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ORIGINAL PAPER

# Synthesis and polymerization of amphiphilic itaconate monomer and some properties of the polymer

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**Abstract** A $\beta$-2-methoxyethyl $\alpha$-3-[tris(trimethylsiloxy)silyl]propyl itaconate (**1**) was synthesized successfully as a novel amphiphilic itaconate monomer, and its radical homopolymerization and copolymerization with styrene (St) were investigated. The polymerization rate (Rp) is expressed with $\mathrm{Rp} = \mathrm{k}[\mathbf{1}]^{2.73}[\mathrm{AIBN}]^{0.51}$. Overall activation energy in the radical homopolymerization was determined to be 52.9 kJ/mol. The **1** copolymerized with St in bulk in a highly alternating tendency. The *Q*, *e* values of the **1** were obtained to be 1.05 and 0.69, respectively, and the **1** was found to be a conjugative and electron-accepting monomer. Membranes containing the **1** unit, prepared by the copolymerization of **1** with *N*-vinylpyrrolidone (NVP) and by the terpolymerization of **1**, NVP, and 2-hydroxyethyl methacrylate, showed higher oxygen permeability than corresponding ones without the **1** unit, and also they have better transparency than membranes containing 3-[tris(trimethylsiloxy)silyl]propyl methacrylate unit.

**Keywords** Amphiphilic · Synthesis · Radical polymerization · Itaconate · Membrane

## Introduction

Contact lens (CL) is known well as the lens equipped on a cornea for vision correction, and the CL materials are required both the oxygen permeable property for breathing of corneal cell and the hydrophilic property for not repelling a tear and

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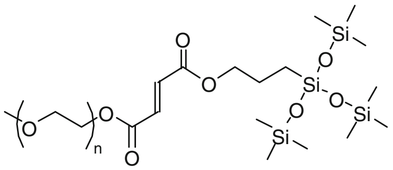
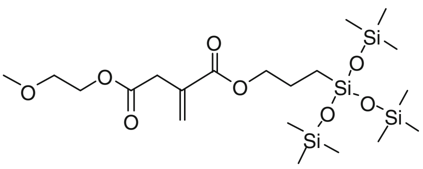
to protect a lipid deposition [1]. However, compounds having substituents with high oxygen permeability, for example, siloxy group as substituents, are hydrophobic, and they are immiscible with compounds having hydrophilic substituents. Therefore, when the polymers with a hydrophobic group are mixed with the polymers with a hydrophilic group, phase separation takes place to form opaque materials, not suitable for CL. To dissolve the problem, we focused on fumarate monomers, because they can possess two substituents different in size and property in the molecule. Previously, we prepared amphiphilic fumarate monomers having both a hydrophilic alkoxyethyl group such as 2-methoxyethyl (**E1SiFu**), 2-(2-methoxyethoxy)ethyl (**E2SiFu**), and 2-(2-(2-methoxyethoxy)ethoxy)ethyl (**E3SiFu**), and a hydrophobic bulky 3-[tris(trimethylsiloxy)silyl]propyl group and investigated the polymerization behavior and the thermal property of the resulting polymers, and also, some properties required in CL materials such as oxygen permeability, hydrophilicity and transparency [2]. However, those monomers showed poor homopolymerization reactivities, especially **E1SiFu** was no homopolymerizable. Homopolymerization reactivity of the vinyl-type monomers significantly depends upon the substitution mode. Generally, 1,2-disubstituted ethylene monomers are less reactive than 1,1-disubstituted ethylene ones [3]. Therefore, to obtain the amphiphilic monomers with much higher homopolymerization reactivity, we focused on itaconate monomers as 1,1-disubstituted ethylene-type monomer. First report on homopolymerization of itaconic acid and its derivatives appeared in 1959 [4], and after that, many itaconic acid derivatives have been prepared and their polymerization behaviors have been investigated [5, 6]. It was reported that polymerization reactivities of the itaconates significantly depend upon the substituent on the side chain, especially substituent in the $\alpha$-position [7].

In this work, to find a high performance materials suitable for CL, we synthesized a novel amphiphilic monomer, $\beta$-2-methoxyethyl $\alpha$-3-[tris(trimethylsiloxy)silyl]propyl itaconate (**1**), which has a hydrophobic 3-[tris(trimethylsiloxy)silyl]propyl group with high oxygen permeability and a nonionic, hydrophilic 2-methoxyethyl group, and investigated the homopolymerization kinetics, copolymerization with styrene (St), and the thermal properties of the resulting polymers. Moreover, we prepared membranes containing the **1** unit and compared in oxygen permeability, water content, and transparency with the membranes containing the **E1SiFu** unit reported previously.



**E1SiFu: n=1**
**E2SiFu: n=2**
**E3SiFu: n=3**



**1**

## Experimental

### Measurements

$^{1}$H and $^{13}$C NMR spectra were taken on JEOL JNM-EX270 and JNM-A500 FT NMR spectrometers using chloroform-*d* with a tetramethylsilane as an internal standard at room temperature. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on a Yanaco CHN Corder MT-5. Number-average molecular weights, $M_n$, of homopolymers and copolymers were estimated by gel permeation chromatography (GPC) on a JASCO PU-1580 equipped with JASCO RI-930 detector and two TSKgel MultiporeH$_{XL}$-M columns (bead size with 5 μm, molecular weight range $5.0 \times 10^{2}$–$2.0 \times 10^{6}$) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 ml/min and polystyrene standard for calibration at room temperature. The solution viscosity of **1** in benzene was measured with an Ostwald viscometer at 50 °C. Relative viscosities ($\eta_{rel}$) of the monomer were calculated from the flow times. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with SII EXSTAR6000 series, DSC6220 and TG/DTA6200, at a heating rate of 10 °C/min under nitrogen.

### Materials

Styrene (St, bp 52 °C/30 mmHg) was washed with 2% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, stirred over calcium hydride, and then distilled. Benzene (bp 80 °C) was washed with a concentrated sulfuric acid, and water, dried over anhydrous magnesium sulfate, refluxed over metal sodium for 24 h, and then distilled. Diethyl ether (bp 35 °C) was refluxed over metal sodium for 6 h, and then distilled. 2,2′-Azobis(isobutylonitrile) (AIBN) was recrystallized from methanol. 3-[Tris(trimethylsiloxy)silyl]propyl methacrylate (SiMA, bp 115 °C/0.2 mmHg), *N*-vinylpyrrolidone (NVP, bp 70 °C/2.0 mmHg), and 2-hydroxyethyl methacrylate (HEMA, bp 82 °C/2.0 mmHg) were purified by distillation. Ethylene dimethacrylate (EDMA), itaconic acid anhydride, 2-methoxyethanol, triethylamine, lithium aluminum hydride, 4-(*N*,*N*-dimethyl)aminopyridine (DMAP), 1-ethyl-3-(3-*N*,*N*-dimethylaminopropyl) carbodiimide hydrochloride (EDC), chloroform, dichloromethane, diisopropyl ether, and ethyl acetate were used as received.

### Monomer synthesis

#### *3-[Tris(trimethylsiloxy)silyl]propyl alcohol*

Lithium aluminum hydride (670 mg, 18 mmol) was dissolved in dry diethyl ether (80 ml), and the mixture was cooled to 0 °C with stirring. Into the resulting solution was added dropwise a solution of 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (5.0 g, 12 mmol) in dry diethyl ether (20 ml), and stirred at 0 °C for 1 h. The reaction mixture was added slowly into 1*N* hydrochloric acid solution, and extracted with diethyl ether (100 ml × 2). The extracts were combined, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent to give a viscous residue, which was dissolved in a small amount of chloroform. The resulting solution was passed through a silica gel column (diameter 6 cm × length 30 cm) by using chloroform as an eluent. The first elution band was collected and placed under reduced pressure to give 3.3 g (79% yield) of 3-[tris(trimethylsiloxy)silyl]propyl alcohol as a colorless liquid. IR (NaCl, $cm^{-1}$): 3346 (O–H), 2960 (C–H), 1064 (Si–O–Si). $^1H$ NMR (270 MHz, $CDCl_3$, $\delta$, ppm): 3.62-3.56 (m, 2H), 1.68–1.57 (m, 2H), 1.50–1.43 (m, 1H), 0.51–0.45 (m, 2H), 0.12 (s, 27H). $^{13}C$ NMR (68 MHz, $CDCl_3$, $\delta$, ppm): 65.2 ($CH_2OH$), 26.6 ($CH_2$), 10.3 ($CH_2$), 1.7 ($CH_3$). Anal. Calcd for $C_{12}H_{34}O_4Si_4$: C, 40.63; H, 9.66; O, 18.04; Si, 31.67%. Found: C, 40.05; H, 9.40%.

### *Itaconic acid β-2-methoxyethyl ester (**2**)*

A mixture of itaconic acid anhydride (1.0 g, 8.92 mmol) and 2-methoxyethanol (0.565 g, 7.43 mmol) was heated at 60 °C for 12 h, after then the reaction mixture was added into 1*N* hydrochloric acid solution, and extracted with diethyl ether (100 ml × 2). The extracts were combined, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent to give a viscous residue, which was dissolved in a small amount of dichloromethane, and the resulting solution was passed through a silica gel column (diameter 6 cm × length 30 cm) by using a mixture solution of dichloromethane and ethyl acetate (=99/1, v/v) as an eluent. The second elution band was collected and placed under reduced pressure to give 0.87 g (62% yield) of **2** as a colorless liquid, which was further purified by recrystallization from diisopropyl ether. Yield, 0.35 g (25% yield). Mp 38 °C. IR (NaCl, $cm^{-1}$): 34470 (O–H), 2890 (C–H), 1,733 and 1,702 (C=O), 1,636 (C=C), 1,200 (C–O–C). $^1H$ NMR (270 MHz, $CDCl_3$, $\delta$, ppm): 9.53 (s, 1H), 6.47 (s, 1H), 5.85 (s, 1H), 4.27 (t, $J = 4.8$ Hz, 2H), 3.60 (t, $J = 4.8$ Hz, 2H), 3.39 (s, 5H). $^{13}C$ NMR (68 MHz, $CDCl_3$, $\delta$, ppm): 171.1 (C=O), 170.6 (C=O), 133.2 (C=C), 130.7 (C=C), 70.2 ($CH_2$), 63.9 ($CH_2$), 58.8 ($CH_3$), 37.1 ($CH_2$).

### *β-2-Methoxyethyl α-3-[tris(trimethylsiloxy)silyl]propyl itaconate (**1**)*

A solution of **2** (0.66 g, 3.51 mmol), 3-[tris(trimethylsiloxy)silyl]propyl alcohol (1.0 g, 2.82 mmol) and DMAP (36 mg, 0.29 mmol) in dichloromethane (6.0 ml) was cooled to 0 °C and into the resulting solution was added EDC (1.12 g, 5.84 mmol). After stirring at ambient temperature for 95 h, the reaction mixture was added into 1*N* hydrochloric acid solution, and extracted with dichloromethane (100 ml × 3). The extracts were combined, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove solvent to give a viscous residue, which was dissolved in a small amount of dichloromethane, and the resulting solution was passed through a silica gel column (diameter 6 cm × length 30 cm) by using dichloromethane as an eluent. The first elution band was collected and placed under reduced pressure to give 0.86 g (58% yield) of **1** as a colorless liquid. IR (NaCl, $cm^{-1}$): 2958 (C–H), 1744 (C=O), 1641 (C=C), 1254 and 842 (Si–C), 1,131 (O–Si–O), 1054 (C–O–C). $^1H$ NMR (270 MHz, $CDCl_3$, $\delta$, ppm): 6.33

(s, 1H), 5.71 (s, 1H), 4.25 (t, $J = 4.7$ Hz, 2H), 4.10 (t, $J = 6.8$ Hz, 2H), 3.59 (t, $J = 4.7$ Hz, 2H), 3.38 (s, 5H), 1.72–1.58 (m, 2H), 0.51–0.45 (m, 2H), 0.10 (s, 27H). $^{13}$C NMR (68 MHz, $CDCl_3$, $\delta$, ppm): 170.7 (C=O), 166.1 (C=O), 133.9 (C=C), 128.2 (C=C), 70.3 ($CH_2$), 67.3 ($CH_2$), 63.9 ($CH_2$), 58.9 ($CH_3$), 37.5 ($CH_2$), 22.7 ($CH_2$), 10.4 ($CH_2$), 1.7 ($CH_3$). Anal. Calcd for $C_{20}H_{44}O_8Si_4$: C, 45.75; H, 8.45; O, 24.38; Si, 21.40%. Found: C, 45.96; H, 8.74%.

## Polymerization procedure

### *Radical homopolymerization*

Given amounts of **1**, AIBN as a radical initiator, and benzene as a solvent if necessary, were placed in a glass tube for polymerization, and degassed by freeze-thaw method (repeated three times), and sealed. It was placed in an oil bath controlled at a constant temperature. After polymerization for a given time, the tube was cooled to a liquid nitrogen temperature to stop the polymerization. A small amount of dichloromethane was added into it to dissolve the reaction mixture, and then the resulting solution was poured into an excess of methanol to precipitate the polymer. The obtained polymer was purified by three cycles of dissolution-reprecipitation method using dichloromethane as a solvent and methanol as a precipitant, respectively, and then placed under reduced pressure. Monomer conversion was determined gravimetrically.

### *Radical copolymerization*

Given amounts of **1**, St, AIBN were placed in a tube for polymerization, and it was degassed by freeze-thaw method (repeated three times), and then purged with nitrogen gas, and sealed. It was placed in an oil bath thermostated at 60 °C for a given time. The rest of procedure was similar to the above-mentioned homopolymerization case. The copolymer composition was determined by the integral peak area ratio at 7–6 ppm due to the aromatic protons for the St unit, to that at 0.1 ppm due to methyl protons for the **1** unit in the $^{1}$H NMR spectrum. Chloroform-*d* without a trimethylsilane as an internal standard was used for the determination of copolymer composition.

## Membrane property

Membranes were prepared as follows: Given amounts of **1**, NVP and/or HEMA, small amount of EDMA (0.3 wt%) as a cross-linking agent, and AIBN (0.3 wt%) were placed in two $20^{\phi}$ mm holes on Teflon spacer sheet with 0.2 mm thickness and sandwiched between nylon sheet and glass plate, and then set in a thermostated oven chamber. The polymerization was performed by heating at 60 °C for 60 min, 90 °C for 90 min, and 110 °C for 60 min to attain complete conversion. After cooling to room temperature, membranes were taken out from the Teflon sheet and then immersed into water for 24 h.

Water content (W.C. wt%) of the membranes was estimated by a following equation: W.C. (wt%) = $(W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{wet}} \times 100$. $W_{\mathrm{dry}}$ is a weight of a membrane after drying at 80 °C for 2 h and $W_{\mathrm{wet}}$ is a weight of a membrane swollen in water for 24 h.

Oxygen permeability (Dk) of membranes was evaluated according to the international standard methodology ISO 9913-1. As Dk values generally depend upon the film thickness, $\mathrm{Dk}_{0.2}$ value, which is the value extrapolated to the membrane with 0.2 mm thickness, was used in this work and compared among the membranes.

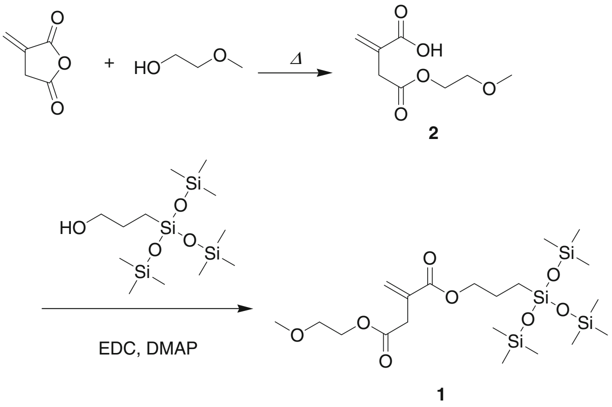
The transparency of the membranes was determined by measuring a light transmittance. The membranes (0.2 mm thickness) were swollen in water for 24 h and then used for measurement.

## Results and discussion

### Monomers synthesis

An amphiphilic itaconate monomer (**1**) was synthesized in two steps according to the procedure as shown in Scheme 1.

Compound **2** was prepared as a colorless liquid in 62% yield by reaction of itaconic acid anhydride with 2-methoxyethanol according to the method reported previously [8], and then purified by recrystallization from diisopropyl ether to give white needles with the melting point of 38 °C in 25% yield. Monomer **1** was obtained as a colorless liquid in 58% yield by reaction of **2** with 3-[tris(trimethylsiloxy)silyl]propyl alcohol in the presence of DMAP and EDC as a condensation agent. The chemical structure of **1** was confirmed by IR, $^{1}$H NMR, $^{13}$C NMR, and elemental analysis. $^{1}$H NMR spectrum of **1** is shown in Fig. 1, where each peak could be assigned to the respective protons of the chemical structures illustrated therein.



**Scheme 1** Monomer synthesis

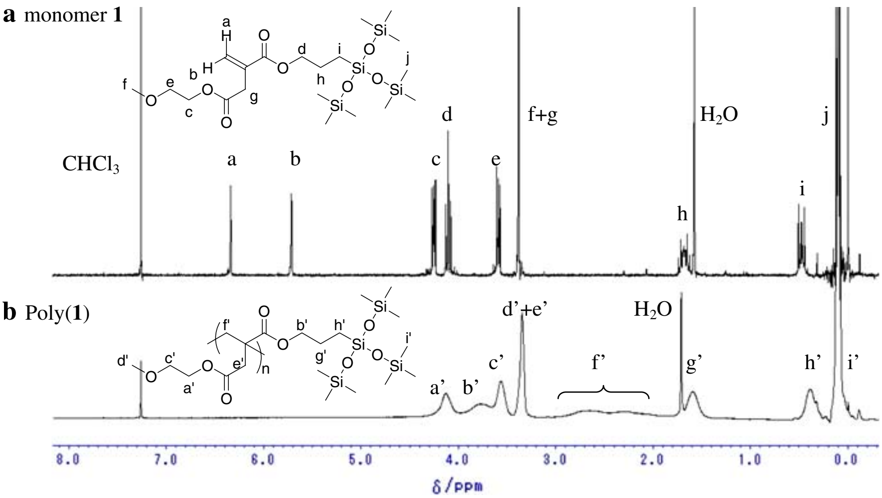


**Fig. 1** $^1$H NMR spectra (**a**) monomer **1** and (**b**) poly(**1**) in $CDCl_3$

## Homopolymerization

Solution polymerization of **1** was carried out at 45, 50, 55 and 60°C in benzene under the conditions of a monomer concentration of 1.0 mol/l and of a AIBN initiator concentration of 0.05 mol/l. Each conversion was determined from the weight of the resulting polymer. The polymerization results are summarized in Table 1. The polymer of **1** (poly(**1**)) was obtained as white solids with $M_n$ of 8,000–35,000. $^1$H NMR spectra of the isolated poly(**1**) and **1** are shown in Fig. 1, where each peak could be assigned to the respective protons of the chemical structure illustrated therein. The olefin proton peaks (6.33 and 5.71 ppm) observed in the monomer **1** disappeared, and a broad peak appeared at 2–3 ppm, assignable to the methylene proton in the poly(**1**).

Time-conversion plots for the polymerization of **1** are shown in Fig. 2. The conversions linearly increase against polymerization time at all temperatures. From the slopes of these time-conversion plots, the polymerization rates (Rp) are estimated and summarized in Table 2.

Moreover, the polymerization of **1** was carried out at 65, 70 and 75 °C under the same condition and the observed Rp are shown in Table 2. The Arrhenius plot of the Rp is shown in Fig. 3, where Rp decreases at 65, 70 and 75 °C. This indicates that at higher temperatures over 65 °C, contribution of the depolymerization becomes significant. It is reported that on the polymerizations of itaconate monomers such as dicyclohexyl itaconate, dipropyl itaconate, and dimethyl itaconate, depropagation significantly affects the polymerization rate in the temperature higher than 100 °C [9]. Depropagation in the polymerization of **1** becomes significant at lower temperature in comparison with alkyl itaconates, due to the presence of the bulky tris(trimethylsiloxy)silyl group in monomer **1.** Yamada et al. [10] reported the method to determine the ceiling temperature (Tc) from the plots of log Rp vs 1/T.

**Table 1** The results of homopolymerization of **1** in benzene at various temperatures

| Run (Nos) | Temperature (°C) | Time (h) | Yield/mg (%) | $M_n$ ($10^3$) | $M_w$ ($10^3$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| 1 | 45 | 3 | 6.7 (4.3) | 35.4 | 48.1 | 1.36 |
| 2 | ″ | 4 | 7.6 (4.8) | 34.5 | 48.0 | 1.39 |
| 3 | ″ | 7 | 16.0 (10.2) | 34.5 | 49.3 | 1.43 |
| 4 | ″ | 8 | 22.7 (14.4) | 33.8 | 46.3 | 1.37 |
| 5 | 50 | 2 | 4.1 (2.6) | 17.7 | 24.4 | 1.38 |
| 6 | ″ | 4 | 12.2 (7.7) | 23.6 | 35.6 | 1.51 |
| 7 | ″ | 5 | 13.9 (8.9) | 21.2 | 28.2 | 1.33 |
| 8 | ″ | 8 | 23.6 (15.0) | 21.1 | 27.8 | 1.32 |
| 9 | 55 | 2 | 5.8 (3.7) | 16.0 | 20.4 | 1.28 |
| 10 | ″ | 3 | 13.4 (8.5) | 15.8 | 20.2 | 1.28 |
| 11 | ″ | 4 | 20.3 (12.2) | 16.8 | 22.5 | 1.34 |
| 12 | ″ | 6 | 24.8 (15.8) | 13.3 | 17.6 | 1.35 |
| 13 | 60 | 1 | 7.0 (4.5) | 7.8 | 9.8 | 1.26 |
| 14 | ″ | 2 | 11.6 (7.4) | 15.3 | 17.8 | 1.16 |
| 15 | ″ | 3 | 17.3 (11.0) | 15.5 | 18.2 | 1.18 |
| 16 | ″ | 4 | 22.6 (14.4) | 20.0 | 26.6 | 1.33 |

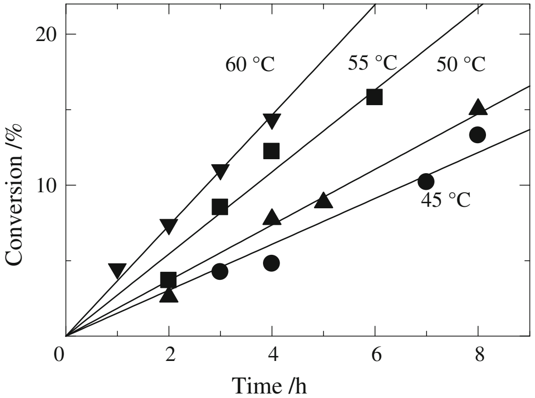


**Fig. 2** Time-conversion curves for the solution polymerization of **1** in benzene at 45 (*filled cirlcle*), 50 (*filled triangle*), 55 (*filled square*) and 60 (*filled inversed triangle*). [**1**] = 1.0 mol/l and [AIBN] = 0.05 mol/l

From the Fig. 3, Tc in the polymerization of **1** is determined to be 80 °C. From the slope of linear part of the plot, the overall activation energy (Ea) of the polymerizations for **1** is estimated to be 52.9 kJ/mol. This value is similar to that of diethyl itaconate (Ea = 70.7 kJ/mol) [11].

We investigated the order of dependence of Rp on the **1** and initiator concentrations at 50 °C. The results are summarized in Table 3. The order of dependence of Rp on AIBN concentration at 50 °C, where **1** is a constant concentration of 1.0 mol/l, is shown in Fig. 4.

The order of dependence of Rp on initiator is to be 0.51. The Rp is dependent on the square root of the initiator concentration, indicating usual bimolecular

**Table 2** The Rp[a] of **1** at various temperatures

| Temperature (°C) | 1/K ($10^{-3}$) | Rp (mol/l s) | Log Rp |
|---|---|---|---|
| 45 | 3.14 | $4.2 \times 10^{-6}$ | −5.37 |
| 50 | 3.10 | $5.1 \times 10^{-6}$ | −5.29 |
| 55 | 3.05 | $7.5 \times 10^{-6}$ | −5.12 |
| 60 | 3.00 | $10.0 \times 10^{-6}$ | −4.99 |
| 65 | 2.96 | $10.3 \times 10^{-6}$ | −4.99 |
| 70 | 2.92 | $7.7 \times 10^{-6}$ | −5.11 |
| 75 | 2.87 | $0.28 \times 10^{-6}$ | −6.56 |

[a] [**1**] = 1.0 mol/l (157 mg, 0.300 mmol) and [AIBN] = 0.05 mol/l (2.5 mg, 0.015 mmol)

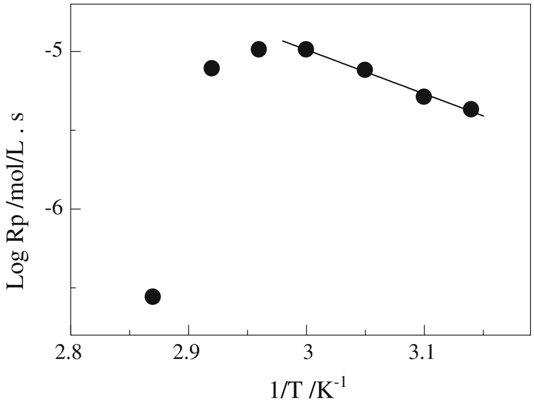


**Fig. 3** Arrhenius plots of Log Rp versus 1/T for the polymerizations of **1**

**Table 3** The Rp of the homopolymerizations of **1** at various condition of **1** ([**1**]) and AIBN ([AIBN]) concentrations in benzene at 50 °C

| Run (Nos). | [**1**] (mol/l) | [AIBN] (mol/l) | Rp ($10^{-6}$ mol/l s) | Log [**1**] | Log [AIBN] | Log Rp | Log $(\mathrm{Rp}/(\eta_{\mathrm{rel}})^{0.5})$ |
|---|---|---|---|---|---|---|---|
| 1 | 1.0 | 0.025 | 4.4 | 0 | −1.6 | −5.36 | |
| 2 | 1.0 | 0.10 | 8.8 | 0 | −1.0 | −5.05 | |
| 3 | 1.0 | 0.05 | 5.1 | 0 | −1.3 | −5.29 | −5.47 |
| 4 | 0.75 | 0.05 | 1.8 | −0.13 | −1.3 | −5.73 | −5.96 |
| 5 | 1.25 | 0.05 | 7.2 | 0.097 | −1.3 | −5.14 | −5.40 |

termination in this polymerization. The order of dependence of Rp on **1** concentration at 50 °C, where AIBN is a constant concentration of 0.05 mol/l, is shown in Fig. 5.

The order of dependence of Rp on monomer **1** concentration is determined to be 2.73. The order with respect to monomer concentration is significantly greater than unity, and this behavior is similar to the radical polymerizations of itaconates reported previously [12]. Therefore, the polymerization rate (Rp) is expressed as follows:

**Fig. 4** Dependence of Rp on [AIBN] in benzene at 50 °C. [**1**] = 1.0 mol/l

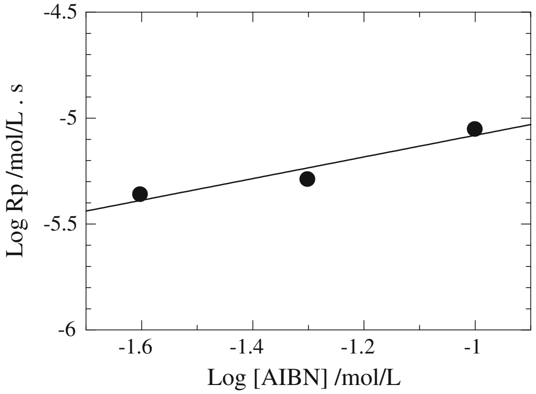


**Fig. 5** Dependence of Rp (*filled circle*) and Rp/($\eta_{rel}$)$^{0.5}$ (*filled inversed triangle*) on [**1**] in benzene at 50°C. [AIBN] = 0.05 mol/l

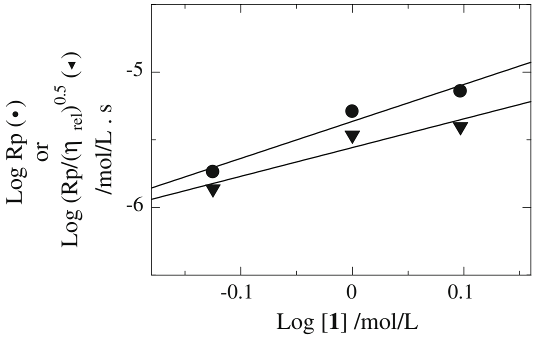


**Table 4** Relative viscosity ($\eta_{rel}$) of **1** in benzene at 50 °C

| [**1**] (mol/l) | $\eta_{rel}$ |
|---|---|
| 0 | 1.00 |
| 0.75 | 1.78 |
| 1.00 | 2.25 |
| 1.25 | 3.35 |

$$\mathrm{Rp} = k[\mathbf{1}]^{2.73}[\mathrm{AIBN}]^{0.51}$$

A kinetics order higher than unity with respect to the monomer is thought to be the effect of the increasing viscosity of the polymerization solution with the monomer concentration. Therefore, the viscosity of polymerization system at 50 °C was measured and the results are presented in Table 4.

The relative viscosity ($\eta_{rel}$) of **1** in benzene appreciably increases with an increase in monomer concentration. The rate of diffusion-controlled termination in radical polymerization should be proportional to the reciprocal of $\eta_{rel}$ of the polymerization system [12]. Therefore, the Rp is rewritten as follow:

$$\mathrm{Rp} = k'(\eta_{\mathrm{rel}})^{0.5}[\mathbf{1}]^{n}[\mathrm{AIBN}]^{0.51}$$

The logarithm of $\mathrm{Rp}/(\eta_{\mathrm{rel}})^{0.5}$ is plotted against monomer concentration as shown in Fig. 5. From the slope of the straight line in Fig. 5, Rp may be expressed as follow:

$$\mathrm{Rp}/(\eta_{\mathrm{rel}})^{0.5} = k'[1]^{2.14}[\mathrm{AIBN}]^{0.51}$$

The kinetics order is still higher than unity in spite of considering the viscosity. Sato et al. [13] investigated the polymerization of di-2-[2-(2-methoxyethoxy)ethoxy]ethyl itaconate and observed the higher kinetic order with respect of monomer concentration. The reason might be explained in terms of solvent effect reported in the polymerization of the alkyl itaconates [11, 12].

## Copolymerization with St

The radical copolymerization of **1** with St was carried out in bulk at 60 °C. The copolymer compositions were determined by $^1$H NMR measurement, and the copolymerization results are summarized in Table 5 and the copolymerization composition curve is shown in Fig. 6. Monomer reactivity ratios were determined to be $r_1 = 0.10$ and $r_2 = 0.33$ by the Kelen-Tüdös method [14], and also $r_1 = 0.12 \pm 0.02$ and $r_2 = 0.34 \pm 0.03$ by non-linear least squares computer fit of the copolymer equation [15], respectively. The product of these values, $r_1 \times r_2$ (=0.041), is nearly close to zero, indicating that the copolymerization of **1** with St proceeds in a highly alternating tendency. From the monomer reactivity ratios, the $Q$, $e$ values of **1** are calculated to be 1.05 and 0.69, respectively, indicating that **1** is a conjugative and electron-accepting monomer. These values are similar to those of di-2-[2-(2-methoxyethoxy)ethoxy]ethyl itaconate ($r_1 = 0.20$, $r_2 = 0.53$, $Q = 0.57$ and $e = 0.7$) [13].

## Thermal property

Thermal analyses (DSC and TG) of the poly(**1**) and the poly(**1-*co*-St**) were carried out under nitrogen. The copolymer with the **1**/St ratio of 49.2/50.8 in mol% was used for measurement. Figure 7 shows their DSC curves.

**Table 5** Copolymerization results of **1** with St in bulk at 60 °C

| Run (Nos.) | Monomer in feed | | | | | Copolymer composition[a)] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1** (mg) | St (mg) | **1** (mol%) | AIBN (mg) | Time (h) | Yield (%) | 1 (mol%) | St (mol%) | $M_n$ ($M_w/M_n$) ($10^4$) |
| 1 | 100 | 179 | 10 | 21 | 2 | 9.8 | 23 | 77 | 1.8 (1.2) |
| 2 | 100 | 80 | 20 | 11 | 4 | 11.1 | 29 | 71 | 2.3 (1.3) |
| 3 | 100 | 37 | 35 | 6 | 15 | 2.0 | 38 | 62 | 2.5 (1.2) |
| 4 | 100 | 13 | 60 | 3.5 | 2 | 2.1 | 48 | 52 | 2.6 (1.4) |
| 5 | 512 | 21 | 83 | 11.7 | 1 | 11.2 | 61 | 39 | 3.6 (1.2) |

[a] Determined by $^1$H NMR measurement

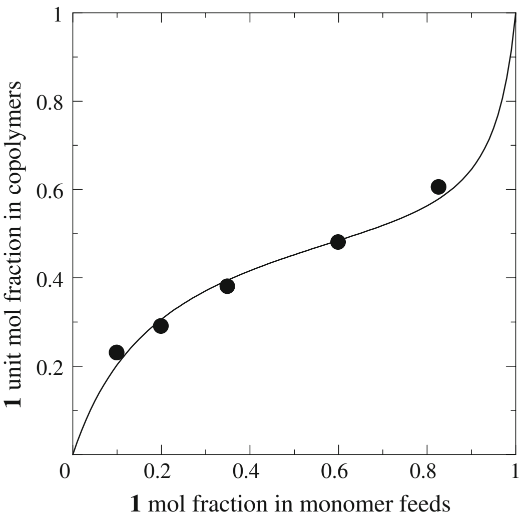


**Fig. 6** Copolymer composition curve for the copolymerization of the **1**-St system in bulk at 60 °C. *Filled circles* were measured. The *solid curve* was calculated with the Mayo-Lewis equation with $r_1 = 0.10$ and $r_2 = 0.33$

Glass transition temperature ($T_g$) of the poly(**1**) was observed at 2.6 °C and considerably lower than $T_g$ value of the poly(dibutyl itaconate), which is reported to be 17 °C [16]. This comes from the presence of both flexible alkoxyethyl and siloxy groups as the side chain in **1**. While, $T_g$ of the poly(**1**-*co*-**St**) was found at 21.3 °C, and it was a little higher to that (16.0 °C) of the poly(**E1SiFu**-*co*-**St**) [2]. Figure 8 shows TGA curves of the poly(**1**) and the poly(**1**-*co*-**St**), together with that of poly(**E1SiFu**-*co*-**St**). The poly(**1**) starts to decompose about 250 °C, and the temperature at 5% weight loss ($T_d^5$) is to be 294 °C. The poly(**1**-*co*-**St**) starts to decompose about 300 °C, and the $T_d^5$ is to be 325 °C. The copolymer is thermally stable than the homopolymer, due to the presence of the St unit with high thermal stability. While, $T_d^5$ of poly(**E1SiFu**-*co*-**St**) is to be 352 °C and poly(**1**-*co*-**St**) is less thermally stable compared with poly(**E1SiFu**-*co*-**St**). The difference in the chemical structure between **1** unit and **E1SiFu** unit affects obviously the $T_g$ and thermally stability.

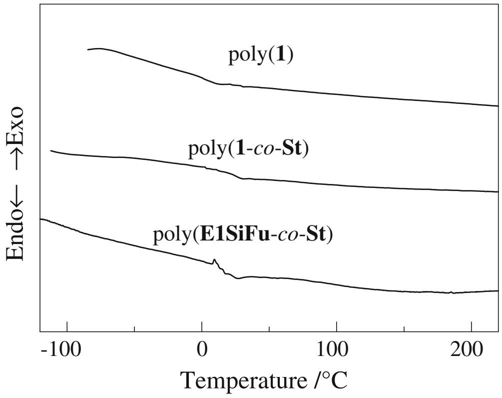
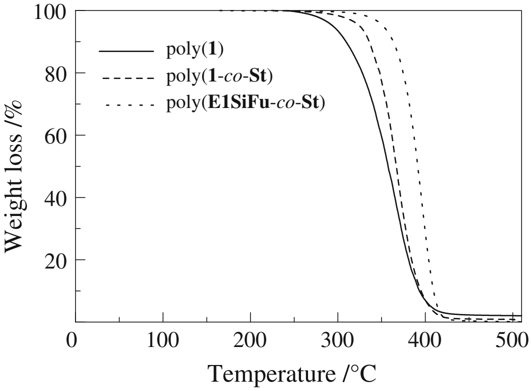


**Fig. 7** DSC curves of the poly(**1**) ($M_n = 33{,}500$, $M_w/M_n = 1.5$), the poly(**1**-*co*-**St**) (**1**: 49.2 mol%, $M_n = 42{,}900$, $M_w/M_n = 1.32$) and the poly(**E1SiFu**-*co*-**St**) (**E1SiFu** : 50.8 mol%, $M_n = 43{,}000$, $M_w/M_n = 1.43$) [2] under nitrogen. Heating rate: 10 °C/min

**Fig. 8** TGA curves of the poly(**1**) ($M_n = 33{,}500$, $M_w/M_n = 1.50$), the poly(**1**-*co*-**St**) (**1**: 49.2 mol%, $M_n = 42{,}900$, $M_w/M_n = 1.32$) and the poly(**E1SiFu**-*co*-**St**) (**E1SiFu** : 50.8 mol%, $M_n = 43000$, $M_w/M_n = 1.43$) [2] under nitrogen. Heating rate: 10 °C/min



## Membrane property

We prepared the membranes containing the **1** unit by copolymerization of **1** with NVP, and by terpolymerization of **1**, NVP, and HEMA in the presence of AIBN (0.3 wt%) and compared with the corresponding membranes containing the **E1SiFu** unit reported previously [2]. Small amount of EDMA (0.3 wt%) was added as a cross-linking agent for both polymerizations to obtain the membranes. Copolymer and terpolymer compositions are almost same compositions in the monomer feeds because all polymerizations were carried out until complete conversion. $Dk_{0.2}$ and W·C. of these membranes were measured and the results are summarized in Table 6.

The membranes containing the **1** unit show $Dk_{0.2}$ values of 23–33 × $10^{-11}$(cm$^2$/s)·(mLO$_2$/mL × Hg) and W.C. values of 24–43 wt%. The relationship of the $Dk_{0.2}$ with water content (W.C.) of the membranes containing the **1** unit (*filled circle*) is shown in Fig. 9, together with the corresponding values for the membranes containing the **E1SiFu** unit (×) and only hydrophilic monomer units (*filled triangle*) reported previously [2] for comparison. The oxygen permeability of the membranes containing the **1** unit is higher than that of the membranes without the **1** unit, and independent of water content, though oxygen permeability of the membranes without the **1** unit is significantly dependent upon the water content. Moreover, the membranes containing the **1** unit have almost same $Dk_{0.2}$ values to the membranes containing the **E1SiFu** unit.

Next, to investigate the effect of the **1** unit on the transparency of the membranes, we measured the light transmittance of the each membrane at various wavelength. The results are shown in Fig. 10, together with the data for the membranes containing the **E1SiFu** unit or the 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (SiMA) unit reported previously for comparison. The membranes of run no. 4 (38.0%) and of run no. 5 (43.8%) show much better light transmittance than the membranes containing the SiMA (3.2% and 23.1%), indicative of better transparency of the membranes containing the **1** unit. However, the transparency of those membranes is worse in comparison with the membranes containing the **E1SiFu** unit

**Table 6** $Dk_{0.2}$ and water content (W.C. wt%) of membranes

| Run (Nos.) | Monomer in feed (wt%) | | | $Dk^{a}_{0.2}$ | W.C.[b] (wt%) |
|---|---|---|---|---|---|
| | **1** | NVP | HEMA | | |
| 1 | 70 | 30 | 0 | 28 | 24 |
| 2 | 60 | 40 | 0 | 33 | 35 |
| 3 | 60 | 27 | 13 | 23 | 36 |
| 4 | 50 | 50 | 0 | 23 | 44 |
| 5 | 50 | 33 | 17 | 23 | 43 |

The polymerization was performed by heating at 60 °C for 60 min, 90 °C for 90 min, and 110 °C for 60 min. 0.3 wt% of EDMA and 0.3 wt% of AIBN were added in these polymerizations

[a] $Dk_{0.2}$:$\times 10^{-11}$ ($cm^2/s$)·($mLO_2/ml \times Hg$)

[b] W.C. (wt%): $\{(W_{wet} - W_{dry})/W_{wet}\} \times 100$. $W_{dry}$ = weight of a membrane after drying at 80 °C for 2 h. $W_{wet}$ = weight of the membrane swollen in water for 24 h

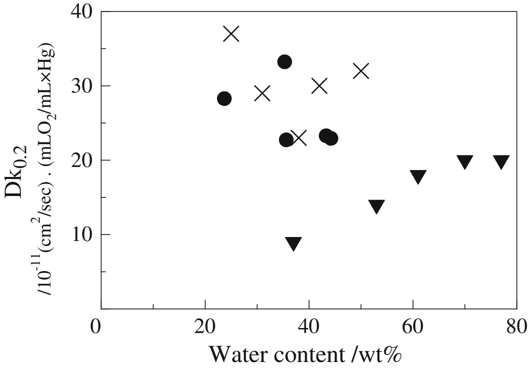


**Fig. 9** The relationship of $Dk_{0.2}$ with water content for the membranes containing the **1** unit (*filled circle*), the those without the **1** unit (*filled triangle*), and the those containing the **E1SiFu** unit (×) [2]

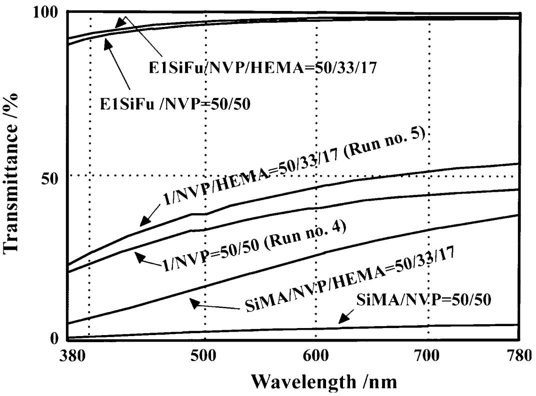


**Fig. 10** Light transmittance of the membranes of run no. 4 (**1**/NVP = 50/50), run no. 5 (**1**/NVP/HEMA = 50/33/17) in Table 6, (SiMA/NVP = 50/50) (SiMA/NVP/HEMA = 50/33/17) (**E1SiFu**/NVP = 50/50), and (**E1SiFu**/NVP/HEMA = 50/33/17) [2]. All membranes have the thickness of about 0.2 mm

(96.6 and 97.5%). This is due to the presence of a hydrophobic methylene group in the **1** unit, leading to the less amphiphilic property.

## Conclusions

Amphihilic *β*-2-methoxyethyl *α*-3-[tris(trimethylsiloxy)silyl]propyl itaconate (**1**), which has a hydrophobic 3-[tris(trimethylsiloxy)silyl]propyl group with high oxygen permeability and a nonionic, hydrophilic 2-methoxyethyl group, was successfully synthesized. Ceiling temperature of **1** was found to be 80 °C. The order of dependence of Rp on initiator and monomer were investigated and $\mathrm{Rp} = \mathrm{k}\,[\mathbf{1}]^{2.73}\,[\mathrm{AIBN}]^{0.51}$ was obtained as the polymerization rate equation. The *Q*, *e* values of **1** were obtained to be 1.05 and 0.69, respectively, indicating that **1** is a conjugative and electron-accepting monomer. The copolymer is thermally more stable than the homopolymer because of the presence of thermally stable aromatic ring. The membranes prepared by the copolymerization of the **1** with NVP and by terpolymerization of **1**, NVP and HEMA showed similar oxygen permeability to ones containing the **E1SiFu** unit, but their transparency was insufficient compared to membranes containing the **E1SiFu** unit.

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