Naphthalene-Based Spiro Cyclic Monomer Undergoing Selective Radical and Cationic Polymerization

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Cyclic compounds that undergo radical and/or cationic ring-opening polymerization are important for the preparation of functional polymers having various groups such as ether, ester, ketone, sulfide, and carbonate in the polymer backbone, which cannot be attained by vinyl polymerization.[1,2] These cyclic monomers show a smaller degree of shrinkage during polymerization than vinyl monomers such as styrene and methyl methacrylate because of their compact structure. For instance, a cyclic ketene acetal is one of the cyclic monomers with a highly electron-rich double bond that undergoes cationic and radical polymerization. The degree of ring opening of a cyclic ketene acetal in radical ring-opening polymerization depends on the ring size and substituents. Seven-membered non-substituted or phenyl-substituted cyclic ketene acetals undergo ring-opening polymerization with complete ring opening to afford corresponding polyesters,[3] which are important materials whose biodegradability and medical applications have been widely studied and applied.[4] However, ring-opening polymerization of five- and six-membered cyclic ketene acetals is accompanied by vinyl polymerization. Cho et al. reported that a five-membered cyclic acetal of spiro type, 8-methylene-1,4-dioxaspiro-6,9-diene, could be selectively subjected to both radical and cationic ring-opening polymerization to give polyarylene ethers, although the ring strain is small.[5] This is due to the formation of a stable aromatic ring as the driving force during both polymerization. With this driving force, previously, we have also demonstrated the synthesis of well-defined polymers containing anthracene units in the main chain by radical ring-opening polymerization via reversible addition−fragmentation transfer (RAFT) process.[6] Thus, we investigated the polymerization and synthesis of a new spiro-type five-membered cyclic acetal which could undergo both radical and cationic polymerization. In this communication, we describe the radical and cationic polymerization of a naphthalene-based spiro cyclic monomer, 1-methylene-4-spiro[2′,5′-dioxolane-1,4-[2*H*]-naphthalene] (**1**).

A spiro cyclic monomer, 1-methylene-4-spiro[2′,5′-dioxolane-1,4-[2*H*]-naphthalene] (**1**), was prepared by the Wittig reaction of *p*-naphthoquinone ethylene acetal,[7] which was synthesized by the reaction of 1-naphthol and a large excess of ethylene glycol with iodobenzene diacetate. It was obtained as a white solid after purification by recrystallization from pentane with a small amount of 1,4-diazabicyclo[2.2.2]octane as a stabilizer in 24% yield. The structure of **1** was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, in addition to elemental analysis. Figure 1a shows the ^{1}H NMR spectrum of **1**. The vinyl protons of **1** were observed at 5.90−6.32 and 6.57 ppm, and the two methylene protons assignable to the acetal group were also observed at 4.31−4.42 ppm, indicating the successful methylation of oxygen atom in **1** by the Wittig reaction with the remaining the acetal group.

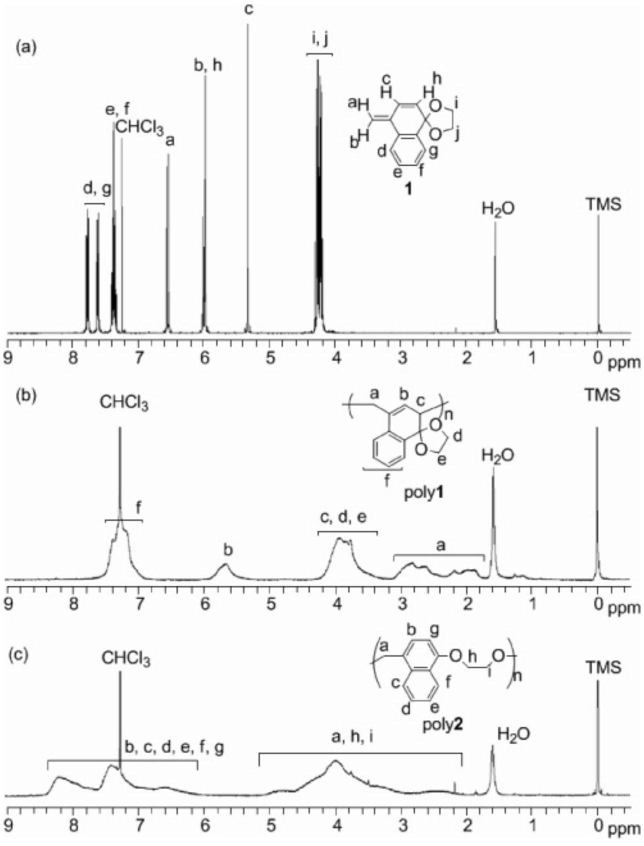

Figure 1. ^{1}H NMR spectrum of (a) **1**, (b) poly**1** obtained by the polymerization of **1** with AIBN at 60 °C for 20 h in PhCl (2 M), and (c) poly**2** obtained by the polymerization of **1** with BF_3OEt_2 at −78 °C for 3 h in CH_2Cl_2 (2 M).

Radical polymerization of **1** was conducted using 2,2′-azobis-(isobutyronitrile) (AIBN), benzyl peroxide (BPO), and *tert*-butyl peroxide (TBPO) ([**1**]/[I] = 50) as initiators in chlorobenzene (PhCl) for 20 h by the sealed tube technique. The results are summarized in Table 1. The obtained polymers were collected as a white powder insoluble in methanol. The polymers were readily soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, DMF, and THF. When the polymerizations were carried out in dilute condition, both the conversion and the molecular weight of the obtained polymers (poly**1**) were low, and the molecular weight distribution was very wide due to the bimodal elution peaks in the SEC profiles (runs 1 and 2). In contrast, the polymerization in high concentration conditions afforded the corresponding polymers with higher molecular weight and in higher conversion. The molecular weight distributions of the poly**1** were narrower than those in a dilute condition, and its SEC curves showed unimodal peaks (runs 3−5). The structure of poly**1** obtained under the conditions described in Table 1

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Table 1. Radical Polymerization of 1[a]

run	initiator	concn (mol/L)	temp (°C)	convn[b] (%)	M_n[c]	M_w/M_n[c]
1	AIBN	0.15	60	39	7400	2.97
2	AIBN	0.5	60	53	10 000	2.18
3	AIBN	1.0	60	69	13 200	1.63
4	AIBN	2.0	60	85	16 600	1.66
5	BPO	2.0	80	97	15 600	2.40
6	DTBP	2.0	120	98	40 500	5.09

[a] Conditions: run 1 (0.10 g, 0.50 mmol), chlorobenzene, initiator (2.0 mol %), and reaction time (20 h). [b] Determined by ^1H NMR spectroscopy. [c] Estimated from SEC (polystyrene standard; eluent = DMF containing 50 mM lithium bromide).

was confirmed by ^1H and ^{13}C NMR spectroscopies. The ^1H NMR spectrum of poly**1** from run 4 showed the absence of characteristic signals at 5.90−6.32 and 6.57 ppm, assignable to *exo*-methylene protons of **1**. A new signal appeared at 5.30−6.21 ppm, which was assigned to vinyl proton **b** as shown in Figure 1b. In ^{13}C NMR spectrum, characteristic peaks assignable to methine and vinyl groups were observed at 38.4−46.2 and 110.5 ppm, respectively (see Supporting Information, Figure 1S). These data indicate that the radical polymerization of **1** proceeds predominantly via the formation of 1,4-adduct unit.

Furthermore, the cationic polymerization of **1** was also carried out using boron trifluoride diethyl etherate (BF_3OEt_2) as an initiator at −78 °C in CH_2Cl_2 (2 M) for 3 h in a nitrogen atmosphere. The polymer was obtained as a white powder after the precipitation into methanol, and ^1H NMR spectrum revealed a polymer conversion of 89%. The M_n and M_w/M_n of the obtained polymer (poly**2**) were estimated to be 5200 and 1.82, respectively. Figure 1c illustrates the ^1H NMR spectrum of poly**2**. No signals of vinyl protons of **1** were observed, and new signals appeared at 6.02−9.02 ppm, which was assigned to aromatic protons. The ^{13}C NMR spectrum of poly**2** showed the presence of characteristic signals at 104.2 and 155.0 ppm, which was assignable to aromatic carbons appeared by the formation of 1,9-adduct units (see Supporting Information Figure 1S), indicating that the cationic polymerization of **1** proceeds effectively through aromatization by ring-opening of ethylene acetal, i.e., the selective formation of a naphthalene ring.

The UV spectra also supported the 1,4-type and 1,9-type polymerization of **1** (Figure 2). Although λ_{max} of the monomer **1** is observed at 261 nm, λ_{max} of poly**1** (M_n = 16 600) shifted slightly to the long wavelength region (270 nm), suggesting that the repeating unit of poly**1** is the 1,4-adduct consisting of a structure similar to that of **1**. That is, the radical polymerization of **1** proceeded mainly according to a 1,4-type polymerization mode. In contrast, λ_{max} of poly**2** shifted dramatically to the long wavelength region (298 nm assignable to naphthalene ring) than that of **1** and poly**1**. This finding clearly supported the cationic polymerization of **1** proceeds selectively in accordance with a 1,9-type ring-opening polymerization.

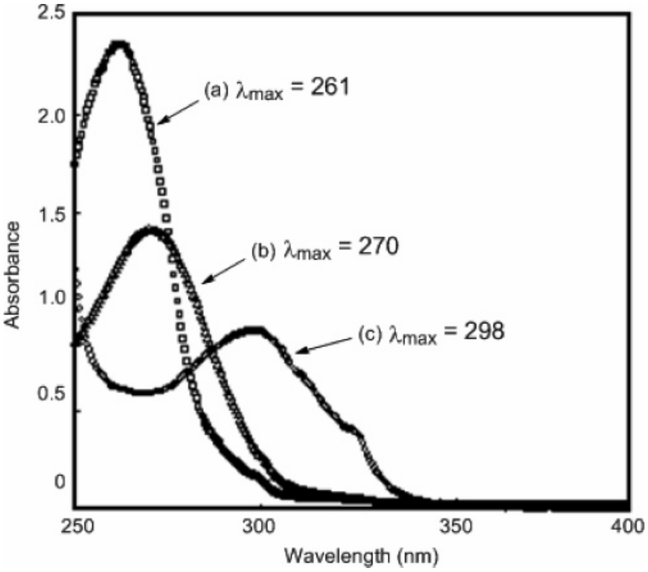
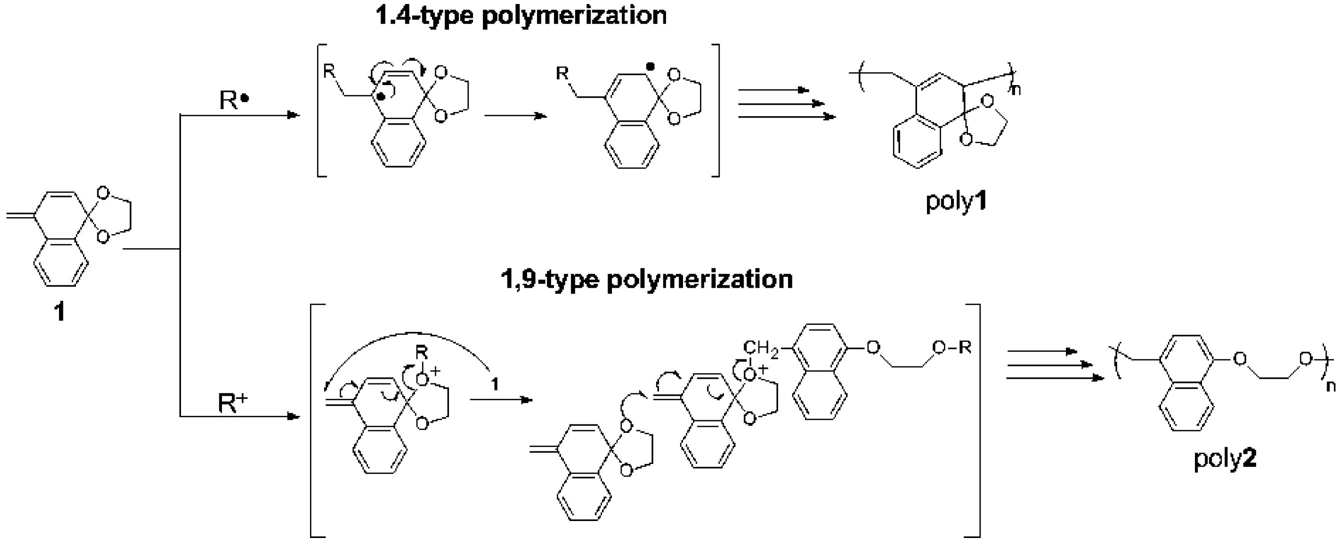


Figure 2. UV spectrum [CH_2Cl_2 (0.05 g/L)] of (a) **1**, (b) poly**1** obtained by the polymerization of **1** with AIBN at 60 °C for 20 h in PhCl (2 M) (run 4 in Table 1), and (c) poly**2** obtained by the polymerization of **1** with BF_3OEt_2 at −78 °C for 3 h in CH_2Cl_2 (2 M).

Scheme 1 shows the plausible mechanism of the radical and cationic polymerization of **1**. The radical polymerization of **1** can be regarded as that of a 1,3-butadiene derivative that is a typical electron-donating monomer. Generally, the radical polymerization of 1,3-butadiene was accompanied by 1,2- and 1,4-type polymerization. However, the radical polymerization of **1** proceeds via only a 1,4-type polymerization neither a 1,2-type nor a 1,9-type polymerization, and the 1.4-H-transfer gives a radical, which is stabilized by its neighboring cyclic ethylene acetal group. In the cationic ring-opening polymerization, a nucleophilic attack of the oxygen atom to the cationic initiator affords oxonuim cation species. Then, the oxygen atom of

Scheme 1. Plausible Mechanism of Radical and Cationic Polymerization of 1



another monomer molecule **1** nucleophilically attacks the α-position of the double bond in the cyclic oxonuim ion, and the chain reaction of those processes gave poly**2** having a naphthalene ring in the main chain.

Thermal properties of the obtained polymers were evaluated by DSC and TGA analysis under nitrogen (see Supporting Information, Figures 2S and 3S). Poly**1** ($M_n = 16\,600$) and poly**2** lost their 10% weight at 342 and 344 °C, respectively, suggesting that each polymer having 1,4-type and 1,9-type structures are high thermal stability. Glass transition temperatures (T_gs) of poly**1** and poly**2** were observed at −61 and 126 °C, respectively. These results suggest that the structures of poly**1** and poly**2** consist of a flexible poly(1,3-butadiene) derivative and rigid naphthalene ring in their backbone, respectively

In summary, we have demonstrated the selective synthesis of 1,4- and 1,9-type polymers by the radical and cationic polymerization of 1-methylene-4-spiro[2′,5′-dioxolane-1,4-[2*H*]-naphthalene] (**1**), which was prepared by the Wittig reaction of *p*-naphthoquinone ethylene acetal derived from 1-napthol. In the radical polymerization, **1** was subject to only a 1,4-type polymerization to synthesize the poly(1,3-butadiene) derivative carrying aromatic spiro cyclic acetal in the side chain. The cationic ring-opening polymerization allowed the preparation of a 1,9-type polymer alternatively containing oxymethylene-1,4-naphthalene and oxyethylene units in the main chain. To the best of our knowledge, this is the first attempt to synthesize nonconjugated polymers with low or high T_gs from one monomer by selecting radical or cationic polymerization modes.

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Supporting Information Available: Text giving typical experimental procedures and figures showing the ^{13}C NMR spectrum, and the DSC and TGA profiles of poly**1** and poly**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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