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Cationic Polymerization of 3-Phenyl-3-(phthalimidomethyl)oxetane Leading with Quantitative Dehydration to an Oligo(indene) Having the C−C Backbone

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A number of polymerization processes accompanied by elimination of relatively small molecules, such as water, alcohols, hydrogen halides, etc., have been long known in the field of polycondensation.[1] In contrast to step-growth polymerization, no elimination generally takes place in chain-growth polymerization. However, some exceptions categorized in condensative chain polymerization[2] have been reported: for instance, decarboxylation in the ring-opening polymerization of oxazolidine-2,5-diones[3] or cyclic carbonates,[4] desulfoxylation in the ring-opening polymerization of cyclic sulfites,[5] evolution of nitrogen in the $BF_3{\cdot}Et_2O$-catalyzed polymerization of diazomethane,[6] and elimination of diaryl ketone in the ring-opening polymerization of 2,2-diaryl-4-methylene-1,3-dioxolanes.[7] In most cases, elimination occurs, though not always quantitatively, during the isomerization of propagating species irrespective of the polymerization modes involved.

More recently, we have reported that 3-phenyl-3-(phthalimidomethyl)oxetane (**1**) undergoes cationic cyclo-oligomerization to yield mainly two geometric isomers of substituted 1,3-dioxanes (**4** and **5**).[8] These dimerized products differ from an eight-membered cyclic ether expected from the well-known "*back-biting*" in the cationic polymerization of cyclic ethers.[9] The cyclodimerization was accompanied by the formation of small amounts of very low-molecular-weight oligomers, but the details were not elucidated. We have now succeeded in quantitatively obtaining the higher oligomer. Surprisingly, it is oligo(2-phthalimidomethyl-1,2-indanylene) (**7**) that can be derived formally by subtracting H_2O from **1** (Scheme 1). In this paper we report the novel cationic polymerization of **1** involving quantitative dehydration without any side reaction and discuss the mechanistic aspects.

The polymerization of **1** with CF_3SO_3H was carried out in chlorobenzene at 130 °C for 11 days to give the oligomer (**7**) quantitatively (exp no. 5 in Table 1).[10] Contrary to our initial expectation that a polyether having an oxytrimethylene backbone would be formed, **7** gave very peculiar IR and NMR spectra (Figures 1 and 2). To elucidate the structure of the repeating unit, **7** was analyzed by matrix-assisted laser-desorption-ionization time-of-flight (MALDI-TOF) mass spectroscopy (Figure 3).[11] Two different series of peaks with relatively stronger and weaker counts were observed, ranging from *m*/*e* 1000 to about 5000. Crests of two consecutive peak clusters were separated alternately by approximately 129 and 146 Da. This regular repetition can be explained by (i) the fact that the chains were composed of the repeating units having FW = 275 and (ii) the possibility that the smaller clusters were caused by fragmentation of one phthalimide moiety (FW = 146). However, the mass of the repeating unit is not consistent with that of the feed monomer **1** (FW = 293), indicating that the repeating unit is derived by the loss of one molecule of water from **1**.

Table 1. Cationic Polymerization of 1 with CF_3SO_3H[a]

exp no.	catalyst, mol %	time, h	product distribution,[b] %						
			2	**3**	**4**	**5**	**6**	**7**	(M_n[c])
1[d]	5	0.15	100	0	0	0	0	0	
2	5	0.15	0	1	58	36	0	5	(682)
3	5	72	0	7	28	18	11	36	(717)
4	5	132	0	7	0	0	10	83	(748)
5	20	264	0	0	0	0	0	100	(1207)
6[e]	20	264	0	0	0	0	0	100	(1072)
7[f]	5	72	0	10	32	18	32	8	
8[f]	5	120	0	0	0	0	8	92	(699)
9[g]	20	264	0	0	0	0	0	100	(1505)

[a] Polymerization conditions: **1**, 0.10 g (0.34 mmol); chlorobenzene, 0.34 mL; temperature, 130 °C. [b] Determined by ^1H NMR. [c] Estimated by GPC (based on polystyrene standards). In GPC, **4** and **5** were eluted at the same retention time corresponding to $M_n = 481$. [d] The reaction was carried out at 80 °C. [e] In the presence of 5.2 mol % of 2,6-di-*tert*-butyl-4-methylphenol as a radical scavenger. [f] Trimethylsilyl trifluoromethanesulfonate was used as a catalyst. [g] In the presence of an equimolar amount (6.2 μL) of water to **1**.

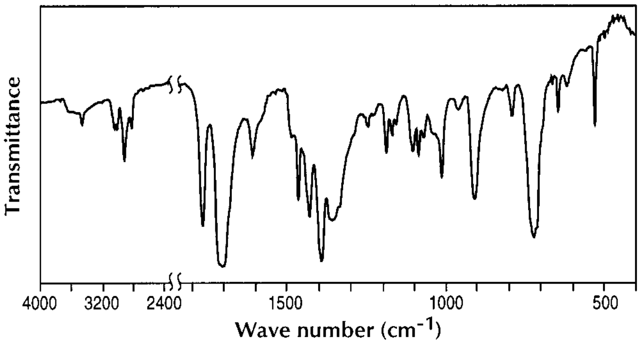
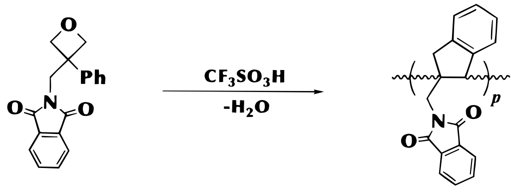


Figure 1. IR spectrum of **7** (KBr disk).

Scheme 1



1

7

The structure of **7** was most clearly characterized by IR spectroscopy (Figure 1).[12] Strong stretching bands at 1780 and 1710 cm^{-1} were ascribed to the imide carbonyl group, but no absorption assignable to any ether linkage appeared. On the basis of this interpretation, the most probable structure of **7** is deduced as oligo(2-phthalimidomethyl-1,2-indanylene). As for the polymerization of indene and its related compounds, numerous investigations now appear in the literature, but no example using any oxetane monomer has been

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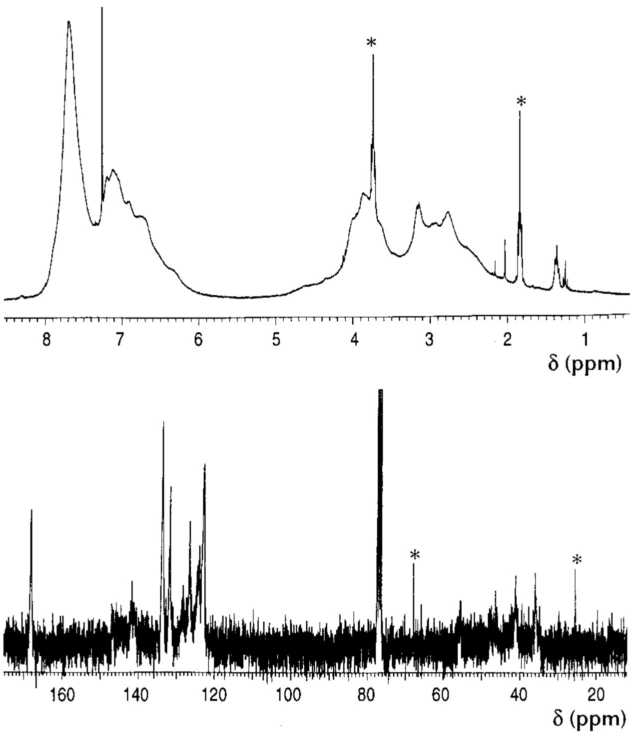


Figure 2. ^{1}H and ^{13}C NMR (270 MHz for ^{1}H nuclei) spectra of **7** in CDCl$_3$. Asterisked signals are due to THF used for reprecipitation.

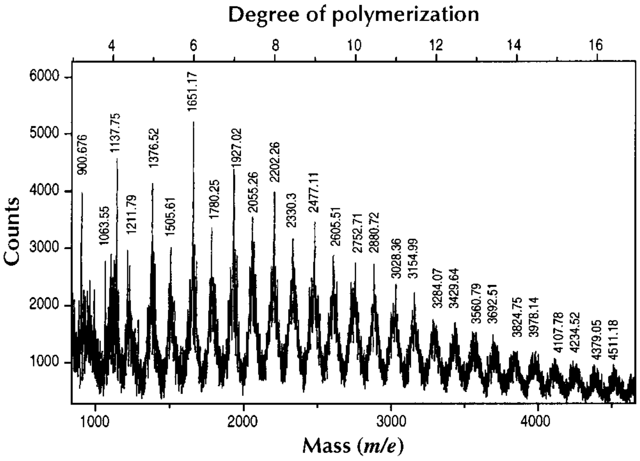
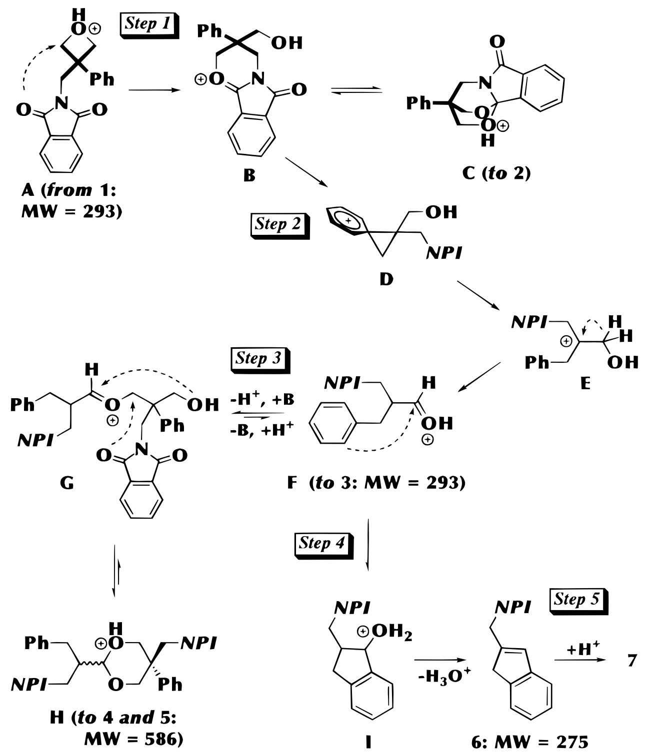


Figure 3. MALDI-TOF-MS spectrum of **7** ($M_{\mathrm{n\,GPC}}$ = 1730) purified by reprecipitation of a THF solution with diethyl ether.

reported yet. Similar to poly(unsubstituted indene), the ^{1}H and ^{13}C NMR spectra of **7** also showed extremely broadened signals due to restricted mobility of the main chain (Figure 2). Nevertheless, the relative signal intensities between the aromatic and aliphatic protons, as well as four different ^{13}C signals appearing in the aliphatic region, supported the expected structure of **7**.

Table 1 shows the change of the product distributions in the polymerization of **1** with CF$_3$SO$_3$H in chlorobenzene at 130 °C. Various intermediates (**2**–**6**) were found to be formed during the reaction, although the formation of bicyclic acetal (**2**) was confirmed only in a very early stage of the reaction at the low temperature of 80 °C (exp no. 1). All of these intermediates finally disappeared by employing both a relatively large amount of the catalyst and a prolonged reaction time, resulting in **7** as a single product. The production of **4** and **5** was so rapid as to reach completion within 10 min (exp no. 2), whereas the rate of formation of **7** was extremely slow, perhaps by less than a five-hundredth of the above. The course of polymerization was unaltered in the presence of 2,6-di-*tert*-butyl-4-methylphenol (exp no. 6). This indicates that no radical process is involved irrespective of the elevated temperature. As reported in the preceding paper, the cyclodimerization of **1** with Lewis acids also gave the same products, **2**–**5**, but not **6**. The close similarity of the intermediate products in the polymerization of **1** and its cyclodimerization strongly suggests that both reactions proceed by a very similar mechanism. In contrast to the cases of cyclodimerization,[8] the Lewis acids, such as BF$_3$·OEt$_2$ and benzylthiolanium hexafluoroantimonate, were not effective for the purpose of yielding **7**. This is probably because of the water liberated during the reaction. Therefore, trimethylsilyl trifluoromethanesulfonate, which can hydrolyze to CF$_3$SO$_3$H, brought about a polymerization similar to that of **1** (exp nos. 7 and 8). Although a rather low yield of **6** was always obtained throughout the polymerization reaction, we succeeded in isolating **6**, and it proved to be 2-(phthalimidomethyl)indene,[13] corresponding to the olefinic monomer of **7**.

Scheme 2. Plausible Mechanism for the Cationic Polymerization of 1 Involving Quantitative Dehydration[a]



[a] NPI: phthalimido group. Counteranions are omitted.

A plausible mechanism for the polymerization of **1** in the presence of a proton source is illustrated in Scheme 2. Although the mechanism is complicated, it can be explained reasonably by analogy to the mechanism proposed for the cyclodimerization of **1**.[8] Thus, the cyclodimerization involves three successive elementary steps: (1) isomerization of **1** to **2** via an intermediate cation **B** by the intramolecular nucleophilic attack of the imide carbonyl group; (2) skeletal rearrangement of **B** to an aldehyde **3** by consecutive cation transfer; and (3) intermolecular addition of **3** to **B**, followed by internal cyclization of the resulting dimer cation **G** leading to **4** and **5**. For the oligomerization process, additional steps besides the above should be required. Step 4 seems to proceed utilizing proton as a condensing agent in a manner similar to that of a Bischler−Napieralski reaction.[14] Thus, protonated aldehyde **F** brings about an intramolecular aromatic electrophilic substitution, followed by dehydration of oxonium **I** to give **6**. Finally, the olefinic monomer **6** undergoes proton-initiated polymerization to give **7**. Water liberated at step 4 does not decompose the Brønsted acid CF_3SO_3H used as a catalyst and does not interfere with the subsequent oligomerization process because most of the water should be vaporized as an azeotrope with chlorobenzene at 130 °C. Even when an amount of water equimolar to **1** was added externally (exp no. 9), **7** was obtained in a similar quantitative yield. Previously, we demonstrated that **3**−**5** are interconvertible via a common intermediate **G** and that the equilibrium is largely shifted to the dimer side, more preferably to **4**.[8] In the polymerization of **1**, however, the cyclic dimers are not thermodynamically stable products but a precursor pool for supplying the real monomer **6** via **3**.

In the present reaction system, there exist at least three cationically polymerizable monomers, namely, **1**, **2**, and **6**. We recently have reported that oxetanes and styrene can be copolymerized cationically.[15] Nevertheless, neither copolymerization with **6** nor homopolymerization of **1** or **2** took place. The reason is attributable to (i) a great difference in reaction rate between the cyclodimerization of **1** and the oligomerization of **6** and (ii) the bulkiness of the neophyl-type skeleton around the electrophilic sites of cationic species **A**−**C**, as shown by the heavy lines in Scheme 2.

In conclusion, the cationic polymerization of **1** using CF_3SO_3H as a proton source was found to afford **7** with quantitative dehydration. This new type of polymerization should be distinguished from conventional polycondensation or condensative chain polymerization, in that elimination of water takes place prior to the polymerization process. Thus, **1** is transformed in turn into a bicyclic acetal (**2**), an aldehyde (**3**), substituted 1,3-dioxanes (**4** and **5**), and then 2-(phthalimidomethyl)-indene (**6**) by proton-catalyzed multi-isomerization, followed by internal condensative dehydration. Regardless of this being a one-pot reaction, a sequence of complicated processes via the above various intermediates proceeded in an extremely ordered manner. The oligomer **7** composed of indanyl units is characterized by the possession of phthalimide groups which can be easily converted into amino groups.[16]

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Supporting Information Available: Experimental details for the synthetic procedures and characterization of **1**−**7** together with copies of NMR (270 MHz for ^1H nuclei) spectra for **6** (4 pages). Ordering information is given on any current masthead page.

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(8) Kanoh, S.; Nishimura, T.; Ando, K.; Senda, H.; Ogawa, H.; Motoi, M.; Tanaka, T. *Macromolecules*, **1998**, *31*, 7988−7991 [*t*-5-Phenyl-*c*-5-phthalimidomethyl-*r*-2-(1-benzyl-2-phthalimidoethyl)-1,3-dioxane (**4**) and *c*-5-phenyl-*t*-5-phthalimidomethyl isomer (**5**)].

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(10) Typically, to a glass tube containing **1** (0.10 g, 0.34 mmol) was charged anhydrous PhCl (0.34 mL) containing CF_3SO_3H (68 μmol) by a syringe in a nitrogen stream, and the resulting solution was allowed to stand at 130 °C for the designated time. After the addition of anhydrous Et_3N (0.1 mL), the mixture was evaporated to dryness. A small amount of the crude products was subjected to ^1H NMR and gel permeation chromatography (GPC) analyses to determine the product distribution and the molecular weight (M_n) distribution, respectively, of the produced oligomer.

(11) MALDI-TOF mass spectroscopic analyses were performed on a PerSeptive Biosystems Voyager Elite. To a matrix layer, deposited by evaporation of 0.3 μL of 0.1% dithranol solution in THF, was added 0.3 μL of a sample solution of **7** in THF (2.0 mg/mL). A mixture of angiotensin and ACTH 7−38 was used for calibration.

(12) The crude oligomer obtained in exp no. 5 was dissolved in THF and precipitated by adding diethyl ether to separate it into two fractions having lower and higher molecular weights: $M_n = 916$ and 1 730 and isolated yield = 28 and 41%, respectively. The higher-M_n part was used for analytical purposes. **7**: ^1H NMR ($CDCl_3$) δ 2.0−3.4 (m, 3H, CH_2 and CH in indane moiety), 3.4−4.8 (m, 2H, NCH_2), 6.0−7.3 (m, 4H, H_{Ar} in indane moiety), 7.3−8.1 (m, 4H, H_{Ar} in phthalimide moiety); ^{13}C NMR ($CDCl_3$) δ 36.2, 41.4, 47.7, 55.6, 122.9, 124.0, 126.6, 128.3, 141.7, 131.8, 133.8, 147.1, 168.2; IR (KBr) 1780, 1710 ($\nu_{\text{imide C=O}}$) cm^{-1}. Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.93; H, 4.60; N, 4.50.

(13) The reaction of **1** was carried out using 5 mol % of CF_3SO_3H at 130 °C for 3 days by a method similar to that of the polymerization. PTLC separation of the crude products on EM Aluminiumoxid 60 PF_{254} Type E, using ethyl acetate−hexane (1:1 v/v) as an eluent, gave **6** in 9%, which was further purified by recrystallization from CH_2Cl_2-hexane. **6**: yield, 4%; colorless needles; mp 192−193 °C; TLC on EM aluminum sheets Aluminiumoxid 60 F_{254} neutral, $R_f = 0.95$, ethyl acetate−hexane (1:1 v/v); ^1H NMR ($CDCl_3$) δ 3.41 (s, 2H, 1-CH_2), 4.73 (s, 2H, NCH_2), 6.77 (s, 1H, 3-CH), 7.13 (td, $J_1 = 7.3$ Hz, $J_2 = 1.7$ Hz, 1H, either 5- or 6-H_{Ar}), 7.21 (t, $J = 6.9$ Hz, 1H, either 5- or 6-H_{Ar}), 7.29 (d, $J = 6.9$ Hz, 1H, either 4- or 7-H_{Ar}), 7.37 (d, $J = 7.3$ Hz, 1H, either 4- or 7-H_{Ar}), 7.73, 7.87 (each dd, $J_1 = 5.3$ Hz, $J_2 = 3.0$ Hz, each 2H, carbonyl *m*- and *o*-H_{Ar}); ^{13}C NMR ($CDCl_3$) δ 37.8, 40.1, 121.0, 123.4, 123.6, 124.7, 126.4, 130.0, 132.1, 134.1, 142.9, 143.2, 144.3, 168.0; IR (KBr) 1770, 1708 ($\nu_{\text{imide C=O}}$), 1615 ($\nu_{C=C}$) cm^{-1}; HRMS found, *m/e* 275.0947 (calcd for $C_{18}H_{13}NO_2$, *m/e* 275.0946). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.48; H, 4.81; N, 5.04.

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