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Polymerization of [2,5-bis(trifluoromethyl)phenyl]acetylene and polymer properties

Kenji Tsuchihara[1], **Toshio Masuda**[1], **Toshinobu Higashimura**[1], **Masakazu Nishida**[2], and **Hiroshige Muramatsu**[3]

[1]Department of Polymer Chemistry, Kyoto University, Kyoto, 606 Japan
[2]Government Industrial Research Institute, Nagoya, 462 Japan
[3]Department of Applied Chemistry, Gifu University, Gifu, 501-11 Japan

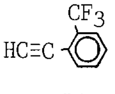
SUMMARY

[2,5-Bis(trifluoromethyl)phenyl]acetylene [BTFPA; $HC{\equiv}CC_6H_3$-2,5-$(CF_3)_2$] polymerized with W, Mo, and Nb catalysts to produce methanol-insoluble polymers in high yields. The poly(BTFPA) produced by the $W(CO)_6$-based catalyst at 30 °C was soluble in $\underline{p}$-$(CF_3)_2C_6H_4$, and had relatively high molecular weight ($[\eta]$ = 0.352 dL/g in $\underline{p}$-$(CF_3)_2C_6H_4$). The main chain of the polymer was composed of alternating double bonds, and the polymer was a dark brown solid. The temperature at which the weight loss of the polymer started was higher than 300 °C. The polymerization behavior and polymer properties for BTFPA are compared with those for phenylacetylene and [$\underline{o}$-(trifluoromethyl)phenyl]acetylene.

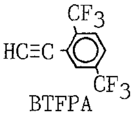
INTRODUCTION

Fluorine-containing polymers often show unique properties such as high thermal stability and resistance to chemicals (1). Rather few fluorine-containing polyacetylenes, however, have been known, whose recent examples include; $\{CH{=}C\underline{n}C_4F_9\}$ (2), $\{CMe{=}CC_6F_5\}$ (3), poly[1-ethynyl-5-(trifluoromethyl)naphthalene] (4).

Recently, we have obtained from $\underline{o}$-(trifluoromethyl)phenylacetylene ($\underline{o}$TFMPA) a soluble polymer whose weight-average molecular weight ($\overline{M}_w$) reaches $1{\times}10^6$ (5,6). This polymer is film-forming unlike poly(phenylacetylene), and possesses thermal stability higher than that of poly(phenylacetylene). In the polymerization of substituted acetylenes by groups 5 and 6 transition-metal catalysts, a general tendency has been observed that when the substituent of monomer possesses suitable bulkiness, a high-molecular-weight polymer is formed (7). Further, it is expected that a polymer with high fluorine content shows unique properties. From these viewpoints, it is of interest to study the polymerization of phenylacetylenes having more than one CF_3 groups.



$\underline{o}$TFMPA

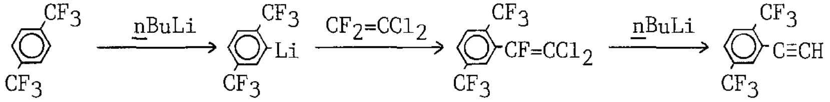


BTFPA

In the present study, we investigated the polymerization of [2,5-bis(trifluoromethyl)phenyl]acetylene (BTFPA) and polymer properties. This monomer is featured by steric crowding and high fluorine content. The results obtained are compared with those for $\underline{o}$TFMPA.

EXPERIMENTAL

The monomer, BTFPA was prepared according to the following procedure reported by Okuhara et al. (8):



Overall yield 55%; bp 65 °C (30 mmHg); d^4_{20} 1.310

The transition-metal compounds and organometallic cocatalysts were commercially obtained, and used without further purification.

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

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).

RESULTS and DISCUSSION

Polymerization of [2,5-Bis(trifluoromethyl)phenyl]acetylene(BTFPA)

Table I summarizes results for the polymerization of BTFPA by groups 5 and 6 transition-metal catalysts. When W catalysts such as WCl_6-Ph_4Sn and $W(CO)_6$-hν were used, methanol-insoluble polymers were obtained virtually quantitatively. Among Mo catalysts, $MoCl_5$-Ph_4Sn produced a polymer in high yield, while no polymer was obtained with $Mo(CO)_6$-based catalyst. Interestingly, $NbCl_5$-Ph_4Sn also produced a polymer in good yield, and methanol-soluble part was cyclotrimers. It has been known that

Table I

Polymerization of $HC{\equiv}CC_6H_3$-2,5-$(CF_3)_2$ by Various Catalysts[a]

Catalyst	Monomer convn,%	Polymer[b] yield,%
WCl_6-Ph_4Sn	96	95
$W(CO)_6$-hν[c]	100	94[d]
$MoCl_5$-Ph_4Sn	89	86
$Mo(CO)_6$-hν[c]	10	0
$NbCl_5$-Ph_4Sn[e]	100	73
$TaCl_5$-Ph_4Sn[e]	10	0

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [Cat] = [Ph_4Sn] = 20 mM.
[b] Methanol-insoluble product.
[c] Polymerized in CCl_4; [Cat] = 10 mM.
[d] [η] = 0.352 dL/g (in p-$(CF_3)_2C_6H_4$, 30 °C)
[e] Polymerized at 80 °C.

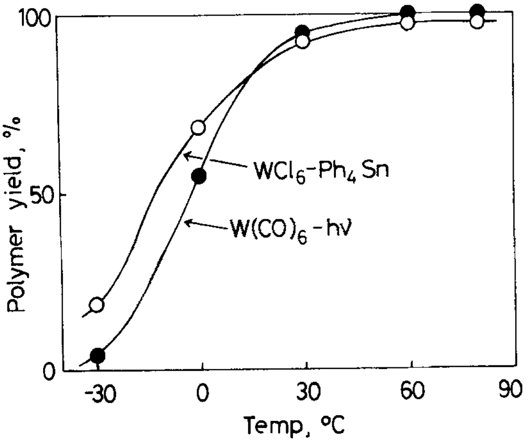


Figure 1. Effect of temperature on the polymerization of $HC{\equiv}CC_6H_3$-2,5-$(CF_3)_2$ (WCl_6-Ph_4Sn(1:1), in toluene, 24 h, $[M]_o$ = 0.50 M, $[WCl_6]$ = 20 mM; in CCl_4, $[W(CO)_6]$ = 10 mM in case of the $W(CO)_6$-based catalyst)

$NbCl_5$-based catalysts selectively give cyclotrimers from most monosubstituted acetylenes except those with bulky substituents (6). *o*TFMPA provides only cyclotrimers in the presence of $NbCl_5$. Hence, it can be concluded that the meta CF_3 group of the present monomer sterically plays an important role in polymerization. The intrinsic viscosity of the polymer obtained with $W(CO)_6$-hν at 30 °C was 0.352 dL/g in *p*-$(CF_3)_2C_6H_4$ suggesting that the polymer has a relatively high molecular weight.

Figure 1 shows temperature dependences of the polymerizations by WCl_6-Ph_4Sn and $W(CO)_6$-hν both of which produced polymer in good yields.

Table II
Solvent Effect on the Polymerization of $HC{\equiv}CC_6H_3$-2,5-$(CF_3)_2$ by WCl_6-Ph_4Sn (1:1)[a]

Solvent	Monomer convn, %	Polymer[b] yield, %
toluene	96	95
$(CH_2Cl)_2$	100	94
CCl_2FCClF_2	100	80
m-$(CF_3)_2C_6H_4$	100	78
anisole	25	0
acetophenone	0	0

[a] Polymerized at 30 °C for 24 h ; $[M]_o$ = 0.50 M, $[WCl_6]$ = 20 mM.
[b] Methanol-insoluble product.

The polymer yield with these catalysts remained low at a low temperature of -30 °C. In contrast, polymers were obtained virtually quantitatively at 30 °C and above. Though the $W(CO)_6$-based catalyst is generally less active than the WCl_6-based catalyst, these catalysts show similar activities for the present monomer.

Table II shows solvent effects on the polymerization of BTFPA by WCl_6-Ph_4Sn. Polymers were obtained in good yields not only in toluene but also in chlorine- and fluorine-containing solvents. No substantial difference in the polymerization behavior was observed between the polymerization in $(CH_2Cl)_2$ (nonsolvent of the polymer) and that in fluorine-containing solvents (relatively good solvents of the polymer). On the other hand, no polymer was obtained in oxygen-containing solvents such as anisole and acetophenone.

To compare the reactivity of the present monomer with that of *o*TFMPA, copolymerization of BTFPA with *o*TFMPA was examined (Figure 2). *o*TFMPA reacted faster than BTFPA. In general, a monomer with less bulky substituent is more reactive in the copolymerization of substituted acetylenes (7). Further, the ^{13}C NMR chemical shifts of acetylenic carbons of these monomers were similar to each other. Therefore, it can be said that the meta CF_3 group of BTFPA affected the copolymerization sterically to reduce its reactivity.

Structure and Properties of Polymer

The elemental composition of the polymer agreed well with the one expected for the addition polymerization products (Anal. Cald. for $(C_{10}H_4F_6)_n$: C 50.45%, H 1.67%, F 47.88% Found: C 51.03%, H 1.43%, F 47.54%)

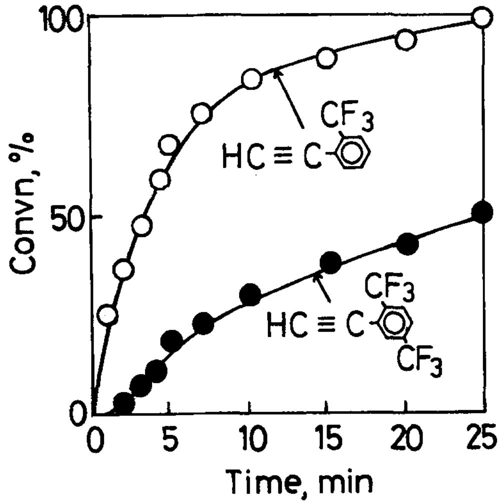


Figure 2. Copolymerization of $HC{\equiv}CC_6H_3$-2,5-$(CF_3)_2$ with $HC{\equiv}CC_6H_4$-*o*-CF_3 by WCl_6-Ph_4Sn (1:1)
(in toluene, 30 °C, 24 h, $[M_1]_o = [M_2]_o = 0.50$ M, $[WCl_6] = 20$ mM)

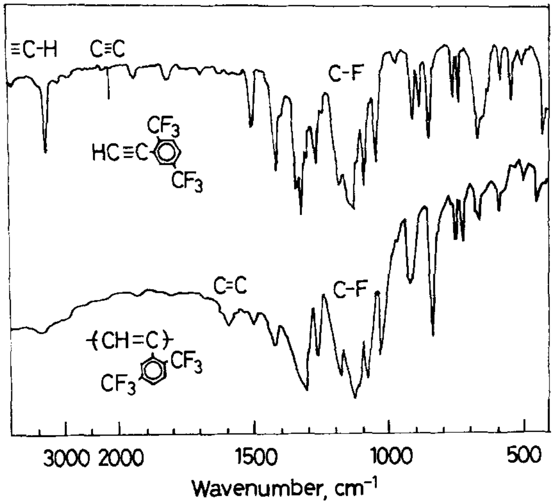


Figure 3. IR spectra of $HC\equiv CC_6H_3$-2,5$(CF_3)_2$ and its polymer (KBr pellet)

Figure 3 exhibits the IR spectra of the BTFPA monomer and its polymer. The spectrum of the polymer shows no absorption characterisitic of the $\equiv$C-H (3300 cm^{-1}) and C$\equiv$C (2200 cm^{-1}) bonds which are 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 absorptions at 1350 - 1000 cm^{-1} are assignable to C-F stretching. Absorptions due to a 1,2,4-trisubstituted benzene are also seen at 780 and 700 cm^{-1}. The analytical and IR spectral data support that the main chain of the polymer is composed of alternating double bonds as shown in Figure 3.

Poly(BTFPA) obtained in the present study was a dark brown solid.

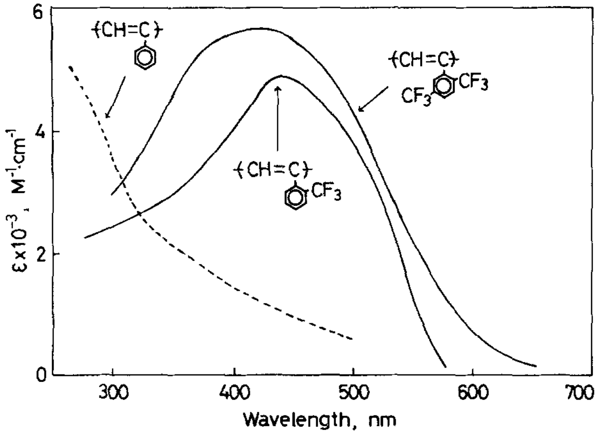


Figure 4. UV-visible spectra of poly(phenylacetylenes)
(in THF, but poly(BTFPA) in p-$(CF_3)_2C_6H_4$)

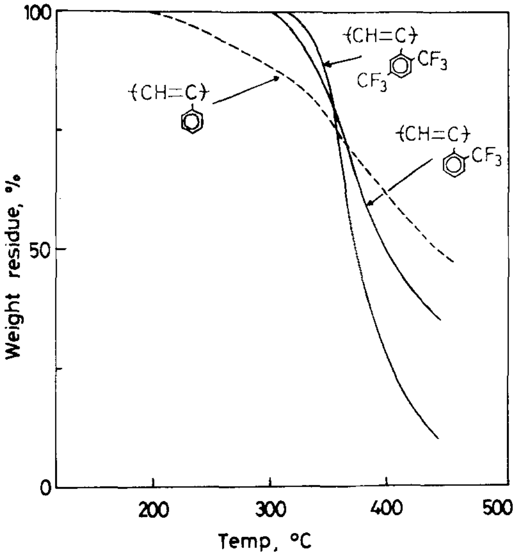


Figure 5. TGA curves of poly(phenylacetylenes) in air

The polymer produced with the $W(CO)_6$-based catalyst was completely soluble in *p*-$(CF_3)_2C_6H_4$, though polymers obtained in other conditions were partly insoluble in this solvent. Regarding other solvents, poly(BTFPA) was partly soluble in tetrahydrofuran, C_6F_6 and CCl_2FCClF_2 (soluble part 30 - 70%), virtually insoluble in toluene and dimethylformamide, and completely insoluble in hexane, $CHCl_3$ and $(CH_2Cl)_2$. The proportion of soluble part varied to some extent with the polymerization conditions. The polymer obtained with $W(CO)_6$ in CCl_4 at 30 °C was the most soluble (the soluble part in C_6F_6 was about 70%). Poly(*o*-TFMPA) is totally soluble in common organic solvents such as toluene and $CHCl_3$, but insoluble in some polyfluorinated hydrocarbons such as C_6F_6 and *p*-$(CF_3)_2C_6H_4$. The difference in solubility in these two polymers should originate from differences in the fluorine-content and the stiffness of the polymer chain.

Figure 4 shows the UV-visible spectrum of poly(BTFPA). An absorption maximum of the polymer lies at about 420 nm, and no absorption is seen above 680 nm. This absorption band is almost similar to that of poly(*o*TFMPA), and is in a region of fairly long wavelength as compared with that of poly(phenylacetylene). Generally, the absorption maximum of an ortho-substituted phenylacetylene polymer shifts to longer wavelength with increasing bulkiness of the substituent (5). Poly(BTFPA) also exhibits this tendency.

Figure 5 shows results of thermogravimetric analysis (TGA) of the present and analogous polymers. Poly(phenylacetylene) begins to lose weight at a relatively low temperature of 200 °C. In contrast, the temperatures at which weight loss starts are 300 °C and 320 °C with poly(*o*TFMPA) and poly(BTFPA), respectively, indicating that these polymers are thermally more stable than poly(phenylacetylene). This is explained in terms that the CF_3 group sterically prevents oxygen from attacking the main-chain double bonds.

ACKNOWLEDGMENT

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