J. Am. Chem. Soc. **1994**, *116*, 2827–2843

Living Cyclopolymerization of 1,6-Heptadiyne Derivatives Using Well-Defined Alkylidene Complexes: Polymerization Mechanism, Polymer Structure, and Polymer Properties

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Received August 23, 1993[⊗]

Abstract: We report here the living cyclopolymerization of 1,6-heptadiyne derivatives (usually 4,4-disubstituted) using well-defined alkylidene complexes as initiators. Diethyl dipropargylmalonate (**2a**), di-*tert*-butyl dipropargylmalonate (**2b**), optically active di-(1*R*,2*S*,5*R*)-(−)-menthyl dipropargylmalonate (**2c**(−)), di-(1*S*,2*R*,5*S*)-(+)-menthyl dipropargylmalonate (**2c**(+)), di-(1*R*)-*endo*-(+)-fenchyl dipropargylmalonate (**2d**), 4,4-bis[[(*p*-tolylsulfonyl)oxy]methyl]-1,6-heptadiyne (**3b**), 4,4-bis[(trimethylsiloxy)methyl]-1,6-heptadiyne (**3c**), the cyclic silyl ether, $PhEtSi(OCH_2)_2C(CH_2C{\equiv}CH)_2$ (**3d**), and *N*,*N*-dipropargyl-2,4,6-triisopropylbenzamide (**5b**) are polymerized to give soluble polymers in high yield using $Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$ (**1a**; Ar = 2,6-*i*-$Pr_2C_6H_3$, $OR_{F6} = OCMe(CF_3)_2$) as the initiator in 1,2-dimethoxyethane (DME). The polymers show a high degree of conjugation ($\lambda_{max} > 500$ nm) and have narrow molecular weight distributions. Poly(**2a**) is soluble in most organic solvents (THF, C_6H_6, toluene, CH_2Cl_2, $CHCl_3$, DME, DMF, MeCN). The mechanism of the polymerization has been investigated by ^{1}H NMR studies and by monomer, initiator, and solvent variations. Symmetric, diphenyl-capped polyenes, "pull–pull" polyenes containing *p*-cyanophenyl end groups, and "push–push" polyenes containing *p*-dimethylamino end groups have all been prepared, as have polyenes that contain optically active substituents and "push–pull" polyenes containing *p*-(dimethylamino)phenyl and *p*-cyanophenyl end groups. 4,4-Bis(carboxyethyl)cyclopent-1-ene and 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene were employed as model compounds in order to quantify five- and six-membered ring structures in the polymer. The substituted polyenes are far more stable at room temperature and in air than unsubstituted polyenes of the same length. Random and block copolymers of **2a**, 2,3-dicarbomethoxynorbornadiene (DCMNBD) and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT) were prepared and characterized. The solution electrochemistry, thin film electrochemistry, and UV/vis spectroelectrochemistry of several homopolymers and copolymers have been examined.

Introduction

Organic polymers and oligomers having conjugated π-systems possess a variety of interesting optical and electrical properties.[1,2] Polyacetylene, one of the simplest of such polymers, has been extensively studied.[1,3] Polyacetylene is highly conductive when doped,[4] particularly when oriented,[5] and possesses a high third-order susceptibility ($\chi^{(3)}$).[6,7] Unfortunately, polyacetylene is insoluble and sensitive to oxygen, properties that make it challenging to manipulate and to document any dependence of potentially useful properties on chain length or average conjugation length. Routes to polyacetylene that involve soluble precursor polymers have been developed,[8–11] but the polyacetylene that is prepared is still intractable. Polyacetylenes prepared from substituted acetylenes usually have a dramatically lower average conjugation length. For example, although λ_{max} is 550 nm for a soluble graft copolymer containing *cis*-polyacetylene and 640 nm for a similar copolymer containing *trans*-polyacetylene,[12] λ_{max} = 315 nm for polyphenylacetylene.[13] Soluble polyacetylenes with relatively high average conjugation lengths have been synthesized from monosubstituted cyclooctatetraenes,[14–18] although even these polyenes tend to aggregate and perhaps cross-link. Substituted acetylenes have been polymerized using $MoOCl_4$/*n*-Bu_4Sn/EtOH,[19] but again conjugation lengths are relatively short. Unfortunately, these polymerizations cannot be classified as living,[20] since the amount and nature of the initiator is unknown in many cases, and in some cases chain-transfer and back-biting reactions are fast.[14,17,21] Therefore, correlating polyene properties with chain length has in general not been possible.

The living ring-opening metathesis polymerization (ROMP) of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT) with well-defined alkylidene complexes of the type

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[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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$M(CHCMe_3)(NAr)(OCMe_3)_2$ (M = W,[22] Mo[23,24]) as initiators has been employed as a route to di-*tert*-butyl capped polyenes (t-Bu(CH=CH)$_n$-t-Bu) (n = 2–13) with a known number of double bonds.[25–27] After quenching the reaction in a Wittig-like manner with pivaldehyde, the polyenes are generated in a retro-Diels–Alder reaction via heating. This method is a living version of that developed using classical olefin metathesis catalysts.[8,9] Polyenes having up to 13 double bonds were isolated and characterized. Longer polyenes (n > 13) could not be isolated due to their insolubility and thermal and oxidative instability, especially in the all-trans form, but longer unsubstituted polyenes (up to 16 double bonds) could be incorporated along with norbornene in block copolymers.[28,29] Such relatively well-defined polyenes are soluble, and therefore optical and electrical properties could be studied as a function of chain length.[28,30]

A potentially interesting class of polyenes are those prepared by cyclopolymerization of 1,6-heptadiyne derivatives with Ziegler–Natta catalysts,[31,32] Pd(II) catalysts,[33–36] and catalysts that are also active for the metathesis of olefins.[37–54] Many variations have been polymerized, but insoluble polymers usually are obtained, and the chain length cannot be controlled because the methods are not living. The most soluble derivatives are polymers made from dipropargyl malonate esters.[44,45,47,49] We became interested in determining whether this type of polymer could be prepared in a living manner using a well-defined alkylidene complex as the initiator and whether the primary structure of such a polymer could be determined and controlled in a rational manner. The initiators of choice are molybdenum complexes of the type $Mo(CHR)(NAr)(OR')_2$,[23,24] which have been used to prepare a variety of polymers from norbornenes and substituted norbornadienes.[55] We recently reported in a preliminary fashion[56] the living polymerization of diethyl dipropargylmalonate (**2a**) to give poly(**2a**) using $Mo(CHCMe_3)(NAr)(OR_{F6})_2$ (**1a**)[23,24,56] as the initiator in 1,2-dimethoxyethane (DME). In this paper we explore this reaction in detail. We also exploit the living nature of the polymerization reaction by synthesizing block and random copolymers containing other ROMP monomers and polyenes terminated with donor or acceptor groups and report the preliminary electrochemistry of many of these new polymers.

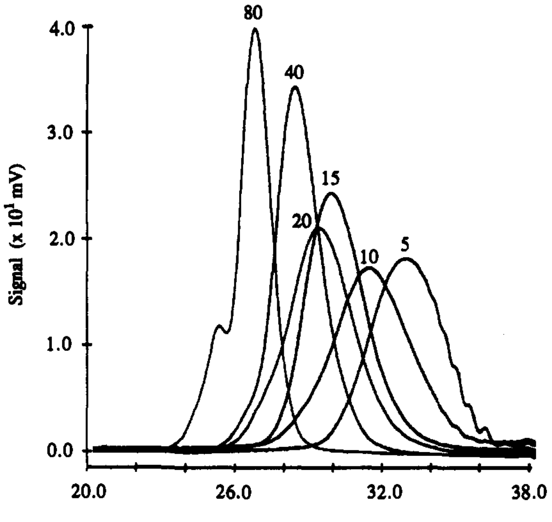

Figure 1. An overlay plot of the GPC concentration profiles for poly(**2a**)$_n$ (n = 5, 10, 15, 20, 40, 80) prepared using **1a** in DME.

Results

Polymerization of Diethyl Dipropargylmalonate (2a). Homopolymers of **2a** were prepared using **1a** as an initiator in DME. The polymerization reaction was terminated in a Wittig-like reaction by adding benzaldehyde. Molecular weights of the polymers were determined by GPC on-line viscometry, and one molecular weight was confirmed by vapor pressure osmometry. The degree of polymerization uniformly is somewhat higher than indicated by the stoichiometry, a circumstance that could be ascribed either to a significantly faster rate of propagation relative to initiation or to systematic error, or to a combination of the two. All initiator is consumed in each polymerization, according to NMR studies (see below). GPC traces (Figure 1) are all unimodal, with one exception; the high molecular weight shoulder at shorter retention times in the GPC trace of poly(**2a**)$_{80}$ corresponds to a polymer with double the molecular weight. Polymerization under more dilute conditions led to a diminished rate, as expected, but the amount of the double molecular weight polymer was also diminished, a fact that suggests that the double molecular weight polymer arises via an intermolecular chain-linking process (see below). All polymers are soluble in several common organic solvents (THF, C_6H_6, toluene, CH_2Cl_2, $CHCl_3$, DME, DMF, MeCN), but are insoluble in pentane and diethyl ether. The molecular weight distributions are uniformly narrow ($M_w/M_n \leq 1.25$), but the polydispersities are not as low as one would expect from a living polymerization reaction that involves

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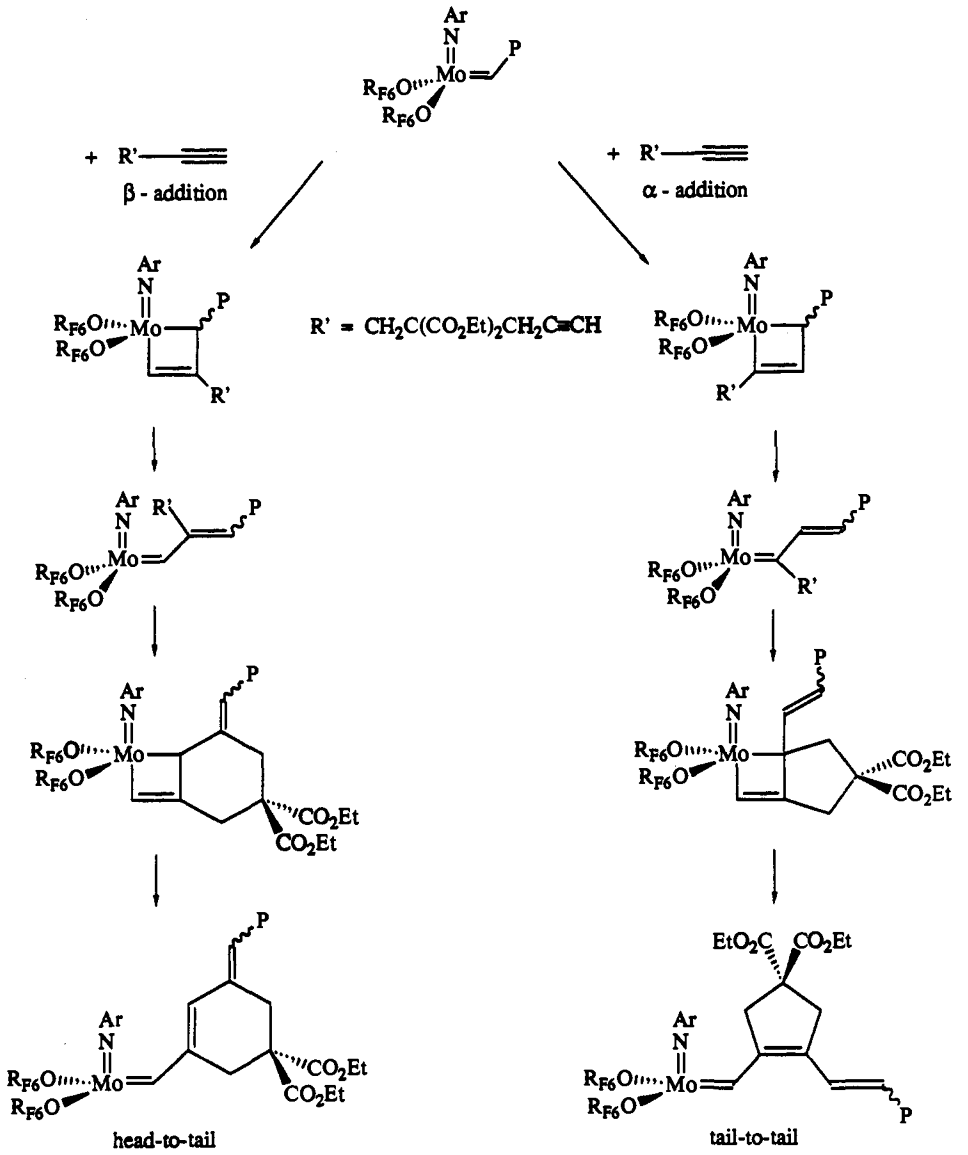
Scheme 1



only one type of propagation step. The reason can be attributed to the bifurcated nature of the polymerization mechanism (see below and Scheme 1).

A plot of the number average molecular weight (M_n) as a function of the number of equivalents of **2a** employed is linear (Figure 2a) and comes close to passing through the origin. This type of plot is what one would expect for a living polymerization reaction. As in any living polymerization reaction, care is required in order to obtain reproducible results. The monomer and initiator must be ultrapure, and significant quantities of initiator must be employed. Similar plots in which initiator **1m** (see later) is employed (Figure 2b) appear to be more accurate and reproducible.

The optical absorption maximum (λ_{max}) for the polymers varies considerably. For example, a plot of the transition energy (in electronvolts) versus $1/N$ (where N is the nominal average number of double bonds) for the series of poly(**2a**) samples in Table 1 is shown in Figure 3. The observed value of λ_{max} for a given number of double bonds does not correspond to the value observed for an unsubstituted polyene,[26,28] even those that contain some cis double bonds. One possible explanation is that the polymer is not rigid and the average conjugation length therefore is shorter than it is in the unsubstituted polyenes. The apparent solvatochromic shift that is observed (MeCN versus THF; Figure 3) could be explained in terms of changes in polymer conformation in the different solvents. However, there is a potential problem beyond experimental error, different structures for different length polymers, etc., that make it difficult to correlate λ_{max} with N with any great degree of accuracy; λ_{max} values for polymers with the same M_n but different polydispersities are not likely to be the same, and neither is likely to equal that expected for a structurally well-defined polymer with a fixed (single) chain length with a molecular weight M_n.[57] Only for a polymer with a specific chain length and regular structure is λ_{max} accurate.

Some other initiators that will polymerize **2a** in a smooth manner are listed in Table 2. Polydispersities of the resulting poly(**2a**) are less than 1.25 in most cases. Complex **1b**[23] afforded poly(**2a**) in high yield, although a significant amount of higher molecular weight polymer was present. We speculate that when intramolecular cyclization does not compete effectively with polymerization through one triple bond, a higher fraction of "dangling acetylenes" are left behind, which react further to link the polymer chains (eq 1; also see below). Tungsten complex **1c**[22] provided a substantially lower yield of polymer. Two possible reasons are a greater incompatibility of the tungsten complex with ester functionalities or a relatively high stability of intermediate tungstacyclobutene complexes toward "ring-opening" to the vinyl alkylidene complex.[55] Use of Mo(NAr)(CHCMe$_2$-

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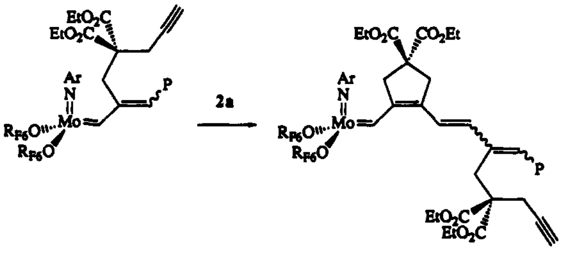

(1)

$Ph)(OR_{F13})_2$ (R_{F13} = $C(CF_3)_2CF_2CF_2CF_3$)[58] yielded a polymer with a significant degree of cross-linking, as judged by the significant fraction of higher molecular weight material observed by GPC. $Mo(NAr)(CHCMe_2Ph)(OR_{F9})_2$ (**1d**; OR_{F9} = $OC(CF_3)_3$),[58] Mo(*N*-1-adamantyl)$(CHCMe_2Ph)(OR_{F6})_2$ (**1f**),[58] Mo(*N*-2-*t*-BuC_6H_4)$(CHCMe_3)(OR_{F6})_2$ (**1g**),[58] $Mo(NAr)(CHPh)(OR_{F6})_2$ (**1i**),[59] $Mo(NAr)[CH\text{-}4\text{-}C_6H_4(NMe_2)](OR_{F6})_2(DME)$ (**1j**),[59] and $Mo(NAr)[C(Me)Ph](OR_{F6})_2$ (**1k**)[59] are all relatively well-behaved initiators. Complex **1k** is an unusual disubstituted alkylidene complex that has not been reported elsewhere. The fact that initiation is fast in an absolute sense, and relative to propagation, may have important implications (see Discussion).

Poly(**2a**) samples can be prepared from difunctional initiators, $[(DME)(R_{F6}O)_2(ArN)Mo]_2(CH)_6$ (**1l**),[59] and 1,4-$[(DME)(R_{F6}O)_2(ArN)Mo{=}CH]_2C_6H_4$ (**1m**) (Table 3); the polymerization is terminated by adding benzaldehyde. A plot of M_n versus monomer equivalents for polymers prepared using initiator **1m** (data in Table 3) is shown in Figure 2b. Poly$(\mathbf{2a})_{20}$ prepared using **1m** had a significantly lower λ_{max} than poly$(\mathbf{2a})_{20}$ prepared using **1l**. We speculate that the central phenyl ring is twisted out of conjugation with the polyene chains, thereby reducing λ_{max} effectively to what it is in a polyene with approximately half the nominal length. Different structures of the polymer near the central initiator block in the two circumstances might contribute directly or indirectly (through chain twisting) to a lower λ_{max}. It should be noted that λ_{max} for other length polyenes in this class does not correspond to the actual conjugation length, although this "average" conjugation length does increase proportionally with the length of the polymer chain, up to a length of approximately 40 double bonds.[26] The dramatic drop in the average conjugation length when moving from poly$(\mathbf{2a})_2$ to poly$(\mathbf{2a})_6$ might be ascribed to different "average" structures for these relatively short polymers or to different solution behavior of the two polymers.

Poly(**2a**) samples capped with π-donating groups (**d**) or π-accepting groups (**a**) at the chain ends have been prepared by employing initiator **1m** and *p*-(dimethylamino)benzaldehyde (**d**) or *p*-cyanobenzaldehyde (**a**) as the capping reagent.[60] Data for poly$(\mathbf{2a})_n$**dd** and poly$(\mathbf{2a})_n$**aa** are listed in Table 4. It is interesting to note that in short polymers the difference in λ_{max} between the "push–push" and the "pull–pull" polyenes is relatively large but that this difference diminishes as the polymer length increases. End group effects are diluted since the effective conjugation length does not correspond to the length of the entire polymer.

Finally, a series of "push–pull" polyenes (poly$(\mathbf{2a})_n$**da**) containing π-donating (**d**) and π-accepting (**a**) capping groups were prepared by using the *p*-dimethylamino benzylidene complex (**1j**) as the initiator and *p*-cyanobenzaldehyde as the capping reagent; the data for such polymers are listed in Table 5. In each case M_n was determined by on-line viscometry and the average number of double bonds was determined from M_n.

The nature of the solvent dramatically affects the cyclopolymerization of **2a**. Table 6 summarizes the polymer data for poly$(\mathbf{2a})_n$ prepared in several solvents other than dimethoxyethane using **1a** or **1d** as initiators. Molecular weight distributions are significantly broader than they are for polymers prepared in DME, and GPC traces are often multimodal. Only DME leads to a unimodal GPC trace and relatively narrow molecular weight distributions. Solvent undoubtedly plays a critical role in determining the rate of cyclization to give five- or six-membered rings, the rate of propagation relative to initiation, and the rate of cyclization relative to formation of chains that contain dangling acetylenes. Solvent effects are not understood at this stage.

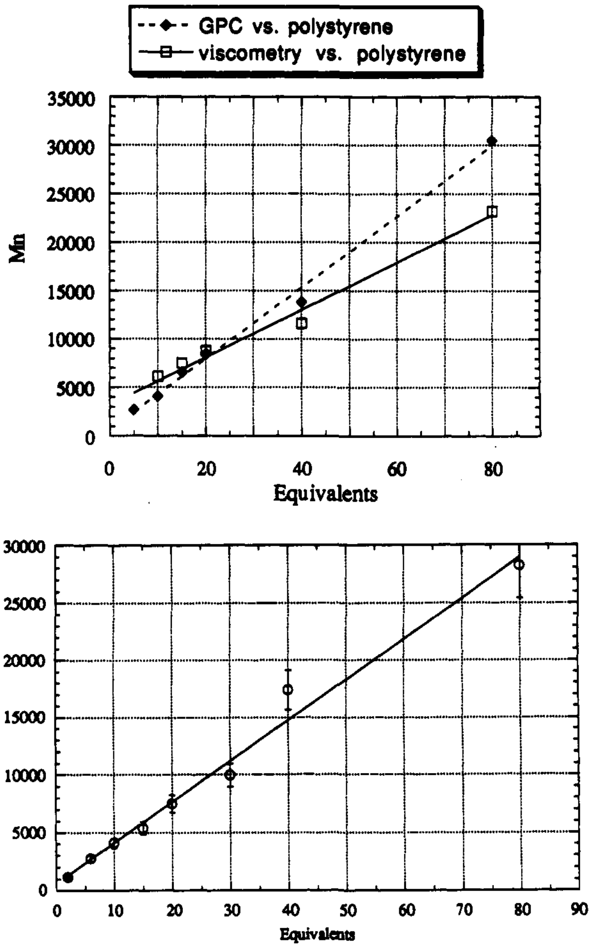

Figure 2. (a, top) A plot of M_n versus number of equivalents of monomer for the series of samples of poly(**2a**) prepared using **1a**. (Data are listed in Table 1.) (b, bottom) A plot of M_n versus number of equivalents of monomer for the series of samples of poly(**2a**) prepared using initiator **1m**. (Data are listed in Table 3.)

The thermal stability and oxidative stability of poly(**2a**) are enhanced greatly over the stability of analogous unsubstituted polyenes, as has been noted in other studies in the literature.[49] Decomposition of a film of poly$(\mathbf{2a})_{80}$ (static cast) was monitored by UV/vis spectroscopy. Initially, the thin film was transparent and deep purple, with λ_{max} = 544 nm. The slight metallic luster of the film was lost after 48 h in air, and the film changed from deep purple to a red-orange; λ_{max} decreased steadily over that time. The absorption gradually becomes less intense as the color fades, consistent with decomposition of the polyene framework, but even after 7 weeks the film could be redissolved in THF. A THF solution of poly$(\mathbf{2a})_{80}$ in air was bright purple (λ_{max} = 554 nm). λ_{max} changed little with time upon exposure of the THF solution to air, although the magnitude of the absorbance decreased steadily and three absorptions corresponding to short polyene segments grew in at 234, 272, and 292 nm.[26] Over a period of several weeks, the fraction of long conjugated chains decreased as the fraction of short chains increased.

When the polymerization of **2a** by **1a** was carried out in the

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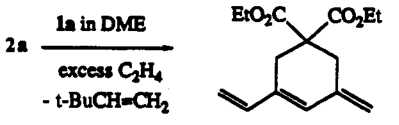
Table 1. GPC, UV/Vis, and Yield Data for Poly(**2a**)$_n$ Prepared Using **1a** as the Initiator in DME[a]

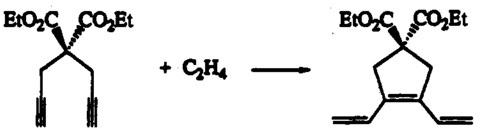
polymer	M_n[b]	M_w/M_n[b]	M_n[c]	$[\eta]$ (dL/g)[b]	λ_{max} (nm)[d]	DP[e]	yield (%)
poly(**2a**)$_5$	3640	1.21	2690	0.051	514 (504)	15	98
poly(**2a**)$_{10}$	6110	1.24	4080	0.064	534 (524)	26	93
poly(**2a**)$_{15}$	7520[f]	1.18	6560	0.107	548 (544)	32	99
poly(**2a**)$_{20}$	8790	1.25	8460	0.123	548 (544)	37	100
poly(**2a**)$_{40}$	11 600	1.16	13 800	0.164	552 (554)	49	96
poly(**2a**)$_{80}$	23 200	1.23[g]	30 500	0.272	556 (574)	98	97

[a] Details of the procedure are described in the Experimental Section. [b] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [c] By GPC versus polystyrene standards. [d] In THF or acetonitrile (in parentheses). [e] Calculated from M_n in column 2. [f] M_n = 7550 (±1200) was obtained by vapor pressure osmometry. [g] A small amount of double molecular weight material was observed by GPC.

presence of an excess of ethylene, 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene could be isolated in 62% yield (eq 2). It is known that a DME-stabilized methylene complex is generated when **1a** reacts with ethylene.[59] Reaction of this methylene complex with **2a** to give a β-substituted metallacyclobutene intermediate, followed by ring-opening, cyclization, and metathesis of the resulting alkylidene by ethylene (cf. Scheme 1), would complete the formation of the observed product. It should be noted that formation of a cyclohexene ring corresponds to a head-to-tail cyclization, the type that is usually assumed to take place in polymerizations reported in the literature. The other plausible cyclization step is formation of a cyclopentene ring via a tail-to-tail cyclization (eq 3). We could not confirm that the divinylcyclopentene is also formed in the reaction between **2a** and **1a** in the presence of an excess of ethylene. Therefore the divinylcyclopentene could not be used as a model for the cyclopentene ring formed in the cyclopolymerization. However, 4,4-bis(carboxyethyl)cyclopentene could be prepared readily[61] and was adequate as a model in NMR studies. The ^{13}C NMR spectra of the cyclopentene and cyclohexene model compounds have quaternary carbon resonances near 54 and 57 ppm, respectively (Figure 4a,b).

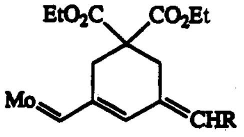


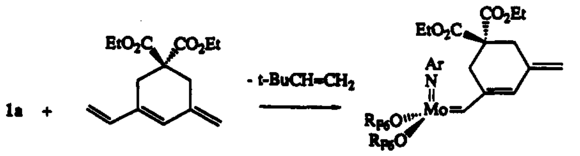
(2)



(3)

The reaction between **2a** and **1a** was monitored by ^1H NMR. Upon adding 2.5 equiv of **2a** to a solution of **1a**, the alkylidene proton resonance at 12.14 ppm for **1a** diminished in intensity by half and two new alkylidene H_α resonances appeared at 13.03 and 12.41 ppm. All **2a** was consumed, and there was no evidence for any product formed by insertion of a single acetylene into the Mo=C bond. The resonance at 12.41 is assigned to the alkylidene proton of an alkylidene complex that contains a six-membered ring attached to the alkylidene carbon atom, viz., on the basis of comparison with the product of the reaction between **1a** and 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene (eq 4), which exhibits a resonance at 12.44 ppm for the alkylidene proton in CD_2Cl_2. We can ascribe the resonance at 13.03 ppm to another isomer of the propagating alkylidene complex, e.g., the one containing a five-membered ring, but we cannot be certain because no model compound has been prepared. Since initiator is still present in this experiment, more than 1 equiv of **2a** must have reacted; evidently the H_α resonance is relatively insensitive to the nature of the second unit away from the metal in this experiment. In contrast, proton NMR spectra of poly(**2a**)$_{80}$ prepared using **1a** in DME exhibit broad H_α resonances.





(4)

More information can be obtained about the structure of poly(**2a**) by ^{13}C NMR spectroscopy. The high-field ^{13}C NMR spectrum of poly(**2a**)$_{80}$ (Figure 5) reveals two resonances for the carbonyl carbon atoms at 170.8 and 172.0 ppm, indicating that there are two different carbonyl environments in the polymer. Moreover, there are numerous olefinic resonances in the range 120–140 ppm, two major clusters of peaks between 50 and 60 ppm for the quaternary carbon atoms adjacent to the esters, and many resonances for the allylic methylene groups. The two clusters of resonances for the quaternary carbon atoms (Figures 4c and 6a) can be assigned to quaternary carbons in five-membered rings (57–58 ppm) and in six-membered rings (54–55 ppm), respectively. The several resonances within each group can be ascribed to carbons in different local environments within the polymer chain (e.g., a five-membered ring between two six-membered rings, etc.) or to the presence of cis/trans isomerism in the double bond formed between monomer ring units. The ratio of the two clusters of quaternary carbon atom resonances is the same as the ratio of carbonyl carbon atom resonances, approximately 1:1. We propose that five- and six-membered rings originate from initial α- and β-additions of the first triple bond to the Mo=C bond followed by cyclization and ring-opening (Scheme 1). Evidently formation of five- or six-membered rings via these two pathways proceeds at *approximately* the same rate on the average. (There may be some tendency for a five-membered ring to be followed by a six-membered ring, for example, but these polymers are not regular enough to address such questions.) A difference in the rates of formation of five- and six-membered rings is yet another of the several characteristics that would lead to a broadening of the molecular weight distribution.

The relative amounts of five- and six-membered rings formed in poly(**2a**) prepared with a variety of initiators are listed in Table 7; ^{13}C spectra are shown in Figure 6. Both the carbonyl and quaternary carbons were employed in order to determine the relative amounts of five- and six-membered rings. In general, solvent appears to play a negligible role in determining the ratio of five- to six-membered rings. Minor modifications of the initiator such as changing the alkoxide ligands from OR_{F6} (**1a**) to OR_{F13} (**1e**) or the substituents on the arylimido ligand (**1a** versus **1h**) resulted in only small changes in the ratio of rings. A significant change in the ring ratio was found when the adamantyl imido initiator (**1f**) was employed; ~80% six-membered rings were formed. In previous work, e.g., poly(**2a**) prepared using a

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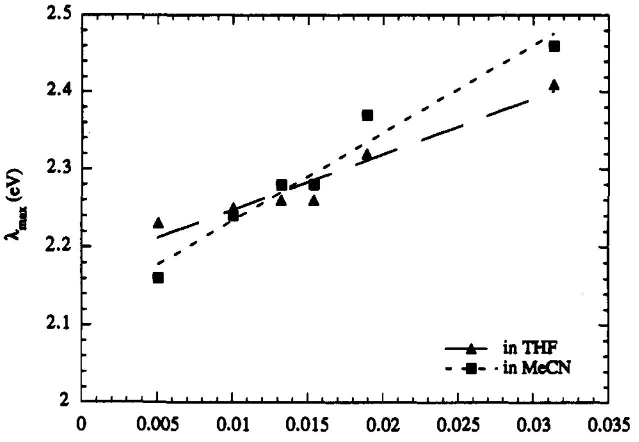
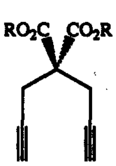


Figure 3. Dependence of the optical absorption maximum (λ_{max}) in THF and MeCN versus the reciprocal of the number of double bonds (*N*) in poly(**2a**)$_n$ prepared using **1a**.

1:1 mixture of $MoCl_5$ and $(n\text{-}Bu)_4Sn$ in dioxane,[49] the polymer structure was proposed to consist of six-membered rings. We have examined poly(**2b**) prepared in this manner and find that it contains (according to its ^{13}C NMR spectrum; Figure 6f) ~70% *five*-membered rings. The overall similarities between the polymers prepared with well-defined alkylidene initiators described here and the polymers obtained using classical metathesis catalysts *suggest* that the active catalyst in the classical system contains a metal–carbon double bond, as has been assumed by previous workers.[62–64]

Further assignments of the quaternary carbon resonances in ^{13}C NMR spectra of samples of poly(**2a**) can be made (Figures 4c and 6a). There are two groups of resonances for quaternary carbons in five-membered rings at approximately 57 and 58 ppm. In the polymer containing ~70% five-membered rings (Figure 6f) the major resonance is found at 57 ppm, and in the polymer containing ~80% six-membered rings (Figure 6e) the major resonance is found at 58 ppm. Therefore, we can assign the resonances at 57 ppm to five-membered rings adjacent to five-membered rings and the peaks at 58 ppm to five-membered rings adjacent to six-membered rings. A similar assignment for six-membered rings is ambiguous, since chemical shift differences are not as large.

Cyclopolymerization of Other 1,6-Heptadiynes. Other dialkyl malonate esters can be prepared readily from malonyl dichloride and 2 equiv of the appropriate alcohol, and from these the corresponding dipropargyl derivatives can be synthesized in high yield. Di-*tert*-butyl dipropargylmalonate (**2b**), di-(1*R*,2*S*,5*R*)-(−)-menthyl dipropargylmalonate (**2c(−)**), di-(1*S*,2*R*,5*S*)-(+)-menthyl dipropargylmalonate (**2c(+)**), and di-(1*R*)-*endo*-(+)-fenchyl dipropargylmalonate (**2d**) were each prepared and cyclopolymerized employing either **1a** (Table 8) or **1m** (Table 9). As the ester substituent becomes more sterically demanding, five-membered rings are slightly more favored (compare poly(**2a**)$_{92}$ and poly(**2c(+)**)$_{40}$ employing **1f** as an initiator in Table 7). Poly(**2b**) is soluble in all common organic solvents. Poly(**2c(−)**), poly(**2c(+)**), and poly(**2d**) are all soluble in nonpolar organic solvents and insoluble in polar solvents such as acetonitrile.



R = Et (**2a**), t-butyl (**2b**), 1R,2S,5R-(-)-menthyl (**2c(-)**), 1S,2R,5S-(+)-menthyl (**2c(+)**). (1R)-endo-(+)-fenchyl (**2d**).

The UV/vis and CD data for poly(**2c(−)**)$_{40}$, poly(**2c(+)**)$_{40}$, and poly(**2d**)$_{40}$ are listed in Table 10. The UV/vis and CD spectra of **2c(−)** and **2c(+)** are shown in Figure 7a,b, while the UV/vis and CD spectra of poly(**2c(−)**) and poly(**2c(+)**) are shown in Figure 8a,b. The optically active side groups on these conjugated polymers give rise to a strong dissymmetry in the polymer chain. Extreme behavior of this type would be an enforced single-sense helical form of the polymer in solution.[17,65–70]

Other 4,4-disubstituted-1,6-heptadiyne monomers that were prepared from **2a** include 4,4-bis(hydroxymethyl)-1,6-heptadiyne (**3a**), 4,4-bis[[(*p*-tolylsulfonyl)oxy]methyl]-1,6-heptadiyne (**3b**), 4,4-bis[(trimethylsiloxy)methyl]-1,6-heptadiyne (**3c**), and $PhEtSi(OCH_2)_2C(CH_2C{\equiv}CH)_2$ (**3d**) (Scheme 2). The monosubstituted derivative, 4-(carboxyethyl)-1,6-heptadiyne (**4**), was prepared directly from **2a**. Two amide monomers, *N,N*-dipropargylbenzamide (**5a**) and *N,N*-dipropargyl-2,4,6-triisopropylbenzamide (**5b**), were synthesized from dipropargylamine. Surprisingly, **3a** appeared to be polymerized by **1a**, although the polymers were insoluble in organic solvents and therefore could not be characterized. Poly(**3b**) and poly(**3c**) could be prepared smoothly, had narrow molecular weight distributions, and exhibited maximum absorbances between 520 and 560 nm (Table 8). Poly(**3d**) and poly(**4**) had molecular weight distributions that were quite broad and molecular weights that were unusually high; we speculate that polymer chains are cross-linked via dangling triple bonds. Poly(1,6-heptadiyne) was found to be insoluble, as found previously,[31,32,71] as was poly(dipropargylether).[40] Poly(*N,N*-dipropargylbenzamide) was found to be relatively insoluble, but poly(*N,N*-dipropargyl-2,4,6-triisopropylbenzamide) was again soluble. On the basis of these results, it appears that sterically demanding substituents (preferably two) in the 4-position of the monomer encourage intramolecular cyclization. This effect is similar to the "*gem*-dialkyl effect" which has been observed to accelerate intramolecular reactions in a variety of organic reactions.[72–74]

Copolymerizations. Block copolymers containing **2a** and 2,3-dicarbomethoxynorbornadiene (DCMNBD) were prepared employing **1a** as the initiator. (DCMNBD is known to be polymerized in a living manner by **1a** in DME.[59]) The first copolymer was prepared by adding 20 equiv of **2a** to a DME solution of **1a**, followed (after **2a** had been consumed) by 200 equiv of DCMNBD. The living diblock copolymer was capped by addition of benzaldehyde to give poly(**2a**)$_{20}$poly(DCMNBD)$_{200}$ (Table 11). A slightly different block copolymer, poly(DCMNBD)$_{50}$poly(**2a**)$_{20}$, was synthesized by reversing the order of addition; DCMNBD (50 equiv) was polymerized first followed by 20 equiv of **2a** (Table 11). In both cases the yield was high, the polydispersity was low, and λ_{max} was comparable to λ_{max} in poly(**2a**)$_{20}$.

Random copolymers were generated when a mixture of DCMNBD and **2a** was added to **1a**. Poly[(DCMNBD)$_{30}$(**2a**)$_{70}$], poly[(DCMNBD)$_{50}$(**2a**)$_{50}$], and poly[(DCMNBD)$_{70}$(**2a**)$_{30}$] (Table 11) were obtained in high yield and had low polydispersities. Since λ_{max} in each case is significantly less than λ_{max} of poly(**2a**)$_5$

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Table 2. GPC, UV/Vis, and Yield Data for Poly(**2a**)$_n$ Prepared in DME Using Various Alkylidene Complexes as Initiators[a]

initiator		equiv (n)	M_n[a]	M_w/M_n[b]	λ_{max} (nm)[c]	yield (%)
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	**1b**	20	8500[c]	1.24[d]	538	96
W(NAr)(CHCMe$_3$)(OR$_{F6}$)$_2$	**1c**	20	4900[c]	1.46	514	62
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F9}$)$_2$	**1d**	25	7660	1.30	538	98
	1d	50	14 000[c]	1.28	554	94
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F13}$)$_2$	**1e**	80	67 200	1.64[e]	552	100
Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**1f**	20	4200[c]	1.19	534 (544)	93
	1f	92	106 200	1.23	534 (572)	95
Mo(*N*-2-*t*-BuC$_6$H$_4$)(CHCMe$_3$)(OR$_{F6}$)$_2$	**1g**	80	57 700	1.31	548 (572)	99
Mo(NAr′)(CHMe$_2$Ph)(OR$_{F6}$)$_2$	**1h**	80	24 300	1.21[e]	554	100
Mo(NAr)(CHPh)(OR$_{F6}$)$_2$	**1i**	20	9400	1.11	548	100
Mo(NAr)[CH-4-C$_6$H$_4$(NMe$_2$)](OR$_{F6}$)$_2$(DME)	**1j**	20	7800	1.13	544	99
Mo(NAr)[C(Me)Ph](OR$_{F6}$)$_2$	**1k**	20	6200	1.17	546	100

[a] Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, Ar′ = 2,6-Me$_2$C$_6$H$_3$, OR$_{F3}$ = OCMe$_2$(CF$_3$), OR$_{F6}$ = OCMe(CF$_3$)$_2$, OR$_{F13}$ = OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$). [b] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [c] In THF or acetonitrile (in parentheses). [d] M_n determined versus polystyrene standards. [e] A significant amount of higher molecular weight material was present.

Table 3. GPC, UV/Vis, and Yield Data for Symmetric Diphenyl-Capped Polyenes, Poly(**2a**)$_n$, Prepared Using 1,4-[(DME)(OR$_{F6}$)$_2$(NAr)Mo=CH]$_2$C$_6$H$_4$ (**1m**) or [(DME)(OR$_{F6}$)$_2$(NAr)Mo]$_2$(CH)$_6$ (**1l**) in DME

polymer	M_n[a]	M_w/M_n[a]	[η] (dL/g)[a]	λ_{max} (nm)[b]	N[c]	CL$_{avg}$[d]	yield (%)
poly(**2a**)$_2$/**1m**	1150	1.27	0.041	474 (470)	14	12	50
poly(**2a**)$_6$/**1m**	2800	1.19	0.038	466 (460)	28	11	89
poly(**2a**)$_{10}$/**1m**	4100	1.16	0.047	486 (486)	39	14	98
poly(**2a**)$_{15}$/**1m**	5400	1.14	0.073	516 (506)	50	16	100
poly(**2a**)$_{20}$/**1m**	7500	1.14	0.091	530 (528)	68	20	98
poly(**2a**)$_{20}$/**1l**	7600	1.13		548			100
poly(**2a**)$_{30}$/**1m**	10 000	1.14	0.102	538 (542)	88	24	99
poly(**2a**)$_{40}$/**1m**	17 600	1.19	0.197	550 (562)	152	31	85
poly(**2a**)$_{80}$/**1m**	27 900	1.27[e]	0.298	552 (572)	240	36	98
poly(**2a**)$_{160}$/**1m**	76 500	1.63[e]		556 (580)	654	42	95

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In THF or acetonitrile (in parentheses). [c] Average number of double bonds calculated from M_n. [d] Average conjugation length calculated from the relationship $E = 1.9368 + 8.4391/N$ (ref 26), where E is the energy of the transition (in acetonitrile) and N is the number of double bonds in conjugation. [e] Broadened due to doubling in molecular weight.

Table 4. GPC, UV/Vis, and Yield Data for Push–Push Polyenes (Poly(**2a**)$_n$**dd**) and Pull–Pull Polyenes (Poly(**2a**)$_n$**aa**) Prepared Using **1m** in DME

polymer	M_n[a]	M_w/M_n[a]	[η] (dL/g)[a]	λ_{max} (nm)[b]	ϵ_{max} (M^{-1} cm^{-1})[a]	N[c]	yield (%)
poly(**2a**)$_5$**dd**	1530	1.31	0.034	464 (464)	14 700	16	80
poly(**2a**)$_5$**aa**	1750	1.28	0.034	454 (452)	10 300	18	100
poly(**2a**)$_{10}$**dd**	4410	1.23	0.051	508 (504)	15 600	41	90
poly(**2a**)$_{10}$**aa**	2000	1.25	0.040	470 (462)	11 000	21	98
poly(**2a**)$_{15}$**dd**	4710	1.22	0.053	510 (506)	11 600	43	99
poly(**2a**)$_{15}$**aa**	3660	1.24	0.044	492 (488)	11 400	34	98
poly(**2a**)$_{20}$**dd**	5520	1.26	0.093	528 (522)	16 800	50	100
poly(**2a**)$_{20}$**aa**	5780	1.25	0.096	528 (524)	14 800	52	100
poly(**2a**)$_{40}$**dd**	13 420	1.25	0.140	548 (548)	16 200	117	100
poly(**2a**)$_{40}$**aa**	11 500	1.23	0.142	546 (546)	14 800	101	95

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In THF or acetonitrile (in parentheses). [c] Average number of double bonds calculated from M_n.

Table 5. GPC, UV/Vis, and Yield Data for Push–Pull Polyenes, Poly(**2a**)$_n$**da**, Prepared Using **1j** in DME

polymer	M_n[a]	M_w/M_n[a]	[η] (dL/g)[a]	λ_{max} (nm)[b]	ϵ_{max} (M^{-1} cm^{-1})[b]	N[c]	yield (%)
poly(**2a**)$_5$**da**	1510	1.47	0.038	498 (494)	13 700	17	91
poly(**2a**)$_{10}$**da**	3910	1.28	0.050	526 (522)	13 200	38	98
poly(**2a**)$_{15}$**da**	7260	1.18	0.079	542 (538)	14 600	66	96
poly(**2a**)$_{20}$**da**	9100	1.16	0.086	542 (542)	15 200	82	95
poly(**2a**)$_{30}$**da**	18 700	1.18	0.179	552 (562)	16 100	183	89

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In THF or acetonitrile (in parentheses). [c] Average number of double bonds calculated from M_n.

(514 nm; Table 1), the reactivities of DCMNBD and **2a** must be comparable under these conditions and relatively random copolymers must be generated. Consistent with this proposal is the fact that as the fraction of **2a** decreases, λ_{max} decreases because shorter conjugated segments are present in the random copolymer.

Similar random copolymers, poly[(TCDT)$_x$(DCMNBD)$_y$], were prepared from TCDT and DCMNBD employing initiator **1a** in DME (Table 11). Poly(TCDT) eliminates hexafluoro-*ortho*-xylene and generates an unsubstituted polyene chain when heated.[8,9,27–29] Block copolymers have been prepared previously that contain poly(TCDT) sequences as a means of preparing block copolymers that contain relatively well-defined polyene sequences.[27–29] Random copolymers **6f**, **6g**, and **6h** (Table 11) all undergo a small amount of retro-Diels–Alder reaction at room temperature, which gives rise to an absorption at ~342 nm for a short polyene sequence, but after heating the polymers to 125 °C for 10 min in solution, λ_{max} increases according to the percentage of TCDT in the polymers and therefore the average length of the resulting polyene sequences in the copolymer. Since λ_{max} is found at relatively low energies, we conclude that **2a** and

Table 6. GPC and Yield Data for Poly(**2a**)$_n$ Prepared in Various Solvents Using Mo(CH-*t*-Bu)(NAr)(OR_{F6})$_2$ (**1a**) or Mo($CHCMe_2Ph$)(NAr)(OR_{F9})$_2$ (**1d**)

initiator	solvent	equiv	M_n[a]	M_w/M_n[a]	yield (%)
1a	THF	20	7800	1.98[b]	81
1a	CH_2Cl_2	50	30 500	1.26	96
1a	C_6H_5Me	50	43 000	1.62[b]	96
1a	$C_6H_5CF_3$	50	35 700	1.39	95
1a	MeCN	50	36 300	1.32[b]	98
1a	C_6H_5Cl	50	38 800	1.49[b]	99
1d	CH_2Cl_2	50	48 300	1.48	96
1d	C_6H_5Me	50	27 800	1.50[b]	99

[a] Determined by GPC versus polystyrene standards. [b] A significant amount of double molecular weight material was present.

DCMNBD are polymerized at comparable rates with **1a** in DME. Therefore **2a**, TCDT, and DCMNBD are all polymerized at roughly equal rates when **1a** is employed as an initiator in DME.

Random copolymers containing **2a** and TCDT (poly[(TCDT)$_x$(**2a**)$_y$]; **6i**–**6o**, Table 11) were synthesized in high yield and had low polydispersities. As expected for random copolymers, UV/vis spectra of the polymers prior to heat treatment showed that λ_{max} decreases as the fraction of TCDT in the polymer increases. After heating these samples in solution, λ_{max} shifts dramatically to approximately the same low energy (~560 nm in THF; ~580 nm in MeCN), consistent with the retro-Diels–Alder reaction giving rise to a fully conjugated "hybrid" polyacetylene chain. When the chain contains a relatively high fraction of unsubstituted polyene sequences derived from TCDT, then the polymers are no longer readily soluble. The λ_{max} for these random copolymers approach that of poly(**2a**)$_{160}$ (Table 3) even though the copolymers were prepared from only 100 equiv of monomer. We speculate that unsubstituted polyene sequences must increase the average conjugation length of the polymer, perhaps by reducing steric interactions between substituents in the polymer formed from **2a**, and may also increase the total percentage of trans double bonds in the polymer.

Three random copolymers of TCDT and **2c**(+) that each contain a total of 50 equiv of the two monomers were prepared (Table 11). Preparation of these copolymers differed slightly from preparation of the random copolymers of TCDT and **2a** in that the monomer mixture was added to the initiator solution in two equal portions, the second portion being added only after the first had reacted completely. (Addition of the monomer mixture in one batch yielded polymer that contained a significant amount of double molecular weight material, according to GPC analysis; the reason for this molecular weight doubling is discussed below.) The values for λ_{max} before heating were significantly lower in energy than those measured for the random [(TCDT)$_x$(**2a**)$_y$] copolymers containing the same proportions of TCDT. For example, poly[(TCDT)$_{50}$(**2a**)$_{50}$] and poly[(TCDT)$_{25}$(**2c**(+))$_{25}$], both of which contain 50% TCDT, have λ_{max} at 434 and 552 nm, respectively. These results suggest that the "random" copolymers of TCDT and **2c**(+) actually contain largely uninterrupted sequences of poly(**2c**(+)); that is, they are virtually block copolymers. This circumstance can be ascribed to the relatively slow polymerization of **2c**(+), presumably for steric reasons. For the same reason a relatively slow intramolecular cyclization reaction results in the production of "dangling" acetylene groups, which explains why double molecular weight material was produced when the concentration of **2c**(+) was relatively high. TCDT polymerizes first in the presence of the slower reacting **2c**(+), which then reacts to produce the second block. Under these circumstances when the monomer mixture is added in two portions, the resulting polymers will be "blocky", i.e., ($\mathbf{A}_{x/2}$)($\mathbf{B}_{y/2}$)($\mathbf{A}_{x/2}$)($\mathbf{B}_{y/2}$), where **A** and **B** represent the two monomers (*x* and *y* equivalents, respectively). The regions between the "blocks" would consist of relatively random copolymer sequences.

Details of the heat treatment are also consistent with the blocky nature of the "random" copolymers **6p**–**6r**. DSC analysis of pure poly(TCDT) showed that two exotherms occur at ~70 and ~120 °C,[9] which correspond to the retro-Diels–Alder reaction and cis/trans isomerization, respectively. Heat treatment of poly[(TCDT)$_x$(**2c**(+))$_y$] samples at 85 °C for 10 min allows the retro-Diels–Alder reaction to proceed, which generates cis olefins initially,[26] but cis/trans isomerization is minimized. This procedure yielded polyenes that exhibited a λ_{max} at *higher* energy than the unheated samples. Heating those same polymers further at 125 °C for another 10 min effected cis/trans isomerization and yielded polyenes with longer average conjugation lengths, as before, demonstrating that a higher proportion of trans olefins is present. There is no change in λ_{max} after heating the homopolymer poly(**2a**)$_{40}$ to 125 °C.

Three block copolymers containing **2a** and TCDT were prepared. The first, poly(**2a**)$_{20}$poly(TCDT)$_{10}$, was prepared by the usual sequential addition of monomers (Table 11). Heat treatment of this block copolymer at 125 °C for 10 min to effect the retro-Diels–Alder reaction changed λ_{max} only slightly (538 nm in THF, 543 nm in MeCN), although the polymer did remain soluble. The other two block polymers, poly(TCDT)$_{10}$poly(**2a**)$_{20}$poly(TCDT)$_{10}$ and poly(TCDT)$_{10}$poly(**2c**(+))$_{20}$poly(TCDT)$_{10}$, were prepared by adding 20 equiv of **2a** (or **2c**(+)) to **1m** followed by 20 equiv of TCDT and finally termination with benzaldehyde.

Solution Electrochemistry of Poly(2a) and Poly(2c(−)). Solutions of poly(**2a**)$_n$ prepared using **1a** in DME were characterized by cyclic voltammetry in 0.1 M [Et_4N]AsF_6 / CH_3CN. The cyclic voltammogram of poly(**2a**)$_{20}$ at 100 mV/s exhibited a poorly defined anodic peak at 0.75 V in the potential range 0–1.2 V and a corresponding small return wave at 0.65 V. Voltammograms of solutions of poly(**2a**)$_5$ and poly(**2a**)$_{10}$ contained the same anodic features as that of poly(**2a**)$_{20}$, the only differences being slight shifts in peak positions. The voltammogram of a solution of poly(**2a**)$_{80}$ under the same conditions was broad and featureless. Some anodic deposition of polymer onto the electrode was observed when cycling between 0 and 1.25 V. The voltammogram of poly(**2c**(−))$_{20}$ in 0.1 M [*n*-Bu_4N]PF_6/CH_2Cl_2 showed only a very broad anodic feature with no discernible peaks.

Thin Film Electrochemistry of Poly(2(−)). We were unable to study the thin film electrochemistry of poly(**2a**) due to its solubility in most solvents that are suitable for electrochemistry. Poly(**2c**(−)), on the other hand, was insoluble in acetonitrile. Therefore we were able to characterize solution-cast thin films of these polymers by cyclic voltammetry in 0.1 M [*n*-Bu_4N]PF_6/CH_3CN. Films of poly(**2c**(−)) of various lengths exhibited a well-defined, sharp wave at 0.8 V. The cyclic voltammogram of a thin film of poly(**2c**(−))$_{40}$ is shown in Figure 9a. The oxidation peak at 0.85 V and the corresponding reduction peak at 0.8 V are sharp. In addition, the anodic peak current varies linearly with scan rate, as expected for a surface-confined electroactive species.[75] Scanning to 1.2 V results in an oxidation of the polymer and a loss of intensity on the return wave (Figure 9b). The voltammogram of poly(**2c**(−))$_{20}$ contains a similar sharp oxidation at 0.9 V and a corresponding reduction peak at 0.85 V. Scanning to 1.5 V causes the reduction peak to almost completely disappear. Several cycles to 1.5 V caused the film to become red and eventually turn colorless, suggesting that the polymer is decomposing or dissolving under these conditions.

UV/vis spectroelectrochemistry of thin films of poly(**2c**(−))$_{20}$ on indium-tin oxide/glass electrodes demonstrated that the peak at 534 nm which is present for the neutral polymer film disappears upon electrochemical oxidation to 1.0 V vs Ag in 0.1 M [*n*-Bu_4N]PF_6/CH_3CN (Figure 10), and at the same time a new

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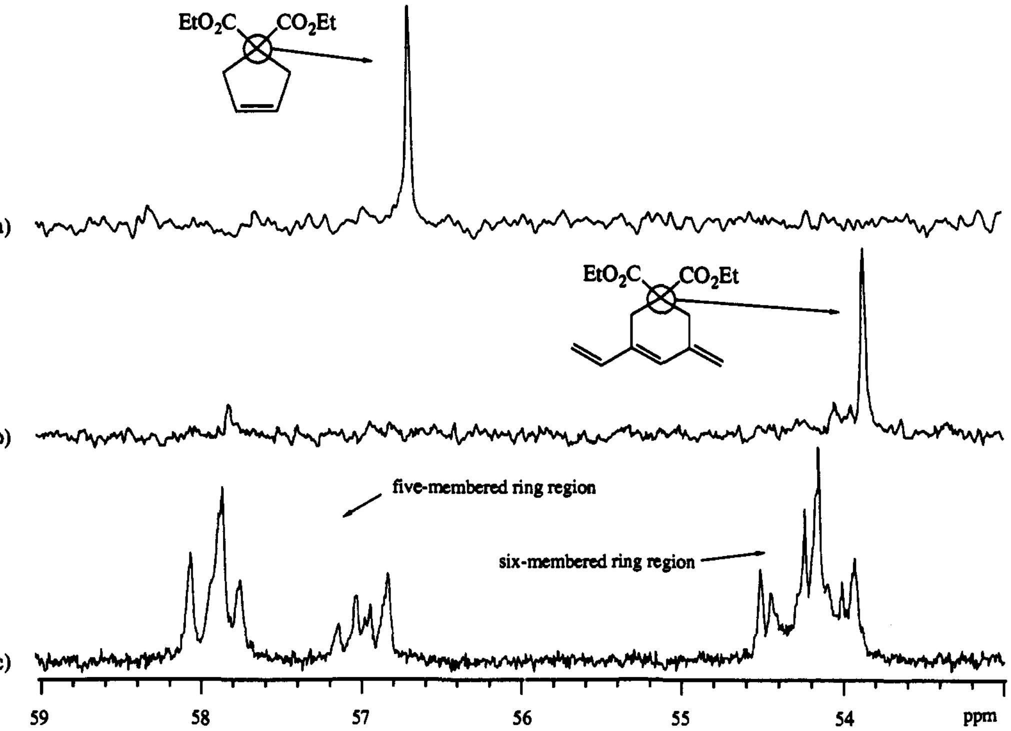

Figure 4. ^{13}C NMR spectra (125 MHz) of the quaternary carbons in ring compounds and poly(**2a**)$_{80}$: (a) the five-membered-ring model compound; (b) the six-membered-ring model compound; and (c) the five- and six-membered rings in poly(**2a**)$_{80}$.

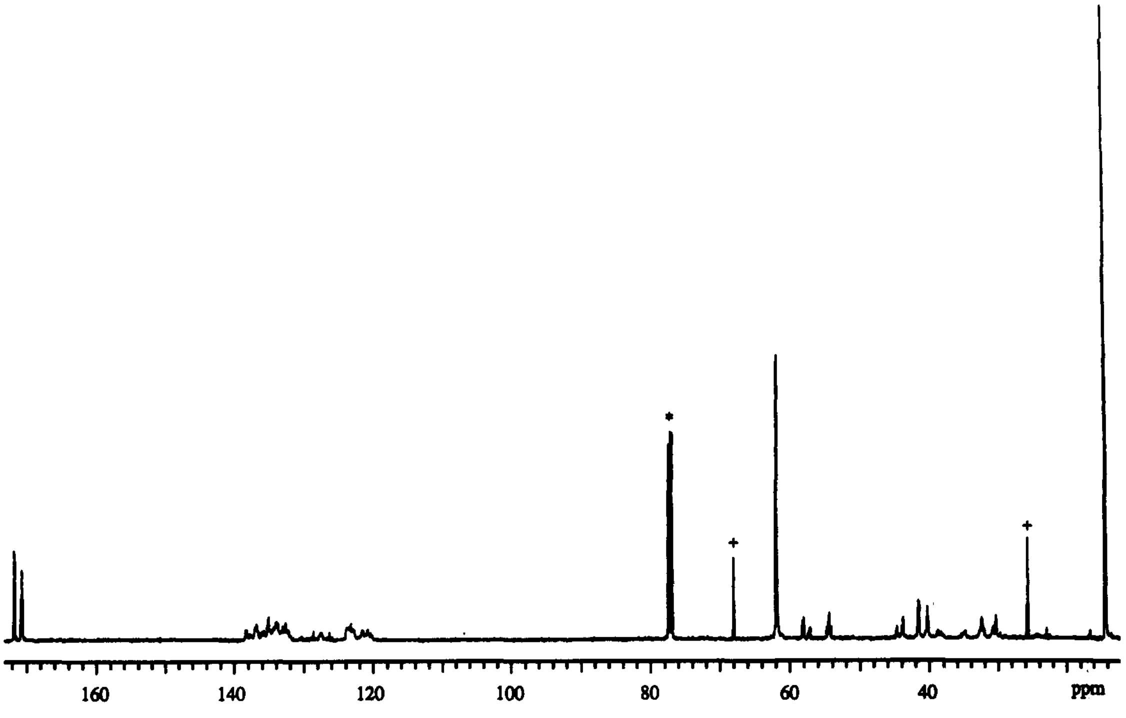

Figure 5. ^{13}C NMR spectrum (125 MHz) of poly(**2a**)$_{80}$ prepared using **1a** in DME (* denotes CDCl$_3$; + denotes residual THF).

absorption appears in the near-IR region. This potential is 100 mV more positive than the oxidation peak in the cyclic voltammogram of this polymer. When the polymer sample is returned to its neutral state (0 V vs Ag), the 534-nm band reappears, although the intensity is reduced. The observed changes in spectral properties are consistent with the absorption changes observed upon oxidative doping of polyacetylene[76] and substituted polyacetylenes.[77]

Microelectrode devices developed in these laboratories may be used for *in situ* potential dependent measurement of the conductivity of solution-cast polymer films. The method has been described previously for the measurement of the conductivities of polyacetylene films.[30] Using this technique, we measured the drain current (I_D) as a function of gate potential (V_G) for thin films of poly(**2c**(−))$_{20}$. The drain current flows between the "source" and "drain" microelectrodes when the sample is conducting due to the small applied drain voltage (V_D). Surprisingly, we found that the drain current was negligible over the potential range 0–1.2 V, implying that the conductivity of poly(**2c**(−))$_{20}$

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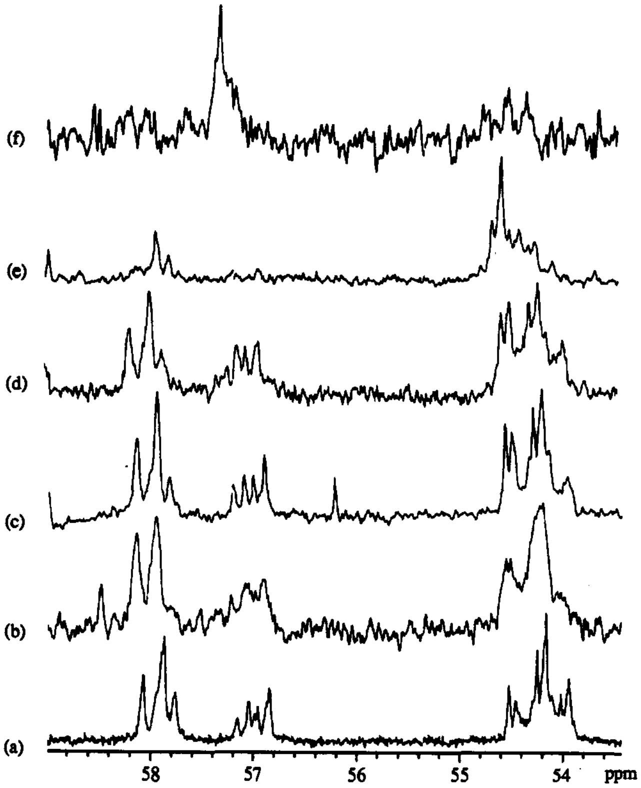

Figure 6. ^{13}C NMR spectra (125 MHz) showing the quaternary carbons in poly(**2a**) prepared using (a) $Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$; (b) $Mo(NAr')(CHCMe_2Ph)(OR_{F6})_2$; (c) $Mo(NAr)(CHCMe_2Ph)(OR_{F13})_2$; (d) $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_3)(OR_{F6})_2$; (e) Mo(*N*-1-adamantyl)$(CHCMe_2Ph)(OR_{F6})_2$ in DME; and (f) $MoCl_5/Sn(n\text{-}Bu)_4$ in 1,4-dioxane.

Table 7. Ring Compositions in Cyclopolymers Determined by ^{13}C NMR[a]

polymer	catalyst	solvent	5 rings	6 rings
poly(**2a**)$_{80}$	**1a**	DME	53(3)	47
poly(**2a**)$_{50}$	**1a**	CH_2Cl_2	51(1)	49
poly(**2a**)$_{50}$	**1a**	$C_6H_5CF_3$	44(3)	56
poly(**3**)$_{80}$	**1a**	DME	59(7)	41
poly(**4**)$_{40}$	**1a**	DME	60(2)	40
poly(**6**)$_{40}$	**1a**	DME	68(1)	32
poly(**2a**)$_{80}$	**1e**	DME	44(3)	56
poly(**2a**)$_{92}$	**1f**	DME	21(0)	79
poly(**2a**)$_{80}$	**1g**	DME	55(2)	45
poly(**2a**)$_{80}$	**1h**	DME	53(0)	47
poly(**2a**)[b]	$MoCl_5/(n\text{-}Bu)_4Sn$	dioxane	67(8)	33
poly(**2c**(+))$_{40}$[c]	**1f**	DME	45(4)	55
poly(**2c**(−))[d]	$MoCl_5/(n\text{-}Bu)_4Sn$	dioxane	80(3)	20

[a] All spectra were obtained at 25 °C in $CDCl_3$ at 125 MHz. The percentages of five- and six-membered rings were determined using carbonyl resonances in the region of 170–175 ppm and quaternary carbon resonances in the region of 50–60 ppm. The average is listed here and the difference between the two within parentheses. [b] $M_n = 103000$, $M_w/M_n = 2.24$ (versus polystyrene); $\lambda_{max} = 548$ nm (THF), 93% yield. [c] $M_n = 18200$, $M_w/M_n = 1.08$ (versus polystyrene); $\lambda_{max} = 564$ nm (THF), 89% yield. [d] $M_n = 151000$, $M_w/M_n = 2.41$ (versus polystyrene); $\lambda_{max} = 556, 594$ nm (THF), 96% yield.

over this potential region is very low ($\sigma < 10^{-6}\ \Omega^{-1}\ cm^{-1}$). This result is quite different from the conductivity of the analogous unsubstituted poly(TCDT)$_{20}$ ($\sigma = 3 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$).[30] The conductivities of other substituted polyacetylenes have been studied, and it has been observed that substituted polyacetylenes containing predominantly cis double bonds have conductivities 2–3 orders of magnitude lower than conductivities of comparable trans materials.[3,16] The extremely low conductivity observed in poly(**2c**(−))$_{20}$ might be ascribed to the presence of cis double bonds in the polymer backbone.

Table 8. GPC, UV/Vis, and Yield Data for Other Soluble Polyenes Prepared Using **1a** in DME

polymer	M_n[a]	M_w/M_n[a]	λ_{max} (nm)[b]	yield (%)
poly(**2b**)$_{20}$	9900	1.26	548 (544)[c]	100
poly(**2b**)$_{40}$	30 800	1.27	554 (548)	97
poly(**2b**)$_{80}$	50 000	1.29	554 (550)[d]	100
poly(**2c**(−))$_{20}$[e]	7110	1.21	544	100
poly(**2c**(+))$_{20}$	6990	1.26	540	93
poly(**2c**(+))$_{40}$	14 400	1.23	561	90
poly(**2d**)$_{20}$	9100	1.32	560	90
poly(**2d**)$_{40}$	26 600	1.20	564 (562)	80
poly(**3b**)$_{20}$	10 600	1.21	544	100
poly(**3c**)$_{20}$	10 300	1.25	548	96
poly(**3d**)$_{20}$	7700	2.21	538	94
poly(**4**)$_{50}$[f]	22 183[g]	1.91[h]	530 (538)	94
poly(**5b**)$_{20}$	16 100	1.20	550 (538)	100
poly(**5b**)$_{40}$	43 400	1.30	548 (526)	97

[a] Determined by GPC versus polystyrene standards. [b] In THF or acetonitrile (in parentheses). [c] $\lambda_{max} = 518$ nm in pentane. [d] $\epsilon_{max} = 14500$ $M^{-1}\ cm^{-1}$ in THF. [e] **1m** was used as the catalyst. [f] Poly(**4**)$_{50}$ prepared in THF. [g] In CH_2Cl_2. [h] Two peaks were observed by GPC.

Thin Film Electrochemistry of Copolymers. The copolymers prepared from **2c**(+) and TCDT (**6p**–**6r**; Table 11) were characterized by cyclic voltammetry on solution-cast thin films on Pt electrodes. Acetonitrile, in which the films were insoluble, was employed as the solvent. The voltammograms of films of **6r** (70% TCDT) and **6p** (50% TCDT), which had been heated to 125 °C for 10 min, are shown in Figures 11 and 12a, respectively. The anodic and cathodic features at 0.7 V for **6p** are broader than those observed for poly(**2c**(−))$_{20}$, but the separation between the anodic and cathodic peaks is still very small. As the content of TCDT is increased to 70% (**6r**), a shoulder appears at 0.9 V in the anodic scan and at 0.55 V on the return cycle (Figure 11). These shoulders are also evident in the voltammogram of **6q** (60% TCDT). Since these copolymers are more like block copolymers than random copolymers, it seems likely that long segments of unsubstituted polyacetylene may be electrochemically independent of the cyclopolymer segments and that these shoulders can be ascribed to electrochemistry of the polyacetylene sequences. (The cyclic voltammogram of poly(TCDT)$_{20}$ under identical conditions contains an anodic peak at 0.9 V and a corresponding reduction at 0.7 V with a shoulder at 0.55 V.) Random copolymers containing TCDT and **2a** also could be characterized in this manner; the cyclic voltammogram of polymer **6l** (50% TCDT; Table 11) is shown in Figure 12b. It is evident that the wave for **6l** is slightly broader than the wave for poly(**2c**(−))$_{20}$.

The potential dependent conductivities of copolymers **6j**, **6l**, **6p**, **6q**, **6r**, and **6u** were determined by recording the I_D–V_G plots[30] for thin films of these polymers. These are shown in Figure 12c for **6p** and in Figure 12d for **6l**. For each of the copolymers studied by electrochemistry, we were able to calculate the average conductivity at the potential where the I_D–V_G plot reaches a maximum; these data are included in Table 11. Several conclusions can be drawn from these data. First, the copolymers **6p**, **6q** and **6r** have conductivities in the $10^{-2}\ \Omega^{-1}\ cm^{-1}$ range, a value that could be expected for unsubstituted polyacetylene samples where the average chain is 20–30 double bonds in length.[30] Assuming the cyclopolymer segments contribute little to the overall conductivity—their homopolymers (e.g. poly(**2c**(−))$_{20}$) are poorly conducting—it seems likely that in **6p**–**6r** the polyacetylene block is roughly 25 double bonds in length, consistent with the blocky structure of these polymers. The average conductivity of **6u** was $3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$, a value that is slightly less than expected for 20 double bonds.[30] If the cyclopolymer block were contributing to the bulk conductivity, the measured conductivity would be greater than the observed value. For the copolymers **6j** and **6l**, in which the structure is more random, the conductivities are proportional to the TCDT content, consistent with short conducting unsubstituted polyene fragments interrupted by cyclopolymer fragments.

Table 9. GPC, UV/Vis, and Yield Data for Optically Active Polyenes, Poly(**2c**(−))$_n$, Prepared using **1m** in DME

polymer	M_n[a]	M_w/M_n[a]	$[\eta]$ (dL/g)[a]	λ_{max} (nm)[b]	ϵ_{max} (M^{-1} cm^{-1})[b]	N[c]	yield (%)
poly(**2c**(−))$_{5}$	4300	1.21	0.044	494	12 600	24	76
poly(**2c**(−))$_{10}$	6300	1.24	0.037	498	9900	33	99
poly(**2c**(−))$_{15}$	10 800	1.20	0.057	530	13 460	48	94
poly(**2c**(−))$_{20}$	12 300	1.19	0.077	546	11 100	59	100
poly(**2c**(−))$_{30}$	25 000	1.17	0.107	558	12 200	115	92
poly(**2c**(−))$_{40}$	27 200	1.17	0.138	560	18 300	124	96
poly(**2c**(−))$_{80}$	68 400	4.09	0.632	566	17 000	305	97

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In THF. [c] Average number of double bonds calculated from M_n.

Table 10. UV/Vis and CD Data for Optically Active Polymers Prepared Using **1a** in DME[a]

	UV/vis		CD	
polymer	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})[b]	$[\theta]$ (deg cm^2 $dmol^{-1}$)[b]	λ (nm)
poly(**2c**(−))$_{40}$	562	16 800	+4700	603
			+4500	575
			−3700	487
poly(**2c**(+))$_{40}$	558	15 700	−5900	566
poly(**2d**)$_{40}$	564	14 800	+2800	601
			+2500	581
			−7600	468

[a] All measurements were taken in THF. [b] Per monomer equivalent.

Discussion

There is abundant indirect evidence in the literature which suggests that the Mo or W initiators cyclopolymerize 1,6-heptadiyne derivatives via an "alkylidene mechanism", i.e., a mechanism in which the triple bond reacts with a M=C bond to give a metallacyclobutene intermediate, which then opens to give a vinyl alkylidene complex (Scheme 1).[37,46,47,53] Nevertheless, to our knowledge no identified and characterized alkylidene complex has been shown to be an initiator for the cyclopolymerization reaction. The results we have reported here substantiate the proposals that alkylidene complexes can be initiators for the cyclopolymerization of 1,6-heptadiyne derivatives. We demonstrated in previous work that the "alkylidene mechanism" for the living polymerization of 2-butyne[64] and acetylene itself[78] was operative in two systems that contained well-defined alkylidene complexes, although controlled living acetylene polymerization by well-defined initiators is still relatively rare. (Systems that contain "classical" metathesis-like catalysts have been shown to polymerize acetylenes, in some cases in a living fashion, probably via alkylidene catalysts.[13,57,79]) Potentially important advantages of controlled living cyclopolymerization reactions of the type reported here are greater tolerance of functionalities, control over the nature of the capping groups, and the ability to prepare block or random copolymers that contain other monomers that can be polymerized by these well-defined initiators. All of these potential advantages have been demonstrated here.

Since the mechanism of polymerization by the well-defined initiators reported here unfortunately is not clear, it is not yet possible to control the cyclopolymerization to the extent that some ROMP reactions of some norbornenes and norbornadienes now can be controlled.[80-83] Ideally we would like to prepare cyclopolymers that have only one size ring and cis/trans and head/tail regularity (when applicable). We believe that the ring size is controlled by the extent of α- addition versus β-addition of the acetylene to the alkylidene, the two modes that presumably give rise to five- and six-membered rings, respectively (Scheme 1). Some of the other uncertainties in catalyst systems of the type employed here are the rate at which alkylidene rotamers interconvert,[82,84] the extent to which the reactivities of the two alkylidene rotamers differ, and the degree of selective formation of one rotamer when a triple bond reacts with a Mo=C bond. From a practical perspective an important feature of the cyclopolymerization to give soluble conjugated polymers is to limit the number of "ordinary" or "monoinsertions" of a triple bond; such "dangling" triple bonds eventually serve to cross-link chains. Therefore intramolecular cyclization must be fast relative to ordinary intermolecular (linear) polymerization through one triple bond per monomer. Cyclization appears to be encouraged by the presence of at least one bulky group in the 4 position, and preferably two, but we are not certain to what extent this preference is linked to any given aspect of the polymerization mechanism. In any case the combination of DME as a coordinating solvent and an electrophilic metal catalyst appears to encourage cyclization.

One relatively surprising finding in this work is the high reactivity of a disubstituted alkylidene (Mo=C(Me)Ph) initiator. We were under the impression that addition of a terminal acetylene to give an α-substituted metallacyclobutene intermediate would be undesirable because such a species would be much *less* reactive than a primary vinyl alkylidene intermediate, perhaps so unreactive as to block further addition of an acetylene. The formation of a high percentage of five-membered rings by tail-to-tail cyclopolymerizations via α-substituted metallacyclobutene intermediates, in the classical systems as well as the well-defined systems described here, is further evidence that the disubstituted alkylidene intermediate is, in fact, surprisingly reactive. The reason for the high reactivity of disubstituted alkylidene complexes could be ascribed simply to a greater lability (for steric reasons) of coordinating solvents or functionalities; it is too early to say with any certainty.

Conductivities of doped 1,6-heptadiyne derivatives prepared with classical catalysts have been found to be low relative to the conductivity of doped polyacetylene. Our findings confirm that conductivities of 1,6-heptadiyne cyclopolymers are inherently much lower than conductivities of unsubstituted polyenes. That result should not be totally unexpected since it is believed that for high conductivity a highly delocalized form of the polymer, preferably trans/transoid in the case of an unsubstituted polyene, should be energetically accessible with minimal distortion of the polymer backbone. The presence of five- and six-membered rings containing bulky substituents enforces a conformation or conformations of the polymer backbone that have a significant degree of conjugation, but at the same time the rings probably severely limit accessibility of highly delocalized, extended excited states. Whether this type of restriction places limits on the nonlinear optical behavior of such materials is currently under investigation.[85]

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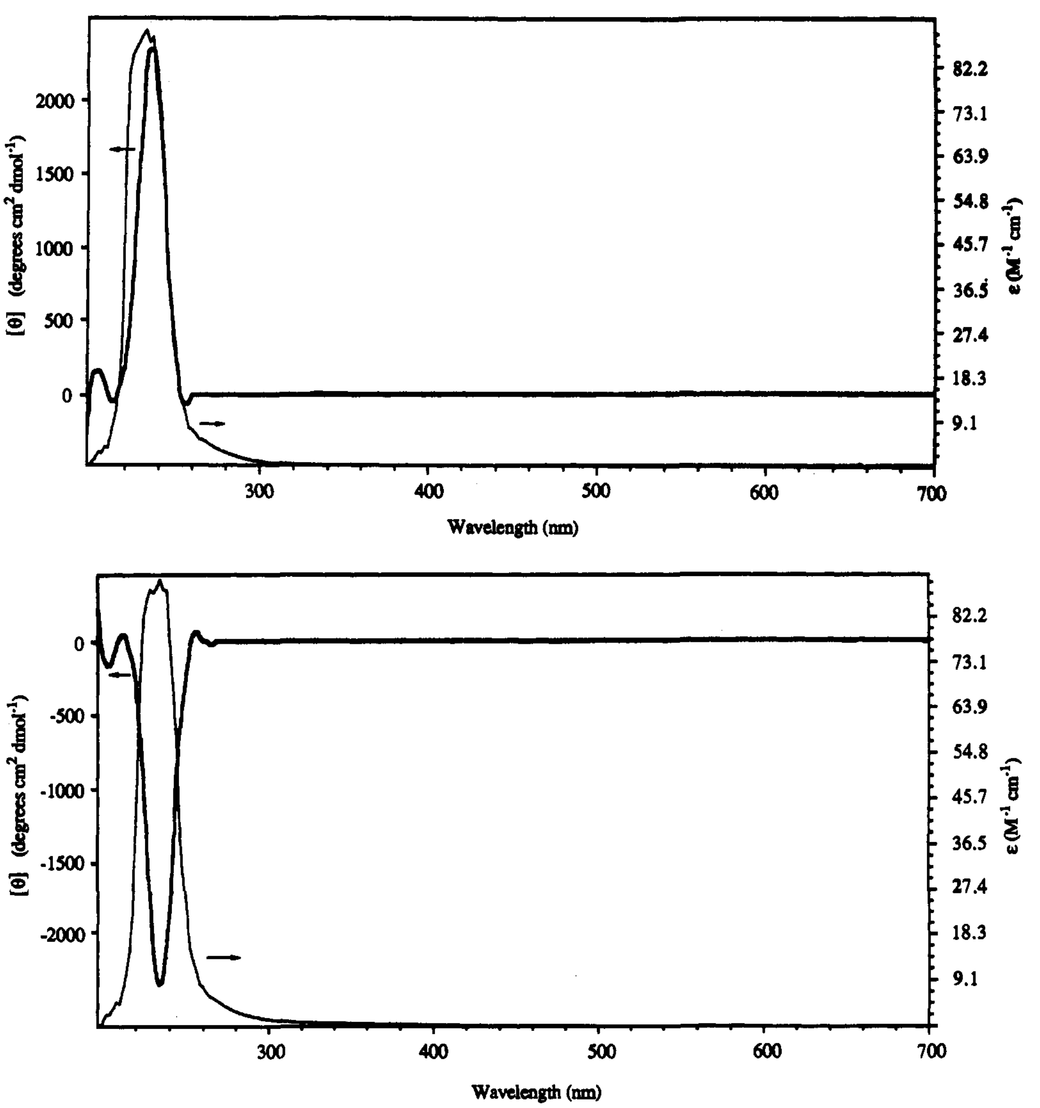

Figure 7. (a, top) CD and UV/vis spectra of di-(1*R*,2*S*,5*R*)-(−)-menthyl dipropargylmalonate (**2c**(−)). (b, bottom) CD and UV/vis spectra of di-(1*R*,2*S*,5*R*)-(+)-menthyl dipropargylmalonate (**2c**(+)).

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Silica gel and alumina were dried (at ~130 °C) in vacuo overnight. Pentane was washed with sulfuric/nitric acid (95:5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from Na/benzophenone under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene, α,α,α-trifluorotoluene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane, chlorobenzene, and acetonitrile were distilled from calcium hydride under nitrogen. Toluene used for polymerizations was stored over a Na/K alloy. Polymerization grade DME and THF were vacuum transferred a second time from Na/benzophenone. Acetonitrile for electrochemistry was Aldrich anhydrous grade; it was filtered through a plug of activated alumina before use. Benzene-d_6 and CD_2Cl_2 were sparged with argon and stored over molecular sieves (4 Å). DME-d_{10} was vacuum distilled from Na/benzophenone. Benzaldehyde was distilled and passed over alumina before use. $[n\text{-}Bu_4N]PF_6$ (Aldrich) was recrystallized from ethanol. $[Et_4N]AsF_6$ was prepared from $[Et_4N]Br$ and $LiAsF_6$ and was recrystallized from acetone/ethanol. Both electrolytes were dried in a vacuum oven overnight.

Gel permeation chromatography (GPC) was carried out using Shodex KF-802.5, 803, 804, 805, and 800P columns, a Knauer differential refractometer, and a Viscotek differential refractometer/viscometer H-500 on samples 0.1–0.3% w/v in THF which were filtered through a Millex-SR 0.5-μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from 1206 to 1.03 × 10⁶ MW. The GPC data were analyzed using Unical 4.03 (Viscotek). UV/vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer in the range 190–820 nm. CD spectra were obtained using an AVIV 62DS spectrometer at 25 °C. A Perkin-Elmer DSC-7 was used for determining the thermal properties of the polymers with a scan rate of 20 °C/min under N_2. Cyclic voltammetry and conductivity (I_D–V_G) measurements were carried out under inert atmosphere using a Pine RDE4 potentiostat. NMR data were obtained at 300 MHz (^1H) and 75.43 MHz (^{13}C; 125.7 MHz where noted) and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in hertz. Spectra were obtained in $CDCl_3$ at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

All chemicals used were reagent grade (Aldrich) and purified by ordinary methods.[86] 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene,[27] diethyl dipropargylmalonate,[87] 2,3-dicarbomethoxynorbornadiene,[88] $Mo(CHCMe_3)(NAr)(OR_{F6})_2$,[23] $Mo(NAr)(CHCMe_2Ph)(OR_{F3})_2$,[23] $W(NAr)(CHCMe_3)(OR_{F6})_2$,[22] $Mo(NAr)(CHCMe_2Ph)(OR_{F9})_2$,[58] $Mo(N\text{-}1\text{-adamantyl})(CHCMe_2Ph)(OR_{F6})_2$,[58] $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_3)(OR_{F6})_2$,[58] $Mo(NAr)(CHCMe_2Ph)(OR_{F13})_2$,[58] $Mo(NAr)(CHPh)(OR_{F6})_2$,[59] $Mo(NAr)[CH\text{-}4\text{-}C_6H_4(NMe_2)](OR_{F6})_2(DME)$,[59] $(DME)(OR_{F6})_2(NAr)Mo(CH)_6Mo(NAr)(OR_{F6})_2$-

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[85] Fox, H. H.; Ledoux, I.; Zyss. J.; Schrock, R. R. Submitted.

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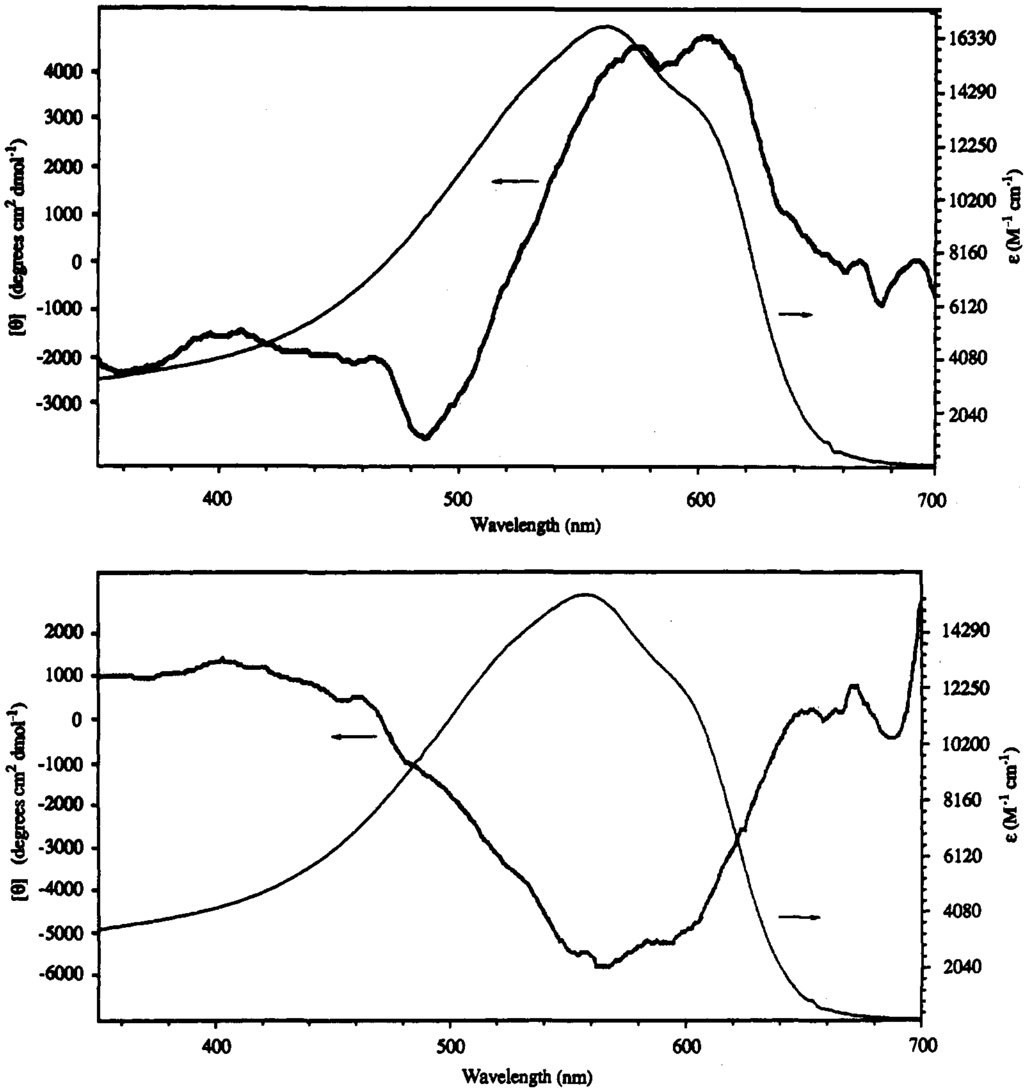
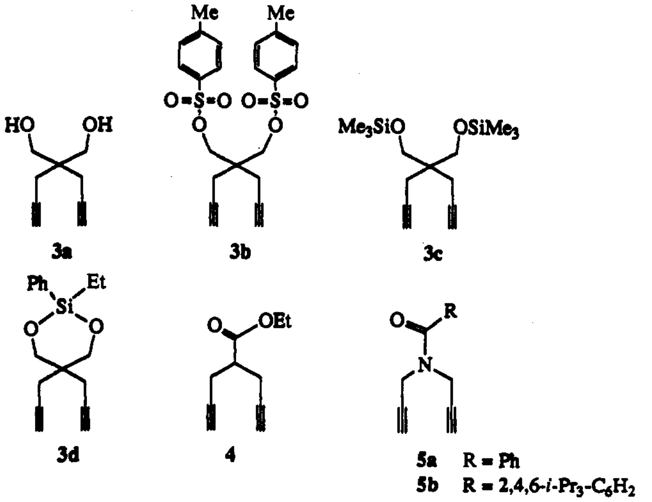


Figure 8. (a, top) CD and UV/vis spectra of poly(**2c**(−))$_{40}$ at 25 °C in THF. (b, bottom) CD and UV/vis spectra of poly(**2c**(+))$_{40}$ at 25 °C in THF.

Scheme 2



(DME),[59] 1,4-{(DME)(OR$_{F6}$)$_2$(NAr)MoCH}$_2$C$_6$H$_4$,[59] and dipropargyl ether[89] were prepared by literature methods.

Di-*tert*-butyl Malonate. Malonyl dichloride (5.05 g, 35.8 mmol) was dissolved in 150 mL of diethyl ether. An excess of *tert*-butyl alcohol (8.15 g, 109.9 mmol) was added. The solution was stirred at room temperature for 24 h. A saturated solution of sodium bicarbonate was added until gas evolution ceased. The layers were separated, and the aqueous layer was washed with 100 mL of diethyl ether. The organic phases were combined and were washed with 100 mL of water. The organic layer was dried over MgSO$_4$, and the volatile components were removed in vacuo. A pale yellow oil remained, which was pure by NMR and was used in the next step of the synthesis (6.57 g, 30.4 mmol, 85%): ^{1}H NMR δ 3.11 (s, 2, CH$_2$), 1.41 (s, 18, CMe$_3$); ^{13}C NMR δ 166.0 (s, CO), 81.4 (t, CH$_2$), 44.2 (s, *C*Me$_3$), 27.9 (q, C*Me*$_3$).

Di-*tert*-butyl Dipropargylmalonate (2b). Di-*tert*-butyl malonate (6.57 g, 30.4 mmol) was added over a period of 5 min to a suspension of NaH (1.46 g, 60.8 mmol) in 200 mL of THF. When bubbling ceased, propargyl bromide (80% in toluene) (9.03 g, 60.8 mmol) was added over 5 min. The solution was stirred for 16 h. Water (100 mL) and pentane (250 mL) were sequentially added to the reaction mixture. The layers were separated, and the aqueous layer was extracted with pentane (3 × 50 mL). The organic phases were combined, washed with water (100 mL), and dried over MgSO$_4$. The solvents were removed in vacuo to afford the product as a white crystalline solid (7.36 g, 25.2 mmol, 83%). The monomer was further purified by dissolving the solid in pentane, passing the solution through a column of Al$_2$O$_3$, and concentrating the solution for crystallization: ^{1}H NMR δ 2.82 (d, 4, $^4J_{CH}$ = 2.7, CH_2C≡CH), 1.97 (t, 2, $^4J_{CH}$ = 2.7, CH$_2$C≡C*H*), 1.41 (s, 18, CMe$_3$); ^{13}C NMR δ 167.7 (s, CO), 82.1 (s, *C*Me$_3$), 78.9 (d, J = 51, CH$_2$*C*≡CH), 71.3 (d, J = 249, CH$_2$C≡*C*H), 56.9 (s, C$_{quat}$), 27.7 (q, J = 127, C*Me*$_3$), 22.3 (t, J = 136, CH_2). HRMS calcd for C$_{17}$H$_{24}$O$_4$: M$^+$ + H, 293.1753. Found: 293.1751.

Di-(1*R*,2*S*,5*R*)-(−)-menthyl Malonate. (1*R*,2*S*,5*R*)-(−)-Menthol (23.86 g, 0.152 mol) was dissolved in 200 mL of diethyl ether containing 2 equiv of pyridine (12.3 mL. 0.304 mol), and the solution was cooled to 0 °C.

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[89] Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971; p 173.

Table 11. Data for Random and Block Copolymers

polymer		M_n[a]	M_w/M_n[a]	λ_{max} (nm)[b] no heat	85 °C	125 °C	σ (Ω^{-1} cm^{-1})[c]	yield (%)
poly(**2a**)$_{20}$poly(DCMNBD)$_{200}$	**6a**	48 000	1.09	548				98
poly(DCMNBD)$_{50}$poly(**2a**)$_{20}$	**6b**	30 100	1.14	546				95
poly[(DCMNBD)$_{70}$(**2a**)$_{30}$]	**6c**	28 700	1.10	378 (432, 358)				94
poly[(DCMNBD)$_{50}$(**2a**)$_{50}$]	**6d**	28 700	1.10	472 (438, 380)				96
poly[(DCMNBD)$_{30}$(**2a**)$_{70}$]	**6e**	29 800	1.12	504 (476)				95
poly[(TCDT)$_{20}$(DCMNBD)$_{80}$]	**6f**	30 200	1.10	342 (360, 326)		360 (438, 408)		99
poly[(TCDT)$_{30}$(DCMNBD)$_{70}$]	**6g**	39 600	1.12	342 (360, 326)		408 (362, 344)		91
poly[(TCDT)$_{40}$(DCMNBD)$_{60}$]	**6h**	32 300	1.13	340 (360, 326)		410 (364)		94
poly[(TCDT)$_{20}$(**2a**)$_{80}$]	**6i**	31 800	1.11	526		560 (582)		88
poly[(TCDT)$_{30}$(**2a**)$_{70}$]	**6j**	31 600	1.12	508		562 (582)	3×10^{-4}	92
poly[(TCDT)$_{40}$(**2a**)$_{60}$]	**6k**	27 600	1.09	476		564 (584)		94
poly[(TCDT)$_{50}$(**2a**)$_{50}$]	**6l**	35 400	1.11	434 (468, 380)		568 (582)	2×10^{-2}	89
poly[(TCDT)$_{60}$(**2a**)$_{40}$]	**6m**	30 400	1.12	430 (408, 380)		556 (580)		90
poly[(TCDT)$_{70}$(**2a**)$_{30}$]	**6n**	34 800	1.09	362 (408, 380)		insoluble		88
poly[(TCDT)$_{80}$(**2a**)$_{20}$]	**6o**	31 100	1.08	362 (406, 382)		insoluble		92
poly[(TCDT)$_{25}$(**2c**(+))$_{25}$]	**6p**	31 500	1.15	552	538	570	4×10^{-2}	96
poly[(TCDT)$_{30}$(**2c**(+))$_{20}$]	**6q**	29 100	1.12	546	534	570	6×10^{-2}	95
poly[(TCDT)$_{35}$(**2c**(+))$_{15}$]	**6r**	22 600	1.17	534	540	568	7×10^{-2}	96
poly(**2a**)$_{20}$poly(TCDT)$_{10}$	**6s**	65 400	1.20	544 (540)		538, 543		91
[poly(TCDT)$_{10}$]$_2$poly(**2a**)$_{20}$	**6t**	74 900	1.17	526		518		87
[poly(TCDT)$_{10}$]$_2$poly(**2c**(+))$_{20}$	**6u**	29 600	1.17	528		524	3×10^{-4}	89

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek) prior to heat treatment of the polymer. [b] In THF or acetonitrile (in parentheses). The UV/vis spectra were measured prior to heat treatment (no heat), after heating at 85 °C for 10 min, and after heating at 125 °C for 10 min. [c] Average maximum conductivity.

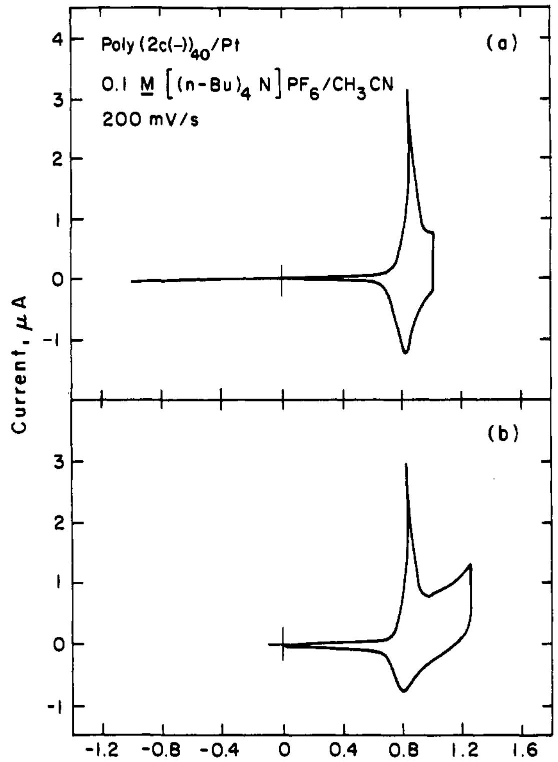


Figure 9. (a) Cyclic voltammogram of a thin film of poly(**2c**(−))$_{40}$ on a Pt electrode in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN from −1.0 to 1.0 V vs Ag. (b) Cyclic voltammogram of poly(**3**)$_{40}$ from 0 to 1.25 V.

Malonyl dichloride (10.7 g, 0.076 mol) was added dropwise to the solution. After stirring for 1 h, the solution was poured into ice water and the aqueous layer was extracted with ether (3 × 50 mL). The ether layers were combined and washed with 100 mL of brine. The ether layer was dried over Na$_2$SO$_4$. The solvent was removed in vacuo, and the product was crystallized from pentane at −80 °C (13.01 g, 0.034 mol, 45%): ^{1}H NMR δ 4.66 (dt, 2, CHO$_2$C), 3.25 (s, 2, CH$_2$(CO$_2$)$_2$), 1.96 (m, 2), 1.84 (d sept, 2, C*H*Me$_2$), 1.63 (m, 2), 1.59 (m, 2), 1.41 (m, 2), 1.31 (m, 2), 1.04 (m, 1), 1.01 (m, 1), 0.97 (m, 1), 0.92 (d, 1), 0.84 (d, 6, CH*Me*$_2$), 0.77 (m, 2), 0.70 (d, 6, CH*Me*$_2$); ^{13}C NMR δ 166.0 (CO), 75.3, 46.8, 42.25, 40.6, 34.1, 31.3, 26.0, 23.3, 21.9, 20.7, 16.2.

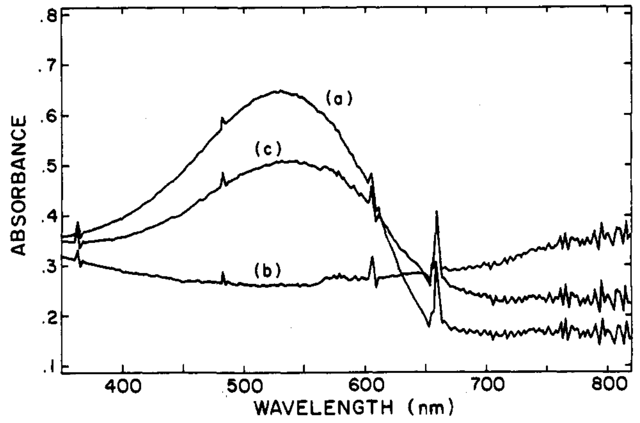


Figure 10. (a) UV/vis spectrum of a thin film of poly(**2c**(−))$_{20}$ on an indium–tin oxide electrode held at 0 V vs Ag in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN. (b) Same film held at 1.0 V. (c) Same film held at 0 V again.

Di-(1*R*,2*S*,5*R*)-(−)-menthyl Dipropargylmalonate (2c(−)). The diester (8.16 g, 0.0214 mol) was dissolved in THF (10 mL) and was added dropwise to a suspension of NaH (1.026 g, 0.0428 mol) in THF (100 mL). After 30 min, 1 equiv of propargyl bromide (80% in toluene) (2.5 mL, 0.0214 mol) was added and stirred. The second equivalent of propargyl bromide (2.5 mL) was added after an additional 30 min. The solution was then refluxed for 16 h. The solution was cooled to room temperature, and H$_2$O (100 mL) was added slowly. The THF layer was extracted with water (3 × 50 mL), and the aqueous fractions were then washed with diethyl ether (3 × 50 mL). The organic layers were combined, extracted with brine (100 mL), and dried over Na$_2$SO$_4$. The volatiles were removed in vacuo, and the product was crystallized from pentane to give 4.98 g (0.011 mol, 51%) of product in one crop: ^{1}H NMR (C$_6$D$_6$) δ 4.88 (dt, 2, RCHO), 3.32 (m, 4, C*H*$_2$C≡CH), 2.20–2.03 (m, 4, menthyl), 1.71 (t, 2, CH$_2$C≡C*H*), 1.51–1.04 (m, 8, menthyl), 0.98–0.56 (m, 24, menthyl); ^{13}C NMR (C$_6$D$_6$) δ 168.1 (CO), 79.0, 75.9, 72.1, 57.2, 47.2, 41.0, 34.3, 31.4, 25.9, 23.1, 23.0, 22.1, 21.0, 16.2. $[\alpha]^{25}_{D}$ (c = 0.1, THF) = −27.3; λ_{max} = 237 nm, ϵ = 90 M^{-1} cm^{-1}; [θ] = 2400 deg cm^2 mol^{-1} at λ = 237 nm. Anal. Calcd for C$_{29}$H$_{44}$O$_4$: C, 76.27; H, 9.71; N, 0.00. Found: C, 76.21; H, 9.38; N, 0.22.

Di-(1*S*,2*R*,5*S*)-(+)-menthyl Malonate. Malonyl dichloride (10.00 g, 71 mmol) was dissolved in 200 mL of diethyl ether. (1*S*,2*R*,5*S*)-(+)-Menthol (22.17 g, 142 mmol) was dissolved in 50 mL of ether. The solution containing the alcohol was added to the acid chloride solution at 0 °C over a period of 2 h. The solution was stirred for 12 h at room temperature. Saturated aqueous NaHCO$_3$ was added to the ether solution until bubbling ceased. The organic layer was extracted with water (3 ×

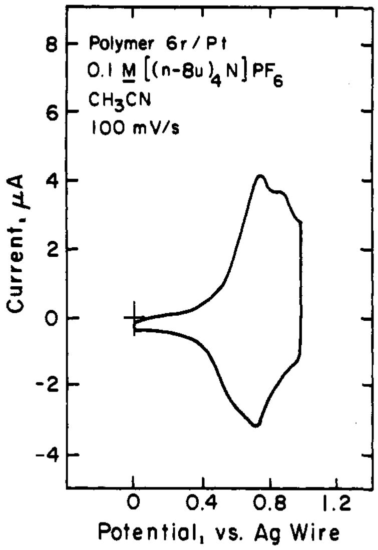


Figure 11. Cyclic voltammogram of a thin film of polymer **6r** on a Pt electrode in 0.1 M [n-Bu$_4$N]PF$_6$ / CH$_3$CN.

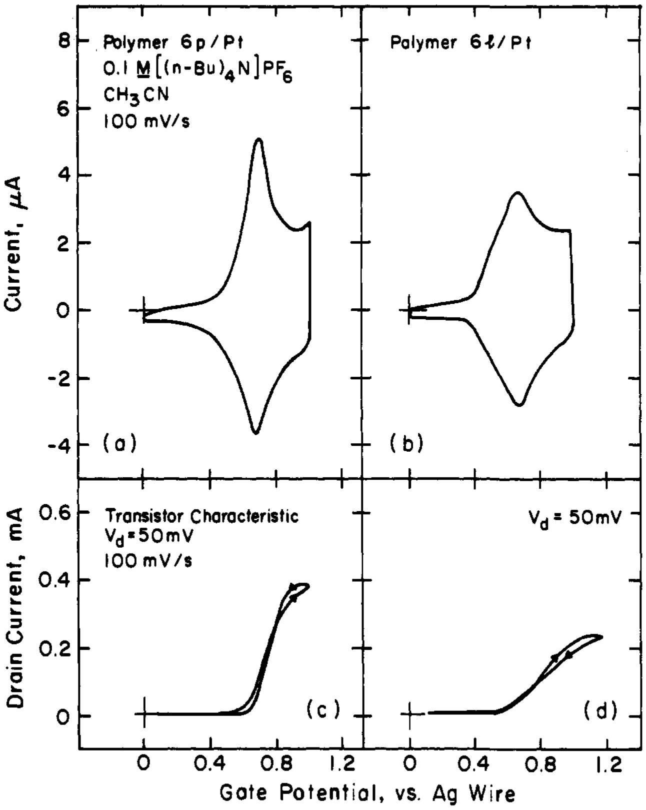


Figure 12. Cyclic voltammograms of copolymer films on Pt electrodes in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN: (a) polymer **6p**. (b) polymer **6l**. I_D–V_G characteristics for copolymer films on interdigitated Pt electrode arrays in 0.1 M [n-Bu$_4$N]PF$_6$/CH$_3$CN. (c) polymer **6p**. (d) polymer **6l**.

50 mL) and washed once with brine (100 mL). The organic fraction was dried over MgSO$_4$. The solution was filtered, and the ether was removed in vacuo. The solid product was crystallized from pentane at -80 °C as white cubes (20.01 g, 0.052 mol, 90%). The NMR data were identical to di-(1*S*,2*R*,5*S*)-(−)-menthyl malonate.

Di-(1*S*,2*R*,5*S*)-(+)-menthyl Dipropargylmalonate (2c(+)). The malonate (10.00 g, 26.3 mmol) was dissolved in 25 mL of dry THF. The solution was added over 30 min to a suspension of NaH (1.26 g, 52.6 mmol) in 200 mL of THF. After the evolution of H$_2$ ceased, propargyl bromide (6.25 g, 52.6 mmol) was added. Gas evolution began again. The solution was stirred for 12 h. Water was added (100 mL) and the organic layer was separated. The organic layer was washed with water and was dried over MgSO$_4$. The solvents were removed to afford a white solid. The product was recrystallized from pentane (9.63 g, 80%): ^{1}H NMR (CDCl$_3$) δ 4.69 (dt, 2, CHO$_2$C), 2.97 (d, 4, $^4J_{HH}$ = 2.6, $C\mathit{H}_2C\equiv CH$), 1.97 (t, 2, $^4J_{HH}$ = 2.6, $CH_2C\equiv C\mathit{H}$), 1.93 (m, 4), 1.67 (m, 2), 1.63 (m, 2), 1.41 (m, 2), 1.36 (m, 2), 0.98 (m, 4), 0.85 (d, 16, CH*Me*$_2$), 0.79 (m, 2), 0.69 (d, 6, CH*Me*$_2$); ^{13}C NMR (CDCl$_3$) δ 168.0 (s, CO), 78.7 (dt, J_{CH} = 50, 9.4, $CH_2\mathit{C}\equiv CH$), 76.1 (d, J = 147, $\mathit{C}H_2C\equiv CH$), 71.6 (d, J = 250, $CH_2C\equiv CH$), 56.7 (pent, J = 5.6, C$_{quat}$), 46.9 (d, J = 125), 40.6 (t, J = 128), 34.1 (t, J = 125), 31.3 (d, J = 125), 25.6 (d, J = 129), 22.9 (t, J = 132), 22.4 (t, J = 128), 21.9 (t), 20.9 (q, J = 124), 15.9 (q, J = 124). $[\alpha]^{25}{}_D$ (c = 0.1, THF) = +26.2; λ_{max} = 234 nm, ϵ = 90 M^{-1} cm^{-1}; $[\theta]$ = −2400 deg cm^2 mol^{-1} at λ = 238 nm.

Di-(1*R*)-*endo*-(+)-fenchyl Malonate. (1*R*)-*endo*-(+)-Fenchyl alcohol (4.38 g, 28.4 mmol) was dissolved in 40 mL of diethyl ether, and malonyl dichloride (2.00 g, 14.2 mmol) was added. After stirring overnight, the solution was neutralized by adding aqueous NaHCO$_3$ until bubbling ceased. The layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The organic fractions were combined and washed with water (50 mL). The organic layer was dried over MgSO$_4$ and filtered, and the solvents were removed in vacuo. A white solid was obtained (3.2 g, 8.5 mmol, 60%): ^{1}H NMR δ 4.35 (s, 2, CHO), 3.35 (s, 2, CH$_2$), 1.63 (m, 4), 1.51 (m, 2), 1.38 (m, 4), 1.14 (s, 2), 1.10 (s, 2), 1.04 (s, 6), 0.99 (s, 6), 0.74 (s, 6); ^{13}C NMR δ 166.7 (CO), 87.3, 48.2, 41.4, 41.3, 39.4, 29.6, 26.4, 25.7, 20.1, 20.0, 19.2.

Di-(1*R*)-*endo*-(+)-fenchyl Dipropargylmalonate (2d). Di-(1*R*)-*endo*-(+)-fenchyl malonate (3.20 g, 8.5 mmol) was added over 5 min to a suspension of NaH (410 mg, 17 mmol) in 50 mL of THF. After bubbling had ceased (~30 min), the propargyl bromide (80% toluene solution) (2.53 g, 17 mmol) was added. Bubbling resumed and continued for 30 min. The mixture was stirred for 16 h. Water (10 mL) was added slowly to the mixture. Additional water (100 mL) and diethyl ether (100 mL) were added. The layers were separated, and the organic layer was washed with water (50 mL). The organic layer was dried over MgSO$_4$. The solvents were removed in vacuo to give the white crystalline product (2.40 g, 4.9 mmol, 58%). The product was further purified by dissolving the solid in pentane, passing the solution through a short column of Al$_2$O$_3$, and concentrating the solution for recrystallization: ^{1}H NMR δ 4.40 (m, 2, CHO), 3.07 (m, 4, $C\mathit{H}_2C\equiv CH$), 2.01 (t, 2, $CH_2C\equiv C\mathit{H}$), 1.69 (m, 4), 1.67 (m, 2), 1.56 (m, 2), 1.43 (m, 2), 1.16 (m, 2), 1.06 (s, 6, Me), 1.04 (s, 6, Me), 1.03 (m, 2), 0.82 (s, 6, Me); ^{13}C NMR δ 168.9 (s, CO), 88.4 (d, J = 151, CHO), 79.2 (d, $^3J_{CH}$ = 52, $CH_2\mathit{C}\equiv CH$), 71.8 (d, $^1J_{CH}$ = 250, $CH_2C\equiv \mathit{C}H$), 57.4 (s, C$_{quat}$), 48.9, 48.2, 41.5, 39.7, 29.7, 26.7, 25.9, 23.0, 20.6, 19.6. $[\alpha]^{25}{}_D$ (c = 0.1 g/10 mL THF) = +20.8; λ_{max} = 238 nm, ϵ = 100 L mol^{-1} cm^{-1}; $[\theta]$ = 370 deg cm^2 mol^{-1} at λ = 233 nm, $[\theta]$ = −1700 deg cm^2 mol^{-1} at λ = 240 nm. HRMS calcd for $C_{29}H_{40}O_4$: M$^+$, 452.2927. Found: 452.2924.

4,4-Bis(hydroxymethyl)-1,6-heptadiyne (3a). Diethyl dipropargylmalonate (21.60 g, 91 mmol) was dissolved in 50 mL of diethyl ether. The solution was added dropwise over a period of 2 h to a suspension of LiAlH$_4$ (6.94 g, 184 mmol) in 200 mL of diethyl ether maintained at 0 °C with an ice water bath. The reaction mixture was stirred for an additional 12 h. Water was added to the gray suspension until it turned white and evolution of H$_2$ was complete (~10 mL). The mixture was filtered through Celite. The solution was dried over MgSO$_4$. The ether was removed in vacuo to yield a white solid that could be recrystallized from ether (11.60 g, 76.4 mmol, 84%): ^{1}H NMR δ 3.70 (s, 4, $C\mathit{H}_2OH$), 2.55 (br s, 2, $O\mathit{H}$), 2.34 (d, 4, $^4J_{HH}$ = 2.7, $C\mathit{H}_2C\equiv CH$), 2.02 (t, 2, $^4J_{HH}$ = 2.7, $CH_2C\equiv C\mathit{H}$); ^{13}C NMR δ 80.2 (d, J = 49.6, $CH_2\mathit{C}\equiv CH$), 71.1 (d, J = 248.6, $CH_2C\equiv \mathit{C}H$), 66.4 (t, J = 143, $\mathit{C}H_2OH$), 42.0 (s, C$_{quat}$), 21.7 (t, J = 132, $\mathit{C}H_2C\equiv CH$). HRMS calcd for $C_9H_{12}O_2$: M$^+$, 152.0837. Found: 152.0838.

4,4-Bis[[(*p*-tolylsulfonyl)oxy]methyl]-1,6-heptadiyne (3b). **3a** (1.20 g, 7.9 mmol) was dissolved in 50 mL of pyridine, and the solution was cooled to 0 °C. Tosyl chloride (2.98 g, 15.8 mmol) was added as a solid, and the solution was stirred for 16 h at room temperature. The mixture was poured into 200 mL of ice water. The water was extracted with ether (3 × 50 mL). The organic fraction was dried over MgSO$_4$. The ether was removed in vacuo to afford a pink solid, which was recrystallized from ether to afford a white crystalline product (3.20 g, 7.0 mmol, 88%): ^{1}H NMR δ 7.72 (d, 4, H$_o$), 7.34 (d, 2, H$_m$), 3.93 (s, 4, OCH$_2$), 2.42 (s, 6, Me), 2.27 (d. 4, $^4J_{HH}$ = 2.7, $C\mathit{H}_2C\equiv CH$), 1.84 (t, 2, $^4J_{HH}$ = 2.7, $CH_2C\equiv C\mathit{H}$); ^{13}C NMR δ 145.1 (s, C$_{ipso}$), 132.0 (s, C$_p$), 129.9 (d, J = 162, C$_o$), 128.0 (d, J = 166, C$_m$), 77.4 (d, J = 50, $CH_2\mathit{C}\equiv CH$), 72.2 (d, J = 249, $CH_2C\equiv \mathit{C}H$), 69.3 (t, J = 151, OCH$_2$), 40.7 (s, C$_{quat}$), 21.6 (q, J = 127, Me), 21.3 (t, J = 134, $\mathit{C}H_2C\equiv CH$). Anal. Calcd for $C_{23}H_{24}S_2O_6$: C, 59.98; H, 5.25; N 0.00. Found: C, 59.60; H. 5.33; N, 0.11.

4,4-Bis((trimethylsiloxy)methyl)-1,6-heptadiyne (3c). **3a** (2.00 g, 13 mmol) was dissolved in CH_2Cl_2, and triethylamine (2.93 g, 28.6 mmol) was added. The solution was cooled to –30 °C, and chlorotrimethylsilane (2.86 g, 26.3 mmol) was added as the solution warmed to room temperature. The mixture was stirred for 12 h. The volatile components were removed in vacuo, and the solid was extracted with 80 mL of diethyl ether. The suspension was filtered through Celite, and the ether was removed in vacuo. The oil was distilled (70–71 °C, 0.5 Torr) from CaH_2 to afford a colorless oil (2.80 g, 10.5 mmol, 81%): ^1H NMR δ 3.47 (s, 4, OCH_2), 2.25 (d, 4, $^4J_{HH} = 2.7$, $C\mathit{H}_2C{\equiv}CH$), 1.92 (t, 2, $^4J_{HH} = 2.7$, $CH_2C{\equiv}C\mathit{H}$), 0.06 (s, 18, $SiMe_3$); ^{13}C NMR δ 81.2 (dt, $J = 50$, 10.2, $CH_2\mathit{C}{\equiv}CH$), 70.2 (dt, $J = 247$, 4.2, $CH_2C{\equiv}\mathit{C}H$), 62.8 (t, $J = 142$, OCH_2), 42.8 (s, C_{quat}), 20.9 (t, $J = 133$, 3.7, $\mathit{C}H_2C{\equiv}CH$), –0.06 (q, $J = 119$, $SiMe_3$). HRMS calcd for $C_{15}H_{28}O_2Si_2$: $M^+ - H$, 295.1550. Found: 295.1548.

$Ph(Et)Si(OCH_2)_2C(CH_2C{\equiv}CH)_2$ (3d). **3a** (0.50 g, 3.3 mmol) was dissolved in CH_2Cl_2, and triethylamine (1.00 g, 7.2 mmol) was added. The solution was cooled to –30 °C, and phenylethyldichlorosilane (0.675 g, 3.3 mmol) was added as the mixture warmed to room temperature. The mixture was stirred for 12 h. The volatile components were removed in vacuo, and the solid was extracted with 40 mL of diethyl ether. The suspension was filtered through Celite, and the ether was removed in vacuo. The oil was distilled (114 °C, 0.5 Torr) from CaH_2 to afford a colorless oil (0.771 g, 2.7 mmol, 83%): ^1H NMR δ 7.61 (d, 2, H aryl), 7.41 (m, 3, H aryl), 4.01 (d, 2, OCH_2), 3.92 (d, 2, OCH_2), 2.65 (d, 2, $^4J_{HH} = 2.7$, $C\mathit{H}_2C{\equiv}CH$), 2.20 (d, 2, $^4J_{HH} = 2.7$, $C\mathit{H}_2C{\equiv}CH$), 2.07 (t, 1, $^4J_{HH} = 2.7$, $CH_2C{\equiv}C\mathit{H}$), 1.98 (t, 1, $^4J_{HH} = 2.7$, $CH_2C{\equiv}C\mathit{H}$), 1.02 (t, 3, $CH_2\mathit{Me}$), 0.85 (q, 3, CH_2Me); ^{13}C NMR δ 134.0 (d, C_o or C_m), 132.5 (s, C_{ipso}), 130.9 (d, C_p), 128.1 (d, C_o or C_m), 79.9 (d, $J = 50$, $CH_2\mathit{C}{\equiv}CH$), 78.8 (d, $J = 50$, $CH_2\mathit{C}{\equiv}CH$), 71.5 (d, $J = 247$, $CH_2C{\equiv}\mathit{C}H$), 71.3 (d, $J = 247$, $CH_2C{\equiv}\mathit{C}H$), 69.5 (t, OCH_2), 40.0 (s, C_{quat}), 22.3 (t, $\mathit{C}H_2C{\equiv}CH$), 21.8 (t, $\mathit{C}H_2C{\equiv}CH$), 5.9 (q, $CH_2\mathit{Me}$), 5.6 (t, $\mathit{C}H_2Me$). HRMS calcd for $C_{17}H_{21}O_2Si$: M^+, 284.1233. Found: 284.1233.

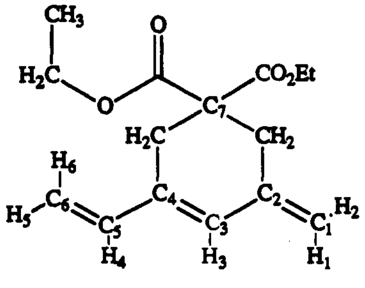
4-(Carboxyethyl)-1,6-heptadiyne (4). The method of Krapcho *et al.*[90] was modified. A solution of **1** (20.0 g, 84.7 mmol), H_2O (1.41 mL, 84.7 mmol), and LiCl (7.04 g, 169 mmol) in DMSO (141 mL) was heated to reflux under argon. The initially clear solution gradually became brown and turbid. After 5 h, the solution was cooled and partitioned between 400 mL of water and 200 mL of hexane. Extraction of the aqueous phase with 2 × 200 mL of hexane followed. The combined hexane phases were dried over $MgSO_4$ and evaporated to leave 98% of crude product. This was distilled, and the fraction boiling at 74–76 °C (0.5 Torr) was collected (11.4 g, 69.5 mmol, 82%): ^1H NMR (acetone-d_6) δ 4.15 (q, 2, $OC\mathit{H}_2Me$), 2.71 (m, 1, CH), 2.59 (dd, 4, $C\mathit{H}_2C{\equiv}CH$), 2.45 (t, 2, $CH_2C{\equiv}C\mathit{H}$), 1.23 (t, 3, $CH_2\mathit{Me}$); ^{13}C NMR δ 172.1 (CO), 80.4 ($CH_2\mathit{C}{\equiv}CH$), 70.4 ($CH_2C{\equiv}\mathit{C}H$), 60.9, 43.0, 19.8, 14.1. HRMS calcd for $C_{10}H_{12}O_2$: $M^+ - H$, 163.0759. Found: 163.0760.

***N,N*-Dipropargylbenzamide (5a).** Dipropargylamine (1.00 g, 10.7 mmol) and 3 mL of triethylamine were dissolved in 10 mL of CH_2Cl_2. A solution of benzoyl chloride (1.51 g, 10.7 mmol) in 5 mL of CH_2Cl_2 was added dropwise over 15 min. The solution was stirred for 16 h. The volatile components were removed in vacuo, and the remaining solid was extracted with diethyl ether. The diethyl ether was removed in vacuo to give a pale yellow oil. The oil was distilled (122 °C, 0.5 Torr), the distillate dissolved in ether/pentane (1:1), and the solution cooled to –40 °C. A white crystalline product was obtained (1.03 g, 5.2 mmol, 49%): ^1H NMR δ 7.51 (d, 2, H_o), 7.39 (m, 3, H_m and H_p), 4.29 (br, 4, $C\mathit{H}_2C{\equiv}CH$), 2.29 (br, 2, $CH_2C{\equiv}C\mathit{H}$); ^{13}C NMR δ 170.6 (CO), 134.6 (C_{ipso}), 130.3 (C_p), 128.4 (C_o), 127.0 (C_m), 78.0 ($CH_2\mathit{C}{\equiv}CH$), 72.8 ($CH_2C{\equiv}\mathit{C}H$), 37.4 ($\mathit{C}H_2C{\equiv}CH$), 34.2 ($\mathit{C}H_2C{\equiv}CH$). HRMS calcd for $C_{13}H_{11}NO$: M^+, 197.0841. Found: 197.0842.

***N,N*-Dipropargyl-2,4,6-triisopropylbenzamide (5b).** 2,4,6-Triisopropylbenzoyl chloride (3.08 g, 11.5 mmol) was dissolved in 50 mL of CH_2Cl_2. A solution of dipropargylamine (1.08 g, 11.6 mmol) and 5 mL of triethylamine in 10 mL of CH_2Cl_2 was added. The solution was stirred for 36 h. The volatile components were removed in vacuo. The remaining solid was extracted with pentane (80 mL) and the mixture filtered through Celite. The product was crystallized from pentane at –30 °C (1.97 g, 6.0 mmol, 52%): ^1H NMR δ 6.98 (s, 2, H_m), 4.56 (d, 2, $^4J_{HH} = 2.4$, $C\mathit{H}_2C{\equiv}CH$), 4.01 (d, 2, $^4J_{HH} = 2.4$, $C\mathit{H}_2C{\equiv}CH$), 2.86 (sept, 1, $C\mathit{H}Me_2$), 2.77 (sept, 2, $C\mathit{H}Me_2$), 2.26 (t, 1, $^4J_{HH} = 2.4$, $CH_2C{\equiv}C\mathit{H}$), 2.24 (t, 1, $^4J_{HH} = 2.4$, $CH_2C{\equiv}C\mathit{H}$), 1.22 (d, 6, $CH\mathit{Me}_2$), 1.21 (d, 6, $CH\mathit{Me}_2$), 1.18 (d, 6, $CH\mathit{Me}_2$); ^{13}C NMR δ 170.3 (s, CO), 149.9 (s, C_{ipso}), 144.7 (s, C_o), 130.3 (s, C_p), 121.3 (d, $J = 154$, C_m), 77.9 (d, $^2J_{CH} = 51$, $CH_2\mathit{C}{\equiv}CH$), 77.5 (d, $^2J_{CH} = 51$, $CH_2\mathit{C}{\equiv}CH$), 73.4 (d, $J = 251$, $CH_2C{\equiv}\mathit{C}H$), 71.9 (d, $J = 251$, $CH_2C{\equiv}\mathit{C}H$), 37.4 (t, $J = 140$, $\mathit{C}H_2C{\equiv}CH$), 34.3 (d, $J = 124$, $\mathit{C}HMe_2$), 32.1 (t, $J = 140$, $\mathit{C}H_2C{\equiv}CH$), 30.9 (d, $J = 124$, $\mathit{C}HMe_2$), 25.1 (q, $J = 128$, $CH\mathit{Me}_2$), 23.9 (q, $J = 128$, $CH\mathit{Me}_2$), 23.4 (q, $J = 128$, $CH\mathit{Me}_2$). HRMS calcd for $C_{22}H_{29}NO$: M^+, 323.2249. Found: 323.2248.

Mo[1-methylidene-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene]-(NAr)(OR_{F6})$_2$. **1a** (45 mg, 0.064 mmol) was dissolved in DME, and 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene (17 mg, 0.064 mmol) was added. The solution was stirred for 24 h. The solvent was removed in vacuo, affording a dark red-brown product. The product was recrystallized from pentane at –40 °C to give dark red crystals (8 mg, 0.008 mmol, 14%). The ^1H NMR is partially assigned: ^1H NMR (CD_2Cl_2) δ 12.44 (s, 1, $MoC\mathit{H}R$), 5.72 (s, 1, H_γ), 4.96 (d, 1, H_ϵ), 4.81 (d, 1, $H_{\epsilon'}$), 3.56 (sept, 2, $C\mathit{H}Me_2$), 2.90 (s, 2, CH_2), 2.68 (s, 2, CH_2), 1.19 (d, 12, $CH\mathit{Me}_2$).

1-Vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene. **1a** (100 mg, 0.142 mmol) was dissolved in 5 mL of DME. Ethylene was loaded in a 60-mL syringe and was bubbled through the solution while stirring as a solution of **2a** (200 mg, 0.846 mmol) in 1 mL of DME was added over 5 min. The solution turned red. Immediately after the addition was complete, the DME was removed in vacuo. The solid residue was extracted with pentane, and the mixture was filtered through Celite. The pentane was removed in vacuo, affording the product as an orange solid (126 mg, 0.09 mmol, 62%): ^1H NMR δ 6.30 (dd, 1, $J = 11.1$, 17.4, H_4), 6.02 (s, 1, H_3), 5.22 (d, 1, $J = 17.4$, H_6), 4.97 (d, 1, $J = 11.1$, H_5), 4.93 (s, 1, H_1 or H_2), 4.91 (s, 1, H_1 or H_2), 3.91 (q, 2, OCH_2), 3.90 (q, 2, OCH_2), 3.02 (s, 2, CH_2), 2.96 (s, 2, CH_2), 0.86 (t, 6, CH_3); ^{13}C NMR δ 170.7 (s, CO), 139.6 (s, C_4 or C_2), 138.2 (d, C_5), 135.3 (s, C_4 or C_2), 129.3 (d, C_3), 114.4 (t, C_6 or C_1), 113.6 (t, C_6 or C_1), 61.4 (t, OCH_2), 53.9 (C_7), 35.7 (t, CH_2), 29.6 (t, CH_2), 13.9 (q, CH_3).



$Mo(NAr)[C(Me)Ph](OR_{F6})_2$. **1a** (290 mg, 0.412 mmol) was dissolved in 2 mL of α-methylstyrene in the presence of 250 μL of DME. After 12 h, the α-methylstyrene and DME were removed in vacuo, leaving a red solid. The product was recrystallized from pentane (2 mL) at –30 °C, affording red crystals (235 mg, 0.317 mmol, 77%): ^1H NMR (CD_2Cl_2) δ 7.30–7.03 (m, 8, H_{aryl}), 3.56 (s, 3, Me), 3.53 (sept, 2, $C\mathit{H}Me_2$), 1.54 (s, 6, $OCMe(CF_3)_2$), 1.05 (d, 12, $CH\mathit{Me}_2$); ^{13}C NMR (CD_2Cl_2) δ 285.8 (s, $Mo\mathit{C}(Me)Ph$), 153.1 (s, C_{ipso} NAr), 148.6 (s, C_{ipso} Ph), 147.8 (s, C_o NAr), 129.1 (d, $J = 161$, C_p NAr), 128.7 (d, $J = 158$, C_o Ph), 128.2 (d, $J = 159$, C_p Ph), 126.8 (d, $J = 160$, C_m Ph), 124.0 (q, $^1J_{CF} = 288$, CF_3), 123.6 (d, $J = 159$, C_m Ph), 82.2 (sept, $^3J_{CF} = 30$, $O\mathit{C}Me(CF_3)_2$), 28.9 (d, $J = 130$, $\mathit{C}HMe_2$), 23.6 (q, $J = 126$, $CH\mathit{Me}_2$), 21.6 (q, $J = 129$, $MoC(\mathit{Me})Ph$), 20.1 (q, $J = 131$, $OC\mathit{Me}(CF_3)_2$). Anal. Calcd for $MoC_{28}H_{31}NF_{12}O_2$: C, 45.60; H, 4.24; N 1.90. Found: C, 45.92; H, 4.57; N, 1.89.

4,4-Bis(carboxyethyl)cyclopent-1-ene. The compound was prepared as reported in the literature:[61] ^1H NMR δ 5.24 (m, 2, H olefinic), 4.19 (q, 4, OCH_2), 2.73 (m, 2, CH_2), 2.43 (m, 2, CH_2), 1.24 (t, 6, Me); ^{13}C NMR δ 170.7 (s, CO), 127.7 (d, C olefinic), 61.5 (t, OCH_2), 56.7 (s, C quaternary), 29.9 (t, CH_2 allylic), 14.1 (q, Me).

Synthesis of Polyenes. In a representative synthesis of poly(**2a**), **1a** (28 mg, 0.04 mmol) was dissolved in 10 mL of DME that had been distilled twice from sodium benzophenone ketyl under dinitrogen. A solution of **2a** (186 mg, 0.79 mmol) in 1 mL of DME was added all at once to the stirring solution. After 60 min, benzaldehyde (8 μL, 0.08 mmol) was added, and the reaction mixture was stirred an additional 60 min. The mixture was concentrated to ~2 mL, and the polymer was precipitated by dropwise addition of the solution to 80 mL of pentane

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[90] Krapcho, A. P.; Weimaster, J. F.; Eldridge. J. M.; Jahngen. E. G. E., Jr.; Lovey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138.

under an inert atmosphere. The polymer was collected by filtration and dried in vacuo overnight to yield a dark purple solid (192 mg, 100%).

Polymerizations of **2a** with **1m** were all performed in one day with the same batch of solvent, **1m**, benzaldehyde, and **2a**. Monomer **2a** had been recrystallized at least three times in the drybox from pentane; each time the solution was passed through a column of activated alumina. Initiator **1m** had been recrystallized several times and was weighed out (~20 mg) for each polymerization. Molecular weights were determined twice by viscometry for each polymer; the average values of M_n, M_w, and M_w/M_n are reported in Table 3.

More polar polymers were precipitated in pentane, and more nonpolar polymers were precipitated in MeCN. Poly(**2c**(−)) was soluble in all common organic solvents and was purified by passing a THF solution through a short column of Al_2O_3. The polymer was always handled under an inert atmosphere. Polymerizations employing the other initiators or different monomer/initiator ratios were carried out under similar conditions. The polymerization time was maintained at a minimum of 1 h and was increased appropriately as the number of equivalents of monomer increased. When the number of equivalents of monomer was greater than 40, the initiator concentration was diluted by a factor of 4 to minimize intermolecular chain linking reactions. When bulky monomers (**2b**, **2c**(−), **2c**(+), or **2d**) were employed, the polymerization was noticeably slower; 20 equiv of monomer was given 2.5 h to reach complete conversion to polymer. Otherwise, polymerizations of different monomers were conducted as directed in this procedure. Polymerizations using the classical catalyst were conducted as specified in the literature.[49]

NMR of Poly(2a)$_{80}$. ^{1}H NMR (300 MHz) δ 6.9–5.9 (br m, 1, olefinic H), 4.2 (br m, 2, OCH_2Me), 3.7–2.8 (br m, 2, CH_2 allylic), 1.2 (br m, 3, OCH_2*Me*); ^{13}C NMR (125.7 MHz) δ 172.0, 170.8 (CO); 138.4, 136.8, 135.1, 134.2, 133.9, 132.6, 124.0, 120.9 (C olefinic); 61.7 (O*C*H_2Me); 58.0, 54.3 (m, C quaternary); 43.8, 41.4, 40.1, 32.3, 30.2 (C allylic); 14.1 (OCH_2*Me*).

Preparation of 2a/DCMNBD Block Copolymers. **1a** (7 mg, 0.01 mmol) was dissolved in 8 mL of DME. A solution of **2a** (47 mg, 0.20 mmol) in 1 mL of DME was added all at once to the stirring solution. After 60 min, 2,3-dicarbomethoxynorbornadiene (417 mg, 2.0 mmol) in 1 mL of DME was added all at once. After 30 min, benzaldehyde (2 μL, 0.02 mmol) was added, and the reaction mixture was stirred an additional 60 min. The mixture was concentrated to ~2 mL and was added dropwise to 80 mL of pentane to precipitate the polymer. The polymer was collected by filtration and dried in vacuo overnight to yield a dark purple solid (453 mg, 98%). The block copolymer prepared in the opposite order (**2a** in the second block) was prepared in an analogous manner, employing only 50 equiv of 2,3-dicarbomethoxynorbornadiene in the first block.

Block Copolymer 2a/TCDT (20:10). **1a** (20 mg, 0.0284 mmol) was dissolved in 8 mL of DME. **2a** (134 mg, 0.568 mmol) dissolved in 1 mL of DME was added to the well stirred solution. After 90 min, the TCDT (75 mg, 0.284 mmol) in 1 mL of DME was added. After a further 50 min the polymerization was terminated with benzaldehyde (30 mg, 0.284 mmol) and the polymer isolated after 20 min by precipitation into pentane (191 mg, 91%).

Triblock Copolymer TCDT/2a/TCDT (10:20:10). **1a** (20 mg, 0.012 mmol) was dissolved in 8 mL of DME. **2a** (57 mg, 0.24 mmol) in 1 mL of DME was added. This was followed after 1 h by TCDT (64 mg, 0.24 mmol) in 1 mL of DME. Stirring was continued for a further 50 min, polymerization was then terminated with benzaldehyde (13 mg, 0.12 mmol), and the polymer was isolated after 20 min by precipitation into pentane (112 mg, 93%).

Random Copolymerizations. These polymerizations were carried out in a standard manner. The preparation of polymer **6l** (Table 11) (50% TCDT/50% **2a**) is given as an example. **1a** (10 mg, 0.014 mmol) was dissolved in 4 mL of DME. TCDT (189 mg, 0.710 mmol) and **2a** (167 mg, 0.710 mmol) were dissolved in 1 mL of DME. The monomer solution was added in one portion to the well stirred initiator solution. After 90 min the polymerization was terminated by addition of benzaldehyde (15 mg, 0.14 mmol), and after 20 min the polymer was isolated by precipitation in pentane to yield, after drying, 325 mg (91%) of a dark brown powder.

The three random copolymers poly[(TCDT)$_x$(**2c**(+))$_y$] were prepared in an analagous manner except that the monomer solution was added in two portions, the second being added 2.5 h after the first.

Electrochemistry. Solution cyclic voltammetry was carried out using a Pt dot working electrode, a Pt mesh counter electrode, and an oxidized silver wire as the quasi-reference electrode. The Pt dot was cleaned by cycling in 0.5 M H_2SO_4 between 1.2 and −0.25 V vs SCE as described previously.[91] Platinum microelectrode arrays for conductivity measurements and cyclic voltammetry of solution-cast thin films were fabricated and mounted as described previously.[92,93] Arrays were cleaned by etching for 10 s with a freshly prepared 3:1 concentrated H_2SO_4/30% H_2O_2 solution, followed by cycling in 0.5 M H_2SO_4 as described above.

Thin films of the polymers were cast from THF solutions directly onto the microfabricated array using a 0.5-μL micropipete. Conductivity measurements were carried out as described previously.[30] In all the experiments, electrodes 1 and 4 were designated "source" and 5 and 8 designated "drain".

The UV/vis spectroelectrochemistry was carried out in an air tight cell using a large Pt mesh counter electrode, oxidized silver wire quasi-reference, and a transparent indium doped tin oxide (Delta Technologies) working electrode.

Acknowledgment. R.R.S. thanks the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy (Contract DE-FG02-86ER13564) for support. M.S.W. thanks the National Science Foundation through the M. I. T. Materials Research Laboratory (NSF DMR 90 22933) for partial support of this research. M.O.W. thanks the Natural Sciences and Engineering Research Council of Canada for a predoctoral fellowship.

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