

## Radical polymerization and copolymerization of bis{3-[tris(trimethylsiloxy)silyl]propyl} fumarate

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### SUMMARY:

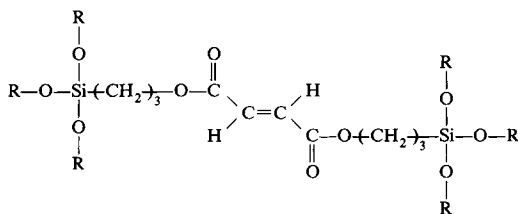
Radical polymerization and copolymerization of bis{3-[tris(trimethylsiloxy)silyl]propyl} fumarate (BSPF (1)) were investigated. The reactivity of BSPF in homopolymerization was found to be very low, and only low-molecular-weight poly(BSPF) was obtained in low yields. On the other hand, copolymerizations of BSPF with diisopropyl fumarate (DiPF) and di-*tert*-butyl fumarate (DtBF) proceed with moderate rates to give high-molecular-weight copolymers. The monomer reactivity ratios were determined to be as follows;  $r_1 = 0,07$ ,  $r_2 = 0,87$  for BSPF ( $M_1$ ) and DiPF ( $M_2$ );  $r_1 = 0,21$ ,  $r_2 = 0,67$  for BSPF ( $M_1$ ) and DtBF ( $M_2$ ). The resulting copolymers are soluble in many common organic solvents. Tough and brittle films were obtained by solution casting of the copolymers of BSPF and DtBF. The copolymers exhibit excellent oxygen permeability.

### Introduction

Dialkyl fumarates (DRFs), i.e., 1,2-disubstituted ethylenes, with bulky alkyl ester substituents were found to homopolymerize readily in the presence of a radical initiator to give high-molecular-weight polymers consisting of a substituted polymethylene structure<sup>1–5</sup>. In polymerization of DRFs, the polymerization reactivity deduced from the yield and the molecular weight of the resulting polymers increases with increasing bulkiness of the ester alkyl substituents, i.e., diisopropyl fumarate (DiPF) and di-*tert*-butyl fumarate (DtBF) give less flexible vinyl polymers in high yields and with high molecular weight. These polymers show different properties from ordinary vinyl polymers on account of their less flexible structure.

On the other hand, the gas separation characteristics of polymer membranes has attracted much interest<sup>6</sup>, especially for the separation of oxygen and nitrogen gases. Although rubbery polymers such as poly(dimethylsiloxane) show high oxygen permeability as compared with glassy polymers<sup>6,7</sup>, a tough membrane cannot be obtained. Recently, it was reported that some glassy polymers from 4-methyl-1-pentene<sup>7</sup>, 1,2-disubstituted acetylenes<sup>8</sup> and 1,2-disubstituted ethylenes<sup>1,9–11</sup> exhibit an excellent oxygen permeability: poly(trimethylsilylpropyne)<sup>8</sup> was found to show the highest oxygen permeability.

Poly(DRF) with bulky alkyl groups also show excellent oxygen permeability<sup>9,10</sup>. If any siloxanyl groups can be introduced into the ester alkyl groups, the oxygen permeability should be still enhanced. In this paper, bis{3-[tris(trimethylsiloxy)silyl]propyl} fumarate (1, BSPF), a monomer bearing primary ester functions with bulky groups, was prepared, and its radical homopolymerization and copolymerization reactivities were investigated and compared with those of the other DRFs.



**1** (BSPF), R = Si(CH<sub>3</sub>)<sub>3</sub>

## Experimental part

**Materials:** BSPF was prepared as follows<sup>12)</sup>: Diallyl fumarate was hydrosilylated with tri-chlorosilane in the presence of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O as a catalyst. The product was mixed with chlorotrimethylsilane, and the mixture obtained was added dropwise to isopropyl alcohol, followed by addition of water. After the addition was complete, the reaction mixture was separated into two layers. BSPF was obtained from the organic layer by distillation (b. p. 195 °C/0,1 mmHg). The other DRFs, DiPF and DtBF, were prepared according to the method<sup>1)</sup> described previously, followed by purification.

2,2'-Azodiisobutyronitrile (AIBN), di-*tert*-butyl peroxide (DTBPO), and 1,1'-azodicyclohexanecarbonitrile (ACN) were used as free-radical initiators after purification.

**Polymerization and copolymerization procedures:** Bulk polymerization and copolymerization were carried out in the presence of a radical initiator in sealed glass tubes. The composition of the resulting copolymers was determined from the peak areas in <sup>1</sup>H NMR spectra, on the basis of the protons of SiCH<sub>3</sub> for BSPF and of CH<sub>3</sub> for DiPF and DtBF. The monomer reactivity ratios (*r*<sub>1</sub> and *r*<sub>2</sub>) were calculated by a non-linear least-squares procedure.

**Measurements:** The number- and weight-average molecular weights ( $\bar{M}_n$  and  $\bar{M}_w$ ) were determined by gel-permeation chromatography (GPC) at 38 °C in tetrahydrofuran (THF) as an eluent, as calibrated with polystyrene standards. GPC was performed with a Tosoh 8000 series GPC system.

<sup>1</sup>H NMR spectra were recorded on JEOL GX-400 or HITACHI R-24B spectrometers in deuteriochloroform with tetramethylsilane (TMS) as an internal standard.

## Results and discussion

The results of bulk polymerization of BSPF (**1**) in the presence of AIBN or DTBPO as a radical initiator, at 60 °C and 120 °C, respectively, are shown in Tab. 1, the results for DiPF and DtBF also being indicated. The polymerization reactivity of BSPF was

Tab. 1. Results of homopolymerization of fumarates in bulk

Fumarate	[Initiator] in mol · L <sup>-1</sup>	Temp. in °C	Time in h	Convsn. in %	10 <sup>-4</sup> · $\bar{M}_n$
BSPF ( <b>1</b> )	AIBN (0,02)	60	50	0,7	0,31
BSPF ( <b>1</b> )	DTBPO (0,02)	120	10	3,1	0,22
DiPF <sup>a)</sup>	AIBN (0,02)	60	10	29,1	11,0
DtBF <sup>a)</sup>	ACN (0,03)	80	6	84,6	10,0

a) Data from ref. 1).

much lower than that of DiPF and DtBF; i.e., BSPF gave low-molecular-weight polymers ( $\bar{M}_n = 3\,100$  and  $2\,200$ ) with low yields (0,7 and 3,1%) at  $60^\circ\text{C}$  and  $120^\circ\text{C}$ , respectively, whereas DiPF and DtBF gave polymers in high yields, with molecular weights higher than  $10^5$  (calibration with polystyrene standards).

In a previous study<sup>1)</sup>, it was shown that homopolymerization reactivities of DRFs increase with increasing bulkiness of the ester alkyl groups, i.e., the polymerization reactivity increases in the following order: primary < secondary < tertiary alkyl esters. The observed low reactivity for homopolymerization of BSPF is consistent with the previous observation, because BSPF is a primary alkyl fumaric ester.

Fig. 1 shows the  $^1\text{H}$  NMR spectra of BSPF monomer and poly(BSPF) obtained. The disappearance of the peak at 6,84 ppm due to the protons on the carbon-carbon double bond indicates that polymerization proceeds via an opening of the double bond in BSPF. From  $^{13}\text{C}$  NMR and IR spectra, the same results were obtained.

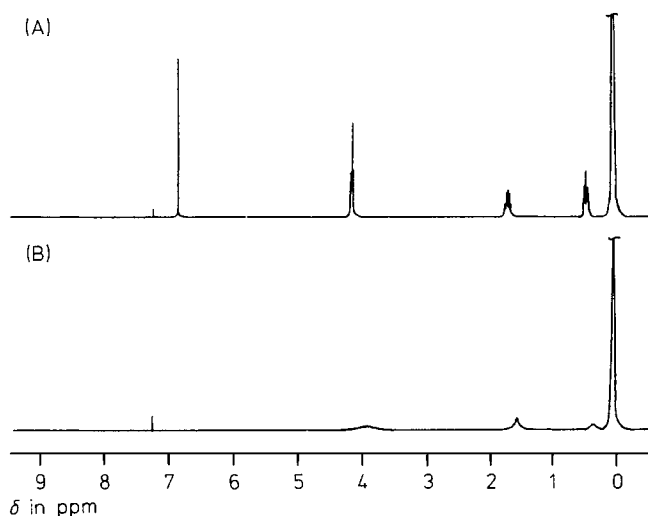


Fig. 1.  $^1\text{H}$  NMR spectra of (A) BSPF (1) and (B) poly(BSPF)

Poly(BSPF) was isolated as a colorless and viscous material, soluble in benzene, toluene, chloroform and THF, and insoluble in methanol. The fluidity of this polymer seems to be due to the high mobility of the siloxanyl groups in the side chain and/or its low molecular weight. Since we could not obtain high-molecular-weight poly(BSPF), it cannot be concluded which factor is more important.

To obtain a polymer exhibiting high toughness, radical copolymerizations of BSPF with other DRFs bearing bulky ester alkyl groups were carried out. The results of bulk copolymerization of BSPF ( $M_1$ ) with DiPF and DtBF ( $M_2$ ) at  $60^\circ\text{C}$  and  $80^\circ\text{C}$ , respectively, are shown in Tab. 2.

Tab. 2. Results of copolymerization of BSPF ( $M_1$ ) with DiPF and DtBF ( $M_2$ ) in bulk

$M_2$	$[M_1]$ in mol-% (in feed)	Time in h	Convsn. in %	$[M_1]$ in mol-% (in copolymer)	$10^{-4} \cdot \bar{M}_n$
DiPF <sup>a)</sup>	25,7	10	17,9	19,8	4,6
	47,2	20	15,7	38,4	2,1
	81,7	30	5,3	53,2	—
	90,9	40	2,4	63,8	—
DtBF <sup>b)</sup>	25,0	2	28,5	25,8	7,1
	50,0	4	30,6	41,8	3,0
	70,2	15	38,5	54,5	1,1
	90,0	30	15,2	71,2	—

a)  $[AIBN] = 0,02 \text{ mol} \cdot \text{L}^{-1}$ , at  $60^\circ\text{C}$ .

b)  $[ACN] = 0,02 \text{ mol} \cdot \text{L}^{-1}$ , at  $80^\circ\text{C}$ .

Copolymers with  $\bar{M}_n > 10^4$  were obtained in higher yields than poly(BSPF). Both the yield and  $\bar{M}_n$  of the resulting copolymers increased with increasing fraction of  $M_2$  in the feed. In Fig. 2, the comonomer-copolymer composition curves are depicted. The copolymerization reactivity ratios were determined to be as follows;  $r_1 = 0,07$ ,  $r_2 = 0,87$  for BSPF and DiPF;  $r_1 = 0,21$ ,  $r_2 = 0,67$  for BSPF and DtBF, indicating that the copolymerization reactivity of BSPF is lower than that of DiPF and DtBF, as is also its homopolymerization ability.

In copolymerizations of DRFs bearing different ester alkyl substituents, it was found that DRF with bulkier alkyl groups has higher monomer reactivity. For example, it has already been reported that DtBF exhibits higher reactivity than dimethyl fumarate (DMF);  $r_1 = 1,88$  and  $r_2 = 0,36$  where  $M_1$  is DtBF and  $M_2$  is DMF<sup>13)</sup>. These results seem to contradict the conventional steric effect. However, in polymerizations of DRF,

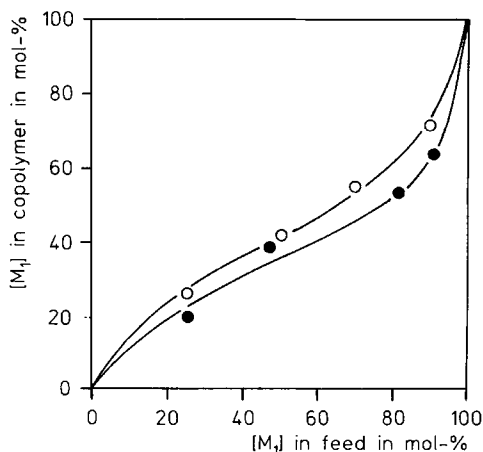


Fig. 2. Comonomer-copolymer composition curves for copolymerization of BSPF ( $M_1$ ); (●): with DiPF ( $M_2$ ) at  $60^\circ\text{C}$ , (○): with DtBF ( $M_2$ ) at  $80^\circ\text{C}$

the propagation rate constant increases with increasing bulkiness of the ester substituents<sup>14-16</sup>. The conformation of the propagating radical and the direction of the addition of DRF to the propagating radical, i. e., *meso* and *racemo* addition, would be important<sup>16</sup>. Accordingly, a prerequisite to the discussion of such viewpoints is to examine the monomer reactivity in the copolymerization.

Although the homopolymerization of BSPF gave only viscous low-molecular-weight polymers, the copolymers of BSPF with DiPF or DtBF were white powders, soluble in many organic solvents such as benzene, chloroform, and THF. A tough and brittle film was obtained by solution casting of the copolymers of BSPF and DtBF.

Preliminary results for oxygen permeation indicated that the copoly(BSPF-DtBF) membranes have excellent oxygen permeabilities, and that the permeability coefficient ( $P_{O_2}$ ) increases with increasing BSPF fraction in the copolymers as follows<sup>12</sup>:  $P_{O_2} = 6,9 \cdot 10^{-9}$  and  $1,17 \cdot 10^{-8} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$  for copolymers containing 20 and 45 mol-% of BSPF, respectively. These values are larger than those for poly(DRF) with alkyl groups reported previously<sup>10</sup>: e. g.,  $P_{O_2} = 4,9 \cdot 10^{-9}$  and  $2,1 \cdot 10^{-9} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$  for poly(*tert*-butyl 4-methylpentyl fumarate) and poly(*tert*-butyl isopropyl fumarate), respectively.

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- <sup>1)</sup> T. Otsu, T. Yasuhara, A. Matsumoto, *J. Macromol. Sci., Chem. A* **25**, 537 (1988), and references cited therein
- <sup>2)</sup> A. Matsumoto, T. Tarui, T. Otsu, *Macromolecules* **23**, 5102 (1990)
- <sup>3)</sup> M. Yoshioka, T. Otsu, *Macromolecules* **25**, 559 (1992)
- <sup>4)</sup> T. Otsu, M. Yoshioka, A. Matsumoto, K. Shiraishi, *Polym. Bull. (Berlin)* **26**, 159 (1991)
- <sup>5)</sup> M. Yoshioka, A. Matsumoto, T. Otsu, I. Ando, *Polymer* **32**, 2741 (1991)
- <sup>6)</sup> W. J. Koros, G. K. Fleming, S. M. Jordan, T. H. Kim, H. H. Hoehn, *Prog. Polym. Sci.* **13**, 339 (1988)
- <sup>7)</sup> S. Pauly, "Polymer Handbook", 3rd ed., Eds. J. Brandrup, E. H. Immergut, Wiley, New York 1989, p. VI-435
- <sup>8)</sup> T. Masuda, E. Isobe, T. Higashimura, K. Takada, *J. Am. Chem. Soc.* **105**, 7473 (1983)
- <sup>9)</sup> H. Ikebe, Y. Murata, T. Otsu, *Polym. Prepr., Jpn.* **34**, 420 (1985)
- <sup>10)</sup> S. B. Choi, A. Takahara, N. Amaya, Y. Murata, T. Kajiyama, *Polym. J.* **21**, 433 (1989)
- <sup>11)</sup> A. Matsumoto, Y. Oki, T. Otsu, *Polym. J.* **23**, 201, 1371 (1991)
- <sup>12)</sup> T. Otsu, M. Yoshioka, to be published
- <sup>13)</sup> M. Yoshioka, A. Matsumoto, T. Otsu, *Macromolecules* **25**, 2837 (1992)
- <sup>14)</sup> T. Otsu, B. Yamada, T. Ishikawa, *Macromolecules* **24**, 415 (1990)
- <sup>15)</sup> B. Yamada, E. Yoshikawa, H. Miura, K. Shiraishi, T. Otsu, *Polymer* **32**, 1892 (1991)
- <sup>16)</sup> M. Yoshioka, A. Matsumoto, T. Otsu, *Polym. J.* **23**, 1249 (1991)