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Cation Radical Polymerization. A Fundamentally New Polymerization Mechanism

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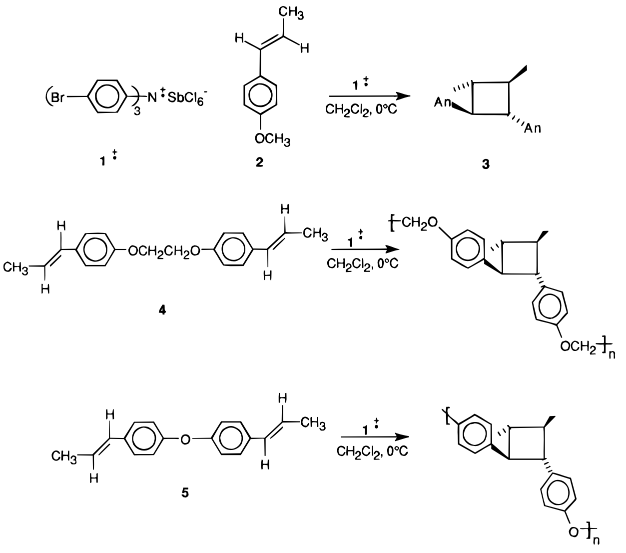
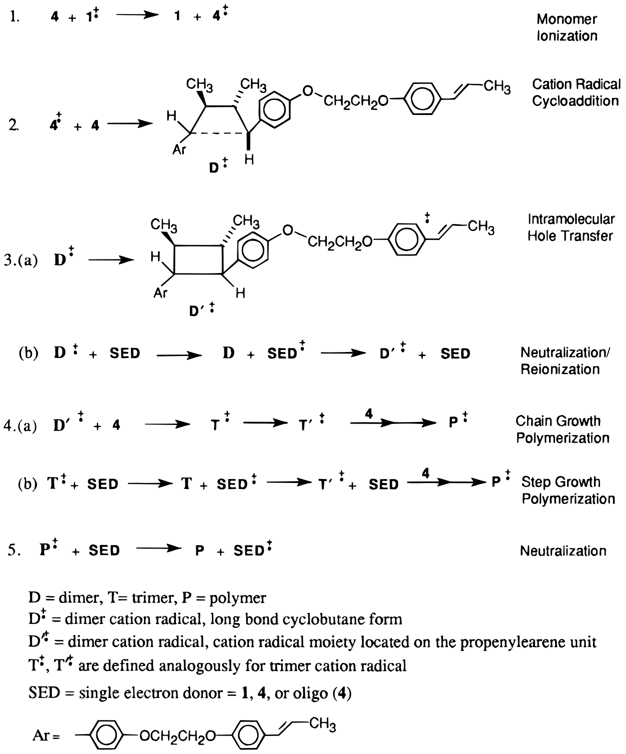
Cycloadditions of cation radicals to neutral molecules have been studied intensively in these laboratories and others for well over a decade.[1,2] The extension of this novel chemistry to a bifunctional context has now provided a fundamentally new mechanism for polymerization which involves cation radical intermediates at every catenation step.

In the presence of catalytic amounts of the stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate ($1^{\cdot+}$) in dichloromethane solvent at 0 °C, *trans*-anethole (**2**) is smoothly converted in less than 5 min to the cyclobutane dimer **3** (Scheme 1).[3] The same reaction can also be induced by photosensitized electron transfer, and in both contexts a mechanism involving the addition of $2^{\cdot+}$ to **2** has been supported.[4] To exploit this reaction type in a difunctional context, monomers **4** and **5** (Scheme 1) were prepared. The former is considered to be a very close analogue of **2**, while **5** is somewhat more loosely analogous. Treatment of **4** (200 mg) in dichloromethane at room temperature with 15 mol % of $1^{\cdot+}$ (80 mg) for 7 min followed by quenching with saturated K_2CO_3/CH_3OH solution and aqueous workup gave a solid (230 mg) which showed no traces of monomeric **4** (TLC, GC). The crude polymer was purified by alumina chromatography (9:1 hexanes: dichloromethane, followed by pure dichloromethane eluent), affording 136 mg (68%) of the pure poly(**4**). The ^1H and ^{13}C NMR spectra of the crude and pure polymers are virtually identical in the aliphatic region (neutral **1** is present in the crude). The high-temperature ^1H NMR spectrum (55 °C, $CDCl_3$) shows broadened absorptions at δ 1.1 (diagnostic for methyl attached to a cyclobutane ring), 1.7 (non-benzylic methine), 2.7 (benzylic methine), 4.1 (ether methylenes), and 6.8, 7.0 (aromatics), with weak propenyl end group absorptions at δ 1.8, 6.0, and 6.3. The high-temperature ^{13}C NMR spectrum (55 °C, $CDCl_3$) has absorptions at δ 18.8, 43.3, 52.5, 66.8, 114.6, 127.7, 136.2, and 157.0. The exceptionally close correspondence of both the ^1H and ^{13}C NMR spectra of poly(**4**) to those of the *trans*-anethole dimer (**3**) are especially noteworthy.[5] Molecular weight measurements on this polymer afford $M_w = 9400$ and a polydispersity index of 5.30.[6] When the reaction is carried out for 15 min, the molecular weight of the polymer increases to $M_w = 37\,000$ (polydispersity 7.31).

Scheme 1. Cation Radical Cyclobutapolymerizations



Scheme 2. Mechanism of Cation Radical Cycloaddition Polymerization of 4



D = dimer, T= trimer, P = polymer
$D^{\cdot+}$ = dimer cation radical, long bond cyclobutane form
$D'^{\cdot+}$ = dimer cation radical, cation radical moiety located on the propenylearene unit
$T^{\cdot+}$, $T'^{\cdot+}$ are defined analogously for trimer cation radical
SED = single electron donor = **1**, **4**, or oligo (**4**)

Extensive mechanistic studies will be required to clarify some of the finer mechanistic details of these polymerizations, but, based upon previous studies of the *trans*-anethole dimerization,[3,4] the gross mechanism shown in Scheme 2 is proposed. The first step, monomer ionization to afford the monomer cation radical, is only mildly endergonic [$E_{OX}(\mathbf{1}) = 1.05$ V; $E_P(\mathbf{4}) = 1.20$ V *vs* SCE] and suitable for initiation even at 0 °C. The second step is a cation radical/neutral cycloaddition (specifically, cyclobutanation), a reaction type which has been studied extensively in this and other laboratories.[3] The reaction is stereospecific and yields only the *trans,-anti,trans*-cyclobutane dimer shown. By analogy with the *trans*-anethole cyclodimerization, the initially formed dimer cation radical presumably has a "long bond" structure ($D^{\cdot+}$) in which both aryl groups symmetrically stabilize the cyclobutane cation radical. This cation radical is then converted to the more stable isomer $D'^{\cdot+}$) in which the cation radical site (the hole) migrates to the propenylarene moiety. This can occur both intramolecularly (step 3a), in a process which is entropically favored, or intermolecularly (step 3b), *via* hole transfer to neutral **1** (formed in the first step) or **4**, followed by re-ionization of the neutral dimer (**D**) by $1^{\cdot+}$. The preference for ionization at the propenylarene site is demonstrated by the observation of a much lower

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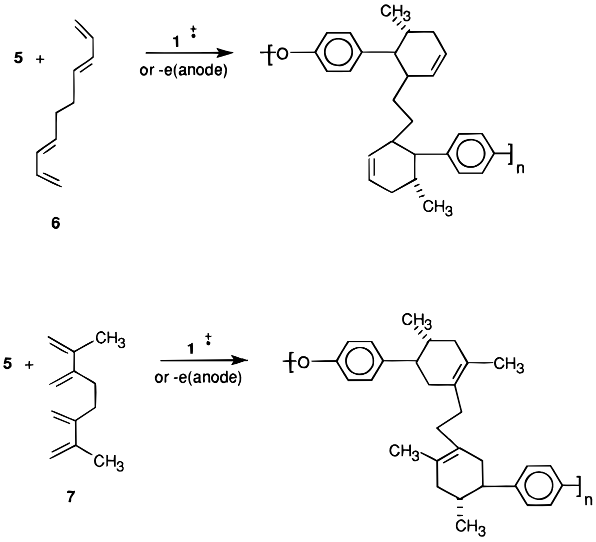
Scheme 3. Cation Radical Diels−Alder Copolymerizations



peak oxidation potential for **4** (1.20 V) than for the *trans*-anethole dimer (1.60 V). The postulated intramolecular hole transfer is thus substantially exergonic. Polymerization then continues by addition of $\mathbf{D}'^{\cdot+}$ to **4** to give a trimer cation radical $\mathbf{T}^{\cdot+}$. Depending upon whether hole transfer occurs intramolecularly or in a stepwise intermolecular process, polymerization occurs respectively *via* a chain or step growth process. In the present instance, it appears likely that a mixture of chain and step growth propagation is involved.

An especially attractive aspect of cation radical polymerization, from a commercial viewpoint, is that, at least in theory, either catalyst or monomer cation radicals can be generated electrochemically. Attempts to polymerize **4** and **5** by generating monomer cation radicals ($\mathbf{4}^{\cdot+}$ or $\mathbf{5}^{\cdot+}$) directly at a reticulated vitreous carbon anode in acetonitrile at electrode potentials appropriate to each monomer were unrewarding. Polymerization occurred to a very limited extent and then ceased rather abruptly, possibly because of formation of a polymer coating on the anode. However, both **4** and **5** are smoothly oligomerized when the aminium ion catalyst was generated by anodic oxidation of **1** at its oxidation potential (1.06 V *vs* SCE) in the presence of **4** or **5**.[7] More specifically, when **4** (50 mg, 0.17 mmol), **1** (8 mg, 0.02 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (10 mg, 0.05 mmol) were dissolved in $CH_3CN:CH_2Cl_2$ (1:3, 15 mL) containing lithium perchlorate electrolyte and the solution was electrolyzed (16.4 C), 33 mg (68%) of the purified oligomer ($M_w = 3300$) was isolated. The ^{1}H and ^{13}C spectra of this oligomer are essentially identical to those observed when the preformed catalyst ($\mathbf{1}^{\cdot+}$) was used. It may be noted that the hindered base was used to preclude any acid-catalyzed reactions.[8] Similar results were obtained for **5** (70% yield of purified oligomer, $M_w = 1600$).

The previously described homopolymerizations of **4** and **5** involve cation radical cyclobutanation. This research group has been especially involved with the development of another cation radical cycloaddition reaction—the cation radical Diels−Alder reaction—in a monofunctional context.[1,2] This latter reaction has now also been extended to a difunctional context. Specifically, Diels−Alder polymerizations of **4** and **5** with bis(dienes), i.e. tetraenes, **6** and **7** have been carried out (Scheme 3). For example, an 82% yield (124 mg) of purified Diels−Alder copoly(**5**,**6**) having $M_w = 10\,800$ was obtained when 100 mg (0.40 mmol) of **5** and 60 mg (0.44 mmol) of **6** in methylene chloride (3 mL) was treated dropwise over 10 min with 98 mg of $\mathbf{1}^{\cdot+}$ in methylene chloride (2 mL) at 0 °C for a total reaction time of 20 min, followed by a conventional two-phase aqueous workup and alumina chromatography (pentane, then dichloromethane). The ^{1}H NMR spectrum of this polymer is virtually superimposable on the corresponding spectrum of the model mono Diels−Alder adduct of tetraene **6** with a monofunctional analogue of **5**, i.e. *trans*-**4**-propenylphenyl phenyl ether. Salient features of these spectra are the two cyclohexene protons (δ 4.9 and 5.05, respectively), methyl protons (δ 0.9), benzylic protons (δ 2.7), non-benzylic methines (δ 1.7), and allylic protons (δ 2.0−2.2). Similarly, a 75% yield of purified Diels−Alder copoly(**5**,**7**) of $M_w = 4000$ was obtained when a 1.1:1 mixture of **7**:**5** was polymerized in the same manner.

The scope of cation radical polymerization appears likely to be very substantial. A variety of cation radical pericyclic reaction types can potentially be applied, including cyclobutanation, Diels−Alder addition, and cyclopropanation. The monomers which are most effectively employed in the cation radical context are diverse and distinct from those which dominate the standard polymerization methods (i.e. vinyl monomers). Consequently, the resulting polymers are structurally distinct from those available by conventional methods, although the M_w's observed thus far are modest. Future work in this area will pursue the possibility of cation radical Diels−Alder homopolymerization and also copolymerization *via* cation radical cyclopropanation. The fundamental mechanistic issue of whether these reactions proceed *via* a chain or catalytic mechanism will also be addressed.

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References and Notes

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(5) The ^{1}H NMR spectrum of **3** has absorptions at δ 1.15, 1.6−2.0, 2.77, 3.7, and 6.7−7.2; the ^{13}C NMR absorptions occur at δ 18.9, 43.3, 52.7, 55.2, 113.8, 127.8, 136.0, and 158.1.

(6) GPC traces were recorded on a Waters Model 510 HPLC with two PLgel 10μ MIXED-B columns (Polymer Laboratories). The GPC working conditions were as follows: injection 50 μL; THF flow rate, 1.0 mL/min. The molecular weights of the samples were determined by the peak position of the GPC elution, based on a polystyrene standard. The calibration curve was obtained from the GPC traces of a series of linear polystyrene standards with the following mlecular weights: 2.0×10^6, 6.7×10^5, 3.9×10^5, 2.0×10^5, 5.37×10^4, 3.5×10^4, 2.04×10^4, 7.5×10^3, 4.0×10^3, 2.0×10^3, 517. The width of the molecular weight distribution was measured by the half peak height. We wish to thank Professors Stephen Webber and Grant Willson for the use of their equipment and Drs. Cao Ti and Qin Anwei for their assistance in making these mesurements.

(7) Electrochemical polymerizations were carried out using an ESC Potentiostat 415, 640 Digital Coulometer, and a 420X power supply. A divided electrochemical cell (25 mL) having a reticulated vitreous carbon working electrode and counter electrode and a Ag/Ag$^+$ reference electrode was used. A lithium perchlorate electrolyte was dissolved in a 1:3 acetonitrile:methylene chloride solvent mixure. Electrolysis was carried out at 1.06V *vs* SCE, the oxidation potential of **1**.

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