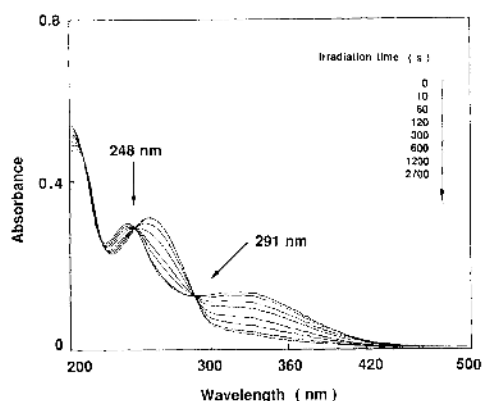


Figure 2. Change in the UV spectrum of P-5 film prepared by the reaction of NBDC with MDA by photo-irradiation.

spectrum was also found. This result indicates that the photochemical valence isomerization of the NBD residue in the main chain of polyamide (P-5) occurred selectively without any side reaction in the film state.

The rates of photochemical valence isomerization of NBD moieties in polyamides P-1, P-3, P-6 were compared with that of P-5 under the same irradiation conditions. As shown in Figure 3, although P-3, P-5, and P-6 films have relatively high photochemical reactivity, the photochemical reactivity of P-1 film was very low. It seems that the photochemical reactivity of polyamides was strongly related to identical optical density in the NBD residues at each wavelength, although the light source also affected to the reaction rate of each polymer. That is, P-3 with strong absorption near 250 nm, and P-5 and P-6 with wide absorption ranges showed higher photochemical reactivity than P-1, even those former polymers were exposed through the filter (UV-25) by the high-pressure mercury lamp.

Accordingly, the photochemical reaction of P-1 film was carried out first with 5 mol% of 4-(*N,N*-dimethylamino)benzophenone (DABP), and then with Michler's ketone (MK) (Figure 4). Interestingly enough, it was found that the photochemical reaction of polyamide

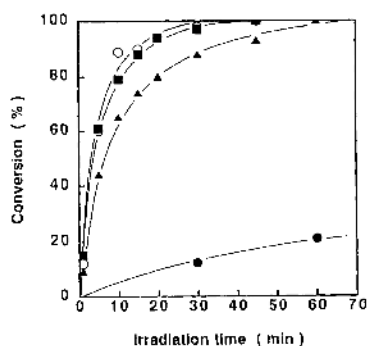


Figure 3. Photochemical valence isomerization of the NBD residue in the polymer film: (●) P-1; (○) P-3; (■) P-5; (▲) P-6.

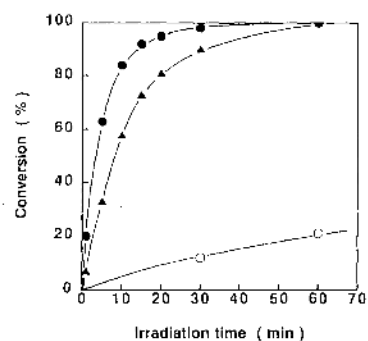


Figure 4. Rate of the photochemical reaction of P-1 film with 5 mol% of the photosensitizer: (▲) with DABP; (●) with MK; (○) without photosensitizer.

P-1 prepared by the reaction of NBDC with DPP was strongly enhanced by the addition of suitable photosensitizers such as DABP and MK in the film state.

Acknowledgment. Further studies of the synthesis of polyamides and copolyamides with NBD residues in the main chain by the reaction of NBDC with diamines, and evaluation of the photochemical reaction of the resulting polymers are now in progress. This work was also supported by a Grant-in-Aid for Scientific Research (No. 03650752) from the Ministry of Education, Science, and Culture of Japan, which is gratefully acknowledged.

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