Synthesis and Cationic Polymerization of 2-Phenyl-1,6-dioxaspiro[4.6]undecane. A Novel Expandable Monomer Undergoing Cationic Double Ring-Opening Polymerization

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Introduction. Spiro cyclic and bicyclic compounds such as spiro orthocarbonates (SOCs), bicyclo orthocarbonates (BOCs), and spiro ortho esters (SOEs) have been reported as candidate monomers for adhesive applications, because they show either no shrinkage or expansion in volume during polymerization.[1] However, the obtained polymers contain carbonate and ester moieties in the main chain, which may be hydrolyzed under certain conditions. In the course of our study on expandable monomers based on spiro cyclic compounds, we have designed a novel spiro cyclic monomer, "spiroketal" capable of undergoing cationic double ring-opening polymerization to afford a polymer (poly(ether−ketone)) without hydrolysis. Although there are some reports of polymers containing a spiroketal skeleton in the polymer chain,[2] spiroketals have never been used as a monomer so far. Spiroketals such as 1,6-dioxaspiro[4.4]-nonane, 1,6-dioxaspiro[4.5]decane, 1,6-dioxaspiro[4.6]-undecane, and 1,7-dioxaspiro[5.5]undecane exist in natural products such as insect pheromons.[3] This article deals with the synthesis and cationic polymerization of a novel spiroketal, 2-phenyl-1,6-dioxaspiro[4.6]undecane, **1**.

Results and Discussion. Synthesis of Monomer 1. Spiroketals are commonly synthesized by the acid-catalyzed intramolecular ketalization of the corresponding dihydroxyketones. However, the synthesis of 1,6-dioxaspiro[4.6]undecane derivatives is very difficult due to the unstable seven-membered acetal ring. Mori et al. have synthesized optically active 2,7-dimethyl-1,6-dioxaspiro[4.6] undecanes from the corresponding optically active alkyl halides and lactones in 9−12% overall yields.[4] Utimoto et al. have reported the cyclization of alkynediols into spiroketals using $PdCl_2$ as a catalyst in 60−85% yields.[5] In this work, we applied Utimoto's method for the synthesis of a novel monomer, 2-phenyl-1,6-dioxaspiro[4.6]undecane, **1**, as shown in Scheme 1. First, 1,5-pentandiol was allowed to react with an equivalent amount of *p*-toluenesulfonyl chloride (*p*-TsCl) in the presence of triethylamine in dichloromethane to afford the monotosylated diol, whose residual hydroxyl group was protected with tetrahydropyranyl (THP) ether. Further, the product was reacted with lithiated trimethylsilylacetylene in a tetrahydrofuran− (THF−) hexamethylphosphoric triamide (HMPA) mixed solvent

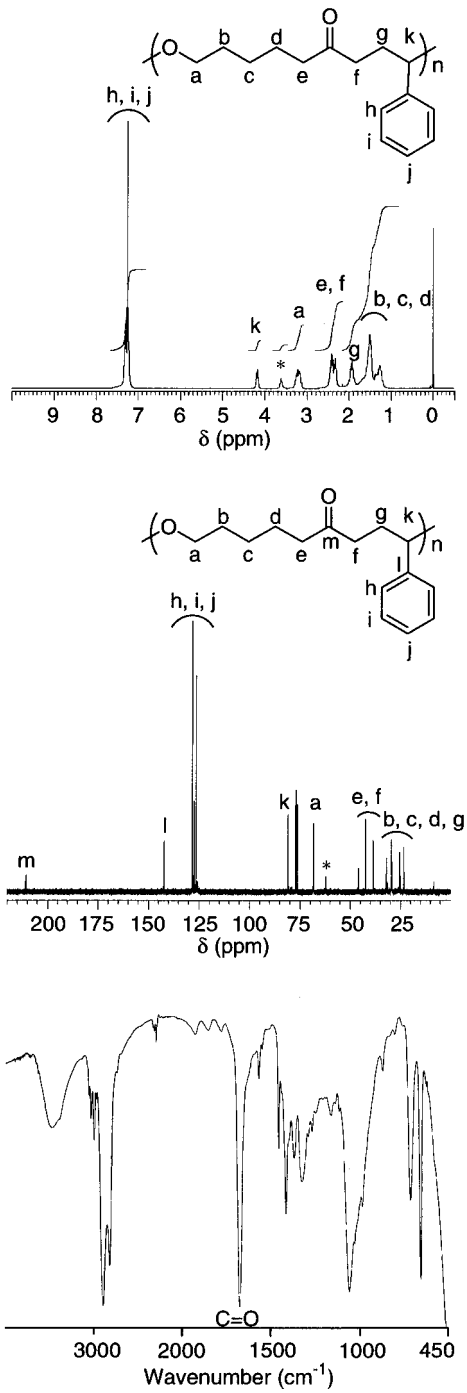

Figure 1. (Top) ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of poly **1** obtained by the cationic polymerization of **1** with 5 mol % of $BF_3{\cdot}Et_2O$ at 80 °C for 2 h (run 3 in Table 1). (Middle) ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of the same sample. (Bottom) IR (neat) spectrum of the same sample. ∗: Signal derived from the polymer end $-CH_2-OH$.

to afford **5**, whose trimethylsilyl (TMS) group was deprotected by reaction with tetrabutylammonium fluoride (TBAF). Compound **7** was prepared by reaction of lithiated **6** and styrene oxide, and subsequently deprotected by acid treatment to form the diol **8**. Finally, the spiroketal **1** was prepared by tandem cyclization of **8** with $PdCl_2$ as catalyst.[6]

Cationic Polymerization of Spiroketal. Polymerization of the spiroketal **1** was carried out with 5 mol %

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Scheme 1

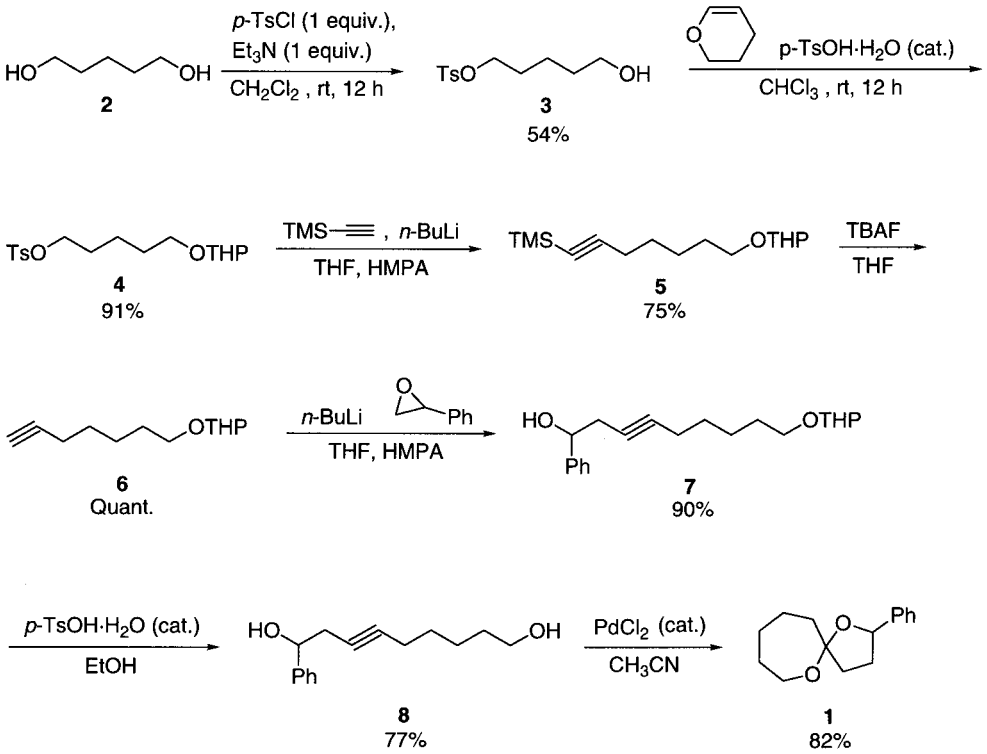


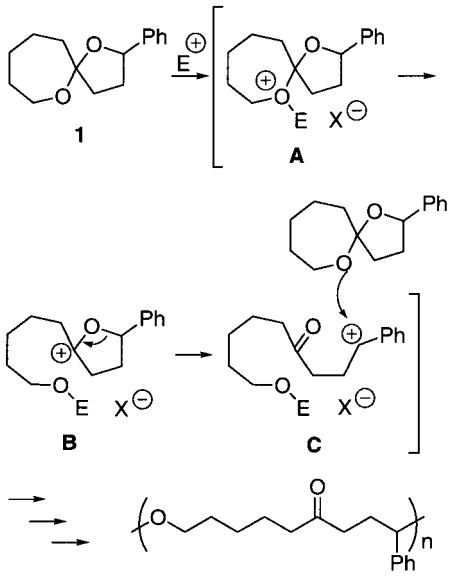
Table 1. Cationic Polymerization of 1[a]

run	init	temp (°C)	convn[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]	vol change[e] (%)
1	$BF_3{\cdot}Et_2O$	rt	<1	0			
2	$BF_3{\cdot}Et_2O$	50	85	81	2900	1.8	
3	$BF_3{\cdot}Et_2O$	80	95	93	3700	3.3	+0.9
4	$BF_3{\cdot}Et_2O$	100	98	94	3300	7.4	+1.1
5	TfOMe	80	87	86	2900	3.6	+1.2
6	TfOH	80	89	86	3100	2.9	+0.9
7	$SnCl_4$	80	91	89	3100	1.9	+1.0

[a] Conditions: **1**, 1 mmol; initiator, 0.05 mmol; CH_2Cl_2, 0.2 mL; polymerization time, 2 h. [b] Estimated by GC using ethylbenzene as an internal standard. [c] Hexane-insoluble part. [d] Estimated by GPC eluted with THF, polystyrene calibration. [e] Measured by the density gradient tube method at 23.5 °C.

of $BF_3{\cdot}Et_2O$, methyl trifluoromethanesulfonate (TfOMe), trifluoromethanesulfonic acid (TfOH), or $SnCl_4$ as a cationic initiator in dichloromethane at room temperature to ~100 °C for 2 h, as summarized in Table 1. No polymerization took place at room temperature, while sticky liquid polymers with number-average molecular weights (M_n) of 2900−3700 were obtained as hexane-insoluble materials in 81−94% yield at 50−100 °C. The monomer conversion, M_n, and polydispersity (M_w/M_n) of the obtained polymer tended to increase as the temperature was raised when $BF_3{\cdot}Et_2O$ was used as the initiator (runs 2−4). Figure 1 depicts the ^1H NMR, ^{13}C NMR, and IR spectra of the polymer obtained in run 3 in Table 1. The IR and ^{13}C NMR spectra of the polymer showed peaks at 1711 cm^{-1} and 211 ppm, respectively, which were based on a ketone unit in the polymer. No ketal center carbon signal was observed around 110 ppm in the ^{13}C NMR spectrum, supporting the absence of a single ring-opened unit in the polymer. All the ^1H and ^{13}C NMR signals could be reasonably assigned for the double ring-opened poly(ether−ketone) structure, as shown in Figure 1. Further, acetic acid 9-chloro-6-oxo-9-phenylnonyl ester, obtained by the reaction of **1** with acetyl chloride, showed spectroscopic patterns similar

Scheme 2



to those of the polymer.[7] These data indicate that **1** underwent cationic double ring-opening polymerization to give poly(ether−ketone).

Scheme 2 illustrates a plausible mechanism of the cationic polymerization of **1**. [8] First, the ether oxygen of the oxepane ring attacks an electrophile to form an oxonium cation (A), which is followed by bond cleavage to form a carbenium ion (B). B rapidly isomerizes into a benzyl cation, where the driving force would be formation of a carbonyl group and the stabilized benzyl cation. Another monomer attacks the benzyl cation, and successive reactions afford the poly(ether−ketone). The selective formation of the double ring-opened unit would be promoted by the strained oxepane ring and the formation of a stabilized benzyl cation. The model reaction of **1** with acetyl chloride quantitatively afforded

acetic acid 9-chloro-6-oxo-9-phenylnonyl ester, which supports this polymerization process.

The densities of the monomer (1.100) and the polymers (1.090−1.087) were measured by the density gradient tube method at 23.5 °C. The polymer samples for the measurement were prepared by the solvent (chloroform) casting method, and dried at 80 °C for 12 h. The spiroketal **1** showed 0.9−1.2% of volume expansion during the polymerization.

Summary. We synthesized a novel expandable spirocyclic monomer, 2-phenyl-1,6-dioxaspiro[4.6]undecane **1**, which underwent cationic double ring-opening polymerization with volume expansion. We are now investigating the hydrolysis resistance of the polymers.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR and IR spectra of **1** (Figure S1), energy profiles of ring-opening addition of phenylspiroketal **1** with methyl cation (Figure S2), ^{1}H NMR spectrum of acetic acid 9-chloro-6-oxo-9-phenylnonyl ester (Figure S3), two-dimensional NMR spectra of poly(spiroketal) (Figures S4 and S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Spectroscopic data of **1**. Bp = 150 °C/1 Torr (Kugelrohr distillation). ^{1}H NMR ($CDCl_3$): δ1.21−2.58 (m, 12H, $-CH_2-\times6$), 3.57−3.76 (m, 1H, $-O-CH_2-$), 3.77−3.98 (m, 1H, $-O-CH_2-$), 5.05 (t, J = 10.2 Hz, 1H, $-O-CH<$), 7.14−7.58 (m, 5H, $-C_6H_5$). ^{13}C NMR ($CDCl_3$): δ 23.13, 23.26, 29.42, 29.45, 30.58, 30.65, 33.89, 34.45, 38.28, 38.53, 38.71, 39.42 ($-CH_2-$), 62.21 ($-O-CH_2-$), 62.64 ($-O-CH_2-$), 79.00 ($-O-CH<$), 81.84 ($-O-CH<$), 110.62 (>C<), 110.64 (>C<), 125.55, 126.05, 126.82, 126.96, 127.95, 128.02, 142.73, 143.76 ($-C_6H_5$). IR (neat): 2932, 2879, 2856, 1604, 1495, 1474, 1451, 1350, 1321, 1284, 1254, 1237, 1215, 1196, 1170, 1150, 1130, 1097, 1067, 1042, 991, 977, 946, 915, 867, 842, 758, 699 (−Ph) cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.62; H, 8.89.

(7) Spectroscopic data of acetic acid 9-chloro-6-oxo-9-phenylnonyl ester. ^{1}H NMR ($CDCl_3$): δ 1.24−1.36 (m, 2H, $-CH_2-$), 1.50−1.66 (m, 4H, $-2(-CH_2-)$), 2.04 (s, 3H, $-CH_3$), 2.25−2.35 (m, 2H, $-CH_2-$), 2.40 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.59 (t, J = 7.5 Hz, 2H, $-CH_2-$), 4.05 (t, J = 6.3 Hz, 2H, $-O-CH_2-$), 4.93 (t, J = 6.9 Hz, 1H, −CHCl), 7.25−7.45 (m, 5H, $-C_6H_5$). ^{13}C NMR ($CDCl_3$): δ 20.92 ($-CH_3-$), 20.96 ($-CH_2-$), 23.25 ($-CH_2-$), 28.34 ($-CH_2-$), 33.59 ($-CH_2-$), 39.60 ($-CH_2-$), 42.62 ($-CH_2-$), 62.83 (−CH−), 64.17 ($-CH_2-$), 126.78 (−CH−), 128.32 (−CH−), 128.61 (−CH−), 141.20 (−C−), 171.08 (−C−), 209.31 (−C−). IR (neat): 2940, 2866, 1738 (C═O), 1714 (C═O), 1494, 1455, 1435, 1411, 1367, 1241, 1117, 1044, 763, 700 (−Ph) cm^{-1}. Anal. Calcd for $C_{17}H_{23}ClO_3$: C, 65.69; H, 7.46. Cl, 11.41. Found: C, 65.51; H, 7.52. Cl, 11.32.

(8) The ether oxygen of the oxolane ring can also attack an electrophile. We have calculated formation energies of the intermediates by the AM-1 Hamiltonian using the PC Spartan Pro semiempirical program (Figure S2). As a result, it has been confirmed that Scheme 2 is the most likely possibility for the polymerization mechanism.

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