

Synthesis and Photoisomerization Properties of Polynorbornenes with Azobenzene Chromophores

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We successfully synthesized the addition-type polynorbornenes (PNB) exhibiting photochromic properties and excellent thermal stability. Three norbornene-based monomers with different azobenzene moiety (R=NO₂, H, OCH₃) were synthesized by transesterification method. The corresponding PNB copolymers were synthesized by transition metal-catalyzed addition polymerization method, and characterized by GPC, UV-Vis spectroscopy, NMR, and thermal analysis. For comparison of the photochromic properties depending on the rigidity of polymer backbone, we prepared the polymethylmethacrylate (PMMA) copolymer with the corresponding azobenzene moiety. We investigated the photoisomerization behavior by means of optical multichannel analyzer with Xe lamp as well as real-time UV-Vis spectroscopy with high-pressure mercury lamp. Among three PNB copolymers, a polymer with azobenzene (R=H) was the most adaptable for observation of photoisomerization behavior. It was found that the rate of photoisomerization and relaxation depended on the structure of azobenzene chromophore, rather than that of polymer backbone.

Keywords : Photochromic, Photoisomerization, Azobenzene, Polynorbornene.

Introduction

A number of optically functional dyes or/and polymers have been proposed for practical and reliable photonic materials. Especially, azobenzene moiety has drawn great attentions because of their interesting optical properties such as nonlinear optic, liquid crystallinity, photochromism, and optically induced birefringence. It is well known that the azo-aromatic group can exist in two configurations, the trans or the cis form. The cis-trans interconversion can be affected by light and heat. When exposed to light with a certain wavelength, the stable trans form can be photoisomerized to the cis form. Cis-to-trans isomerization can occur thermally or/and photochemically. The energy difference between the ground state of the trans and cis isomers is about 50 kJ/mol in the case of neat azobenzene.¹

The isomerization mechanism²⁻⁴ has been under investigation since the early 1950's, which was first suggested that the azo-aromatic groups were isomerized by rotation about the -N=N- bond. An alternative mechanism was later proposed where isomerization occurred *via* the inversion of one or both of the azo-aromatic groups, and both mechanisms are possible in the photochemical isomerization process.⁴⁻⁶

Azobenzene groups in polymer matrices have been studied in many application.⁷⁻¹⁰ A variety of polymers were used in host/guest,¹¹⁻¹³ main-chain,¹⁴ and side-chain^{15,16} systems. Among them, side-chain poly(methylmethacrylate) (PMMA) would be the most famous structure because of the facile synthesis

for functional monomers and polymers therefrom.¹⁷ However, this PMMA had a critical demerit of lack of thermal stability for practical application. This study describes our preliminary attempts to exploit polynorbornene¹⁸ as a new polymer class for thermally stable optical applications. For example, in order to improve the long-term stability of the stored information, thermally stable polymers with high glass transition temperatures^{19,20} are very attractive as a polymer matrix. Unlike general polynorbornenes that were synthesized by a ring-opening metathesis polymerization, addition-type polynorbornenes have very high glass transition temperatures in the range of 300-360 °C. Functional norbornene monomers can be successfully polymerized with transition metallic catalysts to give corresponding functional polynorbornenes. Recently, we have reported the photochromic polynorbornenes with phenoxyquinone moiety.²¹

In this study, we have prepared some polynorbornenes with azobenzene groups as a side-chain, which is applicable to advanced optical materials due to their higher thermal stability than PMMA series. The addition-type polynorbornenes were copolymerized using azobenzene-bearing norbornenes and a hexyl norbornene monomer by a nickel catalyst. We investigated the differences of thermal and photochromic behavior of azobenzene groups in PMMA^{22,27} and polynorbornene system.

Experimental Section

Materials. Starting materials for chromophore synthesis including 4-nitroaniline, aniline, *p*-anidine, 6-chloro-1-hexanol, triethylamine, methacryloyl chloride, and dibutyltin

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oxide were purchased from the Aldrich Chemical Co. Azobased chromophores such as 4-[2-(4-nitrophenyl)-1-diazenyl]phenol were prepared by a general diazonium coupling method. The dibutyltin oxide (98%) was purchased from Acros. 5-Norbornene-2-ethylester, 5-norbornene-2-hexyl monomers, and nickel catalyst were provided by Promerus LLC (a wholly owned subsidiary of Sumitomo Bakelite, formerly the BFGoodrich Electronic Materials Division). Anhydrous toluene (Aldrich Co.) was used as a solvent for polymerization. As an initiator, 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from acetone.

Synthesis of monomer C1. Into a 250 mL three-necked flask equipped with a magnetic stirrer and a reflux condenser, was added 20 g (82.24 mmol) of 4-[2-(4-nitrophenyl)-1-diazenyl]phenol, 12.36 g (90.46 mmol) of 6-chloro-1-hexanol and 100 mL of *N,N*-dimethylformamide (DMF). To this solution, was added 6.252 g (90.46 mmol) of potassium carbonate, and then the reaction mixture was heated to 90 °C and stirred for 24 h. The mixture was cooled to room temperature and poured into cold water to precipitate the product. The product was purified by recrystallization from acetonitrile, yielding 21.1 g (75.0%) of orange crystal solid. UV(THF): λ_{\max} 375 nm; DSC (10 °C/min): m.p. 80 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.9-7.8 (m, 4H, ArH), 7.2-6.9 (m, 4H, ArH), 4.1-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 1.9-1.2 (m, 8H, $-\text{CH}_2-$).

Synthesis of monomers C2 and C3. The compound C2 and C3 were synthesized according to the same procedure as described above.

C2: UV(THF): λ_{\max} 348 nm; DSC (10 °C/min): m.p. 76 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.0-7.9 (m, 4H, ArH), 7.6-7.4 (m, 3H, ArH), 6.2-5.9 (m, 2H, CH=CH), 4.2-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 2.3-1.2 (m, 8H, $-\text{CH}_2-$).

C3: UV(THF): λ_{\max} 356 nm; DSC (10 °C/min): m.p. 106 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.5-8.3 (m, 2H, ArH), 8.1-7.9 (m, 4H, ArH), 7.3-7.0 (m, 2H, ArH), 4.2-4.0 (m, 7H, $-\text{O}-\text{CH}_2-$), 2.2-1.2 (m, 8H, $-\text{CH}_2-$).

Synthesis of monomer M1. Into a 250 mL three-necked flask equipped with a Dean-Stark apparatus and a reflux condenser, was added 6 g (17.47 mmol) of C1 compound and 4.36 g (26.21 mmol) of norbornene ethylester and 90 mL of toluene. After adding 0.22 g (0.87 mmol) of dibutyltin oxide, the solution was heated at reflux for 24 h. The cooled mixture was evaporated to remove solvent under reduced pressure. The crude product was chromatographed on silica gel using a mixture solvent of hexane/ethyl acetate (4/1), giving 5.65 g (70%) of orange crystals. UV(THF): λ_{\max} 375 nm; DSC (10 °C/min): m.p. 80 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.9-7.8 (m, 4H, ArH), 7.2-6.9 (m, 4H, ArH), 6.1-5.9 (m, 2H, CH=CH), 4.1-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.2-2.9 (m, 2H, 2norbornene-H), 1.9-1.2 (m, 13H, $-\text{CH}_2-$, norbornene-H, 2norbornene-2H).

Synthesis of monomers M2 and M3. The monomer M2 and M3 were synthesized according to the same procedure as described above.

M2: UV(THF): λ_{\max} 348 nm; DSC (10 °C/min): m.p. 76 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.0-7.9 (m, 4H, ArH), 7.6-7.4 (m, 3H, ArH), 6.2-5.9 (m, 2H, CH=CH), 4.2-4.0 (m, 4H,

$-\text{O}-\text{CH}_2-$), 3.2-2.9 (m, 2H, 2norbornene-H), 2.3-1.2 (m, 13H, $-\text{CH}_2-$, norbornene-H, 2norbornene-2H).

M3: UV(THF): λ_{\max} 356 nm; DSC (10 °C/min): m.p. 106 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.5-8.3 (m, 2H, ArH), 8.1-7.9 (m, 4H, ArH), 7.3-7.0 (m, 2H, ArH), 6.2-5.9 (m, 2H, CH=CH), 4.2-4.0 (m, 7H, $-\text{O}-\text{CH}_2-$, $-\text{OCH}_3$), 3.2-2.9 (m, 2H, 2norbornene-H), 2.2-1.2 (m, 13H, $-\text{CH}_2-$, norbornene-H, 2norbornene-2H).

Synthesis of monomer M4. The portion of 10.0 g (33.50 mmol) of C2, 6-4-[2-(4-phenyl-1-diazenyl)phenoxy]-1-hexanol was dissolved in 50 mL of tetrahydrofuran at 50 °C. To this solution was added a solution of 4.2 g (40.20 mmol) of methacryloyl chloride in 5 mL of the tetrahydrofuran and 10 mL of triethylamine. The reaction mixture was stirred at 50 °C for 20 h. After cooling, the mixture was filtered off and then concentrated to remove tetrahydrofuran. The crude product was recrystallized from acetonitrile, producing 10.1 g (83.5%) of needlelike crystals.

M4: UV(THF): λ_{\max} 348 nm; DSC (10 °C/min): m.p. 88 °C; $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.0-7.8 (m, 4H, ArH), 7.5-7.4 (m, 3H, ArH), 7.0-6.9 (m, 2H, ArH), 6.1-5.5 (s, 2H, CH=CH), 4.2-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 2.0 (s, 3H, $-\text{CH}_3$), 1.9-1.5 (m, 8H, $-\text{CH}_2-$).

Copolymerization of CP1. Into a dried 50 mL serum bottle, was placed 1.426 g (8 mmol) of 2-hexyl-5-norbornene, 0.927 g (2 mmol) of M1, 25 mL of anhydrous toluene and a magnetic stirring bar. This bottle was sealed with a crimper and degassed by syringe needles for 20 min under argon atmosphere. The Ni catalyst 0.0485 g (0.1 mmol) in 5 mL toluene, which was prepared in a glove box, was injected all at once into the polymerization bottle with vigorous stirring. After 24 h at room temperature, the viscous polymer solution was diluted with toluene. About 5 g of ion exchange resin was added into the solution to remove catalyst and the mixture was stirred for 5 h. After vacuum filtration, the orange polymer solution was poured dropwise into acetone while stirring. The precipitated copolymer was dissolved again in toluene and this polymer solution was poured dropwise again in acetone. The orange powder was collected by filtration and washed thoroughly with acetone, and dried overnight in oven at 80 °C. Yield: 1.70 g (72%). $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.5-8.3 (m, 2H, ArH), 8.0-7.8 (m, 4H, ArH), 7.1-6.9 (m, 2H, ArH), 4.1-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.0-0.1 (m, 14H, norbornene, 21H, $-\text{CH}_2-$ and $-\text{CH}_3$).

Copolymerization of CP2 and CP3. The copolymerizations of the hexyl norbornene with M2 and M3 were carried out by the same procedure as described above, giving the corresponding CP2, and CP3, respectively.

CP2: $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 7.9-7.8 (m, 4H, ArH), 7.2-7.0 (m, 3H, ArH), 7.0-6.9 (m, 2H, ArH), 4.2-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.0-0.1 (m, 14H, norbornene, 21H, $-\text{CH}_2-$, $-\text{CH}_3$).

CP3: $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.0-7.9 (m, 4H, ArH), 7.0-6.9 (m, 4H, ArH), 4.2-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.0-0.1 (m, 14H, norbornene, 21H, $-\text{CH}_2-$, $-\text{CH}_3$).

Copolymerization of CP4. Into a vacuum-sealable 30 mL polymerization bottle, was added the portion of 1.00 g (2.73 mmol) of M4 and 1.09 g (10.92 mmol) of methylmeth-

acrylate, 15 mL of tetrachloroethane, and 3 mol% (based on total monomer content) of AIBN. The monomer solution was degassed by a vacuum-freeze-thaw method three times until the gas was completely removed. The polymerization was carried out at 60 °C for 24 h. The copolymers solution was poured into methanol, and the precipitated solid was dissolved in tetrahydrofuran and poured dropwise into methanol. This procedure was repeated until the monomer was no longer detectable by a thin layer chromatography. The polymer was dried under vacuum to yield 1.5 g (76.0%) of **CP4**. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 8.0-7.9 (m, 4H, ArH), 7.6-7.4 (M, 3H, ArH), 7.1-7.0 (m, 2H, ArH), 4.1-4.0 (m, 4H, $-\text{O}-\text{CH}_2-$), 3.8-3.4 (s, 3H, $-\text{O}-\text{CH}_3$), 2.1-0.7 (m, 18H, $-\text{CH}_2-$ and $-\text{CH}_3$).

Characterization and measurement. $^1\text{H-NMR}$ spectra were obtained on a Varian unity 600 instrument at 600 MHz for proton. UV-visible spectra were recorded on a Hewlett Packard (model 8453) instrument. The thermal properties of the polymers were investigated using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated using an indium standard. For each polymer, two samples were run, and the values quoted are the average values for the second heating cycle; the heating rate in all cases was 10 °C/min.

The photoisomerization spectra were measured with both solution and film samples. The polymer solution was prepared in chloroform. The polymer films were spin-coated onto glass. The copolymer was dissolved in THF/cyclohexanone at a concentration of 3 wt%, to set the desirable absorbance about maximum 1.0. The solution was filtered out using a microfilter. (Millipore, 0.2 μm /Whatman). The substrate was then spun at 750 rpm for 20 s. After coating, the films were heated to 80 °C under reduced pressure for about 15 h to remove residual solvent. The optic set-up for determination of the photoisomerization behavior of solution samples, is shown in Figure 1. The spectrum was obtained by OMA (Optical multichannel analyzer) using Xe lamp as a light source. The black fluorescent light (355 nm, 6.6 mW/cm^2) was used to induce the photoisomerization (*trans* \rightarrow *cis*) of azobenzene molecules. The second harmonic generation wavelength (532 nm) of Nd:YAG laser was irradiated on first photoisomerized solution to induce reverse-photoisomerization (*cis* \rightarrow *trans*). The exposure time and intensity

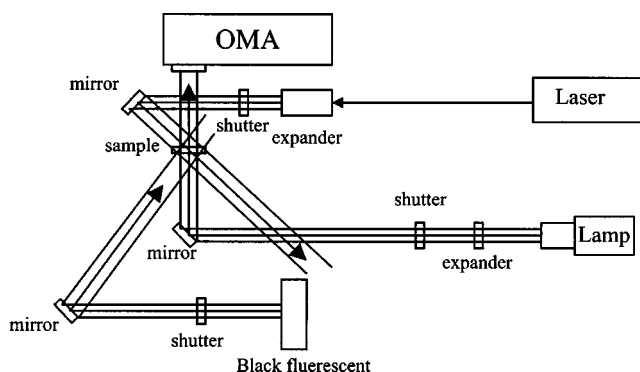


Figure 1. Optical set-up using OMA (Optical Multichannel Analyzer) for measuring the photoisomerization.

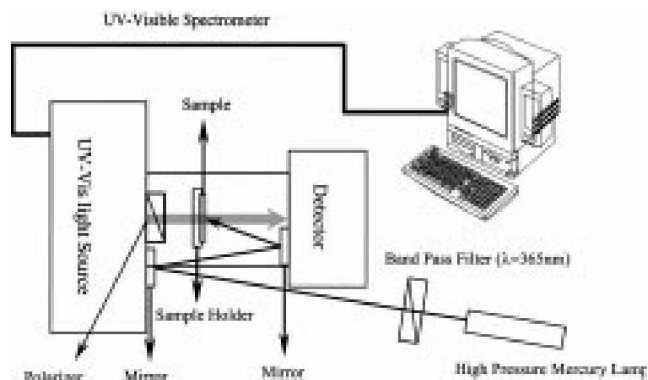


Figure 2. Optical set-up using UV-visible spectroscopy for measuring the photo-isomerization.

was controlled by a shutter and an attenuator, respectively. On the other hand, the optic set-up for determination of the photoisomerization behavior of film samples, is shown in Figure 2. The real-time photoisomerization spectrum was obtained by UV-visible spectrophotometer while irradiating high-pressure mercury lamp (1 kW) with optical fiber cable on the surface of film. The 355 nm band pass filter in front of mercury lamp was used for an irradiation of UV light. The spectrum was recorded by every 5 sec during irradiation. After turning off the UV light, the spectrum was also recorded for determination of the relaxation of the absorbance.

Results and Discussion

Synthesis of monomers and copolymers. The starting materials, azobenzene chromophores with three different substituents ($\text{R}=\text{NO}_2$, H, OCH_3), were easily synthesized by well-known diazotization and coupling method, respectively. The synthetic procedures of norbornene-based monomers are depicted in Figure 3(a). First, the phenoxy compound was reacted with 6-chloro-1-hexanol to produce **C1-C3** with a flexible hexyl spacer. The norbornene-based monomers **M1-M3** were successfully synthesized by transesterification of **C1-C3** with norbornene ethylester using tin catalyst in high yield. All the monomers were obtained as crystals, and their structures were confirmed by $^1\text{H-NMR}$ spectroscopy. We could confirm the $\text{CH}=\text{CH}$ peaks in norbornene unit at 5.9 and 6.2 ppm (*endo*), 6.1 ppm (*exo*). All the monomers had a little higher content of *endo*-isomers than *exo*-isomers (*endo:exo* = 0.55:0.45). For a comparison of photochromic behavior of polynorbornene with poly(methylmethacrylate) (PMMA), we prepared a methacrylate-based monomer, **M4** by esterification with methacryl chloride and **C2**.

The copolymer structures of addition-type polynorbornene (**CP1-CP3**) and PMMA (**CP4**) are shown in Figure 4. Generally, it was well known the polynorbornenes were obtained by a ring opening metathesis polymerization (ROMP), which have $\text{CH}=\text{CH}$ groups in polymer structure. This ROMP-type polynorbornenes have low glass transition temperatures below 50 °C. Fully addition-type polynorbornenes could be synthesized by transition metal catalysts such as palladium and nickel. A certain of polynorbornene has very high glass

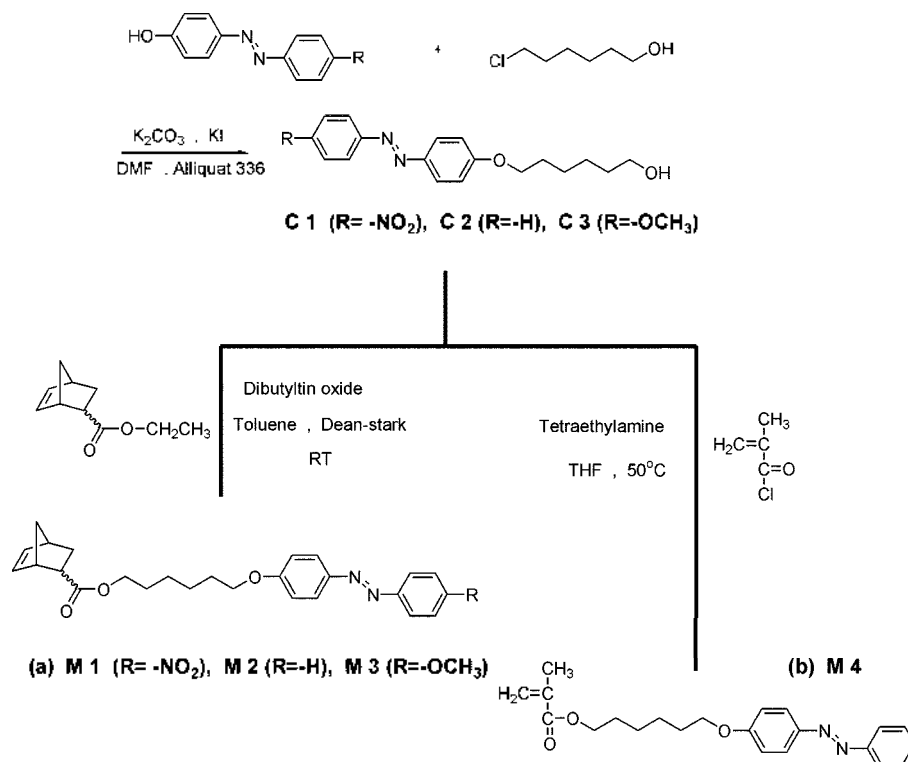


Figure 3. (a) Synthesis of norbornene monomers (**M1**, **M2** and **M3**). (b) Synthesis of methacrylate monomers (**M4**).

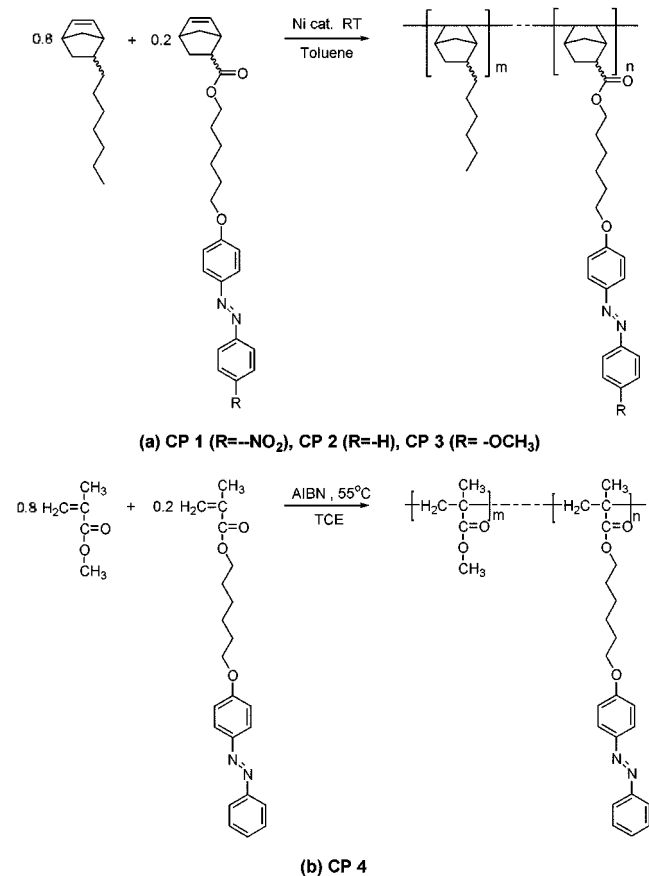


Figure 4. (a) Copolymerization of hexyl norbornene with azobenzene-based norbornene monomers (**CP1**, **CP2** and **CP3**). (b) Copolymerization of MMA with azobenzene-based MMA monomer (**CP4**).

transition temperatures up to 350 °C. Unfortunately, most polymerization produced low molecular weight and low yield because most catalysts were not tolerant enough against polar functional groups. Recently, promising polymerization systems have been developed by B.F. Goodrich Specialty Chemicals (now, Sumitomo Bakelite), which were carried out by using palladium or nickel catalyst.²⁸

In this study, the polynorbornene copolymers were synthesized by nickel catalyzed addition copolymerization of **C1-C3** with hexyl norbornene as a comonomer, respectively. The feed ratio (x:y) of hexyl norbornene monomer and azobenzene comonomer was always 80:20. The catalyst was quite sensitive to moisture and oxygen, and a great care in inert argon atmosphere was taken to prepare the catalyst. The catalyst residue could be removed by stirring with ion exchange resins. Three copolymers were characterized by ¹H-NMR spectroscopy. The CH=CH units of norbornene monomer around 5-6 ppm were disappeared completely and the chemical shift from aromatic protons were appeared as shown in Figure 5. Every polymerization was successfully performed even though these monomers contained polar units such as nitro and ester. The copolymerization results are summarized in Table 1. In all the copolymerization system, azobenzene moieties of **CP1-CP3** were imbedded in 17-21%, which were calculated by the integration of the characteristic chemical shift in ¹H-NMR spectra.

As a result of GPC, it was found that the number-average molecular weight (*M_n*)s of these copolymers (**CP1-CP3**) were in the range of 35,000-44,000. The resulting copolymers were fairly soluble in toluene and chloroform, but not soluble in acetone and DMF. For a comparative polymer

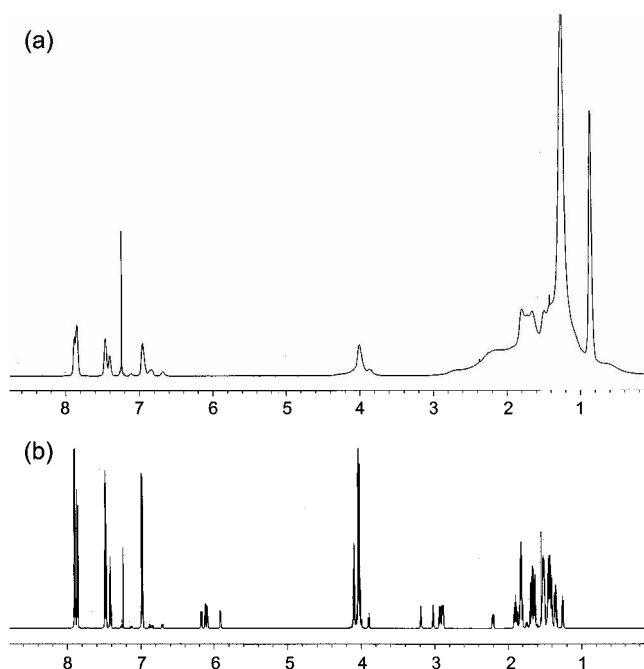


Figure 5. (a) 600 MHz $^1\text{H-NMR}$ spectrum of **CP2** polymer. (b) 600 MHz $^1\text{H-NMR}$ spectrum of **M2** monomer.

Table 1. The Results of copolymerization

No	X Y ^a (mol ^o :/mol ^o %)	Yield (%)	m/n ^b (mol ^o :/mol ^o %)	Mw ^c	Mn ^c	Mw/ Mn ^c
CP1	80:20	72	82:18	87,000	44,000	1.98
CP2	80:20	73	79:21	68,000	35,000	1.93
CP3	80:20	78	83:17	65,000	36,000	1.78
CP4	80:20	76	86:14	128,000	47,000	2.75

^afeed ratio. ^bactual ratio calculated from $^1\text{H-NMR}$ spectrum. ^cmeasured by GPC.

sample, we prepared a PMMA copolymer (**CP4**) bearing **C2** chromophore by a general radical polymerization using AIBN. The number-average molecular weight (M_n)s of **CP4** copolymers were about 47,000. The results of thermogravimetry two samples (**CP2** and **CP4**) are shown in Figure 6. The initial decomposition temperature of norbornene copolymer **CP2** was higher than that of MMA copolymer **CP4**. The onset temperature of decomposition of **CP2** and **CP4** was 402 °C and 330 °C, respectively. The decomposition rate of **CP4** was also quite faster. As we expected, the polynorbornene **CP2** had better thermal stability than **CP4**. The glass transition temperatures of polynorbornene could not be observed on DSC curves, it might be responsible for rigid polymer backbone.

Figure 7 shows the UV-visible spectra of three copolymers (in chloroform). The maximum absorption wavelengths decreased in the order of **CP1** (382 nm, R=NO₂) > **CP3** (361 nm, R=OCH₃) > **CP2** (352 nm, R=H). The **CP2** having no terminal group (R=H) had the lowest λ_{max} of 352 nm (*trans*-isomers) and tiny absorption of 450 nm (*cis*-isomers). In the case of **CP2**, we could observe clearly resolved photoisomerization behavior because the difference between two

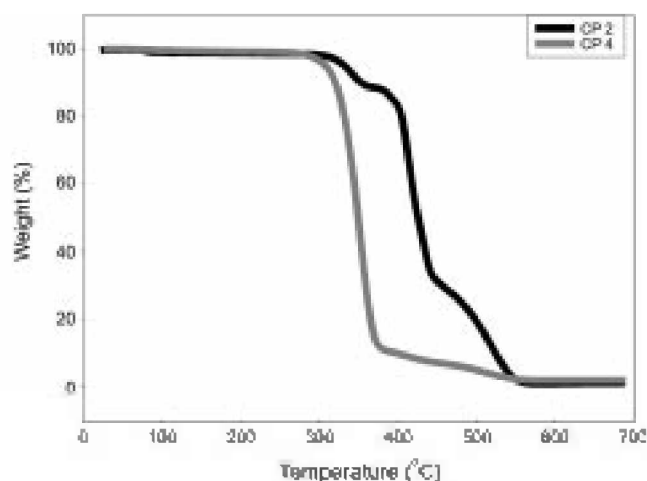


Figure 6. Thermogravimetric curves of **CP2** and **CP4**.

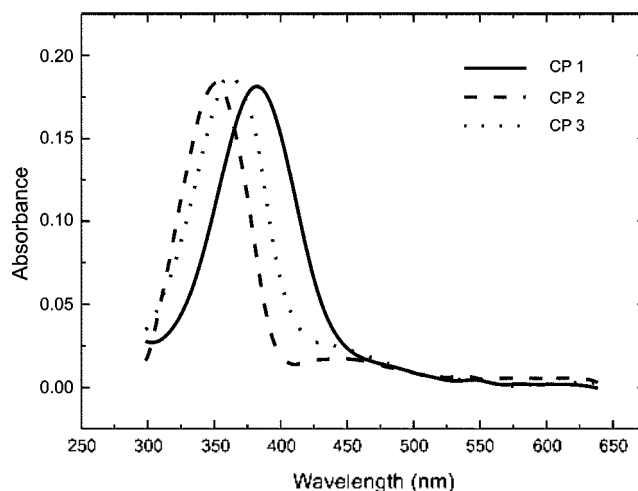


Figure 7. UV-visible spectra of copolymers **CP1-CP3** in chloroform.

absorption peaks was the biggest.

Figure 8(a) shows the absorption spectral change of **CP2** (in solution) during irradiation of UV light (355 nm), which was determined by optical multichannel analyzer (OMA) as drawn in Figure 1. The absorption peak of $\pi \rightarrow \pi^*$ at 352 nm decreased by irradiation of UV light while that of $n \rightarrow \pi^*$ at 450 nm increased, indicating that the *trans* isomer converted to *cis* isomer due to photoisomerization. The absorbance of $\pi \rightarrow \pi^*$ decreased and stabilized in twenty seconds irradiation. The Figure 8(b) shows that the relaxation behavior (*cis* \rightarrow *trans*) of **CP2** after turning off the UV pumping light. We could observe that most of *cis*-isomers of azobenzene changed to *trans*-isomer after about 3 h in this solution state. Figure 8(c) shows the faster reverse *cis* to *trans* isomerization behavior of **CP2** under irradiation of visible light with the wavelength of 532 nm.

The photochromic behavior of **CP1-CP4** films were also measured by real-time UV-vis spectrophotometer with another optical set-up as drawn in Figure 2. The maximum absorption ($\pi \rightarrow \pi^*$) of **CP1**, **CP2**, and **CP3** films were 387, 345, and 366 nm, and the $n \rightarrow \pi^*$ absorption band of copolymer films were 474, 442, and 442 nm, respectively.

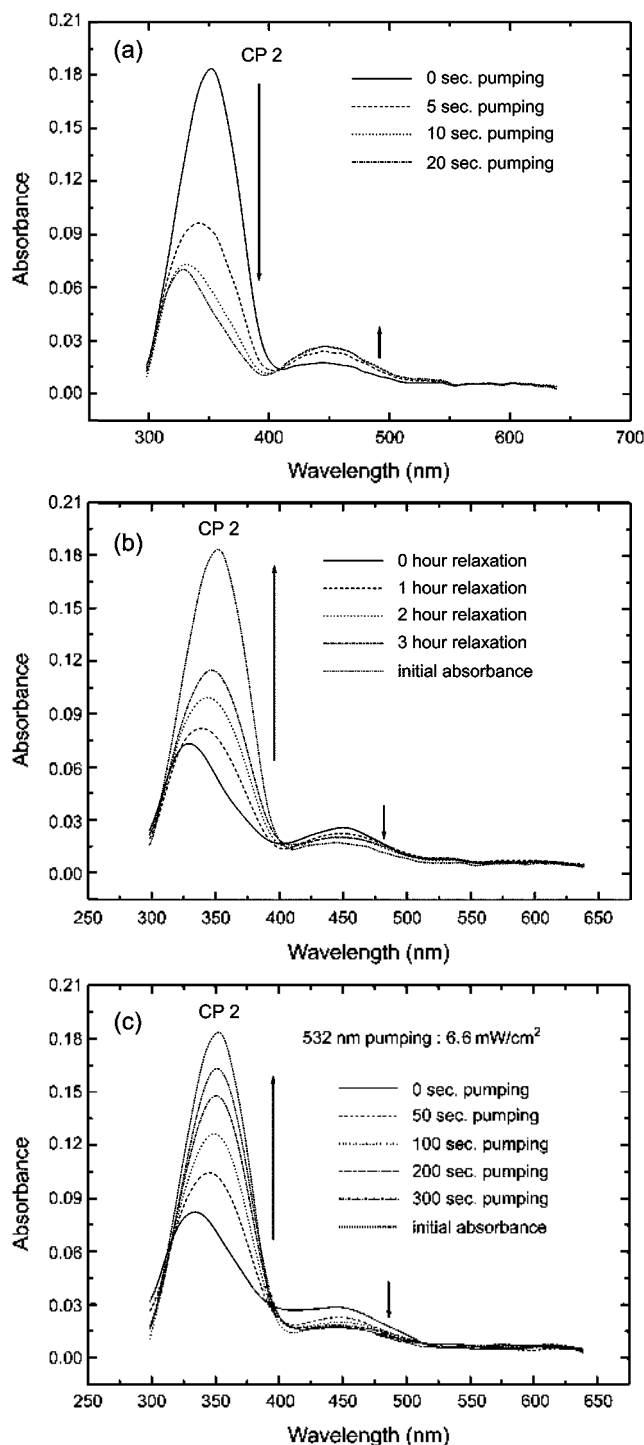


Figure 8. The photoisomerization behavior of **CP2**: (a) Absorption spectrum change on irradiation of UV light (355 nm); (b) Absorption spectrum change after irradiation-off; (c) Absorption spectrum change on irradiation of visible light (532 nm).

There was no remarkable difference of absorption bands between methacrylate-based **CP2** and norbornene-based **CP4**. Figure 9(a) shows that the maximum absorbance due to $\pi \rightarrow \pi^*$ transition decreases after irradiation of 365 nm UV light for 500 s and then the absorbance increase after turning off the pump beam. The **CP1** copolymer showed a smaller decrease of $\pi \rightarrow \pi^*$ band (30%) while **CP2** and **CP3**

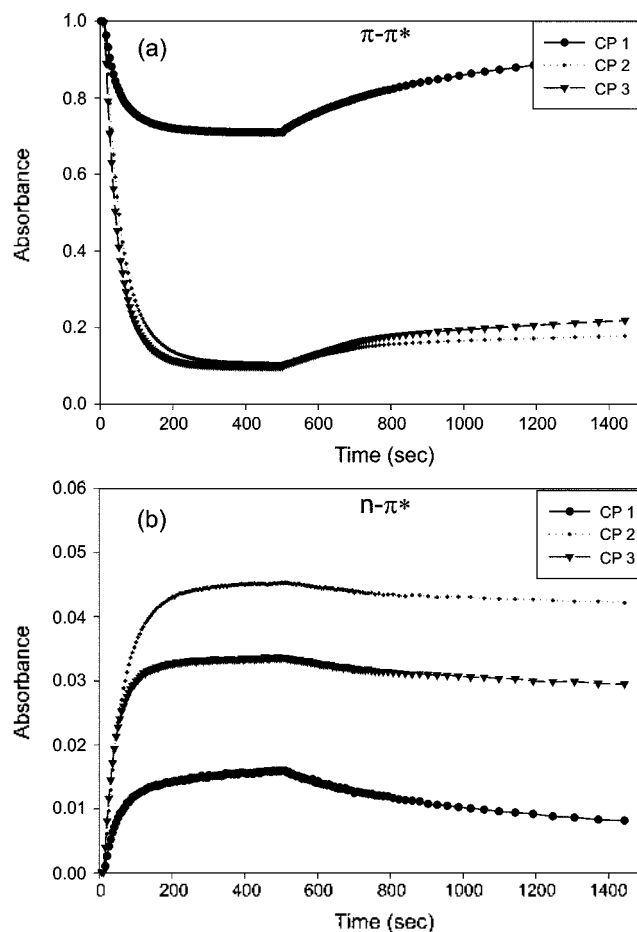


Figure 9. (a) Comparison for photoisomerization ($\pi \rightarrow \pi^*$) and its relaxation behavior of **CP1-CP3**; (b) Comparison for photoisomerization ($n \rightarrow \pi^*$) and its relaxation behavior of **CP1-CP3**.

had larger decrease of $\pi \rightarrow \pi^*$ band (90%). The reason why only a **CP1** with nitro groups had a smaller decrease of $\pi \rightarrow \pi^*$ band, is worthwhile to elucidate. This phenomenon means that trans-azobenzene chromophores of **CP1** are relatively difficult to be transformed to cis-isomers, or cis-azobenzene chromophores of **CP1** are relatively unstable. In case of $n \rightarrow \pi^*$ absorption change in Figure 9(b), the **CP1** exhibited the smallest increase of 0.015, implying that chromophores would not be changed to cis-isomers. In addition, **CP1** showed the fastest relaxation rate after 500 s. In other words, the **CP1** copolymer had the shortest life-time of cis-molecules. Among **CP1-CP3**, the **CP2** (R=H) was the most stable system for cis-isomers of azobenzene. Conclusively, a structure of azobenzene molecules was very important to control photoisomerization rate as well as relaxation rate. For a comparison of photochromic behavior depending on polymer backbone, we carried out the same measurement for **CP2** and **CP4**. Figure 10(a) and (b) shows the photoisomerization and relaxation results of norbornene-based **CP2** and methacrylate-based **CP4**. However, both of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption change was not remarkable as well as the relaxation behavior. As a result, we could conclude that the polymer backbone did not affect on photoisomerization and relaxation rate as much as we expected.

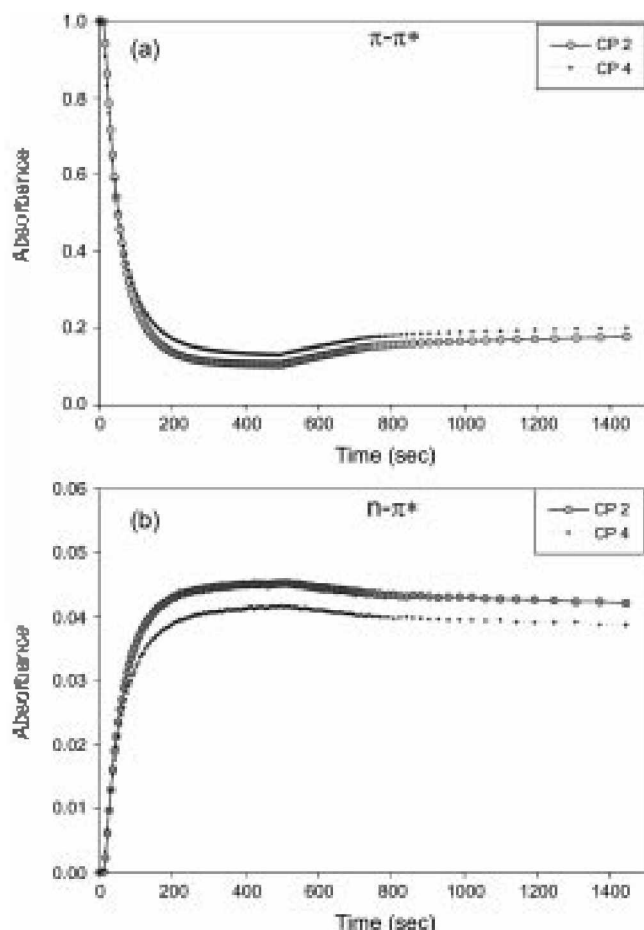


Figure 10. (a) Comparison for photoisomerization ($\pi-\pi^*$) and its relaxation behavior of CP2 and CP4; (b) Comparison for photoisomerization ($n-\pi^*$) and its relaxation behavior of CP2 and CP4.

Conclusions

Azobenzene-based photochromic polynorbornenes were synthesized by nickel-based transition metal catalyst. The polynorbornene copolymer had higher decomposition temperature than polymethylmethacrylate copolymer. Among polynorbornene copolymers (R=NO₂, OCH₃, H), a polymer with azobenzene (R=H) was the most adaptable for observation of photoisomerization behavior, and showed the most stability for *cis*-isomers. For a comparison for photochromic properties depending on the rigidity of polymer backbone, we prepared a comparative polymethylmethacrylate copolymer with the same azobenzene moiety. It was found that the rate of photoisomerization and relaxation is dependent on the structure of azobenzene chromophores rather than the polymer backbone.

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