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Cation radical chain cycloaddition polymerization: a fundamentally new polymerization mechanism

Nathan L. Bauld,* Daxin Gao and J. Todd Aplin

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

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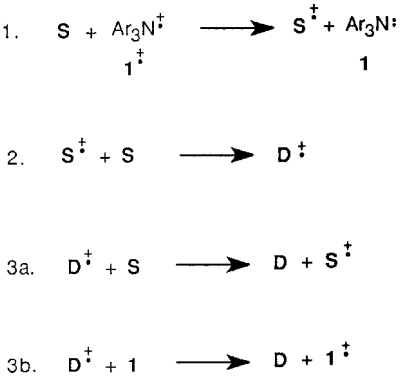
ABSTRACT: Cation radical chain cycloaddition polymerization, a fundamentally new addition polymerization method involving cation radical intermediates in each propagation step, is described and demonstrated. The cycloaddition reactions of appropriately constituted difunctional monomers, catalyzed by tris(4-bromophenyl)aminium hexachloroantimonate in dichloromethane solvent at 0 °C, is shown to afford polymers having average molecular weights of up to 150 000. Both cyclobutanation and Diels–Alder polymers were obtained in this way. The surprising efficiency of these polymerization reactions is believed to be the result of rapid intramolecular hole transfer from the site at which the hole is originally generated in the cycloaddition step to a reactive, terminal alkene moiety. Consequently, chain propagation is much more efficient than in the cycloadditions of corresponding monofunctional compounds, which necessarily involve intermolecular hole transfer. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: cation radical chain cycloaddition polymerization; intramolecular hole transfer; chain propagation

INTRODUCTION

Cation radical cycloaddition reactions potentially can occur via either a catalytic or chain mechanism (Scheme 1). [1] In the specific context of an aminium salt-induced cycloaddition, the substrate molecule (S) is ionized to the corresponding cation radical by intermolecular hole transfer from the aminium salt. The substrate cation radical then cycloadds to a molecule of neutral substrate to yield a cyclodimer cation radical, which then must be neutralized by hole transfer to an appropriate neutral molecule. If the single electron donor is the neutral triarylamine, which is formed in the first step and also by decomposition of the aminium salt,[2] the aminium salt catalyst is regenerated, resulting in a true *catalytic mechanism*. If, on the other hand, the hole transfer is to neutral S as the single electron donor, the cation radical of the substrate is generated and the resulting mechanism is a *cation radical chain mechanism*.

In the context of cation radical cycloadditions of difunctional molecules (Scheme 2), addition polymerization is at least a formal possibility. A key requirement for polymerization is the transfer of the hole, either directly or indirectly, from the site at which it is initially formed in the cycloaddition reaction (which in the example illustrated in Scheme 2 is the cyclobutane ring) to a reactive terminal alkene site. The operation of a catalytic mechanism in the context of the cation radical polymerization of a bifunctional molecule then necessarily



S = ionizable substrate; $S^{\bullet+}$ = substrate cation radical

D = cyclodimer; $D^{\bullet+}$ = cyclodimer cation radical

Chain Mechanism: Step 1 (initiation), steps 2, 3a (propagation)

Catalytic Mechanism: Steps 1,2,3b

Scheme 1. Chain vs catalytic mechanisms of cation radical cycloadditions

**Correspondence to:* N. L. Bauld, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, USA.
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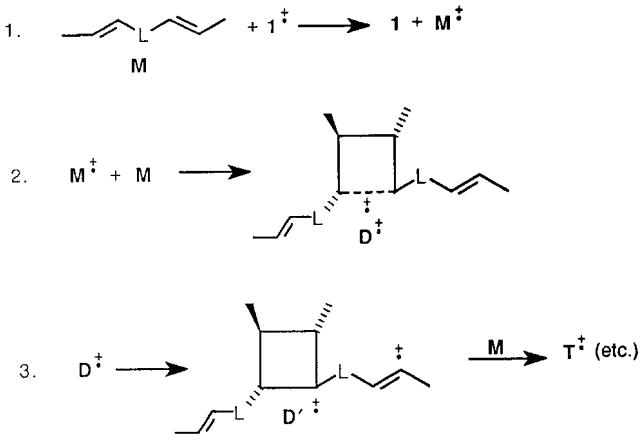
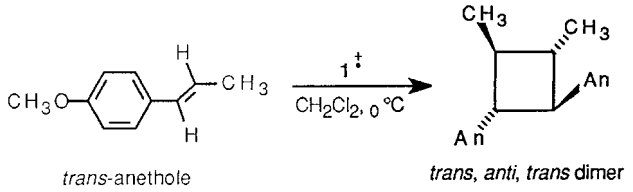


Scheme 2. Cation radical cyclobutanation polymerization

involves a step growth polymerization process (Scheme 3). This follows because, in this mechanism, the dimer cation radical is always neutralized by the triarylamine to the corresponding neutral dimer, and therefore further oligomerization and polymerization must involve the successive re-ionization of the dimer and each higher oligomer, in turn, by the aminium salt. Given the yields in typical cycloaddition reactions of monofunctional substrates (ca 30–80%),[3] and the stringent requirements upon the yields in the individual (consecutive) reactions of an efficient step growth polymerization,[4] the prospects for efficient *catalytic* cation radical cycloaddition polymerization would not appear to be encouraging. Even in the case of a cation radical chain mechanism, one of the two possible scenarios also leads to a relatively undesirable step growth mechanism (Scheme 3). Thus, if the dimer cation radical $D^{+\cdot}$ is neutralized by hole transfer to the monomer prior to intramolecular hole transfer, a step growth process once again results. However, if intramolecular hole transfer to give $D'^{+\cdot}$ is faster than intermolecular hole transfer to the monomer, a chain polymerization process can be the result. Since,

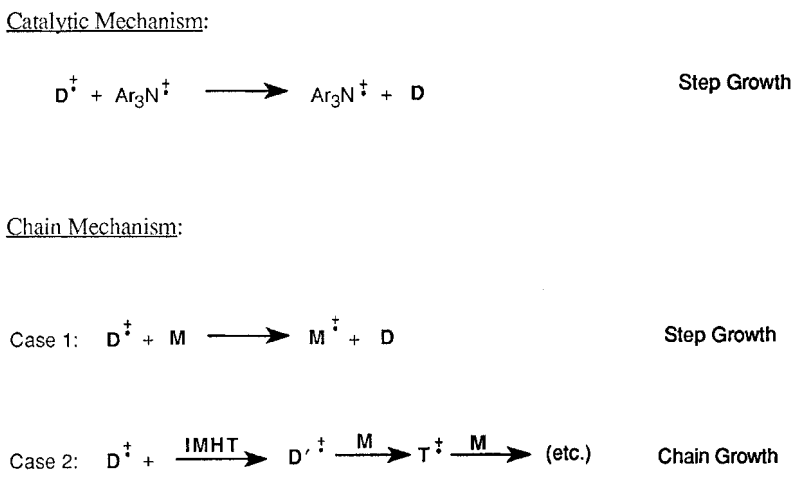


Scheme 4. Cation radical cyclobutadimerization of *trans*-anethole

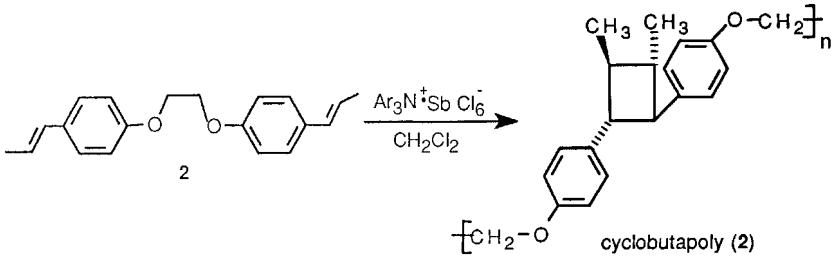
given appropriate linkers and a sufficiently exergonic hole transfer, intramolecular hole transfer can be exceptionally rapid, it appears not unreasonable to postulate an intrinsic advantage for cation radical chain polymerization over cation radical cycloadditions of corresponding neutral monofunctional molecules, based upon the advantage of intramolecular hole transfer over intermolecular hole transfer. Consequently, the possibility of relatively efficient cation radical chain polymerization was considered a realistic one in spite of the modest efficiency of most aminium salt-induced cation radical cycloadditions.

RESULTS AND DISCUSSION

Cyclobutanation was selected as the specific cycloaddition type for initial, exploratory studies, especially since this cycloaddition mode requires only a single, symmetrical difunctional monomer. Further, since the cyclobutadimerization of *trans*-anethole has been studied fairly extensively,[2,5,6] this reaction was chosen as a monofunctional model for these studies (Scheme 4). Monomer **2** (Scheme 5) was therefore selected as an appropriately close difunctional analogue of *trans*-anethole. In fact, **2** has an oxidation potential which is essentially identical with that of *trans*-anethole (both have peak potentials at 1.23V vs SCE[7]). The synthesis of **2** from commercially

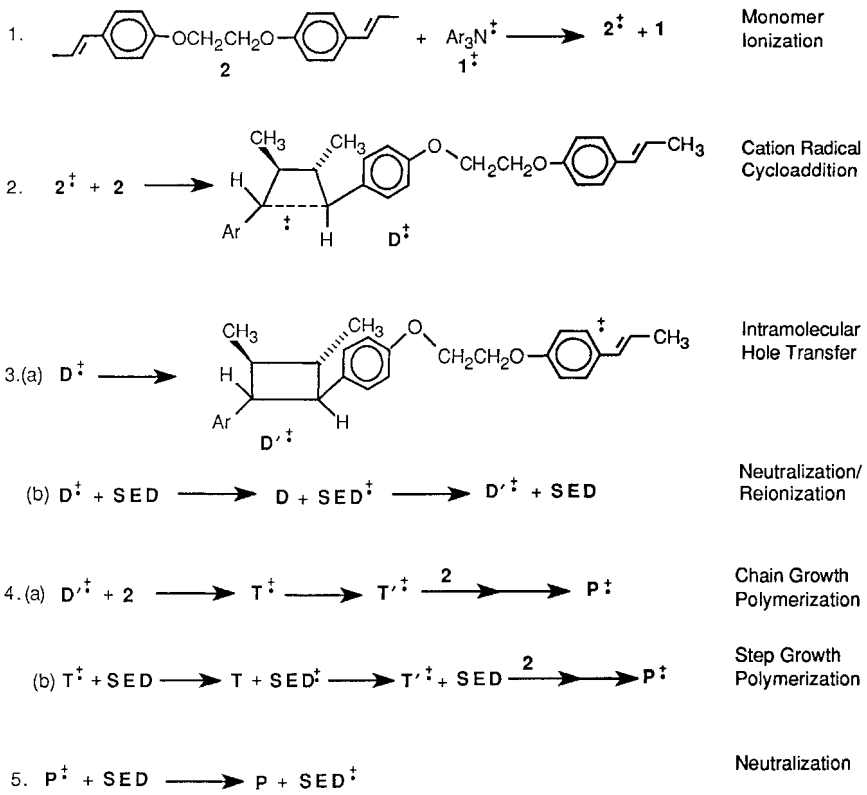


Scheme 3. Chain growth vs step growth polymerization

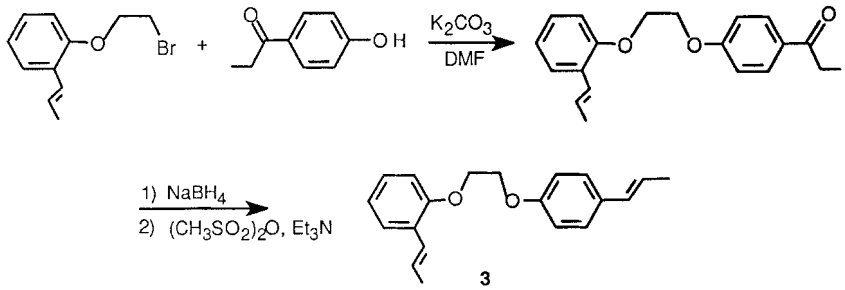


Scheme 5. A cation radical chain cyclobutanation polymerization

available 1,2-diphenoxyethane via propionylation, reduction and dehydration is straightforward. The polymerization of **2** in saturated dichloromethane solution (0.056 M) at ambient temperature (the low solubility of **2** at 0 °C was problematic) in the presence of 15 mol% of tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\cdot}$) proceeded fairly smoothly to the desired cyclobutapolymer (a preliminary report on the cyclobutapolymerization of **2** has already appeared[8]). After a reaction time of 7 min, the monomer had been completely consumed and the resulting polymer had $M_w = 9400$ [polydispersity index (PDI) = 5.30]. The crude polymer was subsequently purified by chromatography on alumina, but the NMR spectra of the crude and purified polymers were essentially identical except for the presence of the spent catalyst (the neutral triarylamine)



Scheme 6. Mechanism of cation radical cycloaddition polymerization of **2**

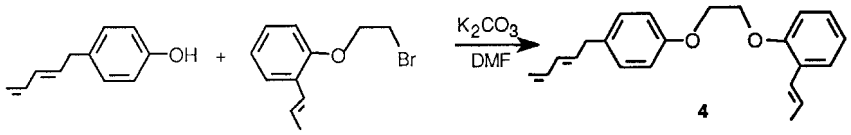


Scheme 7. Synthesis of a more soluble monomer

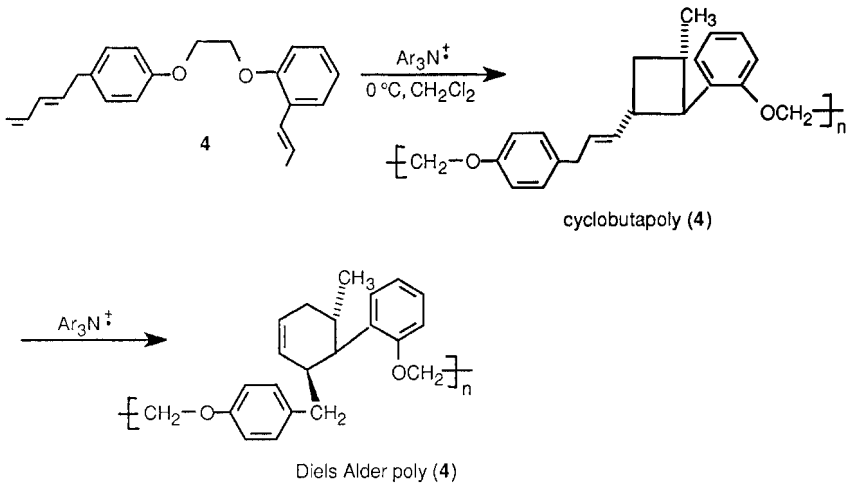
in the crude polymer. The ^{1}H NMR spectrum of the polymer (55 °C, $CDCl_3$) shows broadened absorptions at δ 1.1 (diagnostic for methyl attached to a cyclobutane ring), 1.7 (the non-benzylic methine), 2.7 (the benzylic methine), 4.1 (the ether methylenes) and 6.8,7.0 (aromatic protons), corresponding closely to the absorptions of the *trans,anti,trans*-cyclobutadimer of *trans*-anethole. In addition, weak propenyl end-group absorptions are found at δ 1.8, 6.0 and 6.3. The ^{13}C NMR spectrum under the same conditions has absorptions at δ 18.8, 43.3, 52.5, 66.8, 114.6, 127.7, 136.2 and 157.0, again corresponding very closely to those of the *trans,anti,trans*-cyclobutadimer of *trans*-anethole. When the reaction of **2** is carried out for a longer time (10 min), the polymer has M_w = 37 000 (PDI = 7.31), and the ^{1}H and ^{13}C NMR spectra are closely comparable to those of the lower molecular weight polymer and the *trans*-anethole cyclobutadimer. In addition to the absorption in the ^{1}H NMR at δ 1.1, corresponding to the methyl groups attached to a cyclobutane ring, a much weaker absorption at 0.7–0.9 was also observed, corresponding to methyl groups attached to either acyclic carbons or to a cyclohexane ring. This absorption amounted to no more than 10–15% of the δ 1.1 absorption and was observed, at least to some extent, even when the polymerizations were run in the presence of sodium carbonate or di-*tert*-butylpyridine. Conceivably this could correspond in part to the competing production of some acyclic polymer resulting from acid-catalyzed, carbocation-mediated polymerization or from cationic block polymerization of the termini of the cation radical polymer. However, the fact that the absorptions were found even under basic conditions suggests that, at least in part, these absorptions could be the result of extraneous substances introduced during workup and handling.

The proposed mechanism for the cation radical chain cyclobutapolymerization of **2** induced by the triarylaminium salt $\mathbf{1}^{+\cdot}$ (Scheme 6) is based upon the known mechanism of the *trans*-anethole dimerization and the theoretical considerations discussed in the introduction. In particular, the intramolecular hole transfer shown in step 3(a) should be strongly exergonic, given the difference in the oxidation potentials of the *trans*-anethole dimer (ca 1.6 V9) and *trans*-anethole (1.23 V). Whether the hole transfer from the long bond of the initially formed diarylcyclobutane cation radical to the *trans*-anethole-like terminal site occurs via bonds or through space is not yet clear, but efficient transmission via the ethylenedioxy linkage is by no means implausible. That the cation radical cyclobutapolymerization of **2** is a chain growth process is strongly suggested by the theoretical arguments developed in the introduction, and is further supported by experimental observations. First, the observed polydispersity indices are much higher than the theoretical maximum of 2.0 for a step growth process.[10] Further, studies of the molecular weights of the polymers generated at early reaction times, i.e. under conditions where the monomer is only partially consumed, yield molecular weights which are very much larger than those predicted for a step growth process. Specifically, the M_w in a step growth process is proportional to the monomer molecular weight and to the quantity $(1 + p)/(1 - p)$, where p is the fraction of the monomer which has been consumed.[10] In the case where p = 0.82, the molecular weight of the polymer generated from **2** (which has a molecular weight of 294)) via a step growth process should be 2973, whereas that actually observed was 15 300. Similarly, the predicted molecular weight in the case where p = 0.5 is only 882 (average trimer), whereas an average molecular weight of 5000 was observed experimentally. It is important to note that the efficiency of these polymerizations varies from batch to batch of the initiator and with monomer purity. In comparison experiments, it is therefore essential to run side-by-side experiments.

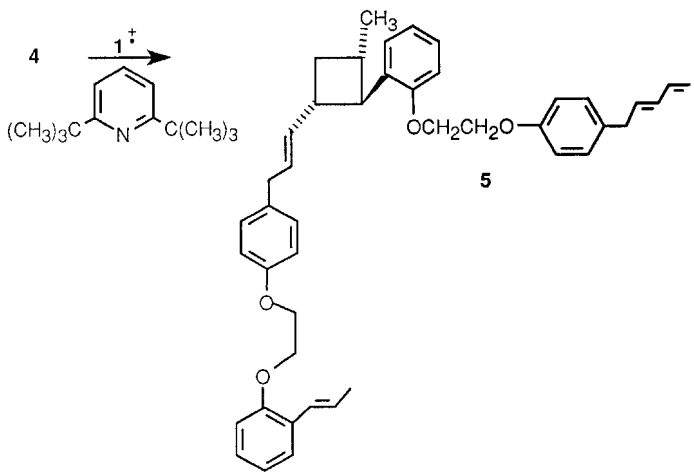
A limiting factor in the case of the cyclobutapolymerization of **2** is its relatively low solubility in dichloromethane at 0 °C (ca 0.05 M). In order to increase the degree of polymerization, an appropriate monomer was sought which would permit polymerization at substantially higher initial monomer concentrations. An unsymmetrical version of monomer **2**, having one propenyl group in an *ortho* position and one in the *para* position of the other ring, was therefore synthesized (monomer **3;** Scheme 7). The polymerization of monomer **3** in the presence of 10 mol% of $\mathbf{1}^{+\cdot}$ at a concentration of 0.192 M for 8 min yielded a cyclobutapolymer having M_w = 86 700 (PDI = 1.84), i.e. roughly twice the average molecular weight obtainable from the polymerization of monomer **2** using 15 mol% of $\mathbf{1}^{+\cdot}$. The cyclobutapolymer



Scheme 8. Synthesis of the Diels–Alder monomer **4**



Scheme 9. Polymerization of monomer **4**

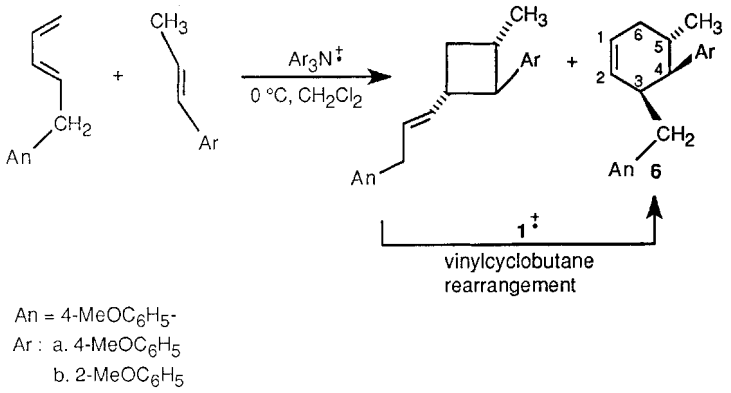


Scheme 10. Cyclobutadimerization/oligomerization of monomer **4**

structure was again readily confirmed by proton NMR and COSY spectra.

Indirect Diels–Alder polymerization

Diels–Alder cycloadditions to s-*cis* conjugated dienes are also a well known reaction of cation radicals such as that of *trans*-anethole.[1,3] In the case of an acyclic diene such as 1,3-pentadiene, the predominant conformation of the conjugated diene linkage is s-*trans*, so that addition initially occurs at least in part to yield a vinylcyclobutane adduct.[11] However, the latter typically rearranges rapidly via a cation radical vinylcyclobutane rearrangement to the cyclohexene product,[12] which can therefore be considered the result of an indirect Diels–Alder reaction. Further, cyclobutanation of a 1,3-pentadiene moiety would involve a sterically unhindered (i.e. unsubstituted) diene terminus, and therefore should proceed relatively rapidly in comparison with addition to a terminal propenyl moiety such as was involved in the case of monomers **2** and **3**. The monomer **4**, which should exhibit analogous chemistry to that observed for 1,3-pentadiene and anisole, was therefore prepared (Scheme 8). The polymerization of **4** in dichloromethane solution (0.31 M) at 0 °C in the presence of 10 mol% of $\mathbf{1}^{+\cdot}$ proceeded efficiently, yielding a polymer of weight average molecular weight 59 000 after 10 min (Scheme 9). When the



Scheme 11. Cation radical cycloaddition of *trans*-anethole and *ortho*-anethole to 4-*trans*-(2,4-pentadienyl)anisole

initial monomer concentration was increased to 0.37 M, the molecular weight increased to 153 000.

To characterize the polymer structure and to obtain information about the relative amounts of cyclobutane and Diels–Alder linkages in the polymer, model compounds for both types of polymer linkage were prepared. First, a mixture of the cyclobutadimer (**5**) of **4**, along with the trimer, tetramer and lower cyclobutaoligomers, was prepared by reacting **4** with $\mathbf{1}^{+\cdot}$ in the presence of excess 2,6-di(*tert*-butyl)pyridine (Scheme 10).[13] Interestingly, no Diels–Alder adducts were noted in the products of this reaction, and it therefore appears that the initial addition of the cation radical of **4** to neutral **4** occurs predominantly via the cyclobutanation mode. Second, the model reaction of 5-anisyl-*trans*-1,3-pentadiene with *trans*-anethole in the presence of $\mathbf{1}^{+\cdot}$ was studied (Scheme 11). Although not a perfect model of the propenyl function of **4**, which is *ortho* to the oxygen function, *trans*-anethole is a readily available compound the cycloadditions of which to various conjugated dienes had already been studied. This reaction, at very short reaction times (very low conversions), led to a mixture of vinylcyclobutane and Diels–Alder adducts, as indicated by GC–MS, but the conversion of the former to the latter was fairly rapid. As a consequence, only the Diels–Alder adduct could be isolated in pure form, and this was apparently a single diastereoisomer (**6a**), that corresponding to the *endo* addition mode. Comparison of the 500 MHz ^{1}H NMR spectrum of the polymer with those of the vinylcyclobutane and Diels–Alder model compounds then revealed that the polymer does consist of a mixture of these two linkages (>4:1 Diels–Alder: cyclobutane), but the relative amount of cyclobutane linkages is substantial even at relatively high degrees of polymerization.

The disparity between the amount of vinylcyclobutane rearrangement in the polymer and in the model reaction with *trans*-anethole appeared significant, and prompted the study of a model reaction which more closely parallels the polymerization of **4**, viz. the reaction of *o*-propenyl anisole with 5-anisyl-1,3-pentadiene. This reaction, in fact, generated a product distribution very similar to that observed in the polymer, with cyclobutane linkages being formed almost exclusively initally and persisting in substantial amounts even to high conversions. Comparison of the proton NMR spectra of this latter mixture of vinylcyclobutane and Diels–Alder adducts with that of the polymer provided clear confirmation of the structure of poly(**4**) as a mixture of these two cycloaddition modes. The percentage of acid-catalyzed (linear) polymer linkages is negligible. As would be expected, the propenyl and pentadienyl end-group absorptions observed in the polymer are comparable to each other in amount. At low degrees of polymerization, the cyclobutane linkages were strongly predominant, but as the polymerization proceeded to higher molecular weights, the percentage of Diels–Alder linkages increased markedly. In the presence of a relatively large amount of the aminium salt catalyst (30 mol%), the cyclobutane linkages of the polymer could be rearranged to a predominantly Diels–Alder structure. Further, the spectra of the crude polymers (from polymerizations carried out to various molecular weights), were virtually superimposable upon those of purified polymers (chromatography) and closely corresponded to (were virtually superimposable upon) the spectra of the cycloadduct mixtures obtained in the more appropriate model reaction.

CONCLUSION

A fundamentally new polymerization method, cation radical chain cycloaddition polymerization, has been proposed and demonstrated. Polymers having average molecular weights of up to 150 000 have been obtained under exceptionally mild thermal conditions and in short reaction times. Both cyclobutapolymerization and indirect Diels–Alder polymerization have been demonstrated. The enhanced efficiency of cation radical chain polymerization as compared with the corresponding reactions of monofunctional compounds appears to be based upon

the efficiency of intramolecular hole transfer, which is unique to the polymerization process, relative to intermolecular hole transfer, which is involved in the corresponding monofunctional chemistry.

EXPERIMENTAL

Analysis. Routine ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC250 spectrometer as solutions in $CDCl_3$. High-field ^{1}H NMR spectra were recorded on a General Electric GN-500 spectrometer. Chemical shifts (δ) are reported in parts per million downfield from a tetramethylsilane reference, and coupling constants (J) are given in Hz. Low-resolution mass spectrometry (LRMS) was performed with a Hewlett-Packard Model 5971A GC–MS system equipped with a DB-1 capillary column (15 m × 0.25 mm i.d.). High-resolution mass spectrometry (HRMS) was carried out on a Dupont (CEC) 21-110B mass spectrometer. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran using a Waters Model 550 HPLC pump, a Waters Model 410 differential refractometer, and a Waters Model 745 data module with an Ultrastyragel 500 Å column connected in series with a Styragel 10^4 Å column. The GPC analyses were calibrated with polystyrene standards.

Solvents, catalyst and reagents. Reagent-grade dichloromethane was distilled from phosphorus pentoxide immediately prior to use. Tris(4-bromophenyl)aminium hexachloroantimonate was used as received from Aldrich. All other reagents used as starting materials were used as received from Aldrich.

Synthesis of Monomer 2. 1,2-Diphenoxyethane (Aldrich) was first subjected to bis(propionylation by a literature procedure.[14] From 15 g of 1,2-diphenoxyethane was obtained 21 g (94%) of 1,2-bis(4-propionylphenoxy)ethane (99% purity by GC): m.p. 112–114 °C; ^{1}H NMR, δ 1.2 (t, 6H), 2.9 (q, 4H), 4.4 (s, 4H), 6.94 (d, 4H), 7.93 (d, 4H); ^{13}C NMR, δ 8.3, 31.4, 66.4, 114.2, 130.2, 133.1, 162.1, 199.4; IR (C═O), 1687; LRMS, *m/z* 326 (M^+), 297, 241, 207, 177, 134, 121 (base). Reduction of this diketone (16.7 g) with sodium borohydride (2:1 molar ratio of hydride to diketone) in a 3:1 solution of ethanol and tetrahydrofuran for 1 h at room temperature, followed by quenching of the reaction at 0 °C with acetic acid (10%) and extraction with dichloromethane, yielded 19 g of the corresponding diol, 1,2-bis [4-(1-hydroxy-1-propyl)phenoxy]ethane, which was used without further purification: m.p. 71–72 °C; ^{1}H NMR, δ 0.8 (t,6H), 1.6–1.8 (m,4H), 1.8 (br s,2H), 4.2 (s,4H), 4.4 (t,2H), 6.8 (d, 4H), 7.2 (d,4H); ^{13}C NMR, δ 10.1,31.7, 66.5,72.1,114.5, 127.2,137.2, 158.0; IR(OH), 3360. Monomer **2** was prepared by the dehydration of the preceding diol: to 6.6 g (0.02 mol) of the diol dissolved in pyridine (25 ml) was added a slight excess (7.0 g, 0.045 mol) of phosphorus oxychloride at room temperature and the solution was refluxed for 1.5 h. After cooling the reaction mixture in an ice bath, water was added slowly, followed by dichloromethane solvent. The crude monomer **2** was obtained by separation of the dichloromethane layer, washing it with water and drying and evaporating the solvent. Column chromatography on alumina (1:1 hexane–dichloromethane) gave 2.48 g (42.4%) of **2**, which was found to be at least 98% pure by GC criteria: m.p. 175–176 °C; ^{1}H NMR, δ 1.8 (dd, 6H), 4.3 (s,4H), 6.1 (dq, 2H, J = 15.8 Hz), 6.3 (d,2H, J = 15.8 Hz), 6.8 (d, 4H), 7.3 (d, 4H); ^{13}C NMR, δ 8.4, 66.6, 114.7, 124.0, 126.9, 130.2, 131.2, 157.1; LRMS, *m/z* 294 (M^+), 164, 133 (base); HRMS, *m/z* calculated for $C_{20}H_{22}O_2$ 294.1619, found 294.1613; E_p = 1.23 V vs SCE.

Polymerization of 2. To a solution of **2** (200 mg, 0.68 mmol) in dry dichloromethane (12 ml) at room temperature under a nitrogen atmosphere, 80 mg (0.1 mmol) of $\mathbf{1}^{+\cdot}$ were added, with stirring. After 7 min the reaction mixture was quenched with an excess of saturated potassium carbonate in methanol. The organic layer was washed with water (3 × 10 ml), dried and the solvent removed to give 230 mg of the polymer. GC analysis of the crude product revealed the absence of any of the starting monomer. The crude polymer was subjected to column chromatography on alumina. The column was first eluted with 9:1 hexane–dichloromethane to remove the neutral triarylamine (**1**), then with dichloromethane to elute the polymer. The NMR specrum of the polymer (see below) was essentially identical before and after chromatographic purification, except for the aromatic absorptions arising from the presence of **1** in the crude material. The weight-average molecular weight (M_w) of this polymer was found (GPC) to be 9460, with a PDI of 5.30. When the same polymerization reaction was carried out in the presence of excess powdered potassium carbonate for either 10 or 30 min to minimize any acid-catalyzed side reactions, the NMR of the polymer was again identical with that obtained in the absence of potassium carbonate. In this case, however, the M_w was lowered to 3700, with PDI = 3.0.

When the polymerization of **2** is carried out under the same conditions as described above, but the reaction is allowed to run for 10 min, the M_w is found to increase to 37 000 (PDI = 7.31). The NMR spectra of this higher molecular weight polymer is virtually identical with those of the two lower molecular weight polymers described above: ^{1}H NMR (55 °C, $CDCl_3$), δ 1.1 (br s, methyl attached to the cyclobutane ring), 1.7 (br s, non-benzylic methine), 2.6 (br s, benzylic methine), 4.1 (br s, ether methylenes), 6.6–7.2 (br, aromatics); ^{13}C NMR (55 °C, $CDCl_3$), δ 18.8 (methyl group attached to CB ring), 43.3 (non-benzylic CB carbon), 52.5 (benzylic CB carbon), 66.8 (ether carbons), 114.8, 127.7, 136.4, 157.2.

1-(2-Bromoethoxy)-2-(2-propenyl)benzene. A mixture of 2-allylphenol (10.05 g, 0.075 mol), 1,2-dibromoethane (28.5 g, 0.15 mol), and potassium carbonate (12.42 g, 0.09 mol) in *N*,*N*-dimethylformamide (25 ml) was stirred at room temperature for 48 h and then subjected to aqueous workup. Column chromatography on silica gel (13:1 hexane–ethyl acetate) afforded the pure product (14 g, 77.5%): ^{1}H NMR ($CDCl_3$, 250 MHz), δ 3.42 (d, 2H, J = 6.67 Hz), 3.68 (t, 2H, J = 6.11 Hz), 4.31 (t, 2H, J = 6.11 Hz), 5.06 (dd, 2H, J = 15.2, 9.51 Hz), 6.0 (m, 1H), 6.82 (d, 1H, J = 8.2 Hz), 6.98 (d, 1H, J = 7.32 Hz), 7.18 (d, 2H, J = 7.2 Hz); LRMS, *m/z* 242 (M + 1); HRMS, *m/z* calculated for $C_{11}H_{13}OBr$ 241.022801, found 241.022823.

1-(2-Bromoethoxy)-2-(trans-1-propenyl)benzene. A catalytic amount of $PdCl_2$ was added to 50 ml of dichloromethane, followed by the addition of 30 drops of acetonitrile. After stirring this mixture for 5 min, 14 g (0.058 mol) of 1-(2-bromoethoxy)-2-(2-propenyl)benzene were added and the solution was stirred for 40 h at room temperature. After aqueous workup, the product was chromatographed (silica gel column, hexane eluent), yielding 14 g (100%) of the pure product: ^{1}H NMR ($CDCl_3$, 250 MHz), δ 1.9 (dd, 3H, J = 6.58, 1.67 Hz), 3.68 (t, 2H, J = 6.28 Hz), 4.3 (t, 2H, J = 6.27 Hz), 6.26 (m, 1H), 6.75 (d, 1H, J = 14.6 Hz), 6.8–7.4 (m, 4H); LRMS, *m/z* 242 (M + 1); HRMS, calculated for $C_{11}H_{13}OBr$ 241.022801, found 241.022461.

Synthesis of monomer 3. A solution of 4′-hydroxypropiophenone (Aldrich) (4.5 g, 0.03 mol), 1-(2-bromoethoxy)-2-(*trans*-1-propenyl)benzene (this paper; 4.82 g, 0.02 mol) and potassium carbonate (4.14 g, 0.03 mol) in *N*,*N*-dimethylformamide solution (80 ml) was stirred at room temperature for 24 h and then subjected to aqueous workup and silica gel chromatography (100:15 hexane–ethyl acetate) to yield the pure product, 1-[2′-(*trans*-1″-propenyl)phenoxy]-2-[4′-(1″-propionyl)phenoxy]ethane (3.2 g, 51%): m.p. 82–83 °C; ^{1}H NMR (deuteroacetone, 250 MHz), δ 1.12 (t, 3H, J = 7.23 Hz), 1.78 (d, 3H, 6.61 Hz), 2.98 (q, 2H, J = 7.25 Hz), 4.40 (t, 2H, J = 4.37 Hz), 4.51 (t, 2H, J = 4.46 Hz), 6.25 (m, 1H), 6.68 (d, 1H, J = 16.78), 6.88–8.00 (m, 8H); ^{13}C NMR (deuteroacetone, 250 MHz), δ 8.2, 19.5, 31.7, 67.8, 68.0, 113.8, 115.2, 122.0, 126.2, 126.5, 128.0, 128.2, 130.9, 131.2, 156.2, 163.0, 199.0; LRMS, *m/z* 311 (M + 1); HRMS, *m/z* calculated for $C_{20}H_{23}O_3$ 311.164720, found 311.165234.

All of this purified product (3.2 g, 0.01 mol) was reduced with sodium borohydride (399 mg, 0.01 mol) in ethanol (36 ml)–tetrahydrofuran (12 ml) solvent for 5 h at room temperature. After quenching with 10% aqueous acetic acid followed by aqueous workup, the pure product, 1-[2′-(*trans*-1″propenyl)phenoxy]-2-[4′-(1″-hydroxypropyl)phenoxy]ethane was obtained (3.22 g, 100%): m.p. 70–72 °C; ^{1}H NMR ($CDCl_3$, 250 MHz), δ 0.89 (t, 3H, J = 7.38 Hz), 1.67–1.80 (m, 2H), 1.84 (dd, 3H, J = 1.65, 6.68), 4.33 (s, 4H), 4.54 (t, 1H, J = 6.59 Hz), 6.25 (m, 1H), 6.71 (d, 1H, J = 15.87 Hz), 6.88–7.45 (m, 8H); ^{13}C NMR ($CDCl_3$, 250 MHz), δ 10.2, 18.9, 31.8, 66.6, 67.2, 75.6, 112.8, 114.6, 121.3, 125.5, 126.5, 127.2, 127.6, 137.8, 155.1, 158.1; LRMS, *m/z* 312 (M^+); HRMS, *m/z* calculated for $C_{20}H_{24}O_3$ 312.172545, found 312.172533.

The product alcohol (1.33 g, 4.26 mmol) was suspended in dry dichloromethane (22 ml), followed by the addition of dry triethylamine (1.19 ml, 8.53 mmol). Triflic anhydride (0.73 ml, 4.26 mmol) was then added all in one portion at −78 °C. The reaction mixture was stirred for 30 min at this temperature and then quenched with dilute sodium hydrogencarbonate solution. After aqueous workup and silica gel column chromatography (100:4 hexane–ethyl acetate), monomer **5** was obtained in pure form (330 mg, 26.4%): m.p. 112–114 °C; ^{1}H NMR ($CDCl_3$, 250 MHz), δ 1.84 (d, 6H, J = 6.56), 4.32 (s, 4H), 6.10 (m, 2H), 6.34 (d, 1H, J = 16.5 Hz), 6.68 (d, 1H, J = 15.55 Hz), 6.78–7.40 (m, 8H); ^{13}C NMR ($CDCl_3$, 250 MHz), δ 18.46, 18.95, 66.70, 67.34 112.8, 114.87, 121.36, 123.76, 126.56, 126.64, 126.96, 127.72, 130.35, 131.8, 155.2, 158.0; LRMS, *m/z* 294(M^+); HRMS, calculated for $C_{20}H_{22}O_2$ 294.161980, found 294.162004.

Polymerization of monomer 3. To monomer **3** (73.5 mg, 2.5 mmol) dissolved in dry dichloromethane (0.8 ml) was added the aminium salt initiator (20.4 mg, 0.25 mmol) dissolved in dry dichloromethane (0.5 ml; the overall monomer concentration is 0.192 M) in one portion at 0 °C. The reaction mixture was stirred for 8 min and then quenched using saturated potassium carbonate–methanol solution. The crude polymer (70 mg, 95%) obtained after aqueous workup was found (GPC) to have M_w = 86 700 (PDI = 1.837): ^{1}H NMR ($CDCl_3$, 500 MHz), δ 1.1–1.2 (br, characteristic of methyl attached to cyclobutane ring), 1.79–1.85 (br), 2.78–2.80 (br), 4.0–4.35 (br), 6.1–6.25 (br), 6.3–7.36 (br).

trans-2,4-Pentadienyl phenyl ether. To a suspension of potassium carbonate (6.1 g, 0.044 mol) in 200 ml of acetone at room temperature was added phenol (7.52 g, 0.08 mol) and then *trans*-2,4-pentadienyl bromide (7.38 g, 89% pure by GC, 0.044 mol). The solution was stirred for 24 h. Aqueous workup yielded a colorless oil, which was purified by column chromatography (silica gel; light petroleum eluent), giving 5.8 g (90%) of the product:[15] ^{1}H NMR (250 MHz), δ 4.5 (d, 2H, J = 5.72 Hz), 5.2–5.26 (dd, 2H, J = 14.57, J = 9.29 Hz), 5.8–5.92 (m, 1H), 6.3–6.4 (m, 2H), 6.85–6.92 (m, 3H), 7.29–7.38 (m, 2H); LRMS, *m/z* 160 (M^+).

trans-2,4-Pentadienyl phenol. To a solution of *trans*-2,4-pentadienyl phenyl ether (1.6 g, 0.01 mol) in dry dichloromethane (100 ml) cooled to −40 to −30 °C was

added boron trifluoride–ether complex (1.52 ml, 0.012 mol). The resulting solution was stirred for 1 h at −40 to −30 °C. After aqueous workup the crude product was chromatographed (silica gel column; 10:1 light petroleum–ethyl acetate), yielding 1.52 g (94.5%) of the pure product:[15] ^{1}H NMR (250 MHz), δ 3.32, (d, 2H, J = 6.84 Hz), 4.92–5.10 (dd, 2H, J = 16.09, 9.18 Hz), 5.8 (m, 1H), 6.08 (m, 1H), 6.3 (m, 1H), 6.75 (d, 2H, J = 8.52 Hz), 7.0 (d, 2H, J = 8.46 Hz); LRMS, *m/z* 160 (M^+).

1-[4′-trans-2″,4″-Pentadienyl)phenoxy]-2-[2′-trans-1″-propenyl)phenoxy]ethane (4). To 30 ml of *N*,*N*-dimethylformamide at room temperature were added 2.19 g (0.0159 mol) of potassium carbonate and 2.13 g (0.0133 mol) of 4-(*trans*-2,4-pentadienyl)phenol. After stirring the mixture for 30 min, 3.83 g (0.00158 mol) of 1-(2-bromoethoxy)-2-(*trans*-1-propenyl)benzene were added and the reaction mixture was stirred for an additional 43 h. Aqueous workup and silica gel chromatography (light petroleum, then 100:1 light petroleum–ethyl acetate) yielded the pure monomer **6** (2.8 g, 66%): m.p. 58 °C; ^{1}H NMR (500 MHz), δ 1.87 (d, 3H, J = 6.68 Hz), 3.40 (d, 2H, J = 6.75 Hz), 4.33 (m, 4H), 5.00–5.14 (dd, 2H, J = 16.65, 10.18 Hz), 5.80–5.86 (m, 1H, —CH_2C*H*=CHCH=CH_2), 6.06–6.15 (m, 1H, —CH_2CH=C*H*CH=CH_2), 6.19–6.27 [dq, 1H, J = 15.85 Hz (d), 6.63 (q) —CH=C*H*CH_3], 6.29–6.37 [dt, 1H, J = 17.06 Hz (d), 10.34 (t), —CH_2CH=CHC*H*=CH_2], 6.70–6.72 (d, 1H, J = 15.93 Hz, —C*H*=$CHCH_3$), 6.9–7.40 (8H, m); ^{13}C NMR (500 MHz, $CDCl_3$), δ 18.85 (CH_3), 38.01 (CH_2), 66.7, 67.3 (—OCH_2CH_2O), 112.6 (Ar-C), 114.8 (Ar-C), 115.6 (—CH_2CH=CHCH=*C*H_2), 121.3 (Ar-C), 125.6 (—*C*H=$CHCH_3$), 126.44 (—CH=$CHCH_3$), 126.54 (Ar-C), 127.65 (Ar-C), 129.6 (Ar-C), 131.8 (—CH_2CH=*C*HCH=CH_2), 132.6 (Ar-C), 133.8 (—CH_2*C*H=CHCH=CH_2), 137.0 (—CH_2CH=CH*C*H=CH_2), 155.25 (Ar-C), 157.2 (Ar-C); HRMS (CI), *m/z* calculated for $C_{22}H_{24}O_2$ 320.1776, found 320.1773. Positional assignments of chemical shifts are based upon H–H COSY and C–H correlation spectra.

Methyl 4-(trans-2′,4′-pentadienyl)phenyl ether. To 4-(*trans*-2′,4′-pentadienyl)phenol (1.27 g, 7.94 mmol) in *N*,*N*-dimethylformamide (30 ml) at room temperature was added 1.1 g (7.97 mmol) of potassium carbonate and the solution was stirred for 30 min. An excess of methyl iodide (0.5 ml) was then added and the reaction mixture was stirred for an additional 3 h. After an aqueous workup, silica gel column chromatography (light petroleum) yielded the product (0.9 g, 65.2%): ^{1}H NMR (250 MHz), δ 3.39 (d, 2H, J = 6.77 Hz), 3.79 (s, 3H), 5.00 (d, 1H, J = 10.14 Hz), 5.10 (d, 1H, J = 16.99 Hz), 5.82 (m, 1H), 6.10 (m, 1H), 6.35 (m, 1H), 6.82 (d, 2H, J = 8.63 Hz), 7.10 (d, 2H, J = 8.47 Hz); ^{13}C NMR (250 MHz, $CDCl_3$), δ 37.973 (CH_2), 55.230 (—OCH_3), 113.829, 115.525, 129.484, 131.716, 132.056, 133.899, 136.935, 157.982; HRMS (CI), *m/z* calculated for $C_{12}H_{15}O$ 175.1123, found 175.1114.

Diels–Alder adduct (6a) of trans-anethole and methyl 4-(trans-2′,4′-pentadienyl)phenyl ether. To a solution of *trans*-anethole (74.1 mg, 0.5 mmol) and methyl 4-(*trans*-2,4-pentadienyl)phenyl ether (87 mg, 0.5 mmol) in dry dichloromethane (1 ml) at 0 °C was added tris(4-bromophenyl)aminium hexachloroantimonate (41 mg, 0.05 mmol) dissolved in 1 ml of dry dichloromethane dropwise over a period of 30 s. The reaction mixture was stirred for 7 min and then quenched with excess saturated potassium carbonate–methanol. Aqueous workup and column chromatography (silica gel, 100:1 hexane–ethyl acetate) gave 45 mg (28%) of the pure product: ^{1}H NMR (500 MHz), δ 0.92 (d, 3H, methyl, J = 6.62 Hz), 1.74–1.82 (m, 2H, H6), 2.09–2.15 (m, 1H, H5), 2.26–2.32 (m, 2H, benzylic methylene), 2.45–2.49 (m, 1H, H3), 2.69–2.72 (dd, 1H, J = 9.03, 5.02 Hz, H4), 3.74 (s, 3H, —OCH_3), 3.8 (s, 3H, —OCH_3), 5.48–5.53 (m, 1H, H2), 5.63–5.68 (m, 1H, H1), 6.72 (d, 2H, J = 6.62 Hz), 6.84–6.87 (dd, 4H, J = 6.02, 5.82 Hz), 7.12 (d, 2H, J = 6.02). Chemical shifts of protons were assigned from H–H COSY spectra. Specifically, irradiation of the signal corresponding to the benzylic methylene protons engendered an intensity increase of 5.11% in the signal corresponding to the proton at C5, whereas the C4 proton signal did not show an NOE effect. Similarly, irradiating the C5 methyl signal caused a small intensity increase in the C4 proton (1.9%) and C3 (1.08%) proton signals and had no effect on the C3 proton signal. These observations indicate that the C5 methyl and the C4 and C3 protons are all *cis*. This corresponds to a net *endo* Diels–Alder addition with suprafacial addition to the dienophile. ^{13}C NMR (250 MHz), δ 20.786 (CH_3), 28.513 (C6), 33.209 (C5), 37.069 (benzylic methylene carbon), 41.134 (C3), 49.811 (C4), 55.179 (— OCH_3), 55.246 (— OCH_3), 113.310, 113.407, 126.023 (C1), 127.718 (C2), 129.907, 130.266, 130.675, 133.073, 157.574, 157.675. The stereochemistry was assigned by NOESY spectra; HRMS *m/z* calculated for $C_{22}H_{26}O_2$ 322.193280, found, 322.193684.

Cyclobutane and Diels–Alder adducts of 2-(trans-1′-propenyl)anisole with methyl 4-(trans-2′,4′-pentadienyl)phenyl ether. To a solution of 2-(*trans*-1′-propenyl) anisole (148.2 mg, 1 mmol) and methyl 4-(*trans*-2′,4′-pentadienyl)phenyl ether (174 mg, 1 mmol) in dichloromethane (2 ml) at 0 °C was added, in one portion, tris(4-bromophenyl)aminium hexachloroantimonate (82 mg, 0.1 mmol) in dichloromethane (2 ml). After stirring the reaction mixture for 10 min at 0 °C, a quenching solution of saturated K_2CO_3 in methanol was added. Aqueous workup and column chromatography (silica gel: first hexane then 1000:5 hexane–ethyl acetate) yielded a 1:1 mixture of cyclobutane and Diels–Alder adducts (52 mg,

16.2%): ^{1}H NMR (500 MHz, $CDCl_3$, chemical shift assignments via H–H COSY spectra): Diels–Alder adducts: δ 0.908 [minor DA adduct (33%); d, 3H, J = 7.03, 0.932 (major DA adduct (67%); d, 3H, J = 6.624), 1.78–1.86 (m, 2H, H6), 2.15–2.22 (m, 1H, H5), 2.24–2.29 (m, 2H, benzylic protons), 2.27–2.32 (m, 1H, H3), 2.57–2.62 (m, 1H, H4), 3.75 (3H, s), 3.80 (3H,s), 5.52–5.56 (m, 1H, H2), 5.64–5.68 (m, 1H, H1), 6.72–7.26 (m, 8H). Cyclobutane adduct: δ 1.1 (d, 3H, J = 6.22), 1.37–1.44 (m, 1H, H4), 2.21–2.25 (m, 2H, H3, H4), 2.75–2.82 (m, 1H, H1), 3.10 (t, 1H, H2, J = 8.23–9.03), 3.24 (d, 1H, J = 6.63, a diastereotopic benzylic methylene); 3.38 (d, 1H, J = 6.62, the other diastereotopic methylene), 3.74 (3H, s), 3.77 (3H, s), 5.48 (m, 1H, vinyl proton distal to CB ring), 5.62 (m, 1H, vinyl proton proximal to CB ring), 6.72–7.26 (m, 8H); HRMS, *m/z* calculated for $C_{22}H_{26}O_2$ 322.193280, found: 322.192844.

Oligomerization of monomer 4 in the presence of a hindered base to form 5. To 200 mg (0.625 mmol) of **4** dissolved in dry dichloromethane (2 ml) was added 2,6-di-*tert*-butylpyridine (74 mg, 0.375 mmol) followed by addition of 255 mg of $\mathbf{1}^{+\cdot}$ (0.313 mmol) in dry dichloromethane (4 ml) over a 2 min period. The reaction mixture was stirred for 15 min and quenched by the addition of saturated K_2CO_3–CH_3OH solution. After aqueous workup and column chromatography (alumina), 42 mg (21%) of the trimer–oligomer mixture (**7**) were obtained: GPC $\overline{M}_W$ 1130 (PDI = 1.027); oligomer $\overline{M}_W$ 8080 (PDI = 2.43); ^{1}H NMR (500 MHz, $CDCl_3$, chemical shift assignments via H–H COSY spectra), δ 1.10 [d, 3H, J = 6.02, methyl attached to a CB ring], 1.41 (m, 1H, one of the CH_2 protons of the CB ring), 1.86 (d, J = 6.42 Hz, CH_3 of propenyl end group), 2.22 (m, 1H, methine on methyl-bearing CB carbon), 2.22 (m, 1H, one of CB methylene protons), 2.86 (m, 1H, allylic methine on the CB ring), 3.14 (t, 1H, J = 8.94–9.23 Hz, benzylic methine), 3.22 (d, 1H, J = 6.62 Hz, one of the diastereotopic benzylic methylenes), 3.36 (d, 1H, J = 6.63 Hz, the other diastereotopic benzylic methylene), 4.28–4.36 (m, 8H, ether methylenes), 5.00–5.19 (dd, 2H, J = 17.06, 10.04 Hz, C=CH_2 of pentadienyl end groups), 5.50 (m, 1H, vinyl proton off the CB ring), 5.63 (dd, 1H, J = 15.25, 6.42 Hz, vinyl proton nearest the CB ring), 5.83 (m, 1H, pentadienyl end groups), 6.10 (dd, 1H, J = 14.65, 13.25 Hz, pentadienyl end group), 6.25 (m, 1H, propenyl end groups), 6.35 (m, 1H, pentadienyl end group), 6.72 (d, 1H, J = 15.93 Hz, propenyl end group), 6.80–7.50 (m, 16H, aryl); ^{13}C NMR (500 MHz; chemical shifts assigned with the assistance of C–H correlation spectra), δ 19 (end group CH_3), 21 (CH_3 attached to CB), 33.6 (CB methylene), 35 (CB methine attached to CH_3), 37.8 (end group benzyl), 38.0 (benzyl attached to vinyl), 41.0 (CB methine attached to vinyl), 49.2 (CB methine attached to aryl), 63.5–63.9 (ether methylenes), 111.5, 112.8, 114.9, 115.0, 115.8 (—CH_2CH=CHCH=CH_2), 121.0, 121.3, 125.7 (—CH=$CHCH_3$), 126.7 (—CH=$CH$$CHCH_3$), 126.9, 127.3, 127.7 (—CH_2CH=CH—CB ring), 127.8, 129.5, 129.6, 131.9 (—CH_2CH=CHCH=CH_2), 133.2, 132.4, 133.8, (—CH_2CH=CHCH=CH_2), 135.4 (—CH_2CH=CH-CB ring), 137.0 (—CH_2CH=CHCH=CH_2), 155.23, 156.58, 156.93, 157.14.

Polymerization of monomer 4 to $\overline{M}_W$ 59300. To 200 mg (0.626 mmol) of **4** dissolved in 1 ml of dry dichloromethane were added, in a dropwise fashion over a 1 min period, 51 mg (0.0625 mol) of $\mathbf{1}^{+\cdot}$ in 1 ml of dry dichloromethane. The reaction mixture was stirred for 10 min and then quenched with saturated K_2CO_3–CH_3OH. The crude polymer obtained after aqueous workup had $\overline{M}_W$ = 59300 (PDI = 1.75). After column chromatography, the ^{1}H NMR spectrum was essentially unchanged. The 500 MHz ^{1}H NMR spectrum revealed an 8:2 ratio of DA:CB linkages. ^{1}H NMR (500 MHz, $CDCl_3$, chemical shift assignments *via* comparison with the model Diels–Alder compound), δ 0.9 (d, 3H, J = 6.62), 1.67–1.76 (m, 2H, H6), 1.80–1.89 (propenyl methyl end groups), 2.14–2.17 (m, 1H, H5), 2.18–2.23 (m, 2H, benzylic protons), 2.42–2.46 (m, 1H, H3), 2.60–2.65 (m, 1H, H4), 3.85–4.40 (br, ether methelenes), 4.9 (d, 1H, J = 9.63), 5.10 (d, 1H, J = 16.46), 5.45–5.51 (m, 1H, H_2), 5.60–5.67 (m, 1H, H_1), 5.76–5.86 (m, 1H), 6.03–6.12 (m, 1H), 6.18–6.26 (m, 1H), 6.27–6.37 (m, 1H), 6.63–6.80 (m, 1H), 6.83–7.40 (brm, 16H).

Polymerization of monomer 4 to $\overline{M}_W$ = 153000. To 300 mg (0.932 mmol) of **4** dissolved in 1.5 ml of dry dichloromethane was added, in a dropwise fashion over a 1 min period, a solution of 77 mg (0.0932 mol) of $\mathbf{1}^{+\cdot}$ in 1.0 ml of dry dichloromethane. After stirring the reaction mixture for 4 min at 0 °C, the mixture was quenched with saturated K_2CO_3–CH_3OH. Following aqueous workup, the polymeric product was found to have $\overline{M}_W$ = 153 500 (PDI = 3.58).

Polymerization of monomer 4 to the predominantly Diels–Alder polymer. To 100 mg (0.313 mmol) of **4** in 2.0 ml of dry dichloromethane were added, in a dropwise fashion over 8 min, 78 mg (0.0939 mmol) of $\mathbf{1}^{+\cdot}$ in 8.0 ml of dry dichloromethane. The reaction mixture was stirred for 20 min and then quenched with K_2CO_3–CH_3OH solution, followed by aqueous workup. The polymer was found to have $\overline{M}_W$ = 173 000 (PDI = 1.59). The 500 MHz ^{1}H NMR spectrum corresponded very closely to those of the Diels–Alder model compounds.

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