

SHORT COMMUNICATIONS

Syntheses of Polymers Containing Pendant Norbornadiene Derivatives by a Phase Transfer Catalysis and Their Photochemical Valence Isomerization

Tadatomi NISHIKUBO,* Akemi SAHARA, and Tsutomu SHIMOKAWA

*Department of Applied Chemistry, Faculty of Engineering,
Kanagawa University, Rokkakubashi, Kanagawa-ku,
Yokohama 221, Japan*

(Received February 24, 1987)

KEY WORDS Phase Transfer Catalysis / Chemical Modification / Pendant Norbornadiene Derivatives / Photochemical Valence Isomerization / Pendant Quadricyclane /

Photochemical valence isomerizations between norbornadiene (NB) derivatives and the corresponding quadricyclane (QC) derivatives have been of interest recently from the standpoint of a solar energy conversion and storage system,^{1–3} because photo-energy can be stored as strain energy in QC produced by the irradiation of NB and then released as thermal energy by contact with certain catalysts. However, this solar energy conversion and storage system has so far been evaluated^{4–6} mostly as a low molecular weight NB–QC system using an insoluble polymeric photosensitizer or other photosensitization processes. The polymer containing pendant NB moiety could be useful in polymeric solar energy storage processes and as a new photo-responsive polymer in the field of imaging technology. Recently, Kamogawa and Yamada⁷ reported radical polymerization of (meth)acrylate monomers containing a norbornadiene moiety and the photochemical reaction of the obtained polymer. However, it seems that the rate of photo-response of the pendant NB moiety in this polymer was very low, because this NB moiety did not have any group causing either a red shift of absorption

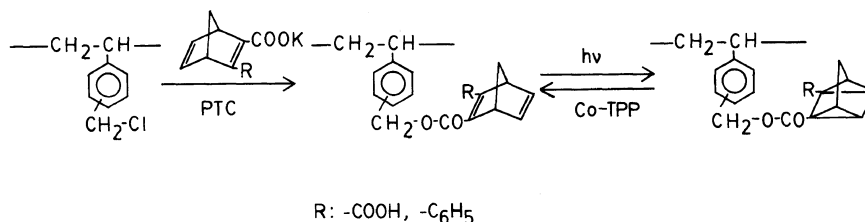
or improvement in photosensitivity.

On the other hand, we investigated extensively the reactions^{8,9} of polymers containing pendant chloromethyl groups such as poly(chloromethylstyrene) (PCMS), and poly(epichlorohydrin) and poly(2-chloroethylvinyl ether) with some nucleophilic reagents using a phase transfer catalyst (PTC), which are practical and very important for the chemical modifications^{10,11} of polymers to yield photosensitive polymers and polymeric photosensitizers under mild reaction conditions.

In this communication, we report the successful syntheses of a polymer containing a pendant NB moiety by substitution reactions of PCMS with potassium salts of 2,5-norbornadiene-2,3-dicarboxylic acid (NBDA) and 3-(phenyl)norbornadiene-2-carboxylic acid (PNBA) using PTC. Also the rate of photochemical valence isomerization of the pendant NB moieties to the QC moieties and the rate of catalytic reversion of QC moieties to the NB moieties are evaluated.

PCMS (reduced viscosity; 0.13, in 0.5 g dl⁻¹ in DMF at 30°C) was prepared by radical polymerization of chloromethyl styrene (mixture of 40% *meta* and 60% *para*) according to the

Scheme 1



reported method.⁸ Potassium salts of NBDA and PNBA were obtained by neutralizing the corresponding acids (mp of NBDA; 164–166°C, mp of PNBA; 125.5–126°C) with potassium hydroxide in methanol and recrystallized twice from benzene. PCMS (4.58 g; 30 mmol) was dissolved in 60 ml of DMF, and then monopotassium salt of NBDA (9.82 g; 45 mmol) and tetrabutylammonium bromide (TBAB) (0.97 g; 3 mmol) was added to the solution. The reaction was carried out at 50°C for 72 h. The reaction mixture was precipitated into 1000 ml of water, reprecipitated twice from THF into methanol, and then dried *in vacuo* at 50°C. The yield of the recovered polymer was 5.93 g. The degree of esterification was 84.4 mol% (calculated from the elemental analysis of chlorine; 20.2 mg g⁻¹). The reduced viscosity of this polymer was 0.22 (0.5 g dl⁻¹ in DMF at 30°C). The IR spectrum (film) of the polymer showed absorptions at 1730 (C=O) and 1610 cm⁻¹ (C=C). The UV spectrum (film) of the polymer showed λ_{\max} at 253 nm. The ¹H NMR spectrum (CDCl₃) of this polymer showed proton signals at δ = 0.8–2.6 (CH–CH₂ in the main chain and C–CH₂–C), 3.9–4.4 (C–CH–C), 4.5 (C–CH₂–Cl), 5.1 (C–CH₂–O), and 6.1–7.6 ppm (CH=CH and aromatic protons).

The reaction of PCMS with potassium salt of PNBA was also carried out under the same reaction conditions at those described. The degree of esterification was 92.9 mol% (calculated from the elemental analysis of chlorine; 7.9 mg g⁻¹). The reduced viscosity of this polymer was 0.18 (0.5 g dl⁻¹ in DMF at 30°C).

The IR spectrum (film) of the polymer showed absorptions at 1690 (C=O), 1600 (C=C), and 1230 cm⁻¹ (C–O–C). The UV spectrum (film) of the polymer showed λ_{\max} at 295 nm. The ¹H NMR spectrum (CDCl₃) of this polymer showed proton signals at δ = 1.0–2.4 (CH₂–CH in main chain and C–CH₂–C), 3.6–4.2 (C–CH–C), 5.0 (C–CH₂–O), and 6.1–7.8 ppm (CH=CH and aromatic protons).

This result suggested that the reaction of PCMS with monopotassium salt of NBDA successfully proceeded with high conversion using PTC under mild reaction conditions, and soluble polymer (P-1) containing a pendant NB moiety was obtained without gelation. The reaction of PCMS with potassium salt of PNBA also proceeded in a high conversion under the same reaction conditions to give the soluble polymer (P-2) containing the other pendant NB moiety.

A solution of P-2 in THF was cast on to the inside wall of quartz cell and dried. The polymer film on the quartz was irradiated by 250 W high pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter at a distance of 30 cm. As shown in Figure 1, the rate of disappearance of the absorption peak at 295 nm was measured by a UV-visible light spectrophotometer (Shimadzu Model UV-240).

Interestingly enough, this result suggests that the rate of photochemical valence isomerization of pendant NB moiety in P-2 to the QC group is very fast in the film state, and the reaction may have proceeded quantitatively without side reactions, because the spectrum showed isosbestic points at 238 and 248 nm.

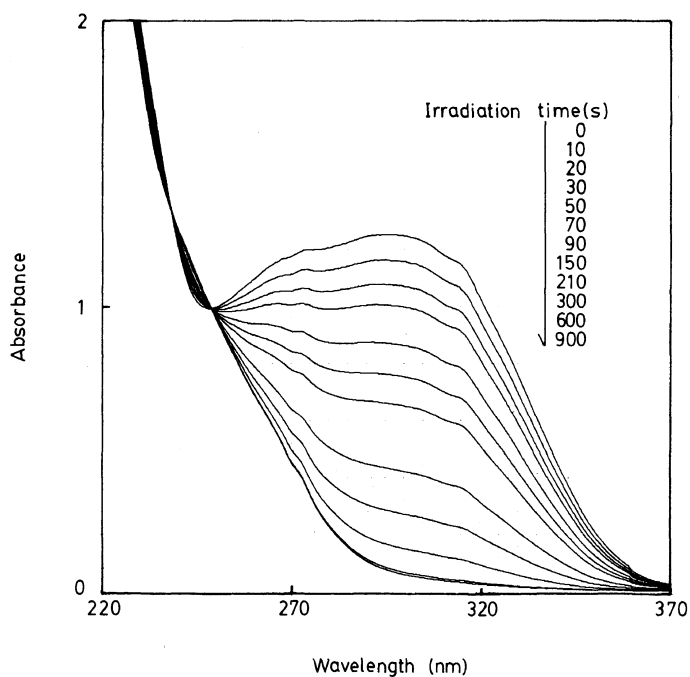


Figure 1. Change in the UV spectrum of P-2 by irradiation.

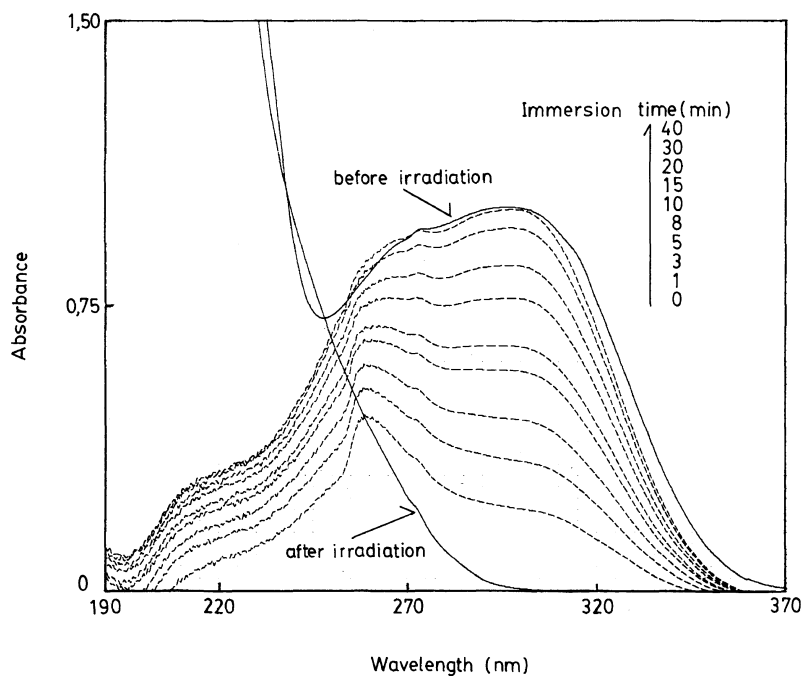


Figure 2. Change in the UV spectrum of P-2 by immersion into the Co-TPP solution of carbon tetrachloride.

The same spectrum change was confirmed in the photochemical valence isomerization of potassium salt of PNBA in water using a polymeric photosensitizer.¹² The observed rate of P-2 obeyed first order kinetics, and the rate constant of this reaction was $7.05 \times 10^{-3} \text{ s}^{-1}$. The photochemical valence isomerization of the pendant NB moiety of P-1 was also carried out in the same manner; however, the rate of reaction for P-1 was lower than that for P-2.

As shown in Figure 2, reversion of the pendant QC group in P-2 to the NB moiety occurred very smoothly when a solution ($1.6 \times 10^{-6} \text{ g ml}^{-1}$) of Cobalt 5, 10, 15, 20-tetraphenylporphyrin (Co-TPP) in carbon tetrachloride was added to the quartz cell in which the irradiated P-2 film had been cast. The observed rate of this reaction also obeyed first order kinetics, and the rate constant of the reaction was $1.16 \times 10^{-3} \text{ s}^{-1}$.

Photosensitization of the pendant NB moiety of P-1 was carried out in film state using benzophenone, *N,N*-dimethylaminobenzophenone and Michler's ketone, which are typical photosensitizers for NB derivatives, since the rate of photochemical valence isomerization for P-1 was lower than that for P-2. As shown in Figure 3, Michler's ketone had higher sensitization efficiency than benzophenone and *N,N*-dimethylaminobenzophenone, and the efficiency of benzophenone was lower than those of the other two.

This result suggest that the pendant NB moiety in the polymer can be sensitized effectively by benzophenone derivatives.

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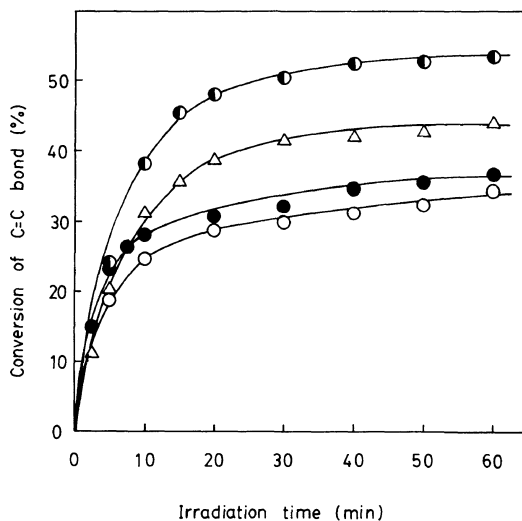


Figure 3. Disappearance rate of the C=C group of the NB moiety in P-1 in the presence of 2 mol% of photosensitizer: (●), with Michler's ketone; (Δ), with *N,N*-dimethylaminobenzophenone; (●), with benzophenone; (○), without photosensitizer.

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