Mechanistic Distinctions between Cation Radical and Carbocation Propagated Polymerization

J. Todd Aplin and Nathan L. Bauld*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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The polymerization of bis[4-(1-propenyl)phenyl] ether in the presence of tris(4-bromophenyl)aminium hexachloroantimonate is found to occur by competing cation radical and carbocation pathways. These pathways involve, respectively, cyclobutanation and linear addition. Methods for favoring each mechanistic type are proposed and explored.

Although addition polymerization reactions propagated by carbocation intermediates are very well-known,[1] only recently have cation radicals been established as viable intermediates for propagating addition polymerizations.[2] The present research describes the polymerization of a monomer under conditions which were designed to be conducive to cation radical polymerization but which result in a competition between cation radical and carbocation propagated polymerization. As a result of the present study, criteria are developed for distinguishing between cation radical and carbocation mechanisms of polymerization, and means for favoring each mechanism are explored.

Results and Discussion

The cation radical cyclobutanation polymerization of monomer **1** (Scheme 1) reported recently[2] represents the first instance in which an addition polymerization reaction has been shown to be propagated by cation radical intermediates. The cation radical chain mechanism shown in Scheme 1 was proposed and supported for this unprecedented polymerization. The initiator is tris(4-bromophenyl)aminium hexachloroantimonate (**2**$^{\bullet+}$), a stable, commercially available cation radical salt. The polymerization of **1** by **2**$^{\bullet+}$ is also unusual in that it is a *cycloaddition* as opposed to a *linear* (or acyclic) addition polymerization. Finally, the joining of monomer units via cyclobutane linkages (i.e. cyclobutanation polymerization) is especially unprecedented in thermal chemistry.

In the course of our research on cation radical cyclobutanation polymerization, attention was directed to **3** (Scheme 2) as an appropriate monomer for study. Although the oxidation potential of **3** (1.42 V vs SCE) is somewhat higher than that of **1** (1.33 V), both are well within the range of oxidizing ability of **2**$^{\bullet+}$ (E_{ox} 1.05 V; range up to 1.6 V). Monomer **3** was conveniently prepared by double Friedel−Crafts propionylation of diphenyl ether, followed by sodium borohydride reduction and elimination via phosphorus oxychloride/pyridine. Polymerization of **3** in the presence of **2**$^{\bullet+}$ (5 mol %) in dichloromethane at 0 °C gave an 81% yield of a polymer which is highly insoluble in all of a wide variety of solvents tried, including diphenyl ether at 250 °C. This observation contrasts sharply with poly(**1**) prepared under comparable conditions, which is highly soluble in dichloromethane or chloroform. The solid-state ^{13}C NMR spectrum of poly(**3**) has broad absorptions centered at δ 12, 20 (weak), 35, 43, 120, 140, and 155. The insolubility of the polymer immediately suggested the possibility of a cross-linked polymer, which is not expected if polymerization occurs by a cation radical cycloaddition route. On the other hand, linear polymerization of **3** via an acid-catalyzed, carbocation-mediated route would be expected to yield a cross-linked polymer (Scheme 2). The generation of strong Bronsted acid under aminium salt induced reaction conditions is well-established, and instances have been presented in which carbocation chemistry prevails over cation radical chemistry.[3,4] The extremely broad ^{13}C NMR absorptions of poly(**3**) presented difficulties in definitively characterizing the polymer structure and especially in distinguishing cyclobutapoly(**3**) from the similar cross-linked, acyclic structure. A special element of difficulty arose when the ^{13}C NMR spectrum of poly(**3**) was compared with those of the *trans*-anethole cyclobutadimers (Scheme 3),[5] which had been projected as NMR spectroscopic models for cyclobutapoly(**3**). Whereas the cyclodimerization of *trans*-anethole (**4**) by **2**$^{\bullet+}$ at 0 °C yields exclusively the trans,anti,trans dimer (^{13}C NMR δ 18, 43, 52) in the aliphatic region, at −30 °C the trans,syn,trans cyclodimer (^{13}C NMR δ 15, 34, 49) is formed in equal amounts. Initially, it was not certain whether cyclobutapoly(**3**) should be expected to have exclusively the anti structure or to be a syn,anti mixture. Thus the ^{13}C NMR spectrum of poly(**3**) might have been considered to be consistent with a mixture of syn and anti cyclobutapoly(**3**), especially if the possibility of solid-state effects on the ^{13}C NMR chemical shifts is considered. Consequently, a soluble polymer of **3** was sought in order to permit its characterization by solution phase ^{13}C and ^{1}H NMR spectroscopy. When a dilute solution of **3** was polymerized by **2**$^{\bullet+}$, a soluble polymer was indeed obtained which had the same ^{13}C NMR absorptions as the previously obtained insoluble polymer, but in addition the ^{1}H NMR spectrum indicated that the poly(**3**) obtained has primarily the acyclic structure. In particular, ex-

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(3) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1994**, *106*, 7993.

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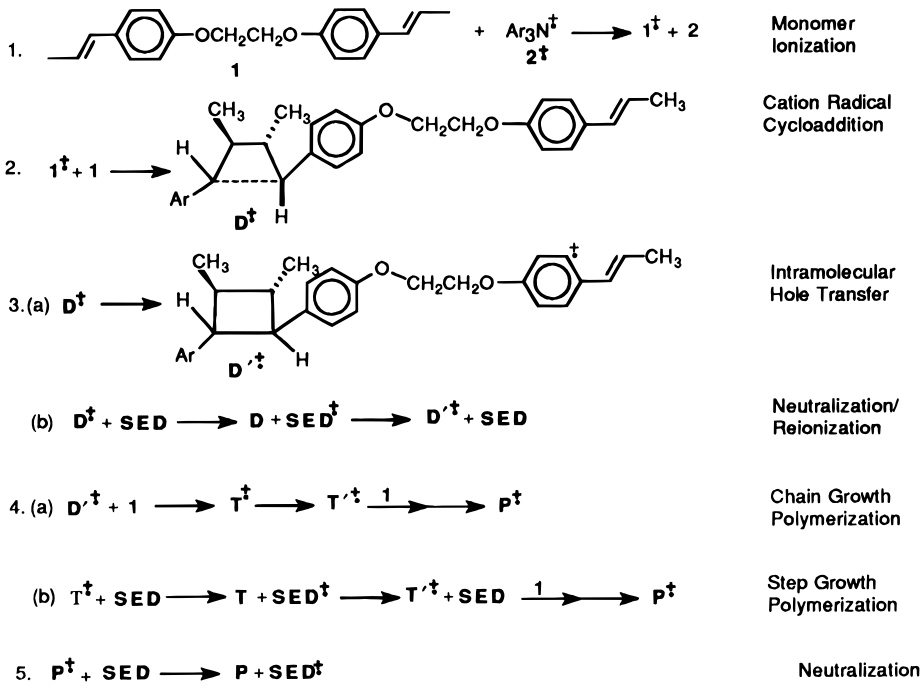
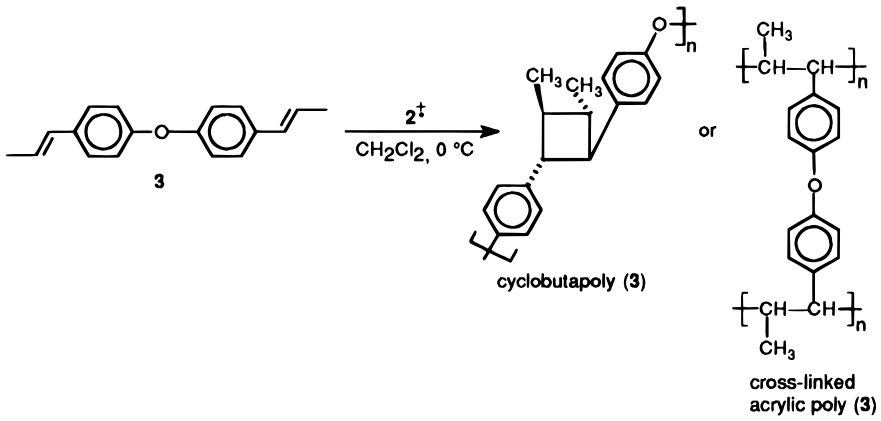
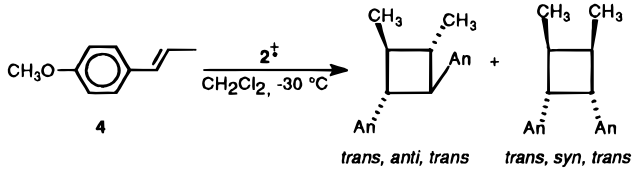
Scheme 1. Mechanism of Cation Radical Cycloaddition Polymerization of 1



Scheme 2. Cation Radical vs Carbocation Polymerization



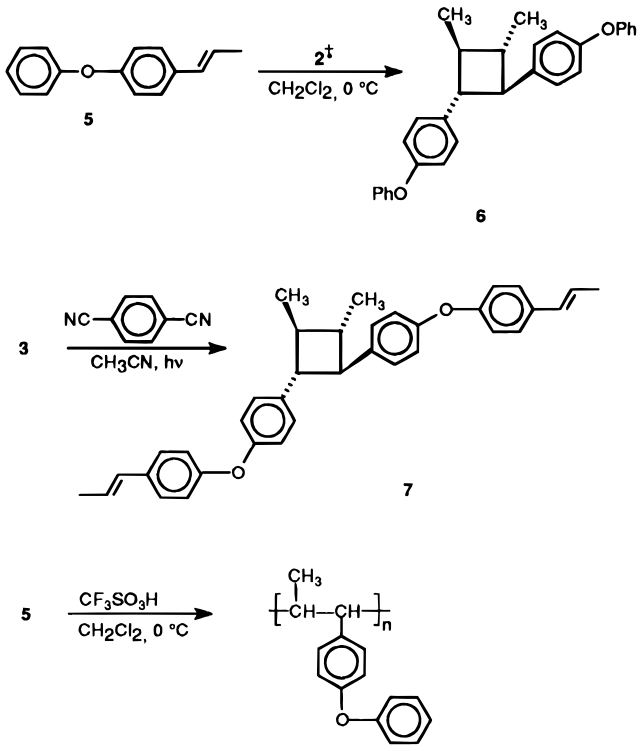
Scheme 3. Cation Radical Cyclodimerization of *trans*-Anethole



tensive previous research has shown that methyl groups attached to cyclobutane rings absorb at appreciably lower fields (δ 1.1−1.2) than do typical aliphatic methyl groups (δ 0.7−0.9) in their ^{1}H NMR spectra.[5] The soluble poly(**3**) had only very weak methyl absorptions in the range of δ 1.1−1.2 region with much stronger absorptions in the δ 0.7−0.9 region. From the relative peak areas in the ^{1}H NMR spectra, the poly(**3**) obtained was estimated to have 90% acyclic (acid-catalyzed) linkages and 10% cyclobutane (cation radical) linkages. This analysis was further supported by the relative ^{13}C NMR peak areas at δ 12 and 20, assuming that the former correspond to acyclic methyl carbons and the latter to methyl groups attached to a cyclobutane ring (see the anti dimer of **4**).

Additional confirmation of the critical ^{13}C and ^{1}H NMR absorptions expected for cyclobutapoly(**3**) were obtained from model compounds which are structurally even more closely related to the polymer than the *trans*-anethole dimers. First, the monopropenyl analogue of **3** (**5**) was treated with $\mathbf{2}^{\bullet+}$ in order to obtain **6** (Scheme 4). Second, **3** itself was subjected to cyclobutadimerization under photosensitized electron-transfer conditions, giving **7**. Both of these model compounds exhibit methyl absorptions in their ^{13}C NMR spectra at δ 18, as well as benzylic

Scheme 4. Cation Radical vs Carbocation Polymerization



cyclobutane carbon absorption at δ 52, and non-benzylic cyclobutane carbons at δ 43, but none of the strong absorptions of poly(**3**) at δ 12 or 35. In contrast, when the monopropenyl substrate **5** was subjected to acid-catalyzed polymerization (triflic acid, 0 °C), the resulting linear polymer (Scheme 4) exhibited signals at δ 13, 34, and 48, corresponding to the absorptions of poly(**3**). Finally, the polymerization of **3** by triflic acid gave a polymer virtually identical in its ^{13}C NMR spectrum to that obtained in the aminium salt catalyzed polymerization.

Hindered nitrogen bases such as 2,6-di-*tert*-butylpyridine are known to suppress acid-catalyzed reactions completely,[3,4] while permitting most cation radical reactions to proceed, albeit with diminished efficiency. Such bases are known to be able to deprotonate the highly acidic cation radical intermediates in competition with their cycloaddition reactions, thus diminishing the efficiency of the latter reactions. When the polymerization of **3** via **2**$^{\bullet+}$ was conducted in the presence of a hindered amine base, the product consisted of a mixture of oligomers up to and including octamers. The ^{1}H and ^{13}C NMR spectra of these oligomers correspond excellently with the model cyclobutadimers **6** and **7** and exhibit none of the δ 12 and 35 absorptions of poly(**3**) prepared in the absence of base.

The suppression of acid-catalyzed polymerization by the use of insoluble bases was also studied. When **3** was polymerized by **2**$^{\bullet+}$ in the presence of solid sodium carbonate, the product consisted of recovered **3** (40%), dimers and low oligomers (16%), and higher polymers (18%). The latter had a 1:1 ratio of cyclic:acyclic linkages.

Finally, the polymerization of **3** was also attempted by anodic oxidation. Direct oxidation of **3** in acetonitrile at a reticulated vitreous carbon anode resulted in the immediate formation of a polymer coating on the anode. When **2** (the neutral triarylamine) was included in the reaction mixture, anodic oxidation resulted in the formation of oligomers having $\bar{M}_w = 1600$ and exclusively the cyclobutane structure.

Mechanistic Considerations. Although **3** has a modestly higher oxidation potential than **1** (ca. 0.1 V), it is still well within the range of oxidizability of **2**$^{\bullet+}$, as shown by the facile cation radical Diels–Alder and cyclobutanation reactions of **5**. It is therefore a matter of mechanistic interest that the cation radical cycloaddition polymerization of **1** is quite efficient but that of **3** is so inefficient as to be overwhelmed by acid-catalyzed carbocation-mediated polymerization. It has previously been proposed that the chain mechanism for cation radical cycloaddition polymerization is far more efficient than the catalytic mechanism, which represents a step growth process.[2] Further, the maintenance of an efficient chain process depends critically upon the existence of an efficient intramolecular transfer of the cation radical moiety (hole) from its initial location following cycloaddition (on the cyclobutane long bond) to the terminal propenyl site required for further cycloaddition (Scheme 1). In the case of **1**, this hole transfer is evidently rapid in comparison to the rate of intermolecular hole transfer to a neutral, ionizable molecule (**1** or **2**), which would convert the chain process into a catalytic, step growth process. In the case of **3** (Scheme 5), the intramolecular hole transfer may be less favorable energetically because the propenyl moiety involved has a higher oxidation potential than was available in the case of **1**. That this is the case is indicated by the circumstance that the hole receptor propenyl moiety in the case of **1** is a β-methylstyrene moiety having a strongly stabilizing *p*-alkoxy substituent ($\sigma^+ = -0.78$ for methoxy), while in the case of **3**, the substituent is the less strongly stabilizing *p*-phenoxy group ($\sigma^+ = -0.50$). The difference in the oxidation potentials between 4-PhO and 4-MeO β-methylstyrene is, in fact, 0.14 V or 3.2 kcal/mol.[6] Since intermolecular hole transfer to **2** (see Scheme 5) is highly exergonic, it is presumably virtually diffusion controlled. Consequently a diminished rate of intramolecular hole transfer could easily result in the prevalence of intermolecular hole transfer.

Conclusions

The polymerization of the bispropenyl derivative of diphenyl ether (**3**) by tris(4-bromophenyl)aminium hexachloroantimonate (**2**$^{\bullet+}$) in dichloromethane at 0 °C proceeds to give a polymer which consists primarily (9:1) of acyclic structural units propagated by an acid-catalyzed, carbocation-mediated mechanism. This polymer is virtually identical to the one generated by the triflic acid catalyzed polymerization of **3**. Cation radical cyclobutanation polymerization contributes more significantly (1:1) when sodium carbonate is included in the reaction medium. When a soluble amine base is included, the efficiency of polymerization overall is diminished, leading to oligomers (dimer to octamer) which are exclusively the result of cation radical cyclobutanation. Anodic oxidation of the same monomer in the presence of neutral triarylamine **2** also yields an oligomeric mixture which involves only cyclobutaoligomerization. The greatly diminished efficiency of the cation radical cyclobutanation polymerization of **3** in comparison to a previously studied monomer is noted, and a mechanistic rationale for this is provided.

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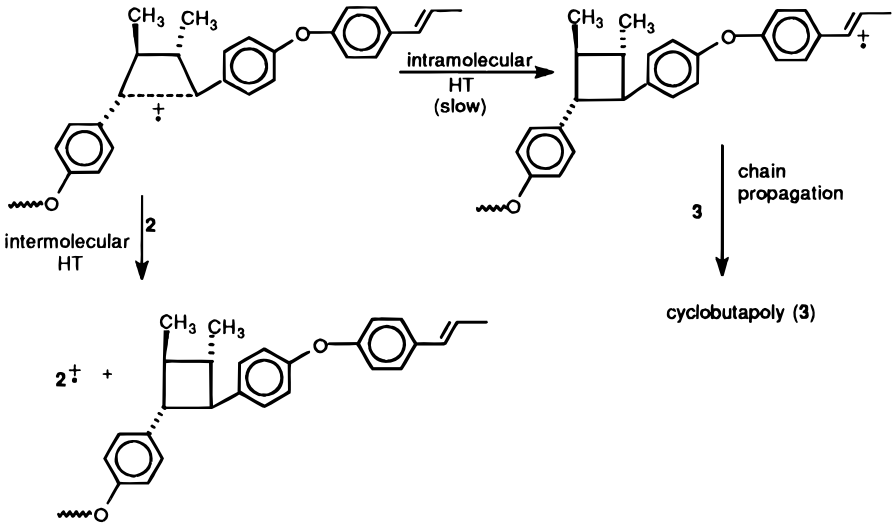
Scheme 5. Intramolecular vs Intermolecular Hole Transfer



Experimental Section

Reagents. Dried solvents were obtained by distillation under nitrogen immediately prior to use. Reagent grade dichloromethane (DCM) and acetonitrile (AN) were distilled from phosphorus pentoxide. Pyridine was distilled from potassium hydroxide. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from a blue solution of sodium (or potassium) and benzophenone. All other reagents were used as received unless otherwise specified. Alumina (neutral) TLC plates and alumina preparative scale TLC (PTLC) plates (Analtech, 1.5 mm layer thickness) were washed with a 1:1 solution of ethyl acetate (EtOAc) and DCM and then dried in a 110 °C oven prior to use. In some instances the PTLC plate was eluted two or three times in an attempt to obtain better separation. After identifying the bands, the adsorbent was scraped from the PTLC plate and was washed with DCM. The adsorbent was filtered off, and the solvent was removed on a rotary evaporator. Column chromatography was performed using neutral or basic alumina. Reagent grade lithium perchlorate used for electrochemistry was dried by heating at 180 °C for 24 h under an N_2 purge and stored in a desiccator containing Drierite. All moisture sensitive reactions were carried out in oven dried glassware which had been flushed with dry nitrogen. All organic product solutions were dried over magnesium sulfate unless otherwise indicated. Solvent removal was performed on a rotary evaporator.

Analysis. Room-temperature ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer as solutions in $CDCl_3$. Two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR spectra were recorded using a General Electric GN-500 spectrometer as solutions in $CDCl_3$. High-temperature ^1H NMR and ^{13}C NMR spectra of polymers were recorded on a General Electric G-500 spectrometer as solutions in $CDCl_3$ at 55 °C. Solid-state ^{13}C NMR spectra were recorded on a Chemagentics CMX-300 spectrometer as fine powders. Chemical shifts are reported in parts per million (ppm) downfield from a tetramethylsilane (TMS) reference. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; br, broad. Solution-state ^1H, ^{13}C and solid-state ^{13}C NMR spectra of polymer samples gave broad signals with little fine structure, so chemical shifts of such samples are reported as the midpoint of the broad signals. Gas chromatographic (GC) analyses were performed on a Varian Model 3700 equipped with a flame ionization detector and a DB-1 (J&W Scientific, 15 m × 0.25 mm, 1 mm film thickness) capillary column using helium as a carrier gas. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5890 gas chromatograph equipped with a DB-1 (15 m × 0.25 mm, 1 mm film thickness) capillary column and a 5917A mass selective detector. Low-resolution chemical ionization mass spectra (CIMS) were recorded on a Finigan MAT TSQ-70 mass spectrometer. High-resolution mass spectra (HRMS) were recorded on a Dupont (CEC) 21-110B mass spectrometer. Cyclic voltammetry (CV) measurements were performed using a BAS model 100 electrochemical analyzer at a scan rate of 100 mV/s. The CV measurements were carried out using a divided cell equipped with a platinum disk working electrode (anode) and a reticulated vitreous carbon counter electrode separated by a glass frit. Ag/Ag^+ reference electrode (silver wire immersed in an acetonitrile solution 0.1 M in $AgNO_3$ and $LiClO_4$), calibrated against ferrocene/ferrocinium ion, was placed in the anode compartment and separated from the bulk solution by a Vycor frit. The peak oxidation potential (E_p^{ox}) measurements vs Ag/Ag^+ were converted to vs SCE by adding 0.3 V to each value. A blank CV trace of the electrolyte solution was recorded prior to analyzing the substrate. The substrate was then added to the cell as a solution in the electrolyte (concentration ~4 mM), and its CV response was recorded. Gel permeation chromatography (GPC) was carried out in DCM or THF (1 mL/min) using a Waters 550 HPLC pump, a Waters 410 differential refractometer, and a Waters 745 data module with an Ultrastyragel 500 Å column connected in series with a μ Styragel 10^4 Å column. The GPC analyses were calibrated with a polystyrene standard. UV−visible spectra were taken on a Hewlett-Packard 8450A spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 205 FT-IR spectrometer using polystyrene as a standard. Liquid samples were run as thin films between NaCl plates. Solid samples were run as thin films on NaCl plates (generated by evaporation of a DCM solution on the plate) or as solutions in CCl_4 using a NaCl solution cell. Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected.

Bis(4-propionylphenyl) Ether. To a dry, round-bottom flask equipped with a magnetic stirrer was added $AlCl_3$ (50.3 g, 0.378 mol) followed by dichloromethane (100 mL). After the temperature was lowered to −20 °C using a dry ice/acetone bath, a solution of diphenyl ether (25.6 g, 0.151 mol) in dichloromethane (50 mL) was added slowly. A solution of propionyl chloride (30 g, 0.45 mol) in dichloromethane (40 mL) was then added dropwise over a period of 10−20 min. After the addition was complete, the dry ice/acetone bath was replaced with an ice bath and the reaction mixture was stirred for an additional 3 h and then poured into a separatory funnel containing crushed ice. The aqueous layer was separated and extracted twice with dichloromethane (2 × 100 mL). The combined dichloromethane layers were then washed with water (500 mL), saturated aqueous $NaHCO_3$ (2 × 500 mL), and water (2 × 500 mL). The dichloromethane solution was then dried and the solvent removed by rotary evaporator. The product (38.1 g, 90%) was obtained as a white solid which was

found to be 99% pure by GC: mp 98.5−99.8 °C; ^{1}H NMR δ 1.2 (t, 6H), 3.0 (q, 4H), 7.1 (d, 4H), 8.0 (d, 4H); ^{13}C NMR δ 8.2, 31.7, 66.3, 118.8, 130.4, 160.2, 199.5; IR (C═O) 1684; LRMS *m/e* 282 (M^+), 271, 197, 196, 139, 120, 92 (base).

Bis[4-(1-hydroxypropyl)phenyl] Ether. The diketone obtained in the preceding reaction (20 g, 0.071 mole) was dissolved in 200 mL of a 3:1 ethanol:tetrahydrofuran mixed solvent, and solid $NaBH_4$ (5.0 g, 0.13 mol) was added. After 1.5 h at room temperature, the reaction was quenched with excess 10% acetic acid at 0 °C. The aqueous solution was extracted with dichloromethane (3 × 100 mL), and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 × 100 mL) and water (2 × 100 mL). The solution was then dried and the solvent removed on a rotary evaporator, giving 20.5 g of the diol product (99.7%) as an oil which was used without further purification: ^{1}H NMR δ 0.9 (t, 6H), 1.6−1.9 (m, 4H), 2.6 (br s, 2H), 4.5 (t, 2H). 6.9 (d, 4H), 7.2 (d, 4H); ^{13}C NMR δ 10.2, 31.9, 75.4, 118.6, 127.4, 139.5, 156.5; IR (O═H) 3360.

Bis[4-(1-propenyl)phenyl] Ether. The diol obtained in the preceding reduction (6.31 g, 0.02 mol) was dissolved in pyridine (25 mL) at room temperature, followed by the addition of $POCl_3$ (7 g, 0.045 mol). The solution was then refluxed for 2 h, cooled in an ice bath, and quenched by adding water slowly. The quenched reaction mixture was then transferred to a separatory funnel containing 100 mL of ethyl acetate, washed with water, and dried, and the solvent was removed by rotary evaporator. The crude product was chromatographed on alumina, yielding 3.96 g (71.8%) of **3**, upon elution with 1:1 hexane:dichloromethane. The product was found to be pure (GC), but consisted of a mixture of *E*,*E* (87%), *Z*,*E* (11%), and *Z*,*Z* (2%) isomers: mp 117−119 °C; λ_{max} 270 nm, log ϵ 2.4; ^{1}H NMR δ 1.9 (dd, 6H), 6.1 (dq, 2H, J_{trans} 15.8), 6.4 (d, 2H, J_{trans} 15.8), 6.9 (d, 4H), 7.4 (d, 4H); ^{13}C NMR δ 18.4, 66.8, 118.8, 124.7, 126.9, 130.2, 131.2, 156.1; IR (C═C) 1590. LRMS *m/e* 250 (M^+), 207, 179, 165, 133, 115 (base), 91; HRMS *m/e* calcd for $C_{20}H_{22}O_2$ 250.1358, found 250.1369; E_p^{ox} 1.36 V (vs SCE).

General Procedure for the Polymerization of 3 Using $2^{\bullet+}$. The polymerizations were run at a monomer concentration of 0.2 M at 0 °C in dry dichloromethane under dry nitrogen. A catalytic amount of $2^{\bullet+}$ (usually 5 mol %) was added to the reaction mixture as a solid in one portion or as a solution in 1−5 mL of dry dichloromethane at 0 °C. The catalyst solution was added slowly over a period of 1−15 min, and the reaction was stirred for an additional 4−10 min. The polymerizations were quenched with a saturated solution of K_2CO_3 in MeOH, and an aqueous workup was performed by adding excess DCM and water and then filtering off any solid that remained. The organic solution was washed three times with water and dried over magnesium sulfate. The solvent was removed, and purification was accomplished using PTLC or column chromatograhy (9:1 hexane and dichloromethane). TLC was performed to verify the separation, and in some instances the oligomers, especially the higher ones, were not cleanly separated. Insoluble material was characterized by solid-state ^{13}C NMR. Soluble material was characterized by one or more of the following methods: room- and high-temperature ^{1}H and ^{13}C NMR, CIMS, TLC, and GPC.

Polymerization of 3 with No Added Base. To 0.990 g (3.96 mmol) of **3** in 8 mL of dry DCM was added 0.170 g (0.21 mmol) of $2^{\bullet+}$ dissolved in 5 mL of dry DCM over 15 min. After 10 min of additional reaction time, no further agitation was observed and the reaction was quenched (the blue-black color of the reaction mixture was slow to dissipate). After workup, 0.805 g (81.3%) of a tan solid was isolated and found to be insoluble in common solvents under any conditions, including diphenyl ether at 250 °C: solid state ^{13}C NMR δ 12, 20, 35, 43, 120, 130, 155.

Polymerization of 3 with Sodium Carbonate. To 0.501 g (2.00 mmol) of **3** in 8 mL of dry DCM was added 3.05 g (28.8 mmol) of Na_2CO_3 followed by the addition of 0.166 g (0.020 mmol) of $2^{\bullet+}$ for 2 min and quenched. After workup and column chromatography, 0.198 g (39.5%) of **3**, 0.078 g (15.6%) of dimer and low oligomers, and 0.090 g (18.0%) of high oligomers/polymer were isolated: ^{1}H NMR for polymer methyl groups δ 0.8 (acid catalysis), 1.1 (cation radical catalysis); the integrated signals gave an acid:CB linkage ration of 1:1; ^{13}C NMR for polymer methyl groups δ 13 (acid), 15.5 (*tst*), and 18.09 (*tat*); CIMS *m/e* 1250 (pentamer), 1002 (tetramer + 2 mass units), 751 (trimer + 1), 501 (dimer + 1), 250 (monomer).

Polymerization of 3 with 2,6-Di-*tert*-butylpyridine (DTBP). To 0.382 g (153 mmol) of **3** in 8 mL of dry DCM was added 0.177 g (0.93 mmol) of DTBP followed by the addition of 0.595 g (0.73 mmol) of $2^{\bullet+}$ dissolved in 5 mL of dry DCM over 1 min. The reaction was stirred for 15 min and quenched. After workup and PTLC, 0.208 g (52.4%) of **3**, 0.77 g (33.2%) of dimer and trimer, and 0.080 g (20.9%) of high oligomers/polymer were isolated. ^{1}H and ^{13}C NMR of the fraction assigned by TLC to be dimer/trimer gave no resonances for acid lingages: CIMS *m/e* 2000 octamer, 1750, 1500, 1250, 751, 501, 250.

Polymerization of 3 at Low Concentration. The polymerization of **3** was performed exactly as above with the exception that the concentration was 0.02 M lower. This resulted in the formation of the acid-catalyzed polymer as before, but the isolated material was soluble.

Acid-Catalyzed Polymerization of 5. To a solution of triflic acid (0.066 g, 8.7%) in 4 mL of dry DCM at 0 °C was added 1.057 g (5.03 mmol) of **5** in 8 mL of dry DCM. After 5 min, 10 mL of saturated aqueous $NaHCO_3$ was added along with 10 mL of additional DCM. The organic layer was isolated, washed with 20 mL of water, and dried to give 0.976 g (92% recovery) of solid. Hexane was used to wash the solid, and 0.140 g (13% yield) of insoluble material was isolated by vacuum filtration. Only the aliphatic resonances are reported: ^{1}H NMR δ 0.8 (methyl), 1.7 (methine), 2.1 (benzyl); ^{13}C NMR δ 13 (methyl), 34 (methine), 48 (benzyl).

PET Synthesis of the *trans,syn,trans*-Cyclobutane Dimer (7) of 3. To a dry Pyrex test tube was added 0.500 g (2.0 mmol) of **3**, 0.025 g (0.19 mmol) of dicyanobenzene, and 10 mL of dry DCM. The test tube was capped with a septum and the reaction irradiated with a medium-pressure mercury lamp for 24 h. The solvent was removed, and column chromatography was performed (9:1 hexane and DCM). The *trans,syn,trans*-cyclobutane dimer (0.200 g, 40% yield) and **2** (0.050 g, 10% recovery) were isolated with no higher oligomers observed. The assignment of the structure of the dimer is based on its similarity to the dimer of *trans*-anethole:[6] ^{1}H NMR δ 1.2 (d, 6H), 1.9 (d, 6H), 2.8 (d, 2H), 3.5 (d, 2H), 6.1 (m, 2H), 6.4 (d, 2H), 6.8 (m, 8H), 7.1 (m, 8H); ^{13}C NMR δ 15.1, 18.4, 34.2, 49.6, 117.7, 118.2, 118.8, 125.0, 126.2, 129.3, 130.1, 136.0, 156.5; LRMS *m/e* 498 (M − 2H), 444, 334, 250 (base), 117.

Preparation of 6 by the Dimerization of 5 Using Tris(4-bromophenyl)aminium Hexachloroantimonate ($2^{\bullet+}$). To 1.047 g (4.99 mmol) of **5** in 20 mL of dry DCM at 0 °C was added 0.204 g (0.25 mmol) of $2^{\bullet+}$ as a solid. After 5 min of stirring, the reaction was quenched with saturated K_2CO_3 in methanol. Excess water and DCM were added, and the organic layer was isolated. The organic solution was washed three times with water and dried. TLC analysis of the crude product mixture showed three spots identified as **5**, the cyclobutane dimer of **5** (**6**), and polymer. Column chromatography (9:1 hexane and DCM) allowed for the isolation of **5** and **6** as a mixture followed by PTLC (hexane) to separate **5** and **6**. After PTLC, 0.67 g (64% recovery) of **5**, 0.18 g (36% yield) of **6**, and 0.15 g (15% of recovered material) of polymer were isolated (95.5% mass balance). The assignment of the structure of the dimer is based on its similarity to the dimer of *trans*-anethole **5**. Only the aliphatic resonances are reported: ^{1}H NMR δ 1.2 (6H, d, trans,syn,trans (*tst*) and trans,anti,trans (*tat*) methyl), 1.88 (2H, m, *tst* benzyl); ^{13}C NMR of *tst* δ 15.2, 34, 49, *tat* δ 18.90, 43.3, 52.4.

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