

Cation radical cycloaddition polymerization: Diels–Alder copolymerization

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ABSTRACT: The Diels–Alder cycloaddition copolymerization of a bis(diene) with ionizable bis(dienophiles) *via* a cation radical mechanism has been accomplished using tris(4-bromophenyl)aminium hexachloroantimonate as a catalyst in dichloromethane solvent. The reactions occur at 0°C and yield Diels–Alder polymers of $\bar{M}_w$ up to ca. 10,000 and a polydispersity index ca. 2. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: cation radical cycloaddition polymerization; Diels–Alder copolymerization

INTRODUCTION

Addition polymerization is well known to occur *via* radical, anionic and cationic mechanisms,¹ but only very recently has polymerization *via* reactive cation radical intermediates been demonstrated.² Especially novel aspects of this new polymerization mechanism are its propensity for cycloaddition and its apparent preference for non-vinyl (e.g. propenyl) monomers. The cation radical cycloaddition polymerization of the dipropenyl monomer **1** (Scheme 1), e.g. initiated by the stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate ($2^{+\cdot}$), has been shown to proceed *via* a cation radical chain mechanism to afford the novel macromolecule cyclobutapoly (**1**). In recent years, a variety of cation radical cycloaddition reaction types have been explored in these and other laboratories.³ These include cyclobutanation, Diels–Alder cycloaddition and cyclopropanation. The present paper describes the development of cation radical Diels–Alder cycloaddition as a novel approach to polymerization.

RESULTS AND DISCUSSION

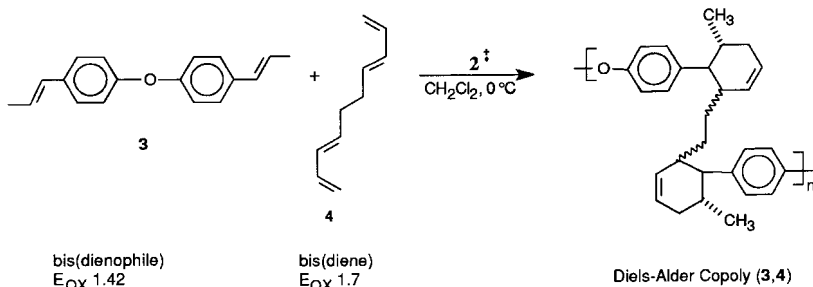
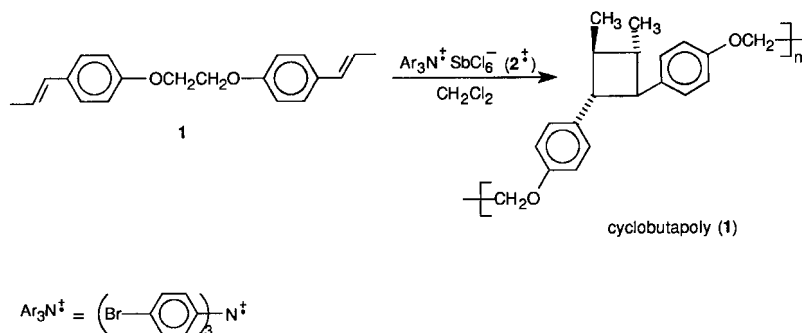
Both homopolymerization and copolymerization formats are potentially available for Diels–Alder cycloaddition polymerization. The copolymerization format was selected for this initial study because it appeared that the synthesis of symmetrical bis(diene) and bis(dienophile) comonomers might be more facile than the synthesis of unsymmetrical monomers containing both diene and

dienophile functionalities. Further, several bis(dienophile) monomers were already available from a previous study of cation radical poly(cyclobutanation).² Previous research had suggested that cation radical Diels–Alder reactions generally occur more efficiently when the reactive cation radical is the ionized dienophile.³ Consequently, a bis(dienophile), **3**, was selected which was known to be readily ionizable by $2^{+\cdot}$ (Scheme 2), while the preferred bis(diene), **4**, was known to be resistant to ionization by $2^{+\cdot}$. Finally, propenyl rather than vinyl moieties were selected for the dienophile functionality because terminal methyl groups sharply enhance the ionizability of the alkene functions and because they also tend to suppress the acid-catalyzed side reactions which sometimes compete with the cation radical reactions when unsubstituted vinyl groups are present. The bis(dienophile) comonomer **3** was readily prepared from diphenyl ether in three steps, while the bis(diene) comonomer **4** was obtained from 5-bromo-1,3-pentadiene *via* copper catalyzed coupling of the corresponding Grignard reagent.

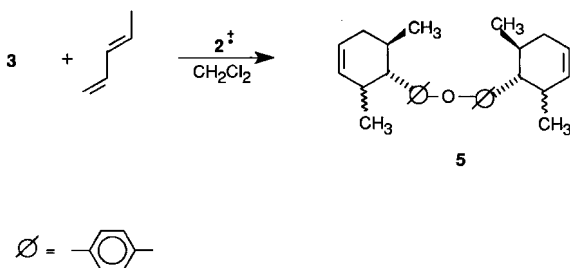
Copolymerization of **3** and **4**

A dichloromethane solution of comonomers **3** (0.04 M) and **4** (1.1-fold excess) was subjected to cation radical Diels–Alder copolymerization at 0°C by adding $2^{+\cdot}$ (30 mol%) dropwise over a period of 10 mins. The reaction was quenched after 20 min by adding excess methanolic potassium carbonate, followed by the addition of water and methylene chloride and separation of the organic phase. Alumina chromatography yielded a polymer (82%) having $\bar{M}_w = 10800$ and a polydispersity index (PDI) of 2.1. Structural characterization of the polymer was achieved by comparing the ^1H NMR

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spectrum of the polymer with that of a model compound (**5**; Scheme 3) prepared by the aminium salt (2^{+})-catalyzed Diels–Alder reaction of **3** with 2 mol of (*E*)-1,3-pentadiene. The ^1H NMR spectra of the model compound **5** and the polymer are virtually superimposable and consist of cyclohexene type protons (δ 4.9 and 5.05), benzylic methine protons (δ 2.7), non-benzylic methine protons (δ 1.7), methylene protons (δ 2.2–2.0) and methyl doublets (δ 0.9). In particular, the existence of cyclobutane linkages which could have resulted from the homopolymerization of **3** or from the incorporation of two or more consecutive molecules of monomer **3** into the polymer chain in substantial amounts can be ruled out. Such cyclobutane linkages are known to exhibit absorptions at δ 1.2, corresponding to methyl groups attached to a cyclobutane ring.² The cation radical Diels–Alder reactions of various dienophiles including *trans*-anethole, a dienophile which is structurally very similar to **3** are regiospecific and stereospecific. Consequently,

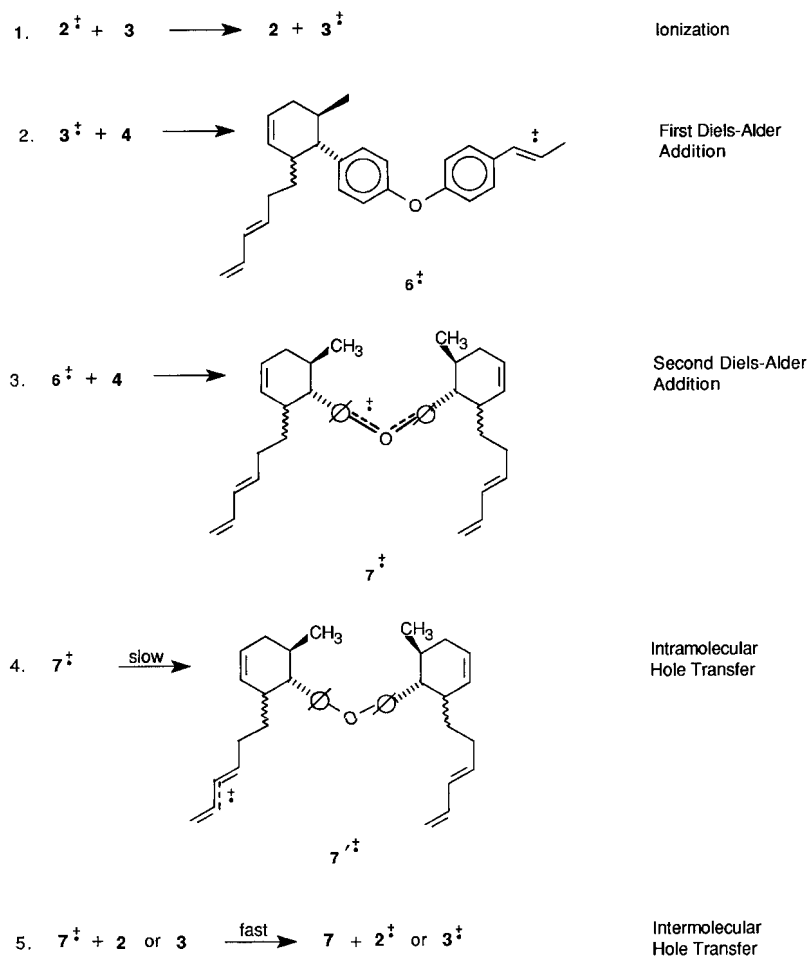


the copolymerization of **3** and **4** is considered to be regio- and stereospecific. However, since cation radical Diels–Alder cycloadditions are not highly *endo* diastereoselective, especially where acyclic dienes are involved, the present polymer structure is not completely tactic, but occurs with the ethano bridges *cis* and *trans* to the aryl substituent on the cyclohexene ring as indicated in the structure of copoly-(**3,4**).

The bis(dienophile) comonomer **1**, an even closer analogue of *trans*-anethole, was also examined. This monomer has previously been observed to undergo especially facile cation radical cyclobutane homopolymerization.² In the presence of a slight excess of the bis(diene) **4**, copolymerization again occurs to form exclusively the Diels–Alder copolymer (75% yield of chromatographed polymer) of $\bar{M}_w = 2520$ and a PDI of 2.3. Interestingly, whereas **1** undergoes homopolymerization much more efficiently than does **3**, the latter is a significantly more effective partner for **4** in copolymerization.

Mechanistic considerations

The observation that alternating Diels–Alder copolymerization of **3** with **4** and of **1** with **4** dominates over the cyclobutane (CB) homopolymerization of **3** or **1** indicates that the Diels–Alder addition of $3^{+\cdot}$ and $1^{+\cdot}$ to **4** is substantially faster than the competing additions of these same cation radicals to neutral **3** or **1**. While this circumstance was obviously not unexpected, it should not

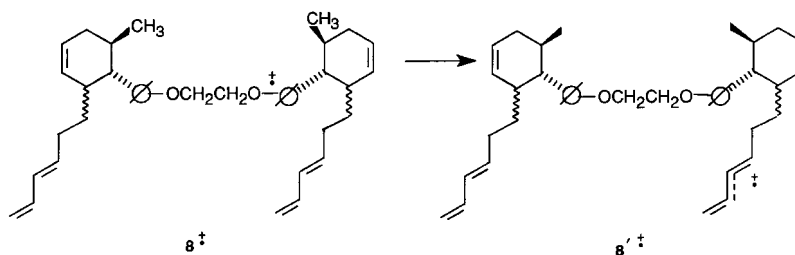


Scheme 4

necessarily be considered to imply a strong inherent preference for DA over CB cycloaddition. In fact, both CB and DA cycloadditions of cation radicals are well known to be extremely facile, and instances when these two reaction modes are competitive are now familiar.³ It appears much more likely that the preference for addition to **4** as opposed to **3** (or **1**) is based upon the now well established steric preference of cation radicals for addition to an unsubstituted alkene (vinyl) terminus over addition to a monosubstituted alkene (propenyl) terminus.⁴

The significantly lower molecular weights observed in these DA copolymerizations than in previously ob-

served CB homopolymerizations (e.g. **1**) is also of mechanistic interest. An inspection of the detailed mechanism of copolymerization (Scheme 4) reveals a major obstacle to the crucial intramolecular hole transfer reaction (step 4 of Scheme 4), which is required in order for the polymerization to propagate as a chain reaction. The reaction of $3^{\cdot+}$ with **4** is expected to proceed efficiently to the 1:1 adduct cation radical $6^{\cdot+}$ (Scheme 4). The cation radical moiety in this adduct is expected initially to reside on that functionality in direct conjugation with the pericyclic (DA) transition state which is most readily ionizable. The two logical candidates are the cyclohexene double bond and the 4-propenylphenoxy-



Scheme 5

phenyl function, and the obvious preference in terms of ionizability is the latter function. Reaction of $6^{+\cdot}$ with **4** can then proceed directly to the 2:1 adduct cation radical $7^{+\cdot}$. At this point, however, significant problems with continuing the chain propagation process become evident. First, hole transfer from the diphenyl ether function of $7^{+\cdot}$ to the diene function of $7'^{+\cdot}$ is required for further chain propagation. This hole transfer is not obviously exergonic and may therefore be relatively slow. Intermolecular hole transfer from $7^{+\cdot}$ to the neutral triarylamine **2** or to the monomer, in contrast, is highly exergonic and may result in the preferential neutralization of $7^{+\cdot}$ (step 5). The net result is that a potentially relatively efficient chain growth polymerization is converted, at least partially, into a less efficient step growth process.

A second potential problem with propagation from the 2:1 adduct cation radical is that even if intramolecular hole transfer were to occur, affording $7'^{+\cdot}$, the reaction of this diene cation radical with neutral **3** is not of the type to be preferred in most cation radical DA cycloadditions (i.e. dienophile cation radical/neutral diene). In fact $7'^{+\cdot}$ is unlikely to react with **3** to yield a DA adduct at all, since it should be formed preferentially in the *s-trans* conformation and would be unable to generate the *s-cis* diene cation radical required for DA reaction.

The even further diminished efficiency of DA copolymerization of **1** with **4** can be readily understood on the same basis. Since **1** has an oxidation potential which is about 0.1 V less than that of **3**, it is not unreasonable to assume that the hole transfer from $8^{+\cdot}$ (Scheme 5) to the diene moiety is even less energetically favorable than that in $7^{+\cdot}$. This proposal is further supported by viewing $7^{+\cdot}$ as a benzene-type cation radical having a stabilizing phenoxy substituent, while $8^{+\cdot}$ is a benzene-type cation radical having a stabilizing alkoxy substituent. Since the $^+$ value of methoxy (-0.78) is much more negative than that of phenoxy (-0.50), the cation radical moiety should be more stabilized in $8^{+\cdot}$ than in $7^{+\cdot}$. This view is supported by the substantially lower oxidation potential of **1** than **3**: $E_{\text{ox}}(\mathbf{1}) = 1.327$, $E_{\text{ox}}(\mathbf{3}) = 1.424$ V vs SCE. Hence it does not appear that the delocalization of the cation radical moiety over the second phenyl ring in $3^{+\cdot}$ provides greater stabilization than that available in $1^{+\cdot}$. Consequently, hole transfer to give $8'^{+\cdot}$ should be energetically even less favorable than from $7^{+\cdot}$ to give $7'^{+\cdot}$.

Evidence has previously been presented that the CB homopolymerization of **1** occurs *via* a chain growth process, at least in the first and most efficient stage of reaction. It is therefore expected, if DA copolymerization is constrained to proceed *via* step growth, that this type of polymerization will be less efficient. The PDIs of the presently observed DA copolymerizations, being *ca* 2 at essentially 100% monomer conversion, are in good accord with the proposal of a step growth mechanism.

Cation radical Diels–Alder homopolymerization

The clear implication of the preceding analysis is that cation radical DA homopolymerization should be a much more efficient process than copolymerization. In the case of the polymerization of a monomer which has both diene and ionizable dienophile functionalities, a readily ionizable dienophilic moiety is available in each propagation step to facilitate intramolecular hole transfer. This concept is currently being investigated.

CONCLUSIONS

The cation radical Diels–Alder copolymerizations of two ionizable, difunctional dienophiles with a simple, acyclic bis(diene) have been demonstrated. The resulting polymers are of modest molecular weight ($\overline{M}_w = 10\,000$ in the best instance). These Diels–Alder polymerizations thus appear to be substantially less efficient than the cation radical homocyclobutane polymerizations of ionizable bis(dienophiles). Nevertheless, the reactions occur under very mild conditions (0°C) and are regio- and stereospecific. The reactions appear to occur by a step growth mechanism ($\text{PDI} \approx 2$), rather than the more efficient cation radical chain mechanism proposed for poly(cyclobutane). The apparent suppression of the chain mechanism is viewed as an inherent problem with the copolymerization format of cation radical Diels–Alder polymerization.

EXPERIMENTAL

Reagents. Dried solvents were obtained by distillation under nitrogen immediately prior to use. Reagent-grade dichloromethane and acetonitrile 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 specified otherwise. 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 dichloromethane, then dried in an oven at 110°C prior to use. 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 indicated otherwise.

Analysis. Room temperature ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer

as solutions in CDCl_3 at 55°C . Solid-state ^{13}C NMR spectra were recorded on a Chemagentic 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 and ^{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 mid-point of the broad signals. Gas chromatographic (GC) analyses were performed on a Varian Model 3700 chromatograph equipped with a flame ionization detector and a DB-1 capillary column (J&W Scientific, $15\text{ m} \times 0.25\text{ mm i.d.}$, 1 mm film thickness) using helium as a carrier gas. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard Model 5890 gas chromatograph equipped with a DB-1 capillary column ($15\text{ m} \times 0.25\text{ mm i.d.}$, 1 mm film thickness) and a Model 5971A 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 (CED) 21-110B mass spectrometer. Cyclic voltammetric (CV) measurements were performed using a BAS Model 100 electrochemical analyzer at a scan rate of $100\text{ mV}^{-1}\text{s}$. 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 (cathode) attached to copper wire which was separated from the working electrode by a glass frit. An Ag/Ag^+ reference electrode (silver wire immersed in an acetonitrile solution 0.1 M in AgNO_3 and LiClO_4), calibrated against ferrocene/ferrocene $^+$, 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 ca 4 mM) and its CV response recorded. Gel permeation chromatography (GPC) was carried out in dichloromethane or THF (1 mL min^{-1}) using a Waters Model 550 HPLC pump, a Waters Model 410 differential refractometer and a Waters Model 745 data module with an Ultrastaygel $500\text{ \AA}$ column connected in series with a $\mu\text{Styragel } 10^4\text{ \AA}$ column. The GPC analyses were calibrated with a polystyrene standard. UV-visible spectra were taken on a Hewlett-Packard Model 845A spectrophotometer. 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 dichloromethane

solution on the plate) or as solutions in CCl_4 using an NaCl solution cell. Melting-points were determined on a Mel-Temp capillary melting-point apparatus and are uncorrected.

Bis[4-(propionyl)phenyl] ether. To a dry round-bottomed flask equipped with a magnetic stirrer, AlCl_3 (500 g , 0.38 mol) was added, followed by dichloromethane (100 mL). After lowering the temperature of the reaction to -20°C (by means of a dry-ice-acetone bath, a solution of diphenyl ether (25.6 g , 0.15 mol) in dichloromethane (40 mL) was added slowly. A 1:1 (v/v) solution of propionyl chloride (41.6 g , 0.45 mol) in dichloromethane was then added dropwise over a period of 15 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 , then carefully poured into a separating funnel containing crushed ice. The aqueous layer was separated and extracted twice with dichloromethane ($2 \times 100\text{ mL}$). The combined dichloromethane layers were washed with water (500 mL), saturated aqueous NaHCO_3 ($2 \times 500\text{ mL}$) and water ($2 \times 500\text{ mL}$) prior to drying (MgSO_4) and solvent removal by a rotary evaporator. The crude product was recrystallized from heptane, yielding 38.1 g (90%) of the pure diketone ($>95\%$ purity, by GC): m.p. $98.5\text{--}99.8^\circ\text{C}$ (lit. 5 100°C); ^1H 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, 118.8, 130.4, 160.2, 199.5; LRMS, m/z 282 (M^+), 271, 253, 197, 196, 139, 120, 92 (base); HRMS, m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}_3$ 282.1256; found 282.1261.

Bis[4-(1-hydroxypropyl)phenyl] ether. The diketone prepared in the previous procedure (2028 g , 0.072 mol) was dissolved in 200 mL of a 3:1 solution of ethanol-THF, followed by the addition of 5.44 g (0.14 mol) of sodium borohydride. After 1.5 h at room temperature, the reaction was quenched with 10% acetic acid at 0°C . The quenched solution was then extracted with dichloromethane ($3 \times 100\text{ mL}$) and the combined extracts were washed with aqueous NaHCO_3 ($2 \times 100\text{ mL}$) and water ($2 \times 100\text{ mL}$), prior to drying (MgSO_4) and solvent removal (rotary evaporator). The oily product diol (20.5 g , 99.7%) was used without further purification: ^1H NMR, δ 0.9 (t, 6H), 1.6–1.9 (m, 4H), 2.6 (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 (OH), 3360 cm^{-1} ; LRMS, m/z 286 (M^+), 254, 250, 115 (base); HRMS, m/z calculated for $\text{C}_{18}\text{H}_{22}\text{O}_3$ 286.1569; found 286.1576.

Bis[4-(1-propenyl)phenyl] ether. To a solution of the diol obtained in the previous procedure (6.31 g , 0.022 mol) in pyridine (25 mL) was added a slight excess of phosphorus oxytrichloride (7.5 g) at room temperature. The reaction mixture was refluxed for 2 h , then cooled in an ice bath. Water was then added slowly to quench any excess POCl_3 . The quenched reaction mixture was then trans-

ferred to a separating funnel, washed with water and dried (MgSO_4) prior to solvent removal (rotary evaporator). The crude product (**3**) was subjected to column chromatography (9:1 hexane–ethyl acetate), yielding 3.96 g (72%) of **3** which was 99% pure but consisted of an 87:11:2 mixture of the *E,E*-, *E,Z*- and *Z,Z*-isomers, respectively, of **3**: m.p. 117–119 °C; λ_{max} 270 nm, $\log \epsilon$ 2.24; ^1H NMR, δ 1.9 (t, 6H), 6.1 (dq, 2H, $J_{\text{trans}} = 15.8$), 6.4 (d, 2H, $J_{\text{trans}} = 15.8$), 6.9 (d, 4H), 7.4 (d, 4H); ^{13}C NMR, δ 18.4, 118.8, 124.7, 130.2, 137.2, 156.1; IR (C=C) 1590; LRMS, m/z 250 (M^+), 207, 179, 165, 133, 115 (base), 91; HRMS, m/z calculated for $\text{C}_{18}\text{H}_{18}\text{O}$ 250.1358; found 250.1369; E_p^{OX} 1.36 V.

(*E,E*)-1,3,7,9-Decatetraene (**4**). A dry 500 ml round-bottomed flask equipped with a reflux condenser, stirrer, nitrogen inlet and addition funnel was placed in an ice bath and 200 ml of 1.0 M vinylmagnesium bromide in THF were added. A solution of 13 ml (0.19 mol) of freshly distilled 2-propenal in 20 ml of THF was then added dropwise. The reaction was stirred for 2 h after the addition was complete. The reaction was then quenched by the addition of saturated NaHCO_3 . The layers were separated and the aqueous layer was extracted with pentane (3×100 ml). The combined organic extracts were dried (MgSO_4) and the solvent removed (rotary evaporator). Distillation gave 8.1 g (50%) of 1,4-pentadiene-3-ol: b.p. 115–120 °C. The crude alcohol was placed in a 250 ml round-bottomed flask equipped with a stirrer, ice bath and addition funnel. With stirring, 25 ml of 48% HBr were added slowly and the reaction was allowed to stir overnight. Once the reaction was complete, the aqueous solution was added with Et_2O (3×100 ml). The combined ethereal solutions were dried and the solvent was removed. Distillation afforded pure 1-bromo-2,4-pentadiene (43% yield, b.p. 28–32 °C at 50 Torr).

Finally, a dry 250 ml round-bottomed flask containing 2.0 g (82 mmol) of magnesium and 50 ml of dry THF was placed in an ice bath and equipped with a reflux condenser, stirrer, nitrogen inlet and addition funnel. Then, a solution of 10 g (68 mmol) of 5-bromo-1,3-pentadiene in 30 ml of THF was added dropwise. After the addition was complete, the reaction mixture was stirred for 3 h at room temperature. The Grignard solution was added *via* a syringe to a vigorously stirred suspension of anhydrous CuCl (7.3 g, 75 mmol) in 30 ml of THF at 0 °C over a period of 30 min. The resulting solution was filtered and work-up performed by addition of 5 ml of 6 M HCl and 100 ml of H_2O . The aqueous layer was extracted with Et_2O and the combined ethereal solutions were dried. After solvent removal, the crude product was purified by distillation at reduced pressure to give 8.24 g (75% yield) of **4**⁶ (95% pure by GC): b.p. 68–70 °C at 39 Torr; ^1H NMR, δ 2.2 (t, 4H), 4.96–5.12 (m, 4H), 6.65–5.79 (m,

2H), 6.0–6.1 (m, 2H), 6.25–6.38 (m, 2H); ^{13}C NMR, δ 32.2, 115, 131.4, 134.2, 137.1; LRMS, m/z 134 (M^+), 119, 106, 92, 79, 67 (base); HRMS, m/z calculated for $\text{C}_{10}\text{H}_{14}$ 134.1096; found 34.110.

Copolymerization of 3 with 4 using 2⁺. To a solution of **3** (100 mg, 0.4 mmol) and a 1.1-fold excess of **4** (59 mg) in 2 ml of dichloromethane at 0 °C was added a solution of 2^+ (0.098 g, 30%) in 8 ml of dichloromethane, dropwise, over a period of 10 min. After 20 min, the reaction was quenched, followed by the addition of water (20 ml) and dichloromethane (20 ml). The combined organic layers were dried and the solvent was removed. Column chromatography gave 124 mg (82%) of polymer whose ^1H NMR spectrum was essentially superimposable on that of the cross-adduct between **3** and *trans*-1,3-pentadiene: $\overline{M}_w = 10\,800$; PDI 2.1.

Copolymerization of 1 with 4 using 2⁺. This polymerization was performed exactly as for **3** with **4** except that 15 ml of dichloromethane were used to dissolve **1**: $\overline{M}_w = 2520$; PDI 2.3.

Reaction of 3 with (E)-1,3-pentadiene. To a dry, 25 ml round-bottomed flask containing 0.198 g (0.792 mmol) of **3** and 0.120 g (1.77 mmol) of (*E*)-1,3-pentadiene dissolved in 10 ml of dichloromethane at 0 °C was added 0.052 g (8.1%) of 2^+ . The reaction was quenched (K_2CO_3 – CH_3OH) after 10 min and worked up in the same manner as described for the polymerization of **3**. The pure Diels–Alder adduct **5** was obtained after chromatography on alumina: ^1H NMR, δ 0.75 (d, 3H), 0.85 (d, 3H), 2.2–2.4 (m, 3H), 2.7 (m, 2H), 5.6 (m, 1H), 5.7 (m, 1H), 6.9 (d, 2H), 7.1 (d, 2H).

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