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Synthesis and Characterization of Poly[[*o*-(trifluoromethyl)phenyl]acetylene]

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ABSTRACT: Polymerization of [*o*-(trifluoromethyl)phenyl]acetylene initiated by 1:1 mixtures of WCl_6 or $MoCl_5$ with various organometallic cocatalysts provided in high yields a substituted polyacetylene having weight-average molecular weight ($\bar{M}_w$) of 2×10^5–16×10^5. A mixture of WCl_6 with Ph_4Sn was especially active as catalyst and achieved a high $\bar{M}_w$ of 16×10^5. The product polymer was a dark brown solid, soluble in such solvents as toluene and chloroform. A tough film could be obtained by solution casting. The polymer was thermally fairly stable in air. The high molecular weight, film formation, and fair thermal stability of the present polymer are notable characteristics, which are not seen in poly(phenylacetylene).

Introduction

Fluorine-containing polyacetylenes are expected to show unique properties and functions not only because of their alternating double-bonds structure in the main chain but also because of the effect of fluorine atoms in the side group. Though polymerization of several fluorine-containing acetylenes has been attempted so far, most of the products are either insoluble polymers or oligomers; e.g., $HC{\equiv}CCF_3$ (insoluble),[1] $CF_3C{\equiv}CCF_3$ (insoluble),[2] $CH_3C{\equiv}C_6F_5$ (insoluble),[3] $NCC{\equiv}C\text{-}n\text{-}C_nF_{2n+1}$ (n = 1–3; mol wt <2500),[4] $\overline{\mathrm{OCH{=}CHC(CF_3){=}C}}\mathrm{C{\equiv}CH}$ (mol wt ~2000).[5]

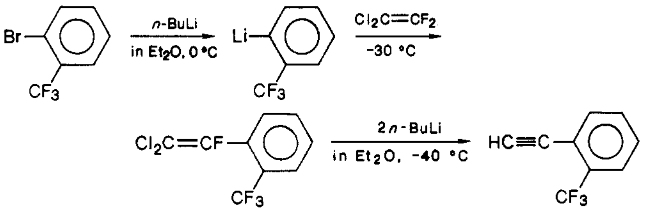
Recently, soluble fluorine-containing poly(phenylacetylenes) have been obtained from the following monomers:[6] $HC{\equiv}CC_6H_4\text{-}o\text{-}CF_3$, $HC{\equiv}C_6H_4\text{-}m\text{-}CF_3$, $HC{\equiv}CC_6H_4\text{-}p\text{-}CF_3$, and $HC{\equiv}CC_6H_4\text{-}p\text{-}F$. Among them, [*o*-(trifluoromethyl)phenyl]acetylene (*o*-TFMPA) yields a polymer whose weight-average molecular weight ($\bar{M}_w$) reaches 1.6×10^6. The employed catalyst is the one obtained by UV irradiation of CCl_4 solution of $W(CO)_6$ [$W(CO)_6$–CCl_4–$h\nu$].

Apart from $W(CO)_6$–CCl_4–$h\nu$ and its Mo counterpart [$Mo(CO)_6$–CCl_4–$h\nu$], WCl_6- and $MoCl_5$-based catalysts (WCl_6 and $MoCl_5$ alone and their mixtures with organometallic cocatalysts) are known to polymerize phenylacetylenes in high yields.[7] The characteristics of these metal chloride based catalysts, as compared with those of the metal carbonyl based catalysts, include the following: (i) various cocatalysts are available; (ii) various polymerization solvents can be used; (iii) the catalyst preparation is facile; (iv) the catalyst activity is generally high. Hence, it seems very interesting to investigate the polymerization of *o*-TFMPA with use of WCl_6- and $MoCl_5$-based catalysts. Further, the structure and properties of the *o*-TFMPA polymer [poly(*o*-TFMPA)] have hardly been revealed yet. Therefore, it is also important to elucidate the influence of the *o*-CF_3 group on polymer properties.

The present paper deals with the polymerization of *o*-TFMPA by WCl_6- and $MoCl_5$-based catalysts and characterization of the product polymer. It is clarified that these catalysts provide brown, soluble, thermally fairly stable poly(*o*-TFMPA).

Experimental Section

Materials. The monomer, *o*-TFMPA was prepared according to the following procedure reported by Okuhara:[8]



Overall yield 55%; bp 68 °C (31 mmHg) [lit.[8b] bp 65.5 °C (30 mmHg)]; d_4^{20} 1.176.

The transition-metal compounds and organometallic cocatalysts were all commercially obtained and used without further purification. Toluene and other polymerization solvents were purified by the standard methods, care being exercised to remove moisture and oxygen as perfectly as possible.

Polymerization. Polymerizations were carried out under dry nitrogen. Catalyst systems composed of a transition-metal compound and an organometallic cocatalyst were allowed to stand (age) in solution at 30 °C for 15 min before use. Metal carbonyl based catalysts were prepared by irradiation of CCl_4 solution of

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Table I
Polymerization of *o*-TFMPA by Various Catalysts[a]

no.	catalyst	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
1	WCl_6	60	54	330	140
2	WCl_6–Ph_4Sn (1:1)	100	100	690	190
3	$W(CO)_6$–CCl_4–$h\nu$[c]	100	100	640	260
4	$MoCl_5$	100	100	200	100
5	$MoCl_5$–Ph_4Sn (1:1)	100	100	800	280
6	$Mo(CO)_6$–CCl_4–$h\nu$[c]	70	65	150	54
7	$Fe(acac)_3$–Et_3Al (1:3)	27	0		
8	$Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$ (1:4)	20	19	37	23
9	$NbCl_5$	25	0		
10	$TaCl_5$	29	0		

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 1.0 M, [Cat.] = 10 mM. [b] Determined by GPC. [c] Polymerized in CCl_4.

Table II
Effects of Organometallic Cocatalysts on the Polymerization of *o*-TFMPA by WCl_6[a]

no.	cocatalyst	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
1	none	0	0		
2	Ph_4Sn	100	100	1600	420
3	n-Bu_4Sn	100	100	1000	390
4	Ph_3SiH	100	100	1400	710
5	Et_3SiH	100	100	1200	520
6	Ph_3Sb	100	100	1500	800
7	Ph_3Bi	100	100	1100	380

[a] Polymerized in toluene at 0 °C for 24 h; $[M]_0$ = 1.0 M, $[WCl_6]$ = [Cocat] = 10 mM. [b] Determined by GPC.

Table III
Solvent Effects on the Polymerization of *o*-TFMPA by WCl_6–Ph_4Sn[a]

solvent	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
toluene	100	100	1600	420
CCl_4	100	96	770	370
$(CH_2Cl)_2$	100	100[c]		
PhOMe	0	0		
PhCOOMe	0	0		
PhCOMe	0	0		

[a] Polymerized at 0 °C for 24 h; $[M]_0$ = 1.0 M, $[WCl_6]$ = $[Ph_4Sn]$ = 10 mM. [b] Determined by GPC. [c] Partly or totally insoluble in any solvents.

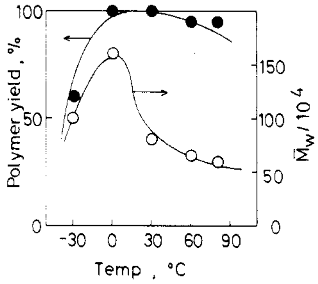

Figure 1. Temperature dependence of the polymerization of *o*-TFMPA by WCl_6–Ph_4Sn (in toluene, 24 h, $[M]_0$ = 1.0 M, $[WCl_6]$ = $[Ph_4Sn]$ = 10 mM).

a metal carbonyl with UV light (200-W high-pressure Hg lamp, distance 5 cm) at 30 °C for 1 h.

A typical polymerization procedure is as follows (see Table II, no. 2 for results): In a Schlenk tube equipped with a three-way stopcock, monomer solution was prepared by mixing *o*-TFMPA (6.0 mmol, 1.0 g, 0.86 mL), chlorobenzene [0.24 mL; standard for gas chromatography (GC)], and toluene (1.3 mL). In another Schlenk tube, WCl_6 (0.050 mmol, 20 mg) and Ph_4Sn (0.050 mmol, 21 mg) were dissolved in toluene (3.0 mL), and this catalyst solution was aged at 30 °C for 15 min. Then 2.0 mL of the monomer solution was added to the catalyst solution. After polymerization at 0 °C for 24 h, the reaction was terminated by addition of a mixture (5 mL) of toluene and methanol (4:1 vol ratio). Monomer conversion was determined by GC (silicone DC550 3 m, 100 °C). The reaction mixture was diluted with toluene (100 mL) and poured into methanol (1 L) under stirring. The precipitated polymer was washed with methanol, filtered, and dried to a constant weight. Polymer yield was determined by gravimetry.

Polymer Characterization. The weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of polymers were determined by gel permeation chromatography (GPC) by using a polystyrene calibration. The GPC measurements were carried out on a Jasco Trirotar liquid chromatograph (eluent, $CHCl_3$; columns, Shodex A804, A806, and A807 polystyrene gels). The IR and UV–visible spectra of polymers were recorded with Shimadzu IR435 and UV190 spectrophotometers, respectively. Gas permeability coefficients for the polymer membrane were measured with a K-315-N gas permeability apparatus (Rikaseiki Co., Japan); membrane thickness ~30 μm.

Results

Polymerization by Various Catalysts. Table I shows results for the polymerization of *o*-TFMPA by several types of transition-metal catalysts.

The three W catalysts in Table I and the corresponding Mo catalysts were all effective in the polymerization of *o*-TFMPA. In contrast, Ziegler catalysts [$Fe(acac)_3$–Et_3Al and $Ti(O\text{-}n\text{-}Bu)_4$–$Et_3Al$], which are useful in acetylene polymerization, did not form or only slightly formed a polymer (methanol-insoluble product). Neither $NbCl_5$ nor $TaCl_5$ gave any polymer (product, cyclotrimers).

Among the three W catalysts, WCl_6–Ph_4Sn polymerized *o*-TFMPA most quickly and gave a polymer with the highest $\bar{M}_w$ (~7×10^5). The same tendency was observed with the Mo catalysts; that is, $MoCl_5$–Ph_4Sn was the most active among the three Mo catalysts. Ph_4Sn is expected to reduce and alkylate WCl_6 and $MoCl_5$, resulting in the increase of the number of active species and/or in the enhancement of their activity.

Polymerization by WCl_6-Based Catalysts. Effects of organometallic cocatalysts containing group 4 and 5 main-group metals were examined (Table II). Since WCl_6–cocatalyst systems were active enough even at 0 °C, polymerizations were carried out at 0 °C to make the polymer molecular weight as high as possible. Whereas WCl_6 alone did not effect polymerization, all the 1:1 mixtures of WCl_6 with the organometallics in Table II polymerized *o*-TFMPA quantitatively. The $\bar{M}_w$ values of the product polymers were 1×10^6 or above. The highest $\bar{M}_w$ (1.6×10^6), which was achieved with WCl_6–Ph_4Sn, is adventitiously the same as that with $W(CO)_6$–CCl_4–$h\nu$.[6] The $\bar{M}_w/\bar{M}_n$ ratios were in the range ca. 2–4, and the molecular weight distributions were close to or somewhat broader than the most probable distribution.

Figure 1 shows the temperature dependence of *o*-TFMPA polymerization by WCl_6–Ph_4Sn. In the range 0–80 °C, polymers are obtained virtually quantitatively. The polymerization at –30 °C was too slugguish to reach 100% conversion within 24 h. The $\bar{M}_w$ of polymer shows a maximum of 1.6×10^6 at 0 °C. Therefore 0 °C is most suitable for the preparation of a high-molecular-weight polymer in high yield.

The present polymerization proceeded in ca. 100% yields in toluene, CCl_4, and $(CH_2Cl)_2$ as polymerization solvents (Table III). However, the $\bar{M}_w$ of polymer formed in CCl_4 was only about half that for toluene, and the polymer obtained in $(CH_2Cl)_2$ did not completely dissolve in any solvents. Further, the polymerization did not occur in oxygen-containing solvents such as anisole. Conse-

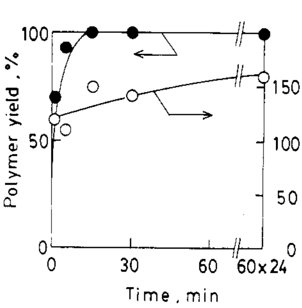

Figure 2. Time course of the polymerization of *o*-TFMPA by WCl_6-Ph_4Sn (in toluene, 0 °C, $[M]_0 = 1.0$ M, $[WCl_6] = [Ph_4Sn] = 10$ mM).

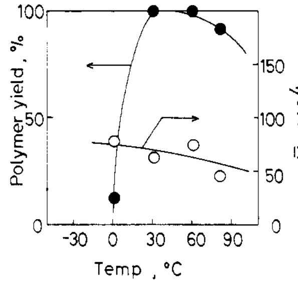

Figure 3. Temperature dependence of the polymerization of *o*-TFMPA by $MoCl_5$-Ph_4Sn (in toluene, 24 h, $[M]_0 = 1.0$ M, $[MoCl_5] = [Ph_4Sn] = 10$ mM).

Table IV
Effects of Organometallic Cocatalysts on the Polymerization of *o*-TFMPA by $MoCl_5$[a]

cocatalyst	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
none	100	100	200	100
Ph_4Sn	100	100	800	280
n-Bu_4Sn	100	75	190	120
Ph_3SiH	100	100	1100	310
Et_3SiH	100	74	430	210
Ph_3Sb	100	100	450	240
Ph_3Bi	53	49	560	290

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[MoCl_5] = [Cocat] = 10$ mM. [b] Determined by GPC.

quently, it can be said that toluene is one of the most favorable solvents for polymerization.

The polymerization by WCl_6–Ph_4Sn is considerably fast; it is completed within 15 min even at 0 °C (Figure 2). No decrease in polymer molecular weight, however, is observed even if the polymerization procedure is continued as long as 24 h. This indicates that no degradation of polymer is induced by the polymerization catalyst. Consequently, the polymerization time can be chosen fairly arbitrarily.

Polymerization by $MoCl_5$-Based Catalysts. Effects of organometallic cocatalysts were studied in the polymerization by $MoCl_5$ (Table IV). Since $MoCl_5$ appeared less active than WCl_6 for the present monomer, polymerization was conducted at 30 °C. At this temperature, *o*-TFMPA polymerized quantitatively even with $MoCl_5$ alone but the polymer molecular weight was rather low ($\bar{M}_w$ 2×10^5). When suitable cocatalysts such as Ph_4Sn and Ph_3SiH were employed, it was possible to enhance the $\bar{M}_w$ of polymer up to 8×10^5–11×10^5 without reducing the polymer yield. The $\bar{M}_w/\bar{M}_n$ ratios lay in the range ca. 1.5–3.5.

In the case of $MoCl_5$–Ph_4Sn, the polymer yield becomes quantitative at 30 °C or above under ordinary conditions (Figure 3). This is indicative of $MoCl_5$–Ph_4Sn being less active than the W counterpart, WCl_6–Ph_4Sn. The molecular weight of polymer does not greatly vary with increasing temperature, but slightly decreases.

Table V
Solvent Effects on the Polymerization *o*-TFMPA by $MoCl_5$-Ph_4Sn[a]

solvent	convn, %	polymer yield, %	polymer $\bar{M}_w/10^3$ [b]	polymer $\bar{M}_n/10^3$ [b]
toluene	100	100	800	280
CCl_4	100	95	510	240
$(CH_2Cl)_2$	100	100	470	230
PhOMe	100	100	250	110
PhCOOMe	100	72[c]		
PhCOMe	0	0		

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[MoCl_5] = [Ph_4Sn] = 10$ mM. [b] Determined by GPC. [c] Partly or totally insoluble in any solvents.

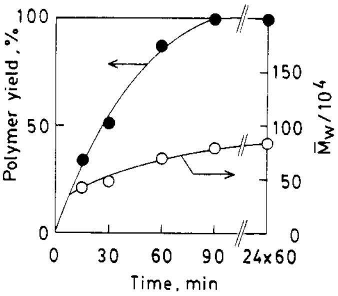

Figure 4. Time course of the polymerization of *o*-TFMPA by $MoCl_5$-Ph_4Sn (in toluene, 30 °C, $[M]_0 = 1.0$ M, $[WCl_6] = [Ph_4Sn] = 10$ mM).

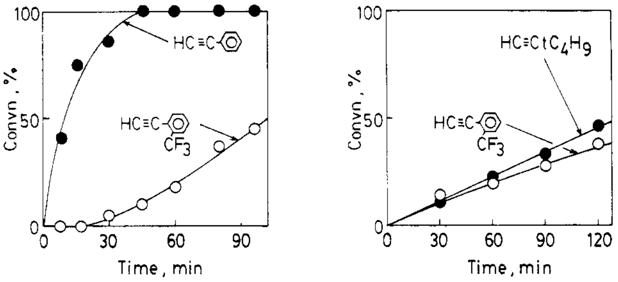

Figure 5. Time courses of the copolymerizations of *o*-TFMPA with phenylacetylene and *tert*-butylacetylene by WCl_6 (in toluene, 30 °C, $[M_1] = [M_2] = 0.50$ M, $[WCl_6] = 10$ mM).

As seen in Table V, the polymerization by $MoCl_5$–Ph_4Sn at 30 °C proceeded not only in toluene and halogenated hydrocarbons but also in some oxygen-containing solvents. The molecular weight of polymer was the highest in toluene as polymerization solvent.

As compared with the polymerization by WCl_6–Ph_4Sn at 0 °C (Figure 2), that by $MoCl_5$–Ph_4Sn at 30 °C is slow and completed in 90 min (Figure 4). This again shows that WCl_6–Ph_4Sn is more active than $MoCl_5$–Ph_4Sn for the present monomer. The molecular weight of polymer does not decrease even though the polymerization system is allowed to stand for 24 h.

Copolymerization. In order to gain knowledge on the relative reactivity of *o*-TFMPA, 1:1 copolymerizations with phenylacetylene or *tert*-butylacetylene by WCl_6 were carried out (Figure 5). In the copolymerization with phenylacetylene, phenylacetylene smoothly polymerizes, and when most of this monomer has been consumed, *o*-TFMPA begins to polymerize. Thus copolymer formation in this system appears difficult. In contrast to this, in the copolymerization with *tert*-butylacetylene *o*-TFMPA is consumed at a rate similar to that of the comonomer. Thus the relative reactivity of these monomers can be expressed as follows: $HC{\equiv}CPh \gg HC{\equiv}CPh(o\text{-}CF_3) \simeq HC{\equiv}t\text{-}Bu$. This order is in correspondence with the previous observation that a bulkier monomer exhibits a lower relative

Table VI
Molecular Weight Change by Heat Treatment in Air for 20 h[a]

	poly(*o*-TFMPA)			poly(PA)[b]		
heat-treated at	$\bar{M}_w/10^3$	$\bar{M}_n/10^3$	$\alpha \times 10^{3c}$	$\bar{M}_w/10^3$	$\bar{M}_n/10^3$	$\alpha \times 10^{3c}$
starting polymer	1600	420		200	60	
100 °C	800	120	1.0	19	8.6	10
120 °C	185	58	2.5	12	6.0	19
150 °C	34	11	15	6.6	2.9	35
room temp[c]	940	350	0.08	38	15	5

[a] $\bar{M}_w$ and $\bar{M}_n$ determined by GPC. [b] Poly(PA) = poly(phenylacetylene). [c] $\alpha \equiv 1/\overline{DP}_n - 1/\overline{DP}_{n,0}$, where $\overline{DP}_{n,0}$ and $\overline{DP}_n$ are the initial and final number-average degrees of polymerization, respectively. [d] In air after one month.

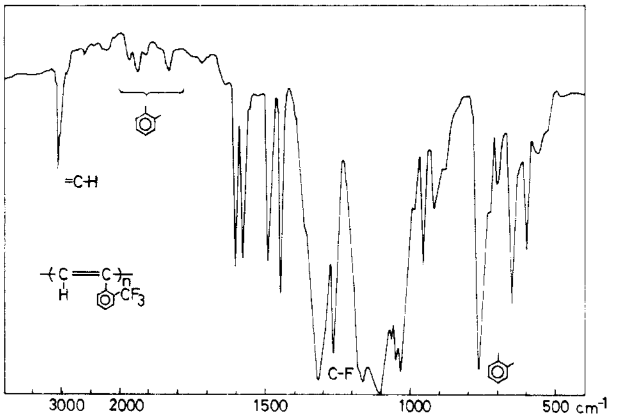

Figure 6. IR spectrum of poly(*o*-TFMPA) (sample from Table II, no. 2; KBr disk).

reactivity owing to decreased coordinating ability in the copolymerization of substituted acetylenes by W and Mo catalysts.[9]

Polymer Structure. The data for elemental analysis of poly(*o*-TFMPA) (sample from Table II, no. 2) agreed well with the theoretical values. Anal. Calcd for $(C_9H_5F_3)_n$: C, 63.53; H, 2.97; F, 33.50. Found: C, 63.71; H, 2.98; F, 33.19.

In the IR spectrum of polymer, strong bands due to C–F stretching are observed at 1310, 1170, and 1100 cm^{-1} (Figure 6). Two small triplets at 1950 and 1850 cm^{-1} as well as one strong absorption at 770 cm^{-1} are characteristic of ortho-substituted benzenes. On the other hand, the absorption at 3300 cm^{-1} assignable to the ≡C—H stretching of the monomer is not seen at all in the polymer. The IR spectrum of polymer did not change with the kind of catalyst.

The ^{13}C NMR spectra of polymers ($CDCl_3$ solution) showed a multiplet only in the region δ 145–115. The two peaks due to acetylenic carbons of the monomers [δ 83.6 (HC≡) and 80.2 (≡CAr)] disappeared in the polymer. No further information was, however, obtained.

The UV–visible spectra of poly(*o*-TFMPA)s (Figure 7) exhibit an absorption maximum at 458 nm whose molar extinction coefficient (ϵ) is ca. 5000 M^{-1} cm^{-1}. This indicates that the present polymers possess conjugated double bonds in the main chain. Very interestingly, the absorption maxima of poly(*o*-TFMPA)s appear at much longer wavelength than those of poly(phenylacetylene)s. If the ortho substituent hampers the conjugation between the main chain and phenyl group, then the maxima should shift to shorter wavelength by ortho substitution; the reason is not clear at present.

The analytical and spectral data above are compatible with the polymer structure composed of alternating double bonds: $-[CH{=}C(o\text{-}CF_3C_6H_4)]_n-$.

Polymer Properties. Poly(*o*-TFMPA) had the form of dark brown solid irrespective of the kind of catalyst.

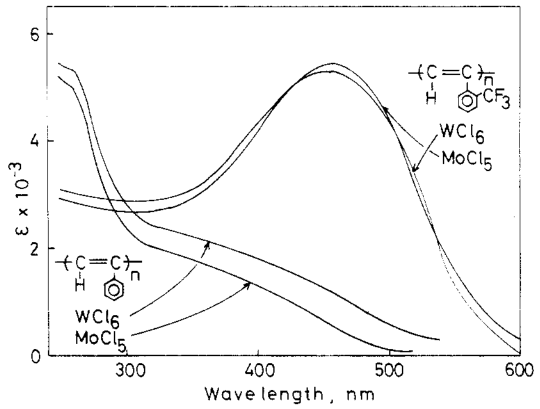

Figure 7. UV–visible spectra of poly(*o*-TFMPA) and poly(phenylacetylene) [poly(*o*-TFMPA) samples from Table I, no. 5, and Table II, No. 2; measured in tetrahydrofuran].

Properties of the present polymer hardly varied with polymerization conditions. Unless otherwise specified, the polymer properties described below are based on the sample of Table II, no. 2.

Poly(*o*-TFMPA) dissolved in aromatic hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons [CCl_4, $CHCl_3$, $(CH_2Cl)_2$, PhCl, PhF, $PhCF_3$], ethers (anisole, 1,4-dioxane, tetrahydrofuran, diethyl ether), ketones (acetone, acetophenone), and esters (ethyl acetate, methyl benzoate). Nonsolvents of the present polymer include aliphatic hydrocarbons (hexane, heptane, cyclohexane), some polyfluorinated hydrocarbons [m-$(CF_3)_2C_6H_4$, C_6F_6, CCl_2FCClF_2], some nitrogen-containing compounds [acetonitrile, $HCON(CH_3)_2$, aniline), dimethyl sulfoxide, and alcohols (methanol, *tert*-butyl alcohol). A very dark brown, tough film can be prepared by casting the polymer from toluene solution.

The softening point of poly(*o*-TFMPA) was 260–264 °C. This polymer showed no exo- or endothermic peak in the range of room temperature to 500 °C in the differential thermal analysis (DTA) under nitrogen. The weight loss of poly(*o*-TFMPA) in air occurs only above 300 °C according to thermogravimetric analysis (TGA), whereas that of poly(phenylacetylene) starts around 200 °C (Figure 8). Table VI shows the change of polymer molecular weights by allowing the polymer to stand in air either at elevated temperature for 20 h or at room temperature for one month. The molecular weight change of poly(*o*-TFMPA) at room temperature after one month is only slight, and that at 100 °C after 20 h is not remarkable either. The probability of main-chain scission (α value) for poly(*o*-TFMPA) is clearly smaller than that for poly(phenylacetylene) at any temperature and is no more than 1/50 at room temperature. Thus both TGA data and molecular weight change by heat treatment indicate that the present polymer is thermally more stable than poly(phenylacetylene).

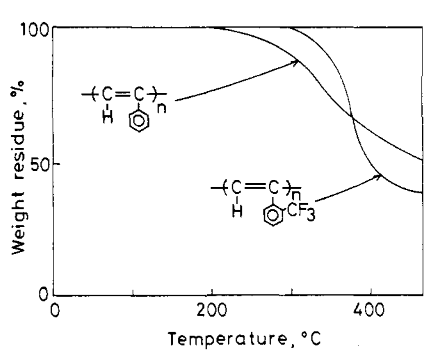

Figure 8. Thermogravimetric analysis of poly(*o*-TFMPA) and poly(phenylacetylene) [poly(*o*-TFMPA) samples from Table II, no. 2; in air, heating rate 10 °C/min].

Though the details will be reported elsewhere,[10] mechanical properties of poly(*o*-TFMPA) were as follows: Young's modulus, 1050 MPa (25 °C); elongation at break, 1.7% (25 °C); tensile strength, 18 MPa (25 °C); glass transition temperature (T_g; determined by dynamic viscoelasticity), 150 °C. Consequently, this polymer proves to be hard and brittle and to have a relatively high T_g.

The electrical conductivity of poly(*o*-TFMPA) at 25 °C in the dark measured with a DC current was 2×10^{-15} $S{\cdot}cm^{-1}$, being in the insulator range ($<1 \times 10^{-10}$ $S{\cdot}cm^{-1}$). The electron spin resonance (ESR) spectrum of poly(*o*-TFMPA) (25 °C, powder) showed a rather broad singlet [line width (ΔH_{msl}) 9.1 G] at $g = 2.0032$. The unpaired-electron density was 6.1×10^{17} $spin{\cdot}g^{-1}$. The *g* value observed suggests that the spin is distributed also on the fluorine atoms to some extent.

Polyacetylenes with bulky substituents often exhibit high gas permeability.[7] A poly(*o*-TFMPA) membrane showed the following permeability property (25 °C): oxygen permeability coefficient (P_{O_2}) 25 barrer; separation factor of oxygen versus nitrogen (P_{O_2}/P_{N_2}) 3.4. It is noted that this P_{O_2} value is close to that of natural rubber (23 barrer), whereas the P_{O_2}/P_{N_2} ratio is fairly large compared to that of natural rubber (2.5).[11]

Discussion

Comparison with Phenylacetylene Polymerization. In homopolymerization, both phenylacetylene[12] and *o*-TFMPA polymerize very quickly in the presence of WCl_6–Ph_4Sn. With $MoCl_5$–Ph_4Sn as catalyst, *o*-TFMPA polymerizes quantitatively, whereas phenylacetylene polymerizes only in moderate yield even under forcible conditions. These facts imply that even if a bulky substituent of CF_3 group is introduced into the ortho position of phenylacetylene, the reactivity in homopolymerization does not decrease. It is a salient feature of the acetylene polymerization by group 5 and 6 transition-metal catalysts that sterically crowded acetylenes like *tert*-butylacetylene and 1-(trimethylsilyl)-1-propyne exhibit high polymerizability.[7] The high polymerizability of *o*-TFMPA is consonant with this general tendency.

On the other hand, *o*-TFMPA is less reactive than phenylacetylene and as reactive as *tert*-butylacetylene in copolymerization. This result of copolymerization reflects the relative reactivity of monomers in propagation and can be explained in terms of the steric effect of monomers;[9] it does not correspond to the overall reactivity in homopolymerization. [*o*-(Trimethylsilyl)phenyl]acetylene, the ortho-substituent of which is electron-donating, shows a reactivity similar to that of *o*-TFMPA.[13] This indicates that the electronic influence of the CF_3 group is not significant.

It is noteworthy that the molecular weight of poly(*o*-TFMPA) ($\bar{M}_w \sim 1 \times 10^6$) is much higher than that of poly(phenylacetylene) ($\bar{M}_w \sim 1 \times 10^4$).[12] This suggests that the bulkier the substituent in the monomer, the higher the polymer molecular weight. Such a trend is also observed in the pair of poly(*tert*-butylacetylene) ($\bar{M}_w \sim 1 \times 10^6$) and poly(1-hexyne) ($\bar{M}_w < 1 \times 10^4$).[7]

Comparison with Poly(phenylacetylene). The two most significant characteristics of poly(*o*-TFMPA), which are not seen in poly(phenylacetylene), are film formation and high thermal stability. Because of its high molecular weght, poly(*o*-TFMPA) can be cast into film from solution. This often makes it easy to study properties and functions of the polymer. In contrast, the film of poly(phenylacetylene) is too brittle to hold its form owing to its low molecular weight. Poly(*o*-TFMPA) is thermally more stable in air than poly(phenylacetylene). For example, the molecular weight of poly(*o*-TFMPA) hardly changes during storage at 0 °C for a long period of time, whereas that of poly(phenylacetylene) gradually decreases.[12b] This stability of poly(*o*-TFMPA) is also favorable in most cases when applications of the polymer are aimed at.

There are some other differences in properties between poly(phenylacetylene) and poly(*o*-TFMPA). One is a deeper color of poly(*o*-TFMPA). It involves interesting problems on polymer configuration and conformation, although an interpretation has not been reached yet. The solubility property of poly(*o*-TFMPA) generally resembles that of poly(phenylacetylene). A minor difference is, however, observed such that poly(*o*-TFMPA) dissolves in (trifluoromethyl)benzene which is a nonsolvent of poly(phenylacetylene).

Conclusions

o-(Trifluoromethyl)phenylacetylene polymerizes in high yields with WCl_6–cocatalyst and $MoCl_5$–cocatalyst systems. The polymer formed has high molecular weight ($\bar{M}_w > 1 \times 10^6$) and is dark brown, soluble, film-forming, and thermally fairly stable in air.

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Registry No. *o*-TFMPA (homopolymer), 96504-22-2; (*o*-TFMPA)(PhC≡CH) (copolymer), 111616-48-9; (*o*-TFMPA)(*t*-BuC≡CH) (copolymer), 111616-49-0; O_2, 7782-44-7; N_2, 7727-37-9; WCl_6, 13283-01-7; Ph_4Sn, 595-90-4; $W(CO)_6$, 14040-11-0; CCl_4, 56-23-5; $MoCl_5$, 10241-05-1; $Mo(CO)_6$, 13939-06-5; $Ti(O\text{-}n\text{-}Bu)_4$, 5593-70-4; Et_3Al, 97-93-8; Bu_4Sn, 1461-25-2; Ph_3SiH, 789-25-3; Et_3SiH, 617-86-7; Ph_3Sb, 603-36-1; Ph_3Bi, 603-33-8.

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Poly(lactones). 9.[†] Polymerization Mechanism of Metal Alkoxide Initiated Polymerizations of Lactide and Various Lactones

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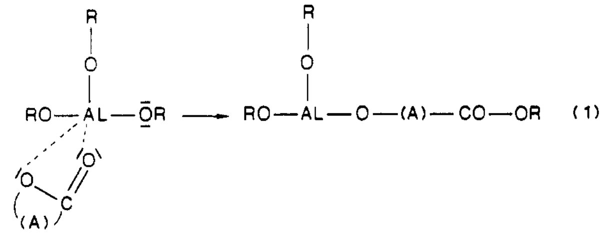
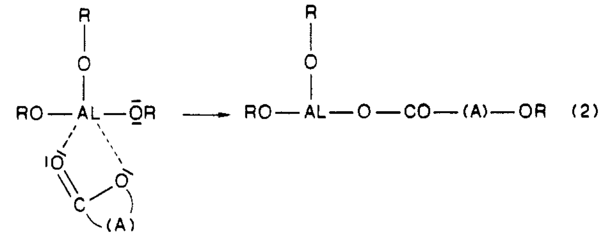
ABSTRACT: Four different lactones, namely, β-propiolactone, D,L-β-butyrolactone, ε-caprolactone, and L,L-lactide, were polymerized in bulk or in solution at temperatures between 50 and 150 °C. Various metal alkoxides, such as magnesium ethoxide, aluminum isopropoxide, zinc or titanium *n*-butoxide, zirconium *n*-propoxide, and dibutyl- or tributyltin methoxide, were used as initiators. Both ^{1}H and ^{13}C NMR spectroscopy clearly prove that in all cases the same initiation and propagation mechanisms take place. The ring opening of the lactones involves cleavage of the acyl–oxygen bond, and the alkoxide groups of the initiator form alkyl ester end groups. It is demonstrated that this so-called insertion mechanism is different from both cationic and anionic mechanisms. ^{1}H NMR end-group analyses also demonstrate that all alkoxide groups of an initiator are active, at least at temperatures above 50 °C. Despite a living character with regard to end-group activities these insertion mechanisms do not yield narrow molecular weight distributions, partially because initiation is not faster than propagation and partially because most initiators cause transesterification. Whereas aluminium isopropoxide does not effect back-biting up to temperatures around 150 °C, other initiators, in particular butyltin methoxides, are so active that cyclic oligomers are formed by degradation of the polylactones even after few hours at 100 °C.

Introduction

Aluminum alkoxides are known to be effective initiators of the polymerization of lactones. Teyssié and co-workers have demonstrated that aluminum isopropoxide[1] and also μ-oxo bimetallic aluminum alkoxides[2,3] initiate the polymerization in such a way that the acyl–oxygen bond of the lactone is cleaved (eq 1) and not the alkyl–oxygen bond (eq 2). It is characteristic of this mechanism (eq 1) that the alkoxide group of the initiator forms the dead end of the growing chain end. Polymerizations conducted with ε-caprolactone at 0 °C also showed that only one alkoxide group per aluminum is active as an initiating species.





In the first part of this series[4] the copolymerization of glycolide and ε-caprolactone by means of aluminum isopropylate (and other initiators) was investigated. The ring-opening mechanism of eq 1 was confirmed; yet at polymerization temperatures $\geq$100 °C all three alkoxide group were found to be active, obviously because at high temperatures aluminum isopropoxide does not undergo self-association in dilute solution. Furthermore, it was found that aluminum isopropoxide does not cause in*ter*molecular transesterification up to a temperature of 150 °C in contrast to alkyltin alkoxides.[5] On the basis of these results the purpose of the present work was threefold:

I. It should clarify whether the ring-opening mechanism of eq 1 is valid for all heavy metal alkoxides or whether the alternative mechanism, eq 2, may also be operating.

II. It should analyze whether all or only one alkoxide group per initiator is active in the initiating process. This information is important for the calculation of the average degree of polymerization ($\overline{\mathrm{DP}}$) from the monomer/initiator ratio (M/I).

III. It should elucidate whether the metal alkoxides cause transesterification of polyester chains under the polymerization conditions. A clear answer to this question is important for the course of copolymerizations, because initiators with high transesterification activity are useful for the preparation of amorphous copolyesters with random sequences, whereas initiators without transesterification activity are worthwhile for the preparation of crystalline block copolymers.

Experimental Section

Initiators. Magnesium ethoxide and aluminum isopropoxide were purchased from Lancaster Chemicals (UK). Potassium *tert*-butoxide, titanium *n*-butoxide, and zirconium *n*-propoxide

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