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Journal of Fluorine Chemistry 71 (1995) 151–153

**JOURNAL OF  
FLUORINE  
CHEMISTRY**

# Anionic polymerization reactivity of 1,2,2-trifluorostyrene

Tadashi Narita\*, Tokio Hagiwara, Hiroshi Hamana, Keiichi Shibasaki, Ikuo Hiruta

*Department of Environmental Engineering, Saitama Institute of Technology, 1690 Okabe, Saitama 369-02, Japan*

Received 17 May 1994; accepted 29 September 1994

## Abstract

The anionic polymerization of 1,2,2-trifluorostyrene ( $\text{CF}_2=\text{CFC}_6\text{H}_5$ ) (TFS) has been undertaken with a view to obtaining preliminary information on the reactivity of TFS which is hardly polymerized under radical polymerization conditions. The solid polymer of TFS was obtained following initiation with triethylaluminum complexed with active methylene chelate compounds although the yields of the polymer were rather low. The characteristic feature of this polymerization system is that the molecular weight distribution of the poly(TFS) obtained is very narrow. The polymer was shown to be produced by an addition polymerization mechanism by analyzing its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

*Keywords:* Anionic polymerization; 1,2,2-Trifluorostyrene; NMR spectroscopy; IR spectroscopy; Molecular weight distribution

## 1. Introduction

Many reports have described the polymerization of 1,2,2-trifluorinated vinyl monomers ( $\text{CF}_2=\text{CFX}$ ) from which it may be concluded that the polymerizations of 1,2,2-trifluorinated vinyl monomers are generally very difficult although chlorotrifluoroethene may be readily polymerized under radical conditions [1]. The radical polymerization of hexafluoro-1,3-butadiene ( $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ ) (HFBD), which is an example of a 1,2,2-trifluorinated vinyl monomer, produces grease-like oligomers [2]. The anionic polymerization of HFBD by initiators containing cesium or rubidium counterions led to a polymer whose structure was similar to that of poly(hexafluoro-2-butyne) [3].

This paper describes another example of the polymerization of a 1,2,2-trifluorinated vinyl monomer, 1,2,2-trifluorostyrene ( $\text{CF}_2=\text{CFC}_6\text{H}_5$ ) (TFS), using several anionic polymerization initiators. Although radical polymerization of TFS under emulsion polymerization conditions has been reported to produce poly(TFS) in fair yield [4], a detailed study of the polymerization reactivity of TFS has not been undertaken. Whereas thermal reaction of TFS takes place to produce cyclobutane derivatives [5], anionic polymerization may be preferable because the electron density of the vinyl group may be reduced by the electron-withdrawing

inductive effect of the fluorine atoms. The  $Q$  value of TFS is reported to be 0.75 while  $e$  is 0.22.

## 2. Experimental details

Experiments related to the polymerization reactions were undertaken under a purified nitrogen atmosphere in order to preclude oxygen and atmospheric moisture.

1,2,2-Trifluorostyrene (TFS) (supplied by Nippon Mektron, Ltd.) was purified carefully by distillation since the purity of the material supplied was less than 70%. The main impurity was bromobenzene which was one of the starting materials used to synthesize TFS. Commercially available  $\text{C}_4\text{H}_9\text{Li}$  and  $\text{C}_4\text{H}_9\text{MgCl}$  were used after determination of the active species by alkalimetry. Alkali metal *t*-butoxide was synthesized from alkali metal and 2-methyl-2-propanol. Organoaluminum compounds were synthesized according to literature methods [6]. Commercial triethylaluminum and diethylzinc were purified by distillation under reduced pressure. Cesium fluoride was used after drying under reduced pressure. Tetrabutylammonium fluoride was used as received. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized with methanol. Tetrahydrofuran (THF) and toluene were purified by the usual methods. 1,2-Dimethoxyethane (DME) was refluxed over calcium hydride and then distilled. The distillate was further purified by refluxing with triethylaluminum followed by distillation under nitrogen.

\* Corresponding author.

Polymerizations were carried out in a sealed glass ampoule which was charged with 1,2,2-trifluorostyrene (TFS) (9.3 mmol), an initiator (0.19 mmol) and solvent. The total volume was 10 ml. After a fixed time, polymerization was terminated by adding hydrochloric acid/methanol. Solid polymer was separated by filtration after precipitation with methanol and was dried to a constant weight.

Gel permeation chromatography (GPC) was undertaken using a Tosoh HLC-802A apparatus employing a TSK gel G4000HXL–G3000HXL–G2000HXL column series with THF as the eluent. The molecular weights of the polymers were estimated by calibration against standardized polystyrene.  $^1\text{H}$  (at 270 MHz) and  $^{13}\text{C}$  (at 67.80 MHz) NMR spectra were registered on a JEOL JNM-GX270 FT NMR spectrometer using THF- $d_8$  as the solvent and tetramethylsilane as internal standard.

### 3. Results and discussion

In order to increase the purity of 1,2,2-trifluorostyrene (TFS), its reactions with organometallic compounds such as butyllithium, Grignard reagent, diethylzinc and magnesium metal were investigated in an attempt to remove bromobenzene which had been used as one of the starting materials in its synthesis. Such treatment, however, had little effect on the purity of TFS with several cyclic dimers being produced in the process of purification. Careful distillation under reduced pressure was the most effective method of purification in our experience. The purity of the TFS obtained by distillation was ca. 75% with the 25% impurity being mainly bromobenzene.

Anionic polymerization of TFS was examined with typical anionic initiators such as butyllithium, butylmagnesium bromide, potassium t-butoxide and cesium t-butoxide. Organoaluminum compounds such as triethylaluminum, diethyl(dimethyl malonato)aluminum, diethyl(ethyl cyanoacetato)aluminum [( $\text{C}_2\text{H}_5$ ) $_2$ AIECA] and diethyl(acetylacetonato)aluminum, some of which are active initiators for the polymerizations of *ortho*-, *meta*- and *para*-trifluoromethylstyrenes [7,8], and diethylzinc were also investigated at polymerization temperatures between 40 °C and 80 °C for 3 d in toluene, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME). The results obtained are listed in Table 1.

Although poly(TFS) was obtained, the polymer yields were generally low. The highest yield (7.0%) of poly(TFS) was obtained using ( $\text{C}_2\text{H}_5$ ) $_2$ AIECA as the initiator; other initiator systems produced only ca. 1% of the polymer. It is therefore concluded that the anionic polymerization reactivity of TFS is very low. CsF, which is active initiator in the polymerization of HFBD [2], gave no polymer. Radical polymerization of TFS with

Table 1  
Polymerization of 1,2,2-trifluorostyrene <sup>a</sup>

Initiator	Solvent	Temp. (°C)	Time (d)	Yield (%)	$M_{\text{GPC}} \times 10^{-4}$
n-C <sub>4</sub> H <sub>9</sub> Li	THF	60	3	trace	0.9
	toluene	60	3	trace	2.3
	DME	60	3	trace	1.7
n-C <sub>4</sub> H <sub>9</sub> MgCl	THF	60	3	trace	1.1
	toluene	60	3	trace	1.4
	DME	60	3	trace	1.7
t-C <sub>4</sub> H <sub>9</sub> OK	THF	60	3	trace	1.0
	toluene	60	3	trace	1.7
	DME	60	3	trace	1.6
t-C <sub>4</sub> H <sub>9</sub> OCs	THF	60	3	0	–
	toluene	60	3	trace	1.9
	DME	60	3	trace	1.5
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	toluene	60	3	0.5	1.3
	DME	60	3	trace	0.9
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> AlDMM <sup>b</sup>	toluene	50	3	0.7	0.7
	toluene	60	3	trace	–
	toluene	60	7	1.3	1.0
	toluene	80	3	0.5	–
	toluene	100	7	trace	–
	DME	40	3	trace	–
	DME	60	3	0.5	–
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> AlIECA <sup>c</sup>	DME	80	3	0.5	–
	toluene	50	3	0.3	–
	toluene	60	3	7.0	0.7
	toluene	80	3	1.0	0.8
	DME	40	3	trace	–
	DME	60	3	0.3	–
	DME	80	3	0.7	0.9
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Alacac <sup>d</sup>	toluene	50	3	0.5	–
	toluene	60	3	0.5	–
	toluene	60	7	0.7	1.0
	toluene	80	3	1.4	1.0
	DME	40	3	trace	–
	DME	60	3	1.8	0.7
	DME	80	3	1.7	0.8
Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	THF	60	3	trace	0.9
	toluene	60	3	0.3	0.9
	DME	60	3	0.4	1.3
CsF	THF	60	3	0	–
	toluene	60	3	0	–
	DME	60	3	0	–
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NF	THF	60	3	0	–
	toluene	60	3	trace	2.0
	DME	60	3	0	–
AIBN	THF	60	3	0	–
	toluene	60	3	0	–
	DME	60	3	0	–

<sup>a</sup> TFS: 9.3 mmol; initiator: 0.19 mmol; total volume, 10 ml.

<sup>b</sup> ( $\text{C}_2\text{H}_5$ ) $_2$ AlDMM: ( $\text{C}_2\text{H}_5$ ) $_2$ Al(CH<sub>3</sub>OCOCHCOOCH<sub>3</sub>).

<sup>c</sup> ( $\text{C}_2\text{H}_5$ ) $_2$ AlIECA: ( $\text{C}_2\text{H}_5$ ) $_2$ Al(NCCHCOOC<sub>2</sub>H<sub>5</sub>).

<sup>d</sup> ( $\text{C}_2\text{H}_5$ ) $_2$ Alacac: ( $\text{C}_2\text{H}_5$ ) $_2$ Al(CH<sub>3</sub>COCHCOCH<sub>3</sub>).

2,2'-azobisisobutyronitrile (AIBN) at 60 °C in toluene, THF and DME for 3 d produced no polymer. The products obtained were white powders, soluble in benzene, toluene, chloroform, acetone and THF, and insoluble in methanol, hexane and dimethyl sulfoxide.

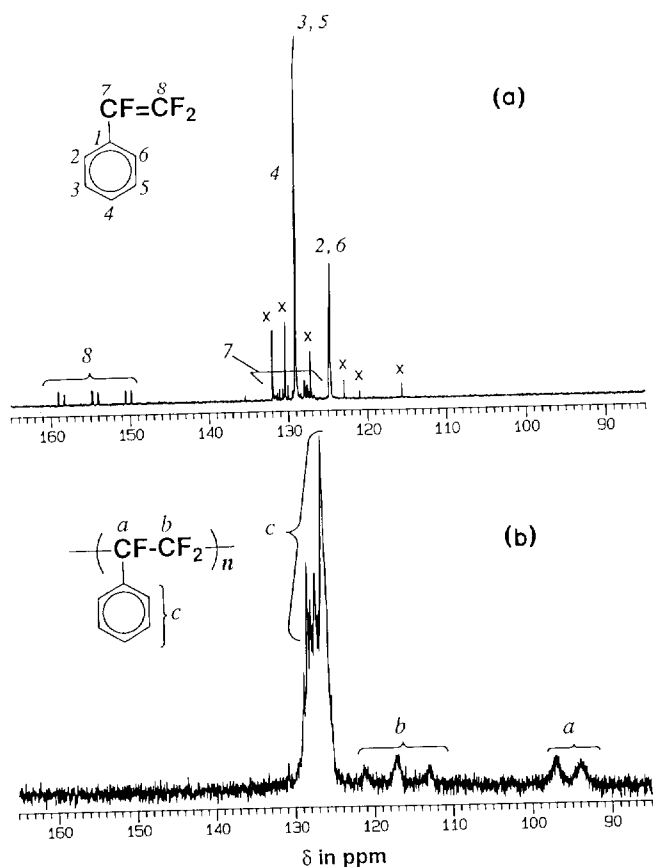


Fig. 1.  $^{13}\text{C}$  NMR spectrum of (a) TFS and (b) poly(TFS) obtained using  $\text{Al}(\text{C}_2\text{H}_5)_3$  as initiator (in DME at  $80^\circ\text{C}$  for 3 d).

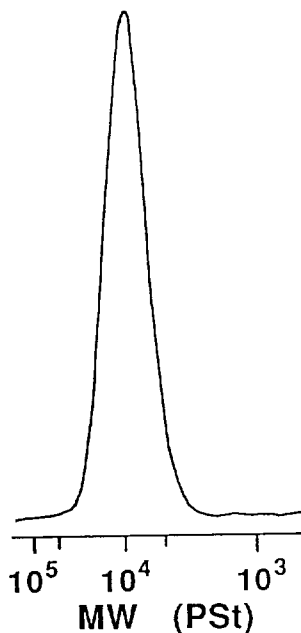


Fig. 2. GPC of poly(TFS) obtained using  $(\text{C}_2\text{H}_5)_2\text{AlIECA}$  in DME at  $60^\circ\text{C}$ .

In order to clarify the structure of the polymer, the  $^{13}\text{C}$  NMR spectra of the monomer and polymer were examined. The results are shown in Fig. 1. The signals at 150–160 ppm which may be assigned to the  $\text{CF}_2=\text{C}$  carbon of the monomer in Fig. 1(a) disappear and new absorptions at 93–97 ppm assigned to the  $-\text{CF}-$  carbon and at 112–122 ppm assigned to the  $-\text{CF}_2-$  carbon are detected in the spectrum of the polymer (Fig. 1(b)). The polymerization of TFS is therefore tentatively concluded to take place by addition polymerization of the vinyl group. This view is supported by the infrared measurements undertaken since the absorption assignable to a vinyl group at  $1757\text{ cm}^{-1}$  observed in the spectrum of the monomer is absent from that of the polymer.

The characteristics of this polymerization system were obtained by measurements of the molecular weights of the polymers generated. Molecular weights and molecular weight distributions of poly(TFS) were examined by gel permeation chromatography (GPC). The result of a typical GPC analysis is shown in Fig. 2. The molecular weight obtained was  $0.9 \times 10^4$  with a very narrow molecular weight distribution since  $M_w/M_n = 1.1$  although the polymer yield was ca. 1%. This is the most characteristic feature of the polymerization systems studied.

In conclusion, poly(TFS) may be produced by anionic polymerization although previously TFS has been reported only producing cyclobutane derivatives. No side-reactions take place once polymerization has started since the molecular weight distribution is very narrow. The polymerization reactivity of TFS is fairly low since the polymer yields are less than 10%.

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