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# Cationic Polymerization of *cis*-2,3-Tetramethylene-1,4,6-trioxaspiro[4,4]nonane Photosensitized by Anthracene

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ABSTRACT: A stereoregular poly(ether ester), poly(*trans*-2-oxycyclohexyl butanoate) (-[*trans*-2-OCHB]$_n$-) (**II**), was obtained by cationic polymerization of *cis*-2,3-tetramethylene-1,4,6-trioxaspiro[4,4]nonane (**I**) initiated by the 9-phenyl-9,10-dihydroanthracen-10-ylium cation (PDAC) obtained by exposing a mixture of (4-octylphenyl)phenyliodonium hexafluoroantimonate (OPIA) and anthracene (**A**) to UV light at 254 nm. The structure of **II**, the polymerization mechanism of **I**, and the relationship between volume changes during polymerization and polymer structure were studied. The polymerization mechanism of **I** proceeded in a regiospecific manner and was determined in terms of the relation among the polymer structure, the steric hindrance sensitized PDAC, and the only intermediate, 1,3-dioxolan-2-ylium carbocation (DOLC). Polymer **II** exhibited high volume expansion (2.09 ± 0.25%) during polymerization compared to that of -[*cis*-2-OCHB]$_n$- (**III**), obtained by polymerization of **I** using $SnCl_4$ as an initiator, which demonstrated high volume shrinkage (−2.49 ± 0.13%) during polymerization. The volume expansion of **II** is caused by the conversion of *cis* substitution at C-2 and C-3 in **I** to the *trans* form during polymerization.

## Introduction

Spiroorthoesters, which act as expanding monomers, undergo cationic double-ring-opening polymerization and, theoretically, show volume expansion during polymerization.[1−6] However, most reported spiroorthoester monomers did not show volume expansion during polymerization initiated by a Lewis acid (e.g., $BF_3 \cdot OEt_2$, $CH_3OSO_2CF_3$, or $SnCl_4$) or a peroxide but always exhibited volume shrinkage.[7−13] The reason for this shrinkage has rarely been further studied in the literature. Photopolymerization initiated by UV light is a method of rapid polymer production. The reaction is completed, or the change from a liquid to a solid takes place within a few seconds or even within a fraction of a second.[14,15] Cationic photopolymerization has several advantages compared to free radical photopolymerization: it is not inhibited by oxygen, the reaction can continue long after irradiation has ceased, and reaction can take place in areas that the light did not reach. It can be used to polymerize important classes of monomers, including epoxides and vinyl ethers. However, to our knowledge, it has rarely been used in initiating double-ring-opening polymerization of spiroorthoesters.[13,16,17]

We have reported that *cis*-2,3-tetramethylene-1,4,6-trioxaspiro-[4,4]nonane (**I**) (Table 1) underwent cationic photopolymerization initiated by a diphenyliodonium salt after direct exposure to UV light at 254 nm or by exposure to UV light at 365 nm in the presence of the nonaromatic photosensitizers, isopropylthioxanthone (ITX) and 2,2-dimethoxy-2-phenylacetophenone (DMPA). The polymer, poly[(*trans*-OCHB)$_{x'}$-(*cis*-OCHB)$_{x''}$-(CHO)$_y$], consisting of poly(*trans*-2-oxycyclohexyl butanoate) ([*trans*-OCHB]$_{x'}$), poly(*cis*-2-oxycyclohexyl butanoate) ([*cis*-OCHB]$_{x''}$), and poly(1,2-cyclohexene oxide) ([CHO]$_y$) segments was produced.[17] The polymer thus formed exhibited volume expansion during polymerization, unlike the polymers obtained by conventional cationic polymerization using Lewis acids as an initiator, which demonstrated volume shrinkage during polymerization. This was because of the higher and optimal molar ratio of (*trans*-OCHB)$_{x'}$/(*cis*-OCHB)$_{x''}$ segments and the lower content of the higher density [CHO]$_y$ segment in the polymer chain.

Fused-ring aromatic compounds such as anthracene (**A**) and perylene often show photosensitizing activity, and they have been used to photosensitize diaryliodonium (or triarylsulfonium) salts to undergo cationic photopolymerization.[18,19] The mechanism and kinetics of the reaction of diaryliodonium salts photosensitized by **A** have been studied thoroughly.[20−22] It could be concluded that **A** is first excited to the singlet state by absorbing photons and then undergoes intersystem crossing to the triplet state. The triplet-state **A** subsequently forms an excited-state complex—an exciplex—with the diaryliodonium salt. In the exciplex, **A** may undergo electron transfer to the diaryliodonium salt,[23] becoming a radical cation. After a series of reactions,[21] the radical cation is converted to a 9-phenyl-9,10-dihydroanthracen-10-ylium cation (PDAC), which acts as an active center to initiate the reaction.

In this paper, the cationic polymerization of **I** initiated by PDAC, obtained by exposing an OPIA/**A** mixture to UV light at 254 nm, was studied. The novel reaction mechanism of **I** initiated by PDAC and the unique stereoregular structure and volume expansion of the polymer thus formed were studied in detail.

## Experimental Section

**Materials.** **I** was prepared by the reaction of *cis*-1,2-cyclohexene oxide with γ-butyrolactone (γ-BL) in the presence of $BF_3 \cdot OEt_2$ in dichloromethane using a previously reported method[24] (bp: 88−89 °C, 2.2 mmHg) and was stored at room temperature under nitrogen. OPIA was used as the photoinitiator. ITX and DMPA were used as nonaromatic photosensitizers, **A** was used as an aromatic photosensitizer, and $SnCl_4$, $CH_3SO_2OCF_3$, and $BF_3 \cdot OEt_2$ were used as conventional cationic initiators. All compounds, except OPIA (Nissho Sangyo) and **A** (Acros), were purchased from Aldrich Co. and used as received without further treatment. Dry dichloromethane was obtained by refluxing over calcium hydride and distillation.

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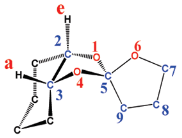
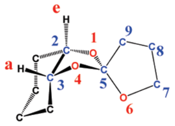
**Table 1. Heats of Formation, Steric Energy, and B3LYP/6-31G(d) Mulliken Net Atomic Charges of I**

| Entry | Structure | Heat of formation (KJ/mole) | Steric energy (KJ/mole) | Mulliken netatomic charge | | |
|---|---|---|---|---|---|---|
| | | | | O-1 | O-4 | O-6 |
| **I** |  | -607.14 | 134.62 | 0.527 | 0.534[e] | 0.517[a] |
| **I'** |  | -601.27 | 139.76 | - | - | - |

**Cationic Photopolymerization with an OPIA/A Initiating System.** In a drybox, $3.89 \times 10^{-2}$ g (0.062 mmol) of OPIA and $9.76 \times 10^{-3}$ g (0.065 mmol) of **A** were dissolved in 1.0 mL of dichloromethane and added to a round Teflon fillister (diameter × depth = 16.5 × 5 mm). A 30 $\mu$m thick transparent polypropylene film was laminated on the top of the fillister to prevent moisture diffusion. The solution was exposed to UV light ($\lambda_{max}$: 254 nm) at 25 °C in a BLX-E254 cross-linker box (Vilber Lourmat, Marne-la-Vallée, France) for 5 min with a light intensity of 6.0 mW/cm$^2$ (measured using a UVX-25 radiometer, European Union). Then, 1.00 g (5.44 mmol) of liquid **I** was immediately added to the fillister and mixed thoroughly with the photoreacted OPIA/**A** solution with a dry glass rod. After standing for 5 min, 10 $\mu$L of trimethylamine was added to the mixture to quench the reaction. After qualitative analysis of the $\gamma$-BL by gas−liquid chromatography (GLC), the solution was washed with water and dried with anhydrous $MgSO_4$. The procedure for separating and purifying the product was performed as described in the literature.[17] Other experimental procedures, such as the cationic polymerization of **I** initiated by a Lewis acid and photoinitiator, were performed as described in the literature.[17]

**Degree of Monomeric Conversion[17].** Homogeneous mixtures of **I**, initiators, and other additives before and after irradiation were coated on the KBr disks. After the solvent was removed under reduced pressure, the samples were recorded on a Fourier-transform infrared (FTIR). The total area of the $\nu_{as,C-H}$ and $\nu_{s,C-H}$ absorptions at 2950 and 2850 cm$^{-1}$ was considered the internal standard (IS). The change in the peak area due to the spiroester group at 1323 cm$^{-1}$ before and after the reaction was monitored, and the degree of conversion (DC) was determined using the following equation

$$\mathrm{DC}\ (\%) = [1 - (A_{1323}/A_{\mathrm{IS}})_a/(A_{1323}/A_{\mathrm{IS}})_b] \times 100$$

where $(A_{1323}/A_{\mathrm{IS}})_a$ is the ratio between the area of spiro absorption at 1323 cm$^{-1}$ and the area of IS absorption after irradiation and $(A_{1323}/A_{\mathrm{IS}})_b$ is the ratio between the area of spiro absorption and the area of IS absorption before irradiation.

**Volume Change Test.** The densities of monomer (liquid) ($\rho_1$) and polymer (liquid) ($\rho_2$) were determined by means of a pycnometer at 25 °C. Volume change was calculated from $(1/\rho_2 - 1/\rho_1)/(1/\rho_1)$.

**Identification of the PDAC Structure.** PDAC was prepared and identified indirectly as follows. In a round Teflon fillister, 0.1000 g (0.1594 mmol) of diaryliodonium pentafluorophosphate (used to simplify the patterns in the $^1$H NMR and high-resolution MS (HRMS) spectra) and 0.0283 g (0.1594 mmol) of **A** were dissolved in 1.0 mL of dry dichloromethane. A 30 $\mu$m thick transparent polypropylene film was laminated on the fillister top. The solution was exposed to UV light ($\lambda_{max}$: 254 nm) at 25 °C for 10 min. Then a 10 wt % alcohol solution of sodium boronhydride (0.02 g) was added to react with any PDAC produced to yield 9-phenyl-9,10-dihydroanthracene. After drying under reduced pressure, the residue was purified by column chromatography using silica gel (Acros, 70−80 mesh, 60 Å) as the stationary phase and $n$-hexane/ethyl acetate (95/5 v/v) as the eluent. 9-Phenyl-9,10-dihydroanthracene[25] ($R_f$(TLC): 0.24) was obtained (< 30 mg) after drying under a vacuum at 60 °C. $^1$H NMR ($CDCl_3$): $\delta$ (ppm) = 3.94−4.06 (m, 2H, benzylic hydrogen), 5.36 (s, 1H, benzylic hydrogen), 7.07−7.39 (m, 13H, aromatic hydrogen). HRMS (EI) calcd for $C_{20}H_{16}$ $[M]^+$: 256.1252; found: 256.1239.

**Measurements.** Fourier-transform infrared (FTIR) spectra of the samples were recorded on a Digilab FTS-1000 spectrometer with a resolution of 4 cm$^{-1}$. Samples for measurement were prepared by coating the polymer or homogeneous mixtures on KBr disks followed by vacuum drying (< 5 Torr) at 40 °C for 10 h. The $^1$H and $^{13}$C NMR spectra of the polymers were recorded on a Bruker AMR 300 NMR spectrometer (Bruker, Madison, WI) in $CDCl_3$ with TMS as an internal standard. HRMS were recorded on a Finnigan MAT 95 mass spectrometer. UV absorption spectra were recorded using a Cary 100 Conc UV−vis spectrophotometer (Varian Inc., Palo Alto, CA). GLC was used to qualitatively analyze the $\gamma$-BL produced by the side reaction. The molecular weight of the polymer was measured using a Jasco PU-980 GPC with a Jasco RI-930 RI detector (Jasco, Easton, MD). A mixed bed column (Jordi DVB gel), 250 × 10 mm in size, was used. DMAc was used as the eluting agent, with polystyrene as a standard.

**Calculations.** The parameters of the optimized-geometry monomer and polymers were calculated using the Spartan 08 software suite (Version 1.2.0, Wave function, Inc., Irvine, CA). The Mullikan net atomic charge on the molecules and the energetically minimized structures of the polymers were determined in the semiempirical PM3 mode, followed by single energy point calculations using the DFT method (B3LYP with a 6-31G(d) basis set). The steric energies of the molecules were calculated using the ChemBio 3D ultra 11 progam (MM2 method) (CambridgeSoft Corp., Cambridge, MA).

## Results and Discussion

**Cationic Photopolymerization of I with an OPIA/A Initiating System.** When **I** was mixed thoroughly with OPIA/**A** (molar ratio: 1.0/1.05) and the mixture was exposed to UV radiation at 254 nm ($\lambda_{max}$), cationic photopolymerization occurred instantly to afford a polymer with an NMR spectrum (Figure 1a) similar to that of the polymer obtained by direct irradiation of **I** with OPIA.[17] Byproducts such as $\gamma$-BL and -[CHO]$_n$- oligomers produced by single-ring-opening side reactions were examined. The structure of the polymer was identified as $[(trans\text{-OCHB})_p\text{-}(cis\text{-OCHB})_q\text{-}(\text{CHO})_s]$. An OPIA/**A** mixture was irradiated with UV of the same wavelength; **I** was then added immediately, and reaction took

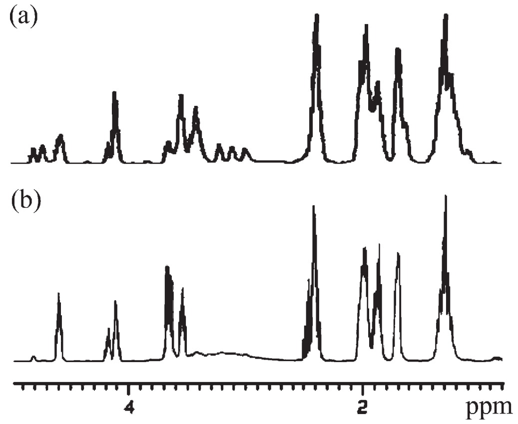


**Figure 1.** $^1$H NMR spectra of polymers obtained by (a) UV exposure of mixture of **I** and OPIA/**A** at wavelength of 254 nm and (b) UV exposure of OPIA/**A** at 254 nm followed by addition of **I**.

place within 3−5 min. The polymer thus formed has a simple $^1$H NMR spectrum (Figure 1b), quite different from that in Figure 1a. The byproduct mentioned above was not detected by GLC or FTIR spectroscopy. This proved that **I** had undergone a full double-ring-opening cationic polymerization without any single-ring-opening side reactions.

**Polymer Structure.** The correlation of the protons of the polymer with the simple $^1$H NMR spectrum (Figure 1b) was achieved using DQF-COSY NMR spectroscopy (Figure 2). The absorption of the -$CH_2CO_2$- at 2.42 ppm was not disturbed by any other absorption of the polymer, and its proton area is almost one-eighth of the total protons area.[12] This indicates that the repeating unit in the polymer contains 16 protons and has the same hydrogen numbers as **I**. It is therefore reasonable to deduce that the structure of the repeating unit is 2-oxycyclohexyl butanoate. It must be emphasized that the chemical shift at 4.60 ppm is the methine hydrogen $\mathbf{H_a}$ of the 2-oxycyclohexyl butanoate unit due to deshielding of the ester group[26] at the *trans* position. The structure of the polymer is thus identified as a stereoregular poly(ether ester) (-[*trans*-2-OCHB]$_n$-) (**II**). The stereochemistry of the repeating unit was proved by the $^1$H NMR spectrum of the pure model isomer *trans*-2-hydroxycyclohexyl butanoate.[17]

**Stereostructure of I.** Before investigating the polymerization mechanism of **I**, the stereostructure of the monomer was first identified. *cis*-2,3-Tetramethylene-1,4,6-trioxaspiro[4,4]-nonane, comprising a five-membered cyclic acetal (2,2-disubstituted-1,3-dioxolane) and a cyclic ether (2,2-disubstituted tetrahydrofuran),[27] has two possible stereoisomers, designated **I** and **I′**. The heats of formation and steric energies of **I** and **I′**, estimated using PM3 and MM2 computations, are listed in Table 1.[27−29] Inspection of the data in Table 1 reveals that the heat of formation and steric energy of **I** are lower than those of **I′**. However, it was confirmed by $^1$H and $^{13}$C NMR spectra that the synthesized monomer has only one type of stereostructure (data not shown). This energy difference could be evidence that the stereostructure of the monomer is **I**, not **I′**.

**UV Irradiation of OPIA.** The exposure of OPIA to UV light at different wavelengths, in the presence or absence of **A**, was studied. 2-Phenylquinoline was used to examine whether or not the photoacid (i.e., $H^+SbF_6^-$), which initiates the cationic polymerization of **I**, was produced during irradiation. Once the 2-phenylquinoline has been protonated by the photoacid (or proton), the 2-phenylquinolinium ion formed shows a significant bathochromic shift in its UV absorption spectrum.[30] Figure 3 shows the UV absorption of 2-phenylquinoline after addition to the OPIA being exposed

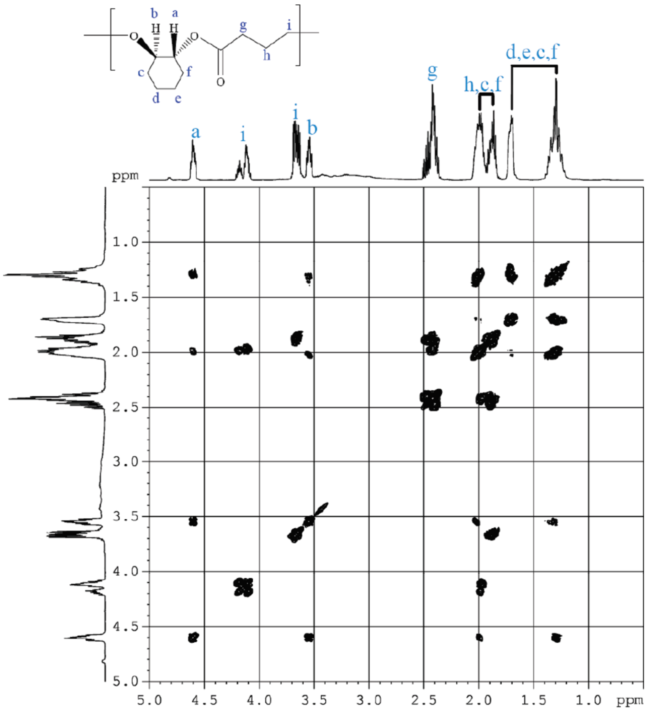


**Figure 2.** DQF-COSY NMR spectrum of **II**.

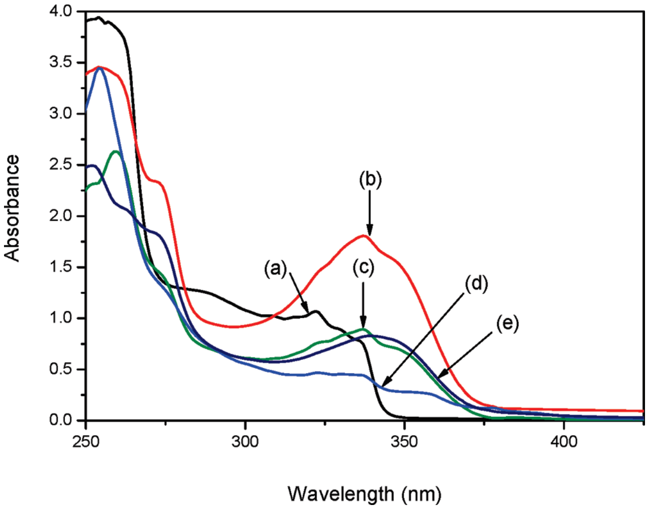
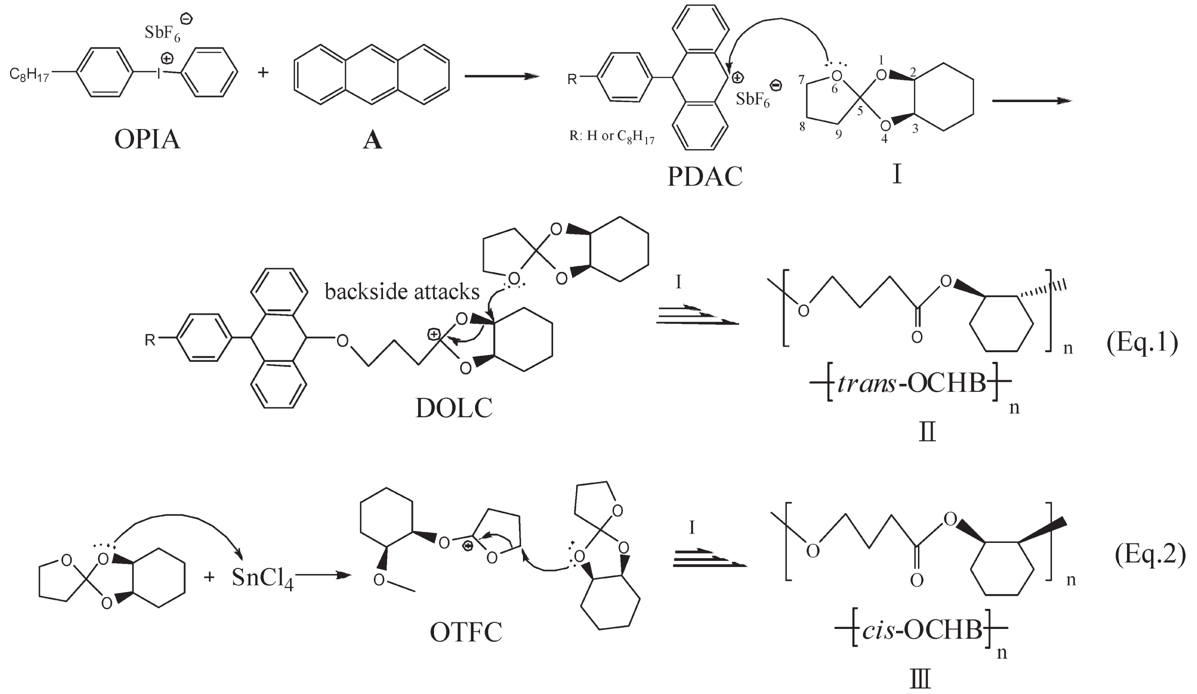


**Figure 3.** UV spectra of 2-phenylquinoline (a) and 2-phenylquinoline in solutions of (b) perchloric acid, (c) OPIA after irradiation at 254 nm, (d) OPIA/**A** after irradiation at 254 nm, and (e) OPIA/**A** after irradiation at 365 nm.

to UV light under various conditions. It was found that, in contrast to direct irradiation of OPIA on its own at a wavelength of 254 nm, which causes the UV absorption of the 2-phenylquinolinium ion to undergo a significant bathochromic shift (curves a−c), the UV irradiated OPIA/**A** mixture shows no bathochromic shift after the addition of 2-phenylquinoline (curve d). When an OPIA/**A** mixture was UV irradiated at 365 nm, the added 2-phenylquinoline was converted to the 2-phenylquinolinium ion and thus showed a significant bathochromic shift in its UV absorption (curve e). These experimental results reveal that when OPIA/**A** is irradiated at 365 nm, electron transfer from the excited **A** to the OPIA in the singlet **A**/OPIA exciplex yielding a photoacid occurs.[31] In contrast, when an OPIA/**A** mixture is exposed to UV at 254 nm, no photoacid is produced; the

**Scheme 1. Polymerization Mechanisms of I Initiated by DPAC and $SnCl_4$**



above-mentioned reaction does not occur. The only reaction may be transfer of an electron from the excited **A** to the OPIA in the triplet **A**/OPIA exciplex to yield a PDAC,[21,23] which can initiate the cationic polymerization of **I**.

However, when an OPIA/A mixture was irradiated at 254 nm in the presence of **I**, it seems that the formation of a triplet exciplex from triplet **A** and OPIA was interfered with to some extent. Some OPIA will be photodecomposed to produce a photoacid during irradiation to induce polymerization of **I**. A surplus **A** residue was thus found in the reaction system (data not shown). It was therefore concluded that when an OPIA/**A** mixture is exposed to UV at 254 nm in the absence of **I**, no photoacid is produced. The only initiating species, PDAC, could be isolated, and its structure was further confirmed by $^1$H NMR and HRMS (see Experimental Section).[25]

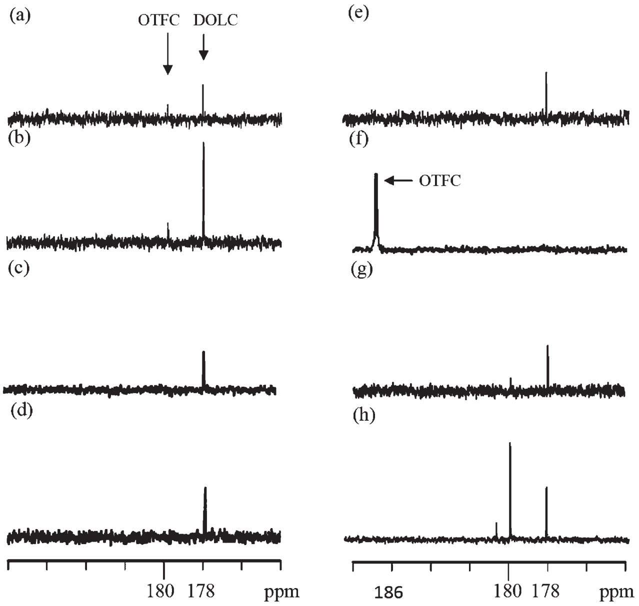


**Figure 4.** $^{13}$C NMR spectra (25 °C, $CDCl_3$) of carbocations produced in the systems (a) TN/DPAC, (b) MTN/DPAC, (c) *trans*-DMTN/DPAC, (d) *cis*-DMTN/DPAC, (e) **I**/DPAC, (f) **I**/$SnCl_4$, (g) **I**/OPIA/DMPA, and (h) **I**/OPIA/ITX. PDAC was obtained by UV exposure of OPIA/**A** at 254 nm without isolation. The molar ratio of spiroorthoester and OPIA/**A** was 1:1.

**Polymerization Mechanism.** The cationic polymerization mechanism of **I** initiated by PDAC to afford **II** with a stereoregular structure is worth studying. The mechanism was determined in terms of the relation among the structures of **I**, **II**, PDAC, and the activated cationic propagating chain end and is shown in eq 1 of Scheme 1. It was deduced that the PDAC attacked the cyclic ether oxygen (O-6) of **I** to afford one type of 1,3-dioxolan-2-ylium cation (DOLC) (Figure 4e).[17,32] The subsequent ring-opening polymerization took place regiospecifically by backside attack by the cyclic ether oxygen of **I** at C-2 or C-3 of DOLC to yield **II**. It seems that PDAC, a bulky and sterically sensitive species, only attacks oxygen atoms, either the cyclic ether oxygen (O-6) or the acetal oxygen (O-1 or O-4), with less steric hindrance. The experimental results shown in Figure 4 could prove this theory. Figure 4a shows the $^{13}$C NMR spectrum of 1,4,6-trioxaspiro[4,4]nonane (TN) after reaction with PDAC. Absorptions of DOLC at ca. 178 ppm and of the 2-oxytetrahydrofuran-2-ylium cation (OTFC)[32] (obtained by attack of the PDAC on the acetal oxygen of **I**) at ca. 180 ppm are both found. Figure 4b shows the spectrum of 2-methyl-1,4,6-trioxaspiro[4,4]nonane (MTN) after reaction with PDAC. The DOLC absorption at ca. 178 ppm is much higher than that of the OTFC, which is only a trace absorption at 180 ppm. Parts c and d of Figure 4 show the spectra of *cis*- and *trans*-2,3-dimethyl-1,4,6-trioxaspiro[4,4]nonanes (*cis*- and *trans*-DMTNs), respectively, after reaction with PDAC. Only the peaks at ca. 178 ppm, corresponding to DOLC, are found, and no OTFC absorption at 180 ppm occurs. The substituted methyl groups at C-2 and C-3 of the DMTNs may prevent the PDAC from attacking the adjacent acetal oxygen because of steric hindrance. It is therefore reasonable to infer that the attack on PDAC by the cyclic ether oxygen

**Table 2. Properties of Polymers II and III**

| Polymer | Monomer DC(%) | Yield (%) | Mn (Mw/Mn) | density (g/cm$^3$) [a] | Volume change (%) | Chain-end distances in oligomer models | |
|---|---|---|---|---|---|---|---|
| | | | | | | $H_3C\text{-}[OCB]_3\text{-}OCH_3$ | $H_3C\text{-}[OCB]_6\text{-}OCH_3$ |
| II | 100 | 82 | 9361 (1.11) | 1.0919 ± 0.0027 | +2.09 ± 0.25 | 23.354 Å[b] | 43.592 Å[b] |
| III | 100 | 78 | 3479 (1.29) | 1.1431 ± 0.0015 | -2.49 ± 0.13 | 13.423 Å[c] | 19.250 Å[c] |

a: The density of I is 1.1147 ± 0.0014 g/cm$^3$; b: *trans* form; c: *cis* form.

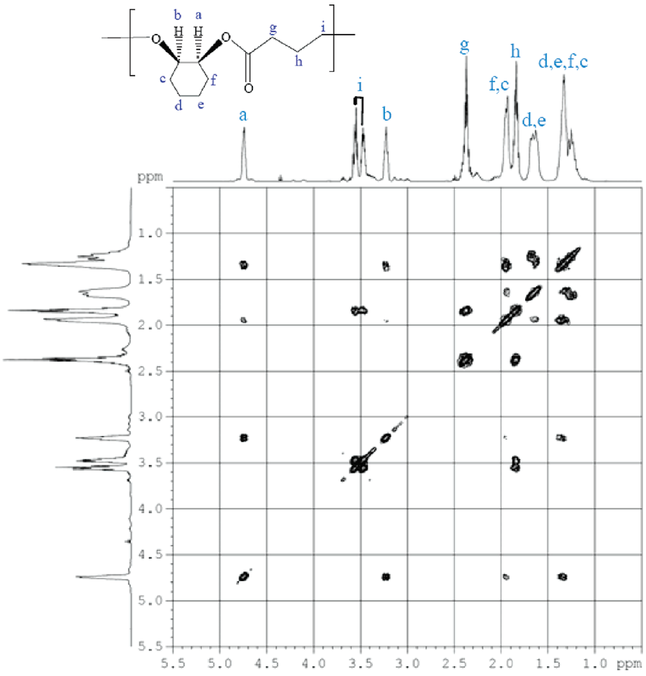


**Figure 5.** DQF-COSY NMR spectrum of **III**.

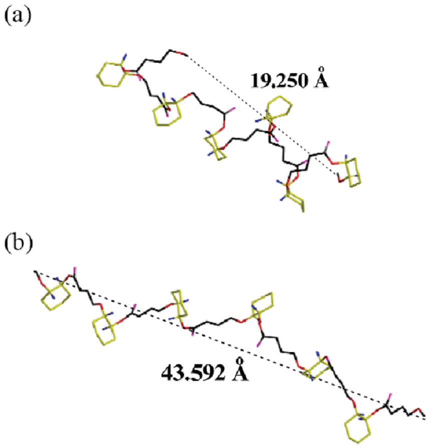


**Figure 6.** Methoxyl-capped six-subunit model oligomers of B3LYP/6-31G(d)-derived geometry-optimized structures of polymers **II** and **III**. The computed distance between the oligomer chain ends (methyl—methyl) is shown.

of **I** (a more complicated structure) is a steric-directing reaction. In addition to the effect of its bulky volume, the resonance stabilization effect of PDAC may play an important role in the regiospecific polymerization of **I**. The Mulliken net atomic charges on the oxygen atoms in **I** were calculated by computer simulation (Table 1).[33] The charges on the oxygen atoms in the cyclic acetal ring (O-1 and O-4) are higher than that on the cyclic ether ring oxygen (O-6). Theoretically, the cation (or Lewis acid) should predominantly attack the cyclic acetal oxygen to afford the OTFC. For example, $SnCl_4$ is a weaker Lewis acid[34] and only attacks the cyclic acetal oxygen to afford the OTFC (Figure 4f); the OTFC then propagates the reaction (eq 2 of Scheme 1) of **I** to yield **III**, a stereoregular poly(ether ester), the structure of which was identified by its DQF-COSY NMR spectrum (Figure 5). However, when **I** undergoes conventional cationic polymerization initiated by $BF_3 \cdot OEt_2$ or $CH_3SO_2OCF_3$ (both are stronger Lewis acids than $SnCl_4$)[35,36] or cationic photopolymerization in OPIA/ITX or an OPIA/DMPA initiating system, both DOLC and OTFC cations are produced (Figure 4g,h). No regiospecific reaction producing the stereoregular poly(ether ester) occurs. The reason is perhaps that the corresponding initiating species such as $BF_3$, $CH_3^+$, $H^+$, and $C_6H_5C(OCH_3)_2^+$ [17,37] thus formed are so energetic that they can attack the oxygen atoms in both the cyclic ether and the acetal without any selectivity with regard to the polymerization route (eq 1 or 2 in Scheme 1).[17] Although $C_6H_5C(OCH_3)_2^+$ cation might be greatly stabilized by two methoxy and a phenyl groups and bulky enough to increase its selectivity in the reaction, the free energy of the transition state of [$C_6H_5C(OCH_3)_2^+ \cdot\cdot$O-6-**I**] (O-6-**I**: cyclic ether oxygen of **I**) (141.08 kJ/mol) is ca. 16.16 kJ/mol (thermodynamic calculation using PM3 method)[16,38] lower than that of [$C_6H_5C(OCH_3)_2^+ \cdot\cdot$O-1-**I** (or O-4-**I**)] (O-1-**I**: cyclic acetal oxygen of **I**) (157.69 kJ/mol). It seems that the difference of free energy is not large enough to prevent the ring-opening reaction of [$C_6H_5C(OCH_3)_2^+ \cdot\cdot$O-1-**I** (or O-4-**I**)] (Figure 4g). For the PDAC, the energy could be also greatly stabilized by its resonance behavior and might be lowered enough to enable selection of the reaction route and exclude side reactions. Theoretically, PDAC should select the cyclic acetal oxygen of **I** to attack because of the higher Mulliken atomic charge on that oxygen (Table 1), but it only attacks the cyclic ether oxygen (eq 1 in Scheme 1) to afford **II**. The result of thermodynamic calculation shows that the free energy of the transition state of [PDAC$\cdot\cdot$O-6-**I**] (11.38 kJ/mol) is ca. 144.15 kJ/mol lower than that of [PDAC$\cdot\cdot$O-1-**I** (or O-4-**I**)] (155.53 kJ/mol). The difference is large enough to let PDAC attack the cyclic ether oxygen of **I** (Figure 4e) in a regiospecific manner to afford **II**. It is therefore reasonable to conclude that the polymerization of **I** initiated by PDAC is controlled by steric factors rather than by electronic factors.

**Volume Changes during Polymerization.** Most spiroorthoester monomers exhibit shrinkage during polymerization.[17] In our study of the cationic polymerization of **I**, however, it was found that the volume of **II** expands by 2.09%, and the volume of **III** shrinks by 2.49%, during polymerization (Table 2). Methoxyl-capped oligomer models of **II** and **III** were designed, and a series of computational simulation studies were undertaken to further understand the macromolecular structures of **II** and **III** to attempt to explain these experimental results. Sequential calculations using the semi-empirical PM3 and DFT (B3LYP with 6-31G(d) basis set) methods were used to obtain the optimized-geometry configurations of the model oligomers (Figure 6). It was found that the methoxyl-capped six-subunit model oligomer ($H_3C$-[*cis*-OCHB$]_6$-$OCHH_3$) of **III** collapses to a more compact configuration with the methyl chain ends 19.250 Å apart (Figure 6a). In contrast, the corresponding chain ends in the model oligomer of **II** were found to be 43.592 Å apart (Figure 6b). By comparing the chain-end distances of the two models (Table 2), it is reasonable to deduce that **II** has a highly extended structure, but **III** collapses to a more compact and coiled configuration.[39,40] The radius of gyration, which is proportional to the chain-end distance,[40] of **II** is much higher than that of **III**. The volume of the former is thus larger than that of the latter because when **I** undergoes polymerization initiated by PDAC, the *cis* substitution at C-2 and C-3 is converted to the *trans* substitution (eq 1 in Scheme 1) during the polymerization.

## Conclusions

**I** underwent cationic polymerization initiated by the PDAC, which was obtained by exposing an OPIA/**A** mixture to UV light at 254 nm. The PDAC was shown to attack the cyclic ether oxygen of **I** to yield the only intermediate, DOLC, which propagates the reaction regiospecifically to afford **II**. The stereoregular structure of **II** was identified by its DQF-COSY NMR spectrum. **II** exhibited high volume expansion (2.09%) during polymerization; in contrast, **III**, obtained using $SnCl_4$ as an initiator, demonstrated high volume shrinkage (−2.49%) during polymerization. The volume expansion of **II** is caused by the conversion of the *cis* substitution at C-2 and C-3 of **I** to *trans* substitution during polymerization. PM3 and B3LYP/6-31G(d) computationally geometry-optimized oligomer models of **II** and **III** were designed to explain the experimental result.

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