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Polymerization of 2-Hexyne and Higher 2-Alkynes Catalyzed by $MoCl_5{\cdot}Ph_4Sn$ and $WCl_6{\cdot}Ph_4Sn$[1]

Toshinobu Higashimura,* Yun-Xiang Deng,† and Toshio Masuda

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
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ABSTRACT: The polymerization of 2-hexyne in toluene catalyzed by an equimolar mixture of $MoCl_5$ and Ph_4Sn provided an extremely high polymer ($\bar{M}_w > 1 \times 10^6$) in virtually quantitative yield. A mixture of WCl_6 and Ph_4Sn also polymerized 2-hexyne (polymer $\bar{M}_w \sim 2 \times 10^5$). $MoCl_5$ and WCl_6 alone were ineffective as catalysts. Similarly, higher 2-alkynes (2-heptyne through 2-decyne) were polymerized by $MoCl_5{\cdot}Ph_4Sn$ or $WCl_6{\cdot}Ph_4Sn$. Elemental and spectral analyses supported polyene structures for the poly(2-alkynes). The poly(2-alkynes) were white solids completely soluble in nonpolar solvents such as toluene and *n*-hexane and afforded sturdy films when cast from solution.

Acetylene and monosubstituted acetylenes can be polymerized to linear polymers by Ziegler-type catalysts. For instance, $Ti(O\text{-}n\text{-}Bu)_4\text{–}Et_3Al$ catalyst is used for the synthesis of polyacetylene film.[4,5] Iron chelates–Et_3Al show high activity for the polymerization of monosubstituted acetylenes such as phenylacetylene,[6,7] 1-hexyne,[8] and isobutoxyacetylene.[9] However, these Ziegler-type catalysts fail to polymerize sterically hindered, disubstituted acetylenes such as 3-hexyne.[3]

There have been only a few papers on the polymerization of aliphatic disubstituted acetylenes owing to their low reactivity: A linear oligomer ($\bar{M}_n$ = 724, mp 90 °C) of 2-hexyne was obtained at high pressure and temperature (23.5 kbar, 255 °C).[10] A mixture of linear polymer and cyclic trimer was formed in the reaction of 3-hexyne catalyzed by diarylcobalts.[11] Recently, Cotton et al. reported that 3-hexyne and 4-methyl-2-hexyne are polymerized by Nb(III)- and Ta(III)-based catalysts.[12]

Earlier we reported that WCl_6 polymerized phenylacetylene to give a soluble high polymer ($\bar{M}_n \sim 1.5 \times 10^4$).[13] Further an equimolar mixture of WCl_6 and tetraphenyltin (Ph_4Sn) was found to polymerize disubstituted aromatic acetylenes such as 1-phenyl-1-propyne[14] and diphenylacetylene[15] in high yields, while WCl_6 by itself was hardly effective. This effect of Ph_4Sn was explained in terms that tungsten(VI) was partly reduced by Ph_4Sn to form an active species. An equimolar mixture of $MoCl_5$ and Ph_4Sn is also active for the polymerization of certain disubstituted aromatic acetylenes like 1-chloro-2-phenylacetylene[16] and phenylpropiolic acid.[17] Thus, mixtures of either WCl_6 or $MoCl_5$ with Ph_4Sn are very useful catalysts for the polymerization of disubstituted aromatic acetylenes. It is interesting to investigate whether these catalysts are effective for disubstituted aliphatic acetylenes. In fact, symmetrical dialkylacetylenes (3-hexyne, 4-octyne, and 5-decyne) formed polymers in high yields with $WCl_6{\cdot}Ph_4Sn$, but the polymers were partly insoluble.[3]

The present study aims at the synthesis of soluble high polymers from disubstituted aliphatic acetylenes. Among the acetylenes examined, 2-alkynes were found to afford such polymers when $MoCl_5{\cdot}Ph_4Sn$ and analogous catalysts were used. Thus this paper reports principally on the polymerization of 2-hexyne and higher 2-alkynes catalyzed by $MoCl_5{\cdot}Ph_4Sn$ and $WCl_6{\cdot}Ph_4Sn$.

Experimental Section

Monomers (2-hexyne, 2-heptyne, 2-octyne, 2-nonyne, and 2-decyne) were purchased from Tokyo Chemical Industry, Co., and distilled from calcium hydride. WCl_6 and $MoCl_5$ (Hermann C. Stark, Berlin) were used without further purification. Ph_4Sn was recrystallized from carbon tetrachloride. Other organometals were used as purchased. Solvents for polymerization were washed with acid and/or alkali solutions and distilled twice from calcium hydride or sodium before use.

Table I
Polymerization of 2-Hexyne by Various Catalyst Systems[a]

no.	catalyst	yield, %	[η], dL g^{-1}	$10^{-5}\bar{M}_w$
1	$MoCl_5$	~0		
2	WCl_6	0		
3	$MoCl_5{\cdot}Ph_4Sn$	88	4.55	11.2
4	$MoCl_5{\cdot}n\text{-}Bu_4Sn$	81	3.46	7.6
5	$MoCl_5{\cdot}(PhCH_2)_3SnCl$	47	5.61	36.4
6	$MoCl_5{\cdot}Ph_3SnCl$	33	3.31	6.0
7	$MoCl_5{\cdot}n\text{-}Bu_3SnCl$	~0		
8	$MoCl_5{\cdot}Ph_3Sb$	43	4.10	7.0
9	$WCl_6{\cdot}Ph_4Sn$	57	0.54	2.0
10	$WCl_6{\cdot}n\text{-}Bu_4Sn$	~0		
11	$WCl_6{\cdot}(PhCH_2)_3SnCl$	0		
12	$WCl_6{\cdot}Ph_3SnCl$	~0		
13	$Mo(CO)_6\text{–}CCl_4\text{–}h\nu$	11		
14	$W(CO)_6\text{–}CCl_4\text{–}h\nu$	~0		
15	$Fe(acac)_3{\cdot}3Et_3Al$	0		
16	$Ti(O\text{-}n\text{-}Bu)_4{\cdot}Et_3Al$	0		

[a] Polymerized at 30 °C for 24 h in toluene (nos. 13 and 14 in CCl_4): $[M]_0$ = 1.0 M, [Cat] = 30 mM.

All polymerization procedures were carried out under dry nitrogen. Catalyst solutions consisting of two components (e.g., $MoCl_5$ and Ph_4Sn) were aged at 30 °C for 20 min before use. Unless otherwise specified, polymerization was conducted at 30 °C for 24 h: $[M]_0$ = 1.0 M. The reaction was terminated by addition of toluene containing 1 vol % of ammoniacal methanol. The polymer produced was precipitated in a large amount of methanol.

Intrinsic viscosities, [η], were measured in toluene at 30 °C. Weight-average molecular weights of poly(2-hexyne) were determined in heptane solution (dn/dc = 0.150 mL g^{-1}) on a Chromatix KMX-6 low-angle laser light scattering photometer. IR and UV–visible spectra were recorded on Shimadzu IR27G and UV190 spectrophotometers, respectively. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ or in a mixture of C_6D_6 and $CDCl_3$ using a JEOL FX90Q spectrometer. Differential thermal analysis (DTA) was carried out under nitrogen with a Shimadzu 20B analyzer.

Results and Discussion

Effectiveness of Catalysts in the Polymerization of 2-Hexyne. Table I lists results for the polymerization of 2-hexyne by various catalyst systems. The catalysts used are classified as follows: (i) $MoCl_5$ and WCl_6 (nos. 1 and 2), (ii) 1:1 mixtures of either $MoCl_5$ or WCl_6 with organometals (nos. 3–12), (iii) $Mo(CO)_6$- and $W(CO)_6$-based

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† Permanent address: Zhongshen (Sun Yatsen) University, China.

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Table II
Polymerization of 2-Hexyne by $MoCl_5·Ph_4Sn$ and $WCl_6·Ph_4Sn$ in Several Solvents[a]

catalyst	solvent	yield, %	[η], dL g^{-1}
$MoCl_5·Ph_4Sn$	toluene	88	4.55
$MoCl_5·Ph_4Sn$	$(CH_2Cl)_2$	29	3.11
$MoCl_5·Ph_4Sn$	1,4-dioxane	6	
$MoCl_5·Ph_4Sn$	acetone	~0	
$MoCl_5·Ph_4Sn$	$CH_3CO_2C_2H_5$	0	
$WCl_6·Ph_4Sn$	toluene	57	0.54
$WCl_6·Ph_4Sn$	CCl_4	22	0.97
$WCl_6·Ph_4Sn$	$(CH_2Cl)_2$	15	0.30

[a] Polymerized at 30 °C for 24 h: $[M]_0 = 1.0$ M, [Cat] = 30 mM.

catalysts (nos. 13 and 14),[18] and (iv) Ziegler-type catalysts (nos. 15 and 16).

Neither $MoCl_5$ nor WCl_6 alone showed any catalytic activity. As described in the introduction, $MoCl_5·Ph_4Sn$ and $WCl_6·Ph_4Sn$ catalyze the polymerization of some disubstituted acetylenes. Therefore, these and analogous catalysts were examined. Catalyst solutions were aged at 30 °C for 20 min, based on the result of polymerization of phenylacetylene by $WCl_6·Ph_4Sn$.[19] Polymerization readily proceeded with $MoCl_5·Ph_4Sn$ and $WCl_6·Ph_4Sn$, especially with the former. The polymerization solution with $MoCl_5·Ph_4Sn$ was no longer fluid at high monomer conversion because of the formation of a high polymer. For $MoCl_5$, n-Bu_4Sn was almost as effective as Ph_4Sn, whereas $(PhCH_2)_3SnCl$, Ph_3SnCl, and Ph_3Sb were less effective; n-Bu_3SnCl was completely ineffective. In the case of WCl_6, no active organometals other than Ph_4Sn were found. The unreacted monomer was always recovered without isomerization.

We have recently found that the $Mo(CO)_6$–CCl_4–$h\nu$ and $W(CO)_6$–CCl_4–$h\nu$ catalysts polymerize various acetylene derivatives.[18] These catalysts, however, did not work well for 2-hexyne. Two Ziegler-type catalysts, $Fe(acac)_3·3Et_3Al$ and $Ti(O$-n-$Bu)_4·4Et_3Al$, did not polymerize this alkyne either.

The poly(2-hexynes) contained no toluene-insoluble fraction. The intrinsic viscosities of the polymers obtained with mixtures of $MoCl_5$ and organometals were remarkably high, and the weight-average molecular weights of some of the polymers exceeded 10^6. The organometals appreciably affected polymer molecular weight. The weight-average molecular weight of the polymer prepared with $WCl_6·Ph_4Sn$ was not so high (~2×10^5).

Influence of Reaction Conditions on the Polymerization of 2-Hexyne by $MoCl_5·Ph_4Sn$ and $WCl_6·Ph_4Sn$. As it was found that $MoCl_5·Ph_4Sn$ and $WCl_6·Ph_4Sn$ were especially effective catalysts for 2-hexyne polymerization, the influence of reaction conditions was examined using these catalysts. At first polymerization in various solvents was studied (Table II). Aromatic hydrocarbons such as toluene were the most favorable solvents. On the other hand, the yields in halogenated hydrocarbons were lower, and those in oxygen-containing solvents were negligible. The polymerization by $MoCl_5·Ph_4Sn$ in carbon tetrachloride was not carried out since the catalyst solubility in this solvent was insufficient. The reason that aromatic hydrocarbons are excellent polymerization solvents seems to be that they are inert to the active species and are good solvents for both catalyst and polymer.

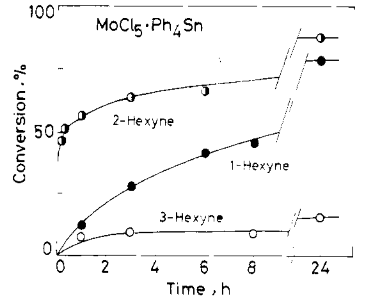

Figure 1. Time courses for the polymerizations of 1-, 2-, and 3-hexynes by $MoCl_5·Ph_4Sn$ (in toluene, 30 °C, $[M]_0 = 1.0$ M, [Cat] = 30 mM).

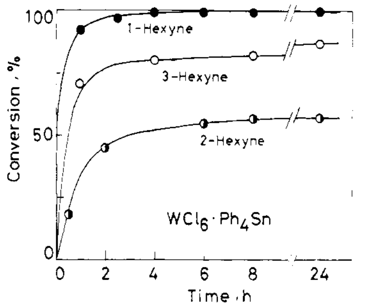

Figure 2. Time courses for the polymerizations of 1-, 2-, and 3-hexynes by $WCl_6·Ph_4Sn$ (in toluene, 30 °C, $[M]_0 = 1.0$ M, [Cat] = 30 mM).

Table III shows results for the effects of reaction conditions (monomer and catalyst concentrations and temperature) on the polymerization by $MoCl_5·Ph_4Sn$ in toluene. An increase in monomer concentration hardly affected the polymer yield but enhanced the polymer molecular weight. As the catalyst concentration was reduced, the polymer yield decreased and the polymer molecular weight increased. Polymerization did not occur at 0 °C, and both polymer yield and molecular weight at 60 °C were lower than those at 30 °C.

Comparison of the Polymerizations of 1-, 2-, and 3-Hexynes. When $MoCl_5$ and WCl_6 alone are used as catalysts, 1-hexyne gives a polymer in good yields[20] but 2-hexyne (vide supra) and 3-hexyne[3] are not at all or hardly polymerized. Figures 1 and 2 show time courses for the polymerizations of these hexynes catalyzed by $MoCl_5·$

Table III
Effects of Monomer and Catalyst Concentrations and Temperature on the Polymerization of 2-Hexyne by $MoCl_5·Ph_4Sn$[a]

$[M]_0$, M	[Cat], mM	$[M]_0$/[Cat]	temp, °C	yield, %	[η], dL g^{-1}	$10^{-5}\bar{M}_w$
0.125	30	4.2	30	88	1.51	
0.25	30	8.3	30	90	3.06	
0.50	30	16.7	30	96	4.18	7.0
1.0	30	33.3	30	88	4.55	11.2
1.0	20	50	30	67	5.37	20.6
1.0	10	100	30	34	6.05	38.0
1.0	30	33.3	0	0		
1.0	30	33.3	60	68	2.20	2.2

[a] Polymerized in toluene for 24 h.

Table IV
Polymerization of Higher 2-Alkynes by $MoCl_5$- and WCl_6-Based Catalysts[a]

no.	monomer	catalyst	yield, %	[η], dL g^{-1}
1	2-heptyne	$MoCl_5·Ph_4Sn$	51	3.50
2	2-heptyne	$MoCl_5·n\text{-}Bu_4Sn$	75	2.46
3	2-heptyne	$WCl_6·Ph_4Sn$	40	0.38
4	2-octyne	$MoCl_5·Ph_4Sn$	63	3.16
5	2-octyne	$MoCl_5·n\text{-}Bu_4Sn$	52	2.20
6	2-octyne	$WCl_6·Ph_4Sn$	20	0.23
7	2-nonyne	$MoCl_5·Ph_4Sn$	60	2.20
8	2-nonyne	$MoCl_5·n\text{-}Bu_4Sn$	67	1.80
9	2-nonyne	$WCl_6·Ph_4Sn$	12	0.20
10	2-decyne	$MoCl_5·Ph_4Sn$	50	2.31
11	2-decyne	$MoCl_5·n\text{-}Bu_4Sn$	42	2.10
12	2-decyne	$WCl_6·Ph_4Sn$	40	0.35

[a] Polymerized in toluene at 30 °C for 24 h: $[M]_0$ = 0.50 M, [Cat] = 30 mM.

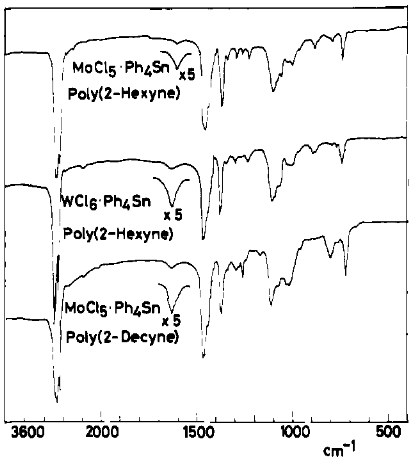

Figure 3. IR spectra of poly(2-alkynes).

Ph_4Sn and $WCl_6·Ph_4Sn$. Monomer reactivities decrease in the following order: 2-hexyne > 1-hexyne > 3-hexyne (with $MoCl_5·Ph_4Sn$); 1-hexyne > 3-hexyne > 2-hexyne (with $WCl_6·Ph_4Sn$). These observations indicate that (i) $MoCl_5·Ph_4Sn$ is the preferred catalyst for the polymerization of 2-hexyne and that (ii) the relative reactivities of 1-, 2-, and 3-hexynes greatly depend on the kind of catalyst.

Poly(1-hexyne) is a yellow tacky polymer, and its molecular weight is only several thousand at the highest.[20] Poly(2-hexyne) is a white soluble solid whose molecular weight exceeds 10^6. On the other hand, poly(3-hexyne) is a white partly insoluble polymer, which makes the measurement of its molecular weight impossible.[3]

Polymerization of Higher 2-Alkynes. To gain knowledge regarding the effect of alkyl chain length, the polymerizations of higher 2-alkynes (2-heptyne, 2-octyne, 2-nonyne, and 2-decyne) were carried out (Table IV). The reaction was catalyzed by $MoCl_5·Ph_4Sn$, $MoCl_5·n\text{-}Bu_4Sn$, and $WCl_6·Ph_4Sn$.

These 2-alkynes, having long alkyl chains, were polymerized in high yields by $MoCl_5·Ph_4Sn$, though they were somewhat less reactive than 2-hexyne. The polymer yield with $MoCl_5·n\text{-}Bu_4Sn$ was comparable to that with $MoCl_5·Ph_4Sn$ for every 2-alkyne. On the other hand, the yields with $WCl_6·Ph_4Sn$ were lower and rather irreproducible.

All the polymers formed were completely soluble in toluene. The intrinsic viscosities of the polymers obtained with $MoCl_5·Ph_4Sn$ and $MoCl_5·n\text{-}Bu_4Sn$ were high (1.8–3.5 dL g^{-1}), while the $WCl_6·Ph_4Sn$ catalyst produced poly(2-alkynes) having much lower viscosities (0.20–0.38 dL g^{-1}).

Table V
Elemental Analysis Data and Thermal Properties of $-(CCH_3{=}CR)-_n$ Obtained with $MoCl_5·Ph_4Sn$

R[a]	elemental analysis		softening point, °C	exotherm in DTA, kcal/mol
$n\text{-}C_3H_7$	% C	87.49 (87.73)[b]	227–231	6.22
	% H	12.32 (12.27)		
$n\text{-}C_4H_9$			234–236	6.12
$n\text{-}C_5H_{11}$	% C	86.67 (87.19)	267–274	4.24
	% H	12.91 (12.81)		
$n\text{-}C_6H_{13}$			255–258	4.13
$n\text{-}C_7H_{15}$	% C	86.51 (86.88)	252–257	1.60
	% H	12.98 (13.12)		

[a] Samples from Table I (no. 3) and Table IV (nos. 1, 4, 7, and 10). [b] Calculated values in parentheses.

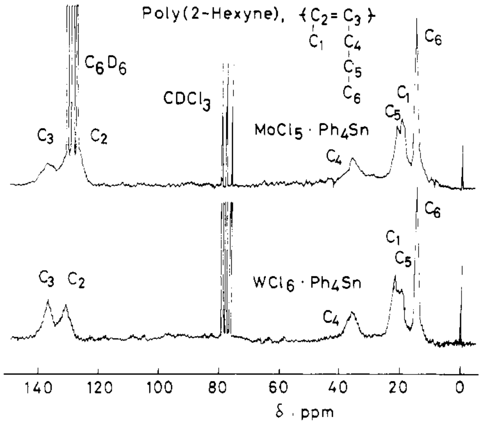

Figure 4. ^{13}C NMR spectra of poly(2-hexyne) (measured in a mixture of C_6D_6 and $CDCl_3$ (vol ratio 4:1) for the $MoCl_5·Ph_4Sn$ polymer and in $CDCl_3$ for the $WCl_6·Ph_4Sn$ polymer).

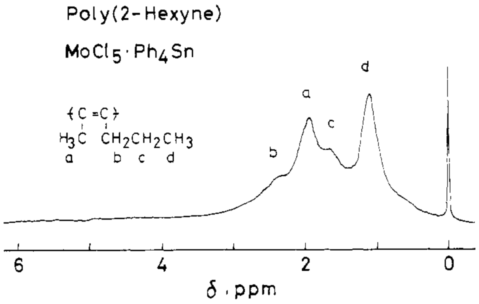

Figure 5. ^1H NMR spectrum of poly(2-hexyne) (measured in a mixture of C_6D_6 and $CDCl_3$ (vol ratio 4:1)).

Polymer Structure. The elemental compositions of the polymers agreed well with the theoretical values, as seen in Table V. Figure 3 shows IR spectra of poly(2-alkynes). The absorption at 1650–1580 cm^{-1} is due to stretching of the conjugated C=C bonds along the main chain. The reason that this absorption is very small is that every main-chain carbon is substituted by alkyl groups, resulting in good symmetry. Absorptions in the 1150–980-cm^{-1} region varied slightly, depending on the kind of catalyst. As seen from the spectrum of poly(2-decyne), the IR spectra of higher poly(2-alkynes) were similar to that of poly(2-hexyne). The ^{13}C and ^1H NMR spectra of poly(2-hexyne) are given in Figures 4 and 5, respectively. Since the poly(2-hexyne) formed with $MoCl_5·Ph_4Sn$ was only partly soluble in $CDCl_3$, its NMR spectra were mea-

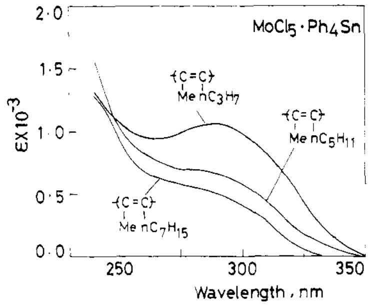

Figure 6. UV spectra of poly(2-alkynes) obtained with $MoCl_5 \cdot Ph_4Sn$ (measured in *n*-hexane).

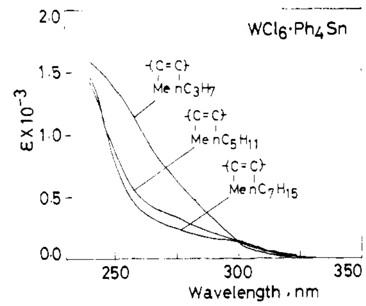

Figure 7. UV spectra of poly(2-alkynes) obtained with $WCl_6 \cdot Ph_4Sn$ (measured in *n*-hexane).

sured in a mixture of C_6D_6 and $CDCl_3$ (vol ratio 4:1). These NMR spectra are consistent with the expected polymer structure, $-(CCH_3{=}C\text{-}n\text{-}C_3H_7)-_n$. The ^1H NMR spectrum of poly(2-hexyne) prepared with $WCl_6 \cdot Ph_4Sn$ was practically identical with that of Figure 5. In the UV spectrum of poly(2-alkynes), no absorption was observed at 350 nm or above (Figures 6 and 7). Every polymer obtained with $MoCl_5 \cdot Ph_4Sn$ exhibited a maximum or a shoulder around 290 nm, while those produced with $WCl_6 \cdot Ph_4Sn$ did not. The higher the 2-alkyne, the weaker the absorption of polymer in the 250–350-nm region.

The following points should be considered regarding polymer structure: (i) elemental composition of the polymer, (ii) repeating unit structure, (iii) extent of conjugation, (iv) geometric structure, and (v) head-to-head structure. (i) The elemental analysis data indicate that no side reactions such as hydrogenation, dehydrogenation, and oxidation take place during polymerization. (ii) The ^{13}C and ^1H NMR spectral data clearly indicate that the polymers have the $-(CCH_3{=}CR)-_n$ structure. Thus the possibility is denied that the polymers contain 1-alkyne units which might be introduced by the polymerization of 1-alkynes formed by isomerization of 2-alkynes. (iii) The IR absorption at 1650–1580 cm^{-1} supports the polyene structure along the main chain. The average extent of conjugation in solution, however, is presumed to be no more than several C=C bonds, according to the UV spectra.[21] This is explained in terms that the main chain is considerably twisted owing to the presence of two substituents per repeating unit. (iv) and (v) No definitive information was obtained concerning these items. Large differences between the UV spectra of the polymers obtained with $MoCl_5 \cdot Ph_4Sn$ and $WCl_6 \cdot Ph_4Sn$, however, suggest a difference either in geometric structure or in head-to-head structure content.

Polymer Properties. The poly(2-alkynes) were all white solids (their films were virtually colorless and transparent). The polymers were soluble in less polar solvents such as benzene, toluene, cyclohexane, *n*-hexane, and tetrahydrofuran, partly soluble in carbon tetrachloride, chloroform, and diethyl ether, and insoluble in more polar solvents like 1,2-dichloroethane, acetone, ethyl acetate, nitrobenzene, and acetonitrile.

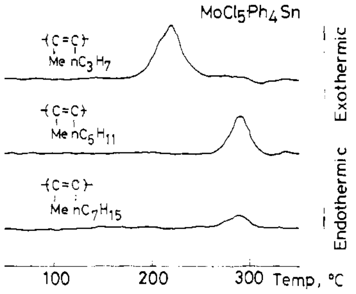

Figure 8. DTA thermograms of poly(2-alkynes).

It was possible to prepare sturdy films by casting toluene solutions of the polymers obtained with the $MoCl_5$-based catalysts. As the side chain of poly(2-alkyne) was longer, the films became more flexible.

The softening points of the polymers obtained with $MoCl_5 \cdot Ph_4Sn$ are shown in Table V. Figure 8 shows DTA thermograms of the poly(2-alkynes) obtained with $MoCl_5 \cdot Ph_4Sn$. Every polymer exhibited an exothermic peak between 200 and 300 °C. The exotherm decreased as the alkyl group of the polymer became longer (see Table V for detailed values). The maxima of the exotherms approximately corresponded to the softening points.

No change in the IR spectrum and intrinsic viscosity occurred when the poly(2-hexyne) obtained with $MoCl_5 \cdot Ph_4Sn$ was allowed to stand in air at room temperature for a month. No change was observed either when this polymer was heated at 100 °C for 3 h in vacuo. On the other hand, after treatment at 100 °C for 3 h in air, an absorption due to C=O stretching appeared in the IR spectrum and the intrinsic viscosity dropped from 4.55 to 0.20 dL g^{-1}.

The electrical conductivity (σ) of poly(2-hexyne) (Table I, sample no. 3) was 10^{-18} Ω^{-1} cm^{-1}, indicating a typical insulator. Further, no unpaired spin was detected in this polymer ($<10^{15}$ spins g^{-1}, even if present). These observations contrast with the fact that polyacetylene (film) is a semiconductor ($\sigma = 10^{-9}$–10^{-5} Ω^{-1} cm^{-1})[22] and paramagnetic (1×10^{19} spins g^{-1}).[23] As has been inferred from the UV spectra of polymers, the main chain of poly(2-alkynes) should be considerably twisted owing to the presence of two substituents per repeating unit. This seems responsible for the observed electrical and magnetic properties of poly(2-hexyne).

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Solid-State Photopolymerization of Diacetylenes

Alfred Prock,† Michael L. Shand, and Ronald R. Chance*

Corporate Research Center, Allied Corporation, Morristown, New Jersey 07960.

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ABSTRACT: A detailed study of the UV photopolymerization of a highly radiation-sensitive diacetylene is presented. The polymerization kinetics, quantum yield, and variation of optical properties on polymerization are analyzed and discussed. The polymerization rate for irradiation of thin diacetylene films is found to decrease markedly as the polymer concentration increases. Quenching of the monomer excited state by the polymer chains present in the partially polymerized samples is shown to provide a reasonable explanation for this behavior. This quenching is probably an important limiting factor in determining overall polymer conversion in the photopolymerization of diacetylenes.

I. Introduction

The solid-state polymerization of diacetylene crystals provides a prime example of a lattice-controlled solid-state reaction.[1] The reaction proceeds via 1,4 addition and can be initiated by heat,[2,3] pressure, UV irradiation,[4,5] high-energy irradiation,[1,6] or exposure to certain gases.[7] In favorable cases, the reaction product is a single-crystal, fully conjugated polymer of macroscopic dimensions.

Much of the work in the poly(diacetylene) area has centered on the kinetics and mechanism of the polymerization process. The thermal polymerization process is temperature activated by about 1 eV, which should represent roughly the energy difference between the monomer and the dimer intermediate to chain propagation. Energetic arguments[3] and recent ESR experiments[8,9] strongly suggest a biradical (rather than a bicarbene) structure for the dimer. At this stage, the dimer can revert to the monomer (which it probably does with highest probability[10]) or proceed forward to initiate a chain. Each propagation event, i.e., each addition of a monomer unit to the chain, is exothermic by ~1.6 eV.[3] Little is known about the chain termination event.

For photopolymerization, the process is viewed to be much the same except that the activation barrier is overcome via the photon energy.[5] Since the photopolymerization process is strictly linear in light intensity (at least in the vicinity of room temperature),[5,11] the dimerization event must involve a monomer excited state interacting with a monomer ground state. Figure 1 illustrates schematically the energetics of these processes.[3] Since the absorbed photon can initiate a chain reaction, quantum yields can be quite high.[5,11] The quantum yield is defined as the number of poly(diacetylene) repeat units produced per absorbed photon and is equal to nq, where q is chain initiation probability and n is the propagation length. Values ranging from $nq = 10^{-4}$ to 50 have been reported for various diacetylenes.[5,11-14] The exothermic nature of the photopolymerization process has been conclusively demonstrated with photoacoustic spectroscopy.[11]

In this paper, we present a detailed study of the UV photopolymerization of a highly radiation-sensitive diacetylene.[6] We discuss the polymerization kinetics, the factors limiting quantum yields, and the variation in optical properties on polymerization. Experimental details are given in section II. Results are presented section III and discussed in section IV.

II. Experimental Section

The diacetylene chosen for this study is 4BCMU, $RC\equiv C-C\equiv CR$, where R is $(CH_2)_4OCONHCH_2COO(n\text{-}C_4H_9)$. BCMU stands for [(butoxycarbonyl)methyl]urethane. This particular diacetylene displays high reactivity to UV or γ irradiation but virtually no thermal reactivity.[6] Some of the experiments described herein employ 4BCMU single crystals, which typically grow as thin platelets (1 × 5 × 0.01 cm).[14] However, most of our photopolymerization studies have been carried out on thin films of 4BCMU. These films, with thicknesses ranging from 1000 to 20 000 Å, were deposited on quartz slides with an air brush. A drop of paraffin oil (purified by passage through silica gel) was then placed on the slide and inserted in a standard 1-cm quartz cuvette so that the paraffin oil formed an interface between the 4BCMU film and the inner surface of the quartz cuvette. This arrangement was used to minimize scattering, which can be quite a problem with an air/film interface. Water and paracyclophane[15] were also used as "index matching" media to ensure that our results were unaffected by the paraffin oil. Spectra were taken before irradiation and after various irradiation dosages. The irradiation source was a 150-W xenon arc lamp with a 260-nm, 10-nm band-pass interference filter and a Corning 754 UV filter. The incident irradiation intensity was typically 2×10^{13} photons/(cm^2·s), determined with a calibrated EG&G photodiode. The band-pass for the spectra was 1 nm.

At the end of the experiment the amount of polymer on the slide was determined by dissolving the film in 2 mL of $CHCl_3$ and measuring the absorbance of the resulting polymer solution ($\epsilon_{max} = 17\,000$ L/(mol·cm) at 470 nm).[16] Average film thickness was

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† Visiting Scientist, Allied Corp., 1980. Current address: Department of Chemistry, Boston University.

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