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Polymerization of Sulfur-Containing Aromatic Disubstituted Acetylenes and Polymer Characterization

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1-Phenylthio-1-alkynes ($PhS{-}C{\equiv}C{-}R$; R = Me, n-Bu, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, and n-$C_{12}H_{25}$) polymerized in 40—80% yields in toluene at 80 °C in the presence of $MoCl_5$–Ph_3SiH (1 : 2) catalyst, but did not polymerize with the corresponding W catalyst. The produced polymers with R=n-C_8H_{17} and longer were soluble in toluene, chloroform, etc., whose weight-average molecular weights ($\overline{M}_w$) reached 2×10^4. 1-Alkylthio-2-phenylacetylenes ($RS{-}C{\equiv}C{-}Ph$; R=Me, Et, n-Bu) polymerized in 10—20% yields with a WCl_6–Ph_3SiH (1 : 2) catalyst, while they did not produce any polymer with Mo catalysts. Only the polymer with R=n-Bu was soluble in several organic solvents, whose $\overline{M}_w$ was ca. 1×10^4. Although 1-phenylthio-2-phenylacetylene ($PhS{-}C{\equiv}C{-}Ph$) polymerized with both $MoCl_5$–Ph_3SiH and WCl_6–Ph_3SiH, the produced polymers were insoluble in all solvents. Poly(1-phenylthio-1-dodecyne) and poly(1-butylthio-2-phenylacetylene) were yellow solids with absorption maxima at around 280 m; their weight loss in a thermogravimetric analysis started at around 200 °C.

In general, sulfur-containing polymers exhibit several unique properties, such as moderate hydrophilicity, complex-forming ability, and chemical reactivity in hydrolysis and oxidation.[1] Although sulfur-containing polyacetylenes are expected to show interesting properties and functions based on their unique structure, only several examples of such polymers have been known so far; e.g., poly[1-chloro-2-(2-thienyl)acetylene],[2] poly(2-ethynylthiophene),[3] poly(3-ethynylthiophene),[4] and poly(dipropargyl sulfide).[5] The yields of these polymers are generally low, and the weight-average molecular weights are 2×10^4 at highest. Such difficulty in the synthesis of high-molecular-weight sulfur containing polyacetylenes in good yields is attributable to the nature of sulfur, in that it can coordinate to catalyst metals to reduce the catalyst activity.

In our previous papers we reported that 1-n-alkylthio-1-propynes[6] and 1-methylthio-1-alkynes,[7] which are sulfur-containing aliphatic acetylenes, polymerize in the presence of Mo catalysts to give in high yields polymers whose weight-average molecular weights ($\overline{M}_w$) reach 1×10^5—2×10^5. The high reactivity of these monomers was attributed to the low basicity of the sulfur atom due to its direct bonding to an acetylenic carbon.

In the present study, we examined the polymerization of 1-phenylthio-1-alkynes (**1**), 1-n-alkylthio-2-phenylacetylenes (**2**), and 1-phenylthio-2-phenylacetylene (**3**) which are sulfur-containing aromatic acetylenes. Consequently, it proved that 1-phenylthio-1-dodecyne (**1a**) and 1-butylthio-2-phenylacetylene (**2a**) produce soluble polymers, while 1-phenylthio-2-phenylacetylene (**3**) does not. The structure and properties of the product polymers were elucidated. The results are discussed while comparing with those of sulfur-containing aliphatic acetylenes.

$Ph{-}S{-}C{\equiv}C{-}n{-}C_{10}H_{21}$ **1a**

$n{-}Bu{-}S{-}C{\equiv}C{-}Ph$ **2a**

$PhS{-}C{\equiv}C{-}Ph$ **3**

Experimental

Monomer Syntheses. Monomers were synthesized with modifications of the literature methods according to the following scheme:[7—9]

$$HC{\equiv}CR + n\text{-}BuLi \rightarrow LiC{\equiv}CR \xrightarrow{PhSSPh} PhSC{\equiv}CR$$

(R=Me,n-Bu,n-C_6H_{13},n-C_8H_{17},n-$C_{10}H_{21}$, and n-$C_{12}H_{25}$)

Table 1. Polymerization of 1-Phenylthio-1-dodecyne by Various Catalysts[a)]

Catalyst	Monomer conversion %	Polymer[b)] Yield/%	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$
$MoCl_5$	63	35	21	6.5
$MoCl_5$–Ph_3SiH	100	61	20	5.3
$MoCl_5$–Ph_4Sn	69	13	13	3.6
$MoCl_5$–Ph_3Sb	56	13	17	6.1
$Mo(CO)_6$–$h\nu$[c)]	47	0	—	—
WCl_6–Ph_3SiH	71	0	—	—
$NbCl_5$–Ph_3SiH	71	0	—	—
$TaCl_5$–Ph_3SiH	43	0	—	—

a) Polymerized in toluene at 80 °C for 24 h; $[M]_0=0.50$ M, [Cat]=20 mM, [Cocat]=40 mM (1 M=1 mol dm^{-3}). b) Methanol-insoluble product. c) Polymerized in CCl_4; $[Mo(CO)_6]=10$ mM.

Table 2. Solvent Effects on the Polymerization of 1-Phenylthio-1-dodecyne by $MoCl_5$–Ph_3SiH (1 : 2)[a)]

Solvent	(DC[c)])	Monomer conversion %	Polymer[b)] Yield/%	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$
Cyclohexane(A)	(1.9)	100	59	22	6.5
Toluene(B)	(2.4)	100	61	20	5.3
(A)+(B) (4 : 1)	(2.0)	100	85	25	6.8
Anisole	(4.3)	100	54	19	6.2
PhCl	(5.8)	100	38	18	5.0
CCl_4	(2.2)	81	0	—	—

a) Polymerized at 80 °C for 24 h; $[M]_0=0.50$ M, $[MoCl_5]=20$ mM. b) Methanol-insoluble product. c) Dielectric constant.

$$HC{\equiv}CPh + n\text{-}BuLi \rightarrow LiC{\equiv}CPh \xrightarrow{RSSR} PSC{\equiv}CPh$$
$$(R = Me, Et, n\text{-}Bu, \text{ and } Ph)$$

A detailed procedure of monomer synthesis has been described elsewhere.[7)]

Procedures. Metal chloride (MCl_n) based catalysts were prepared by mixing MCl_n and organometallic cocatalysts (two molar amounts) in a polymerization solvent and aging the mixtures at 80 °C for 30 min before use. Metal carbonyl $[M(CO)_6]$ based catalysts were prepared by irradiation of a CCl_4 solution of $M(CO)_6$ with a 200-W high-pressure Hg lamp from a distance of 5 cm at 30 °C for 24 h. Monomer consumptions were determined by gas chromatography (GC). The polymers formed were isolated by precipitation into a large amount of methanol. The polymer yields were determined by gravimetry.

The $\overline{M}_w$ and number-average molecular weights ($\overline{M}_n$) of polymers were evaluated by gel permeation chromatography (GPC; eluent $CHCl_3$; polystyrene gel columns) by the use of a polystyrene calibration. Other analyses of polymers were carried out as described in a previous paper.[6)] The ^{13}C NMR spectra of monomers were measured on a JEOL GSX-270 (270 MHz) spectrometer in $CDCl_3$ at 25 °C.

Results and Discussion

Polymerization of 1-Phenylthio-1-dodecyne (1a). Among the various 1-phenylthio-1-alkynes, we examined in detail the polymerization of 1-phenylthio-1-dodecyne because it produced a soluble polymer (see below).

1-Phenylthio-1-dodecyne provided a polymer in good yields only in the presence of $MoCl_5$-based ones among group 5 and 6 transition metal catalysts (Table 1). Even $MoCl_5$ alone was effective to some extent. Both the monomer conversion and the polymer yield increased when Ph_3SiH was used as a cocatalyst. The weight-average molecular weight ($\overline{M}_w$) of the formed polymer was ca. 2×10^4. In contrast, Ph_4Sn and Ph_3Sb rather decreased the polymer yield and, hence, were not as effective as cocatalysts. Further, no methanol-insoluble polymers were produced with $Mo(CO)_6$–$h\nu$ and W catalysts, and most of the products were linear oligomers with average degrees of polymerization of ca. 5. $NbCl_5$- and $TaCl_5$-based catalysts, which are effective to sterically crowded disubstituted acetylenes, produced no methanol-insoluble polymers. As has been clarified in previous papers,[6,7)] the $MoCl_5$–Ph_3SiH (1 : 2) catalyst is also the most effective for sulfur-containing aliphatic acetylenes (1-methylthio-1-octyne, etc.). Consequently, it can be said that 1-phenylthio-1-dodecyne shows a catalyst selectivity similar to those of sulfur-containing aliphatic acetylenes. The methanol-soluble products were linear oligomers; it seems that they formed by the same mechanism as that for the polymeric products, because the molecular weight of the latter is not very high, either.

Table 2 shows solvent effects on the polymerization by the $MoCl_5$–Ph_3SiH (1 : 2) catalyst. In hydrocarbon solvents and anisole, polymers having a $\overline{M}_w$ of ca. 2×10^4 were produced in over 50% yields. Toluene has been employed as a solvent in the polymerization of substituted acetylenes, because it dissolves both the catalyst and polymers well. In the polymerization of 1-phenylthio-1-dodecyne, however, a mixture of cyclohexane and toluene (4 : 1) gave a better result from the viewpoint of both the yield and the molecular weight of the polymer. On the other hand, no methanol-insoluble polymer was produced in CCl_4, the reason of which is not clear at present.

Polymerization of 1-Phenylthio-1-alkynes (1). Polymerization of 1-phenylthio-1-alkynes with different alkyl lengths was examined using $MoCl_5$–Ph_3SiH (1 : 2) (Table 3). The monomer conversions were quantitative and the yields of methanol-insoluble polymers were 40—

Table 3. Polymerization of 1-Phenylthio-1-alkynes by $MoCl_5$–Ph_3SiH (1 : 2)[a)]

PhS–C≡C–R R	Monomer conversion/%	Polymer[b)] Yield/%	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$
CH_3	100	81	Insoluble	
n-C_4H_9	100	63	Insoluble	
n-C_6H_{13}	100	52	Insoluble	
n-C_8H_{17}	100	59	16	6.0
n-$C_{10}H_{21}$	100	61	20	5.3
n-$C_{12}H_{25}$	100	44	19	5.0

a) Polymerized in toluene at 80 °C for 24 h; $[M]_0=0.50$ M, $[MoCl_5]=20$ mM. b) Methanol-insoluble product.

80%, irrespective of the alkyl-chain length. The polymers with shorter alkyl chains (R=Me–n-C_6H_{13}) did not completely dissolve in any organic solvents. The polymers with n-C_8H_{17}, n-$C_{10}H_{21}$, and n-$C_{12}H_{25}$ as alkyl pendants were soluble in toluene, $CHCl_3$, etc., whose $\overline{M}_w$'s were ca. 2×10^4.

Thus, the alkyl-chain length of 1-phenylthio-1-alkynes does not greatly affect the monomer conversion and the polymer yield, but does bring about large differences in the solubility of the polymers formed.

Polymerization of 1-Butylthio-2-phenylacetylene (2a). Table 4 shows the results for the polymerization of 1-butylthio-2-phenylacetylene by various catalysts. Among the several 1-n-alkylthio-2-phenylacetylenes examined, this monomer provides a polymer totally soluble in toluene (see below).

Among the catalysts listed in Table 4, only the WCl_6-based ones formed polymers from 1-butylthio-2-phenylacetylene. The polymer yields were moderate (20—50%) and the $\overline{M}_w$ values were not very high (ca. 1×10^4), either. It is noted that $MoCl_5$–Ph_3SiH, which polymerizes other types of sulfur-containing acetylenes, is ineffective. A few organometallic cocatalysts were examined in the polymerization of 1-butylthio-2-phenylacetylene by WCl_6. In this polymerization, the polymer yield was the highest when no organometallic compound was added. Unlike in the case of 1-phenylthio-1-dodecyne, Ph_3SiH rather decreased the polymer yield, though $\overline{M}_w$ of the polymer hardly changed.

Table 4. Polymerization of 1-Butylthio-2-phenylacetylene by Various Catalysts[a]

Catalyst	Monomer conversion	Polymer[b]		
	%	Yield/%	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$
WCl_6	55	51	9.1	4.8
WCl_6–Ph_3SiH	59	21	10	5.1
WCl_6–Ph_4Sn	30	0	—	—
WCl_6–Ph_3Sb	30	0	—	—
$W(CO)_6$–$h\nu$[c]	24	0	—	—
$MoCl_5$–Ph_3SiH	59	0	—	—
$NbCl_5$–Ph_3SiH	30	0	—	—
$TaCl_5$–Ph_3SiH	30	0	—	—

a) Polymerized in toluene at 80 °C for 24 h; $[M]_0$=0.50 M, [Cat]=20 mM, [Cocat]=40 mM. b) Methanol-insoluble product. c) Polymerized in CCl_4; $[W(CO)_6]$=10 mM.

Table 5. Polymerization of 1-n-Alkylthio-2-phenylacetylenes by WCl_6–Ph_3SiH (1 : 2)[a]

PSC≡CPh	Monomer conversion	Polymer[b]		
R	%	Yield/%	$\overline{M}_w/10^3$	$\overline{M}_n/10^3$
CH_3	41	7	Insoluble	
C_2H_5	38	12	Insoluble	
n-C_4H_9	59	21	10	5.1

a) Polymerized in toluene at 80 °C for 24 h; $[M]_0$=0.50 M, $[WCl_6]$=20 mM. b) Methanol-insoluble product.

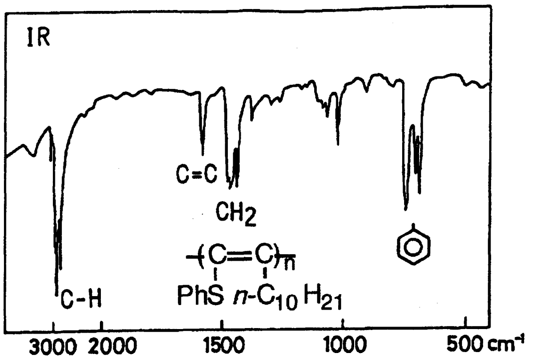
Polymerization of 1-n-Alkylthio-2-phenylacetylenes (2). The polymerization of 1-n-alkylthio-2-phenylacetylenes having different alkyl chain lengths was studied by using the WCl_6–Ph_3SiH (1 : 2) catalyst (Table 5). The polymer yield increased with increasing alkyl-chain length to become ca. 20% with R=n-Bu. The polymers with methylthio and ethylthio groups were insoluble in any organic solvent. On the other hand, poly(1-butylthio-2-phenylacetylene) was totally soluble in toluene, $CHCl_3$, etc., and the $\overline{M}_w$ was 1×10^4.

Polymerization of 1-Phenylthio-2-phenylacetylene (3). The polymerization of 1-phenylthio-

Table 6. Polymerization of 1-Phenylthio-2-phenylacetylene by Various Catalysts[a]

Catalyst	Monomer conversion/%	Polymer[b] yield/%
$MoCl_5$	70	6
$MoCl_5$–Ph_3SiH	69	25
WCl_6	36	5
WCl_6–Ph_3SiH	77	14
$NbCl_5$–Ph_3SiH	50	0
$TaCl_5$–Ph_3SiH	38	0

a) Polymerized in toluene at 80 °C for 24 h; $[M]_0$=0.50 M, [Cat]=20 mM, [Cocat]=40 mM. b) Insoluble in any solvent.



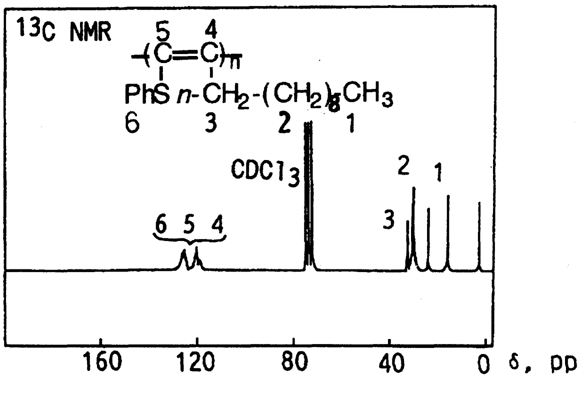


Fig. 1. IR and ^{13}C NMR spectra of poly(1-phenylthio-1-dodecyne) (IR: KBr pellet; ^{13}C NMR: in $CDCl_3$).

Table 7. ^{13}C NMR Chemical Shifts of sp Carbons in Sulfur-Containing Acetylenes

Monomer	δ_{C_α}	δ_{C_β}	$\lvert\delta_{C_\alpha}-\delta_{C_\beta}\rvert$	Catalyst[a]
Ph–S–C_α≡C_β–n-$C_{10}H_{21}$	63.4	98.3	34.9	Mo
Me–S–C_α≡C_β–n-C_8H_{17}	68.6	92.9	24.3	Mo
n-Bu–S–C_α≡C_β–Me	67.8	89.3	21.7	Mo
Ph–S–C_α≡C_β–Ph	80.0	94.2	14.2	Mo, W
n-Bu–S–C_α≡C_β–Ph	79.6	92.8	13.2	W
H–C_α≡C_β–t-Bu	93.1	66.4	26.7	Mo(W)
H–C_α≡C_β–s-Bu	89.0	68.2	20.8	Mo(W)
H–C_α≡C_β–i-Bu	83.4	69.0	14.4	Mo, W
H–C_α≡C_β–n-Bu	84.6	68.1	16.5	W(Mo)
Cl–C_α≡C_β–Alkyl	ca. 57	ca. 69	ca. 12	Mo
Me–C_α≡C_β–n-Pr	79.2	75.4	3.8	Mo(W)
Et–C_α≡C_β–Et	80.8	80.8	0	W(Mo)
Ph–C_α≡C_β–Ph	89.5	89.5	0	W

a) Effective catalyst metals are shown. Those in parentheses denote less active metals.

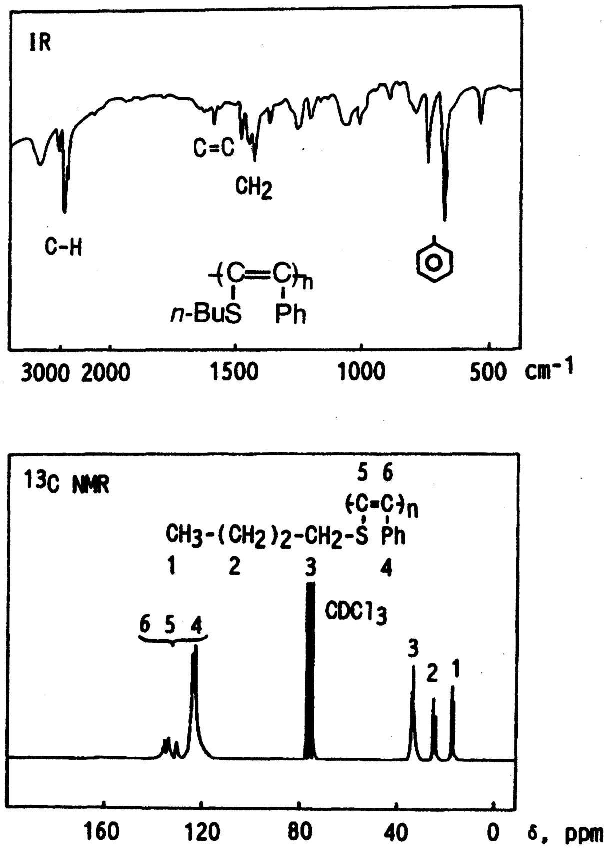


Fig. 2. IR and ^{13}C NMR spectra of poly(1-butylthio-2-phenylacetylene) (IR: KBr pellet; ^{13}C NMR: in $CDCl_3$).

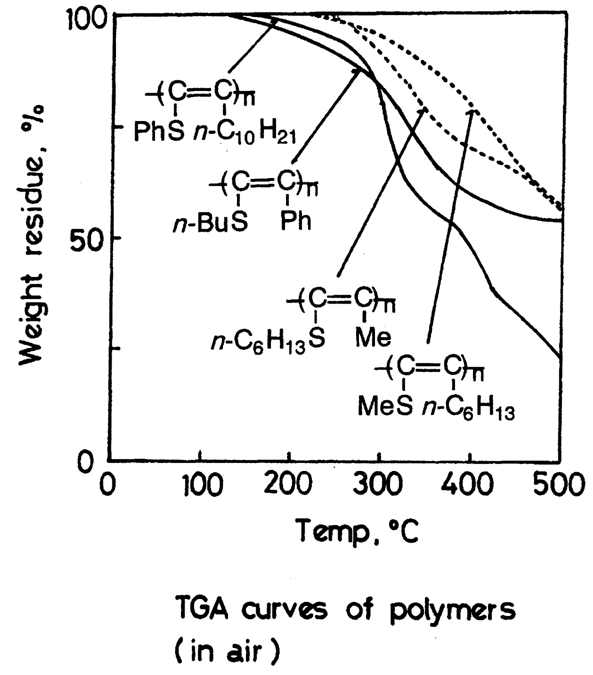


Fig. 3. TGA curves of sulfur-containing polyacetylenes (in air; heating rate 10 °C min^{-1}).

2-phenylacetylene was studied by using various catalysts (Table 6). Unlike the other sulfur-containing acetylenes, it polymerized with both $MoCl_5$–Ph_3SiH and WCl_6–Ph_3SiH. The formed polymers, however, were insoluble in all solvents. $NbCl_5$- and $TaCl_5$-based catalysts gave no methanol-insoluble polymers in spite of the presence of the bulky substituents.

Regarding the Kind of Catalysts. The kind of catalysts suitable for the polymerization of sulfur-containing acetylenes varies depending on monomers, which can be correlated with the difference in the ^{13}C NMR chemical shifts of the two acetylenic carbons (the difference in the chemical shifts reflects the electron density distribution). Thus, if the difference between the chemical shifts of C_β and C_α is large, the monomer polymerizes with Mo-based catalysts, whereas W-based catalysts are effective to monomers whose chemical-shift differences are small (Table 7).

A similar tendency has also been seen in the polymer-

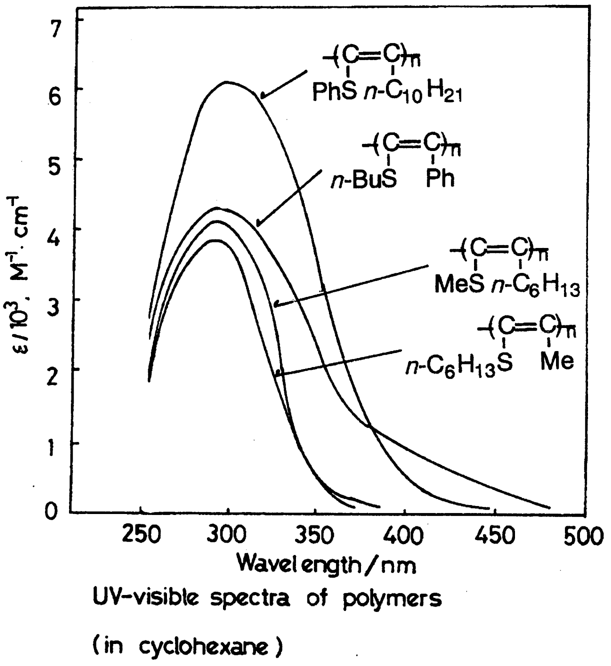


Fig. 4. UV-visible spectra of poly(1-phenylthio-1-dodecyne) and poly(1-butylthio-2-phenylacetylene) (in cyclohexane).

ization of monosubstituted hydrocarbon acetylene.[10) Thus, Mo-based catalysts show higher activities when the value of $|\delta_{C_\alpha}-\delta_{C_\beta}|$ is large, while W-based catalysts are more active when the value is small. This is also the case for the disubstituted acetylenes listed in Table 7.

Polymer Structure. The IR and ^{13}C NMR spectra of poly(1-phenylthio-1-dodecyne) and poly(1-butylthio-2-phenylacetylene) are shown in Figs. 1 and 2, respectively. In the IR spectra of both polymers, a weak absorption at 1600 cm^{-1} is assignable to a stretching of the C=C bond, while the absorptions at 750 cm^{-1} are due to the C–H out-of-plane deformation of the phenyl group. The ^{13}C NMR spectra show signals due to the olefinic and phenyl carbons in the δ=140—120 region. These spectra are compatible with a main-chain structure comprising of alternating C=C double bonds.

Polymer Properties. Poly(1-phenylthio-1-dodecyne) and poly(1-butylthio-2-phenylacetylene) are yellow solids soluble in various organic solvents, such as toluene, hexane, $CHCl_3$, and anisole. Poly(1-phenylthio-2-phenylacetylene) is an ocherous solid insoluble in any solvent.

The thermogravimetric analysis (TGA) curves of the present polymers along with aliphatic counterparts measured in air are shown in Fig. 3. The onset temperatures of the weight loss were 200 °C with poly(1-phenylthio-1-dodecyne) and 180 °C with poly(1-butylthio-2-phenylacetylene). On the other hand, the temperatures for the sulfur-containing aliphatic polymers are all ca. 230 °C,[6,7) indicating that the present sulfur-containing aromatic polyacetylenes are not necessarily thermally more stable. Possible reasons include the rather low molecular weights and/or the long alkyl pendants of the present polymers.

Figure 4 illustrates the UV-visible spectra of poly(1-phenylthio-1-dodecyne) and poly(1-butylthio-2-phenylacetylene) as well as the aliphatic counterparts measured in a cyclohexane solution. The cutoff of the absorption for poly(1-phenylthio-1-dodecyne) is ca. 450 nm, while that for poly(1-butylthio-2-phenylacetylene) is ca. 480 nm. On the other hand, the sulfur-containing aliphatic polyacetylenes have absorption only in the region <400 nm, which corresponds with their colorlessness. These results indicate that the phenyl rings take part in conjugation with the main chain in the present polymers.

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