Polymerization of Acetylenes Containing Heptadecafluorononyloxy Group and Polymer Properties

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ABSTRACT: Polymerizations of two kinds of fluorine-containing aromatic disubstituted acetylenes, 1-[*p*-(heptadecafluorononyloxy)phenyl]-2-phenylacetylene (*p*-C₉F₁₇ODPA) and 1-[*p*-(heptadecafluorononyloxy)phenyl]-1-hexyne (*p*-C₉F₁₇OPH) were studied with groups 5 and 6 transition-metal catalysts. *p*-C₉F₁₇ODPA polymerized with TaCl₅-Et₃SiH catalyst to give a new polymer over 70 yield and its maximum intrinsic viscosity ($[\eta]$) was as high as 2.1 dl g⁻¹. *p*-C₉F₁₇OPH polymerized with Ta and Nb catalysts, but yield and $[\eta]$ of the polymer were lower. Poly(*p*-C₉F₁₇ODPA) and poly(*p*-C₉F₁₇OPH) were in the form of a yellow solid and white solid, and began to lose weight at 410°C and 270°C, respectively, which indicates high thermal stability. Both polymers had a main-chain structure consisted of alternating double bonds, and were completely soluble in some fluorine-containing solvents such as *m*-(CF₃)₂C₆H₄ and CCl₂FCClF₂. Poly(*p*-C₉F₁₇ODPA) formed a tough film by solution casting, and showed high *P*_{O₂} value [4×10^{-8} cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹] comparable to that of poly(dimethylsiloxane).

KEY WORDS Substituted Acetylene / Transition-Metal Catalyst / Metathesis Polymerization / Fluorine-Containing Polymer / Gas Permeability /

The polymerization of various substituted acetylenes has been achieved by Masuda and Higashimura with catalysts based on groups 5 and 6 transition-metals.^{1,2} Among them, polymers of aromatic disubstituted acetylenes show fairly high thermal stability.³ The on-set temperatures of weight loss of poly(diphenylacetylene)⁴ [poly(DPA)] and poly(1-phenyl-1-alkynes),^{5,6} which are representative aromatic disubstituted hydrocarbon polymers, are 500°C and around 300°C, respectively.

Fluorine-containing polyacetylenes are expected to show unique properties and functions because they have unique structures of alternating double-bonds in the main chain and fluorine atoms in the side group. Several fluorine-containing acetylenes have been polymerized. Most, however, are aliphatics or

monosubstituted aromatics, whose recent examples include; HC≡CC₆F₁₃⁷ (intrinsic viscosity $[\eta]$ 0.05 dl g⁻¹), HC≡CC₆H₄-*o*-CF₃^{8,9} [weight-average molecular weight ($\bar{M}_w$) $\sim 1 \times 10^6$], HC≡CC₆H₃-2,4-(CF₃)₂¹⁰ ($[\eta]$ 0.35 dl g⁻¹), HC≡CC₆F₅¹¹ ($[\eta]$ 0.6 dl g⁻¹), HC≡CC₆F₄-*p*-C₄H₉¹¹ ($\bar{M}_w \sim 2 \times 10^6$), CH₃C≡CC₆F₅¹² (insoluble).

1-[*p*-(Heptadecafluorononyloxy)phenyl]-2-phenylacetylene (*p*-C₉F₁₇ODPA) and 1-[*p*-(heptadecafluorononyloxy)phenyl]-1-hexyne (*p*-C₉F₁₇OPH) are new fluorine-containing aromatic disubstituted acetylenes. They are derivatives of diphenylacetylene (DPA) and 1-phenyl-1-hexyne (PH), and are featured by high fluorine content. Thus it is of interest to study their polymerization behavior and properties.

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The present paper deals with the polymerization of p -C₉F₁₇ODPA and p -C₉F₁₇OPH. Soluble, high molecular weight polymers have been successfully obtained from p -C₉F₁₇ODPA and p -C₉F₁₇OPH, and the structures and properties of the polymers have been clarified.

EXPERIMENTAL

Monomer Synthesis

p -C₉F₁₇ODPA and p -C₉F₁₇OPH were prepared with reference to the literature^{13,14} according to the following scheme:

Compound (I) and monomers are new materials. As an example, the procedure for synthesizing p -C₉F₁₇ODPA is described in detail.

p -(Heptadecafluorononyloxy)iodobenzene (I): p -Iodophenol (53 g, 0.24 mol), hexafluoropropene trimers [a mixture of octadecafluoro-3-ethyl-2,4-dimethyl-2-pentene and octadecafluoro-3-(1-methylethyl)-4-methyl-2-pentene; 113 g, 0.25 mol], and dimethylacetamide (250 ml) were placed in a 1-l beaker. To

this mixture, triethylamine (35 ml, 0.25 mol) was added dropwise keeping the mixture below 20°C. After stirring for 3 h at room temperature, the mixture was poured into 2 liters of diluted hydrochloric acid. The separated solid was diluted with dichloromethane and washed with 5% sodium hydroxide solution, and then water. The organic phase was dried over anhydrous sodium sulfate overnight and dichloromethane was evaporated. The crude product was recrystallized from ethanol to afford a colorless solid (I), mp 45°C, yield 82%.

p -C₉F₁₇ODPA: After flushed with nitrogen, a 1-l flask was charged with dry triethylamine (200 ml), (Ph₃P)PdCl₂ (0.14 g, 0.2 mmol), CuI (0.23 g, 1.2 mmol), Ph₃P (0.21 g, 0.8 mmol), and phenylacetylene (20 ml, 0.18 mol), and the mixture was stirred at room temperature for 1 h. A solution of p -(heptadecafluorononyloxy)iodobenzene (97 g, 0.15 mol) in triethylamine (200 ml) was added, and the mixture was heated at 60°C for 3 h with stirring. After completion of the reaction was confirmed by gas chromatography (GC), the mixture was poured into 1 liter of 5% hydrochloric acid. The mixture was extracted with dichloromethane, the organic phase was dried over anhydrous sodium sulfate overnight, and dichloromethane was evaporated. The crude product was recrystallized from methanol to give pure p -C₉F₁₇ODPA as a colorless solid, mp 105°C, yield 67%, purity >99% (GC). The structure of the heptadecafluorononyloxy group of p -C₉F₁₇ODPA was confirmed by ¹⁹F NMR spectrum (chemical shift, δ , ppm from CFC1₃ in CDCl₃): -56.9 (d, 3F), -72.0 (s, 6F), -73.1 (d, 6F), -168.2 (q, 1F), -170.2 (m, 1F).

p -C₉F₁₇OPH was prepared from (I) and 1-hexyne in the same way; the product was sticky oil and purified by distillation, bp 129°C/3 mmHg, yield 67%, purity 98% (GC), d_4^{20} 1.479.

Catalyst Preparation and Polymerization

Transition-metal chlorides and organome-

tallic cocatalysts were commercially obtained and used without further purification. Care was taken that they would not be decomposed by moisture and/or air. Solvents for polymerization were purified by the standard methods.

Polymerizations were performed in pre-baked glass vessels under dry nitrogen. The following polymerization procedure is exemplary (see Table III, no. 3 for the result): In a Schlenk tube equipped with a three-way stopcock, a monomer solution was prepared by mixing $p\text{-C}_9\text{F}_{17}\text{ODPA}$ (1.5 mmol, 0.94 g), 1,2,4-trichlorobenzene (0.20 ml; internal standard for GC) and PhCl (2.17 ml). In another Schlenk tube, TaCl_5 (0.10 mmol, 36 mg) and Et_3SiH (0.20 mmol, 23 mg) were dissolved in PhCl (3.0 ml), and the catalyst solution was aged at 80°C for 15 min. 2.0 ml of the monomer solution were added to the catalyst solution. After polymerization at 80°C for 24 h, the reaction was quenched by adding a mixture (5 ml) of $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ and methanol (4:1 vol ratio). Monomer conversion was determined by GC (silicone DC550 3 m, 170°C). The reaction mixture was diluted with $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ (30 ml), and poured into acetone (1 liter) under stirring. The precipitated polymer was washed with acetone, filtered, and dried to a constant weight. Polymer yield was determined by gravimetry.

Characterization

Intrinsic viscosities ($[\eta]$) of polymers were measured in $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ at 30°C using a Ubbelohde-type viscometer in the concentration (c) range 0.1–0.4 g dl⁻¹. Plots of η_{sp}/c vs. c were all linear.

^{13}C NMR spectra were observed with a JEOL EX270 spectrometer. ^{19}F NMR spectrum of $p\text{-C}_9\text{F}_{17}\text{ODPA}$ monomer was measured at Toray Research Center, Inc. IR spectra and UV-visible spectra were recorded with a JASCO IR700 and Shimadzu UV160A spectrophotometer, respectively. Thermogravimetric analysis (TGA) was conducted with a Seiko TG/DTA200 thermal analyzer (in air,

heating rate $10^\circ\text{C min}^{-1}$). Contact angles of water and n -decane on poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) were measured with Kyowa CA-D goniometer at 25°C .

RESULTS AND DISCUSSION

Polymerization of $p\text{-C}_9\text{F}_{17}\text{ODPA}$

Table I shows the results for the polymerization of $p\text{-C}_9\text{F}_{17}\text{ODPA}$ by groups 5 and 6 transition-metal catalysts, which are effective for the polymerization of various substituted acetylenes. Use of TaCl_5 alone as catalyst afforded only acetone-soluble products (acetone was employed as a precipitant instead of methanol which is often used, because unreacted $p\text{-C}_9\text{F}_{17}\text{ODPA}$ monomer also precipitated in methanol). When a two-fold amount of $n\text{-Bu}_4\text{Sn}$ to TaCl_5 was employed as cocatalyst, acetone-insoluble poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) was obtained in a 70% yield. Since the polymers formed were soluble only in fluorine-containing solvents, their molecular weights were estimated from $[\eta]$ in $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$. $[\eta]$ of the polymer was *ca.* 0.9 dl g⁻¹.

The corresponding Nb, W, and Mo catalysts induced the reaction of $p\text{-C}_9\text{F}_{17}\text{ODPA}$ to some extent, but polymer yields were zero or negligible; the acetone-soluble products were linear oligomers according to gel permeation

Table I. Polymerization of $p\text{-C}_9\text{F}_{17}\text{ODPA}$ by various catalysts^a

Catalyst	Conversion	Polymer ^b	
	%	Yield/%	$[\eta]/\text{dl g}^{-1\text{c}}$
TaCl_5	68	0	
$\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$	100	70	0.87
NbCl_5	3	0	
$\text{NbCl}_5\text{-}n\text{-Bu}_4\text{Sn}$	37	8	
$\text{WCl}_6\text{-}n\text{-Bu}_4\text{Sn}$	58	7	
$\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$	26	0	

^a Polymerized in toluene at 80°C for 24 h; $[\text{M}]_0 = 0.20$ M, $[\text{Cat}] = 20$ mM, $[n\text{-Bu}_4\text{Sn}] = 40$ mM.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ at 30°C .

chromatography (GPC) and IR spectroscopy. These results show that the polymerization behavior of p -C₉F₁₇ODPA is similar to that of DPA.⁴ Hence, the effect of reaction conditions was examined in detail using TaCl₅-based catalyst, aiming at increased polymer molecular weight.

Effects of solvents were studied with use of TaCl₅- n -Bu₄Sn catalyst (Table II). When polymerization was carried out in PhCl, both polymer yield and $[\eta]$ somewhat increased, compared with those obtained in toluene. On the other hand, some fluorine-containing solvents such as PhCF₃, m -(CF₃)₂C₆H₄ and CCl₂FCCL₂F considerably decreased both. These results are probably due to low solubility of the catalyst in fluorine-containing solvents. Consequently, PhCl is a suitable solvent for polymerization of the present monomer.

Table III details effects of organometallic cocatalysts in the polymerization by TaCl₅ in PhCl. When alkylmetals containing group 4 main-group metals such as n -Bu₄Sn and Et₃SiH were used as cocatalysts, the monomer was consumed quantitatively and polymer yields were over 70%. Organometallics involving groups 1–3 main-group metals such as n -BuLi and Et₃Al were also effective to some extent in producing the polymer. Eventually, polymer yield and $[\eta]$ took the highest values when Et₃SiH was employed as cocatalyst.

Table II. Solvent effects on the polymerization of p -C₉F₁₇ODPA by TaCl₅- n -Bu₄Sn^a

Solvent	Conversion	Polymer ^b	
	%	Yield/%	$[\eta]/\text{dl g}^{-1}$ ^c
Toluene	100	70	0.87
PhCl	100	76	1.22
PhCF ₃	88	5	
m -(CF ₃) ₂ C ₆ H ₄	65	18	
CCl ₂ FCCL ₂ F	71	42	0.45

^a Polymerized at 80°C for 24 h; $[M]_0 = 0.20$ M, $[\text{TaCl}_5] = 20$ mM, $[n\text{-Bu}_4\text{Sn}] = 40$ mM.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in m -(CF₃)₂C₆H₄ at 30°C.

Figure 1 illustrates the effects of temperature on polymerization by TaCl₅-Et₃SiH in PhCl. Polymer yield was above 70% in the range of 80–120°C. $[\eta]$ of the polymer gradually decreased with increasing temperature. Thus, about 80°C seems favorable to keep both yield and $[\eta]$ of the polymer high.

The polymerization by TaCl₅-Et₃SiH was completed in 30 min under the conditions shown in Figure 2, being fairly rapid. $[\eta]$ of the polymer stayed almost constant regardless of the polymer yield.

Effects of monomer and catalyst concentrations were studied (Table IV). Under the conditions used, polymer yields were 70–90%. $[\eta]$ of the polymer increased with decreasing $[M]_0$ when $[\text{Cat}] = 20$ mM. Thus it seems that

Table III. Cocatalyst effects on the polymerization of p -C₉F₁₇ODPA by TaCl₅^a

Run	Cocatalyst	Conversion	Polymer ^b	
		%	Yield/%	$[\eta]/\text{dl g}^{-1}$ ^c
1	None	56	0	
2	n -Bu ₄ Sn	100	76	1.22
3	Et ₃ SiH	100	85	1.60
4	n -BuLi	80	56	1.41
5	Et ₃ Al	88	17	

^a Polymerized in PhCl at 80°C for 24 h; $[M]_0 = 0.20$ M, $[\text{TaCl}_5] = 20$ mM, $[\text{Cocat}] = 40$ mM.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in m -(CF₃)₂C₆H₄ at 30°C.

Figure 1. Temperature dependence of the polymerization of p -C₉F₁₇DPA by TaCl₅-Et₃SiH (in PhCl, 24 h, $[M]_0 = 0.20$ M, $[\text{TaCl}_5] = 20$ mM, $[\text{Et}_3\text{SiH}] = 40$ mM),

Figure 2. Time courses of the polymerization of *p*-C₉F₁₇DPA by TaCl₅-Et₃SiH (in PhCl, 80°C, [M]₀ = 0.20 M, [TaCl₅] = 20 mM, [Et₃SiH] = 40 mM).

Table IV. Effects of monomer and catalyst concentrations on the polymerization of *p*-C₉F₁₇ODPA by TaCl₅-Et₃SiH^a

Run	[M] ₀	[Cat]	Conversion	Polymer ^b	
	M	mM	%	Yield/%	[η]/dl g ^{-1 c}
1	0.10	20	100	88	2.10
2	0.20	20	100	85	1.60
3	0.50	20	100	79	1.05
4	0.20	10	100	80	1.22
5	0.20	5	100	72	1.30

^a Polymerized in PhCl at 80°C for 24 h.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in *m*-(CF₃)₂C₆H₄ at 30°C.

lower monomer concentration (0.1–0.2 M) is favorable to attain the high [η]. On the other hand, the decrease of catalyst concentration did not increase [η].

The above results lead to the conclusion that the polymerization conditions in Table IV, run 1 or 2 are optimal to simultaneously achieve high yield and high molecular weight of poly(*p*-C₉F₁₇ODPA).

In order to clarify the influence of *p*-C₉F₁₇O group on the relative monomer reactivity, 1 : 1 copolymerization of *p*-C₉F₁₇ODPA with DPA was carried out (Figure 3). Both monomers were consumed at similar rates. In the copolymerization of substituted acetylenes, a general tendency has been observed that the monomer reactivity increases with decreasing

Figure 3. Copolymerization of *p*-C₉F₁₇DPA with DPA by TaCl₅-Et₃SiH (in PhCl, 80°C, [M]₁₀ = [M]₂₀ = 0.10 M, [TaCl₅] = 20 mM, [Et₃SiH] = 40 mM).

Table V. Polymerization of *p*-C₉F₁₇OPH by various catalysts^a

Catalyst	Conversion	Polymer ^b	
	%	Yield/%	[η]/dl g ^{-1 c}
TaCl ₅	100	4	
TaCl ₅ - <i>n</i> -Bu ₄ Sn	100	54	0.23
NbCl ₅	100	13	
NbCl ₅ - <i>n</i> -Bu ₄ Sn	100	55	0.25
WCl ₆ - <i>n</i> -Bu ₄ Sn	58	7	
MoCl ₅ - <i>n</i> -Bu ₄ Sn	26	0	

^a Polymerized in toluene at 80°C for 24 h; [M]₀ = 0.20 M, [Cat] = [*n*-Bu₄Sn] = 20 mM.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in *m*-(CF₃)₂C₆H₄ at 30°C.

bulkiness of substituent and with increasing electron-donating ability of substituent.^{15,16} Thus, the results of the present study indicate that the *p*-C₉F₁₇O group hardly affects monomer reactivity either sterically or electronically.

Polymerization of *p*-C₉F₁₇OPH

Polymerization of *p*-C₉F₁₇OPH was examined using various catalysts (Table V). TaCl₅ and NbCl₅ alone, which polymerized 1-phenyl-1-alkynes in high yields,⁵ afforded poly(*p*-C₉F₁₇OPH) in rather low yields. The acetone-soluble product was a mixture of linear oligomers and cyclotrimers (acetone, which dissolved cyclotrimers of *p*-C₉F₁₇OPH, was

Table VI. Solvent effects on the polymerization of $p\text{-C}_9\text{F}_{17}\text{OPH}$ by $\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ and $\text{NbCl}_5\text{-}n\text{-Bu}_4\text{Sn}^a$

Run	Solvent	Conversion	Polymer ^b	
		%	Yield/%	$[\eta]/\text{dl g}^{-1\text{c}}$
TaCl ₅ - <i>n</i> -Bu ₄ Sn catalyst				
1	Toluene	100	54	0.23
2	PhCl	97	50	0.35
3	<i>m</i> -(CF ₃) ₂ C ₆ H ₄	95	6	
4	CCl ₂ FCCl ₂ F	98	55	0.67
NbCl ₅ - <i>n</i> -Bu ₄ Sn catalyst				
5	Toluene	96	55	0.25
6	PhCl	72	58	0.40
7	<i>m</i> -(CF ₃) ₂ C ₆ H ₄	91	4	
8	CCl ₂ FCCl ₂ F	97	61	0.51

^a Polymerized at 80°C for 24 h; $[\text{M}]_0 = 0.20\text{ M}$, $[\text{TaCl}_5] = [\text{n-Bu}_4\text{Sn}] = 20\text{ mM}$.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ at 30°C.

Table VII. Cocatalyst effects on the polymerization of $p\text{-C}_9\text{F}_{17}\text{OPH}$ by TaCl_5 and NbCl_5^a

Cocatalyst	Conversion	Polymer ^b	
	%	Yield/%	$[\eta]/\text{dl g}^{-1\text{c}}$
TaCl_5 catalyst			
None	35	0	
$n\text{-Bu}_4\text{Sn}$	98	55	0.67
Et_3SiH	81	32	0.52
$n\text{-BuLi}$	30	2	
Et_3Al	21	17	
NbCl_5 catalyst			
None	74	10	
$n\text{-Bu}_4\text{Sn}$	97	61	0.51
Et_3SiH	92	46	0.24
$n\text{-BuLi}$	12	0	
Et_3Al	100	19	

^a Polymerized in $\text{CCl}_2\text{FCCl}_2\text{F}$ at 80°C for 24 h; $[\text{M}]_0 = 0.20\text{ M}$, $[\text{TaCl}_5] = [\text{Cocat}] = 20\text{ mM}$.

^b Acetone-insoluble part.

^c Intrinsic viscosity measured in $m\text{-(CF}_3)_2\text{C}_6\text{H}_4$ at 30°C.

adopted as precipitant). Use of equimolar $n\text{-Bu}_4\text{Sn}$ as cocatalyst, which is effective for increasing molecular weight of poly(1-phenyl-1-alkynes),⁶ gave poly($p\text{-C}_9\text{F}_{17}\text{OPH}$) in *ca.* 50% yield, and $[\eta]$ was about 0.2 dl g^{-1} . $\text{WCl}_6\text{-}n\text{-Bu}_4\text{Sn}$, and $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$, on the other hand, hardly gave acetone-insoluble products.

Solvent effects on the polymerization by $\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ and $\text{NbCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ were studied (Table VI). Interestingly, $[\eta]$ of the polymer considerably increased when polymerization was carried out in $\text{CCl}_2\text{FCCl}_2\text{F}$. Such a tendency was not seen in the polymerization of $p\text{-C}_9\text{F}_{17}\text{ODPA}$. PhCl was effective to some extent in increasing $[\eta]$ of poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) (see above).

As seen in Table VII, polymer yield was affected by the kind of cocatalyst. The yield was relatively high when $n\text{-Bu}_4\text{Sn}$ or Et_3SiH was used, whereas $n\text{-BuLi}$ hardly produced the polymer.

Consequently, both yield and $[\eta]$ of poly($p\text{-C}_9\text{F}_{17}\text{OPH}$) were considerably lower than those of poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$), irrespec-

tive of polymerization conditions.

Polymer Structure

Analytical data of poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) and poly($p\text{-C}_9\text{F}_{17}\text{OPH}$) did not depend on the polymerization conditions. The data stated below were obtained with the polymer samples from Table III, run 3 and Table VI, run 4.

Elemental analysis data of poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) and poly($p\text{-C}_9\text{F}_{17}\text{OPH}$) agreed well with theoretical values; *Anal.* Poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$): Calcd for $(\text{C}_{23}\text{H}_9\text{F}_{17}\text{O})_n$: C, 44.2%; H, 1.5%; F, 51.7%; O, 2.6%. Found: C, 43.5%; H, 1.3%; F, 52.0%; O, 2.8%. Poly($p\text{-C}_9\text{F}_{17}\text{OPH}$): Calcd for $(\text{C}_{21}\text{H}_{13}\text{F}_{17}\text{O})_n$: C, 41.7%; H, 2.2%; F, 53.4%; O, 2.7%. Found: C, 42.2%; H, 1.4%; F, 52.5%; O, 2.0%.

As seen from Figure 4, the IR spectra of poly($p\text{-C}_9\text{F}_{17}\text{ODPA}$) and poly($p\text{-C}_9\text{F}_{17}\text{OPH}$) do not show absorption due to $\text{C}\equiv\text{C}$ stretching which was observed at 2220 cm^{-1} with the monomers. Strong absorptions characteristic of C-F stretching were seen at $1300\text{--}1200\text{ cm}^{-1}$ in both monomers and polymers.

¹³C NMR spectra of monomers showed two

Figure 4. IR spectra of poly(*p*-C₉F₁₇DPA) and poly(*p*-C₉F₁₇PH) (KBr pellet; samples from Table III, run 3 and Table VI, run 4).

peaks due to two acetylenic carbons at δ 87.7 and 90.1 (*p*-C₉F₁₇ODPA), and at δ 79.1 and 91.2 (*p*-C₉F₁₇OPH), which disappeared in the polymers.

The IR and ¹³C NMR spectra thus support the idea that the polymers possess alternating double bonds in the main chain as shown in Figure 4. No information about the geometric structure of the main chain, however, could be obtained from these spectra.

In the UV-visible spectra of poly(*p*-C₉F₁₇ODPA) and poly(*p*-C₉F₁₇OPH), absorptions continue up to *ca.* 500 nm and *ca.* 400 nm, respectively. Poly(*p*-C₉F₁₇ODPA) has an absorption maximum at 420 nm (ϵ_{max} 5400 M⁻¹cm⁻¹). These spectra suggest that the extent of conjugation of alternating double bonds is not very high; that is, the main chain is considerably twisted.

Polymer Properties

Poly(*p*-C₉F₁₇ODPA) and poly(*p*-C₉F₁₇OPH) have the form of a yellow solid and white solid, respectively, irrespective of polymerization conditions. Other properties of the poly-

Figure 5. UV-visible spectra of poly(*p*-C₉F₁₇DPA) and poly(*p*-C₉F₁₇PH) (CCl₂FCClF₂ solution; samples from Table III, run 3 and Table VI, run 4).

mers were also independent of the polymerization conditions; the samples used are from Table III, run 3 and Table VI, run 4.

Poly(*p*-C₉F₁₇ODPA) and poly(*p*-C₉F₁₇OPH) completely dissolved in some fluorine-containing solvents such as *m*-(CF₃)₂C₆H₄, and CCl₂FCClF₂, and partly dissolved in CCl₂FCCL₂F and hexafluoropropene trimers. Their nonsolvents include benzene, toluene, PhCl, cyclohexane, CHCl₃, and tetrahydrofuran (THF). In general, polymers from symmetrically disubstituted acetylenes are insoluble in any solvent. For example, poly(1-phenyl-1-propyne)⁵ and poly(3-octyne)¹⁷ are soluble in common organic solvents whereas poly(DPA)⁴ and poly(4-octyne)¹⁷ are not. The very poor solubility of poly(PH) is considered to be related to the above tendency.⁵ The introduction of bulky C₉F₁₇O group, therefore, has proved effective in making substituents unsymmetrical to convert insoluble poly(DPA) and poly(PH) into soluble polymers. In this connection, it has recently been revealed that poly(DPA)s containing trimethylsilyl group on one phenyl group are totally soluble in common organic solvents.¹⁸

A tough, free-standing film is accessible from poly(*p*-C₉F₁₇ODPA) by casting its *m*-(CF₃)₂-C₆H₄ solution. Poly(*p*-C₉F₁₇OPH) is too brittle to hold its filmy state, which is probably due to its molecular weight being not high enough.

Figure 6. Thermogravimetric analysis of poly(*p*-C₉F₁₇-DPA) and poly(*p*-C₉F₁₇PH) (in air, heating rate 10°C min⁻¹; samples from Table III, run 3 and Table VI, run 4).

The surface wettability of poly(*p*-C₉F₁₇ODPA) film was evaluated by measuring the contact angles of water and *n*-decane on the film. The contact angles were 115° (water) and 30° (*n*-decane), respectively. These values are close to those for poly(tetrafluoroethylene)¹⁹ [108° (water) and 35° (*n*-decane)], indicating the low surface energy of poly(*p*-C₉F₁₇ODPA).

Poly(*p*-C₉F₁₇ODPA) began to lose weight at about 410°C, in TGA in air (Figure 6). Though this temperature is more or less lower than that of poly(DPA) (500°C), it is higher than those of most substituted polyacetylenes such as poly(1-phenyl-1-propyne)⁵ (280°C). The weight loss of poly(*p*-C₉F₁₇OPH) occurs at 270°C, being comparable to that of poly(1-phenyl-1-propyne). Further, none of the present polymers suffers any molecular weight decrease or oxidation even though they are left in air either at 120°C for 20 h or at room temperature over a few months. Thus the present polymers possess high thermal stability.

Poly(*p*-C₉F₁₇ODPA) did not soften below 400°C, reflecting its stiff backbone due to the presence of two bulky rigid phenyl groups. On the other hand, the softening point of poly(*p*-C₉F₁₇OPH) was about 250°C, which is somewhat lower than those of poly(1-phenyl-1-alkynes) (260–300°C).⁵

The mechanical properties of poly(*p*-C₉F₁₇ODPA) are as follows: Young's modulus

1100 MPa, tensile strength 15 MPa, elongation at break 1.6% at 25°C. These data show that poly(*p*-C₉F₁₇ODPA) is hard and rather brittle.

The oxygen permeability coefficient (*P*_{O₂}) of a poly(*p*-C₉F₁₇ODPA) membrane at 25°C was *ca.* 4 × 10⁻⁸ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹, and the separation factor of oxygen and nitrogen (*P*_{O₂}/*P*_{N₂}) was 1.8. This *P*_{O₂} is comparable with that of poly(dimethylsiloxane) [6 × 10⁻⁸ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹], being fairly large among those of glassy polymers.

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