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Polymerization of 1-Phenyl-1-alkynes by Halides of Niobium and Tantalum[1]

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ABSTRACT: Polymerization of 1-phenyl-1-alkynes (RC≡CPh; R = CH_3, C_2H_5, n-C_4H_9, and n-C_7H_{15}) was examined with the pentahalides of niobium (Nb) and tantalum (Ta) as catalysts. 1-Phenyl-1-propyne yielded a completely soluble, high-molecular-weight polymer ($\bar{M}_w$ 5×10^5–1×10^6) with $TaCl_5$ and $TaBr_5$. Degradation of poly(1-phenyl-1-propyne) occurred after 100% conversion of the monomer in the presence of these catalysts. 1-Phenyl-1-butyne and -1-nonyne gave relatively high polymers ($\bar{M}_w$ 1×10^5–3×10^5) with $NbCl_5$ and $NbBr_5$. 1-Phenyl-1-hexyne afforded an insoluble polymer. Unlike poly(1-phenyl-1-propyne), these polymers did not undergo degradation with Nb or Ta catalysts. All the polymers formed had alternating double bonds along the main chain. They were, however, white, air-stable, electrically insulating solids because of their twisted main-chain conformations resulting from the presence of two substituents per repeating unit.

Introduction

There have been many studies on the polymerization of acetylene and monosubstituted acetylenes with Ziegler catalysts.[2] To our knowledge, however, Ziegler catalysts such as Ti(On-Bu)$_4$–Et_3Al and Fe(acac)$_3$–Et_3Al do not provide polymers from disubstituted acetylenes. We have been studying the polymerization of mono- and disubstituted acetylenes using catalysts based on molybdenum (Mo) and tungsten (W), group 6 transition metals.[3] A feature of these catalysts is that mixtures of $MoCl_5$ or WCl_6 with organometallic cocatalysts [e.g., tetraphenyltin (Ph_4Sn)] polymerize disubstituted acetylenes (1-phenyl-1-propyne, diphenylacetylene, 1-chloro-2-phenylacetylene, 2-alkynes, *sym*-dialkylacetylenes, etc).[4]

Halides of niobium (Nb) and tantalum (Ta), group 5 transition metals, are known to selectively cyclotrimerize acetylene and monosubstituted acetylenes (phenylacetylene, 1-hexyne).[5] On the other hand, it has been reported that organo–Nb(III) and –Ta(III) complexes polymerize disubstituted acetylenes (1-phenyl-1-propyne, 3-hexyne, 4-methyl-2-hexyne).[6] These complexes, however, are sensitive to air and rather difficult to prepare. We have preliminarily reported that simple pentahalides of Nb and Ta polymerize disubstituted acetylenes (1-phenyl-1-propyne, 2-, 3-, and 4-octynes).[7] These halides are stable to air and can be commercially obtained. Thus, they are very interesting potential catalysts for the polymerization of various disubstituted acetylenes.

The present paper deals with the polymerization of 1-phenyl-1-alkynes (RC≡CPh; R = CH_3, C_2H_5, n-C_4H_9, or n-C_7H_{15}) catalyzed by halides of Nb and Ta. The synthesis of polymers having high molecular weights has been achieved with the Nb and Ta catalysts; the polymers other than poly(1-phenyl-1-propyne) are new polymers. The present catalysts are compared with Mo- and W-based catalysts. Further, the structure and properties of the polymers are revealed.

Experimental Section

Materials. Halides of Nb(V) and Ta(V) were commercially obtained (Alfa Products) and used without further purification. 1-Phenyl-1-alkynes were purchased from Farchan Labs and distilled twice at reduced pressures from calcium hydride. Solvents for polymerization were washed with acid and/or alkali solutions and distilled twice from appropriate drying agents.

Polymerization. Polymerization was carried out under dry nitrogen by adding monomer solutions to catalyst solutions. An example of the procedure is as follows: A monomer solution consisting of 1-phenyl-1-propyne (1.5 mL, 1.39 g, 12 mmol), bromobenzene [0.36 mL; internal standard for gas chromatography (GC)], and toluene (4.14 mL) was prepared under dry nitrogen. In a 30-mL Erlenmeyer flask equipped with a three-way stopcock, $TaCl_5$ (71.6 mg, 0.20 mmol) was dissolved in toluene (5 mL) by keeping at 80 °C for 10 min under dry nitrogen. To this catalyst solution, 5 mL of the monomer solution was immediately added at 80 °C [the residual monomer solution (1 mL) was used for GC]. After 6 h, polymerization was terminated by adding a toluene–methanol mixture (volume ratio 4:1; 5 mL). The conversion was determined by measuring the residual-monomer concentration by GC (poly(ethylene glycol) 6000, 2 m; 140 °C): conversion 100%. The reaction mixture was diluted with toluene (80 mL) and poured into methanol (3 L) under stirring. The precipitated polymer was filtered off and dried to a constant weight: polymer yield 0.89 g, 77%.

Characterization of Products. For high-molecular-weight polymers, weight-average molecular weights ($\bar{M}_w$) were determined by the light-scattering method (Chromatix KMX-6 light-scattering photometer; tetrahydrofuran solution); dn/dc (mL·g^{-1}): poly(1-phenyl-1-propyne) 0.230, poly(1-phenyl-1-butyne) 0.285, poly(1-

Table I
Polymerization of 1-Phenyl-1-propyne by Various Catalysts[a]

			polymer		
no.	catalyst	conversion, %	yield, %	10^{-3}MW[b]	[η],[c] dL/g
1	NbF_5	100	0		
2	$NbCl_5$	100	81	4.1 ($\bar{M}_n$)	
3	$NbBr_5$	100	61	3.1 ($\bar{M}_n$)	
4	NbI_5	0	0		
5	TaF_5	100	0		
6	$TaCl_5$	100	41	2.6 ($\bar{M}_n$)	
7[d]	$TaCl_5$	100	77	500 ($\bar{M}_w$)[f]	2.70
8	$TaBr_5$	82	57	920 ($\bar{M}_w$)	3.55
9	TaI_5	0	0		
10[e]	$MoCl_5 \cdot Ph_4Sn$	27	~0		
11[e]	$WCl_6 \cdot Ph_4Sn$	85	57	3.9 ($\bar{M}_n$)	

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 1.0$ M, [Cat.] = 20 mM. [b] $\bar{M}_w$ by the light-scattering method, and $\bar{M}_n$ by VPO. [c] Measured in toluene at 30 °C. [d] Polymerized for 6 h. [e] Polymerized at 60 °C; [Cat.] = 30 mM. [f] According to GPC, $\bar{M}_w = 570 \times 10^3$, $\bar{M}_n = 280 \times 10^3$, $\bar{M}_w/\bar{M}_n = 2.0$.

phenyl-1-nonyne) 0.195. For low-molecular-weight polymers, number-average molecular weights ($\bar{M}_n$) were determined by vapor pressure osmometry (VPO) (Hitachi 117 MW apparatus; benzene solution, 45 °C). Some molecular weights and their distributions (MWD) of reaction products were examined by gel permeation chromatography (GPC) (Jasco Triroter chromatograph; column, Shodex A802, 804, 806 polystyrene gel; eluent, chloroform; a polystyrene calibration used). Intrinsic viscosities of polymers ([η]) were measured in toluene at 30 °C. Elemental analyses were performed at the Laboratory for Organic Elemental Microanalysis, Kyoto University. IR, UV, and NMR spectra were measured on Shimadzu IR27G, Shimadzu UV190, and JEOL FX90Q spectrometers, respectively. Softening points were determined with a Yanaco MP-300 micro-melting-point apparatus. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with a Shimadzu 20B thermal analyzer at a heating rate of 10 °C/min. Electrical conductivities (σ) were measured at 20 °C as described elsewhere.[8]

Results and Discussion

Polymerization of 1-Phenyl-1-propyne. Table I shows results for the polymerization of 1-phenyl-1-propyne by various catalysts. The reactions were usually carried out in toluene at 80 °C for 24 h.

Among the halides of Nb(V) and Ta(V), $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$ yielded methanol-insoluble polymers. The molecular weights of the polymers obtained with $NbCl_5$ and $NbBr_5$ were no more than several thousand. On the other hand, the polymers formed with $TaCl_5$ after 6 h and with $TaBr_5$ after 24 h were as high as several hundred thousand. The high molecular weights of polymers are endorsed by their high intrinsic viscosities. A ratio of weight- to number-average molecular weight tentatively determined by GPC was about 2, suggesting that this polymerization is homogeneous (see Table I, footnote *f*). Rather surprisingly, the molecular weight of the polymer produced with $TaCl_5$ after 24-h polymerization was only several thousand. This is due to a degradation reaction of the polymer formed, which will be described in more detail below.

Though the conversions with NbF_5 and TaF_5 reached 100%, all the products were soluble in methanol. The products were mixtures of linear oligomers (dimer to ~ decamer) according to GPC, which have probably formed by a cationic mechanism because NbF_5 and TaF_5 are strong Lewis acids. The iodides of Nb(V) and Ta(V) did not effect any reaction of 1-phenyl-1-propyne.

For comparison, polymerization was tried by using $MoCl_5 \cdot Ph_4Sn$ and $WCl_6 \cdot Ph_4Sn$ (see also ref 4a). Consequently, $WCl_6 \cdot Ph_4Sn$ gave a low-molecular-weight polymer in moderate yield, while $MoCl_5 \cdot Ph_4Sn$ did not. Unlike Nb and Ta catalysts, WCl_6 alone (without the Ph_4Sn cocatalyst) did not exert any catalytic activity.

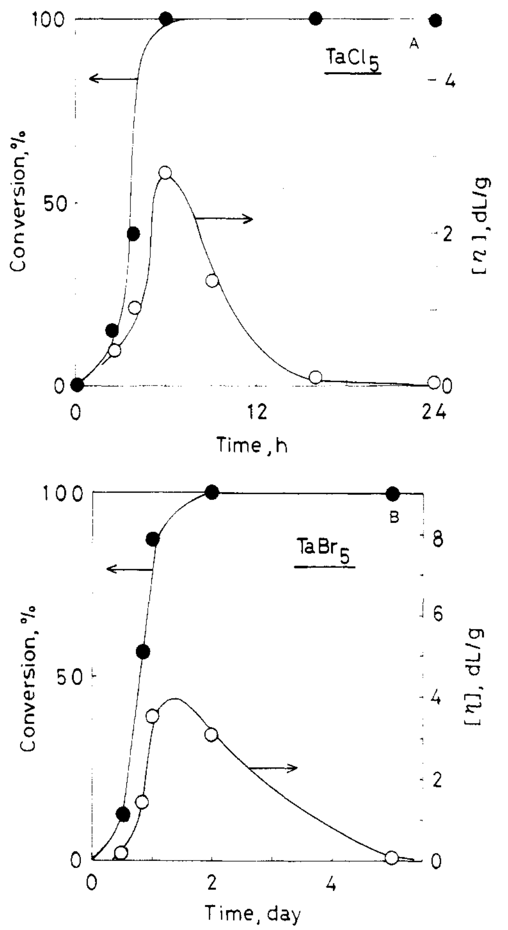

Figure 1. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by Ta catalysts (polymerized in toluene, 80 °C, $[M]_0 = 1.0$ M, [Cat.] = 20 mM; [η] measured in toluene at 30 °C).

Figure 1 shows the changes of conversion and intrinsic viscosity (measured in toluene at 30 °C) of polymer with time in the polymerizations by $TaCl_5$ and $TaBr_5$. The polymerization by $TaCl_5$ proceeded slowly at first and later accelerated to reach 100% in about 6 h. The intrinsic viscosity of the polymer increased with monomer conversion up to 2.7 dL/g, whereas after 100% conversion it decreased steeply with time to become lower than 0.1 dL/g after 24 h. The polymer degradation took place also with $TaBr_5$; in this case, the maximum molecular weight was observed rather adventitiously around 24 h. As Figure 2 shows, not only the Ta catalysts but $NbCl_5$ and $NbBr_5$ also effected polymer degradation. The maximum intrinsic viscosities with $NbCl_5$ and $NbBr_5$ were, however, ~0.6 and ~0.3 dL/g, respectively, not so large as those for Ta catalysts.

Characteristics of the present polymer degradation include the following: (i) The degradation product consists of linear oligomers with a wide molecular weight distribution (dimer to ~20-mer) according to GPC. (ii) The molecular weight of an isolated poly(1-phenyl-1-propyne) did not change when left in solution in the absence of $TaCl_5$, but decreased in the presence of $TaCl_5$. This means that the polymerization catalysts such as $TaCl_5$ induce the polymer degradation. (iii) The polymer degradation occurs only after the monomer has been completely consumed. This should be due to the fact that the coordinating ability

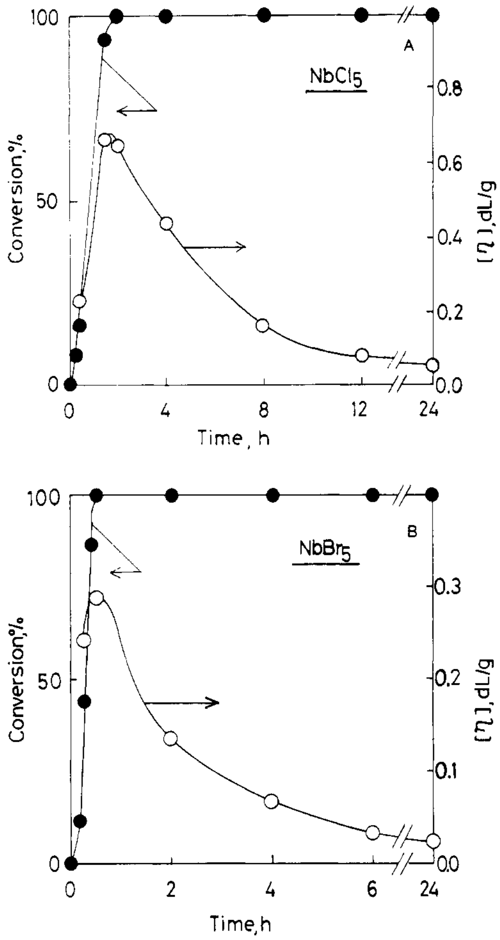

Figure 2. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-propyne by Nb catalysts (polymerized in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM; [η] measured in toluene at 30 °C).

of the monomer (an acetylene) to transition metals is greater than that of the polymer (a polyene). (iv) Interestingly, this polymer degradation could be prevented by use of organometallic cocatalysts such as tetraphenyltin (Ph_4Sn).[9] For instance when polymerization was carried out with a 1:1 mixture of $TaCl_5$ and Ph_4Sn under the conditions shown in Figure 1, the conversion reached 100% in 1 h, and the intrinsic viscosity of polymer (3.26 dL/g) was unchanged even after 24-h polymerization. A detailed study on the effect of cocatalysts is in progress.

Even when no polymer degradation occurred in the polymerization by $TaCl_5$ and $TaBr_5$ (that is, when conversion was less than 100%), considerable amounts of methanol-soluble product were simultaneously obtained (e.g., Table I, no. 8). This methanol-soluble product proved to be a cyctotrimer according to its GPC (unimodal distribution), molecular weight measurement, and IR and ^1H NMR spectra. This indicates that two kinds of active species exist at the same time; one should be a metal carbene which provides the polymer, and the other a metallocyclopentadiene which gives the cyclotrimer.[3,5]

The polymerization of 1-phenyl-1-propyne was studied in more detail with $TaCl_5$ as catalyst (Table II). Regarding polymerization temperature, reaciton hardly occurred at 50 °C, a high-molecular-weight polymer was formed in high yield at 80 °C, and polymer degradation seems to have taken place following the polymerization at 100 °C. This polymerization proceeded in hydrocarbons and halogenated hydrocarbons but did not occur in oxygen-containing solvents like 1,4-dioxane. Generally hydrocarbons achieved higher molecular weights as polymerization solvents than did halogenated hydrocarbons.

Table II
Effects of Temperature and Solvent on the Polymerization of 1-Phenyl-1-propyne by $TaCl_5$[a]

			polymer		
solv	temp, °C	conversion, %	yield, %	$10^{-3}\bar{M}_w$[b]	[η],[c] dL/g
toluene	50	10	0		
toluene	80	100	68	340	1.80
toluene	100	100	51	4.8	0.038
cyclohexane	80	100	83	410	1.96
$(CH_2Cl)_2$	80	96	29	56	0.340
CCl_4	80	64	15	5.4	0.042
1,4-dioxane	80	0	0		
$PhCOOCH_3$	80	0	0		
$PhCOCH_3$	80	0	0		

[a] Polymerized for 8 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] Calculated from viscosities. [c] Measured in toluene at 30 °C.

Table III
Polymerization of 1-Phenyl-1-butyne by Various Catalysts[a]

			polymer		
no.	catalyst	conversion, %	yield, %	$10^{-3}\bar{M}_w$[b]	[η],[c] dL/g
1	NbF_5	100	0		
2	$NbCl_5$	100	~100	220	2.80
3	$NbBr_5$	100	86	260	3.60
4	NbI_5	0	0		
5	TaF_5	100	0		
6	$TaCl_5$	100	46	43[e]	0.62
7	$TaBr_5$	79	45	48	0.73
8	TaI_5	0	0		
9[d]	$MoCl_5 \cdot Ph_4Sn$	13	~0		
10[d]	$WCl_6 \cdot Ph_4Sn$	100	~100	44[e]	0.63

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] By the light-scattering method. [c] Measured in toluene at 30 °C. [d] Polymerized at 60 °C; [Cat.] = 30 mM. [e] Calculated from viscosity.

Table IV
Effects of Temperature and Solvent on the Polymerization of 1-Phenyl-1-butyne by $NbCl_5$[a]

			polymer		
solv	temp, °C	conversion, %	yield, %	polymer $10^{-3}\bar{M}_w$[b]	[η],[c] dL/g
toluene	50	100	82	120	1.26
toluene	80	100	~100	220	2.80
toluene	100	100	78	200[d]	2.60
cyclohexane	80	100	96	110	1.66
$(CH_2Cl)_2$	80	100	87	88[d]	1.20
CCl_4	80	100	84	50	0.75

[a] Polymerized for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 20 mM. [b] By the light-scattering method. [c] Measured in toluene at 30 °C. [d] Calculated from viscosity.

Polymerization of Higher 1-Phenyl-1-alkynes. Like 1-phenyl-1-propyne, 1-phenyl-1-butyne afforded methanol-insoluble polymers in toluene only with the chlorides and bromides among the four kinds of halides of Nb(V) and Ta(V) (Table III). The molecular weights of polymers obtained with Nb catalysts were about 2 × 10^5, higher than those with Ta catalysts. This trend is opposite to the case of 1-phenyl-1-propyne. Though the polymer yield with $WCl_6 \cdot Ph_4Sn$ was virtually quantitative, the molecular weight was lower than those with Nb catalysts.

The polymerization of 1-phenyl-1-butyne by $NbCl_5$ proceeded in high yields in a temperature range of 50–100 °C (Table IV). Cyclohexane and halogenated hydrocarbons were also useful as polymerization solvents though the molecular weights were lower than that with toluene.

The polymerization behavior of 1-phenyl-1-hexyne resembles that of 1-phenyl-1-butyne, though the former

Table V
Polymerization of 1-Phenyl-1-hexyne by Various Catalysts[a]

no.	catalyst	conversion, %	yield, %
1	NbF_5	100	0
2	$NbCl_5$	100	60
3	$NbBr_5$	100	68
4	NbI_5	0	0
5	TaF_5	100	0
6	$TaCl_5$	100	31
7	$TaBr_5$	31	17
8	TaI_5	0	0
9[b]	$MoCl_5{\cdot}Ph_4Sn$	30	~0
10[b]	$WCl_6{\cdot}Ph_4Sn$	100	86

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 1.0$ M, [Cat.] = 20 mM. [b] Polymerized at 60 °C; [Cat.] = 30 mM.

Table VI
Polymerization of 1-Phenyl-1-nonyne by Various Catalysts[a]

			polymer		
no.	catalyst	conversion, %	yield, %	$10^{-3}\bar{M}_w$[b]	$[\eta]$,[c] dL/g
1	NbF_5	100	0		
2	$NbCl_5$	100	82	100	0.95
3	$NbBr_5$	100	77	120	1.35
4	NbI_5	0	0		
5	TaF_5	100	0		
6	$TaCl_5$	100	40	76[e]	0.70
7	$TaBr_5$	100	36	32	0.46
8	TaI_5	0	0		
9[d]	$MoCl_5{\cdot}Ph_4Sn$	24	~0		
10[d]	$WCl_6{\cdot}Ph_4Sn$	100	~100	24[e]	0.26

[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0 = 1.0$ M, [Cat.] = 20 mM. [b] By the light-scattering method. [c] Measured in toluene at 30 °C. [d] Polymerized at 60 °C; [Cat.] = 30 mM. [e] Calculated from viscosity.

yields smaller amounts of methanol-insoluble polymer (Table V). A characteristic of poly(1-phenyl-1-hexyne) as compared with other poly(1-phenyl-1-alkynes) is that it is hardly soluble, which makes the molecular weight measurement impossible. Thus, the polymerization of this monomer was not further studied.

Tables VI and VII show data for the polymerization of 1-phenyl-1-nonyne. Polymers of $\bar{M}_w$ ca. 1×10^5 were obtained in good yields by using $NbCl_5$ and $NbBr_5$. The corresponding Ta catalysts yielded less polymer, and $WCl_6{\cdot}Ph_4Sn$ gave a polymer with lower molecular weight. The effects of temperature and solvent on the polymerization by $NbCl_5$ are similar to those for the polymerization of 1-phenyl-1-butyne by $NbCl_5$.

We examined whether the polymer degradation occurs also in the polymerizationof 1-phenyl-1-butyne and -1-nonyne (see Figures 3 and 4). Like 1-phenyl-1-propyne, both monomers were consumed after ca. 2 h with $NbCl_5$ and ca. 6 h with $TaCl_5$. 1-Phenyl-1-butyne and -1-nonyne, however, did not undergo polymer degradation at all even after 24 h. This gives a striking contrast to the case of 1-phenyl-1-propyne. Poly(1-phenyl-1-butyne) and poly(1-phenyl-1-nonyne) are sterically more hindered and therefore should be less easy to coordinate to the active species than are poly(1-phenyl-1-propyne). This seems the most probable cause for the observed difference regarding polymer degradation.

To our knowledge, poly(1-phenyl-1-butyne), poly(1-phenyl-1-hexyne), and poly(1-phenyl-1-nonyne) are new polymers. The polymerization of 1-phenyl-1-butyne, -1-hexyne, and -1-nonyne is featured as follows (compare with the case of 1-phenyl-1-propyne): (i) $NbCl_5$ and $NbBr_5$ give polymers with higher molecular weights in better yields than $TaCl_5$ and $TaBr_5$ do [though poly(1-phenyl-1-hexyne) is insoluble]. (ii) Polymer degradation does not occur after polymerization, though cyclotrimerization takes place simultaneously to polymerization.

Table VII
Effects of Temperature and Solvent on the Polymerization of 1-Phenyl-1-nonyne by $NbCl_5$[a]

			polymer		
solv	temp, °C	conversion, %	yield, %	$10^{-3}\bar{M}_w$[b]	$[\eta]$,[c] dL/g
toluene	50	61	27	25[d]	0.27
toluene	80	100	82	100	0.95
toluene	100	100	51	93	1.28
cyclohexane	80	100	70	67	0.89
$(CH_2Cl)_2$	80	100	68	25	0.30
CCl_4	80	100	34	19	0.15

[a] Polymerized for 24 h; $[M]_0 = 1.0$ M, [Cat.] = 20 mM. [b] By the light-scattering method. [c] Measured in toluene at 30 °C. [d] Calculated from viscosity.

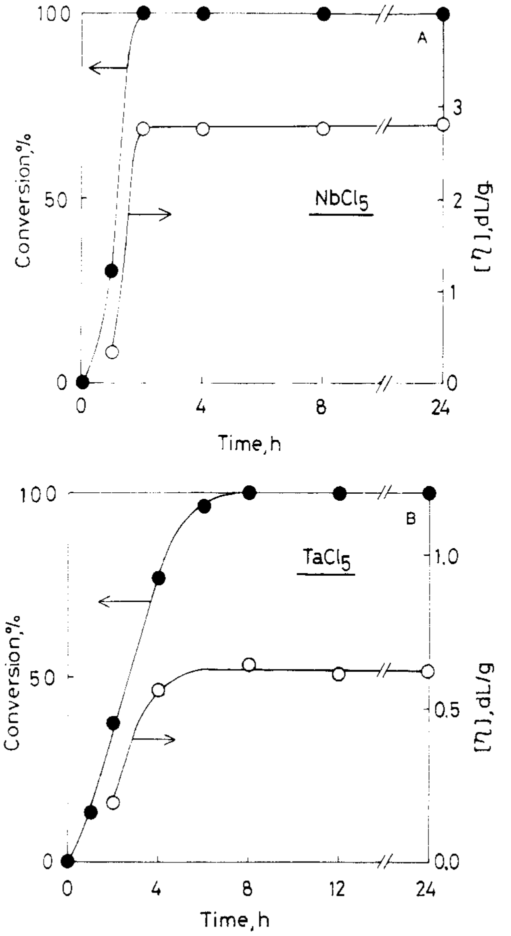

Figure 3. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-butyne by $NbCl_5$ and $TaCl_5$ (polymerized in toluene, 80 °C, $[M]_0 = 1.0$ M, [Cat.] = 20 mM; $[\eta]$ measured in toluene at 30 °C).

Polymer Structure. The elemental-analysis data of poly(1-phenyl-1-propyne) are as follows. Calcd for $(C_9H_8)_n$: C, 93.06; H, 6.94. Found: C, 92.82; H, 7.11. Not only these observed values but also those for other poly(1-phenyl-1-alkynes) agreed well with their calculated values.

The ^{13}C NMR spectra of poly(1-phenyl-1-alkynes) show signals at δ 145–125 owing to the phenyl and main-chain sp^2 carbons, and at δ 35–15 owing to the side-chain alkyl carbon(s) (Figure 5).

The spectrum of poly(1-phenyl-1-propyne) shows that this polymer does not involve the isomerized unit, $-CH{=}C(CH_2Ph)-$. Thus, the polymer structures shown in Figure 5 are supported. ^1H NMR spectra exhibit signals

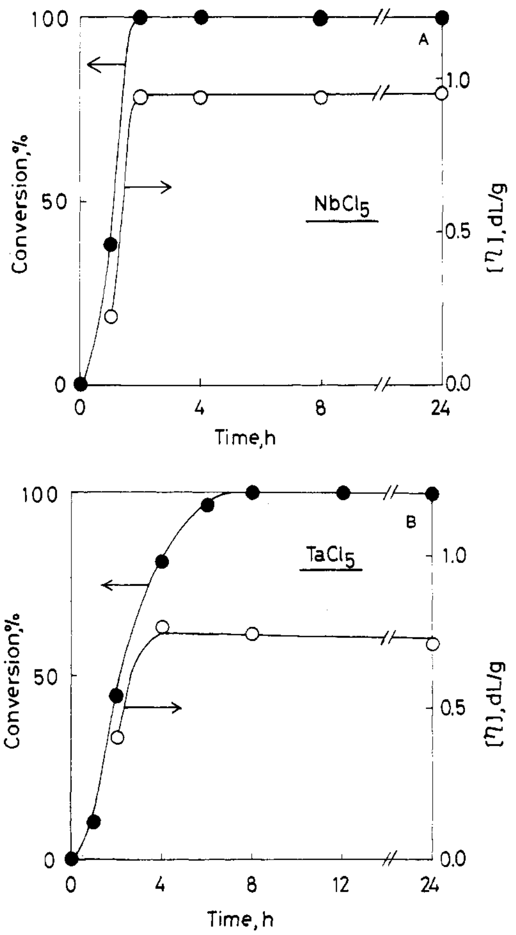

Figure 4. Time dependences of conversion and polymer molecular weight in the polymerization of 1-phenyl-1-nonyne by $NbCl_5$ and $TaCl_5$ (polymerized in toluene, 80 °C, $[M]_0$ = 1.0 M, [Cat.] = 20 mM; [η] measured in toluene at 30 °C).

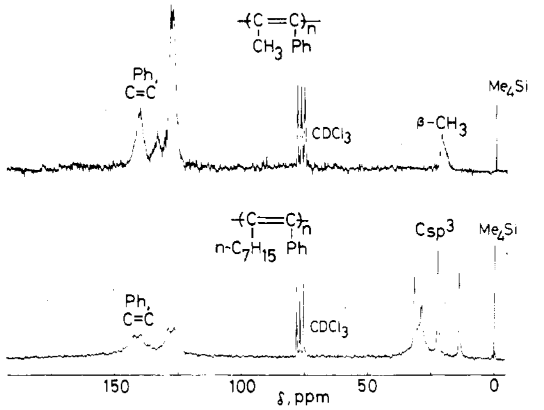

Figure 5. ^{13}C NMR spectra of poly(1-phenyl-1-propyne) and poly(1-phenyl-1-nonyne) (samples from Table I, no. 7, and Table VI, no. 2; measured in $CDCl_3$).

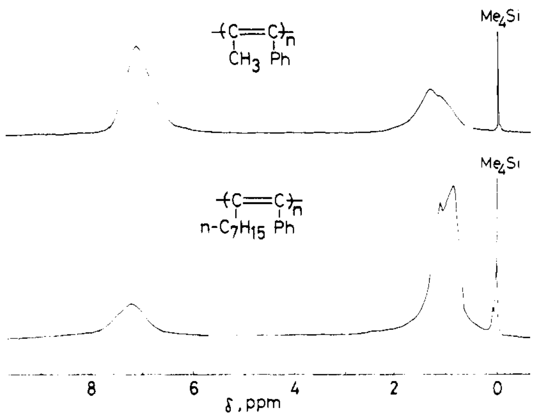

Figure 6. ^1H NMR spectra of poly(1-phenyl-1-propyne) and poly(1-phenyl-1-nonyne) (samples from Table I, no. 7, and Table VI, no. 2; measured in $CDCl_3$).

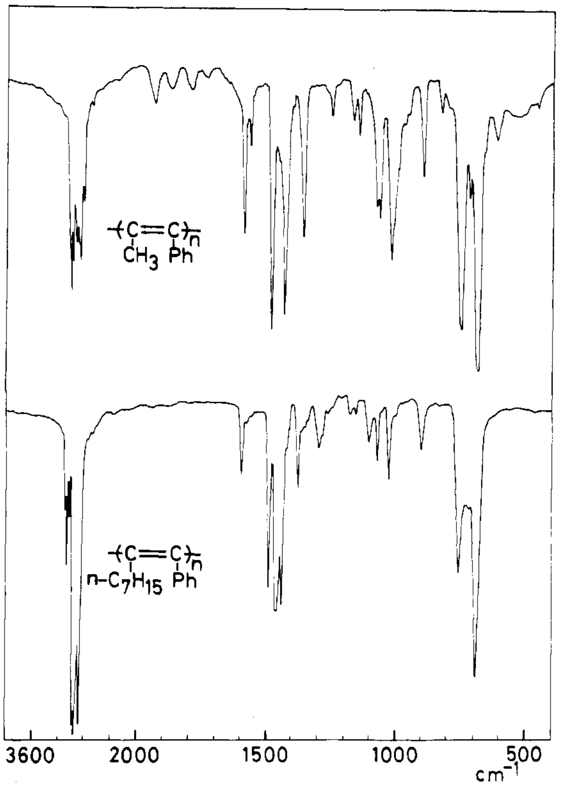

Figure 7. IR spectra of poly(1-phenyl-1-propyne) and poly(1-phenyl-1-nonyne) (samples from Table I, no. 7, and Table VI, no. 2).

at the aromatic and aliphatic regions, whose area ratios coincided well with those for the expected structures (Figure 6).

In the IR spectrum of poly(1-phenyl-1-propyne), the band due to the alternating C=C bonds appears around 1650 cm^{-1} as a shoulder of a different band (Figure 7). Bands characteristic of the phenyl (2000–1700, 750, 690 cm^{-1}) and methyl (1450, 1380 cm^{-1}, etc.) groups are also seen. As the alkyl group of polymer became longer, the bands due to methylene groups (2950, 2880, 1465 cm^{-1}) remarkably increased. As seen in Figure 8, the UV spectrum of poly(1-phenyl-1-propyne) shows an absorption maximum (ε 2500) at 285 nm. Besides this absorption, polymers of higher 1-phenyl-1-alkynes exhibit an absorption (ε around 3000) at 325 nm. No absorption was observed above 400 nm in any polymer. These absorptions in UV spectra are small and their wavelengths are significantly short as compared with polyacetylene ($\lambda_{max} \sim$ 600 nm[10]) and β-carotene (λ_{max} 483 nm, ϵ_{max} 111 000; etc.).

From the above IR and NMR data, it can be concluded that the poly(1-phenyl-1-alkynes) generally possess the structure $-(CR{=}CPh)_n-$ (R = CH_3, C_2H_5, n-C_4H_9, n-C_7H_{15}). Polymers obtained with different catalysts (NbX_5, TaX_5, $WCl_6 \cdot Ph_4Sn$) from the same monomer showed practically identical spectra. No information on the geometric structure of the main chian was obtained from the above spectra.

Polymer Properties. Poly(1-phenyl-1-alkynes) are all white solids.

The polymers from 1-phenyl-1-propyne, -1-butyne, and -1-nonyne are all completely soluble in aromatic hydrocarbons (toluene, Tetralin), halogenated hydrocarbons with

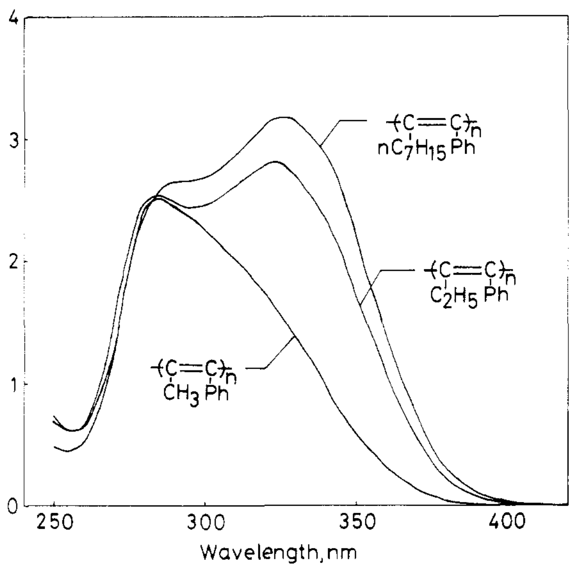

Figure 8. UV spectra of poly(1-phenyl-1-alkynes) (samples from no. 2 of Table I, III and VI; measured in cyclohexane).

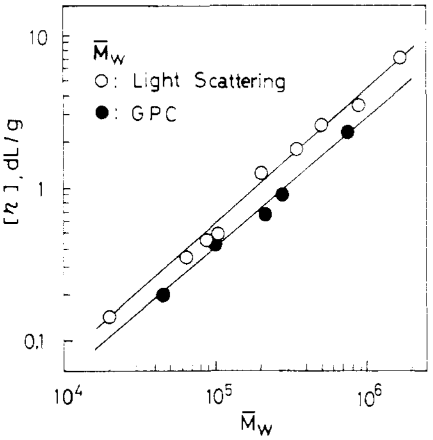

Figure 9. Relationship between the intrinsic viscosity and weight-average molecular weight of poly(1-phenyl-1-propyne) ([η] measured in toluene at 30 °C).

low polarities (CCl_4, $CHCl_3$), tetrahydrofuran, and so on. When inspected in more detail, poly(1-phenyl-1-propyne) dissolves in 1,4-dioxane, 1,2-dichloroethane, and nitrobenzene, whereas poly(1-phenyl-1-nonyne) does not or hardly dissolves in these solvents; the opposite relationship holds with heptane as solvent. Highly polar solvents such as methanol, acetone, and dimethyl sulfoxide are generally nonsolvents of these polymers. Casting of the polymer solutions affords tough films.

On the other hand, poly(1-phenyl-1-hexyne) was hardly soluble in any solvents. This is apparently surprising. In this connection, high polymers from symmetrical disubstituted acetylenes (2-butyne,[11] 3-hexyne,[4e] 4-octyne,[4e] 5-decyne,[4e] cyclooctyne,[11] diphenylacetylene,[4b] and hexafluoro-2-butyne[12]) are all known to be insoluble. This insolubility can be attributed to, besides the rigidity of the main chain, small free volumes in these polymers, and in turn little interaction with solvents. Poly(3-octyne), the repeating unit of which has a relatively high symmetry, is also hardly soluble.[7] The poor solubility of poly(1-phenyl-1-hexyne) should be due to the same reason.

A good linear relationship held between the intrinsic viscosity and weight-average molecular weight (measured by the light-scattering method) of poly(1-phenyl-1-propyne) (Figure 9). When "apparent" weight-average molecular weights obtained by GPC were employed, another linear relationship was obtained in parallel with the above-stated line. The weight-average molecular weights determined by GPC were approximately 1.5 times as large as those by the light-scattering method. Poly(1-phenyl-1-butyne) and poly(1-phenyl-1-nonyne) gave similar linear relationships between intrinsic viscosity and weight-average molecular weight.

Table VIII
Constants a and K for $[\eta] = K\bar{M}_w{}^a$

	poly(1-phenyl-1-propyne)^a	poly(1-phenyl-1-butyne)	poly(1-phenyl-1-nonyne)
a	0.89 (0.85)	0.92	1.15
K, dL/g	2.00×10^{-5} (2.19×10^{-5})	3.39×10^{-5}	2.40×10^{-6}

[a] Figures in parentheses were calculated by using $\bar{M}_w$s obtained by GPC.

Table IX
Softening Points and Electrical Conductivities of $-(CR{=}CPh)_n-$^{a}

R	softening point, °C	σ, S cm^{-1}
CH_3	272	7×10^{-18}
C_2H_5	289–295	$<10^{-18}$
n-C_4H_9	>300	$<10^{-18}$
n-C_7H_{15}	261–266	$<10^{-18}$

[a] Samples from Table I, no. 7; Table III, no. 2; Table V, no. 2; Table VI, no. 2.

Table VIII lists exponents a and coefficients K for eq 1, calculated by the least-squares method. Some of the

$$[\eta] = K\bar{M}_w{}^a \qquad (1)$$

weight-average molecular weights in Tables II–VII were calculated by using these constants from viscosities. The a values in Table VIII are ca. 0.9–1.2, being larger than those usually observed for vinyl polymers (0.5–0.8). This suggests that the present polymers are more rigid than common vinyl polymers.

The softening points of the poly(1-phenyl-1-alkynes) are about 260 °C or above (Table IX). In DTA analysis under nitrogen, no exo- or endothermic peak was observed from room temperature to 250 °C, and a small broad exothermic peak ($\Delta H \leq -0.5$ kJ/mol) appeared in a range of 250–450 °C in every polymer. Temperature dependences of the weight loss of polymers, measured by TGA in air were as follows: poly(1-phenyl-1-propyne), 5% 330 °C, 50% 390 °C; poly(1-phenyl-1-nonyne), 5% 260 °C, 50% 370 °C. As the alkyl group in polymer was longer, the weight loss generally started at a lower temperature. The molecular weight of poly(1-phenyl-1-propyne) ($\sim 5 \times 10^5$) did not change after the polymer had been left in air either at 160 °C for 1 day or at room temperature for 3 months.[13]

The electrical conductiveties (σ) of the polymers are in a range for insulators (Table IX). Their unpaired electron densities were lower than the detection limit (10^{15} g^{-1}) in electron spin resonance (ESR) spectroscopy. These low values indicate that the alternating double bonds along the main chain are little conjugated to one another.

The above findings on the structure and properties of polymers lead to a conclusion that, though the present polymers have the alternating polyene structure $-(CR{=}CPh)_n-$ (NMR, IR), their main chains take twisted conformations (color, UV, σ, ESR) and their backbones are fairly rigid (exponent a, softening point).

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Poly[*p*-(formyloxy)styrene]: Synthesis and Radiation-Induced Decarbonylation

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ABSTRACT: Poly[*p*-(formyloxy)styrene] is prepared by chemical modification of poly(*p*-hydroxystyrene) or free-radical-initiated polymerization of the corresponding monomer. Unlike poly(*p*-acetoxystyrene), which undergoes a partial photochemical Fries rearrangement, poly[*p*-(formyloxy)styrene] decarbonylates smoothly when exposed to UV irradiation in solution or in the solid state. The difference in reactivity between the two acylated polymers is likely due to the lower stability of the formyl radical which is formed in the first stage of the photo-Fries reaction. In addition, while uniform irradiation of a 1-μm film of poly(*p*-acetoxystyrene) is impossible because of the formation of a strongly absorbing and UV stabilizing polymer at the surface of the exposed film, poly[*p*-(formyloxy)styrene] can be used in microlithographic processes to produce high-resolution relief images. The images can be developed with positive or negative tone by differential dissolution of the exposed and unexposed areas of the polymer film by using solvents of appropriate polarities.

Introduction

The photo-Fries rearrangement of aromatic esters and amides which was first reported by Anderson and Reese[1] has been tested with a number of polymeric materials such as aromatic polyesters[2-4] and polyamides.[5] Early interest in this photoinduced rearrangement was mainly due to its applicability to the problem of polymer stabilization. Thus, Cohen et al.[4] have shown that the rearrangement of fully aromatic polyesters produces polymers containing *o*-hydroxy-substituted units which confer great UV stability to the rearranged polymer. The general photostabilizing action of *o*-hydroxy aromatic compounds has been reviewed recently by Allen[6] and by Ranby and Rabek.[7] Similarly, much work on polymers containing aromatic ester or amide pendant groups[3,8] has confirmed that the photo-Fries rearrangement of these polymers is accompanied by the generation of photostabilizing groups. Following a thorough study of the photo-Fries reaction, Guillet et al. concluded that the enhanced stability of the rearranged products was due in part to their high extinction coefficients and in part to their ability to dissipate the absorbed energy through nonphotochemical pathways.[9]

Our interest[10,11] in polymeric imaging systems for application in microelectronics has led us to consider the applicability of the photo-Fries reaction of polymers containing aromatic ester or amido groups. For example, it is expected that the light-induced Fries rearrangement of poly(*p*-acetoxystyrene) will yield a rearranged polymer containing pendant phenolic groups. Such rearrangement would afford a basis for development of an image from a thin film of the polymer as the unexposed and exposed areas of the polymer would have greatly dissimilar polarities and could thus be resolved by differential dissolution in appropriate solvent systems.

Results and Discussion

Our initial study was focused on the photo-Fries rearrangement of poly(*p*-acetoxystyrene) (I), which can be prepared by free-radical polymerization of the corresponding monomer.[12] Progress of the photoinduced rearrangement was monitored by Fourier transform infrared or by UV spectroscopy using 1-μm films of the polymer cast on sodium chloride or quartz disks. As the starting polymer absorbs weakly in the deep UV near 270 nm, a high-pressure mercury–xenon lamp with quartz optics was used for the irradiation experiments. The results of these experiments show that the photo-Fries rearrangement of poly(*p*-acetoxystyrene) does occur but only with low efficiency.

The infrared spectrum of the polymer changes as exposure dose is increased with the appearance of a new carbonyl band at 1642 cm^{-1} and a weak hydroxyl band centered at 3483 cm^{-1}; the appearance of these two bands, which correspond to the newly formed *o*-hydroxy ketone

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