4822 *Macromolecules* **2010**, *43*, 4822–4826
DOI: 10.1021/ma100527f

Macromolecules
NOTE

Synthesis and Photo-Cross-Linking Reaction of Noria Derivatives Containing Photoreactive Groups

Hiroto Kudo,[†] Nobumitsu Niina,[‡] Rieko Hayashi,[†] Ken Kojima,[†] and Tadatomi Nishikubo*[,†]

[†]*Department of Material and Life Chemistry Faculty of Engineering, Kanagawa University Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan, and* [‡]*Science Frontier, Department of Applied Chemistry, Graduate School of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*

Received August 6, 2009

Introduction

Ultraviolet (UV)-curable resins are photofunctional materials based on polymers and oligomers containing polymerizable groups, such as radical- or cation-polymerizable groups, and have contributed substantially to progress in the electronic and optoelectronic industries. The photochemical reactivity of UV-curable resins depends primarily on the polymer or oligomer structure. Generally, the photochemical reactivity of linear oligomer derivatives is greater than that of polymer derivatives because the molecular motions of the main chains and functional groups of linear oligomers are more active than those of polymers.[1] However, the physical properties, such as mechanical properties, thermal stability, and film-forming properties, of linear oligomer derivatives are inferior to those of polymer derivatives. Recently, we reported that a cyclic oligomer, calixarene, is potentially useful as a UV-curable resin. Calixarene derivatives containing polymerizable groups, such as vinyl ether,[2] methacrylate,[3] propargyl ether,[2] oxetane,[4] oxirane,[4] and spiro ortho-ester groups,[5] showed high photochemical reactivity and excellent physical properties; i.e., these photofunctional cyclic oligomers combine the advantages of linear oligomer and polymer.[6]

We recently synthesized a new ladder-type cyclic molecule, noria (water wheel in Latin), by the reaction of resorcinol and 1,5-pentanedial in one pot.[7] This molecule contains 24 hydroxyl groups and has 6 cavities in the side and a large hydrophobic hole through the center of the molecule, resembling a water wheel in appearance. We reported that noria derivatives containing *tert*-butyloxycarbonyl groups,[8,9] *tert*-butyl ester groups,[10] acetal groups,[11] and adamantyl groups[12] are candidates for novel EB and EUV resist materials and can generate clear line and space patterns at resolutions of 26−70 nm. Very recently, Atwood and co-workers[13] reported that noria and noria derivatives showed selective adsorption of CO_2 over H_2 and N_2 because of the large hole in the molecule. Furthermore, we considered that noria would be applicable as a novel UV-curable material because many polymerizable groups can be introduced by substitution of the hydroxyl groups. The resulting noria derivatives are expected to have good physical properties and excellent photochemical reactivity.

In this paper, we examined the synthesis, properties, and photo-cross-linking reactions of noria derivatives containing methacryloyl, vinyl ether, and oxetanyl groups to assess the suitability of these compounds for application as novel UV-curable materials.

Experimental Section

Materials. Tetrahydrofuran (THF), 1-methyl-2-pyrrolidinone (NMP), triethylamine (NEt_3), glycidyl methacrylate, and 2-chloroethyl vinyl ether were dried over CaH_2 and purified by distillation before use. Commercial grade methacryloyl chloride, ethyl acetate, sodium hydrogen carbonate, hydrogen chloride aqueous solution (12 N), sodium hydride (55−60% grade), tetrabutylammonium bromide (TBAB), 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one (Irgacure 907), and bis[4-(diphenylsulfonium hexafluorophosphate)phenyl] sulfide (DPSP) were used without further purification.

Measurements. Infrared (IR) spectra were measured on a Thermo Electron model Nicolet 380 spectrometer. The ^{1}H NMR spectra were recorded on JEOL model JNM α-500 (500 MHz for ^{1}H NMR) instruments in DMSO-d_6 using Me_4Si (TMS) as an internal standard reagent for ^{1}H NMR. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) with the use of a Tosoh model HLC-8120 GPC equipped with refractive index and ultraviolet detectors using TSK gel columns (eluent DMF, calibrated with narrow molecular weight polystyrene standards). The T_gs of the polymers were measured on a Seiko Instruments differential scanning calorimeter (DSC) model EXSTAR6000/DSC6200 at a heating rate of 10 °C/min under nitrogen. Thermal analysis was performed on a Seiko Instruments thermogravimetric analyzer (TGA) model EXSTAR6000/TG/DTA6200 at a heating rate of 10 °C/min under nitrogen. The rate of photochemical reaction was measured by real-time IR (RT-IR) spectroscopy (Bio-Rad model Excalibur FTS3000MX spectrometer).

Synthesis of Noria Derivative Containing Methacryloyl Groups (Noria-MA$_{100}$). Methacryloyl chloride (5.0 g, 48 mmol) was added slowly to a solution of noria (1.71 g, 1.0 mmol) in NEt_3 (35 mL) at 25 °C, and the resulting solution was stirred for 24 h and then concentrated in a rotary evaporator. Ethyl acetate (50 mL) was added to the residual mass, and the insoluble part was removed by filtration. The organic phase was washed with saturated aqueous sodium hydrogen carbonate, 1 N hydrogen chloride solution, and water. The obtained organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The residue was purified by silica gel column chromatography eluted with ethyl acetate, followed by precipitation from *n*-hexane (200 mL) to obtain a white solid. The degree of introduction (DI) of methacryloyl groups was calculated from the ^{1}H NMR integration ratios of the vinyl moieties at 5.46−6.32 ppm and methine protons at 3.68−4.68. DI > 99%. Yield = 2.57 g (87%). IR (KBr, cm^{-1}): 2929 (ν CH), 1739 (ν C=O of ester), 1637 (ν C=C of methacryloyl), 1496 (ν C=C of aromatic), 1294 and 1128 (ν C(O)−O of ester). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.37−2.71 (m, 108H, $-(CH_2)_3-$ of noria and $-CH_3$ of methacryloyl), 3.68−4.68 (m, 12H, $\rangle$CH− of noria), 5.46−6.32 (m, 48H, $CH_2=$), 6.34−7.90 (m, 24H, aromatic H).

Synthesis of Noria-MA$_{83}$. The noria derivative (noria-MA$_{83}$) with DI of methacryloyl groups = 83% was obtained using noria (1.71 g, 1.0 mmol) and methacryloyl chloride (3.75 g, 36 mmol) in the same way as described for the synthesis of noria-MA$_{100}$. Yield = 1.83 g (62%). IR (KBr, cm^{-1}): 3500 (ν OH), 2929 (ν CH), 1737 (ν C=O of ester), 1637 (ν C=C of methacryloyl),

---

*To whom all correspondence should be addressed. E-mail: nishikubot@kanagawa-u.ac.jp.

1496(ν C=C of aromatic), 1294 and 1131 (ν C(O)−O of ester). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.37−2.71 (m, 95.8H, $-(CH_2)_3-$ of noria and $-CH_3$ of methacryloyl), 3.68−4.68 (m, 12H, $\rangle$CH− of noria), 5.46−6.32 (m, 39.8H, $CH_2=$), 6.34−7.90 (m, 24H, aromatic H), 8.61−9.50 (broad m, 4.1H, −OH).

Synthesis of Noria-MA$_{57}$. The noria derivative (noria-MA$_{57}$) with DI of methacryloyl groups = 57% was obtained using noria (1.71 g, 1.0 mmol) and methacryloyl chloride (1.25 g, 12 mmol) in the same way as described for the synthesis of noria-MA$_{100}$. Yield = 0.95 g (34%). IR (KBr, cm^{-1}): 3446 (ν OH), 2927 (ν CH), 1733 (ν C=O of ester), 1635 (ν C=C of methacryloyl), 1497 (ν C=C of aromatic), 1295 and 1150 (ν C(O)−O of ester). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.48−2.43 (m, 77.0H, $-(CH_2)_3-$ of noria and $-CH_3$ of methacryloyl), 3.68−4.62 (m, 12H, $\rangle$CH− of noria), 5.60−6.42 (m, 27.4H, $CH_2=$), 6.43−7.71 (m, 24H, aromatic H), 8.60−9.50 (broad m, 10.3H, −OH).

Synthesis of Noria-MA$_{28}$. The noria derivative (noria-MA$_{28}$) with DI of methacryloyl groups = 28% was obtained using noria (1.71 g, 1.0 mmol) and methacryloyl chloride (0.75 g, 7.2 mmol) in the same way as described for the synthesis of noria-MA$_{100}$. Yield = 1.46 g (66%). IR (KBr, cm^{-1}): 3450 (ν OH), 2930 (ν CH), 1721 (ν C=O of ester), 1630 (ν C=C of methacryloyl), 1500 (ν C=C of aromatic), 1297 and 1148 (ν C(O)−O of ester). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.51−2.35 (m, 56.2H, $-(CH_2)_3-$ of noria and $-CH_3$ of methacryloyl), 3.95−4.54 (m, 12H, $\rangle$CH− of noria), 5.60−6.50 (m, 13.4H, $CH_2=$), 6.52−7.75 (m, 24H, aromatic H), 8.45−9.76 (broad m, 17.3H, −OH).

Synthesis of Noria Derivative Containing 2-Hydroxy-3-methacryloylpropanoxy Groups (Noria-HMAP$_{100}$). Glycidyl methacrylate (GMA) (5.0 g, 48 mmol) was added slowly to a solution of noria (1.71 g, 1.0 mmol) and TBAB (0. 39 g, 1.2 mmol) in NMP (5 mL) at 25 °C, and the resulting solution was stirred at 100 °C for 48 h. Ethyl acetate (50 mL) was added, and the resulting organic phase was washed with 1 N hydrogen chloride solution and water, dried over $MgSO_4$, and concentrated in a rotary evaporator. The residue was poured into a large amount of cyclohexane to precipitate the solid, which was then dried *in vacuo* at 25 °C for 12 h. The degree of introduction (DI) of methacryloyl groups was calculated from the ^{1}H NMR integration ratios of the vinyl moieties at 5.69−6.02 ppm and aromatic protons at 6.39−7.70 ppm. DI > 99%. Yield = 4.72 g (92%). IR (KBr, cm^{-1}): 3438 (ν OH), 2931 (ν CH), 1714 (ν C=O of ester), 1634 (ν C=C of methacryloyl), 1502 (ν C=C of aromatic), 1296 and 1172 (ν C(O)−O of ester). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): 1.83−2.17 (m, 108H, $-(CH_2)_3-$ of noria and $-CH_3$ of methacryloyl), 3.58−5.60 (m, 156H, $\rangle$CH− of noria and $-CH_2-CH(OH)-CH_2-$), 5.69−6.02 (m, 48H, $CH_2=$), 6.39−7.70 (m, 24H, aromatic H).

Synthesis of Noria Derivative Containing Oxetanyl Groups (Noria-OX$_{100}$). Sodium hydride (NaH) (1.44 g, 60 mmol) was added slowly to a solution of noria (1.71 g, 1.0 mmol) and TBAB (0. 39 g, 1.2 mmol) in NMP (6 mL) at 25 °C, and the resulting mixture was stirred for 1 h. 3-Chloromethyl-3-ethyloxetane (9.64 g, 72 mmol) was added, and the resulting solution was stirred at 80 °C for 48 h. Ethyl acetate (50 mL) was added, and the mixture was washed three times with water. The obtained organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The residue was poured into a large amount of *n*-hexane to precipitate the solid, which was then dried *in vacuo* at 25 °C for 24 h. The degree of introduction (DI) of oxetanyl groups was calculated from the ^{1}H NMR integration ratios of methylene and methyl protons at 0.68−1.91 ppm and aromatic protons at 5.42−7.81 ppm. DI > 99%. Yield = 2.89 g (70%). IR (KBr, cm^{-1}): 2962 (ν OH), 2935 (ν CH), 1502 (ν C=C of aromatic), 1292 and 1107 (ν C(O)−O of ester), 980 (ν C−O−C of oxetane moiety). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.68−1.91 (m, 156H, $-(CH_2)_3-$ of noria and $-CH_2-CH_3$ of oxetane), 3.96−4.95 (m, 156H, $\rangle$CH− of noria, $-OCH_2-$ and $-CH_2-O-CH_2-$ of oxetane moiety), 5.42−7.81 (m, 24H, aromatic H).

Synthesis of Noria Derivative Containing 2-Vinyloxyethoxyy Groups (Noria-VE$_{100}$). Sodium hydride (NaH) (1.15 g, 48 mmol) was added slowly to a solution of noria (1.71 g, 1.0 mmol) and TBAB (0. 39 g, 1.2 mmol) in NMP (6 mL) at 25 °C, and the resulting mixture was stirred for 1 h. 2-Chloroethyl vinyl ether (5.09 g, 48 mmol) was added, and the resulting solution was stirred at 80 °C for 48 h. Then, ethyl acetate (50 mL) was added, and the resulting solution was washed three times with water. The obtained organic phase was dried over $MgSO_4$ and concentrated in a rotary evaporator. The residue was poured into a large amount of methanol to precipitate the solid, which was then dried *in vacuo* at 25 °C for 24 h. The degree of introduction (DI) of vinyl ether groups was calculated from the ^{1}H NMR integration ratios of vinyl, methylene, and methyl protons at 3.65−4.75 ppm and aromatic protons at 6.00−7.50 ppm. DI > 99%. Yield = 2.64 g (78%). IR (KBr, cm^{-1}): 2939 (ν CH), 1617 (ν C=C of vinyl), 1500 and 1455 (ν C=C of aromatic), 1294 and 1158 (ν C(O)−O of ester), 1005 (ν C−O−C). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): 0.28−2.37 (m, 36H, $-(CH_2)_3-$ of noria), 3.65−4.75 (m, 156H, $\rangle$CH− of noria, $-OCH_2CH_2O-$, $CH_2=$), 6.00−7.50 (m, 48H, aromatic H and $=CH-$).

Photoradical Cross-Linking-Reaction of Thin Films of Noria-MA$_{100}$, Noria-MA$_{83}$, Noria-MA$_{57}$, and Noria-HMAP$_{100}$. A typical procedure for the photoradical cross-linking-reaction is as follows: A solution of a noria derivative (0.3 g), Irgacure 907 (9 mg) as a photoradical initiator, and 2-ethylanthraquinone (2-EAQ) (3 mg) as a photosensitizer in THF (2.0 mL) was cast on a KBr plate and dried *in vacuo* at room temperature to obtain a film. The resulting film was irradiated with a 250 W high-pressure mercury lamp (8.0 mW/cm^2 at 254 nm) through a monochromator (Jasco model CT-10). The decrease of the peak at 1637 or 1634 cm^{-1} assignable to methacryloyl groups was followed with an RT-IR spectrophotometer.

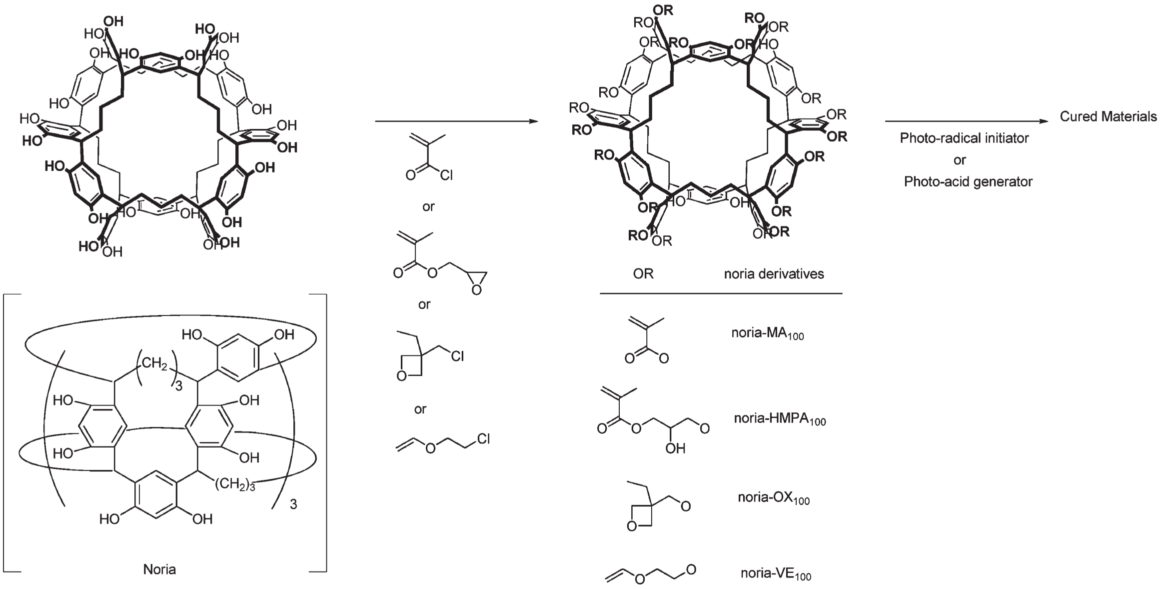
Photocationic Cross-Linking Reaction of Thin Films of Noria-OX$_{100}$ and Noria-VE$_{100}$. A typical procedure for the photocationic cross-linking reaction is as follows. A solution of a noria derivative (0.3 g) and DPSP (9 mg) as a photocationic initiator in $CHCl_3$ (2.0 mL) was cast on a KBr plate and dried *in vacuo* at room temperature to obtain a film. The resulting film was irradiated with a 250 W high-pressure mercury lamp (8.0 mW/cm^2 at 254 nm) through a monochromator (Jasco model CT-10). The decrease of the peak at 980 cm^{-1} assignable to oxetanyl groups or that at 1617 cm^{-1} assignable to vinyl ether groups was followed with an RT-IR spectrophotometer.

Results and Discussion

Synthesis of Noria-MA$_x$. All of the hydroxyl groups of noria were converted to methacryloyl groups by reaction with methacryloyl chloride in NEt_3 at 25 °C for 24 h, affording noria-MA$_{100}$ in 87% yield (Scheme 1). The structure of noria-MA$_{100}$ was confirmed by IR and ^{1}H NMR spectroscopy. Noria derivatives with other conversion rates of methacryloyl groups were also synthesized by the controlling the feed ratio of methacryloyl chloride and noria. Noria-MA$_{83}$ with degree of introduction of methacryloyl groups (DI = 83%), noria-MA$_{57}$ (DI = 57%), and noria-MA$_{28}$ (DI = 28%) were synthesized in 62, 34, and 66% yields, respectively.

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity ratio (M_w/M_n) were determined by means of SEC. The values of M_n and M_w of noria-MA$_x$ (x = 100, 83, 57, and 28) increased with increasing value of DI. However, the values of M_w/M_n were all the same, i.e., 1.01, indicating that the ratio of DI could be controlled very precisely (Figure 1). However, the MALDI-TOF mass spectra of noria-MA$_x$ (x = 83, 57, and 28) could not be observed.

Scheme 1. Synthesis and Photochemical Reaction of Noria Derivatives



Synthesis of Noria Derivatives Containing 2-Hydroxy-3-methacryloylpropanoxy Groups (Noria-HMAP$_{100}$), Oxetanyl Groups (Noria-OX$_{100}$), and 2-Vinyloxyethoxyy Groups (Noria-VE$_{100}$). Other photopolymerizable groups were introduced into noria (Scheme 1). The noria derivative with pendant 2-hydroxy-3-methacryloylpropanoxy groups (noria-HMAP$_{100}$) was synthesized by the reaction of noria and glycidyl methacrylate (GMA) in the presence of TBAB in NMP at 100 °C for 48 h. The noria derivatives with pendant oxetanyl groups (noria-OX$_{100}$) and 2-vinyloxyethoxy groups (noria-VE$_{100}$) were synthesized by the reaction of noria with 3-chloromethyl-3-ethyloxetane or 2-chloroethyl vinyl ether, respectively, in the presence of TBAB in NMP at 80 °C for 48 h. Introduction of these photopolymerizable groups was quantitative, as confirmed by ^{1}H NMR and IR spectroscopy.

Physical Properties of Noria-MA$_x$ (x = 100, 83, 57, and 28), Noria-HMAP$_{100}$, Noria-OX$_{100}$, and Noria-VE$_{100}$ (Solubility, Film-Forming Ability, Thermal Stability). We next determined the solubility, film-forming ability, and thermal stability of noria-MA$_x$ as physical properties relevant to UV-curable resin applications. Noria was soluble in DMSO, DMAc, DMF, toluene, and cyclohexane but insoluble in other solvents. On the other hand, noria-MA$_x$ were soluble in common organic solvents, though not in water. Film-forming ability was examined using films cast on a glass plate (with noria or noria-MA$_x$ 50 mg in THF 1.0 mL) and dried *in vacuo* at room temperature. The film-forming abilities of noria-MA$_{100}$, noria-MA$_{83}$, and noria-MA$_{57}$ were good, whereas that of noria-MA$_{28}$ was poor.

With the apparatus used, the T_g's of the noria and noria derivatives could not be observed. Thermal decomposition of noria-MA$_x$ was examined by TGA. The initial decomposition temperature (T_d^i) and 5 wt % loss of temperature ($T_d^{5\%}$) are summarized in Table 1. These results show that the thermal stability increased with increasing ratios of methacryloyl groups; for example, noria-MA$_{100}$ had excellent thermal stability, with T_d^i = 387 °C and $T_d^{5\%}$ = 418 °C. Furthermore, the thermal decomposition temperatures T_d^i and $T_d^{5\%}$ of other noria derivatives are also summarized in Table 1. The T_d^i and $T_d^{5\%}$ values of noria derivatives with DI > 99% were excellent, being in the range of 332−387 °C and 365−418 °C, respectively. The noria derivatives showed higher thermal stability than noria. This might be because the hydroxyl groups had been replaced with polymerizable groups, i.e., hydroxyl groups promote the thermal decomposition reaction of noria.

Table 2 summarizes the solubility and film-forming ability of noria and its derivatives (noria-MA$_{100}$, noria-HMPA$_{100}$, noria-OX$_{100}$, and noria-VE$_{100}$). Since the solubility of noria is poor, noria does not show good film-forming ability. This is presumably because of the effect of intermolecular hydrogen bonds involving the hydroxyl groups of noria. On the other hand, the synthesized noria derivatives showed good solubilities in common organic solvents and excellent film-forming abilities.

Photochemical Reactions of Noria-MA$_x$ (x = 100, 83, 57, and 28). The photochemical reactions of noria-MA$_x$ were examined using films including a photoradical initiator. Radical polymerization of methacryloyl groups to afford the cured materials was expected to occur. A solution of noria-MA$_{100}$, Irgacure907, and 2-ethylanthraquinone (EAQ) as a photosensitizer in THF was cast on a KBr plate to prepare a thin film, and the resulting film was dried *in vacuo* at room temperature for 3 h. The conversion of methacryloyl groups was calculated from the decrease of the RT-IR peak at 1637 cm^{-1}, assignable to C=C of methacryloyl groups, under photoirradiation using a 250 W high-pressure mercury lamp. The photochemical reactions of noria-MA$_{83}$ and noria-MA$_{57}$ were similarly examined, but noria-MA$_{28}$ could not be evaluated because its film-forming ability was insufficient. The time courses of the cross-linking reactions of noria-MA$_x$ are depicted in Figure 2. The photoradical polymerization of noria-MA$_x$ proceeded with conversions of noria-MA$_{100}$, noria-MA$_{83}$, and noria-MA$_{57}$ amounting to 35%, 24%, and 12%, respectively, after 15 min, quantitatively affording the corresponding cured films. These results show that photochemical reactivity increased with increasing ratio of methacryloyl groups, presumably due to the increase in the density of radical polymerizable groups as same as to decrease of phenol groups. This means that noria-MA$_{100}$ is a more suitable material than the other noria-MA$_x$ (x = 83, 57, and 28) from the viewpoints of photochemical reactivity and thermal stability. On the other hand, cured noria-MA$_x$ (x = 83 and 57) are expected to have higher hydrophilicity due to the residual hydroxyl groups and so might exhibit better adhesion to the substrate.

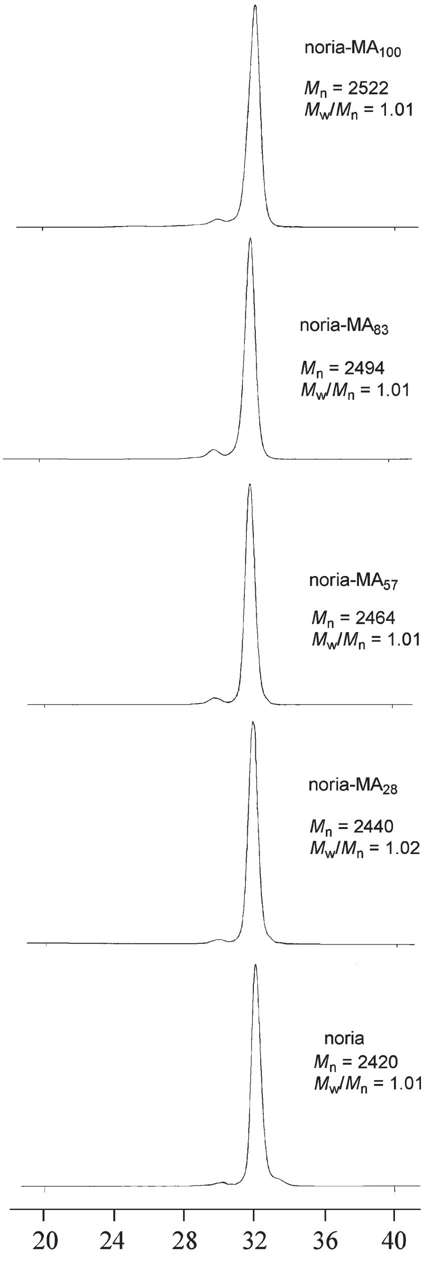


Figure 1. GPC profiles of noria-MA$_{100}$, noria-MA$_{83}$, noria-MA$_{57}$, and noria-MA$_{28}$.

Table 1. Thermal Decomposition Temperatures (T_d^i and $T_d^{5\%}$) of Noria Derivatives

noria derivative	$T_d^{i\,a}$	$T_d^{5\%\,b}$
noria	333	365
noria-MA$_{28}$	345	392
noria-MA$_{57}$	368	418
noria-MA$_{83}$	374	426
noria-MA$_{100}$	387	418
noria-HMPA$_{100}$	332	365
noria-OX$_{100}$	347	387
noria-VE$_{100}$	336	365

[a] T_d^i: initial thermal decomposition temperature. [b] $T_d^{5\%}$: 5 wt % loss thermal decomposition temperature.

Table 2. Solubility and Film-Forming Ability of Noria and Noria Derivatives[a]

solvent	noria	noria-MA$_{100}$	noria-HMPA$_{100}$	noria-VE$_{100}$	noria-OX$_{100}$
water	−	−	−	−	−
DMSO	++	++	++	++	++
NMP	++	++	++	++	++
DMF	+−	++	++	+−	++
methanol	−	−	−	−	−
acetone	−	++	++	++	++
2-propanol	−	+−	+−	++	++
THF	−	++	++	++	++
ethyl acetate	−	++	++	++	++
chloroform	−	++	++	++	++
n-hexane	−	−	−	−	++
PGMEA	+−	++	++	++	++
2.5 wt % TMAH(aq)	++	−	−	−	−
film-forming ability	×	○	○	○	○

[a] Symbols: ++, soluble at room temperature; +, soluble by heating; +−, partially soluble; ○, possible; ×, impossible.

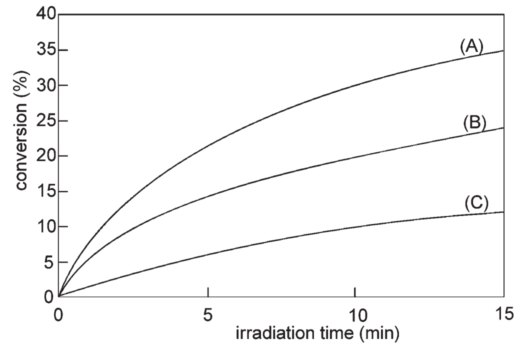


Figure 2. Photochemical reaction of noria-MA$_{100}$ (A), noria-MA$_{83}$ (B), and noria-MA$_{57}$ (C).

UV-Curing Reaction of Noria Derivatives. The photochemical reaction of noria-HMPA$_{100}$ was performed in the film state in the same way as for noria-MA$_{100}$. In the case of noria-OX$_{100}$ and noria-VE$_{100}$, DPSP was used as a photoacid generator. The conversion of vinyl ether groups of noria-VE$_{100}$ could be calculated from the decrease of the RT-IR peaks at 1617 cm^{-1}, assignable to vinyl groups, under photoirradiation with a 250 W high-pressure mercury lamp. Similarly, the photochemical reaction of noria-OX$_{100}$ could be determined from the decrease of the RT-IR peaks at 980 cm^{-1} assignable to C−O−C of oxetanyl groups. The time courses of conversion in these photochemical reactions of noria derivatives are illustrated in Figure 3.

In the case of noria-MA$_{100}$, the photochemical radical polymerization of methacryloyl groups reached 24% after 400 s. In the case of noria-HMPA$_{100}$, the conversion reached 38%. Furthermore, the photochemical cationic polymerization of vinyl ether groups and oxetanyl groups proceeded smoothly to reach 60% conversion. These results also showed that noria-OX$_{100}$ has the highest photochemical reactivity.

Then, the corresponding cured materials could be obtained quantitatively, and their thermal stabilities were investigated by means of TGA. The values of T_d^i and $T_d^{5\%}$ were almost the same as those of the noria derivatives before photoirradiation. This result seems to be characteristic of the photocuring reaction of noria derivatives. Generally, the thermal stability of resins increases after photocuring reaction because of the restriction of segmental and molecular motions resulting from the cross-linking. In the case of noria derivatives, the reason why large changes of segment and molecular motions do not occur during photocuring may be that the monomer already has a rigid structure.

In summary, the synthesis, properties, and photochemical reactivity of noria derivatives noria-MA$_x$ [x = 100, 83, 57,

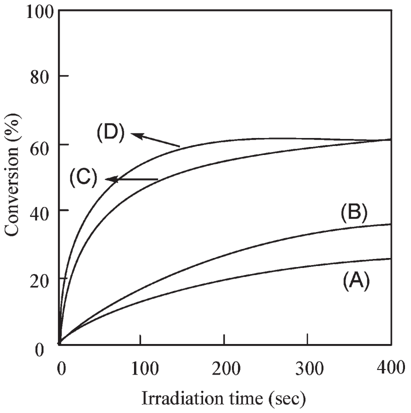


Figure 3. Photochemical reaction of noria-MA_{100} (A), noria-$HMPA_{100}$ (B), noria-VE_{100} (C), and noria-OX_{100} (D).

and 28 mean degree of introduction (DI) of methacryloyl groups] were examined. The physical properties (solubility, film-forming ability, and thermal stability) and photochemical reactivity improve with increasing values of DI. Other noria derivatives, noria-HMPA with pendant 2-hydroxy-3-methacryloylpropanoxy groups, noria-VE with pendant vinyl ether groups, and noria-OX with pendant oxetanyl groups, were also synthesized. These noria derivatives had good physical properties and good photochemical reactivities. Noria derivatives with pendant polymerizable groups are considered to be good candidates for application as UV-curing resins.

Acknowledgment. This work was supported by Nanospace Chemistry for the Creation of Functional Materials at Kanagawa University.

References and Notes

(1) Review: Nishikubo, T.; Kameyama, A.; Kudo, H. *Polym. J.* **2003**, *35*, 213–229.
(2) Nishikubo, T.; Kameyama, A.; Tsutsui, K.; Iyo, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1805–1814.
(3) Iyo, M.; Tsutsui, K.; Kameyama, A.; Nishikubo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3071–3078.
(4) Fujita, J.; Onishi, Y.; Ochiai, Y.; Matsui, S. *Appl. Phys. Lett.* **1996**, *68*, 1297–1299.
(5) Nishikubo, T.; Kameyama, A.; Kudo, H.; Tsutsui, K. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1293–1302.
(6) Review: Kudo., H.; Nishikubo, T. *Polym. J.* **2010**, in press.
(7) Kudo, H.; Hayashi, R.; Mitani, K.; Yokozawa, T.; Kasuga, N. C.; Nishikubo, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7948–7952.
(8) André, X.; Lee, J. K.; DeSilva, A.; Ober, C. K.; Cao, H. B.; Deng, H.; Kudo, H.; Watanabe, D.; Nishikubo, T. *SPIE* **2007**, *6519*, 65194B–10.
(9) Tanaka, M.; Rastogi, A.; Kudo, H.; Watanabe, D.; Nishikubo, T.; Ober, C. K. *J. Mater. Chem.* **2009**, *19*, 4622–4626.
(10) Kudo, H.; Watanabe, D.; Nishikubo, T.; Maruyama, K.; Shimizu, D.; Kai, T.; Shimokawa, T.; Ober, C. K. *J. Mater. Chem.* **2008**, *18*, 3588–3592.
(11) Kudo, H.; Watanabe, D.; Nishikubo, T. *Kobunshi Ronbunshu* **2009**, *66*, 10–16.
(12) Nishikubo, T.; Kudo, H.; Suyama, Y.; Oizumi, H.; Itani, T. *J. Photopolym. Sci.* **2009**, *1*, 73–76.
(13) Tian, J.; Thallapally, P. K.; Dalgarno, S. J.; McGrail, P. B.; Atwood, J. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 5492–5495.