Macromolecules 1990, *23*, 4902-4907

Synthesis and Properties of Poly[1-(*n*-alkylthio)-1-propynes][1]

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Received December 5, 1989; Revised Manuscript Received March 1, 1990

ABSTRACT: 1-(*n*-Alkylthio)-1-propynes ($CH_3C{\equiv}CSR$; R = CH_3, C_2H_5, *n*-C_4H_9, *n*-C_6H_{13}, *n*-C_8H_{17}, and *n*-$C_{10}H_{21}$) could be polymerized in high yield (50–80%) in toluene at 80 °C in the presence of $MoCl_5$–Ph_3SiH (1:2) catalyst. The corresponding W, Nb, and Ta catalysts were less effective. The product polymers possessed weight-average molecular weights up to 1×10^5–2×10^5, higher than any other sulfur-containing polyacetylenes so far synthesized. Spectroscopic data supported that the polymer structure was $-(CCH_3{=}CSR)_n-$. Except for poly[1-(methylthio)-1-propyne], the present polymers totally dissolved in common solvents such as toluene and $CHCl_3$. They were colorless, film forming, thermally fairly stable in air, electrically insulating, and moderately permeable to gases.

Introduction

In general, sulfur-containing polymers exhibit moderate hydrophilicity, complex-forming properties, chemical reactivity in hydrolysis and oxidation, and so on.[2] Sulfur-containing polyacetylenes are expected to show properties and functions peculiar to their structure. Previous examples,[3,4] however, are virtually limited to several polymers having thiophene as the pendant group. Their low molecular weights ($<\sim 2 \times 10^4$) are attributable to the presence of sulfur whose lone-pair electrons might deactivate the catalyst.

We have been interested in the group 5 and group 6 transition-metal-catalyzed synthesis of high molecular weight polymers from various substituted acetylenes.[5] Among those polymers, 2-alkynes[6] (1) and 1-chloro-1-alkynes[7] (2) can be polymerized by $MoCl_5$-based catalysts to give polymers with very high molecular weight [weight-average molecular weight ($\bar{M}_w$) $\sim 1 \times 10^6$]: $CH_3C{\equiv}CR$ (1, R = *n*-C_3H_7, *n*-C_5H_{11}, *n*-C_7H_{15}); $ClC{\equiv}CR$ (2, R = *n*-C_4H_9, *n*-C_6H_{13}; *n*-C_8H_{17}); $CH_3C{\equiv}CSR$ (3, R = CH_3, C_2H_5, *n*-C_4H_9, *n*-C_6H_{13}, *n*-C_8H_{17}, *n*-$C_{10}H_{21}$).

The present paper deals with the polymerization of 1-(*n*-alkylthio)-1-propynes (**3**), sulfur-containing analogues of 2-alkynes. It should be noted that the sulfur in monomers **3** is directly bonded to an acetylenic carbon, which will reduce the basicity of the sulfur, unlike the previous sulfur-containing acetylenic monomers. Consequently, new, colorless, soluble, film-forming polymers have been obtained whose molecular weights ($\bar{M}_w = 1 \times 10^5$–$2 \times 10^5$) are 1 order of magnitude larger than those of any other sulfur-containing polyacetylenes so far reported. The structure and properties of the polymers are also discussed.

Results and Discussion

Polymerization of 1-(*n*-Butylthio)-1-propyne. We chose to study 1-(*n*-butylthio)-1-propyne as monomer in order to establish optimum reaction conditions.

As seen in Table I, Mo catalysts were most effective among group 5 and 6 transition-metal catalysts in producing polymers. This monomer reacted usually quantitatively with Mo catalysts to give acetone-insoluble[8] polymers in ca. 40–60% yields. The $\bar{M}_w$ values of the polymers, which were determined by gel permeation chromatography (GPC) on the basis of a polystyrene calibration, were ca. 1×10^5–2×10^5. These values are higher than any other values so far reported for sulfur-containing polyacetylenes. The number-average molecular weights ($\bar{M}_n$) of the formed polymers were ca. 2×10^4–7×10^4, and the $\bar{M}_w/\bar{M}_n$ ratios are ca. 2.5–5.0. The acetone-soluble products were mainly linear oligomers with $\bar{M}_w$ of a few thousand according to GPC and IR spectroscopy. The $MoCl_5$–Ph_3SiH catalyst gave the highest yield and $\bar{M}_w$ among the Mo catalysts in Table I. In contrast, W catalysts yielded primarily linear oligomers. Nb and Ta catalysts gave mixtures of linear oligomers and cyclotrimers, which is the same tendency as in the polymerization of monomers 1 and 2.[5,7]

Table I
Polymerization of 1-(*n*-Butylthio)-1-propyne by Various Catalysts[a]

cat.	monomer convn, %	polymer[b] yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
$MoCl_5$	100	39	110	35
$MoCl_5$–Ph_3SiH	100	63	180	71
$Mo(CO)_6$–$h\nu$[d]	85	43	100	19
$MoOCl_4$	100	45	145	50
$MoOCl_4$–Ph_3SiH	100	45	101	21
WCl_6	100	12		
WCl_6–Ph_3SiH	100	14		
$W(CO)_6$–$h\nu$[d]	21	0		
$NbCl_5$	56	0		
$NbCl_5$–Ph_3SiH	87	5		
$TaCl_5$	83	0		
$TaCl_5$–Ph_3SiH	71	13		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 0.50 M, [cat.] = 20 mM, [cocat.] = 40 mM. [b] Acetone-insoluble product. [c] Determined by GPC. [d] Polymerized in CCl_4; $[M(CO)_6]$ = 10 mM.

Use of organometallic cocatalysts affected the yield and molecular weight of polymer in the $MoCl_5$-catalyzed polymerization (Table II). Thus, addition of organosilicon, -tin, and -antimony compounds clearly increased both yield and $\bar{M}_w$ of polymer. Not Sn compounds but Ph_3SiH gave the highest yield. Therefore, Ph_3SiH was usually employed as cocatalyst in further experiments.

Table III gives results for the polymerization by $MoCl_5$–Ph_3SiH in various solvents. Aromatic solvents with low polarity such as toluene, chlorobenzene, and anisole gave relatively good polymer yields above 50%. The $\bar{M}_w$ values of the polymers obtained in these solvents were 12×10^4–18×10^4, fairly large. Thus toluene turns out to be one of the most useful and convenient polymerization solvents. Though various hydrocarbons, halogenated hydrocarbons, and ethers may be available in this polymerization, both yield and molecular weight of polymer depend on them.

The conversion of this polymerization reaches 100% at 50 °C and above under the reaction conditions (Figure 1). Polymer yield maximizes at ca. 80 °C, whereas no polymer

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Table II
Effect of Organometallic Cocatalysts on the Polymerization of 1-(*n*-Butylthio)-1-propyne by $MoCl_5$[a]

		polymer[b]		
cocat.	monomer convn, %	yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
none	100	39	110	35
Ph_3SiH	100	63	180	71
Et_3SiH	100	53	190	58
Ph_4Sn	96	45	120	43
n-Bu_4Sn	97	53	220	81
Ph_3Sb	100	61	190	58
Ph_3Bi	100	44	14	6
n-BuLi	83	40	210	91
Et_3Al	61	5		

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM, [cocat.] = 40 mM. [b] Acetone-insoluble product. [c] Determined by GPC.

Table III
Solvent Effect on the Polymerization of 1-(*n*-Butylthio)-1-propyne by $MoCl_5$–Ph_3SiH (1:2)[a]

		polymer[b]		
solvent	monomer convn, %	yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
toluene	100	63	180	71
cyclohexane	100	55	180	51
n-heptane	86	45	120	31
PhCl	100	61	120	32
CCl_4	91	21	87	25
$(CH_2Cl)_2$	97	27	210	57
$PhOCH_3$	100	54	160	51
$PhCOOCH_3$	96	22	120	42
$PhCOCH_3$	83	0		

[a] Polymerized at 80 °C for 24 h; $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM. [b] Acetone-insoluble product. [c] Determined by GPC.

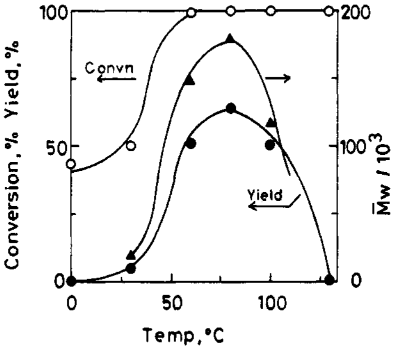

Figure 1. Temperature profile of the polymerization of 1-(*n*-butylthio)-1-propyne by $MoCl_5$–Ph_3SiH (1:2) (in toluene, 24 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM).

forms at 0 and 130 °C. The $\bar{M}_w$ of the polymer also maximizes around 80 °C. These findings indicate that the propagating species tend to decompose at temperatures of 100 °C and above. Hence the choice of temperature is significant in this polymerization.

The polymerization of 1-(*n*-butylthio)-1-propyne gradually reaches 100% after 24 h (Figure 2). In contrast, analogous monomers such as 2-alkynes[6] and 1-chloro-1-alkynes[7] polymerize much faster with $MoCl_5$-based catalysts even at 30 °C. This difference is probably due to the inherent low reactivity of sulfur-containing monomers and/or the reduction of catalyst activity by coordination of the sulfur atom. The yield and $\bar{M}_w$ of the present polymer increase gradually and monotonously with time. The increase of $\bar{M}_w$ with conversion suggests the presence of long-lived propagating species and the absence of polymer degradation during polymerization.

Figure 3 depicts the effect of Ph_3SiH concentration at a constant concentration of $MoCl_5$ (20 mM). Monomer

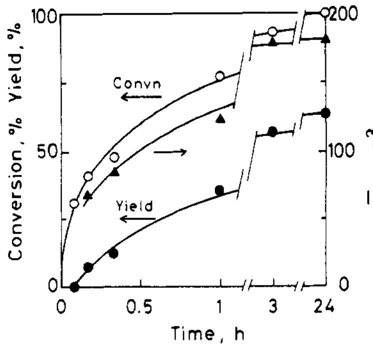

Figure 2. Time course of the polymerization of 1-(*n*-butylthio)-1-propyne by $MoCl_5$–Ph_3SiH (1:2) (in toluene, 80 °C, $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM).

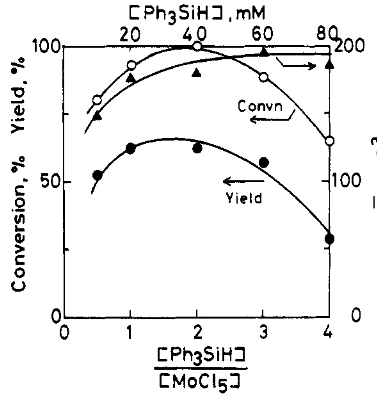

Figure 3. Effect of cocatalyst concentration on the polymerization of 1-(*n*-butylthio)-1-propyne by $MoCl_5$–Ph_3SiH (in toluene, 80 °C, 24 h, $[M]_0$ = 0.50 M, $[MoCl_5]$ = 20 mM).

conversion and polymer yield maximize around a $[Ph_3SiH]/[MoCl_5]$ ratio of 2. The $\bar{M}_w$ of polymer increases with increasing $[Ph_3SiH]/[MoCl_5]$ ratio below 2 and virtually levels off above 2. Therefore, the $[Ph_3SiH]/[MoCl_5]$ ratio should be about 2 to obtain an effective catalytic activity.

The above results lead to the conclusion that the polymerization conditions shown in Table I using the $MoCl_5$–Ph_3SiH catalyst are optimal for a simultaneously high yield and high molecular weight of polymer.

This polymerization seems to proceed by the metal carbene mechanism like the polymerization of other substituted acetylenes by Mo and W catalysts.[5] Some knowledge supporting the metal carbene mechanism has gradually accumulated.[9]

Polymerization of Various 1-(Alkylthio)-1-propynes. Since optimal conditions have been established in the polymerization of 1-(*n*-butylthio)-1-propyne, polymerizations of various 1-(alkylthio)-1-propynes are now compared under such conditions. Table IV lists results for the $MoCl_5$- and $MoCl_5$–Ph_3SiH-catalyzed polymerizations of 1-(*n*-alkylthio)-1-propynes with different alkyl lengths. Poly[1-(methylthio)-1-propyne], the polymer with the shortest alkylthio pendant, was insoluble in any solvent, probably because the substituents could not interact with solvent sufficiently. Other 1-(*n*-alkylthio)-1-propynes with alkyls from ethyl to *n*-decyl polymerized similarly to one another; that is, their monomer conversions, polymer yields, and $\bar{M}_w$ values were not very different. In general, $MoCl_5$–Ph_3SiH gave a somewhat higher yield and $\bar{M}_w$ of polymer than $MoCl_5$ did.

No large differences were observed among toluene, chlorobenzene, and anisole as polymerization solvents. Monomer conversions reached 100%, while polymer yields were ca. 40–80% for each monomer (see Table IV, nos. 7–12 and Table V). Tendencies seen in toluene are confirmed

Table IV
Polymerization of 1-(*n*-Alkylthio)-1-propynes by Mo Catalysts[a]

no.	MeC≡CSR R	monomer convn, %	polymer[b] yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
		Catalyst: $MoCl_5$			
1	CH_3	95	26[d]		
2	C_2H_5	87	58	140	49
3	n-C_4H_9	100	39	110	35
4	n-C_6H_{13}	100	46	87	17
5	n-C_8H_{17}	93	38	95	15
6	n-$C_{10}H_{21}$	100	61	140	36
		Catalyst: $MoCl_5$–Ph_3SiH (1:2)			
7	CH_3	100	45[d]		
8	C_2H_5	100	58	130	35
9	n-C_4H_9	100	63	180	71
10	n-C_6H_{13}	100	60	110	34
11	n-C_8H_{17}	100	73	130	25
12	n-$C_{10}H_{21}$	100	78	170	39

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 0.50$ M, $[MoCl_5] = 20$ mM. [b] Acetone-insoluble product. [c] Determined by GPC. [d] Insoluble in any solvent.

Table V
Polymerization of 1-(*n*-Alkylthio)-1-propynes in Two Solvents by $MoCl_5$–Ph_3SiH (1:2)[a,b]

MeC≡CSR R	monomer convn, %	polymer[c] yield, %	$\bar{M}_w/10^3$ [d]	$\bar{M}_n/10^3$ [d]
	Solvent: Chlorobenzene			
CH_3	100	54[e]		
C_2H_5	100	79	79	16
n-C_4H_9	100	61	120	32
n-C_6H_{13}	100	37	110	30
n-C_8H_{17}	100	74	76	25
n-$C_{10}H_{21}$	100	35	120	63
	Solvent: Anisole			
CH_3	100	56[e]		
C_2H_5	100	59	140	43
n-C_4H_9	100	54	160	51
n-C_6H_{13}	100	36	89	31
n-C_8H_{17}	100	69	85	33
n-$C_{10}H_{21}$	100	52	130	62

[a] Polymerized at 80 °C for 24 h; $[M]_0 = 0.50$ M, $[MoCl_5] = 20$ mM. [b] See Table IV, nos. 7–12 for the results with toluene as polymerization solvent. [c] Acetone-insoluble product. [d] Determined by GPC. [e] Insoluble in any solvent.

Table VI
Polymerization of 1-(Butylthio)-1-propynes by Mo and W Catalysts[a]

MeC≡CSR R	cat.	monomer convn, %	polymer[b] yield, %	$\bar{M}_w/10^3$ [d]
n-C_4H_9	$MoCl_5$–Ph_3SiH	100	63	180
n-C_4H_9	WCl_6–Ph_3SiH	100	14	
sec-C_4H_9	$MoCl_5$–Ph_3SiH	100	20	57
sec-C_4H_9	WCl_6–Ph_3SiH	100	0	
tert-C_4H_9	$MoCl_5$–Ph_3SiH	21	0	
tert-C_4H_9	WCl_6–Ph_3SiH	30	0	

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 0.50$ M, [cat.] = 20 mM, $[Ph_3SiH] = 40$ mM. [b] Acetone-insoluble product. [c] Determined by GPC.

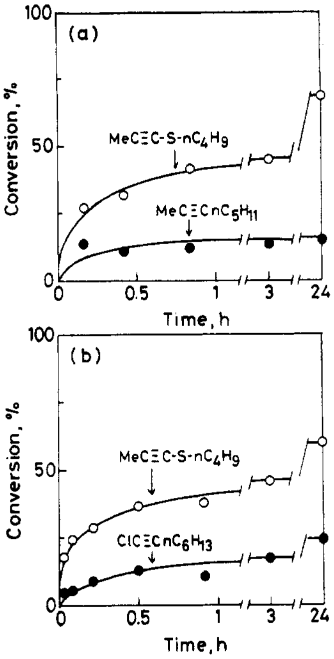

Figure 4. Copolymerizations of 1-(*n*-butylthio)-1-propyne with 2-octyne (a) and 1-chloro-1-octyne (b) by $MoCl_5$–Ph_3SiH (1:2) (in toluene, 80 °C, $[M_1]_0 = [M_2]_0 = 0.50$ M, $[MoCl_5] = 20$ mM).

also in other solvents; i.e., (i) polymerizability hardly depended on the alkyl chain length in the monomer, and (ii) poly[1-(methylthio)-1-propyne] was insoluble in any solvent.

Polymerizations of 1-(*sec*-butylthio)- and 1-(*tert*-butylthio)-1-propynes were carried out for the sake of comparison (Table VI). 1-(*sec*-Butylthio)-1-propyne polymerized quantitatively with Mo and W catalysts, but even the polymer yield with $MoCl_5$–Ph_3SiH was no more than 20%. 1-(*tert*-Butylthio)-1-propyne was much less reactive and formed no polymer. The corresponding Nb and Ta catalysts did not give any polymer from these monomers.

Thus, it has been proven that the polymerizability of 1-(alkylthio)-1-propyne hardly depends on the alkyl chain length but is greatly affected by the alkyl chain branching. This is a tendency similar to those in the Mo-catalyzed polymerization of 2-alkynes[10] and 1-chloro-1-alkynes;[7] MeC≡C-*n*-alkyl ≫ MeC≡C-*sec*-alkyl; MeC≡C-*tert*-alkyl unreactive; ClC≡C-*n*-alkyl ≫ ClC≡C-*sec*-alkyl.

Copolymerization of 1-(*n*-Butylthio)-1-propyne. From the monomer reactivity in the copolymerization of substituted acetylenes, one can know the relative coordinating ability of monomers to the active species.[11,12] The following orders of monomer reactivity have been observed: HC≡C-n-C_4H_9 > HC≡CPh > HC≡C-*sec*-C_4H_9 > HC≡C-*tert*-C_4H_9;[11] MeC≡C-n-C_5H_{11} > n-C_3H_7C≡C-n-C_3H_7 > MeC≡CPh > n-C_4H_9C≡CPh.[12] These orders reflect differences in coordinating ability, which originate from the steric crowding of monomer. It is interesting to study the relative reactivities in the copolymerization of 1-(*n*-butylthio)-1-propyne with 2-octyne (a 2-alkyne) or 1-chloro-1-octyne (a 1-chloro-1-alkyne) whose steric effects are not very different from one another.

In the copolymerization of these monomers, the sulfur-containing monomer was clearly more reactive than the other two monomers (Figure 4). This also should stem from differences in the coordinating ability of the monomer. Eventually, the observed relative reactivity can be attributed to the presence of lone-pair electrons in the sulfur-containing monomer. This is the first example that the monomer reactivity is governed by the electronic effect of the monomer in the copolymerization of substituted acetylenes.

As stated above, 1-(*n*-butylthio)-1-propyne is less reactive than 2-octyne and 1-chloro-1-octyne in homopolymerization. It should, however, be noted that the apparent reactivity in homopolymerization involves many factors, leading to no direct conclusions.

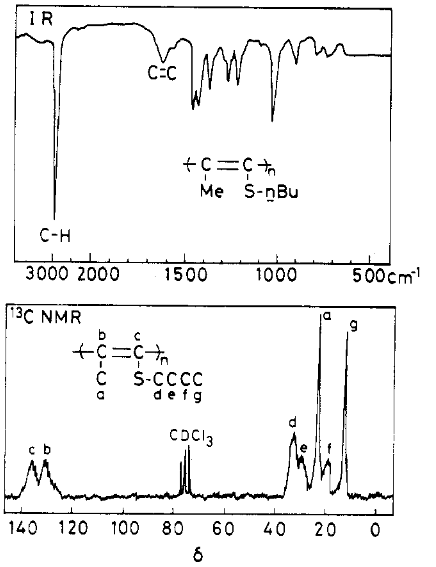

Figure 5. IR and ^{13}C NMR spectra of poly[1-(*n*-butylthio)-1-propyne] (sample from Table IV, no. 9; IR: KBr pellet; ^{13}C NMR: CDCl$_3$ solution).

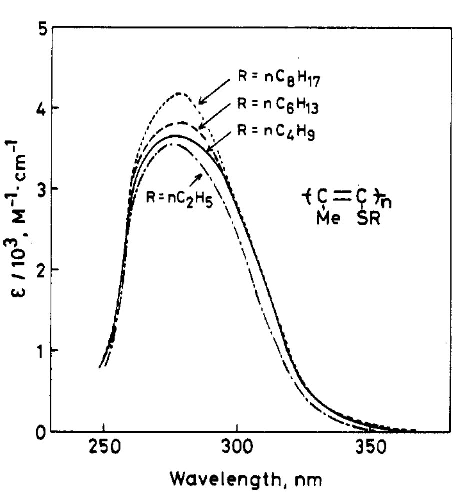

Figure 6. UV-visible spectra of poly[1-(*n*-alkylthio)-1-propynes] (sample from Table IV, nos. 8–11; measured in cyclohexane).

Polymer Structure. The structure of poly[1-(*n*-butylthio)-1-propyne] (sample from Table IV, no. 9) was studied. The elemental composition of the polymerization product was in good agreement with the theoretical one. Anal. Calcd for $(C_7H_{12}S)_n$: C, 65.57; H, 9.43; S, 25.00. Found: C, 64.75; H, 9.47; S, 24.82.

The IR spectrum of poly[1-(*n*-butylthio)-1-propyne] exhibits a C=C stretching at 1620 cm^{-1}, and the C≡C stretching in the monomer around 2100 cm^{-1} has disappeared (Figure 5). In the ^{13}C NMR spectrum, olefinic and alkyl carbons appear in reasonable regions. Though no direct information on sulfur is available in these spectra, it can be concluded that this polymer has alternating carbon–carbon double bonds along the main chain as shown in Figure 5.

The UV–visible spectra of poly[1-(*n*-alkylthio)-1-propynes] show around 280 nm absorption maxima whose molar absorptivities (ϵ_{max}) are 3600–4200 M^{-1} cm^{-1} (Figure 6); the specific data for poly[1-(*n*-butylthio)-1-propyne] is ϵ_{max} = 3670 M^{-1} cm^{-1} (λ_{max} 278 nm). The absorptions disappear above ca. 350 nm. These findings suggest that the main chain is considerably twisted. This is also the case for most disubstituted acetylene polymers.[5] When compared with the absorption maxima of poly(2-alkynes) ($\epsilon_{max} \leq 1000$ M^{-1} cm^{-1}, λ_{max} 280 nm) and poly(1-chloro-1-alkynes) ($\epsilon_{max} \sim 2000$ M^{-1} cm^{-1}, λ_{max} 270 nm), the absorption maxima of poly[1-(*n*-alkylthio)-1-propynes] are somewhat larger, while their positions are close.

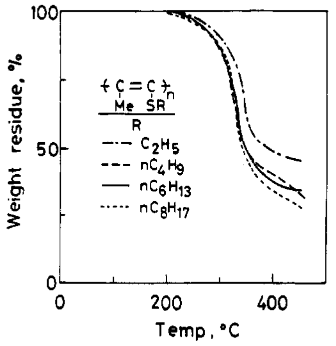

Figure 7. Thermogravimetric analyses (TGA) of poly[1-(*n*-alkylthio)-1-propynes] (samples from Table IV, nos. 8–11; measured in air at a heating rate of 10 °C/min).

Polymer Properties. The present polymers are all colorless solids. General properties are discussed below with samples from Table IV, nos. 7–12.

Poly[1-(methylthio)-1-propyne] did not dissolve in any common organic solvent examined. Poly[1-(ethylthio)-1-propyne] and poly[1-(*n*-butylthio)-1-propyne] were soluble in toluene, hexane, cyclohexane, CCl$_4$, CHCl$_3$, tetrahydrofuran, anisole, diethyl ether, di-*n*-butyl ether, di-*n*-butyl sulfide, and di-*n*-butyl disulfide but were insoluble in (CH$_2$Cl)$_2$, 1,4-dioxane, acetone, acetophenone, ethyl acetate, methyl benzoate, nitrobenzene, acetonitrile, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. The solubility of poly[1-(*n*-decylthio)-1-propyne], a polymer with a very long alkylthio pendant, was somewhat different; that is, it was only partly soluble in anisole and di-*n*-butyl disulfide but insoluble in diethyl ether and di-*n*-butyl ether. The solubilities of poly[1-(*n*-hexylthio)-1-propyne] and poly[1-(*n*-octylthio)-1-propyne] were in between. Transparent films could be prepared by casting these polymers from toluene solution onto a glass plate.

The contact angle of water on the membrane surface of poly[1-(*n*-butylthio)-1-propyne] in air at 25 °C was ca. 100°, close to the values of poly(2-octyne) and poly(1-chloro-1-octyne).[13] Therefore, this sulfur-containing polymer is hydrophobic, which may be because the sulfur is near the main chain and hidden by the alkyl group.

Figure 7 shows thermogravimetric analysis (TGA) curves for poly[1-(*n*-alkylthio)-1-propynes]. The temperatures at which their weight loss started were ca. 220 °C irrespective of the alkyl chain length. The corresponding temperatures for poly(2-alkynes)[14] and poly(1-chloro-1-alkynes)[7] are ca. 200 and 250 °C, respectively. Therefore, the sulfur-containing polyacetylenes are thermally more stable than poly(2-alkynes) but less stable than poly(1-chloro-1-alkynes).

The thermal stability can also be estimated from the so-called α value, which is the probability of main-chain scission on heat treatment in air at 120 °C for 20 h.[14] The α values of the present polymers are in the range 3.8×10^{-3}–1.8×10^{-3} (Table VII), whereas the values of poly(2-alkynes)[14] and poly(1-chloro-1-alkynes)[7] are 40×10^{-3}–55×10^{-3} and 0.12×10^{-3}–0.38×10^{-3}, respectively. These values also suggest that the thermal stabilities of the present polymers lie between those of poly(2-alkynes) and poly(1-chloro-1-alkynes).

As the alkyl chain of poly[1-(*n*-alkylthio)-1-propyne] was lengthened, the polymer became softer and slightly ductile (Table VIII). These tensile properties resemble those of poly(2-alkynes) and poly(1-chloro-1-alkynes),[15] though the

Table VII
Molecular Weight Change of Poly[1-(*n*-alkylthio)-1-alkynes] [-(C(Me)=C(SR))$_n$-] with Heat Treatment[a]

	R[b]			
	C_2H_5	n-C_4H_9	n-C_6H_{13}	n-C_8H_{17}
$\bar{M}_w/10^3$				
before	130	180	110	130
after	60	84	65	62
$\bar{M}_n/10^3$				
before	35	71	34	25
after	15	24	21	20
$10^3\alpha$[c]	3.8	3.5	2.8	1.8

[a] Heat-treated in air at 120 °C for 20 h. [b] Samples from Table IV, nos. 8–11. [c] α denotes the probability of main-chain scission on heat treatment and is defined as follows:

$$\alpha \equiv \frac{\overline{\mathrm{DP}}_{n,0} - \overline{\mathrm{DP}}_n}{\overline{\mathrm{DP}}_n(\overline{\mathrm{DP}}_{n,0} - 1)} \simeq \frac{1}{\overline{\mathrm{DP}}_n} - \frac{1}{\overline{\mathrm{DP}}_{n,0}}$$

where $\overline{\mathrm{DP}}_{n,0}$ and $\overline{\mathrm{DP}}_n$ are initial and final number-average degrees of polymerization.

Table VIII
Mechanical Properties of Poly[1-(*n*-alkylthio)-1-propynes] [-(C(Me)=C(SR))$_n$-][a,b]

	R[c]				
	C_2H_5	n-C_4H_9	n-C_6H_{13}	n-C_8H_{17}	n-$C_{10}H_{21}$
E,[d] MPa	1600	820	340	170	130
σ_B,[e] MPa	53	37	18	11	8
γ_B,[f] %	5	5	20	18	21
T_g,[g] °C	200	180	160	130	90
T_s,[h] °C	240	220	210	190	170

[a] Tensile properties (E, σ_B, and γ_B) and T_g from ref 16. [b] Tensile properties measured at 25 °C. [c] Samples from Table IV, nos. 8–12. [d] Young's modulus. [e] Tensile strength. [f] Elongation at break. [g] Glass transition temperature; determined from dynamic viscoelasticity. [h] Softening temperature.

Table IX
Gas Permeation Behavior of Poly[1-(*n*-alkylthio)-1-propynes] [-(C(Me)=C(SR))$_n$-]

	P,[a] barrer[b]					
R	He	H_2	O_2	N_2	CO_2	CH_4
C_2H_5	60	90	30	9	160	20
n-C_4H_9	58	69	79	18	160	89
n-C_6H_{13}	43	76	38	14	150	45
n-C_8H_{17}	57	91	50	19	180	48
n-$C_{10}H_{21}$	42	78	46	16	190	58

[a] Gas permeability coefficient; measured at 25 °C. Samples from Table IV, nos. 8–12. [b] 1 barrer = 1×10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg).

present polymers are more brittle, probably because of their lower molecular weight.

The glass transition temperature (T_g) of poly[1-(ethylthio)-1-propyne] is 200 °C, fairly high like those of many substituted polyacetylenes,[15] and the T_g decreases progressively with increasing alkyl chain length. The softening temperatures (T_s) of these polymers were higher than their T_g's by ca. 40–80 °C, also decreasing with alkyl chain length.

Poly[1-(*n*-butylthio)-1-propyne] was an electrical insulator with a conductivity of 3×10^{-17} S·cm^{-1} at 20 °C. Unpaired electrons were undetectable in the ESR spectrum of this polymer.

High permeability to gases is one of the salient features of substituted polyacetylenes, especially poly[1-(trimethylsilyl)-1-propyne].[17] Table IX gives data of the gas permeability of the present polymers. The oxygen permeability coefficients (P_{O_2}) of these polymers are in the order of 10 barrer, being medium among various substituted polyacetylenes. This leads to a conclusion that the alkylthio pendant, irrespective of its length, exerts a "neutral" effect on the gas permeability. This contrasts with the fact that globular groups (e.g., Me_3Si) often favor gas permeability while planar groups (e.g., phenyl) disfavor gas permeability.[17b]

Experimental Section

Monomer Synthesis. Monomers were synthesized with some modifications of the method of Pourcelot[18,19] (eq 1). The overall yields of the monomers on the basis of 3-chloro-1-propyne were ca. 50–70%, and their purities were >98% according to gas chromatography (GC). The monomers with n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, and *sec*-C_4H_9 are new compounds. The synthesis of 1-(*n*-butylthio)-1-propyne (**3a**) is detailed below.

$$\mathrm{HC{\equiv}CCH_2Cl + NaS\text{-}\mathit{n}\text{-}C_4H_9 \rightarrow \underset{\mathbf{4a}}{HC{\equiv}CCH_2S\text{-}\mathit{n}\text{-}C_4H_9} \xrightarrow{^{-}OH} \underset{\mathbf{3a}}{MeC{\equiv}CS\text{-}\mathit{n}\text{-}C_4H_9}} \quad (1)$$

3-(*n*-Butylthio)-1-propyne (**4a**): A 2-L, three-necked flask equipped with a pressure-equalizing dropping funnel and a reflux condenser was flushed with dry nitrogen. Anhydrous ethanol (500 mL) was placed in the flask, and Na (11.5 g, 0.50 mol) was gradually added with magnetic stirring and ice cooling. After Na had reacted completely, *n*-butanethiol (53.6 mL, 0.50 mol) was added dropwise at room temperature, and the solution was stirred for an additional 1 h. 3-Chloro-1-propyne (36.2 mL, 0.50 mol) was added dropwise under ice cooling (the reaction was exothermic and the system became turbid). The reaction was monitored for completeness by GC to be finished after 1 h. The reaction mixture was washed with water, and the aqueous phase was extracted with ether. The combined ether extracts were dried ($CaCl_2$) overnight, the solvent was evaporated, and the product, **4a**, was distilled at reduced pressure. Bp 70 °C (15 mmHg), yield 80%.

1-(*n*-Butylthio)-1-propyne (**3a**): A 1-L flask was flushed with dry nitrogen and charged with KOH (39.3 g, 0.70 mol) and tetrahydrofuran (350 mL). **4a** (44.9 g, 0.35 mol) was added dropwise at room temperature with magnetic stirring (the solution changed from yellow to red). The reaction was continued overnight, and its completion was confirmed by GC (silicone DC, 3 m, 120 °C; **4a**, the intermediate allene, and **3a** appeared in this order in GC). The reaction mixture was washed with water, the aqueous phase was extracted with ether, and the organic phase was dried ($MgSO_4$). The ether was evaporated, and the monomer, **3a**, was distilled twice at reduced pressure from CaH_2. Bp 82 °C (32 mmHg), yield 88%, $d^{20}{}_4$ 0.8955 g/dL.

Other Materials. Transition-metal compounds were purchased from Strem Chemicals and used without further purification. Organosilanes (Shin-Etsu Chemicals, Japan) and other organometallics (Aldrich Chemical Co. or Tokyo Kasei, Japan) were also commercially obtained. All solvents and starting materials were of the highest purity commercially available. Solvents for polymerization were further purified by the standard methods,[20] care being exercised to remove trace moisture and oxygen.

Polymerization. Polymerizations were carried out under dry nitrogen in a prebaked, 30-mL flask equipped with a three-way stopcock. Liquid reagents were transferred from one vessel to another with hypodermic syringes. Catalyst solutions were prepared as described before.[7]

The following procedure using 1-(*n*-butylthio)-1-propyne (**3a**) as monomer is representative (see Table IV, no. 9 for results): Monomer solution (3.0 mL) was prepared by mixing **3a** (0.86 mL, 6.0 mmol), bromobenzene (0.60 mL), and toluene (1.5 mL). The catalyst solution (7.5 mL) was separately prepared by dissolving $MoCl_5$ (54.6 mg, 0.20 mmol) and Ph_3SiH (104 mg, 0.40 mmol) in toluene (7.4 mL) and allowed to stand (age) at 80 °C for 30 min before use. Polymerization was initiated by adding 2.5 mL of the monomer solution to the catalyst solution (7.5 mL) and was continued at 80 °C for 24 h. Then the reaction was quenched with a toluene/methanol (volume ratio 4:1) mixture (2 mL), and monomer conversion was measured by GC (silicone DC, 3 m, 130

°C) using bromobenzene as internal standard. The reaction mixture was diluted with toluene (30 mL) and was slowly poured into acetone (800 mL) under magnetic stirring. The polymer precipitated was filtered off, washed with acetone, and dried to a constant weight. Polymer yield was determined by gravimetry.

Polymer Characterization. The $\bar{M}_w$ and $\bar{M}_n$ values of the polymers were measured by GPC on a Jasco Trirotar liquid chromatography [eluent $CHCl_3$; Shodex A804, A806, and A807 columns (Showa Denko, Co. Japan), exclusion limit 2×10^7; RI detector; polystyrene calibration]. GPC analysis of oligomers were carried out with Shodex A802, A803, and A804 columns (exclusion limit 3×10^5).

Elemental analysis was carried out at the Laboratory for Organic Elemental Microanalysis, Kyoto University. IR spectra (KBr pellet) and UV–visible spectra (cyclohexane solution) of polymers were recorded with Shimadzu IR435 and UV190 spectrophotometers, respectively. ^{13}C NMR spectra were observed in $CDCl_3$ solution on a JEOL FX90Q spectrometer. TGA was conducted with a Shimadzu 20B thermal analyzer (in air, heating rate 10 °C/min). The gas permeabilities of the polymers were measured on a K-315-N gas permeability apparatus (Rikaseiki Co., Japan) as stated elsewhere.[17b] Other analyses were performed as described before.[7,12]

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 63550686).

References and Notes

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Registry No. **1** (homopolymer), 105691-94-9; **2** (homopolymer), 129572-09-4; **3** (homopolymer), 120469-13-8; **4** (homopolymer), 129572-11-8; **5** (homopolymer), 123778-87-0; **6** (homopolymer), 129572-13-0; ($MeC{\equiv}CSBu$-*sec*) (homopolymer), 129572-15-2; He, 7440-59-7; H_2, 1333-74-0; O_2, 7782-44-7; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8; $MoCl_5$, 10241-05-1; $MoCl_5$–Ph_3SiH, 789-25-3; $Mo(CO)_6$, 13939-06-5; $MoOCl_4$, 13814-75-0; WCl_6, 13283-01-7; Et_3SiH, 617-86-7; Ph_4Sn, 595-90-4; *n*-Bu_4Sn, 1461-25-2; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8; *n*-BuLi, 109-72-8; Et_3Al, 97-93-8; PhCl, 108-90-7; CCl_4, 56-23-5; $(CH_2Cl)_2$, 107-06-2; $PhOCH_3$, 100-66-3; $PhCO_2CH_3$, 93-58-3; toluene, 108-88-3; cyclohexane, 110-82-7; *n*-heptane, 142-82-5.