**Full Paper:** The zinc glutarate catalyzed copolymerization of sulfur dioxide (SO_2) and propylene oxide (PO) was investigated in detail by varying temperature, time, monomer feed ratio, and PO feed per catalyst as well as by using solvents, such as PO and chloroform. An optimized copolymerization [PO]/[catalyst] = 300, and no solvent at $60\,°C$, 40 h, [PO]/[SO_2] = 1, resulted in poly(propylene sulfite) (PPS) with high molecular weight $\overline{M}_n = 42\,000$ ($\overline{M}_w/\overline{M}_n = 2.1$) never achieved before. PPS was obtained in a yield of 66.9 g per g of catalyst (namely, 12.93 kg per mol of catalyst) and determined to consist of 90.4 mol-% sulfite-linkage and 9.6 mol-% ether-linkage. A polymer containing a large amount of ether-linkages was additionally formed as a minor component. However, no formation of cyclic propylene sulfite as byproduct was detected. In addition, zinc hexacyanoferrate(III) was prepared and used in the copolymerization as a catalyst, but showed almost no catalytic activity.
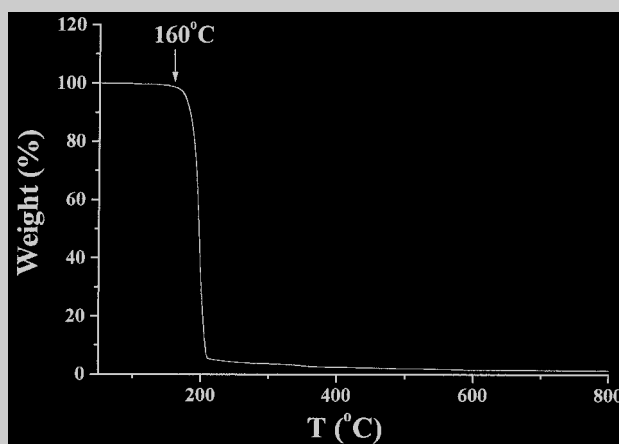
TGA thermogram of a PPS product containing 90.4 mol-% sulfite-linkages and 9.4 mol-% ether-linkages: $\overline{M}_n = 42\,000$ with $\overline{M}_w/\overline{M}_n = 2.1$

Synthesis and characterization of poly(propylene sulfite) from sulfur dioxide and propylene oxide using zinc derivatives as catalysts

Byeongdu Lee, Jae Hwan Jung, Moonhor Ree*

School of Environmental Engineering, Department of Chemistry, BK21-Functional Polymer Thin Film Group, and Polymer Research Institute, Pohang University of Science & Technology, San 31, Hyoja-dong, Pohang 790–784, Korea
ree@postech.edu

Introduction

Sulfur dioxide (SO_2) does not polymerize by itself but undergoes radical copolymerizations with various olefins to form polysulfones[1]. The radical copolymerizations have been investigated in details and their various aspects reviewed in the literature[1–3]. As one result of these research efforts, poly(1-butene sulfone), which is the representative of sulfur dioxide copolymers, is widely used in the microelectronic industry as an electron-beam resist material[4].

SO_2 can also copolymerize ionically with oxirane monomers, leading to polysulfites[1,5–8]. In the late 1960s the cationic copolymerization of SO_2 with propylene oxide (PO) was first reported by Schaefer and coworkers[7,8]. In the cationic copolymerization they used $SnCl_4$, $SbCl_5$, or $Zn(C_2H_5)_2$ as initiators of the Lewis acid type. The $TiCl_3 \cdot Al(C_2H_5)_3$ system was also examined as an initiator in the copolymerization[1,9]. There were, however, oligomeric products obtained to have a low molecular weight of 1 000–2 000 and furthermore to contain a relatively low content (28–64 mol-%) of sulfite-linkage, depending upon the reaction conditions as well as the sort of comonomer.

On the other hand, the anionic copolymerization of SO_2 was attempted with oxiranes using organic Lewis bases, such as pyridine, quinoline, α-picoline, and phosphines, as initiators[10–14]. The copolymerization products contained ≤98 mol-% of sulfite-linkages. The copolymer composition is known to be independent upon the feed ratio of comonomers[10,12]. The copolymers were obtained with a molecular weight of 1 000–15 000, depending upon the sort of oxirane comonomer[10,12,13]. This molecular weight still is too low for applications in the industrial field. These copolymers were reported to be very

unstable, because of the back-biting reaction initiated by the sulfite ions at the chain ends[14]. In addition to the oligomeric product, cyclic propylene sulfite (CPS) was found to be always formed: in the copolymerization catalyzed by pyridine, the CPS was obtained in 3.5% yield relative to the oligomeric product[13].

As described above, polysulfites of a high molecular weight could not be obtained, contrary to the polysulfones, so that there is still a big challenge to synthesize high molecular weight copolymers from SO_2 and oxirane. The reactivity of oxirane towards SO_2 is known to be in the increasing order of epichlorohydrin < glycidyl acetate < propylene oxide < butyl glycidyl ether < ethylene oxide < cyclohexene oxide[14]. Because of the relatively high reactivities, cyclohexene oxide and ethylene oxide have been investigated extensively for the copolymerization with SO_2. In contrast, PO, which is a major downstream product from naphtha cracking, has been rarely studied for the copolymerization.

In the present study, the copolymerization of SO_2 with PO was further investigated using zinc glutarate and zinc hexacyanoferrate(III) as catalysts, in order to achieve high molecular weight poly(propylene sulfite) (PPS). The copolymerization was carried out by varying temperature, time, monomer loading, and catalyst loading. The copolymer products were characterized by nuclear magnetic resonance spectroscopy, infrared spectroscopy, viscometry, gel permeation chromatography, differential scanning calorimetry, and thermogravimetry.

Experimental part

Materials

Propylene oxide (PO) was obtained from SK Oxichemical Company (Korea) and was purified by distillation over CaH_2 just before use. Sulfur dioxide (99.5% purity) was purchased from Shin-Ahn Gas Company (Korea) and used without further purification. Pyridine and chloroform, purchased from Aldrich Chemical Company (USA), were purified in conventional manners, respectively. Other chemicals used in this study were supplied from Aldrich, and used as received.

Synthesis of catalysts

The zinc glutarate catalyst was prepared from zinc oxide and glutaric acid, in accordance to a method[15] described previously, as follows. Zinc oxide of 8.137 g (100 mmol) was added to toluene of 150 mL in a two neck, round bottom flask of 250 mL which was equipped with magnetic stirrer, condenser, Dean-Stark trap, and heating mantle. To this reaction mixture 12.95 g (98 mmol) of glutaric acid, dissolved in the reaction solvent were added. The reactants were stirred vigorously at 55 °C for 2 h, followed by refluxing for additional 4 h. After cooling down to room temperature, the white powders were filtered off and washed several times using acetone and then dried in a vacuum oven at 80 °C: the yield was 100%

based on the glutaric acid used. In addition, zinc hexacyanoferrate(III) was prepared with a yield of 100% by a synthetic scheme reported previously in the literature[16].

Copolymerization

The copolymerization of SO_2 and PO was conducted in an autoclave (250 mL capacity, Parr Instrument Company) by varying reaction temperature, time, monomer feed ratio, and monomer feed per catalyst. In particular, the reaction temperature was in the range of 40–100 °C and the reaction time in the range of 24–60 h. This copolymerizations were carried out with and without using solvents. Here, the zinc glutarate synthesized as described above was used as a catalyst. The reaction products obtained from each copolymerization were dissolved in chloroform and transferred to a separating funnel. Then the catalyst residue was extracted from the product solution by adding an amount of diluted hydrochloric acid. The extraction was repeated several times. The product solution was subsequently washed two times with water. The product solution was concentrated to a proper volume using a rotary evaporator, and poured into an excess of methanol. The polymer precipitate was filtered off, followed by drying in a vacuum oven at room temperature. In the same manner, using the zinc hexacyanoferrate(III) catalyst the copolymerization was also carried out.

Measurements

Fourier transform infrared (FTIR) spectroscopic analysis was carried out with a resolution of 2 cm^{-1} using an ATI Mattson FTIR spectrometer (Model: Research Series). In addition, proton nuclear magnetic resonance (^1H NMR) spectroscopic analysis was performed using a Bruker NMR spectrometer (Model: ASPECT 300 MHz). In the ^1H NMR spectroscopic measurement, chemical shifts were calibrated with the chemical shifts of the chloroform-d_1 solvent used.

Thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer thermogravimeter (Model: TGA7). During the measurement dry nitrogen gas was purged at a flow rate of 100 mL/min, and a ramping rate of 10.0 K/min was employed.

Number average molecular weight ($\overline{M}_n$) and polydispersity of the polymer products were estimated using a gel permeation chromatography (GPC) system of Polymer Labs (Model: PL-GPC 210) with a set of 4 columns (Alltech Jordi 100 Å, 1000 Å, 10000 Å, and 100000 Å). The GPC system was calibrated by a series of polystyrene standards with a weight average molecular weight ($\overline{M}_w$) of 2000–1260000 and a polydispersity ($\overline{M}_w/\overline{M}_n$) of <1.01, that were supplied from Polysciences Inc. Tetrahydrofuran (THF, HPLC grade) was used as an eluent. In addition, intrinsic viscosity [η] measurements were carried out in THF at 25.0 °C using an Ubbelohde suspended level capillary viscometer. All the solutions were filtered through 0.5 μm Fluoropore filters (Millipore Co.) before measurement. For a given polymer product, the relative and specific viscosities were measured at four different concentrations over the range of 0.10–1.00 g/dL, and the [η] value was determined by extrapolation of the reduced and inherent viscosities to infinite dilution.

Results and discussion

Copolymerization

In the present study, zinc glutarate was found to exhibit a reasonably high catalytic activity for the copolymerization of SO_2 and PO. For example, the copolymerization of SO_2 and PO in an equivalent molar concentration (0.75 mol) was conducted at 60 °C for 40 h, without using any solvent. Here, the zinc glutarate catalyst was used in [catalyst]/[PO] = 1/300. The reaction mixture was sampled in a small amount and then examined by ^{1}H NMR spectroscopy after dissolving it in $CDCl_3$. In the NMR spectrum a cyclic propylene sulfite (CPS) byproduct could not be detected, indicative of no formation of cyclic propylene sulfite from the copolymerization. This result is quite different from the copolymerizations using other catalysts reported previously[1,5–13]: CPS is always formed in the copolymerizations catalyzed with pyridine, quinoline, α-picoline, phosphines, $SnCl_4$, $SbCl_5$, $Zn(C_2H_5)_2$, and $TiCl_3 \cdot Al(C_2H_5)_3$. However, there was unreacted PO observed. The formation of propylene ether linkages was detected from the reaction product mixture, in addition to the formation of propylene sulfite linkages. The total reaction conversion was estimated from the consumption of PO loaded in the copolymerization to be 70.4 mol-%. Here, the total PO consumption was obtained from integration of the characteristic chemical shifts for the propylene ether and propylene sulfite units formed in the copolymerization.

From the copolymerization, the methanol soluble product, which includes a high content of propylene ether linkage, was obtained in a yield of 9.2 g per gram of catalyst. The methanol insoluble product was obtained in a yield of 66.9 g per gram of catalyst (namely, 12.93 kg per mol of catalyst).

The methanol insoluble polymer product was further characterized by FTIR and ^{1}H NMR spectroscopy. As shown in Fig. 1, the product exhibits vibrational stretching
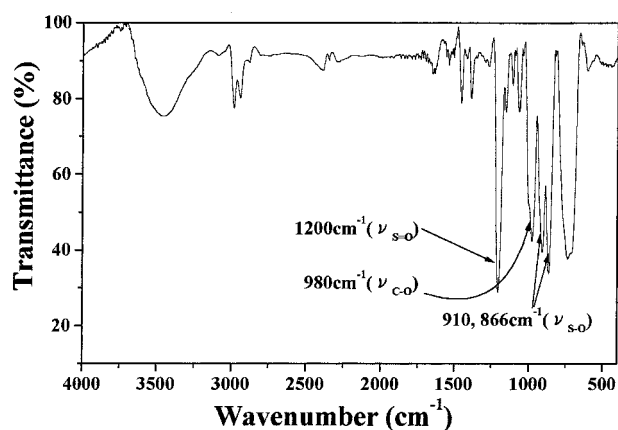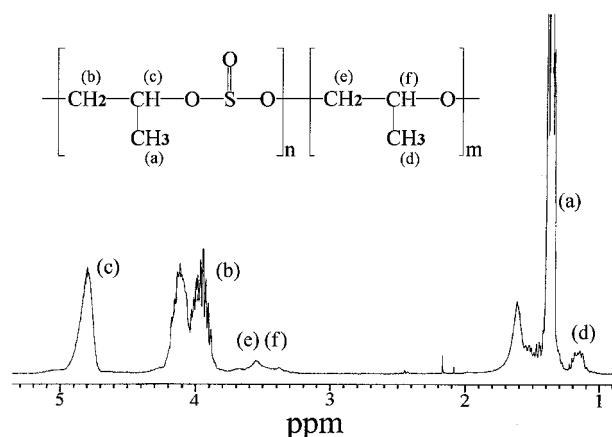
Fig. 2. ^{1}H NMR spectrum of the methanol insoluble polymer product obtained from the copolymerization of SO_2 and PO

frequencies of S=O, C—O, and S—O bonds in the IR spectrum: ν(S=O) at 1200 cm^{-1}, ν(C—O) at 910 cm^{-1}, and ν(S—O) at 866 cm^{-1}. This result indicates that the polymer product contains sulfite-linkages in the backbone. Fig. 2 shows a ^{1}H NMR spectrum of the polymer product: ^{1}H NMR (CDCl$_3$): δ = 0.07–1.24 (3H; C$\underline{H}_3$ of propylene ether linkage), 1.25–1.48 (3H; C$\underline{H}_3$ of propylene sulfite linkage), 3.25–3.42 (1H; CH$_2$C$\underline{H}$ of propylene ether linkage), 3.42–3.65 (2H; C$\underline{H}_2$CH of propylene ether linkage), 3.80–4.30 (2H; C$\underline{H}_2$CH of propylene sulfite linkage), 4.70–5.00 (1H; CH$_2$C$\underline{H}$ of propylene sulfite linkage). The ^{1}H NMR spectrum indicates that the polymer product contains propylene sulfite linkages as well as propylene ether linkages. From the integration of the chemical shifts assigned, the content of propylene sulfite units in the polymer product was estimated to be 90.4 mol-%. That means, poly(propylene sulfite) (PPS) containing 9.6 mol-% ether-linkages [namely: poly(propylene ether-*co*-sulfite)] was obtained. Its intrinsic viscosity [η] was measured to be 0.382 in THF at 25.0 °C. The molecular weight was further measured by GPC analysis: $\overline{M}_n$ = 42000 and $\overline{M}_w/\overline{M}_n$ = 2.1 (polydispersity). This molecular weight is maked by a high value, never achieved before.

In fact, the copolymerization mechanism of SO_2 and PO was not investigated in the present study. However, we may speculate a mechanistic feature from the copolymerization results as well as the consideration of the followings. First, we should think about the active site of the zinc glutarate catalyst. This catalyst consists of an electrophilic zinc metal center and nucleophilic carboxylates. Here, the electrophilicity of the zinc metal center is known to be weaker than the nucleophilicity of the carboxylate[17,18]. In addition, the carboxylate group in zinc carboxylate catalysts was previously reported to be detected at the end of a polycarbonate chain, produced by the catalyzed copolymerization of CO_2 and PO[17,19]. Thus, the copolymerization of SO_2 and PO is anticipated to proceed via an anionic mechanism rather than via a cationic

Fig. 1.   FT-IR spectrum of the methanol insoluble polymer product obtained from the copolymerization of SO_2 and PO

mechanism. Second, the reactivities of SO_2 and PO towards the zinc gluatarate catalyst, as well as the insertion sequence of SO_2 and PO towards the zinc glutarate catalyst should be considered. The sulfur atom of SO_2 is more electrophilic than the methylene carbon of PO. On the other hand, PO has a relatively high strain in the ring. Thus, it is not easy to judge which one is the more reactive species towards the zinc glutarate catalyst. However, to the zinc glutarate catalyst the first insertion of SO_2 leads to a $Zn—OS(O)O(O)C—$ bond which seems to be unstable, whereas the first insertion of PO results in a $Zn—OCH(CH_3)CH_2O(O)C—$ bond which is relatively stable. Therefore, the insertion of PO into the zinc glutarate may occur favorably at the first step of the copolymerization. Third, it was reported that zinc complexes containing more than one zinc(II) atom increase the probability of the complex to be catalytically active for the polycarbonate formation from CO_2 and oxirane[17, 19].

Fourth, the morphological structure of the zinc glutarate has not been investigated in detail yet because of its insolubility. But our X-ray absorption near edge spectroscopic study of the zinc glutarate indicates that the zinc metal is coordinated by four or five oxygen atoms of carboxylate groups and the length of $Zn—O$ coordination is $1.96\,\text{Å}$[20]. In addition a bimolecular Zn complex, which has a distance of 3.19 between two Zn metal ions, was detected[20]. Finally, in an infrared spectroscopic study the zinc glutarate was found to exhibit both *syn-anti* and *syn-syn* bridging bidentate coordinated zinc dicarboxylate characteristics[21]. Adapting all these aspects considered, we propose a structural model of the zinc glutarate and its anionic mechanistic feature for the copolymerization of SO_2 and PO as elucidated in Scheme 1.

In addition to zinc glutarate, zinc hexacyanoferrate(III), which is known as an active catalyst for the copolymerization of CO_2 and PO[16], was prepared and then used in

Scheme 1: A proposed model structure of zinc glutarate and its anionic mechanistic feature in the copolymerization of PO and SO_2
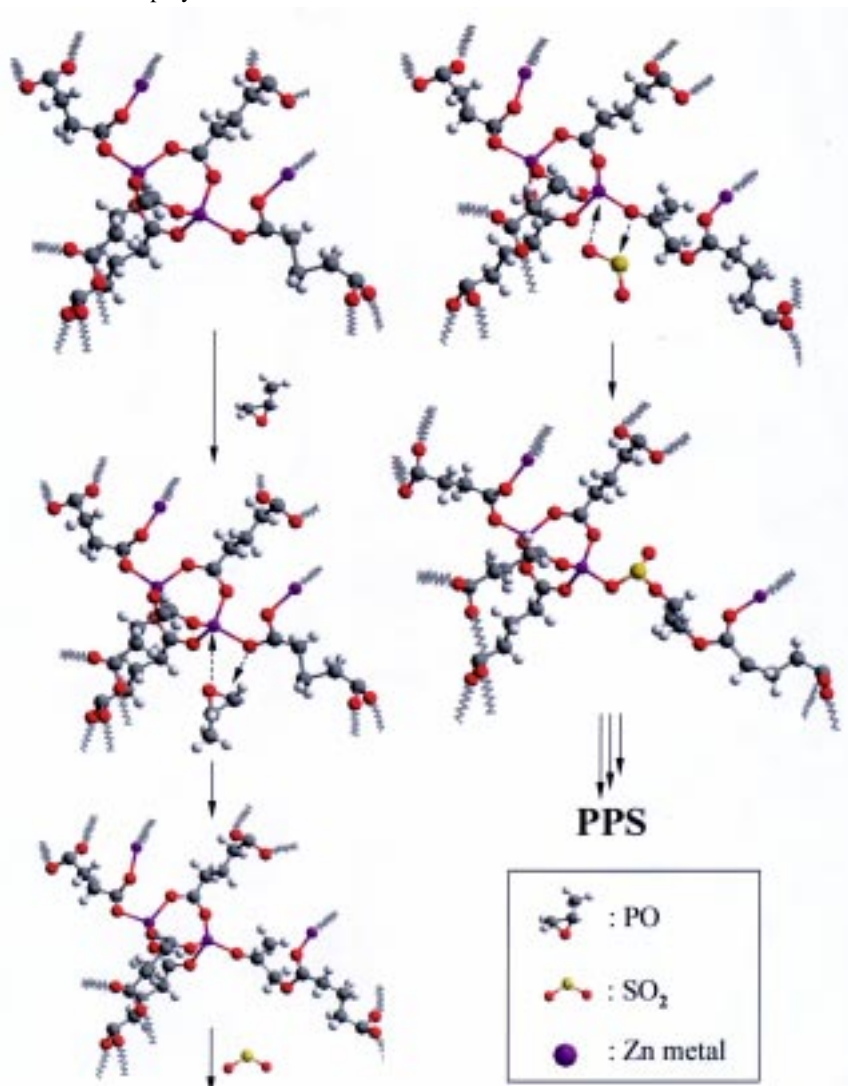
Tab. 1.   Effect of time on the copolymerization of PO with SO_2 in excess using a zinc glutarate catalyst[a]

Time $\dfrac{}{h}$	Total conversion[b] $\dfrac{}{\%}$	Product (g/g of cat.)			PPS[e]	
		CPS[c]	PPOS[d]	PPS[e]	$[\eta]$ [f] $\dfrac{}{dL/g}$	Composition[g] (PS/PE)
24	–	–	–	4.4	0.068	–
40	–	0	–	42.5	0.125	86.4/13.6
50	58.2	0	14.0	52.6	0.149	86.0/14.0
60	53.6	0	13.2	49.9	0.142	84.8/15.2

[a]   Polymerization condition: [PO], 0.75 mol; [SO_2], excess; [PO]/[cat.] = 300; 60 °C.
[b]   Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ¹H NMR spectroscopy.
[c]   Cyclic propylene sulfite.
[d]   Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[e]   Poly(propylene sulfite) insoluble in methanol.
[f]   Intrinsic viscosity was measured in THF at 25 °C.
[g]   Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ¹H NMR spectroscopy.

the copolymerization as a catalyst. However, only a trace amount of methanol soluble product with a low molecular weight was obtained. In conclusion, the zinc hexacyanoferrate(III) has a very poor catalytic activity for the copolymerization of SO_2 of PO.

Using the zinc glutarate which showed a good catalytic activity, the copolymerization was further investigated by changing reaction conditions, including temperature, time, monomer feed per catalyst, comonomer feed ratio, and solvent as described in the following sections. The obtained products were characterized by viscometry and ¹H NMR spectroscopy.

Effect of reaction time

The copolymerization of PO with SO_2 in excess was carried out at 60 °C by varying the reaction time over 24–60 h: here, the catalyst was used in [catalyst]/[PO] = 1/300. The results are summarized in Tab. 1.

The total reaction conversion was ≤58.2 mol-%, depending upon the reaction time: a maximum conversion was achieved for the reaction time of 50 h. A CPS byproduct was not formed, regardless of the reaction time. However, methanol soluble products (namely, products containing a large amount of ether linkage) were obtained with a yield of ≤14.0 g per gram of catalyst, depending upon the reaction time. On the other hand, the yield of methanol insoluble PPS product increased with reaction time and to reach a maximum at 50 h. Then, the yield slightly decreased with further increasing reaction time. The intrinsic viscosity [η] of the products (namely: molecular weight) also increased initially with time, to reach a maximum value at 50 h, and turned to decrease slightly with further increasing time. However, the viscosity was relatively low even for the PPS product obtained from the copolymerization at 50 h: [η] = 0.068–

0.149, depending upon the reaction time. The content of sulfite-linkage in the PPS product was in the range of 84.8–86.4 mol-%. This indicates that the mol-% of sulfite-linkage in the PPS is apparently little sensitive to reaction time. In conclusion, a reaction time of 50 h gave a PPS product of the relative highest yield and molecular weight.

Effect of PO feed per catalyst

The effect of PO feed per catalyst on the copolymerization was investigated. For the copolymerization, the SO_2 was fed in excess, and the reaction temperature and time were hold constant at 60 °C and 40 h, respectively. The [PO]/[catalyst] ratio varied over the range of 300–500. With increasing of PO feeding, the yield of PPS product increased (see Tab. 2). The yield of methanol soluble product also increased with increasing PO feed. The [η] of PPS products increased with increasing PO feeding to reach a maximum value (0.128) at [PO]/[catalyst] = 400. Thereafter, [η] decreased with further increasing PO feed. However, the content of sulfite-linkage in the PPS product decreased with increasing PO feeding: a maximum content of sulfite-linkage (86.4 mol-%) was obtained at [PO]/[catalyst] = 300. Considering both, molecular weight and sulfite-linkage content, there is conclusively a recommended ratio [PO]/[catalyst] = 300–400 for the copolymerization of PO and SO_2.

Effect of comonomer feed ratio

The copolymerization of PO and SO_2 was carried out with varying their feed ratio as illustrated in Tab. 3. The amount of zinc glutarate catalyst used for all copolymerization runs was 0.50 g. An excess feeding of SO_2 delivered a PPS product with low molecular weight in a rela-

Tab. 2. Effect of monomer feed per catalyst on the copolymerization of PO with SO_2 in excess using a zinc glutarate catalyst[a]

[PO]/[Cat.][b]	Total conversion[c] %	Product (g/g of cat.)			PPS[f]	
		CPS[d]	PPOS[e]	PPS[f]	$[\eta]$ [g] dL/g	Composition[h] (PS/PE)
300	–	0	–	42.5	0.125	86.4/13.6
400	–	0	–	42.9	0.128	83.4/16.6
500	49.8	0	27.4	63.6	0.062	81.0/19.0

[a] Polymerization condition: [cat.], 0.5 g; [SO_2], excess; 60 °C; 40 h.
[b] Molar ratio of propylene oxide (PO) and zinc glutarate catalyst.
[c] Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ^{1}H NMR spectroscopy.
[d] Cyclic propylene sulfite.
[e] Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[f] Poly(propylene sulfite) insoluble in methanol.
[g] Intrinsic viscosity was measured in THF at 25 °C.
[h] Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ^{1}H NMR spectroscopy.

Tab. 3. Effect of comonomer feed ratio on the copolymerization of PO with SO_2 using a zinc glutarate catalyst[a]

[PO]/[Cat.][b]	Total conversion[c] %	Product (g/g of cat.)			PPS[f]	
		CPS[d]	PPOS[e]	PPS[f]	$[\eta]$ [g] dL/g	Composition[h] (PS/PE)
<1.0 (SO₂ in excess)	–	0	–	42.5	0.125	86.4/13.6
1.0	70.4	0	9.2	66.9	0.382	90.4/9.6
1.9	23.3	0	13.5	40.4	0.204	83.8/16.2

[a] Polymerization condition: [cat.], 0.5 g; 60 °C; 40 h.
[b] Molar ratio of propylene oxide (PO) and SO_2.
[c] Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ^{1}H NMR spectroscopy.
[d] Cyclic propylene sulfite.
[e] Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[f] Poly(propylene sulfite) insoluble in methanol.
[g] Intrinsic viscosity was measured in THF at 25 °C.
[h] Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ^{1}H NMR spectroscopy.

tively low yield. A similar result was obtained from the copolymerization with an excess of PO feeding. The excess of PO feeding gave a relatively higher molecular weight PPS than the excess of SO_2 feeding. However, the content of sulfite-linkage was slightly higher in the PPS product prepared from the excess of SO_2 feeding than from the excess of PO feeding. Different from these cases, an equimolar feeding of comonomers gave the relatively highest yield of PPS product with the relatively highest molecular weight. Further, this PPS product contains the relatively largest amount of sulfite-linkages in the backbone. These results inform us that the feed ratio of comonomers (SO_2 and PO) is one of the critical factors in this type of copolymerization. This is quite different from the results observed for the copolymerization catalyzed by amine catalysts[10, 12]: the copolymerization catalyzed with amine compounds always delivers oligomeric alkylene sulfite, having chemical composition independent from the feed ratio of comonomers.

Effect of reaction temperature

The copolymerization of PO with SO_2 in excess was carried out during 40 h at various temperatures between 40–100 °C: here, the PO monomer was fed with [PO]/[catalyst] = 300. The product yield increased with temperature to reach a maximum value at 80 °C, and turned to decrease with further elevating temperature (see Tab. 4). In particular, a reaction temperature of 40 °C gave very low yield of product. The $[\eta]$ and sulfite-linkage content in the PPS products decreased with elevating temperature, respectively. According to these results, the most proper reaction temperature for this copolymerization is 60 °C.

In the copolymerization, the formation of CPS byproduct was observed to be restricted below 80 °C. However, CPS was found to form with a yield of 4.1 g per gram of catalyst from the copolymerization at 100 °C. This evidences that CPS can be formed even in the zinc glutarate

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Tab. 4. Effect of temperature on the copolymerization of PO with SO_2 in excess using a zinc glutarate catalyst[a]

$\dfrac{T}{°C}$	$\dfrac{\text{Total conversion}^{b)}}{\%}$	Product (g/g of cat.)			$PPS^{e)}$	
		$CPS^{c)}$	$PPOS^{d)}$	$PPS^{e)}$	$\dfrac{[\eta]^{\ \ f)}}{dL/g}$	Composition$^{g)}$ (PS/PE)
40	–	0	–	0.5	–	–
50	23.7	0	6.1	14.7	0.172	87.2/12.8
60	–	0	–	42.5	0.125	86.4/13.6
80	–	0	–	62.7	0.122	82.0/18.0
100	47.0	4.1	9.7	32.9	0.033	73.4/26.6

[a] Polymerization condition: [PO], 0.75 mol; [SO_2], excess; [PO]/[cat.] = 300; 40 h.
[b] Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ^{1}H NMR spectroscopy.
[c] Cyclic propylene sulfite.
[d] Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[e] Poly(propylene sulfite) insoluble in methanol.
[f] Intrinsic viscosity was measured in THF at 25 °C.
[g] Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ^{1}H NMR spectroscopy.

Tab. 5. Effect of temperature on the copolymerization of equimolar PO and SO_2 using a zinc glutarate catalyst[a]

$\dfrac{T}{°C}$	$\dfrac{\text{Total conversion}^{b)}}{\%}$	Product (g/g of cat.)			$PPS^{e)}$	
		$CPS^{c)}$	$PPOS^{d)}$	$PPS^{e)}$	$\dfrac{[\eta]^{\ \ f)}}{dL/g}$	Composition$^{g)}$ (PS/PE)
50	62.7	0	2.7	76.8	0.288	89.4/10.6
60	70.4	0	9.2	66.9	0.382	90.4/9.6
80	60.4	0	9.4	46.4	0.179	77.6/22.4

[a] Polymerization condition: [PO], 0.75 mol; [SO_2], 0.75 mol; [PO]/[cat.] = 300; 40 h.
[b] Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ^{1}H NMR spectroscopy.
[c] Cyclic propylene sulfite.
[d] Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[e] Poly(propylene sulfite) insoluble in methanol.
[f] Intrinsic viscosity was measured in THF at 25 °C.
[g] Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ^{1}H NMR spectroscopy.

catalyzed copolymerization. However, the formation of CPS byproduct seems to require relative high temperatures. In conclusion, the copolymerization should be conducted at temperatures ≤80 °C in order to prevent the formation of CPS byproduct.

With these results, the effect of reaction temperature was further studied for the copolymerization of PO and SO_2 in an equivalent molar ratio over 50–80 °C. The results are summarized in Tab. 5. The total conversion of PO increased with increasing temperature to reach a maximum at 60 °C. Thereafter, the total conversion was turned to decrease with further increasing temperature. However, the yield of polymer containing a large amount of ether-linkages increased continuously with increasing temperature. In contrast, the yield of PPS product decreased as the reaction temperature increased. The copolymerization at 60 °C gave the relatively highest molecular weight and sulilite-linkage content of PPS products even though its PPS yield was lower compared to that of the copolymeri-

zation at 50 °C. However, the PPS product yield here is still larger than that from the copolymerization of PO with SO_2 in excess at 60 °C, described above. In conclusion, PPS products with a high molecular weight and a high content of sulfite-linkages can be obtained from the equimolar comonomer fed coplymerization at 60 °C.

Effect of solvent

The solvent effect on the copolymerization was investigated using chloroform and PO as reaction solvents. The results are summarized in Tab. 6. For the copolymerization at 60 °C, the utilization of PO as a reaction medium gave a PPS product with a relatively high molecular weight in a high yield, compared to the usage of chloroform as a solvent. However, a PPS product with a relatively high content of sulfite-linkages was obtained from the copolymerization using chloroform as a solvent. The high content of

Tab. 6. Effect of solvent on the copolymerization of equimolar PO and SO$_2$ using a zinc glutarate catalyst[a]

T °C	Solvent	Total conversion[b] %	Product (g/g of cat.)			PPS[e]	
			CPS[c]	PPOS[d]	PPS[e]	$[\eta]$[f] dL/g	Composition[g] (PS/PE)
60	PO	44.4[h]	0	13.5	40.4	0.204	83.8/13.2
60	CHCl$_3$	14.3	0	1.8	17.0	0.156	92.2/7.8
80	CHCl$_3$	60.6	5.6	4.9	71.5	0.200	93.6/6.4

[a] Polymerization condition: [PO], 0.75 mol; [SO$_2$], 0.75 mol; [PO]/[cat.] = 300; [PO] + [solvent], 100 mL; 40 h.
[b] Total conversion of reaction was estimated from the consumption of loaded PO in the reaction by ^{1}H NMR spectroscopy.
[c] Cyclic propylene sulfite.
[d] Poly(propylene ether-*co*-sulfite) soluble in methanol: that is, highly ether-linkage containing polymer.
[e] Poly(propylene sulfite) insoluble in methanol.
[f] Intrinsic viscosity was measured in THF at 25 °C.
[g] Molar fractions of propylene sulfite (PS) and propylene ether (PE) units in the PPS product were determined by ^{1}H NMR spectroscopy.
[h] Estimated from the PO of 0.75 mol which was fed initially.

sulfite-linkages in the PPS product further increased with elevating reaction temperature towards 80 °C. By elevating the reaction temperature towards 80 °C, the PPS yield was also enhanced significantly. And, the methanol soluble polymer product was formed in a much lower yield than in the copolymerization using PO as a solvent. This suggests that the use of chloroform as a solvent contributes positively to restrict the formation of propylene ether homopolymer from the PO monomer component itself.

On the other hand, a CPS byproduct was detected to be formed in the reaction in chloroform at 80 °C. As at forementioned, the CPS byproduct was formed in the reaction at a relative high temperature, e. g. 100 °C. Thus, the reaction temperature to induce the formation of CPS byproduct is apparently lowered by using chloroform as a reaction medium for copolymerization. That is, the formation of CPS byproduct in the copolymerization is accelerated by chloroform solvent.

In conclusion, the copolymerization of PO and SO$_2$ is further dependent upon the reaction solvent, in addition to the reaction temperature, time, monomer feed ratio, and monomer feed per catalyst.

Properties

The obtained PPS products are amorphous. They are optically transparent and sticky solids at room temperature. For the PPS product having the highest molecular weight ($\overline{M}_n$ = 42 000; $[\eta]$ = 0.382), the glass transition temperature (T_g) was measured to be 13.5 °C. This T_g value is lower than that (38 °C) of poly(propylene carbonate)[15], in spite of their similarity in the chemical backbone structure. In fact, the PPS product contains 9.6 mol-% of propylene ether linkages in the backbone. Thus, the relatively low T_g of PPS products may be attributed to its chemical structure containing ether-linkages.
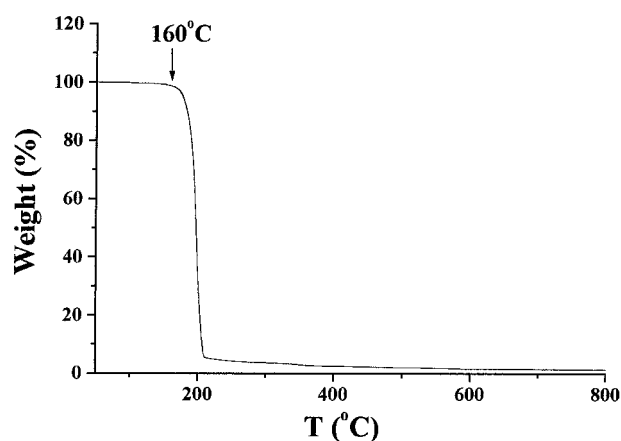

Fig. 3. TGA thermogram of a PPS product containing 90.4 mol-% sulfite-linkages and 9.4 mol-% ether-linkages: $\overline{M}_n$ = 42 000 with $\overline{M}_w/\overline{M}_n$ = 2.1

Fig. 3 shows a TGA thermogram measured from the PPS product with the highest molecular weight. In the TGA run under nitrogen atmosphere, the weight loss was started at 160 °C and then increased sharply with further increasing temperature. That is, the thermal stability of the PPS product is limited up to 160 °C. This thermal stability is also lower than that (252 °C) of poly(propylene carbonate)[15]. The low thermal stability might originate from its inherently low stability.

Conclusions

In the presence of a zinc glutarate catalyst the copolymerization of SO$_2$ and PO proceeds slower than the anionic copolymerization initiated by amines[13, 14]. However, when maintaining appropriate reaction parameters (i. e., temperature, time, comonomer feed ratio, catalyst loading, and solvent) no cyclization processes occur and

copolymer products of much higher molecular weights can be obtained than in the copolymerization catalyzed by amines. In this study an optimized copolymerization resulted in poly(propylene sulfite) (PPS) with high molecular weight, $\overline{M}_n = 42\,000$, never achieved before. PO homopolymerization also proceeds in the system studied, but its rate is much lower than that of alternating copolymerization. For the zinc glutarate catalyst, the nucleophilicity of the carboxylate oxygen atoms is stronger than the electrophilicity of the zinc metal center, so that we propose an anionic mechanistic feature for the zinc glutarate catalyzed copolymerization of SO_2 and PO.

In addition to the zinc glutarate, zinc hexacyanoferrate(III) was investigated as a catalyst for the copolymerization, but exhibited almost no catalytic activity.

[1] Z. Florjanczyk, *Prog. Polym. Sci.* **16**, 509 (1991)

[2] N. Tokura, "*Encyclopedia of Polymer Science and Technology*", H. F. Mark, N. G. Gaylord, Eds., Vol. 9, Interscience, New York 1968, p. 460

[3] H. F. Fawcette, "*Encyclopedia of Polymer Science and Engineering*", Vol. 10, Wiley, New York 1987, p. 408

[4] M. J. Bowden, L. F. Thompson, *Solid Stat. Technol.* **22**, 72 (1979)

[5] Z. Florjanczyk, D. Raducha, *Makromol. Chem., Rapid Commun.* **14**, 207 (1993)

[6] Z. Florjanczyk, D. Raducha, *Makromol. Chem.* **194**, 2605 (1993)

[7] J. Schaefer, R. J. Kern, R. J. Katnik, *Macromolecules* **1**, 107 (1968)

[8] J. Schaefer, *Macromolecules* **1**, 111 (1968)

[9] A. D. Jenkins, "*Proc. IUPAC Intl. Symp. On Macromol. Chem.*", Vol. 1, Budapest, Hungary, 1969, p. 417

[10] K. Soga, I. Hattori, J. Kinoshita, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* **15**, 745 (1977)

[11] K. Soga, K. Kiyochara, I. Hattori, S. Ikeda, *Makromol. Chem.* **181**, 2151 (1980)

[12] Z. Florjanczyk, D. Raducha, *Makromol. Chem., Rapid Commun.* **12**, 393 (1991)

[13] B. Lee, J. H. Jung, M. Ree, *Proc. Polymer Soc. Korea* **23**(2), 117 (1998)

[14] Z. Florjanczyk, D. Raducha, A. K. Szalkowska, *Macromolecules* **29**, 826 (1996)

[15] M. Ree, J. Y. Bae, J. H. Jung, T. J. Shin, *J. Polym. Sci., Part A: Polym. Chem.* **37**, 1863 (1999)

[16] U.S. Patent No. 4 500 704 (1985), invs.: W. J. Kruper Jr., D. J. Swart

[17] W. Kuran, T. Listos, *Macromol. Chem. Phys.* **195**, 977 (1994)

[18] S. Inoue, M. Kobayashi, T. Tozuka, *J. Organomet. Chem.* **81**, 17 (1974)

[19] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **153**, 155 (1996)

[20] M. Ree, J. Y. Bae, S. J. Cho, J. H. Jung, to be submitted

[21] M. Ree, J. Y. Bae, J. H. Jung, T. J. Shin, T. Chang, *Polym. Eng. Sci.*, in press