Unusual Optical Absorption Behavior, Polymer Structure, and Air Stability of Poly(1,6-heptadiyne)s with Substituents at the 4-Position

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ABSTRACT: We report here the effect of size and type of substituents upon the fine and conformational structure and unusual optical absorption behavior for the substituted poly(1,6-heptadiynes). 4-(Carboxy-3-(trimethylsilyl)-1-propyl)-1,6-heptadiyne (**1a**), 4,4-bis(3-(trimethylsilyl)-1-propyl) dipropargylmalonate (**1b**), 4,4-bis[(acetoxy)methyl]-1,6-heptadiyne (**2a**), 4,4-bis[(ethylcarboxy)methyl]-1,6-heptadiyne (**2b**), 4,4-bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (**3a**), and 4,4-bis[(*tert*-butyldiphenylsiloxy)methyl]-1,6-heptadiyne (**3b**) were all prepared and polymerized to give organo-soluble polymers in high yield with $MoCl_5$-based catalysts. From a series of λ_{max} values of the polymers, we have found that incorporation of a bulkier substituent in the 4-position of 1,6-heptadiyne forces the conjugated polyene into a more planar structure, as indicated by the bathochromic shift of maximum absorption bands resulting from the $\pi-\pi^*$ transition of the conjugated polymer backbone. It appears that chain twisting of the substituted poly(1,6-heptadiynes) is determined primarily by the bulk of the substituent group at the 4-position rather than by the point of attachment to the polymer chain which usually decreases the effective conjugation length of the polymer π-system. When an extremely bulky substituent was introduced at the 4-position, the resulting polymer had predominantly a symmetric single repeat unit with a five-membered ring and a trans vinylene group. The polymer **3b** ($\lambda_{max} = 606$ nm) with a nearly 100% five-membered ring structure is environmentally very stable: there is no observable change in IR, NMR, and UV−visible spectra upon exposure to air for 6 weeks. This stability of backbone to air oxidation is thought to be due to effective shielding of the highly conjugated backbone by the bulky substituents.

Introduction

During the past two decades, extensive studies[1] on polymerization of simple mono- and disubstituted acetylenes have been made to overcome some problems of polyacetylene such as its lack of processability and its thermal and environmental instability. However, polymerization of substituted acetylenes resulted in materials with very low effective conjugation lengths, as shown by their high-energy visible absorption spectra and comparatively low iodine conductivities.[1−3] Grubbs and co-workers[4−9] have recently prepared a family of substituted poly(cyclooctatetraenes) (poly-RCOT) using a ring-opening metathesis polymerization (ROMP). Although these polyacetylene-like polymers exhibited desired combination of solubility in organic solvents and relatively long π-conjugation lengths, these polyenes tended to aggregate and perhaps cross-link.

In a recent series of papers, we have reported that $MoCl_5$- and WCl_6-based catalyst systems are very effective for the cyclopolymerization of 1,6-heptadiyne derivatives and dipropargyl derivatives giving highly π-conjugated double bonds in the cyclic recurring unit.[10−20] It has been also reported that these cyclic polymers obtained by both a classical metathesis catalyst and a well-defined alkylidene initiator produced five- and six-membered rings of a certain ratio, which depended on the polymerization conditions and kinds of catalysts used.[21,22] It is very interesting that some of these polymers showed good solubility in common organic solvents, long term stability toward oxidation even with enough conjugation length, and high electrical conductivity as compared to mono- and disubstituted polyacetylenes.

However, there was no systematically performed study on the effect of size and type of substituents upon the fine and conformational structure for this potentially interesting class of cyclic polyenes. In this paper we report the effect of steric bulkiness of substituents at the 4-position of a series of 1,6-heptadiyne derivatives upon the structure of the polymer repeat unit, polymer conformation, and its unusual optical absorption behavior.

Experimental Section

Materials. Propargyl bromide (Aldrich Chemicals, 80% solution of toluene) was dried over calcium hydride and fractionally distilled. Molybdenum(V) chloride (Aldrich Chemicals Co., resublimed 99.9%) was used without further purification. Tetra-*n*-butyltin and ethylaluminum dichloride (Aldrich Chemicals Co.) were used as received. All solvents were used after purification according to conventional methods. Special care was taken to ensure complete removal of moisture and oxygen. All chemicals used were reagent grade (Aldrich) and purified by the ordinary methods.[24] Diethyl dipropargylmalonate,[25] dipropargylmalonic acid,[14] dipropargylmalonyl dichloride,[14] and dipropargylacetic acid[15] were prepared as described in the literature.

Instruments for Characterization. ^1H and ^{13}C NMR spectra were recorded using Bruker AM-200, -300, -500 spectrometers, and the chemical shifts were reported in ppm units with TMS as the internal standard. Infrared spectra

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were measured on a Bomem MB-100 Fourier Transform spectrophotometer using KBr pellets. UV−visible absorption spectra were obtained in chloroform on a Shimadzu UV-3100S spectrophotometer. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a wahrus flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer.

Polymerization. All procedures for the catalyst system preparation and polymerization were carried out under the dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent (0.1 M solutions) before use. A typical polymerization procedure was as follows: Solvent, catalyst solution, and when needed, cocatalyst solution were injected into a 20 mL ampule equipped with a rubber septum in the order given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, monomer dissolved in each solvent was injected into the polymerization ampule. After the mixture was allowed to react at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in THF and precipitated with an excess of methanol. The polymer was filtered from solution and dried under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry.

Synthesis of 4-(Carboxy-3-(trimethylsilyl)-1-propyl)-1,6-heptadiyne (1a). A mixture of 3-(chloropropyl)trimethylsilane (12 g, 80 mmol), dipropargylacetic acid (10.2 g, 87 mmol), K_2CO_3 (12 g, 87 mmol), and DMF (150 mL), is gently refluxed for 10 h. The solution was cooled and poured into water and was extracted with diethyl ether. The extracting layer was dried over anhydrous $MgSO_4$. The volatile components were removed in vacuo. The resulting oil was distilled (88−90 °C, 0.5 Torr) to afford a colorless oil (14.5 g, 58 mmol, 77%): ^{1}H NMR δ 4.1 (t, 2H, OCH_2), 2.70 (m, 1H, CH), 2.59 (dd, 4H, $CH_2C\equiv$), 2.05 (t, 2H, $\equiv$CH), 1.59 (m, 2H, OCH_2CH_2), 0.51 (m, 2H, CH_2Si), 0.01 (s, 9H, $SiCH_3$); ^{13}C NMR δ 172.2 (CO), 80.5 ($-C\equiv$), 70.5 ($\equiv$CH), 67.1, 43.0, 23.9, 19.9, 12.5, −2.1. Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86; Si, 11.22. Found: C, 67.12; H, 8.89; Si, 11.18.

Synthesis of Bis(3-(trimethylsilyl)-1-propyl) Dipropargylmalonate (1b). Under the nitrogen atmosphere, a flask was charged with an ether solution (100 mL) of 3-(trimethylsilyl)-1-propanol (10.4 g, 79 mmol) and pyridine (13.75 g, 174 mmol). Dipropargylmalonyl dichloride (8 g, 37 mmol) was then added dropwise at 0 °C over a period of 1 h. The reaction was completed by stirring the mixture at room temperature for 12 h. Saturated aqueous $NaHCO_3$ was added to the ether solution until bubbling ceased. The organic layer was washed with water. The organic fraction was dried over anhydrous $MgSO_4$. The solution was filtered, and the ether was removed in vacuo. The resulting oily product was chromatographed using hexane as an eluent to give pure product (12.50 g, 31 mmol, 83%): ^{1}H NMR δ 4.12 (t, 4H, OCH_2), 2.96 (d, 4H, $CH_2C\equiv$), 1.98 (t, 2H, $\equiv$CH), 1.58 (m, 4H, OCH_2CH_2), 0.49 (m, 4H, CH_2Si), −0.04 (s, 18H, $SiCH_3$); ^{13}C NMR δ 168.2 (CO), 79.0 ($-C\equiv$), 72.2 ($\equiv$CH), 68.1, 57.1, 23.6, 23.1, 12.4, −2.2. Anal. Calcd for $C_{21}H_{36}O_4Si$: C, 61.72; H, 8.88; Si, 13.74. Found: C, 61.63; H, 8.92; Si, 13.71.

Synthesis of 4,4-Bis(hydroxymethyl)-1,6-heptadiyne (2).[22] Diethyl dipropargylmalonate (33.0 g, 140 mmol) was dissolved in 80 mL of diethyl ether. The solution was added dropwise over a period of 1 h to a suspension of $LiAlH_4$ (8.83 g, 220 mmol) in 300 mL of diethyl ether at room temperature. The reaction mixture was stirred for an additional 6 h. Water was added dropwise to the gray suspension until it turned white and evolution of H_2 ceased. The solution was dried over anhydrous $MgSO_4$. The ether was removed in vacuo to give a white solid that could be recrystallized from ether (17.6 g, 110 mmol, 82%): ^{1}H NMR δ 3.69 (s, 4H, OCH_2), 2.55 (brs, 2H, OH), 2.34 (d, 4H, CH_2), 2.01 (t, 2H, $\equiv$CH); ^{13}C NMR δ 80.1 ($-C\equiv$), 71.0 ($\equiv$CH), 66.3 (OCH_2), 42.0 (C_{quat}), 21.6 ($CH_2C\equiv$). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.99.

Synthesis of 4,4-Bis[(acetoxy)methyl]-1,6-heptadiyne (2a). Acetyl chloride (7.90 g, 100 mmol) was dissolved in 100 mL of diethyl ether. **2** (7 g, 46 mmol) was dissolved in 20 mL of ether. The solution containing alcohol was added dropwise to the acid chloride solution at 0 °C over a period of 1 h. The solution was stirred for 20 h at room temperature. Saturated aqueous $NaHCO_3$ was added to the ether solution until bubbling ceased. The organic layer was washed with water (3 × 70 mL) and dried over anhydrous $MgSO_4$. The solution was filtered, and the ether was removed in vacuo. The remaining oily product was distilled (104−108 °C, 1 Torr) to give a pure oily product (10.0 g, 42 mmol, 92%): ^{1}H NMR δ 4.00 (s, 4H, OCH_2), 2.30 (d, 4H, $CH_2C\equiv$), 1.98 (t, 2H, $\equiv$CH), 1.96 (s, 6H, CH_3); ^{13}C NMR δ 170.4 (CO), 78.7 ($-C\equiv$), 71.7 ($\equiv$CH), 64.8 (OCH_2), 39.8 (C_{quat}), 22.0 (CH_3), 20.6 ($CH_2C\equiv$). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.01; H, 6.92.

Synthesis of 4,4-Bis[(*tert*-butylcarboxy)methyl]-1,6-heptadiyne (2b). This compound was prepared using the same procedure described for **2a**. The crude product was distilled, and the fraction boiling at 132−135 °C (1 Torr) was collected (87%): ^{1}H NMR δ 4.04 (s, 4H, OCH_2), 2.37 (d, 4H, $CH_2C\equiv$), 1.99 (t, 2H, $\equiv$CH), 1.16 (s, 18H, CH_3); ^{13}C NMR δ 177.7 (CO), 78.7 ($-C\equiv$), 78.7 ($-C\equiv$), 71.6 ($\equiv$CH), 64.8 (OCH_2), 40.4 (C_{quat}), 38.9, 27.1, 22.2. Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.23; H, 8.81. Found: C, 71.21; H, 8.82.

Synthesis of 4,4-Bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (3a). **2** (7 g, 46 mmol) was dissolved in DMF, and imidazole (9.4 g, 138 mmol) and *tert*-butyldimethylsilyl chloride (15.25 g, 100 mmol) were added at room temperature. The mixture was stirred at 40 °C for 24 h. The reaction solution was cooled and poured into cold water and was extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$. The volatile compounds were removed in vacuo. The resulting oil was distilled (130−134 °C, 1 Torr) to afford a colorless oil (13.3 g, 35 mmol, 76%): ^{1}H NMR δ 3.61 (s, 4H, OCH_2), 2.28 (d, 4H, $CH_2C\equiv$), 1.97 (t, 2H, $\equiv$CH), 0.84 (s, 18H, CH_3), 0.03 (s, 12H, $SiCH_3$); ^{13}C NMR δ 80.4 ($-C\equiv$), 70.8 ($\equiv$CH), 66.5 (OCH_2), 42.0 (C_{quat}), 25.7, 21.4, 18.1, −5.71. Anal. Calcd for $C_{21}H_{40}O_2Si_2$: C, 66.26; H, 10.56; Si, 14.75. Found: C, 66.22; H, 10.63; Si, 14.73.

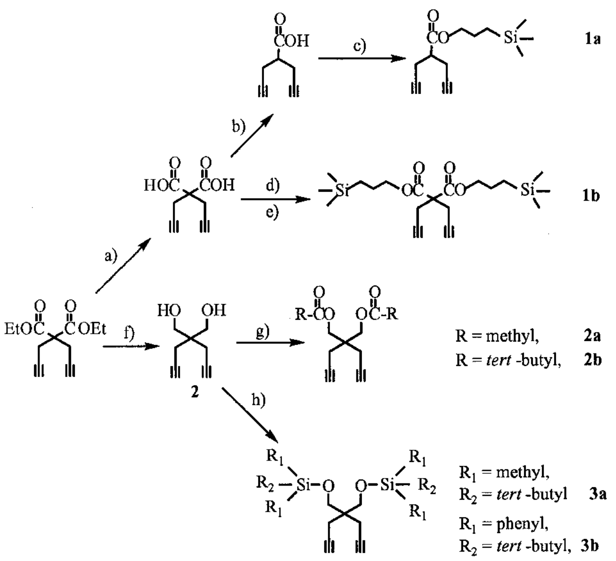
Synthesis of 4,4-Bis[(*tert*-butyldiphenylsiloxy)methyl]-1,6-heptadiyne (3b). This compound was prepared using a procedure similar to that described for **3a**. The crude solid product was recrystallized from hexane to give a white crystalline product (54%): ^{1}H NMR δ 7.7−7.28 (m, 20H, phenyl), 3.70 (s, 4H, OCH_2), 2.46 (d, 4H, $CH_2C\equiv$), 1.89 (t, 2H, $\equiv$CH), 1.04 (s, 18H, CH_3); ^{13}C NMR δ 135.7, 133.3, 129.6, 127.6 (phenyl), 80.9 ($-C\equiv$), 70.5 ($\equiv$CH), 64.1 (OCH_2), 44.2 (C_{quat}), 26.9 (CH_3), 21.4 (CH_2), 19.3 (SiC). Anal. Calcd for $C_{41}H_{48}O_2Si_2$: C, 78.29; H, 7.69; Si, 8.93. Found: C, 78.23; H, 7.75; Si, 8.91.

Results and Discussion

Synthesis of Monomers. The synthetic routes for the monomers are shown in Scheme 1. In order to investigate the size effect of substituents on the fine and conformational structure for a series of poly(1,6-heptadiyne)s, we synthesized dipropargylmalonate/dipropargylacetate with 3-(trimethylsilyl)-1-propyl group and various 4,4-disubstituted-1,6-heptadiyne monomers.

Polymerization. The polymerizations were carried out using $MoCl_5$- and WCl_6-based catalysts in 1,4-dioxane or chlorobenzene under a dry nitrogen atmosphere. Cyclopolymerization was effectively carried out only by the $MoCl_5$-based catalysts and their optimized polymerization results are summarized in Table 1. All polymers were highly soluble in several common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, and chlorobenzene but were insoluble in hexane and methanol. Molecular weights of the polymers were determined by the GPC analysis with polystyrene standards calibration. It was observed that the degrees of polymerization based on the number-average molecular weights were higher than 100 in most cases. In general, in the case

Scheme 1



a) KOH / EtOH (90 %); b) H_2O / reflux (68 %) ;) 3-chloropropyltrimethyl-silane / K_2CO_3 / DMF (71 %) ; d) $SOCl_2$ / pyridine / ether (52 %) ; e) 3- (trimethylsilyl)-1-propanol / TEA / ether (83 %) ; f) $LiAlH_4$ / ether (82 %) ; g) RCO-Cl / TEA / ether ,R = methyl (92 %), R = *tert* -butyl (87 %), ; h) $ClSi(R_1)_2R_2$ / imidazole / DMF, [R_1 = methyl, R_2 = *tert* - butyl (76 %)], [R_1 = phenyl, R_2 = *tert* -butyl (54 %)]

Table 1. Polymerization Conditions[a] and Data for the Resulting Polymers

exp no.	monomer	cat. syst (mole ratio)	yield (%)[b]	$M_n/10^c$	$M_w/M_n{}^c$
1	**1a**	$MoCl_5-(n\text{-}Bu)_4Sn$ (1:4)	98	56.5	1.74
2	**1a**	$MoCl_5$	94	27.4	2.73
3	**1b**	$MoCl_5$	97	112.6	4.23
4	**1b**	$MoCl_5-EtAlCl_2$ (1:4)	98	102.2	2.87
5	**2a**	$MoCl_5$	97	73.0	2.86
6	**2a**	$MoCl_5-EtAlCl_2$ (1:2)	96	47.4	3.01
7	**2b**	$MoCl_5$	96	121.5	2.56
8	**3a**	$MoCl_5-EtAlCl_2$ (1:4)	98	118.4	2.15
9	**3a**	$MoCl_5$	94	88.8	2.49
10	**3b**	$MoCl_5-(n\text{-}Bu)_4Sn$ (1:4)	99	331.9	2.86
11	**3b**	$MoCl_5$	99	236.1	3.35

[a] Polymerization was carried out in 1,4-dioxane at 60 °C for 24 h. $[M]_0 = 0.25$, Mole ratio of monomer to catalyst = 50. [b] Methanol-insoluble polymer. [c] Values were obtained by GPC analysis with polystyrene standards calibration.

that the degrees of polymerization were over a certain value, polymer chain lengths had little effect on UV–visible absorption wavelength. The polymers were black lustrous solids, indicative of a highly conjugated nature of the backbone.

Structure. FT-IR spectra of the polymers did not show a ≡C–H stretching band around 3300 and C≡C stretching bands around 2100 cm^{-1}, while these two stretching bands were present in monomers. Infrared spectra results and an excellent solubility of the polymers suggest that the intramolecular cyclization is fast relative to the intermolecular linear polymerization through one triple bond per diyne monomer, and so leads to a complete cyclopolymerization. From a recent series of studies on the cyclopolymerization of 1,6-heptadiyne derivatives using classical metathesis catalysts based on $MoCl_5$ and WCl_6, we find that the organo-soluble cyclic polymers can be obtained by introducing at least one substituent in the 3- or 4-position. From a series of λ_{max} values, we found that incorporating a bulkier substituent in the 4-position of 1,6-heptadiyne forces the conjugated polyene into a more planar structure, as indicated by the bathochromic shift of maximum absorption bands from the $\pi-\pi^*$ transition of the conjugated polymer backbone (see Figure 1). These results provide remarkable contrast to mono- and disubstituted polyacetylenes and monosubstituted polycyclooctatetraenes by ROMP, in which the steric bulk at the point of attachment to the polymer chain increases; the effective conjugation length decreases because of twisting around the single bonds on polyacetylene, as a result of steric repulsions between the side groups. The unusual optical absorption behavior could not be explained by the planar transoidal conformation of unsubstituted poly(1,6-heptadiyne) proposed by Gibson et al.[23] Recently, Schrock et al.[21,22] reported the authentic polymerization mechanism of diethyl dipropargylmalonate using well-defined alkylidene initiators. They proposed that a five- and six-membered ring are produced by attaching the α- and β-additions of the first triple bond to the Mo=C bond followed by cyclization and ring opening. It is believed that the well-defined alkylidene complexes behave differently from the classical metathesis catalysts based on $MoCl_5$ and WCl_6 in such a way that their steric bulkiness should cause an important effect on the direction of the first triple bond addition. As shown in Chart 1, the classical catalyst is sterically very small compared to well-defined alkylidene complexes. The α-addition of the first triple bond leading to a five-membered ring structure may be sterically less hindered than the β-addition, yielding a six-membered ring. The structures of the polymers were almost independent of the type of classical catalysts used: the polymers prepared only with $MoCl_5$ were almost identical to the corresponding polymers with $MoCl_5$ cocatalyst systems. The

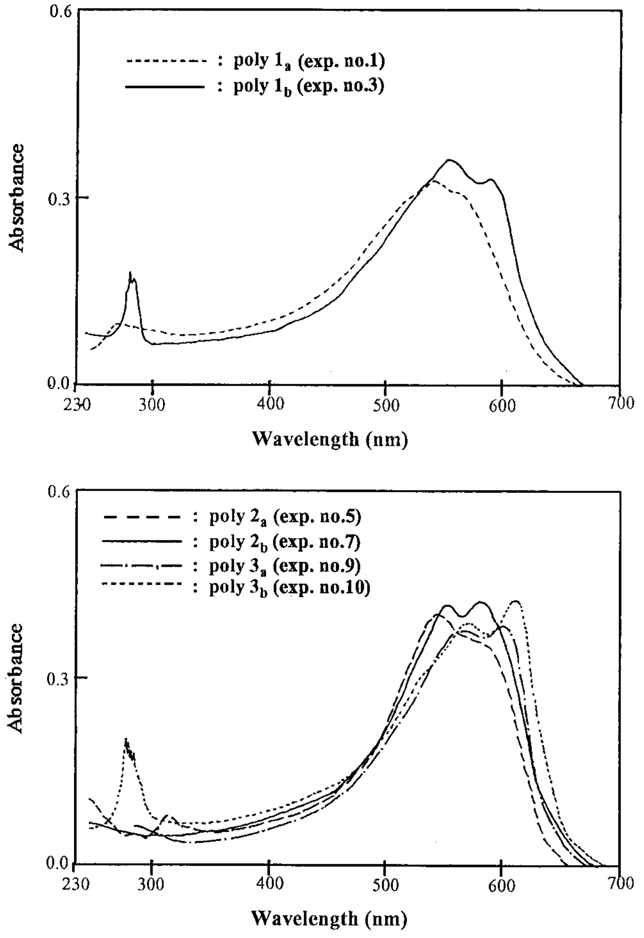
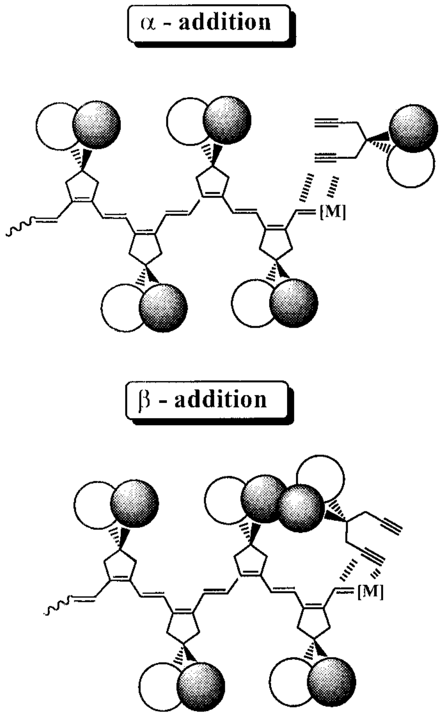


Figure 1. UV–visible spectra of the polymers in chloroform.

Chart 1



ratio between five-membered and six-membered structures increased with the size and number of substituents at the 4-position. In particular, when an extremely bulky substituent such as the (*tert*-butyldiphenylsiloxy)-methyl group was introduced at the 4-position, the ^{1}H NMR spectrum (see Figure 2) shows a broad single peak at 6.5 ppm due to newly forming vinylic protons, while poly(1,6-heptadiyne)s with a five- and six-membered ring repeat unit exhibited broad multiple peaks.[12,14] In addition, the ^{13}C NMR spectrum of polymer **3b** (as well as the polymers with other bulky substituents such as polymer **2b**) also shows two sharp peaks at 138 and 123 ppm. These peaks can be attributed to the presence of a quaternary olefinic carbon and a vinylene carbon of the conjugated π-system, respectively, as well as one sharp quaternary carbon on the ring at around 46 ppm (see Figure 2). On the other hand, polymers **1a**, **1b**, and **2a** and poly(DEDPM) were identified to have both five- and six-membered ring structures. They showed numerous olefinic resonances in the range between 120 and 140 ppm, and two clusters of peaks for the quaternary carbon atoms and many resonances for the allylic methylene groups. Such a difference in NMR spectra and two sharp olefinic carbon peaks suggests that polymer **3b**, containing extremely bulky substituents has predominantly a symmetric single repeat unit with a five-membered ring and a vinylene structure, as shown below.

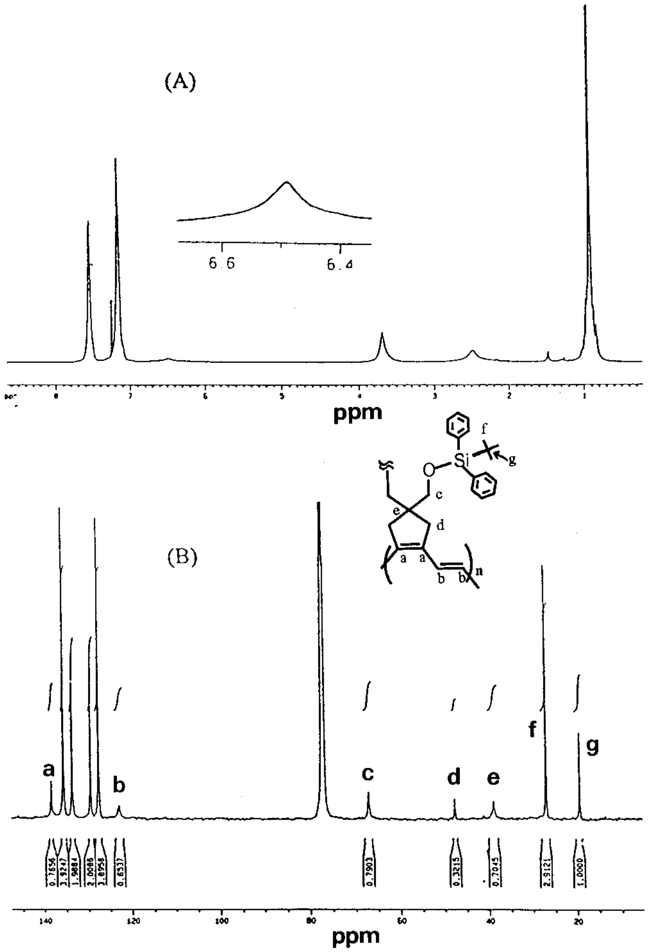
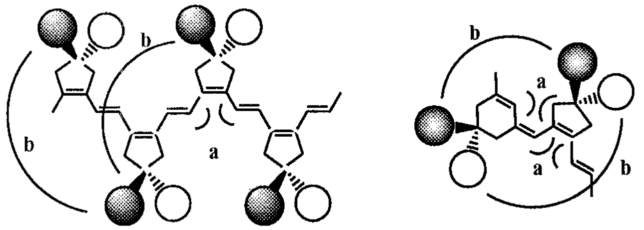


Figure 2. ^{1}H NMR (A) and ^{13}C NMR spectra (B) of the polymer **3b** in CDCl$_3$.

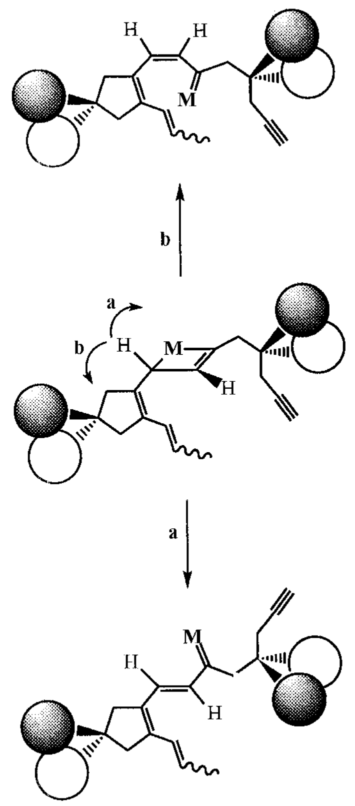
The ratio of trans and cis vinylene groups is believed to be governed by the relative ease of ring opening of the metallacyclobutene, as shown in Scheme 2. The formation of trans double bond through rotation a should lead to a lower-energy transition state than the rotation b because of less steric interaction between the substituents attached to the newly forming vinylene group, and hence trans double bond should predominate. From the spectroscopic results of polymers and considering the mechanism forming the vinyl group of the polymer backbone, we propose the trans−cis structure as the main structure of poly(1,6-heptadiyne)s containing bulky substituents at the 4-position. With such a trans−cis structure the longer distance among the substituents reduces the steric hindrance between the substituents and thus a more planar π-conjugated polyene is retained. On the basis of unusual optical behavior with a bulkier substituent at the 4-position, and the polymer structures proposed here, it appears that chain twisting of the substituted poly(1,6-heptadiyne)s may be limited primarily by the bulk of the substituent group at the 4-position (b interaction) rather than by the point of attachment to the polymer chain (a interaction) which usually decreases the effective conjugation length of the polymer π-system.



The X-ray diffractograms of the present polymers show typical broad amorphous patterns: The ratios between the half-height width and diffraction angle ($\Delta 2\theta/2\theta$) were found to be greater than 0.35 for all polymers.

Environmental Stability. Although thermal and oxidative stabilities of poly(1,6-heptadiyne)s reported previously were greatly enhanced over those of analogous unsubstituted polyenes, decomposition of the long

Scheme 2



conjugated polyene framework could not be avoided completely, especially with polymers having a sterically small substituent at the 4-position.[12,13,22] However, polymer **3b** (λ_{max} = 606 nm) with an extremely bulky substituent such as the (*tert*-butyldiphenylsiloxy)methyl group is environmentally more stable than other polymers currently available: no observable change in IR, NMR, and UV–visible spectra was detected upon exposure to air for 6 weeks. This stability of the backbone to air oxidation is thought to be due to effective shielding of the highly conjugated backbone by the bulky substituents. These findings are particularly important in synthetic polyene chemistry, since they can offer the possibility of obtaining polyacetylenes possessing stability and processibility. This can be attributed to their interesting electrical and optical properties due to their extended π-conjugation. Cyclopolymerization of 1,6-heptadiynes should provide a relatively simple route to a variety of potentially useful polymers whose properties may be "tuned" by changing the substituent and its bulkiness. A more detailed description on the structure and the nonlinear optical behavior of these series of polymers will be reported elsewhere.

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