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Polymerization of (perfluoro-*n*-alkyl)acetylenes by WCl_6-Ph_4Sn and polymer properties

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SUMMARY

(Perfluoro-n-alkyl)acetylenes ($HC\equiv CR_f$; R_f = n-C_6F_{13}, n-C_4F_9) polymerized with the WCl_6-Ph_4Sn catalyst to produce methanol-insoluble polymers in good yields. The intrinsic viscosities of the polymers (in C_6F_6) were ca. 0.05 dL/g, being relatively small. No large difference was observed between the polymerization in toluene (heterogeneous) and that in C_6F_6 (homogeneous). The main chain of the polymers was composed of alternating double bonds. These polymers were white solids soluble in C_6F_6. The temperatures at which the weight loss of the polymers started were higher than 200°C, which indicates improved thermal stability as compared with the corresponding poly(1-alkynes).

INTRODUCTION

Fluorine-containing polymers such as poly(tetrafluoroethylene) are known to show unique properties such as water and oil repellency, thermal stability, and resistance to chemicals. Thus far several polymers have been obtained from fluorine-containing aromatic acetylenes by using groups 5 and 6 transition metal catalysts; e.g., poly(1-pentafluorophenyl-1-alkynes) (insol.),[1] poly[o-(trifluoromethyl)phenylacetylene] (high MW),[2,3] poly[1-ethynyl-5-(trifluoromethyl)naphthalene] (medium MW).[4]

On the other hand, the polymerization of fluorine-containing aliphatic acetylenes is virtually restricted to a few examples as follows: polymerizations of $HC\equiv CCF_3$ with $PdCl_2$/DMF or n-BuLi[5] and of $CF_3C\equiv CCF_3$ with /KF,[6] both of which only produce insoluble polymers.

This note reports on the polymerization of (perfluoro-n-alkyl)-acetylenes having relatively long perfluoroalkyl groups ($HC\equiv CR_f$; R_f = n-C_6F_{13}, n-C_4F_9). These monomers polymerized with WCl_6-Ph_4Sn catalyst to produce new polymers which are white, totally soluble in C_6F_6, and more stable than the corresponding poly(1-alkynes).

EXPERIMENTAL

Monomers were offered by Japan Halon Co., Ltd.: $HC\equiv C$-n-C_6F_{13} bp 96°C/760mmHg, purity [gas chromatography (GC)] 99%; $HC\equiv C$-n-C_4F_9 bp 47°C/760mmHg, purity (GC) 98%. W and Mo compounds and organometallic cocatalysts were commercially obtained, and used without further purification.

All the procedures for catalyst preparation and polymerization were carried out in dry nitrogen. Monomer conversions were determined by GC, and yields of methanol-insoluble polymers were determined by gravimetry.

Intrinsic viscosities of polymers were measured in C_6F_6 at 30°C. Infrared (IR) and ultraviolet(UV)-visible spectra were recorded on Shimadzu IR435 and UV190 spectrophotometers, respectively. Thermogravimetric analysis (TGA) was performed with a Shimadzu 20B thermal analyzer (heating rate 10°C/min., in air). Other analyses were carried out as described elsewhere.[7]

RESULTS AND DISCUSSION

Polymerization of (Perfluoro-n-alkyl)acetylenes

Table I lists results for the polymerization of (perfluoro-n-hexyl)acetylene. When polymerization was carried out with WCl_6-Ph_4Sn as catalyst in toluene solution, a methanol-insoluble polymer was obtained in ca. 50% yield. The methanol-soluble product was a mixture of linear oligomers and cyclotrimers. Apart from toluene as solvent, polymers could be obtained in CCl_4 and various fluorine-containing solvents. The polymer yields in these solvents, however, were 15 - 30%, being lower than that in toluene. The intrinsic viscosities of the polymers produced in toluene and CCl_2FCClF_2 were in the range of ca. 0.05 - 0.08 dL/g, indicating that the molecular weights of the polymers are rather low like poly(1-alkynes). The intrinsic viscosities of the polymers did not greatly change with the kind of polymerization solvents. It is noted that no substantial difference in the yield and molecular weight of polymer is observable between toluene or CCl_4 (non-solvents of the polymer) and fluorine-containing solvents (relatively good solvents of

Table I
Polymerization of (Perfluoro-n-hexyl)acetylene[a]

Catalyst	Solvent	Conversion	Polymer[b]	
		%	Yield,%	[η],dL/g[c]
WCl_6-Ph_4Sn	toluene	72	52	0.047
WCl_6-Ph_4Sn	CCl_4	100	30	
WCl_6-Ph_4Sn	C_6F_6	80	30	
WCl_6-Ph_4Sn	C_6H_4-m-$(CF_3)_2$	25	15	
WCl_6-Ph_4Sn	CCl_2FCClF_2	100	30	0.080
WCl_6	toluene	24	0	
$W(CO)_6$-hν[d]	CCl_4	0	0	
$MoCl_5$-Ph_4Sn	toluene	0	0	

[a] Polymerized at 30°C for 24 h after aging catalyst solutions at 30°C for 15 min.; [M]o = 0.50 M, [Cat] = [Cocat] = 20 mM.
[b] Methanol-insoluble product.
[c] Measured in C_6F_6 at 30°C.
[d] Polymerized at 30°C after irradiation with UV light for 1 h; [M]o = 0.50 M, [Cat] = 10 mM.

Table II

Polymerization of (Perfluoro-n-butyl)acetylene[a]

Catalyst	Solvent	Conversion	Polymer[b]	
		%	Yield,%	[η],dL/g[c]
WCl_6-Ph_4Sn	toluene	100	86	0.050
WCl_6-Ph_4Sn	C_6F_6	100	82	0.059
WCl_6-Ph_4Sn	CCl_2FCClF_2	100	76	0.062
$W(CO)_6$-hν[d]	CCl_4	0	0	
$MoCl_5$-Ph_4Sn	toluene	8	0	

[a] Polymerized at 30°C for 24 h after aging catalyst solutions at 30°C for 15 min.; [M]o = 0.50 M, [Cat] = [Cocat] = 30 mM.

[b] Methanol-insoluble product.

[c] Measured in C_6F_6 at 30°C.

[d] Polymerized at 30°C after irradiation with UV light for 1 h; [M]o = 0.50 M, [Cat] = 10 mM.

the polymer). When WCl_6 alone was used as catalyst, or when n-Bu_4Sn, Ph_3SiH, Et_3SiH, Ph_3Bi, and Ph_3Sb were added as cocatalysts to WCl_6, no methanol-insoluble polymer was obtained. No reaction occurred with $W(CO)_6$-hν or $MoCl_5$-Ph_4Sn. Ziegler-catalysts such as $Fe(acac)_3$-$3Et_3Al$ and $Ti(OBu)_4$-$4Et_3Al$ produced only methanol-soluble oligomers. Thus it has turned out that the effective catalyst for this monomer is restricted to WCl_6-Ph_4Sn.

Table II gives data for the polymerization of (perfluoro-n-butyl)-acetylene, a homologue with a shorter perfluoroalkyl group. When the WCl_6-Ph_4Sn catalyst was used in conjunction with the solvents shown in the table, monomer was completely consumed and methanol-insoluble polymers were obtained in high yields around 80%. The intrinsic viscosities of the produced polymers were 0.05 - 0.06 dL/g, no large difference being observed irrespective of the kind of solvents.

Copolymerization of (perfluoro-n-hexyl)acetylene with 1-octyne by WCl_6-Ph_4Sn catalyst was attempted (polymerization conditions: in toluene, 30°C, 24 h, $[M_1]_o = [M_2]_o = 0.25$ M, [Cat] = 20 mM). Consequently, 1-octyne was completely converted within 1 h, while (perfluoro-n-hexyl)-acetylene was not consumed at all even after 24 h. Further, 1-(perfluoro-n-hexyl)-1-pentyne (n-$C_6F_{13}C{\equiv}C$-n-C_3H_7) was not consumed at all in the polymerization by $MoCl_5$-n-Bu_4Sn catalyst[8] (polymerization conditions: in toluene, 30°C, 24 h, $[M]_o = 0.25$ M, [Cat] = 20 mM); it gives striking contrast to the fact that internal alkynes polymerize well in the presence of $MoCl_5$- and/or WCl_6-based catalysts.[9] These results suggest that the coordinating ability of fluorine-containing acetylenes are inferior to that of the corresponding aliphatic acetylenes.

Structure and Properties of Polymers

The structure and properties of the present polymers did not essentially differ with polymerization conditions. Hence, the data for the polymer samples prepared with WCl_6-Ph_4Sn in toluene will be described below.

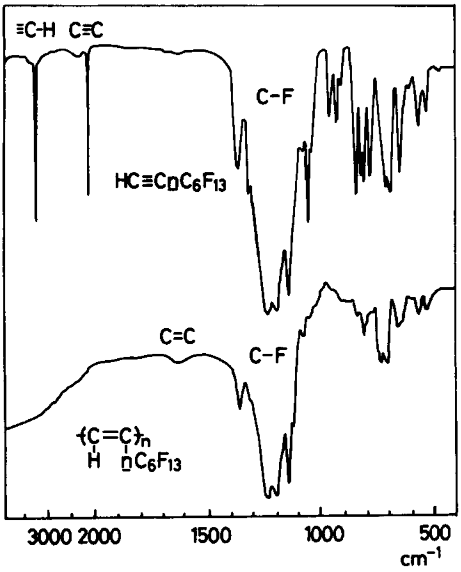

Figure 1. IR spectra of (perfluoro-n-hexyl)acetylene and its polymer (KBr pellet).

The elemental analysis values for the polymers agreed fairly well with the values calculated for the addition polymerization products (e.g., Anal Calcd for $(C_8H_1F_{13})_n$: C, 27.91%; H, 0.30%; F, 71.80% Found: C, 28.30%; H, 0.45%; F, 70.21%).

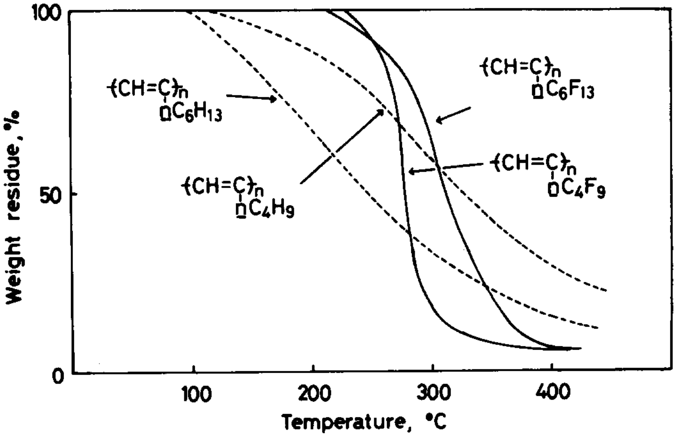

Figure 2. TGA curves of poly[(perfluoro-n-alkyl)-acetylenes] and poly(1-alkynes) (heating rate 10°C/min, in air).

Figure 1 exhibits the IR spectra of (perfluoro-n-hexyl)acetylene and its polymer. The spectrum of the polymer shows no absorptions characteristic of the ≡C-H and C≡C bonds which are clearly seen in the spectrum of the monomer. Instead, an absorption due to the C=C bond is observed at 1620 cm^{-1} in the polymer. The strong complicated band at 1350 - 1000 cm^{-1} is due to C-F stretching. These analytical and IR spectral data indicates that the polymer has alternating double bonds along the main chain as shown in Figure 1.

The poly[(perfluoro-n-alkyl)acetylenes] obtained in the present study are white solids. These polymers completely dissolved in C_6F_6, and were partly soluble in other fluorine-containing solvents such as CCl_2FCClF_2, but did not dissolve in hydrocarbons and ethers at all. Poly(1-alkynes), corresponding hydrocarbon polyacetylenes, are soluble in hydrocarbon solvents such as toluene. Thus it is evident that polymer solubility greatly differs owing to the presence or absence of the fluorine atoms.

TGA curves of poly[(perfluoro-n-alkyl)acetylenes] in air are shown in Figure 2. Poly(1-alkynes) have poor thermal stability; their weight loss starts below 150°C in TGA.[9] In contrast, the temperatures at which these fluorine-containing polymers started to lose weight were fairly high (220 - 230°C), indicating enhanced thermal stability. It can be said that the present polymers have fairly good thermal stability among mono-substituted acetylene polymers because of bulkiness of the side chain and/or lack of H atom in the perfluoroalkyl groups.[9]

As shown in Figure 3, the UV-visible spectra of poly[(perfluoro-n-alkyl)acetylenes] exhibited an absorption maximum at around 250 - 300 nm, and no absorption above 340 nm. These absorption bands are in a shorter wavelength region than are those of the corresponding poly(1-alkynes). This can be explained in terms that the bulky perfluoroalkyl groups twist the polymer backbone to reduce the extent of conjugation. These spectra correspond well with the fact that the present

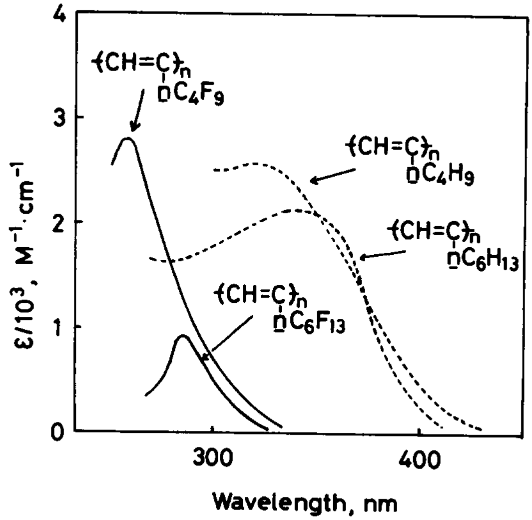

Figure 3. UV-visible spectra of poly[(perfluoro-n-alkyl)acetylenes] and poly(1-alkynes) (in C_6F_6 or CCl_4).

polymers are white, whereas the poly(1-alkynes) are yellow to orange. The absorption of the present polymers weakened with increasing length of perfluoroalkyl group.

The electrical conductivities of poly[(perfluoro-n-alkyl)acetylenes] were in the order of 10^{-17} S•cm^{-1}, indicative of typical electrical insulators.

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