Synthesis and Photo Valence Isomerization of Polyamide Bearing Norbornadiene Unit

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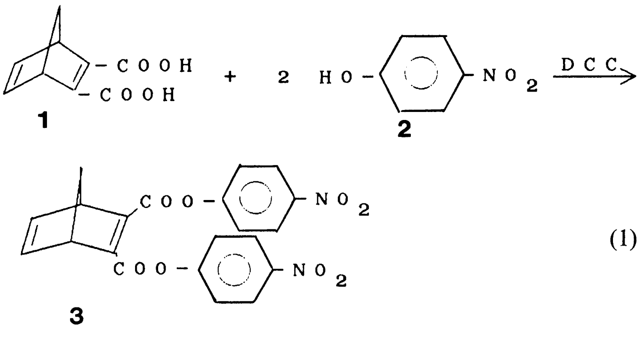
Synopsis. Polyamides bearing norbornadiene (NBD) unit were prepared by the reaction of either bis(*p*-nitrophenyl) 2,3-NBD-dicarboxylate or a mixed anhydride bearing the NBD moiety with various diamines. Films made of the polyamides indicated reversible UV-spectrum changes with UV irradiation, suggesting the occurrence of the photo-valence isomerization between the NBD and quadricyclane units.

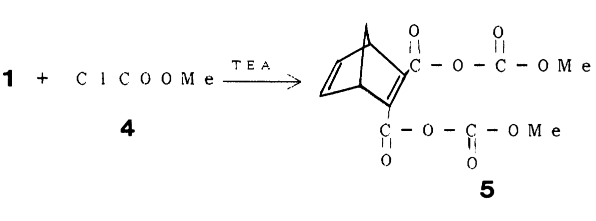
In previous studies,[1,2] we have reported the first syntheses of vinyl polymers bearing the norbornadiene (NBD) unit as pendant via the synthesis of the corresponding vinyl monomers and the results of investigations on the photo-valence isomerization characteristics of the polymers thus prepared.

Nishikubo and coworkers have also prepared vinyl polymers bearing the NBD unit for the purpose of solar energy storage.[3]

Since, in the previous publication,[2] the carboxamide group as 2- and/or 3-substituent of NBD was found to be effective for both improvement of photosensitivity and red shift of UV absorption spectrum, the present study is intended to report the first preparation of the polyamides bearing 2,3-NBDdicarboxylic acid as acid component and the results of investigation on their photo-valence isomerization characteristics.



(1)



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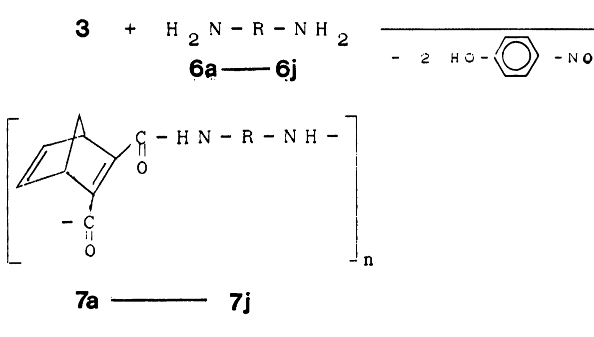
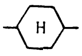
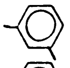
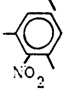
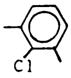
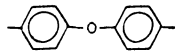
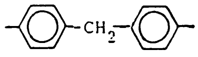
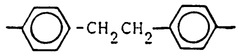
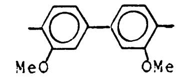
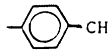


(3)

$$5 + \mathbf{6a—6j} \xrightarrow[-2\,CO_2]{-2\,MeOH} \mathbf{7a—7j} \tag{4}$$

Table 1. Polyamides **7a—j** and a Reference Diamide **7k** Prepared According to Either Eqs. 3 or 4

Compd	R	$[\eta]^{a)}$ dL/g	Preparative method
7a	$-CH_2CH_2-$	0.42	Eq. 3
7b	$-CH(CH_3)CH_2-$	0.36	Eq. 3
7c		1.42	Eq. 3
7d		0.40	Eq. 3
7e		0.18	Eq. 4
7f		0.17	Eq. 4
7g		0.15	Eq. 4
7h		0.63	Eq. 3
7i		0.16	Eq. 4
7j		0.53	Eq. 3
7k			Eq. 4

a) Intrinsic viscosity in DMF at 25 °C.

Polyamides bearing the NBD unit were prepared according to the reaction sequences shown in Eqs. 1, 2, 3, and 4.

where R represents groups given in Table 1.

Experimental

2,3-NBDdicarboxylic acid (**1**) was prepared from cyclopentadiene and 1,2-acetylenedicarboxylic acid.[4]

Bis(*p*-nitrophenyl) 2,3-NBDdicarboxylate (3). Dicyclohexylcarbodiimide (DCC; 8.3 g, 40 mmol) was gradually added to a solution of **1** (3.6 g, 20 mmol) and *p*-nitrophenol (**2**; 6.6 g, 40 mmol) in DMF (45 ml) cooled down to −5 °C, followed by stirring at this temperature for 30 min. Upon standing at 5 °C overnight, the reaction mixture was filtered to remove some insoluble dicyclohexylurea (DCurea). The filtrate was taken up in chloloform (200 ml) and the resulting solution was washed first with 5% aq $NaHCO_3$ then thoroughly with water. The organic layer was worked up as usual and the residue was dissolved in ethyl acetate (20 ml), followed by standing in a refrigerator overnight and subsequent filtration. The filtrate was then chromatographed on a silica-gel (Wakogel C-300) column using benzene as eluting solvent. Recrystallization of crude product from ether provided colorless crystal of mp 131—132 °C in 6% yield. Found: C, 59.96; H, 3.32; N, 6.66%. Calcd for $C_{21}H_{14}N_2O_8$: C, 59.72; H, 3.34; N, 6.63%. IR ($CHCl_3$) 1740, 1520, 1340 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.4 (q, 2H, CH_2), 4.2 (s, 2H, 2-CH<), 7.2 (s, 2H, 2=CH-), 7.5 (d, 4H, ArH), 8.3 (d, 4H, ArH). MS *m/z* 423 (M^+).

Preparation of Polyamides 7a—j According to Eq. 3. A solution of **3** (1.3 g, 3 mmol) and a diamine (**6a—j**; 3 mmol) in DMF (5 ml) was stirred at 20 °C overnight. The reaction mixture was poured into ether-H_2O (1 : 1 v/v) to isolate polymer. IR (KBr) 1650 (-CONH-) cm^{-1}.

Preparation of 7a—j According to Eqs. 2 and 4. Methyl chloroformate (0.95 ml, 10 mmol) was added gradually to a solution of **1** (0.9 g, 5 mmol) and triethylamine (TEA; 1.0 ml, 10 mmol) in DMF (10 ml) cooled to −15—−5 °C with vigorous stirring. A solution of a diamine (**6a—j**; 5 ml) and TEA (1.0 ml, 10 mmol) in $CHCl_3$ (10 ml) was further added with stirring, followed by stirring at 0 °C for one hour and at 20 °C overnight. The reaction mixture was filtered and the filtrate was poured into ether-H_2O (1 : 1 v/v) to precipitate polymer. IR (KBr) 1650 (-CONH-) cm^{-1}.

Preparation of Polyamide Films. A DMF solution containing **7a—j** (3 mg) was spread over the inner wall of a quartz cell (1×3 cm) and dried at 40 °C overnight to afford polymer film ca. 0.004 mm in thickness within the cell.

The cell was then purged with N_2 for 30 min and sealed.

Irradiation of the Films. UV-Irradiation (>310 nm) of the film was carried out at a distance of 10 cm from a 75 W high-pressure Hg lamp (Toshiba SHL100UV), with a Toshiba UV31 filter fitted. The light applied for cycloreversion was obtained by passing the light from the lamp through a grating monochromator (JASCO GT-10S).

Results and Discussion

In order to obtain a polyamide with a high molecular weight following Eq. 3, it was necessary to remove the by-product DCurea hardly separable completely from crude product **3** at the sacrifice of yield until to afford satisfactory analytical results. As regards the method by Eqs. 2 and 4, the intermediate **5** was not isolated as usual.[5,6] As is known from the values of [η] in Table 1, however, molecular weights of the polyamides obtained by Eq. 4 appear to be considerably lower than those by Eq. 3, although polymerization conditions were both very mild. Compound **7k** is a low-molecular weight diamide for reference purpose.

Typical changes of UV absorption spectra for the polyamide films with irradiation by light (>310 nm) in N_2 atmosphere are given in Fig. 1.

These spectral changes are reversible and correspond with those of the NBD–quadricyclane (QC) photovalence isomerization (Eq. 5).[2]

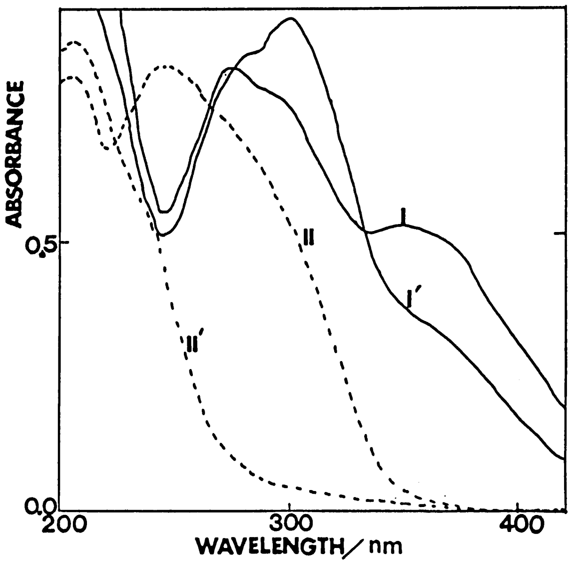
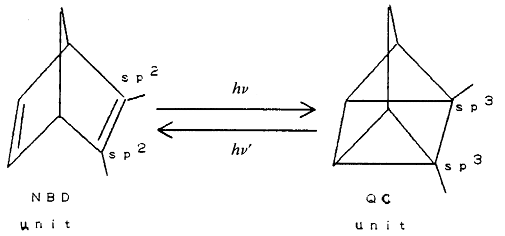


Fig. 1. Typical changes of UV absorption spectra for polyamide films with irradiation by UV light (>310 nm) in nitrogen atmosphere. —— Polyamide **7j**; I: before irradiation (NBD); I′: upon 30 min irrad. (>310 nm). ---- Polyamide **7c**; II: before irrad. (NBD); II′: upon 30 min irrad. (>310 nm).

Table 2. First-Order Rate Constants for the NBD-QC Photo-Valence Isomerization in **7a—k**

Compd	NBD→QC[a]		λ_i[b]	QC→NBD[a]	
	λ_{max}[c]	k_N[e]		λ_{max}[d]	k_Q[f]
	nm	×10^{-2} min^{-1}	nm	nm	×10^{-3} min^{-1}
7a	None	20(320)[h]	227	213	85(220)[g]
7b	241	17	225	200	23(210)[g]
7c	248	12	225	210	9(220)[g]
7d	None	2(330)[h]	295	238	46(250)[g]
7e	None	4(310)[h]	246	<200	Undetermined
7f	None	3(320)[h]	290	239	98(220)[g]
7g	None	3(320)[h]	262	<250	12(230)[h](230)[g]
7h	None	4(320)[h]	275	252	69(250)[g]
7i	None	2(320)[h]	271	225	46(230)[g]
7j	356	7	341,275	301	17(280)[g]
7k[i]	308	20	281	<250	Undetermined

a) NBD: norbornadiene unit; QC: quadricyclane unit. b) Isosbestic point. c) λ_{max} before irradiation at longer wavelengths than λ_i. d) λ_{max} which appeared as a result of irradiation (>310 nm). e) First-order rate constant (NBD→QC) at λ_{max}. f) First-order rate constant (QC→NBD) at λ_{max}. g) Wavelength (nm) of light appllied for cycloreversion. h) Determined at the wavelength (nm) in parentheses. i) Embedded in poly(vinyl methyl ether).



(5)

The 1st order kinetics were found to hold in the reversible spectral changes apparently due to the [2+2] photocycloaddition (NBD→QC) by light of longer wavelengths than 310 nm and the cycloreversion (QC→NBD) by light of shorter wavelengths than isosbestic points. First-order rate constants (k_{N} and K_{Q}) for the polyamides and the reference diamide, together with λ_{max} and isosbestic point (λ_{i}), are summarized in Table 2.

It is known that λ_{i} for the polyamides with an aromatic moiety such as **7d**—**j** are located at longer wavelengths than those with an aliphatic moiety such as **7a**—**c**. It is further known that the values of k_{N} (NBD →QC) for **7a**—**c** are significantly larger than those for **7d**—**j**, presumably suggesting larger steric hindrances suffered in the latters to the conformation changes required for the NBD-QC conversion ($\mathrm{sp^2C}$–$\mathrm{sp^3C}$; Eq. 5) in the solid state. This is demonstrated by the value of k_{N} for the reference **7k** with toluidine residues embedded in a glassy film of poly(vinyl methyl ether), which is comparable to that for **7a**.

The value of k_{Q} (QC→NBD) may depend on irradiation wavelength. However, within the scope of the present study, the values obtained by irradiating light of shorter wavelengths than λ_{i} to the QC form are generally of the same order as those of k_{N}.

In conclusion, polyamides with the NBD moiety introduced into the principal molecular chain in the manner of the present study appear to be subject to significant steric hindrances in the solid state to the conformation change required for the photo-valence isomerization, so that more flexible aliphatic diamine components may provide larger 1st order rate constants (NBD→QC) than more rigid aromatic ones do, although with shorter isosbestic wavelengths.

References

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