

SHORT COMMUNICATIONS

**Successful Cationic Polymerization of Vinyl Ether
Containing Pendant Norbornadiene Moiety**

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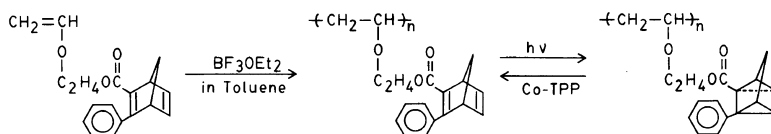
Photochemical valence isomerization between norbornadiene (NBD) derivatives and corresponding quadricyclane (QC) derivatives is well known as a conventional reaction for solar energy conversion and storage systems,¹⁻³ because photoenergy can be stored as strain energy in a QC moiety from which about 96 kJ mol⁻¹ of thermal energy can be released upon contact with some catalysts. However, this solar energy conversion and storage system has so far been investigated mostly for low molecular weight NBD derivatives.

Recently, we reported^{4,5} the synthesis of poly(styrene)s having norbornadiene moieties such as esters of 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNBA) and 3-phenylcarbamoyl-2,5-norbornadiene-2-carboxylic acid by the substitution reactions of poly(chloromethylstyrene) with potassium salts of these acids in the presence of phase transfer catalyst (PTC). The polymers with pendant NBD moieties appear to be useful as new functional-

ity polymers for switch or device material in the opto-electronics and also new photoreactive polymers in imaging technology as well as in solar energy storage systems.

It has been reported⁶⁻⁸ that the cationic polymerization of monomers containing two different C=C groups of both vinyl ether and α,β -unsaturated carboxylate ester groups, such as 2-vinylloxyethyl acrylate, 2-vinylloxyethyl methacrylate, or 2-vinylloxyethyl cinnamate, selectively gives poly(vinyl ether)s containing photoreactive pendant α,β -unsaturated carboxylate esters.

From the viewpoint of the synthesis of functional monomers and selective polymerization of the monomers, this communication reports on the synthesis of a new vinyl ether monomer containing the NBD moiety, its selective cationic polymerization, the photochemical valence isomerization, and catalytic reversion of the resulting polymer.



2-(3-Phenyl-2,5-norbornadiene-2-oxycarbonyl)ethyl vinyl ether (PNVE) was synthesized by the reaction of potassium salt of PNBA (5.01 g, 0.02 mol) with 2-chloroethyl vinyl ether (CEVE) (21.31 g, 0.2 mol) in the presence of tetrabutylammonium bromide (TBAB) (0.644 g, 2 mmol) as a PTC under reflux for 5 h. The yield of PNVE was 4.57 g (81%) (bp 149–152°C/0.43 mmHg). The IR spectrum of PNVE (neat) showed absorption peaks at 1700 (C=O), 1640, 1620 (C=C), 1237 (C–O–C; ester) and 1100 cm⁻¹ (C–O–C; ether). ¹H NMR spectrum (CDCl₃) showed proton signals at δ =2.2 (–CH₂–, q, 2H), 3.8–4.4 (O–CH₂–OCO, CH₂=C, C–H, m, 8H), 6.4 (C=CH–O, dd, 1H), 6.9 (CH=C, m, 2H) and 7.4 ppm (aromatic protons, m, 5H).

A typical procedure for the cationic polymerization of PNVE was as follows: boron trifluoride etherate (BF₃·OEt₂) (0.0341 g, 0.24 mmol) in toluene (0.8 ml) was added dropwise to the toluene (8 ml) solution of PNVE (2.259 g, 8 mmol) at –75°C with stirring, and kept stirring for 3 h. The polymerization was terminated by the addition of a small amount of triethylamine, and the solution was poured into methanol to give precipitation, which was reprecipitated twice from tetrahydrofuran (THF) into methanol and dried *in vacuo* at 50°C. Yields of resulting soluble polymer and insoluble product, which was filtered by 3G type glass filter from THF solution of the polymer, were 76.3 and 4.5%, respectively. The polymerization conditions

and results are summarized in Table I.

The IR spectrum of the soluble PNVE polymer thus obtained showed an absorption peak at 1620 cm⁻¹ due to C=C bond and disappearance of the absorption peak of C=C bond due to vinyl ether group at 1640 cm⁻¹. The ¹H NMR spectrum of the polymer dramatically changed from the spectrum of PNVE monomer, and showed the disappearance of the signal at δ =6.4 ppm based on C=CH–O, although a signal at δ =6.8 due to CH=C still remained, and new appearance of signals at δ =1.6 and 2.5 ppm derived from methylene and methyne of the polymer backbone, respectively.

This means that the polymer containing pendant NBD moiety was successfully obtained by the cationic polymerization of PNVE using BF₃·OEt₂ as a catalyst. That is, selective cationic polymerization of the vinyl ether group in PNVE occurred in toluene using BF₃·OEt₂, although small amounts of insoluble products were obtained. It might be possible that a small amount of C=C double bond at the 5-position in the NBD moiety copolymerized with the vinyl ethers, because the C=C at the 5-position is not electron-withdrawing. The yield of polymer slightly increased with reaction temperature in the range –75~–10°C; however, no further information about the yield of gel products or the degree of polymerization in relation to the reaction conditions was available.

The polymer solution in THF was cast onto

Table I. Conditions and results of cationic polymerization of PNVE^a

Run No.	Temperature/°C	Initiator/mol%	Yield of polymer/%		
			Soluble	Insoluble	η_{sp}/c^b
1	–75	3	76.3	4.5	0.12
2	–75	5	72.8	7.8	0.19
3	–40	3	85.2	9.7	0.13
4	–10	3	92.9	3.1	0.16

^a Polymerization was performed in toluene using BF₃·OEt₂.

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

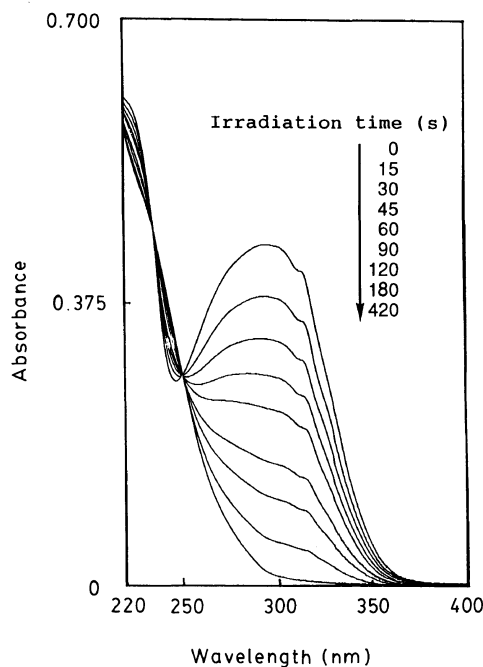


Figure 1. Change in the UV spectrum of the polymer having the pendant NBD moiety by photo-irradiation.

the inside wall of a quartz cell and dried. The cell was photo-irradiated using a 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) at a distance of 30 cm. As illustrated in Figure 1, the rate of disappearance of the absorption maximum at 295 nm of the NBD moiety in polymer film (recorded on a UV-VIS spectrophotometer, Shimadzu Model UV-240) obeyed first order kinetics, and the rate constant of the disappearance was $1.32 \times 10^{-2} \text{ s}^{-1}$. The photochemical valence isomerization of the pendant NBD moiety to the corresponding QC group in the present polymer was found to be faster than that ($7.05 \times 10^{-3} \text{ s}^{-1}$) for poly(styrene)⁴ system having the same NBD moiety. It seems that the observed difference would be due to flexibility of the polymer chain. In addition, the UV spectrum change showed two isosbestic points at 237 and 242 nm indicating that the photochemical valence isomerization of the pendant NBD moieties occurred selectively

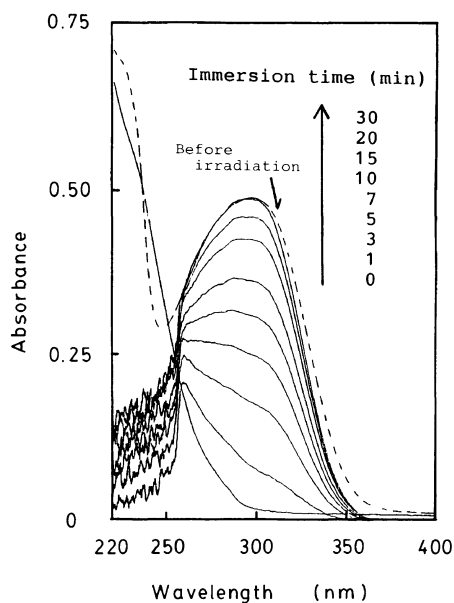


Figure 2. Change in the UV spectrum of the irradiated polymer having pendant QC groups by immersion in a Co-TPP solution of carbon tetrachloride.

without any side reactions in the film state.

As shown in Figure 2, when the irradiated film of the polymer on the quartz cell was immersed in a solution of 5,10,15,20-tetraphenyl-porphyrinato cobalt(II) (Co-TPP) ($1.6 \times 10^{-6} \text{ g ml}^{-1}$) in carbon tetrachloride, its UV spectrum immediately reverted to the original absorption maxima. This suggests that the pendant QC groups in the polymer catalytically reverted to the corresponding NBD moieties upon contact with the Co-TPP solution. The observed rate of the reversion also obeyed first order kinetics, and the rate constant was $2.29 \times 10^{-3} \text{ s}^{-1}$.

Furthermore, it was found that the photo-irradiated PNVE polymer film released about 86.5 kJ mol^{-1} of thermal energy, which was measured by DSC analysis (Perkin-Elmer DSC system 4).

Further studies of cationic or radical polymerization and copolymerization of this monomer, and evaluation of the resulting polymers are now in progress.

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