Macromolecules **1991,** *24,* 3489–3495

Preparation of Discrete Polyenes and Norbornene–Polyene Block Copolymers Using $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ as the Initiator

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Received November 13, 1990; Revised Manuscript Received January 22, 1991

ABSTRACT: Ring-opening metathesis polymerization of TCDT-$(CF_3)_2$ [7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene] by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-diisopropylphenyl) as a route to polyenes was found to be as controlled as polymerization employing $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$, while both TCDT-$H_2$ and TCDT-$(CO_2Me)_2$ gave low yields. Living polyenes could be formed in the Mo system from living poly-TCDT-$(CF_3)_2$ and were found to isomerize from the cis to the trans form at the first C=C bond next to the Mo=C bond. Rates of the retro-Diels–Alder reaction and the cis/trans isomerization in both the Mo and W systems were determined by NMR studies. The retro-Diels–Alder in the first unit next to the Mo=C bond takes place approximately 30 times faster than cis/trans isomerization. Living polyenes can be capped with triene dialdehydes to give relatively long polyenes under fairly mild conditions. Acetylene also can be polymerized by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ in a more controlled manner than by $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$, although the higher trans content in such polyenes contributes to their greater insolubility and/or tendency to cross-link, even when present as the center block in triblock copolymers containing polynorbornene.

Introduction

The synthesis of polymers by ring-opening metathesis of cyclic olefins has been known for some time,[1] but only relatively recently have well-defined catalysts for living polymerizations been perfected.[2,3] Complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (M = W or Mo, Ar = 2,6-diisopropylphenyl) have proven to be especially useful for cyclic olefins that have a relatively reactive double bond, e.g., norbornenes and 2,3-disubstituted norbornadienes,[3b,c] since the alkylidene at the end of the chain does not react readily with internal double bonds within the polymer chain. Polymers prepared with these catalysts can have polydispersities (M_w/M_n) as low as 1.05, and block copolymers can be prepared.[3a] An interesting application is the controlled polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (TCDT-$(CF_3)_2$) by $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ as a means of preparing di-*tert*-butyl-capped polyenes[4] or block copolymers containing polyenes and polynorbornene.[5] These reactions are controlled versions of the polymerization of TCDT-$(CF_3)_2$ by classical metathesis catalysts, an indirect means of preparing oriented polyacetylene.[6] $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ also has been used to polymerize acetylene directly to give polyenes and block copolymers containing polynorbornene.[7]

$Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ is now available in significant quantities in four high-yield steps.[8] In some circumstances it may be a more desirable initiator than $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ for two reasons; functionalities appear to be tolerated to a greater degree and intermediate $Mo(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$ species appear to be more stable.[9] We report here a study of $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ as an initiator for the synthesis of polyenes, either using TCDT-R_2 derivatives (R = H, CF_3, CO_2Me) or acetylene itself, as well as the synthesis of block copolymers containing polyenes and norbornene. A comparison of these results with those obtained by using the analogous tungsten catalyst reveals that in several respects the molybdenum catalyst is superior, at least as far as living characteristics are concerned, and therefore is preferred if the greatest control over the polymerization process is desired.

Results and Discussion

Synthesis of Polyenes. The general synthetic route for preparing polyenes from TCDT-R_2 derivatives is shown in Scheme I. Under ideal circumstances, addition of TCDT-R_2 to $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (M = Mo or W) yields living oligomers from which metal-free poly-TCDT-R_2 can be generated in a Wittig-like reaction with an aldehyde. Poly-TCDT-R_2 can be separated readily from $M(O)(NAr)(O\text{-}t\text{-}Bu)_2$, the initial metal-containing product of the Wittig reaction. ($M(O)(NAr)(O\text{-}t\text{-}Bu)_2$ decomposes, especially in concentrated solution, in an as yet undefined manner.) Heating poly-TCDT-R_2 induces a retro-Diels–Alder reaction that gives an *o*-xylene derivative (for R = H, benzene is formed) and di-*tert*-butyl-capped polyenes. Mixtures of polyenes can be analyzed by HPLC methods and individual polyenes of a given chain length can be isolated from the mixture by means of low-temperature column chromatography (at −40 °C on silica gel under a nitrogen atmosphere).[4] When pivaldehyde is used as the capping reagent, a distribution of polyenes containing an odd number of double bonds is formed. The distribution of chain lengths should be centered about chains containing $2n + 1$ double bonds when n equivalents of monomer are employed, if the rate of initiation and the rate of propagation are comparable.[10]

Three TCDT-R_2 monomers were polymerized by the molybdenum catalyst (R = H, CO_2Me, and CF_3). The time required to fully consume the monomer did not vary significantly as a function of R. Conversion of poly-TCDT-R_2 to the polyene mixtures could be monitored qualitatively by a change in color from a yellow-orange to a deep red (if longer polyenes are formed) and quantitatively by HPLC analysis. The temperature required for this conversion (in toluene) varied significantly with R. Poly-TCDT-H_2 was most easily converted to polyenes (90 °C for 2–3 min). Solutions of poly-TCDT-$(CF_3)_2$ required heating at 120 °C for approximately 3 min and solutions of poly-TCDT-$(CO_2Me)_2$ had to be heated to 120 °C for approximately 10 min. (Polyenes containing up to nine double bonds do not decompose to any significant extent under the harsher conditions.[4]) The retro-Diels–Alder rates show the same trend as reported by Feast and co-

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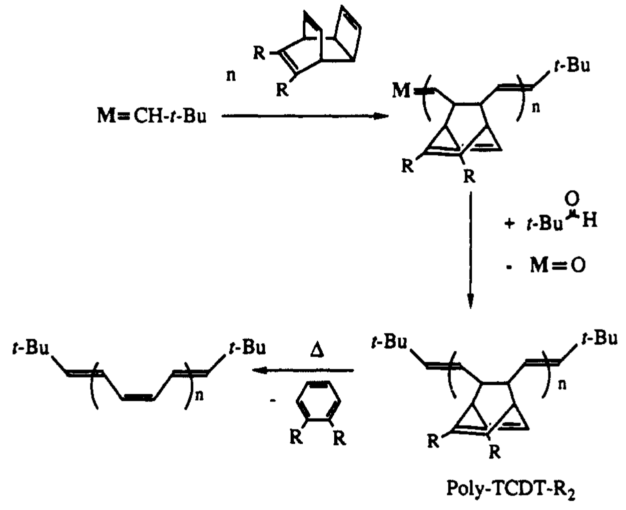
Scheme I



M = M(NAr)(O-*t*-Bu)$_2$
M = Mo or W
Ar = 2,6-diisopropylphenyl
R = CF$_3$, CO$_2$Me, H

Table I
Yields of Di-*tert*-butyl-Capped Polyenes in a Reaction Employing 4 equiv of Monomer and M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (M = Mo or W) as the Initiator[a]

	yield, %	
monomer	Mo	W
TCDT-H$_2$	35	25
TCDT-(CO$_2$Me)$_2$	70	
TCDT-(CF$_3$)$_2$	100	100

[a] Yields were determined by HPLC methods as described in the Experimental Section. The error is estimated to be ±5%.

workers in studies in which these monomers were polymerized by classical catalysts.[6] As shown in Table I, the total yields of polyenes obtained in reactions employing 4 equiv of TCDT-H$_2$ are low, somewhat lower with W than with Mo. A most likely explanation is that the 3,4 double bond in tricyclo[4.2.2.0]deca-3,7,9-triene is not the only C=C bond attacked by intermediate living alkylidene complexes. Either the 9,10 double bond or the 7,8 double bond could be attacked, a reaction that would lead to cross-linking and a decrease in the yield of the expected polyene. In either case the more active tungsten catalyst should be less successful than the molybdenum catalyst, as observed. The yield of polyenes from TCDT-(CO$_2$Me)$_2$ is also quite low compared to the yield from TCDT-(CF$_3$)$_2$. Since the molybdenum catalyst is known to tolerate ester functionalities,[3c,11] we believe that the problems associated with polymerizing TCDT-(CO$_2$Me)$_2$ by the Mo catalyst are related to the secondary metathesis processes described above for TCDT-H$_2$, even though the tetrasubstituted 7,8 double bond should not be attacked and the 9,10 double bond should be protected sterically to some extent by the carbomethoxy substituents. Polyene yields from either TCDT-H$_2$ or TCDT-(CO$_2$Me)$_2$ were not improved when THF was employed as the reaction solvent instead of toluene, a technique that has led to dramatically improved tolerance of functionalities such as a cyano group in norbornene monomers.[3c] Polymerization of TCDT-(CO$_2$Me)$_2$ by the tungsten catalyst was not attempted.

Polyenes were formed quantitatively when TCDT-(CF$_3$)$_2$ was employed with either the molybdenum or tungsten[4] catalyst. There was no evidence of the decomposition that complicated the reactions involving the two monomers already discussed. The yield and distribution of polyenes is the same when the reaction is carried out in THF instead of toluene. We propose that TCDT-(CF$_3$)$_2$ is successful largely because the CF$_3$ groups protect one side of the 9,10 double bond—the cyclobutene ring protects the other side of the 9,10 double bond—leaving only one side of the 3,4 double bond open to attack. The superior behavior of TCDT-(CF$_3$)$_2$ vs TCDT-H$_2$ and TCDT-(CO$_2$Me)$_2$ as a means of synthesizing polyacetylene by employing classical catalysts has been noted previously.[6]

The reaction of TCDT-(CF$_3$)$_2$ with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ appears to be well-behaved. The distribution of polyenes is shifted slightly toward longer chains than would be predicted if $k_p \leq k_i$. For example, 4 equiv of the monomer yields a distribution of polyenes that is centered around chains containing 11 double bonds instead of 9, a result that can be explained if the rate of propagation is slightly greater than the rate of initiation. This was confirmed by measuring[3b] the ratio k_p/k_i for the reaction of TCDT-(CF$_3$)$_2$ with the molybdenum catalyst (1.8 ± 0.2), a value that is similar to that estimated for the analogous tungsten catalyst (estimated to be 2–3[4]). Polydispersities of poly-TCDT-(CF$_3$)$_2$ samples containing up to 250 equiv of monomer are somewhat higher than usually is observed for well-behaved polymerizations (equiv/PDI = 30/1.16; 60/1.15; 150/1.11; 250/1.18), since the retro-Diels–Alder reaction occurs slowly at room temperature and therefore complicates GPC measurements. (Conversion of pure poly-TCDT-(CF)$_3$ to poly-TCDT-(CF)$_3$ containing some polyene sequences leads to broadening of the GPC peak and an apparent increase in dispersity.)

The total yield of polyenes with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is quantitative when 3–4 equiv of TCDT-(CF$_3$)$_2$ is used. The longest chains obtained under these conditions are the 13-ene and a small amount of the 15-ene (Figure 1, top). Employing more than 4 equiv of TCDT-(CF$_3$)$_2$ leads to progressively lower yields (Figure 1, bottom). Living poly-TCDT-(CF$_3$)$_2$ is relatively stable (see below), so the long polyenes themselves must decompose to give insoluble materials. It is believed that the thermal stability of polyenes decreases rapidly with increasing chain length and that cross-links form between the polyene chains.[4] A less likely possibility is that long polyenes isomerize readily and that the resulting polyenes, which contain a large number of trans double bonds, are simply extremely insoluble and therefore are not observed by HPLC under the conditions employed.

Generation of Living Polyenes and Alternative Syntheses of Polyenes. A ^{1}H NMR of the reaction of 1.0 equiv of TCDT-(CF$_3$)$_2$ with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is shown in Figure 2. The two doublets at approximately 11.1 and 11.2 ppm are assigned to alkylidene protons of the first and second insertion products, respectively (α_n in Scheme II). With time and at higher temperatures new resonances begin to appear at ~8 and 12.5 ppm. The group of resonances between 12.45 and 12.65 ppm can be ascribed to alkylidene H$_\alpha$ protons (α'_n) in the *cis*-vinylalkylidene species obtained when the retro-Diels–Alder reaction takes place next to the metal. With time a third set of H$_\alpha$ resonances at ~12 ppm appears that can be ascribed to the alkylidene protons in the analogous *trans*-vinylalkylidene complexes (α''_n). The alkylidene ligand lies in the N/Mo/C plane and can be oriented so that the growing chain points either toward the nitrogen atom in the imido ligand (syn rotamer) or away from the nitrogen atom in the imido ligand (anti rotamer).[8] Thus, two rotamers are observed for the vinylalkylidene species described above. The signals de-

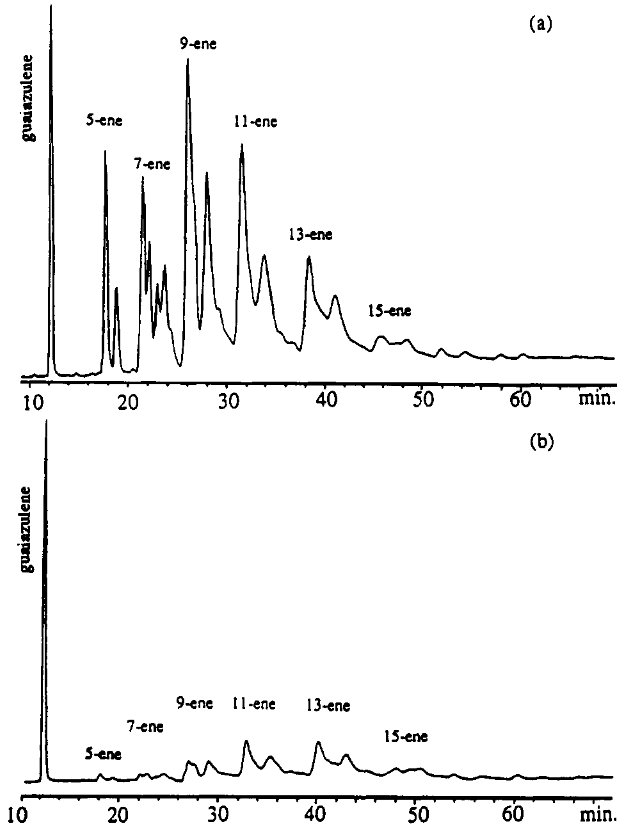


Figure 1. HPLC trace of the polyenes obtained from the reaction of 4 equiv of TCDT-(CF$_3$)$_2$ with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, followed by capping with pivaldehyde (top). The same experiment using 10 equiv of TCDT-(CF$_3$)$_2$ (bottom). Guaiazulene was added as an internal standard.

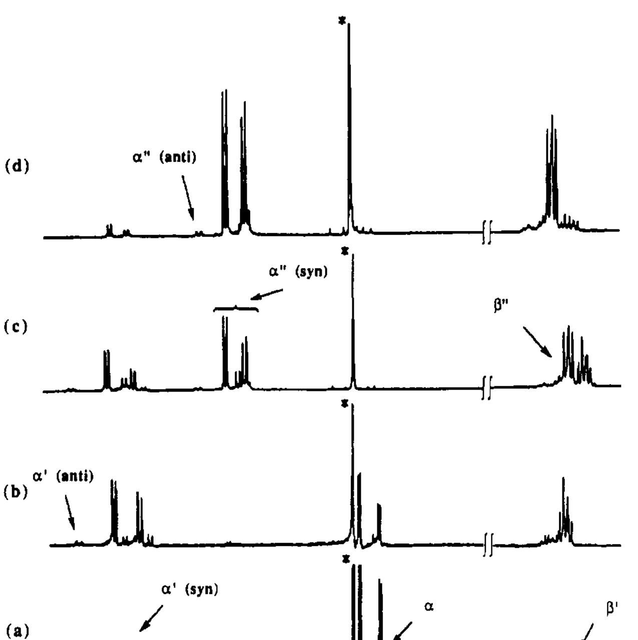
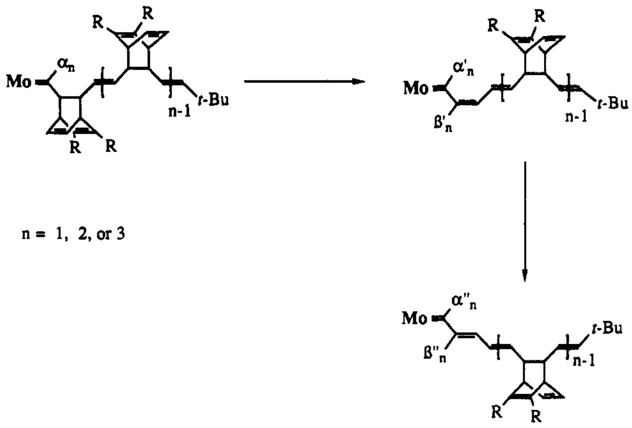


Figure 2. A solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in C$_6$D$_6$ containing 1.0 equiv of TCDT-(CF$_3$)$_2$ after (a) 20 min at 25 °C, (b) 60 min at 25 °C, (c) heating to 50 °C for 30 min, and (d) heating to 50 °C for 90 min. Labels (α, α', β', β'') are defined in Scheme II.

Scheme II



scribed above for α'_n and α''_n arise from the syn rotamers of the *cis*- and *trans*-vinylalkylidenes, respectively. There is a small signal at ~12.8 ppm that is assigned to the anti form of the *cis*-vinylalkylidene species; a small signal at ~12.1 ppm is assigned to the anti form of the *trans*-vinylalkylidene species. These assignments correspond to the assignments made for other vinylalkylidene species.[12] There is no significant decomposition of these alkylidene species during this time period relative to an internal standard. Addition of 25 equiv of norbornene at any stage generates a doublet at 11.5 ppm characteristic of alkylidene protons in living polynorbornene bound to Mo(NAr)(O-*t*-Bu)$_2$. Resonances due to the first three insertion products can be identified and are listed in Table II.

Analogous studies employing W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ showed that although similar species could be observed, vinylalkylidene species were not stable in benzene-d_6. THF-d_8 proved to be more suitable, but instability was still a problem over the long term and especially at higher temperatures. We originally reported that the tungsten-derived living polyenes appeared to be stable.[4] That now does not appear to be the case.

The rate of the retro-Diels–Alder reaction in the monomer unit adjacent to the metal and the rate of the cis to trans isomerization of the resulting vinylalkylidene complex were determined for the molybdenum system in both benzene-d_6 and THF-d_8. There was no appreciable solvent effect on either rate. The rates obtained (by standard NMR methods) for tungsten (in THF-d_8) and molybdenum are given in Table III. The value for k_2 (the cis to trans isomerization of the first C=C bond next to the Mo=C bond) for tungsten is approximately $^1/_{30}$th the magnitude of k_2 estimated earlier,[4] most likely because the earlier estimate was based on the incorrect assumption that living polyenes containing tungsten were relatively stable in benzene-d_6. We are more confident about k_2 for W determined here because the solvent employed was THF-d_8 and the method employed more primary data and NMR methods. Note that the rates of both the Diels–Alder reaction and the cis/trans isomerization are slightly faster for molybdenum than for tungsten. For both Mo and W the retro-Diels–Alder reaction is approximately 1 order of magnitude faster than the rate of cis/trans isomerization of the resulting vinylalkylidene complex.

When the living Mo-poly-TCDT-(CF$_3$)$_2$ is heated in a closed system to 85 °C in THF for 10 min, living polyenes are formed that can then be cleaved from the metal by reaction with pivaldehyde. HPLC analysis indicates that the yield of polyenes derived from living polyenes containing up to nine double bonds is the same as that obtained for polyenes prepared when the capping reaction is carried out before the retro-Diels–Alder reaction. Polyenes pre-

Table II
Chemical Shifts of α and β Protons in Living Oligomers Made from 1, 2, or 3 equiv of TCDT-$(CF_3)_2$ as Shown in Scheme II[a]

n	α_n	α'_n[b]	β'_n	α''_n[b]	β''_n
1	11.21 ($J_{\alpha\beta} = 5.5$)	12.63 ($J_{\alpha\beta} = 10.5$)	8.03 ($J_{\alpha\beta} = J_{\beta\gamma} = 10.5$)	11.96 ($J_{\alpha\beta} = 9.5$)	8.11 ($J_{\alpha\beta} = 9.5$, $J_{\beta\gamma} = 14.5$)
2	11.09 ($J_{\alpha\beta} = 6.5$)	12.48 ($J_{\alpha\beta} = 11.5$)	8.00 ($J_{\alpha\beta} = J_{\beta\gamma} = 10.0$)	11.85 ($J_{\alpha\beta} = 10.0$)	8.10 ($J_{\alpha\beta} = 10.0$, $J_{\beta\gamma} = 14.5$)
3	11.12 ($J_{\alpha\beta} = 6.0$)	12.42 ($J_{\alpha\beta} = 10.5$)		11.89 ($J_{\alpha\beta} = 10.5$)	8.10 ($J_{\alpha\beta} = 10.0$, $J_{\beta\gamma} = 14.5$)

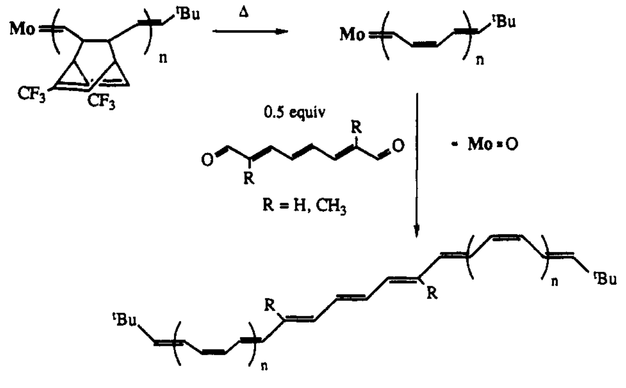
[a] Chemical shifts are in ppm, coupling constants are in hertz; n is the number of monomer units inserted; see Scheme II. [b] The chemical shifts reported here correspond to the syn rotamers of the *cis*- and *trans*-vinylalkylidenes. The anti rotamers appear somewhat downfield of their syn counterparts: ~12.8 (α') and ~12.1 ppm (α'').

Table III
Rates of Formation (k_1) and Isomerization (k_2) of Vinylalkylidene Complexes[a]

	rate, min^{-1}	
	Mo	W
k_1	1.06×10^{-2}	8.9×10^{-3} [b]
k_2	1.80×10^{-3}	5.3×10^{-4} [c]

[a] The rates for k_1 and k_2 for the molybdenum system were determined in both THF-d_8 and benzene-d_6. There was no significant difference in rates in the two solvents; the rates for the tungsten system were determined in THF-d_8 only due to the instability of the tungsten vinylalkylidenes in benzene-d_6. [b] Reported as 6.5×10^{-3} min^{-1} in ref 4. [c] Estimated as 1.7×10^{-2} min^{-1} in ref 4; see text.

Scheme III



pared in this manner have a higher trans content than those obtained by capping first, since cis/trans isomerization of the C=C bond next to the M=C bond is essentially finished before the retro-Diels–Alder reaction throughout the living polyene chain is complete. However, longer living polyenes (11 double bonds and longer) cannot be prepared in this manner either; these species are apparently no more stable (or soluble) than the polyenes themselves.

A way of preparing longer polyenes under relatively mild conditions that takes advantage of the stability of relatively short living polyenes is shown in Scheme III. One-half equivalent of the triene dialdehyde in which R = H or CH_3 reacts with two living polyenes to give one relatively long polyene in high yield. In Figure 3 (top) is shown the products obtained from the reaction of 1 equiv of TCDT-$(CF_3)_2$ with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in THF. The distribution consists primarily of all-trans 3-ene and 5-ene. When the same reaction mixture is treated with 0.5 equiv of 2,7-dimethyl-2,4,6-octatriene-1,8-dial instead of pivaldehyde, the distribution shown in Figure 3 (bottom) is obtained. The retention times of the methyl-substituted polyenes are longer than those of the corresponding unsubstituted polyenes. Their UV/vis spectra also are significantly red-shifted (by ~30–40 nm for the shorter polyenes, somewhat less for the longer polyenes) with respect to their unsubstituted counterparts, an effect that has been observed in studies of carotenes.[13] The 7-, 9-, and 11-enes are the expected dominant products and are the ones that are observed. Because the living polyenes have a relatively high trans content and the dialdehydes used contain only trans double bonds, polyenes produced by this method contain almost exclusively trans double bonds. The products therefore are relatively insoluble. Use of 2,7-dimethyl-2,4,6-octatriene-1,8-dial instead of the unsubstituted 2,4,6-octatriene-1,8-dial enhances the solubility of the resulting polyenes somewhat. This method allows us to synthesize relatively long polyenes without subjecting them to the high temperature required for the retro-Diels–Alder reaction. However, the longer chains are still too insoluble or prone to cross-linking (even at 25 °C) to be isolated.

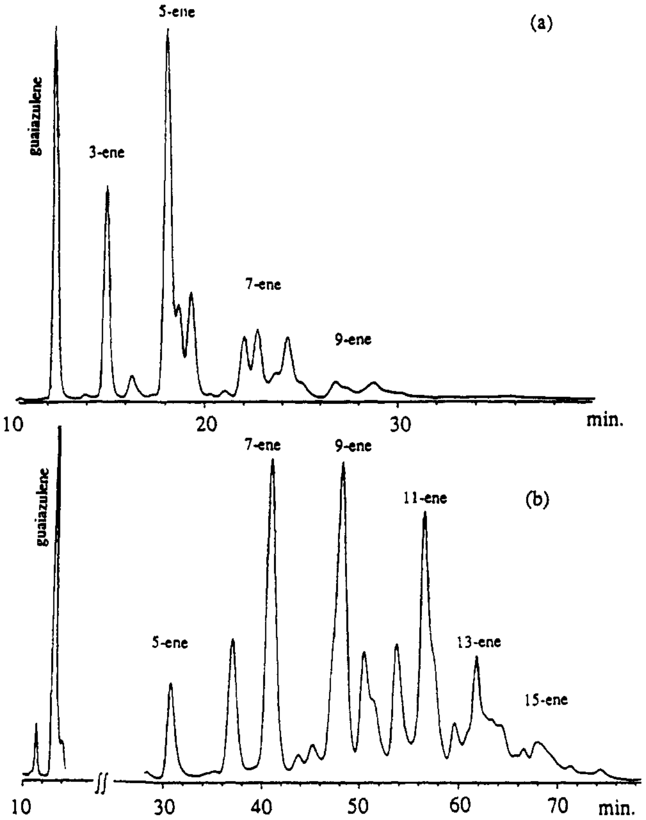
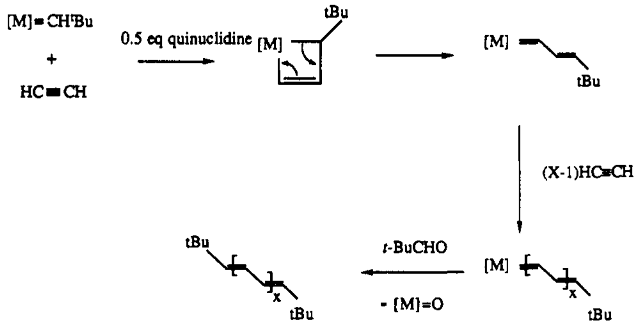


Figure 3. HPLC trace of the polyenes obtained from the reaction of 1 equiv of TCDT-$(CF_3)_2$ with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, followed by capping with pivaldehyde (top). HPLC trace of polyenes obtained in a similar experiment employing 2,7-dimethyl-2,4,6-octatriene-1,8-dial as the capping agent (bottom). Guaiazulene was added to these reactions as an internal standard. Note that the retention times of the methyl-substituted polyenes (bottom trace) are longer than for the unsubstituted polyenes (top trace).

Reactions of Acetylene with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Polyenes can also be prepared by the direct polymerization of acetylene by Mo(CH-*t*-Bu)(NAr)(O-*t*-

Scheme IV



[M] = Mo(NAr)(O^{t}Bu)$_2$
NAr = 2,6-diisopropylphenylimido

Table IV
Polydispersities of Triblocks Synthesized from Norbornene and Acetylene Employing Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in Toluene[a]

NBE	HC≡CH	NBE	M_w	M_n	PDI
50	5	50	21 220	19 826	1.07
50	7	50	17 671	16 780	1.05
50	9	50	20 904	19 938	1.05
50	11	50	21 899	20 856	1.05
50	13	50	18 709	17 506	1.07
50	15	50	79 609	23 907	3.33
50	20	50	141 493	26 106	5.42
50	25	50	214 334	31 627	6.78

[a] GPC data were obtained in dichloromethane vs polystyrene standards. A single slightly unsymmetrical peak was observed in all cases. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ concentration in toluene, 0.025 M.

Bu)$_2$ (Scheme IV). In most respects the results are very similar to those obtained by using W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ as the initiator.[7] In the absence of quinuclidine, addition of acetylene to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ yields polyacetylene immediately, even when only a few equivalents of acetylene is used. In the presence of excess quinuclidine, acetylene is polymerized smoothly to give primarily all-trans polyenes after cleaving the chain from the metal with pivaldehyde. We believe that quinuclidine coordinates to the metal in the living polyenes and thereby decreases k_p/k_i to a magnitude that allows the polymerization to be living. Since both even and odd polyenes are generated, separation of discrete polyenes (whether on a preparative or on an analytical scale) is impractical. Also, the insolubility of the all-trans polyenes hinders isolation and manipulation. Therefore, oligomerization of acetylene appears to be of limited use in the preparation of discrete polyenes of any significant length.

Polymerization of acetylene is shown to be living by the successful introduction of polyene sequences into block copolymers. Triblocks (50–x–50) can be synthesized by adding 50 equiv of norbornene to a mixture of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and quinuclidine, followed by x equiv of acetylene, 50 equiv of norbornene, and finally excess pivaldehyde. Table IV lists the results of GPC analyses on the triblocks synthesized in this manner with up to 25 equiv of acetylene. When up to 11 equiv of acetylene is used, GPC analysis shows that a distribution of triblocks with a low polydispersity and the expected molecular weight is obtained (Figure 4, top), indicative of a well-behaved polymerization. However, when more than 11 equiv of acetylene is used, a bimodal distribution is obtained (Figure 4, bottom). The lower molecular weight peak is approximately the same as that obtained with 11 equiv of acetylene. The higher molecular weight polymer is at least twice the molecular weight of the first and is proposed to result from cross-linking or aggregation of the individual polyene chains in the triblocks.[5] Therefore it appears that living polymers containing up to ~11 equiv of acetylene are stable under the reaction conditions and are well-behaved, but longer versions are subject to some form of aggregation or cross-linking. As the number of equivalents of acetylene used is increased, the percentage of the higher molecular weight polymer increases relative to the polymer with the expected molecular weight. These results are entirely consistent with the observation that living polyenes generated in THF from living poly-TCDT-(CF$_3$)$_2$ are relatively stable up to about 9 double bonds in length for molybdenum.

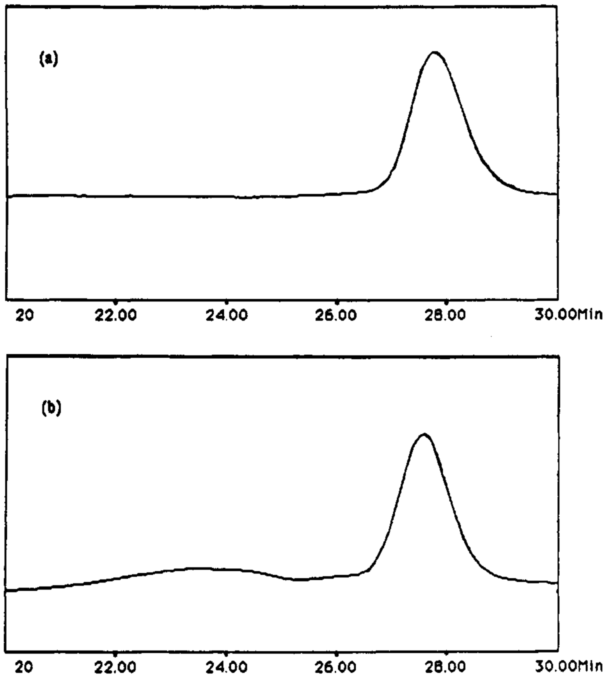


Figure 4. GPC trace (refractometer data) of a 50–7–50 triblock (top) and a 50–15–50 triblock (bottom). The bottom trace exhibits a broad higher molecular weight peak thought to be due to the cross-linking of individual polyene chains with one another.

The analogous tungsten system is less well-behaved, as determined by analysis of similar 50–x–50 triblocks. When greater than 9 equiv of acetylene is used, a trimodal distribution of molecular weights is obtained. The middle molecular weight peak corresponds to the expected polymer; the highest molecular weight peak corresponds to the cross-linked material described above. Formation of a material with a molecular weight approximately half that of the expected polymer suggests that the third block of polynorbornene does not form for a significant fraction of the chains; i.e., some chain termination takes place during the acetylene polymerization step. In the molybdenum system there is no evidence for an analogous chain termination. It is not known whether chain termination is an intrinsic problem for tungsten, or the result of the greater sensitivity of living polyenes of tungsten to impurities.

Synthesis of Block Copolymers Containing Polyenes Employing TCDT-(CF$_3$)$_2$. Block copolymers containing polyene sequences in polynorbornene have been synthesized by use of TCDT-(CF$_3$)$_2$ as the source for the polyene block and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ as the initiator.[5] The polyene sequence was generated by heating the poly-TCDT-(CF$_3$)$_2$/poly-NBE block copolymer after it was cleaved from the metal. In general, the diblock and triblock polymers had low polydispersities, but some relatively high molecular weight material formed via aggregation or cross-linking. One phenomenon that was not satisfactorily explained at the time was the appearance in UV/vis spectra of triblock copolymers of peaks characteristic of polyene sequences containing three, five, and seven double bonds.[5] Diblocks (containing one norbornene block and one polyene block) did not exhibit the higher energy absorptions characteristic of the shorter polyenes. We now have shown that polyenes containing three, five, and seven double bonds are generated via formation of some random copolymer of TCDT-$(CF_3)_2$ and norbornene.

There are two pieces of evidence in favor of the random copolymer hypothesis. The first is that in UV/vis studies of triblocks synthesized by using acetylene as the means of forming the polyene block, only the broad lower energy absorption envelope characteristic of relatively long polyenes is observed. The second is that the appearance of the short polyenes in triblocks synthesized by using TCDT-$(CF_3)_2$ depends on the time that is allowed for polymerization of TCDT-$(CF_3)_2$. If all TCDT-$(CF_3)_2$ is consumed in formation of the second block, then no short polyenes are observed. Therefore, we now believe that short polyene chains observed in the original triblocks[5] resulted from incomplete reaction of TCDT-$(CF_3)_2$ before addition of the second batch of norbornene; i.e., some random copolymer of norbornene and TCDT-$(CF_3)_2$ was formed, which when heated generated some short polyene sequences. Short polyene sequences were not observed in diblocks since a capping agent (pivaldehyde) was the only species competing with TCDT-$(CF_3)_2$ for the alkylidene end of the living polymer. The same problem could arise if diblocks are prepared by adding TCDT-$(CF_3)_2$ to the initiator followed too quickly (before all TCDT-$(CF_3)_2$ is consumed) by norbornene.

Conclusions

Only ring-opening metathesis of TCDT-$(CF_3)_2$ by Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ was found to be a feasible route to polyenes; TCDT-H_2 and TCDT-$(CO_2Me)_2$ both gave low yields. Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ offers greater flexibility than W(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ as a catalyst because living polyenes can be formed and are stable at temperatures as high as 80 °C for up to 30–45 min if they contain less than about nine double bonds. These living polyenes can be capped with difunctional conjugated aldehydes, although insolubility of polyenes containing more than 13 double bonds in the chain remains a significant problem. Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ is also useful as a catalyst for the controlled polymerization of acetylene itself. Block copolymers containing polyene sequences can be prepared by employing either acetylene or TCDT-$(CF_3)_2$, but cross-linking or aggregation of the polyene chains within these block copolymers is still a significant problem. It was shown that formation of norbornene/TCDT-$(CF_3)_2$ random copolymer gave rise to material containing relatively short polyene sequences in the synthesis of triblock copolymers containing polyenes between two blocks of polynorbornene.

Experimental Section

General Methods. All reactions were carried out in a Vacuum Atmospheres Glovebox or by standard Schlenk techniques. Mo(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$[8] and W(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$[14] were prepared by routes described elsewhere. Pivaldehyde (Aldrich) was distilled and passed over alumina before use. Silica gel (Merck grade 60, 3 × 40 cm) was dried (at ~130 °C) in vacuo overnight. 2,7-Dimethyl-2,4,6-octatriene-1,8-dial was used as received from Hoffman-LaRoche. Cyclooctatetraene was supplied by BASF and was distilled before use. Guaiazulene was used as received from Aldrich. Norbornene (Aldrich) was distilled over sodium. Acetylene (Airco) was passed through a column of activated alumina and introduced into reaction mixtures via gastight syringe. Solvents were dried under dinitrogen by standard procedures and degassed. Toluene used for polymerizations was stored over a Na/K alloy. Benzene-d_6 was passed over activated alumina and THF-d_8 was vacuum distilled from Na/benzophenone. HPLC grade solvents were used in GPC and HPLC runs and were degassed prior to use. UV/vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer in the range of 190–820 nm with dichloromethane as the solvent. NMR data are listed in parts per million downfield from TMS.

HPLC Analyses. Samples were first dissolved in dichloromethane, then diluted with acetonitrile (15%/85% v/v), and filtered through Celite before being injected into a Hewlett-Packard 1090M HPLC equipped with a 250-mm reverse-phase (C18) Econosil analytical column (Alltech Associates). HPLC runs were carried out at 30 °C with a flow rate of 0.5 mL/min. A ternary solvent system was used: the initial solvent composition consisted of acetonitrile, dichloromethane, and water (90/5/5); a continuous gradient over a period of 30 min was used to arrive at a solvent composition of acetonitrile and dichloromethane (95/5). (The dichloromethane and acetonitrile were premixed.) The HPLC 1090M was equipped with a diode array detector; UV/vis spectra were recorded continuously over the course of the HPLC run, with a wavelength range of 240–600 nm; HPLC traces were monitored over the range from 250 to 450 nm. Yields of polyenes were determined by HPLC[4] by normalizing the peak areas of individual polyenes to that of an internal standard (guaiazulene). The yields shown in Table I represent the sum of the yields of the individual polyenes obtained for each of the monomers.

GPC Analyses. Gel permeation chromatographic (GPC) analyses were carried out using Shodex Kf-802.5, 803, 804, 805, 800P columns connected to a Knauer differential refractometer and a Spectroflow 757 absorbance detector. Samples were prepared in dichloromethane (0.1–0.3% w/v) and were filtered though a Millex-SR 0.5-μm filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) which ranged from 1206 to 2.75×10^6 MW.

Monomer Syntheses. TCDT-H_2 and TCDT-$(CO_2Me)_2$ were prepared as described in the literature.[15] TCDT-$(CF_3)_2$ was prepared by a somewhat modified version of the reported route.[16] Cyclooctatetraene (0.29 mol) and hydroquinone (0.01 mol) were placed in a high-pressure reaction apparatus. Hexafluoro-2-butyne (0.33 mol) was added. The reaction was stirred at 140 °C for 15 h. After the reaction vessel was cooled, the contents were distilled under full vacuum by using a Bower-Cooke column. The desired product was obtained as a clear, colorless oil, which distilled at 32 °C (yield 30%). It was crucial in the distillation of this material that no oxygen be present in order to prevent polymerization.

Synthesis of Polyenes (Route 1, Analytical Scale). For each reaction, 1.08×10^{-5} mol of M(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ (M = Mo or W) in 250 μL of toluene was used. A solution of monomer [$n \times 1.08 \times 10^{-5}$ mol)] TCDT-R_2 (R = CF_3, CO_2Me, H) in ($n \times 50$ μL) toluene (where *n* is the number of monomer units used) was added to the catalyst solution and allowed to stir at room temperature for an appropriate length of time depending on the number of equivalents of monomer added. For 4.5–5.0 equiv of any of the monomers, a 15-min reaction time proved optimal with either catalyst. A 250-μL aliquot of a stock solution of pivaldehyde (3.83×10^{-5} mol in 250 μL) was then added and the reaction was stirred for 15 min. The reaction was then heated (as described in the text) to complete the retro-Diels–Alder reaction. After heating, the reactions were cooled by the partial removal of solvent in vacuo and then filtered through silica gel to remove the metal–oxo complex generated upon reaction of the living poly-TCDT-$(R)_2$ with aldehyde. A 25-μL aliquot of a guaiazulene stock solution (5.17×10^{-5} mol of guaiazulene in 800 μL of toluene) was then added as an internal standard and the solvent was removed in vacuo. These samples were then prepared for HPLC analysis as described above.

Synthesis of Polyenes (Route 2, Analytical Scale). For each reaction, 1.08×10^{-5} mol of M(CH-*t*-Bu)(NAr)(O-*t*-$Bu)_2$ (M

= Mo or W) in 250 μL of toluene was used. A solution of monomer [$n \times (1.08 \times 10^{-5}$ mol)] TCDT-$\mathrm{R_2}$ (R = $\mathrm{CF_3}$, $\mathrm{CO_2Me}$, H) in ($n \times$ 50 μL) toluene (where n is the number of monomer units used) was added to the catalyst solution and allowed to stir for an appropriate length of time. The reaction was then heated to complete the retro-Diels–Alder reaction. Heating to 85 °C for 10 min gave the optimum yields. After heating, the reactions were cooled by the partial removal of solvent in vacuo. A 1.95 $\times 10^{-5}$ mol aliquot of 2,4,6-octatriene-1,7-dial or 2,7-dimethyl-2,4,6-octatriene 1,7-dial in 250 μL of THF or 3.83 $\times 10^{-5}$ mol of pivaldehyde in 250 μL of THF was then added and the reaction was stirred for 15 min. The solution was then filtered through silica gel to remove the metal–oxo complex generated upon addition of the aldehyde to the living poly-TCDT-$(\mathrm{CF_3})_2$. Guaiazulene was then added as above and the solvent was removed in vacuo. The samples were then prepared as described previously for HPLC analysis.

Synthesis of Polyenes (Route 1, Preparative Scale). Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (1.74×10^{-3} mol) was dissolved in 20 mL of toluene. A solution of TCDT-$(\mathrm{CF_3})_2$ (8.67×10^{-3} mol) in 20 mL of toluene was then added dropwise to the first solution and the reaction was allowed to stir for 15 min. Pivaldehyde (4.64×10^{-3} mol) was then added to the solution and stirring was continued for an additional 15 min. The solution was then diluted to 200 mL with toluene and was transferred into two Fisher-Porter bottles. A drop of anhydrous hydrazine was added to each of the bottles. The sealed bombs were then heated to 120 °C for 4.5–5.0 min. (The color of the solutions turned from a clear yellow-orange to a deep red during heating.) The solutions were then cooled as quickly as possible to room temperature and were filtered through a bed of Celite and silica gel. The solvent was then removed in vacuo. The product was extracted with pentane and filtered a second time through a bed of Celite; the solvent was again removed in vacuo. This mixture of products was then chromatographed under inert atmosphere on a silica gel column approximately 17 in. long at −40 °C using a pentane/dichloromethane gradient beginning with 95% pentane by volume and gradually reaching 70% pentane by volume. The solvent used to elute the purified polyenes was then removed in vacuo. Isolated polyenes were then identified by UV/vis spectra.

Preparation of Poly-TCDT-$(\mathrm{CF_3})_2$. The following stock solutions were prepared: 2.05×10^{-5} mol of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in 10 mL of THF; $n \times (2.05 \times 10^{-6}$ mol) of TCDT-$(\mathrm{CF_3})_2$ in $n \times 10$ μL of THF; 1.03×10^{-3} mol of pivaldehyde in 1 mL of THF. For each reaction 100 μL of the catalyst solution was used. The monomer solution ($n \times 10$ μL) was then added while the solution was stirred rapidly; the solution was stirred for up to 35 min (for the addition of 250 equiv of monomer). Pivaldehyde solution (100 μL) was then added and stirring was continued for an additional 20 min. The polymer was then precipitated as a slightly yellowish solid from the THF solution by adding excess pentane (~200 mL). The polymer was isolated by filtration and washed with more pentane. Samples were prepared for GPC analysis as described above. GPC analyses were run immediately upon preparation of the polymer samples in order to avoid a significant amount of retro-Diels–Alder reaction in the poly-TCDT-$(\mathrm{CF_3})_2$.

Synthesis of Polyenes Using Acetylene (Route 3). To 90 μL of a 0.1 M solution of Mo(CHC(Me)$_3$)(NAr)(O-*t*-Bu)$_2$ (9 μmol) in toluene was added 90 μL of a 0.5 M solution of quinuclidine in toluene. The solutions were stirred for 5 min, after which the vial was sealed with a septum. Acetylene (1.0 mL, 45 μmol, 5 equiv) was then added via a gas-tight syringe at a rate of 0.5 mL/30 s. The color of the reaction mixture changed from yellow to red. The reactions were quenched by the addition of 35 μL (3.22 mmol) of pivaldehyde. After 30 min, the solutions were filtered through silica gel and the solvent was removed in vacuo. HPLC samples were prepared as described above with guaiazulene added as an internal standard.

Synthesis of Norbornene–Acetylene–Norbornene Triblock Copolymers. For each reaction, 180 μL of a 0.5 M solution of quinuclidine (92 μmol) in toluene was added to a rapidly stirred solution containing 180 μL of a 0.1 M solution of molybdenum catalyst (18 μmol) in toluene. After 5 min, 180 μL of a 5.0 M solution of norbornene (900 μmol) was added dropwise to the solution. The solution was stirred for 10 min, after which the vial was sealed with a septum. Acetylene (5–50 equiv) was introduced to the reaction via a gas-tight syringe. The reaction mixture was allowed to stir for 10–15 min (depending on the amount of acetylene used). During this time, the color of the solution varied from yellow (5 equiv of acetylene) to dark purple (greater than 25 equiv). This was followed by the dropwise addition of 180 μL of a 5.0 M solution (900 μmol) of norbornene. After 10 min, the reaction was quenched by the addition of an excess of pivaldehyde (35 μL, 3.22 mmol). After 30 min, the reaction was filtered through silica gel followed by removal of the solvent in vacuo. GPC samples were then prepared as described above.

Synthesis of Norbornene–TCDT-$(\mathrm{CF_3})_2$-Norbornene Triblock Copolymers. Synthesis of such triblocks has been described previously.[5] UV/vis spectra were acquired in dichloromethane.

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. W.E.C. thanks NIH for a postdoctoral fellowship. We gratefully acknowledge Hoffman-LaRoche for 2,7-dimethyl-2,4,6-octatriene-1,8-dial and BASF for cyclooctatetraene.

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Registry No. TCDT-$(\mathrm{CF_3})_2$, 19640-25-6; TCDT-$\mathrm{H_2}$, 21604-76-2; TCDT-$(\mathrm{CO_2Me})_2$, 25733-20-4; poly-TCDT-$(\mathrm{CF_3})_2$, 87366-06-1; poly-TCDT-$(\mathrm{CO_2Me})_2$, 89871-68-1; poly-TCDT-$\mathrm{H_2}$, 89871-67-0; poly(1,2-ethenediyl), 26571-64-2; acetylene, 74-86-2; Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = diisopropylphenyl), 108969-04-6.