Catalytic double ring-opening polyaddition of spiro orthoester with acid chloride for shrinkage-controlled molding

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Abstract

In order to develop a casting resin for precision molding, a curing method without shrinkage during the polymerization was achieved by the double ring-opening addition reaction of spiro orthoester (SOE) and acid chloride using cationic catalysts. Tetraphenylphosphonium halides (TPPXs) were found to be effective catalysts for the reaction. The catalytic reaction of SOE with acid chloride proceeded even at 25 °C to give the corresponding adduct. Polyaddition of a bifunctional SOE-XII with trifunctional 1,3,5-pentanetricarbonyl trichloride gave a cured material at 30 °C in the presence of tetraphenylphosphonium bromide (TPPB) of 1 mol%, accompanied by a negligible shrinkage of 0.21%. Gelation time was shortened with increase in the amount of catalyst and reaction temperature in the curing process. The obtained products were crosslinked copolymers that showed variable mechanical properties dependent on the curing temperature and monomer structure. This is the first demonstration of shrinkage-controlled molding in the absence of heating or cooling process.
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Keywords: Spiro orthoester; Ring-opening copolymerization; Shrinkage control
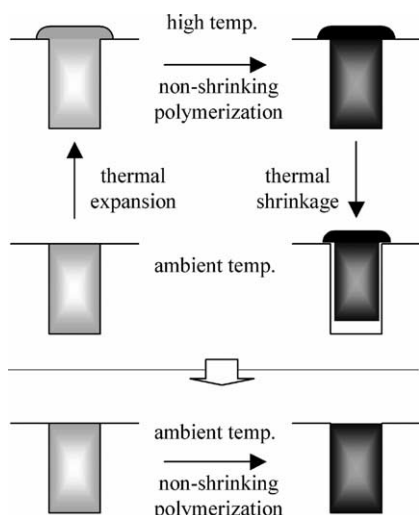
1. Introduction

Polymerization of common monomers, such as vinyl monomers, is always accompanied by a significant degree of volume shrinkage [1–4]. In the field of adhesive and coating applications, this tendency to shrink leads to the formation of voids and micro-cracks in the formed materials, which remarkably diminish their mechanical properties. On the other hand, some kinds of cyclic monomers such as spiro orthoester (SOE), spiro orthocarbonate (SOC), and bicyclo orthoester (BOE) have been reported to maintain their volume or actually expand during the double ring-opening polymerization [5,6]. The mechanism responsible for the volume change during the polymerization of SOE, SOC and BOE has been explained by Bailey, Endo, and their co-workers, that is, three covalent bonds of carbon to oxygen atoms and one van der Waals distance are changed to one double bond, one covalent bond, and two van der Waals distances, causing the expansion in volume [7]. This characteristic of expandable monomers is expected to be incorporated into applications for adhesive, molding, and coating materials, compensating for the tendency of common monomers to shrink.

Generally, the double ring-opening reaction of SOE requires high temperatures of more than 100 °C [8–11]. The total polymerization of SOE proceeds in three stages: (1) the heating stage up to the polymerization temperature, (2) the isothermal polymerization stage at this temperature, and (3) the cooling stage to ambient temperature (Scheme 1). This total process accompanies a considerable level of thermal expansion and shrinkage of monomer and polymer during the heating and cooling stages, respectively, [3]. Even when using the expandable monomers, the volume expansion during the double ring-opening polymerization may be canceled out by the thermal shrinkage in the cooling stage. This means, when the polymerization process takes

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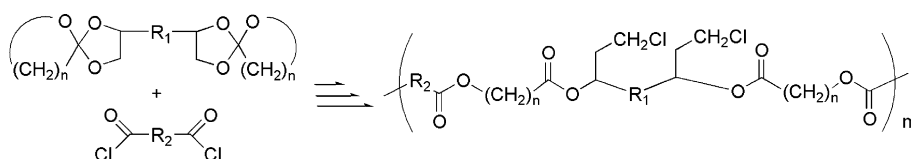E-mail address: hnishida@mol-eng.fuk.kindai.ac.jp (H. Nishida).

Scheme 1. Polymerization process for the moldings at high temperature and ambient temperature.

2. Experimental section

2.1. Measurement

^{1}H NMR spectra were recorded on Hitachi R-24B and Varian Inova 400 VLX spectrometers using tetramethylsilane (TMS) as an internal standard in chloroform-*d* (CDCl$_3$). FT-IR spectra were recorded on a Hitachi 260–30 spectrometer, and transmission spectra were measured by neat on a NaCl disk.

Mechanical properties of the cured products were measured by a tensile testing machine (Tensilon UTM-II, Toyo Boldwin Co., Ltd) at 23 °C with the crosshead speed adjusted to 2 mm min^{-1}. The tensile strength and elongation were estimated from the observed stress–strain diagram. The elastic modulus under tension was also calculated from the value of the stress at 10% strain.
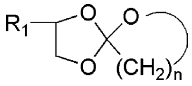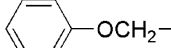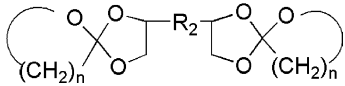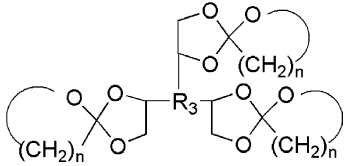
2.2. Materials

All solvents for syntheses and reactions were dried by ordinary methods, and then purified by distillation. All catalysts listed in Table 2 including Lewis acids, onium salts, and phosphine derivatives were commercially purchased and used without further purification. SOEs (SOE-I–VII, IX, XI–XV) in Table 1 were prepared according to the literature in 11–66% yields [13,14]. Almost all the acid chlorides, acetic anhydride, and benzyl chloride listed in Table 4 were reagent grade, and used without further purification.

2.3. Syntheses of SOE-VIII, X, XVI, and XVII

In a typical procedure, a solution of 38.01 g (0.267 mol) of 1,2,7,8-diepoxyoctane in 100 ml of anhydrous dichloromethane was added drop-wise over a period of 1 h at a temperature below 10 °C in a nitrogen atmosphere to a solution of 80.18 g (0.801 mol) of δ-valerolactone and 0.5 ml of boron trifluoride etherate (BF$_3 \cdot$OEt$_2$) as a catalyst in 200 ml of anhydrous dichloromethane. After the addition was completed, the mixture was stirred for 1 h at the same temperature and stirring continued overnight at room temperature. The reaction was quenched by the addition of 5 ml of triethylamine. The reaction mixture was poured into 500 ml of 10% NaOH aqueous solution and stirred for a moment. The mixture was then permitted to stand until the organic layer had separated from the aqueous layer. The organic layer was taken out, washed with three portions of

The article deals with the double ring-opening polyaddition of SOEs with acid chlorides at even lower temperatures. It consists of (1) screening catalysts for the reaction of SOEs with benzoyl chloride, (2) investigating phosphonium salts as effective catalysts in the reaction, and (3) analyzing the curing behavior of bi- or trifunctional SOEs and acid chlorides with phosphonium salts, and then (4) evaluating the volume change and the mechanical properties of the cured products.

place at a higher temperature, it is difficult to meet the requirements for precise molding. Such precision molding using the expandable or non-shrinking monomers needs to be processed under milder conditions.

One promising way of improving the properties of homopolymers is to copolymerize them with active comonomers. So far, Klemm and Haase have reported the copolymerization of SOE with maleic anhydride at 160 °C to obtain the corresponding polyester and poly(ether–ester), for which the copolymerization behavior was not fully characterized [12].

In our previous report [13,14], we succeeded in a selective polyaddition of bifunctional SOEs with bifunctional acid chlorides, in which the double ring-opening reaction of SOEs occurred repeatedly to obtain the corresponding copolymers with very little volume change in a range of 0.2% expansion to 1.3% shrinkage (Scheme 2). This double ring-opening polyaddition proceeded at lower temperatures (~60 °C) than those required for the homopolymerization of SOEs.

Scheme 2. Polyaddition of bifunctional spiro orthoester with bifunctional acid chloride accompanying the double ring-opening reaction.

Table 1
List of spiro orthoesters

	R	n=3	4	5	—CHCH3 / -CH2·CH2
R1 structure	CH3OCH2–	I	II	III	
	ClCH2–			IV	
	BrCH2–			V	
	(phenyl)—OCH2–		VI	VII	
	HOCH2–		VIII		
R2 structure	–CH2O–(CH2)2–OCH2–		IX		X
	–CH2O–(CH2)2–OCH2–	XI	XII	XIII	
	–CH2O–(CH2)6–OCH2–			XIV	
	—CH2O–C(CH3)2–OCH2—			XV	
	—(CH2)4—				
	–(CH2)4–		XVI		
R3 structure	—CH2O–C(CH2–O–)(C2H5)–OCH2—		XVII		

water, and dried over anhydrous magnesium sulfate overnight. After the filtration and evaporation of the solvent under a reduced pressure, the residue was distilled fractionally to yield 44.7 g (49%) of SOE-XVI. Bp: 154 °C at 0.05 mmHg, ^{1}H NMR (CDCl$_3$, δ): 1.0–2.3 (m, 16H), 3.3–4.5 ppm (m, 10H). IR (neat): 910, 940, 970, 1030, 1070, 1090 (ν_{C-O-C}) cm^{-1}. Elem. anal. calcd for C$_{18}$H$_{30}$O$_6$: C, 63.14; H, 8.83%. Found: C, 62.91; H, 8.93%.

SOE-VIII was synthesized from glycidol and δ-valerolactone by a similar procedure to that for SOE-XVI. Yield: 8%. Bp: 72 °C at 0.02 mmHg, ^{1}H NMR (CDCl$_3$, δ): 1.3–2.1 (m, 6H), 3.5–4.1 ppm (m, 7H). IR (neat): 975, 1030, 1070, 1150 (ν_{C-O-C}), 3450 (ν_{O-H}) cm^{-1}.

SOE-X was also synthesized from ethylene glycol diglycidyl ether and γ-valerolactone by a similar procedure. Yield: 20%. Bp: 189–191 °C at 0.17 mmHg, ^{1}H NMR (CDCl$_3$, δ): 1.25 (d, 6H), 1.4–2.35 (m, 8H), 3.3–4.55 (m, 12H), 3.60 ppm (s, 4H). IR (neat): 980, 1040, 1110 (ν_{C-O-C}) cm^{-1}. Elem. anal. calcd for C$_{18}$H$_{30}$O$_8$: C, 57.74; H, 8.08%. Found: C, 57.07; H, 8.15%.

Trifunctional SOE-XVII was obtained as a viscous liquid from trimethylolpropane triglycidyl ether and ε-caprolactone with BF$_3$·OEt$_2$ as a catalyst by a similar procedure. Crude product was purified by liquid–liquid extraction with n-hexane to yield a milky white viscous liquid quantitatively, ^{1}H NMR (CDCl$_3$, δ): 0.6–1.0 (t, 3H), 1.0–2.0 (m, 20H), 3.0–4.6 ppm (m, 27H). IR (neat): 970, 1015, 1065, 1090, 1145 (ν_{C-O-C}) cm^{-1}. Elem. anal. calcd for C$_{30}$H$_{50}$O$_{12}$: C, 59.78; H, 8.36%. Found: C, 59.91; H, 8.86%.

2.4. Synthesis of trifunctional acid chloride

Trifunctional acid chloride: 1,3,5-pentanetricarbonyl trichloride (PTC) was prepared from 1,3,5-pentanetricarboxylic acid (PTA) and phosphorus pentachloride. Phosphorus pentachloride 179 g (860 mmol) was added to PTA 50.0 g (245 mmol) in benzene 250 ml in a cold bath. The mixture was stirred at ambient temperature for 1 day, and then the solvent and phosphoryl chloride as a by-product were evaporated. After the filtration, the filtrate was treated by liquid–liquid extraction with anhydrous n-hexane to isolate PTC as a slightly yellowish viscous liquid. Yield: 54.0 g (84.9%). ^{1}H NMR (CDCl$_3$, δ): 1.7–2.6 (m, 4H), 2.6–3.4 ppm (m, 5H). IR (neat): 1780 cm^{-1} ($\nu_{C=O}$). Elem. anal. calcd for C$_8$H$_9$Cl$_3$O$_3$: C, 37.03; H, 3.50; Cl, 40.98%. Found: C, 36.95; H, 3.41; Cl, 41.49%.

2.5. Effect of various catalysts on the reaction of SOE-II and benzoyl chloride

To a mixture of SOE-II 1.0 g (5.31 mmol) and an equivalent amount of benzoyl chloride (BC) 0.75 g (5.31 mmol) in a 5 ml test tube, a catalyst (0.5 mol% based on the amount of SOE moiety: [SOE]) was added. The tube was sealed, and heated and kept at 100 °C for 2 h. Thereafter, the reaction mixture was cooled, dissolved in CDCl$_3$, and then its ^{1}H NMR spectrum was measured to determine the conversion of the double ring-opening reaction of SOE-II.

2.6. Reaction of various types of SOEs with BC in the presence of tetraphenylphosphonium bromide

To a mixture of SOE 1.0 g and benzoyl chloride (equivalent amount to [SOE]) in a 5 ml test tube, tetraphenylphosphonium bromide (TPPB) 0.5 mol% based on [SOE] was added as a catalyst. The tube was sealed, and heated and kept at 100 °C for 2 h. After the reaction, the mixture was cooled, dissolved in CDCl$_3$, and then its ^{1}H NMR spectrum was measured to determine the conversion of the double ring-opening reaction of SOE moiety.

2.7. Reaction of SOE-II with various types of acid chlorides and related compounds in the presence of TPPB

To a mixture of SOE-II 1.0 g (5.3 mmol) and acid chloride or related compound (equivalent amount to [SOE]) in a 5 ml test tube, TPPB 0.5 mol% based on [SOE] was added. The tube was sealed, and heated at 60 or 100 °C. After the desired time, the reaction mixture was cooled, dissolved in CDCl$_3$, and then its ^{1}H NMR spectrum was measured to determine the conversion of the double ring-opening reaction of SOE-II.

2.8. Effect of the reaction temperature on the reaction of SOE-II with adipoyl chloride in the presence of TPPB

To a mixture of SOE-II 1.88 g (9.99 mmol), adipoyl chloride 0.92 g (5.0 mmol), and CDCl$_3$ 1.5 g in a NMR sample tube, TPPB 0.5 mol% based on [SOE] was added. The sample tube was sealed, and heated at a predetermined temperature. After the desired time, the reaction mixture was cooled, and the ^{1}H NMR spectrum was measured to determine the conversion of the double ring-opening reaction of SOE-II.

2.9. Curing reaction of SOEs and PTC

A curing reaction of SOE-XII with PTC in the presence of TPPB was carried out to measure the gelation time, volume change, and mechanical properties of the products.

A mixture of PTC 0.50 g (1.92 mmol) and a prescribed amount of TPPB was added to a SOE-XII 1.16 g (2.88 mmol) in a 5 ml tube. The tube was sealed, and then stirred under predetermined conditions. The gelation time was defined as the time it took for the reaction mixture to lose its fluidity.

The volume change during the curing reaction of SOE-XII and PTC was monitored with a calibrated meniscus cylinder of 5.00 ml as a dilatometer at 30 °C. PTC 2.58 g (9.94 mmol), SOE-XII 6.00 g (14.93 mmol), and TPPB 0.125 g (0.298 mmol, 1 mol% based on [SOE]) were mixed to form a homogeneous solution. A part (5.23 g) of the mixture was poured into a dilatometer and then the headspace of the meniscus cylinder was replaced with nitrogen. The bottom level of the mixture surface flush with

the gaseous phase in the meniscus was monitored by cathetometer during the curing reaction and the corresponding volume change was calculated from this bottom level.

To evaluate the mechanical properties of the cured products, test pieces of the dumbbell shape were prepared with a Teflon template. Polyfunctional SOE, PTC and TPPB were mixed in prescribed amounts, and the mixture was transferred into the template as a reactor, after which the reactor was settled at 2 atm in a high-pressure polymerization apparatus. After the curing reaction under the prescribed conditions, the mechanical properties of the cured products were evaluated with a tensile testing machine at 23 °C.

3. Result and discussion

3.1. Effect of various catalysts on the reaction of SOE and acid chloride

At first, catalytic activity on the double ring-opening addition reaction of SOE and acid chloride was estimated using various catalysts. According to the reported cationic mechanism of the reaction [14], two groups of reagents for the cationic reaction were tested as the catalysts: (1) Lewis acids and derivatives and (2) onium salts. The reaction of monofunctional SOE, 2-methoxymethyl-1,4,6-trioxaspiro [4,5] decane (SOE-II), and benzoyl chloride (BC) was carried out in the feed ratio [SOE]:[–COCl] = 1:1 with catalysts of approximately 0.5 or 3 mol% based on [SOE] at 100 °C for 2 h in bulk. On the basis of the previous report [14], the conversion of SOE was determined by ^{1}H NMR analysis of the reaction mixture. After the reaction, a signal of methine proton (C^2–H) in SOE ring shifted downfield to appear at 5.2 ppm as an isolated quintuplet (signal *a* in Fig. 1). Thus, this signal intensity (*I*) was used to calculate the conversion of SOE moiety according to the following Eq. (1):

Conversion (%)

$$= [I_a/(I_{\text{total signals}}/\text{total number of protons})] \times 100 \qquad (1)$$

Results are listed in Table 2 (run 2–18). In the absence of catalyst, the conversion was 17% under the conditions (run 1). Almost all reagents accelerated the reaction except for (Ph)$_3$SnCl. These results indicate that the reaction proceeded through a cationic mechanism. Especially, in the presence of SnCl$_4$, tetraphenylphosphonium halides (TPPXs, X: halogen), or tetraphenylarsonium chloride (TPAC), the conversion of SOE-II drastically increased to higher than 86%, and nearly total consumption was achieved using 0.5 mol% tetraphenylphosphonium chloride (TPPC), tetraphenylphosphonium bromide (TPPB), and TPAC (run 11, 12 and 14). Onium salts also showed relatively high catalytic activity, however, the reaction was
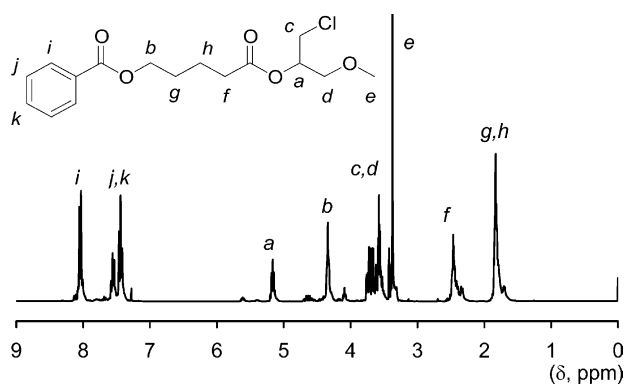
Fig. 1. ^{1}H NMR spectrum of the reaction mixture of SOE-II and BC in the presence of TPPB 0.5 mol% based on [SOE] at 100 °C for 2 h.

not completed. This result suggests the important role of halogen anions in the reaction mechanism.

To examine the high catalytic activity of phosphonium halides, some phosphine derivatives (run 19–21 in Table 2) were also used as catalysts for the reaction under the same conditions. Since, as results, the conversions of SOE-II using phosphine derivatives were relatively low, in a range of 16–28%, the catalytic activity of TPPX must be a characteristic property of the combination (phosphonium cation + halogen anion).

Fig. 1 shows the ^{1}H NMR spectrum of the as-prepared product obtained in the reaction of SOE-II and BC in the presence of 0.5 mol% TPPB (run 12 in Table 2). All the main signals in the spectrum were assigned to the corresponding protons in the structure of an adduct shown in Fig. 1, which agreed with the spectrum of the product obtained without any catalyst as reported previously [13, 14]. Therefore, the product was determined to be the equimolar adduct of SOE-II and BC, and it is clear that TPPB acted as a catalyst on the double ring-opening addition reaction of SOE and acid chloride (Scheme 3).

3.2. Effect of various types of SOEs and acid chlorides

Reactions of various types of SOEs with BC were carried out in both the absence and presence of TPPB at 100 °C for 2 h in bulk. The results are listed in Table 3. In the previous report [14], the order of reactivity of SOEs with adipoyl chloride (AC) in the absence of catalyst was found to be $(5+7) \gg (5+6) > (5+5)$ membered rings (e.g. SOE-III $\gg$ SOE-II $>$ SOE-I), which agreed with that of the ring strain. In the presence of

Table 2
Catalytic activity on ring-opening reaction of SOE-II with BC

Run	Catalyst	(mol%)[a]	Conversion of SOE-II[b] (%)
1	–		17
2	$BF_3 \cdot O(Et)_2$	0.50	17
3		3.00	94
4	$AlCl_3$	0.48	26
5		2.85	63
6	$SnCl_4$	0.50	91
7	$(Ph)_2SnCl_2$	0.51	41
8		2.94	100
9	$(Ph)_3SnCl$	0.49	15
10		2.98	19
11	$(Ph)_4P^+ \ ^-Cl$	0.51	100
12	$(Ph)_4P^+ \ ^-Br$	0.51	97
13	$(Ph)_4P^+ \ ^-I$	0.50	86
14	$(Ph)_4As^+ \ ^-Cl$	0.50	98
15	$(Ph)_3C^+ \ ^-BF_4$	0.51	28
16		3.00	79
17	$(Ph)_3C^+ \ ^-PF_6$	0.50	32
18		2.99	78
19	$(Ph)_3P$	0.50	28
20	$(Ph)_2PCl$	0.50	21
21	$(Ph)PCl_2$	0.50	16

Conditions: [SOE]:[–COCl] = 1:1, 100 °C, 2 h, in bulk.
[a] Based on [SOE].
[b] Determined by ^{1}H NMR analysis.

TPPB, the catalyst accelerated the reactions of all SOEs with BC under the conditions (100 °C, 2 h).

Reactions of SOE-II with various types of acid chlorides were carried out in both the absence and presence of TPPB at 60 °C for 1 or 3 h in bulk. The results are listed in Table 4. In all cases, the conversion of SOE-II increased in the presence of TPPB. In the absence of catalyst, the reactivity of aliphatic acid chlorides was in an order of mono- > bi- > trifunctional structure. This order can be explained in terms of the inductive effect of the substituent. However, in the presence of TPPB, the reactivity was changed to the order tri- ≈ bi- > monofunctional structure. This suggests that there is a kind of cooperative action by neighboring acid chlorides. The reactivity of aromatic acid chlorides was less than that of aliphatic ones because of the lower electrophilicity of the acyl cation caused by the resonance effect.

In Table 4, some reference reactions were also conducted without acid chloride and with acid anhydride and benzyl chloride at 100 °C for 2 h in bulk. No conversion of SOE-II was found in these cases. These results suggest that the creation of the chlorine anion from acid chloride is essential in the catalytic reaction.
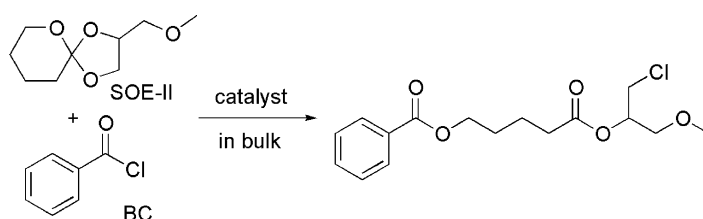
Scheme 3. Double ring-opening addition reaction of SOE-II and BC in the presence of TPPB.

Table 3
Addition reaction of SOEs and benzoyl chloride

Run	SOE	Conversion of SOE[a]		
		n	Without TPPB	With TPPB[b]
1	I	3	15	100
2	II	4	17	97
3	III	5	36	100
4	IV	5	17	97
5	V	5	19	89
6	VI	4	10	75
7	VII	5	25	100
8	VIII	4	100	100
9	IX	4	15	92
10	X	3^l	37	100
11	XI	3	29	91
12	XIII	5	72	100
13	XIV	5	84	85
14	XV	5	86	89
15	XVI	4	13	85

Conditions: [SOE]:[–COCl] = 1:1, 100 °C, 2 h, in bulk.
[a] Determined by ^{1}H NMR analysis.
[b] 0.5 mol% TPPB based on [SOE].

3.3. Effect of the reaction temperature

To clarify the effect of temperature, the catalytic reaction of SOE-II with AC was carried out at various reaction temperatures in the feed ratio [SOE]:[–COCl] = 1:1 in CDCl$_3$. Fig. 2 shows the plots of conversion of SOE-II against reaction time. In this figure, the initial value of approximately 20% of the conversion means the conversion during the sample preparation process in the presence of TPPB 0.5 mol%. At 100 °C, SOE-II was smoothly consumed and the conversion reached 100% within 20 min. The consumption rate decreased when the reaction temperature was lowered, however, the reaction smoothly proceeded at 40 °C and, surprisingly, the reaction was found to proceed gradually even at 25 °C (room temperature) to reach the

conversion of 90% after 20 h. This suggests that this catalytic reaction can give a cured product without requiring any heating or cooling steps throughout the total polymerization process.

3.4. Curing reaction of polyfunctional SOEs and PTC

The curing reaction of bi- or trifunctional SOEs and acid chlorides was carried out in the feed ratio [SOE]:[–COCl] = 1:1 with TPPB in bulk. Bifunctional SOE-XII and trifunctional 1,3,5-pentanetricarbonyl trichloride (PTC) were chosen as comonomers. In order to evaluate the curing rate, the gelation time was measured under the various TPPB concentrations in the range of 0.02–1 mol% based on [SOE] at 25, 60 and 100 °C, in which the gelation time

Table 4
Addition reaction of SOE-II and various types of acid chlorides and related compounds

Run	Acid chlorides and related compounds	Temp. (°C)	Time (h)	Conversion of SOE-II[a]	
				Without TPPB	With TPPB[b]
1	CH$_3$COCl	60	1	38	47
2			3	65	72
3	ClCO–(CH$_2$)$_4$–COCl	60	1	31	72
4			3	54	94
5	ClCO–CH$_2$CH$_2$–CH(COCl)–CH$_2$CH$_2$–	60	1	24	71
6	COCl (PTC)		3	41	94
7	Isophthaloyl dichloride	60	1	7	34
8			3	11	63
9	1,3,5-Benzenetricarbonyl trichloride	60	1	21	61
10			3	30	88
11	–	100	2	–	0
12	CH$_3$C(=O)–O–C(=O)CH$_3$	100	2	–	0
13	Ph–CH$_2$Cl	100	2	–	0

Conditions: [SOE]:[–COCl] = 1:1, in bulk.
[a] Determined by ^{1}H NMR analysis.
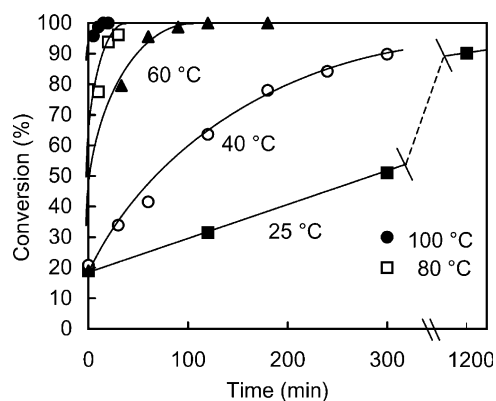[b] 0.5 mol% TPPB based on [SOE].

Fig. 2. Changes in the conversion of the reaction of SOE-II and adipoyl chloride at various temperatures. The reaction was carried out at a feed ratio [SOE]:[–COCl] = 1:1 in the presence of TPPB 0.5 mol% based on [SOE] in CDCl$_3$.

Fig. 3. Volume change in the reaction of SOE-XII with PTC at a feed ratio [SOE]:[–COCl] = 1:1 in the presence of TPPB 1 mol% based on [SOE]. The reaction was carried out at 30 °C in bulk under a nitrogen atmosphere.

means the time during which the reaction mixture lost fluidity. The results are listed in Table 5.

The gelation time was shortened with increases in TPPB concentration and reaction temperature. In particular, the addition of 1 mol% TPPB led to gelation occurring within 39 min at 60 °C and 20 h even at 25 °C. The structure of the gel product was determined with FT-IR. The FT-IR spectra of products in run 1′ and 1″ showed characteristic peaks at 1740 and 750 cm^{-1} attributable to the vibration of C=O and C–Cl stretching, whereas the characteristic peaks of SOE-XII (ν_{C-O-C}) and TPC ($\nu_{C=O}$) had almost disappeared, meaning that the reaction had almost finished by the time that the reaction mixture had set to gel. A similar result was also obtained by the gel product in run 1 at 25 °C after 144 h. This indicates that the curing reaction of SOE-XII and PTC can be completed even at room temperature in the presence of TPPB.

In order to examine the network structure of the products, the cured products were immersed in a range of organic solvents at room temperature for 3 days. No change in appearance of the products was found for isopropanol and n-hexane, whereas swelling was observed against methanol, ethyl acetate, chloroform and benzene. These facts indicate that the gelled products were the crosslinked copolymers as expected.
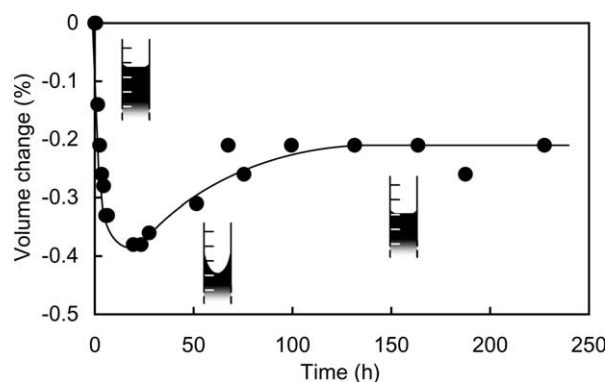
3.5. Volume change during the curing reaction

Volume change during the curing reaction of a mixture of SOE-XII and PTC in the feed ratio [SOE]:[–COCl] = 1:1 with TPPB (1 mol% based on [SOE]) was monitored using a dilatometer at 30 °C for 227.5 h. Fig. 3 shows a plot of the volume change against the reaction time during the reaction. It was observed that the level of the center of the mixture surface flush with the gaseous phase in the meniscus cylinder was rapidly lowered to show an apparent volume shrinkage of 0.38% at 19.5 h, after which the surface gradually recovered a flat shape to show 0.21% volume shrinkage after 100 h. The irregular volume changes in Fig. 3 may be due to the high viscosity of the mixture and the heterogeneous curing process in the dilatometer. The curing must start rapidly from internal surface of dilatometer to cause the lowering of level at the center of surface in the meniscus cylinder, and thereafter it is likely that the diffusion rate overcame the curing rate to become a homogeneously cured product. This shrinkage value 0.21% is reasonable because it is within the range of values (0.2% expansion to −1.3% shrinkage) reported for the reaction previously [13].

This result demonstrates that it is possible, without any heating and cooling processes, to form the cured product with negligible volume shrinkage using the double

Table 5
Curing reaction of SOE-XII and PTC

TPPB (mol%)[a]	Run	Gelation time[b] at 25 °C (h)	Run	Gelation time at 60 °C (min)	Run	Gelation time at 100 °C (min)
0.05	1	<72	1′	130	1″	10
0.1	2	<48	2′	125	2″	<5
0.2	3	<48	3′	97	3″	<5
0.5	4	<48	4′	55	4″	<5
1	5	<20	5′	39	5″	<5

Conditions: [SOE]:[–COCl] = 1:1, in bulk.
[a] Based on [SOE].
[b] Time of missing the fluidity of mixture.

Table 6
Mechanical properties of cured products of SOEs and PTC

Run	SOE	Curing conditions[a]		Mechanical properties of product[b]		
		Temp. (°C)	Time (h)	Tensile strength[c] (10^5 Pa)	Elastic modulus in tension[c,d] (10^7 dyn cm^{-2})	Elongation[c] (%)
1	XII	25	96	2.9	1.5	22.2
2		60	3	3.5	4.0	9.4
3			5	4.4	3.0	15.2
4			20	3.5	2.6	14.1
5			24	3.9	3.3	12.9
6		100	1	5.4	2.9	19.2
7			2	5.0	3.1	17.1
8			4	6.1	3.0	23.9
9	XVI	60	5	5.7	4.9	13.0
10		100	2	6.7	4.1	19.7
11	XII+XVII[e]	25	96	6.3	6.7	11.7
12		60	5	7.6	6.0	13.0

[a] Conditions: [SOE]:[–COCl]=1:1, in bulk, 1 mol% TPPB based on [SOE].
[b] Measured at 23 °C; crosshead speed, 2 mm min^{-1}.
[c] Estimated from stress–strain diagram.
[d] Calculated from the value of stress at 10% strain.
[e] [SOE]$_{XII}$=[SOE]$_{XVII}$.

ring-opening polyaddition system of SOE and acid chloride with phosphonium halides as catalyst.

3.6. Mechanical properties of cured materials

Mechanical properties of cured products, which were prepared from some kinds of polyfunctional SOEs and PTC at a fixed feed ratio: [SOE]:[–COCl]=1:1 with TPPB 1 mol% based on [SOE] at various temperatures, were evaluated by the tensile mode at 23 °C. The results are listed in Table 6.

The tensile strength of the cured products increased with increase in the reaction temperature to show 2.9, 3.5–4.4, 5.0–6.1×10^5 Pa at 25, 60 and 100 °C, respectively. However, the elastic modulus was constant at around 3× 10^7 dyn cm^{-2} except for the product at 25 °C (run 1 in Table 6). The difference in the tensile strength of the products cured at 60 and 100 °C may be due to some differences in network structures of the products.

On the other hand, both the tensile strength and the elastic modulus were improved by using SOE-XVI and XVII (run 9–12 in Table 6). The improvement of the mechanical properties was dependent on the structure of SOE. SOE-XVI has shorter linker between SOE moieties, and does not have the flexible ether linkage found in SOE-XII. SOE-XVII is a trifunctional SOE, which is expected to

Table 7
Tension property of cured product in various feed ratio of SOEs and PTC

Run	SOE	Curing[a] [SOE]/[–COCl]	Mechanical properties of cured product[b]		
			Tensile strength[c] (10^5 Pa)	Elastic modulus[c,d] (10^7 dyn cm^{-2})	Elongation[c] (%)
1	XII	1.00	3.6	2.1	18.1
2		0.95	4.5	4.1	11.8
3		0.90	3.2	2.7	11.6
4		0.85	–	2.2	–
5		0.80	3.7	1.6	26.3
6		0.75	2.3	1.1	22.4
7		0.70	0.9	0.4	26.5
8	XVI	1.00	4.9	3.5	16.6
9		0.95	6.3	3.8	17.7
10		0.90	4.4	2.7	17.6
11		0.85	1.9	1.1	20.5
12		0.80	2.2	1.1	21.1

[a] Conditions: at 60 °C, 5 h, in bulk, and 1 mol% TPPB based on [–COCl].
[b] 23 °C, crosshead speed at 2 mm min^{-1}.
[c] Estimated from the observed stress–strain diagram.
[d] Calculated from the stress value at 10% strain.
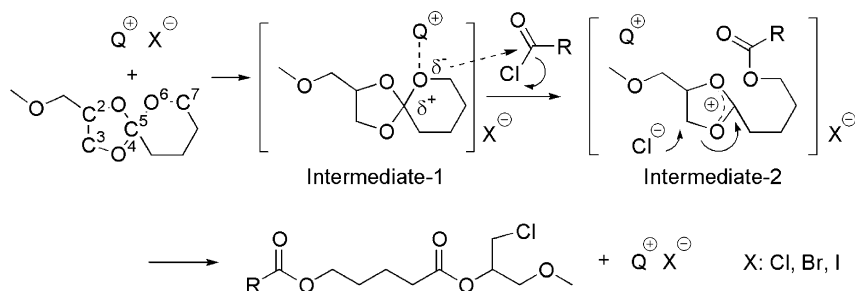
Scheme 4. Plausible reaction pathway for the double ring-opening addition reaction of SOE-II and acid chloride in the presence of catalyst ($Q^+ X^-$).

form a more highly crosslinked structure than SOE-XII. This was shown in the results with products obtained using SOE-XVI and XVII, showing significant increases in both tensile strength and the elastic modulus up to 7.6×10^5 Pa and 6.0×10^7 dyn cm^{-2}, respectively.

In our previous report [13], it was suggested that the homopolymerization of SOE moiety by the acyl cation also occurred as a minor reaction. Taking into account the homopolymerization of SOE moiety, the curing reaction was examined at various feed ratios in a range of [SOE]: [–COCl]=1:1.0–0.7. The curing reactions of SOE-XII and XVI with PTC were conducted in bulk at 60 °C for 5 h with 1 mol% TPPB based on [–COCl]. The mechanical properties of the obtained curing products are listed in Table 7. The highest values of both tensile strength and elastic modulus were found generally at the feed ratio of 1:0.95 in both cases of SOE-XII and XVI. These results might be due to the cationic homopolymerization of SOE moiety initiated by the acyl cation, which proceeded in a lower level as a side reaction.

3.7. Plausible reaction mechanism

Scheme 4 depicts the plausible reaction pathway for the double ring-opening addition reaction of SOE-II and an acid chloride, in which Q^+X^- denotes a pair of phoshonium cation (Q^+) and halogen anion (X^-) as a catalyst. It is considered that, in this reaction, phoshonium cation interacts with O^6 in an oxane ring of SOE moiety to produce a corresponding intermediate-1. The interaction causes the scission of the C^5–O^6 bond, followed by the addition of an alkoxy anion ($^-O^6$–C^7) with an acyl cation derived from acid chloride to form intermediate-2. The intermediate-2 is the same as the intermediate of the reaction in the absence of catalyst reported previously [14]. Finally, the intermediate-2 reacts with the chlorine anion at C^3 to form a carbonyl group ($>C^5=O^4$) and give the corresponding adduct. Nishikubo and co-workers also reported a similar mechanism, in which they discussed a ring-opening addition reaction of epoxides with chloroformate in the presence of quaternary onium salts such as TPPB as catalyst [15,16].

In this reaction mechanism, the formation of intermediate-1 must be an important process, because its formation makes the activation energy for the intermediate-2 formation decrease.

4. Conclusions

To achieve the curing reaction of spiro orthoester (SOE) and acid chloride at lower temperature, the reaction was carried out with catalysts, such as tetraphenylphosphonium halides (TPPXs). The addition of TPPXs drastically accelerated the reaction to lower the reaction temperature to 25 °C (room temperature). The reaction product was confirmed to have an expected structure, which had formed according to the double ring-opening addition mechanism, and was identical to that produced from SOE and acid chloride in the absence of catalyst. This catalytic reaction was adaptable to various types of SOEs and acid chlorides.

The curing reaction of bifunctional SOE-XII and trifunctional 1,3,5-pentanetricarbonyl trichloride proceeded at 30 °C in the presence of 1 mol% TPPB and led to the crosslinked material accompanied by only 0.21% shrinkage. This is the first demonstration of a curing system using the shrinkage-controlled monomers without any heating or cooling processes.

The mechanical properties of the cured products were also evaluated, resulting in an improvement of the properties by the selection of proper polyfunctional SOEs, acid chlorides, and curing conditions.

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