Mono- and bifunctional six-membered cyclic carbonates synthesized by diphenyl carbonate toward networked polycarbonate films

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ABSTRACT: The synthesis of six-membered cyclic carbonates from diols utilizing less toxic and easily-handled diphenyl carbonate (DPC) is carried out based on the reactivity and selectivity at different conditions. Commercially-available neopentylglycol (NPG) or di(trimethylolproapane) (DTMP) react effectively with DPC at 140°C and converted to their corresponding monofunctional NPG-carbonate (NPGC) or bifunctional DTMPC-carboante (DTMPC), respectively. The selectivity of these carbonates changes depending on a feed ratio of DPC and these diols. After a NPG/DPC mixture with the DPC/NPG feed ratio of 4 was heated at 140°C for 48 h, the NPGC is isolated with a yield of 74%. A 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-catalyzed ring-opening polymerization (ROP) of NPGC with DTMPC can form effectively networked structures. By only drying of THF solutions containing NPGC, DTMPC, and a catalytic amount of DBU at 60°C for 12 h, the ROP efficiently proceeds and networked polycarbonate films with well transparency and flexibility are easily obtained. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41956.

INTRODUCTION

Aromatic polycarbonates, as exemplified by bisphenol A-based polycarbonates, are one of widely-used polymers in various industrial applications because of their well transparency, high thermal stability, and mechanical properties.[1–8] While, aliphatic polycarbonates feature biocompatibility and degradability, which inspires many scientists to explore the application to carriers of drugs and genes.[9–13] Furthermore, antimicrobial activities of the aliphatic polycarbonates have been studied by introduction of quaternary ammonium ions in the side chains and/or main chains of the polycarbonates for several years.[10,14–19]

In practical usages, the film processing of such the functionalized polycarbonates is frequently required.[20–23] To fabricate polycarbonate films, the formation of covalently-bridged network structures, which effectively stabilizes the film states, are generally applied. In addition, it is expected that the networked structures promote the thermal stability and the mechanical strength.[24,25] The networked structures are easily formed by copolymerization of six-membered cyclic carbonate monomers (monofunctional carbonate) with six-membered cyclic carbonate dimers (bifunctional carbonates).[24] Especially, the bifunctional carbonates can be also applied to synthesize poly(hydroxyurethane)s, which are attracting a huge interest because they are promising alternatives

to widely-used polyurethanes involving harmful isocyanates as starting materials. The poly(hydroxyurethane)s reported are generally synthesized by the reaction of bifunctional carbonates having a five-membered cyclic structure with diamines.[26–31] Although various structured bifunctional carbonates bearing a five-membered cyclic structure are nowadays reported, the studies of those bearing a six-membered cyclic structure are rarely performed.[24,31,32] Recently, it has been reported that a new bifunctional carbonate with a six-membered cyclic structure can be derived from di(trimethylolpronane) (DTMP) through the reaction with ethyl chlorocarbonate.[24] Although such the chlorocarbonate esters are widely applied because of their less toxicity compared to phosgene, they are derived from phosgene itself through the reaction with alcohols. Thus, the usage of these chlorocarbonate esters involves phosgene in whole processes and it is important to explore another routes without using phosgene derivatives.

Dialkyl carbonates are promising candidates for transesterification agents in respect with environmental and industrial aspects.[33,34] Simply-structured dimethyl carbonate (DMC) or diethyl carbonates (DEC) are sometimes employed for the transesterification to give five- or six-membered cyclic carbonates.[35–39] A 1,1'-carbonydiimidazole,[40] which is structurally

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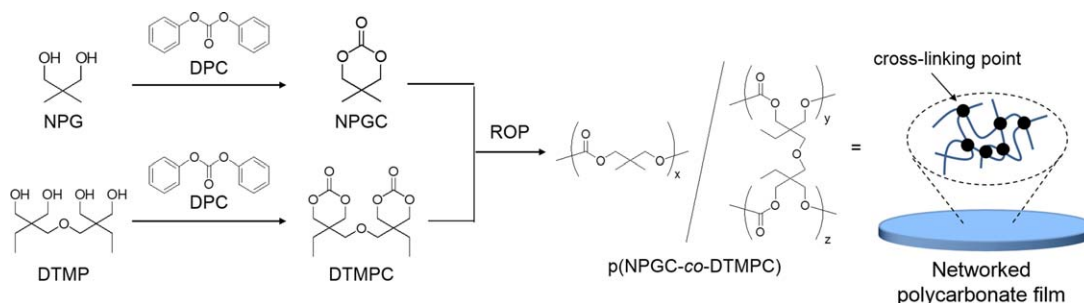
Scheme 1. Schematic illustration of the fabrication of networked polycarbonate films. Phosgene derivative-free synthesis of mono- or bifunctional carbonates bearing a six-membered cyclic structure and fabrication of networked polycarbonate films by the DBU-catalyzed ROP of NPGC and DTMPC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

similar to dialkyl carbonates, and carbon dioxide[33,41] also used for the synthesis of six-membered cyclic carbonates. Among these transesterification agents, we focus on diphenly carbonate (DPC). In our laboratory, it has been reported that the phosgene-free synthesis of polypeptides that applies the tentative generation of N-carbonyl anhydrides from amino acids and DPC and subsequent polymerization of them by amine initiators.[42] Compared to DMC and DEC, DPC consists in a leaving group with higher activity (phenol) and it is expected that the transesterification between alcohols and DPC proceeds at lower temperature without catalysts. Additionally, DPC can be synthesized not only by the reaction of phosgene with phenol but also by the transesterification between DMC and phenol.[43–46] DMC can be synthesized from five-membered cyclic carbonates and methanol. In other way, DMC is catalytically synthesized by the reaction of methanol and carbon oxide and oxygen molecules.[45] In addition, the palladium-catalyzed synthesis of DPC from phenol and carbon oxide is reported.[43,44,46] These synthetic routes are environmentally begins. As a result, the synthesis of six-membered cyclic carbonate using DPC is truly the phosgene derivative-free route in whole processes. However, the reactivity of these carbonate esters containing DPC is quite lower than that of the conventional phosgene and its derivatives. To progress the transesterification, a larger amount of thermal energies is required. Unfortunately, the transesterification at higher temperature causes undesired oligomerizations, resulting in a decrease in yields.[36] To overcome this challenge, DPC modified with electron withdrawing groups such as fluorine and nitro groups are synthesized.[47–49] Nowadays, these compounds are commercially available but highly expensive. Therefore, it is required to explore the synthetic routes to six-membered cyclic carbonates from polyols using DPC without the unfavorable oligomerization.

Here we report the facile synthetic approach to six-membered cyclic carbonates through the transesterification with DPC. From simply-structured and commercially available neopentylglycol (NPG) and DTMP, the corresponding mono- or bifunctional carbonate with a six-membered cyclic structure (NPGC and DTMPC) are synthesized (Scheme 1). By changing the synthetic conditions such as temperature, reaction time, feed ratio of diols to DPC and catalysts, we elucidate how the reactivity of these diols and the selectivity of the corresponding carbonates are affected. In addition, by the ring-opening polymerization

(ROP) of these carbonate monomers, we explored the facile fabrication route to networked polycarbonate films and investigated their transparency, thermal, and mechanical properties.

EXPERIMENTAL

Reagents

NPG was obtained from Tokyo Chemical Industry. DTMP was purchased from Aldrich. DPC was supplied by Asahi Kasei Chemicals. A series of magnesium salts with different counter ions (F^-, Cl^-, or ClO_4^-) and DBU were purchased from Wako Pure Chemical. THF was refluxed with sodium and benzophenon for longer than 12 h and distilled and then used for the ROP of six-membered cyclic carbonates. Other reagents and solvents were purchased from commercially sources and used without purification.

Synthesis

Synthesis of Monofunctional Carbonate (NPGC). NPGC was synthesized from NPG and DPC with a different DPC/NPG feed ratios of 1–15. A general procedure is as follows. To DPC 85.7 g (400 mmol) was added NPG 10.4 g (99.9 mmol) at 140°C and the solution was stirred for 48 h. After cooled to ambient temperature, the solution was purified by silica gel column chromatography with an eluent with a n-hexane/ethyl acetate volume ratio of 1 to give white solids with a yield of 10.4 g (80.4%). The crude product was recrystallized from solvents mixed with a n-hexane/ethyl acetate volume ratio of 4/3 and then collected by suction filtration. After washing with n-hexane and drying under reduced pressure, NPGC was obtained as a white crystal. Yield: 9.64 g (74.2%). mp 114.4–114.8°C. ^1H NMR (400 MHz, CDCl$_3$, δ): 4.06 (s, 4H, CH$_2$O), 1.10 (s, 6H, CH$_3$). ^{13}C NMR (400 MHz, CDCl$_3$, δ): 148.2 (C=O), 77.6 (CH$_2$O), 28.5 ((CH$_3$)$_2$—C— (CH$_2$O)$_2$), 21.2 (CH$_3$). IR (ATR): $v = 2963$ (w; v(CH$_2$)), 1739 (s; v(C=O)), 1190–1118 cm^{-1} (s; v(C—O)). Anal. calcd for C$_6$H$_{10}$O$_3$: C 54.90, H 7.68; found: C 55.37, H 7.74.

Synthesis of Bifunctional Carbonate (DTMPC). DTMPC was synthesized from DTMP and DPC with different DPC/DTMP feed ratios from 2 to 10. A general procedure is as follow. To DPC 85.7 g (400 mmol) was added DTMP 10.0 g (39.9 mmol) at 140°C and the solution was stirred for 48 h. After cooled to ambient temperature, the solution was purified by silica gel column chromatography (eluent: n-hexane/ethyl acetate = 1/4 by

Vol.) followed by recrystallization from a mixed solvent of a n-hexane/ethyl acetate volume ratio of 1/3. DPMPC was obtained as white solids. Yield: 9.92 g (82.0%). mp 104.3–105.6°C. ^{1}H NMR (400 MHz, CDCl$_3$, δ): (ppm): 4.30–4.16 ($d \times d$, $J = 11.0$ Hz, 8H; CH$_2$O—COO), 3.51 (s, 4H, —CH$_2$—O—CH$_2$—), 1.53–1.47 (q, $J = 7.5$ Hz, 4H; CH$_3$—CH_2—), 0.94–0.90 (t, $J = 7.4$ Hz, 6H; CH$_3$). ^{13}C NMR (400 MHz, CDCl$_3$, δ): 148.5 (C=O), 72.9 (—CH$_2$—OCOO), 70.9 (—CH$_2$—O—CH$_2$—), 35.5 ((CH$_2$)$_2$—C—(CH$_2$O)$_2$), 23.7 (CH$_3$—CH$_2$—), 7.5 (CH$_3$). IR (ATR): $v =$ 2967–2881 (w; v(CH$_2$)), 1733 (s; v(C=O)), 1170–1105 cm^{-1} (s; v(C—O)). Anal. calcd for C$_{14}$H$_{22}$O$_7$: C 55.49, H 7.50; found: C 55.62, H 7.33.

Synthesis of Polycarbonate (pNPGC). NPG 520 mg (4.00 mmol) was added in a Schlenk flask and filled with nitrogen gas. To the flask were added THF 0.60 mL and a THF solution of DBU (200 mM, 0.40 mL, 2 mol %). The reaction mixture (initial monomer concentration ($[M]_0$) = 4.0 M, $[M]_0$/[DBU] = 50/1) was stirred at 60°C for 18 h. After the solution was cooled to ambient temperature, a few drop of acetic acid was added to the solution. After stirred at ambient temperature within 10 min, the solution was added to methanol 200 mL and then allowed to stand at 4°C for several hours. The resulting precipitates were collected by suction filtration and washed thoroughly with methanol. After drying under reduced pressure, polycarbonates pNPGC were obtained as white solids. Yield: 482 mg (92.5%). $M_{n,GPC} = 9,900$ g mol^{-1}, $M_w/M_n = 1.29$, relative to polystyrene standards. pNPGC was prepared at the condition of different $[M]_0$ and results were as follows. $[M]_0 = 3.0M$; Yield: 335 mg (85.7%), $M_{n,GPC} = 6000$ g mol^{-1}, $M_w/M_n = 1.25$. $[M]_0 = 2.0M$; Yield: 196 mg (75.4%), $M_{n,GPC} = 4800$ g mol^{-1}, $M_w/M_n = 1.14$.

Synthesis of Networked Polycarbonate (p(NPGC-co-DTMPC)). NPGC 515 mg (3.96 mmol) and DTMPC 12 mg [0.04 mmol, 1 mol % with respect to total monomers (NPGC + DTMPC)] were added in a Schlenk flask and purged with nitrogen gas and sealed. To a flask, anhydrous THF 0.60 mL and a THF solution of DBU (200 mM, 0.40 mL, 2 mol %) were added. The reaction mixture ($[M]_0 = 4.0M$, [NPGC]$_0$/[DTMPC]$_0$/[DBU] = 99/1/2) was stirred at 60°C for 18 h. THF 3.0 mL and a few drop of acetic acid were added in the resulting viscous solution at ambient temperature and the solution was stirred for about 10 min and then added to methanol 200 mL. The resulting precipitates were collected by suction filtration and washed with methanol. The precipitates were dried under reduced pressure to give a networked polycarbonate p(NPGC-co-DTMPC) as a white solid. Yield: 489 mg (92.8%). $M_{n,GPC} = 16,400$ g mol^{-1}, $M_w/M_n = 6.25$, relative to polystyrene standards.

Fabrication of Networked Polycarbonate Films (p(NPGC-co-DTMPC) Films). NPGC 293 mg (2.25 mmol) and DTMPC 76 mg (0.25 mmol, 10 mol % with respect to total monomers) were dissolved in anhydrous THF 1.88 mL. A THF solution of DBU (1.0M, 0.125 mL, 5 mol %) was added in the solution. The solution ($[M]_0 = 1.25M$, [NPGC]$_0$/[DTMPC]$_0$/[DBU] = 18/2/1) was poured to a petri-dish made from PTFE with a diameter of 5.0 cm and a height of 1.0 cm and covered with a glass plate and then allowed to stand for 12 h at 60°C in a Sanso Vacuum Drying Oven SVD10P (width: 20 cm, depth: 25 cm, height: 20 cm) under ambient atmosphere. During the treatments, THF was gradually removed and the ROP proceeded. After cooled to ambient temperature, the resulting film was carefully detached from the petri-dish and then immersed in methanol for several hours. After drying under ambient atmosphere, a networked polycarbonate film was obtained. Polycarbonate films were also fabricated by the ROP of NPGC and DTMPC with different DTMPC/NPGC feed ratios by the same procedure.

CHARACTERIZATION

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 NMR spectrometer operating 400 MHz with tetramethylsilane as an internal reference. Fourier transform infra-red (FTIR) spectroscopy was performed with a Thermo Fisher Scientific Nicolet iS10 equipped with an ATR instrument. Number average molecular weight (M_n) and polydispersity index (M_w/M_n) were calculated by size exclusion chromatography (SEC) using THF as eluents with polystyrene standards at a flow rate of 0.5 mL/min at 40°C. The SEC measurements were conducted on a Tosoh HLC-8320GPC equipped with an analytical column (6 mm Ø × 15 cm) and a refractive index detector. Thermogravimetry (TG) was carried out with a Seiko Instrument Inc. TG/DTA 6200 at a heating rate of 10°C min^{-1} under nitrogen gas at a flow rate of 200 mL min^{-1}. UV/Vis/near infrared (NIR) spectra were recorded on a Jasco V570 UV/VIS/NIR spectrophotometer equipped with Pbs power supply instruments. Stress–strain curves were measured with a Shimazu EZ Test EZ-LX with a operation rate of 500 mm min^{-1} and mechanical parameters were analyzed with a TRAPEZIUM X software.

Investigation of Time-Course Analysis of the Reaction of NPG with DPC

To DPC 1.71 g (8.00 mmol) was added NPG 208 mg (2.00 mmol) at 85°C and the mixture was stirred for 24–180 h. To analyze the degree of the proceeding of the reaction, small parts of the mixture was collected by 24 h. Each aliquot was subjected to ^{1}H NMR spectroscopy and the conversion of NPG and the mole fractions of the products were evaluated. In the case at 140°C, the NPG/DPC mixture was stirred for 2–48 h and also analyzed by the same method.

Synthesis of NPGC by DPC Catalyzed with Magnesium Salts with Different Counter Ions

To mixtures of NPG 208 mg (2.00 mmol) and DPC with different DPC/NPG feed ratios of 3–10 was added Mg(ClO$_4$)$_2$, MgF$_2$, or MgCl$_2$ (1 mol % with respect to NPG) and then the mixture was stirred at 100°C for 20 h. After that, the mixture was measured by ^{1}H NMR spectroscopy for the conversion of NPG and the selectivity of NPGC production. Time-course analysis of the reaction of NPG with DPC at the presence of Mg(ClO$_4$)$_2$ was also carried out. The mixture of NPG 208 mg (2.00 mmol) and DPC 2.14 g (10.0 mmol) containing Mg(ClO$_4$)$_2$ 4.5 mg (0.020 mmol, 1 mol % with respect to NPG) was stirred at 85°C within 94 h. The solution was taken up by about 24 h and each aliquot was analyzed by ^{1}H NMR spectroscopy.
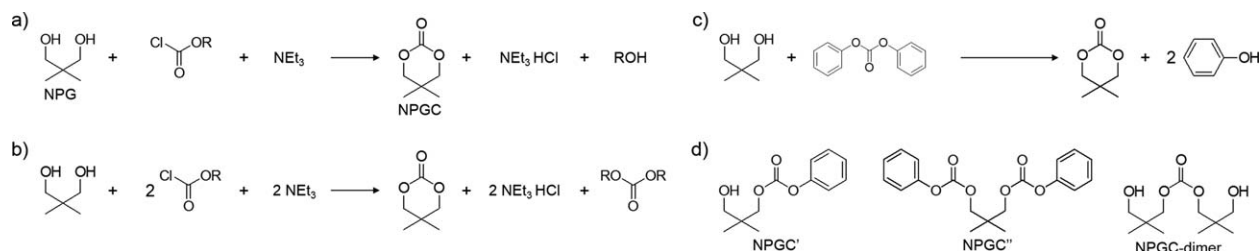
Scheme 2. (a, b) Synthesis of NPGC from NPG, chloroformate ester, and triethylamine. Using 2 equiv. of chloroformate ester and triethylamine, the resulting alcohol and Cl⁻ can be quenched. (c) Synthesis of NPGC from NPG and DPC. (d) Possible main by-products of the reaction of NPG and DPC. Left: NPGC-intermediate (NPGC′). Center: NPGC″. Right: NPGC-dimer.

RESULTS AND DISCUSSION

Synthesis of Mono- and Bifunctional Six-Membered Cyclic Carbonate Using DPC

The reaction of NPG with conventional chloroformate ester is shown in Scheme 2(a). A OH group of a NPG reacts with chloroformate ester to be esterized with an alkoxycarbonyl group and subsequently the other OH group of the NPG attacks intramolecularly to the carbonyl group to give NPGC. Through the overall reaction, one HCl and one alcohol are generated, which are generally trapped by an addition of 2 equiv. of chloroformate ester and triethylamine [Scheme 2(b)].[50] In the case of DPC, one DPC can form one cyclic carbonate and two phenol are produced [Scheme 2(c)]. Through the overall reaction, the reaction using DPC produces less amount of by-products compared to that using chloroformate esters. However, described above, the transesterification usually requires high temperature due to the less activity of carbonate esters. In that condition, cyclic carbonates produced are attacked by non-reacted diols to be oligomerized. It is expected that such the side reaction can be reduced by an addition of an excess amount of DPC. In this case, acyclic compounds depicted in Scheme 2(d) are considered to be mainly generated as by-products.

First, we used an excess amount of DPC and explored the temperature at which the transesterification proceed efficiently and NPGC is preferentially formed. A NPG and 4 equiv. of DPC were mixed and heated at 85°C for 24–168 h. DPC melts at 80–82°C and can serve as a solvent at above 85°C. The mixture was analyzed by ¹H NMR spectroscopy (Figures S1–S3 in Supporting Information). The mixture heated for 24 h showed three signals assigned to phenol at 6.9, 6.8, and 5.2 ppm, indicating the progress of the transesterification. From the spectrum, it was revealed that 6.2% of NPG was reacted and the mole fraction of NPGC was less than 1%. Concomitantly, two by-products depicted in Scheme 2(d) were detected: NPGC intermediate reacting with DPC by one OH group and dimer of NPGC, which are denoted as NPGC′ and NPGC-dimer, respectively. Although an excess amount of DPC was added, an acyclic by-product modified bifunctionally with phenoxycarbonyl groups (NPGC″), which is also depicted in Scheme 2(d), was not confirmed. We consider that when one OH group is esterized by DPC, the cyclization process would be favored. The mole fraction of NPG, NPGC, NPGC′, and NPGC-dimer were plotted as a function of reaction time in Figure 1(a). After the

mixture was stirred for 168 h, the mole fraction of NPG was above 10%. The fraction of NPGC was reached to 30% while about 25% of NPGC-dimer was generated. Thus, it is clear that the reaction at 85°C is not proper for the efficient synthesis of NPGC. Next, the solution was stirred at the temperature higher than 85°C for 48 h and the conversion of the NPG and the selectivity of NPGC formation were monitored by ¹H NMR spectroscopy. The results were shown in Figure 1(b). When the reaction temperature was elevated to 100°C, 75% of NPG was converted and NPGC was produced with a selectivity of 40%. The 60% of residual fraction was by-products. With an increase in the temperature, both the conversion and the selectivity were
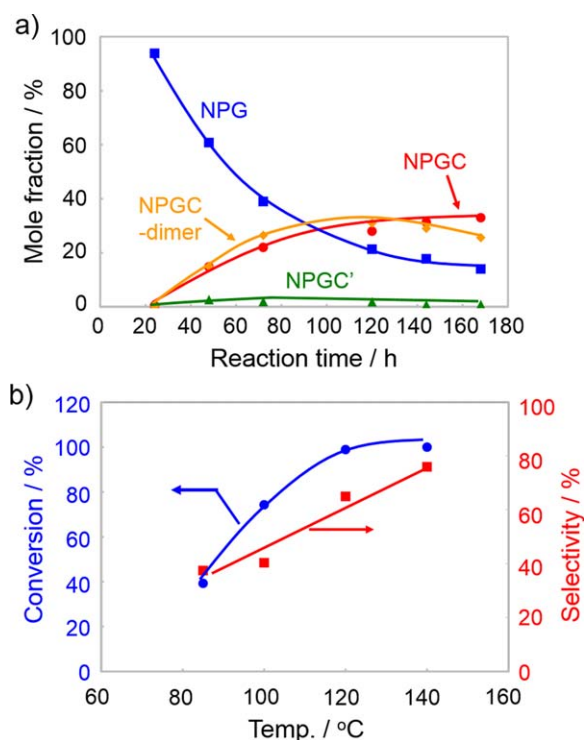

Figure 1. Investigation of the effect of reaction temperature on the formation of NPGC from a NPG/DPC mixture with a DPC/NPG feed ratio of 4. (a) Relationship between mole fractions and reaction time for the NPG/DPC mixture at 85°C. ■: NPG. ●: NPGC. ▲: NPGC′. ◆: NPGC-dimer. (b) Changes in the conversion of NPG (left axis) and selectivity of NPGC formation (right axis) as a function of temperature. In all conditions, the reaction time was 48 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
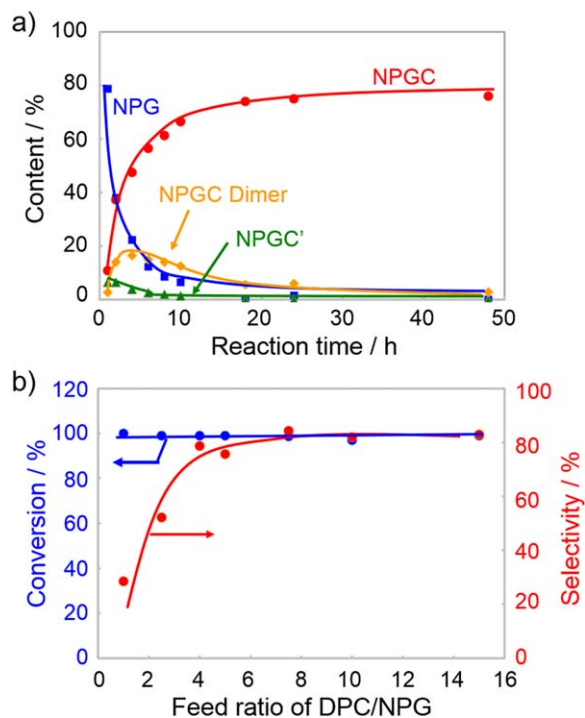
Figure 2. (a) Time-course analysis of the mole fraction in a NPG/DPC mixture with a DPC/NPG feed ratio of 4 at 140°C. ■: NPG, ●: NPGC, ▲: NPGC', ◆: NPGC-dimer. (b) The effect of DPC/NPG feed ratio on the conversion of NPG (left axis) and the selectivity of NPGC production (right axis) after reaction at 140°C for 20 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased. At 140°C, almost all NPG were converted and NPGC was formed with a selectivity of 76%. These results indicate that the reaction temperature should be set at 140°C.

Next, we investigated the time-course changes in the mole fractions of NPG, NPGC, NPGC-intermediate, and NPGC-dimer in reaction mixtures with a DPC/NPG feed ratio of 4 at 140°C. The results were shown in Figure 2(a). It was found that within 10 h, more than 90% of NPG was converted and about 70% of NPGC was selectively formed. Differing from the condition at 85°C, the fraction of NPGC-dimer decreased after the reaction time was longer than 5 h. After 48 h, NPGC-dimers completely disappeared and the main product was NPGC. The decrease in the fraction of NPGC-dimer at higher temperature can be explained by the further reaction of the dimer with DPC and/or by the shift of the chemical equilibrium to the direction in which the entropy is increased. Indeed, for the efficient synthesis of NPGC, it is required to rise the reaction temperature. We further investigated the conversion of NPG and the selectivity of NPGC formation at 140°C by changing the DPC/NPG feed ratios from 1.0 to 10. Reaction mixtures were stirred for 15–20 h and the reaction was monitored by ^{1}H NMR spectroscopy. The conversion of NPG and the selectivity of NPGC production were plotted as a function of DPC/NPG feed ratio in Figure 2(b). With 10 equiv. of DPC, almost all NPG reacted and 80% of NPGC was produced. Without the increase in DPC/NPG feed ratios, the conversion of NPG was not changed. On the other hand, the selectivity of NPGC formation was deeply depended on the feed ratios and was decreased dramatically when the feed ratio is below 4. From these results, more than 4–5 equiv. of DPC is needed for synthesizing NPGC in high yields. Actually, NPGC was isolated at a yield of 74% from the mixture of NPG with 4 equiv. of DPC heated at 140°C for 48 h after purified by column chromatography followed by recrystallization. The ^{1}H and ^{13}C NMR spectra of isolated NPGC are shown in Figure 3. The two proton signals assigned to the methylene groups neighboring to carbonate ester and methyl
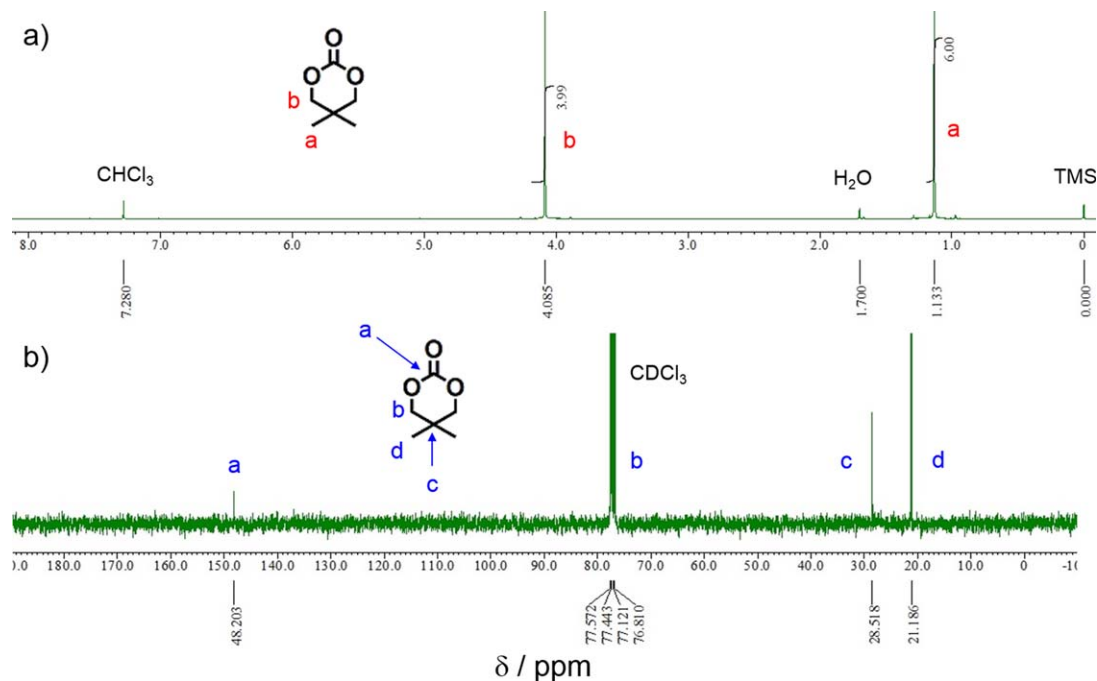

Figure 3. (a) ^{1}H and (b) ^{13}C NMR spectra of NPGC purified by column chromatography followed by recrystallization. Solvent: CDCl$_3$ containing 0.03 (v/v %) of TMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Analysis of the NPG/DPC Mixture with a DPC/NPG Feed Ratio of Four Containing Mg Salts (1 mol % with Respect to NPG) with Various Counter Ions After Heating at 100°C for 20 h

Entry	DPC/NPG Feed Ratio	Catalyst[a]	Temp. (°C)	Time (h)	Conv. (%)[b]	Selectivity of NPGC (%)[b]
1	5.0	MgF_2	100	20	>99	78.6
2	5.0	$MgCl_2$	100	20	>99	77.5
3	5.0	$Mg(ClO_4)_2$	100	20	>99	82.7

[a] 1 mol % with respect to NPG.
[b] Determined by ^1H NMR spectroscopy.

groups were generated at 4.1 and 1.1 ppm, respectively. In addition, ^{13}C NMR spectrum shows a characteristic signal of carbonyl groups at 148 ppm, which is supported by the presence of a strong stretching vibration originating from carbonyl groups at 1738 cm^{-1} (Figure S4, Supporting Information). These results clearly indicate that the NPGC is adequately purified.

In respect with environmental and industrial aspects, it is important to synthesize such the cyclic carbonates by lower energy. We selected magnesium ions as catalysts. The ion is expected to interact coordinatively with an oxygen atom of carbonyl groups in DPC and assist OH groups of NPG to easily

Figure 4. (a) Time-course analysis of the mole fraction of the components in the NPG/DPC mixture with a DPC/NPG feed ratio of four containing $Mg(ClO_4)_2$ (1 mol % with respect to NPG) at 85°C. (b) The effect of DPC/NPG feed ratios on the conversion of NPG (left axis) and the selectivity of NPGC production (right axis) after the NPG/DPC solutions containing 1 mol % of $Mg(ClO_4)_2$ were reacted at 100°C for 20 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

attack a carbon atom of the carbonyl groups, resulting in the decrease in an activation energy of the transesterification. Using a series of magnesium salts with different counter ions (1 mol % with respect to NPG), mixtures of NPG with 5 equiv. of DPC were stirred at 100°C for 48 h and then we checked whether the reaction proceed or not. The results were summarized in Table I. In the case of MgF_2, almost all NPG were converted and NPGC was produced with a selectivity of 78.6% (Entry 1). These values are same as those obtained from noncatalyzed mixtures reacted at 140°C. In despite of counter ions (F$^-$, Cl$^-$, or ClO$_4$$^-$), NPGC was formed with a high selectivity (Entry 2 and 3). The effect of $Mg(ClO_4)_2$ on the conversion of NPG and the selectivity of NPGC formation at 85°C were investigated and plotted as a function of reaction time in Figure 4(a). Even at 85°C, the mixture progressed the transesterification more efficient than that reacted at noncatalytic condition [Figure 1(a) and 4(a)]. After 94 h, the NPG was completely reacted and the selectivity of NPGC reached to 68%. The conversion of NPG and the selectivity of the formation of NPGC is plotted as a function of DPC/NPG feed ratios in Figure 4(b). The effect of the DPC/NPG feed ratios was quite similar to that at the noncatalytic condition [Figure 2(b) and 4(b)]. Consequently, it revealed that using nonexpensive magnesium salts as catalysts, NPGC was effectively synthesized with a high selectivity at temperature lower than 140°C.

For DTMP, we investigated the conversion of DTMP and the selectivity of DTMPC formation by changing the DPC/DTMP feed ratios from 2 to 10. The result was shown in Figure 5.
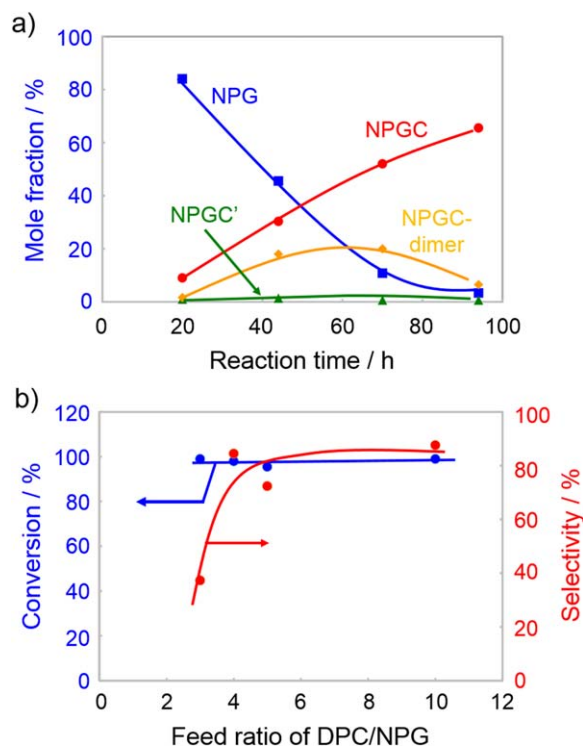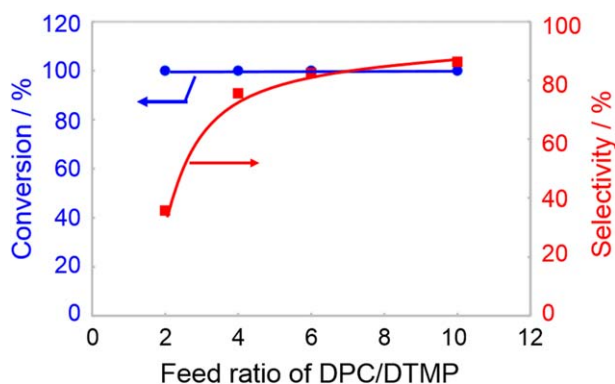

Figure 5. The effect of DPC/DTMP feed ratios on the conversion of DTMP (left axis) and the selectivity of DTMPC production (right axis) after the DTMP/DPC solutions were reacted at 140°C for 48 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
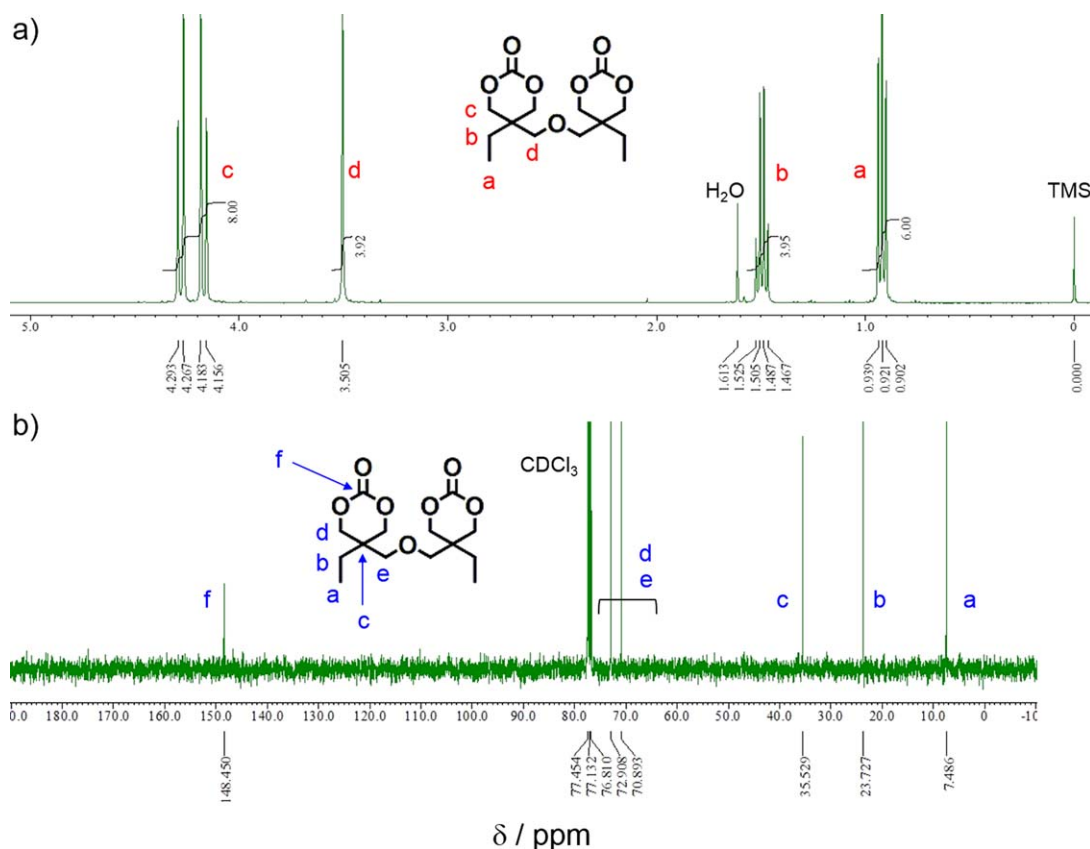
Figure 6. (a) ^{1}H and (b) ^{13}C NMR spectra of DTMPC purified by column chromatography followed by recrystallization. Solvent: CDCl$_3$ containing 0.03 (v/v %) of TMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

When the feed ratio was 4 (2 equiv. of DPC with respect to diol), almost all DTMP were reacted and DTMPC was formed with a selectivity of more than 70%. The selectivity was improved with an increase in the DPC/DTMP feed ratio. With the feed ratio of 10, the selectivity of DTMPC formation reached up to 90%. These results indicate that the production of DTMPC was more favorable than that of NPGC. In actual, DTMPC was isolated with a yield of 82% from the mixture of

DTMP and 10 equiv. of DPC at 140°C for 48 h after purification. The ^{1}H and ^{13}C NMR spectra of the DTMPC were shown in Figure 6. The ^{1}H NMR spectrum shows the signals at 4.29–4.16, which are ascribed to the methylene protons adjacent to carbonate groups. FTIR spectrum give the characteristic stretching vibration of carbonyl groups at 1734 cm^{-1} (Figure S5, Supporting Information). The formation of six-membered cyclic structures was also confirmed by the presence of a signal at 148 ppm in ^{13}C NMR spectrum.

Anionic ROP of NPGC and Fabrication of Networked Polycarbonates

First, we investigated the ROP of NPGC in the THF solution states. At a presence of 2 mol % of DBU, NPGC was polymerized and polycarbonates (pNPGC) were obtained after precipitation by methanol. The pNPGC gives the shift of proton signals to the high magnetic field in ^{1}H NMR spectroscopy [Figure S6(a)] and ^{13}C NMR spectra are also changed [Figure S6(b)]. The SEC trace of pNPGC shows a single peak at a retention time of 4.5 min [Figure 7(a)]. From the trace, M_n and M_w/M_n were calculated to be 9900 g mol^{-1} and 1.29, respectively. This narrow M_w/M_n value indicates that the back biting and the decarbonation reactions are sufficiently prohibited during polymerization. The ROP of NPGC was affected by the initial monomer concentration ($[M]_0$). With decreasing the $[M]_0$, M_n was slightly decreased while M_w/M_n was slightly narrowed (Figure S7, Supporting Information). Next, we added a 1 mol % of
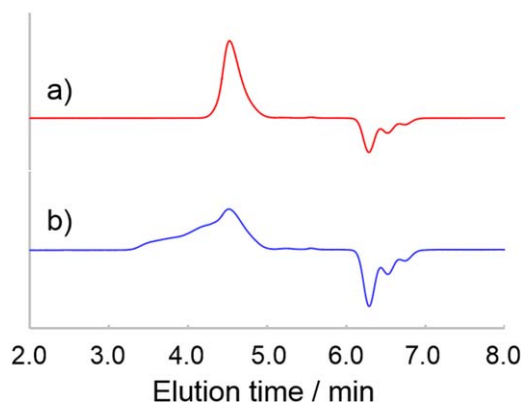

Figure 7. SEC traces of (a) pNPGC and (b) p(NPGC-co-DTMPC) prepared by the ROP of NPGC with 1 mol % of DTMPC with respect to $[M]_0$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
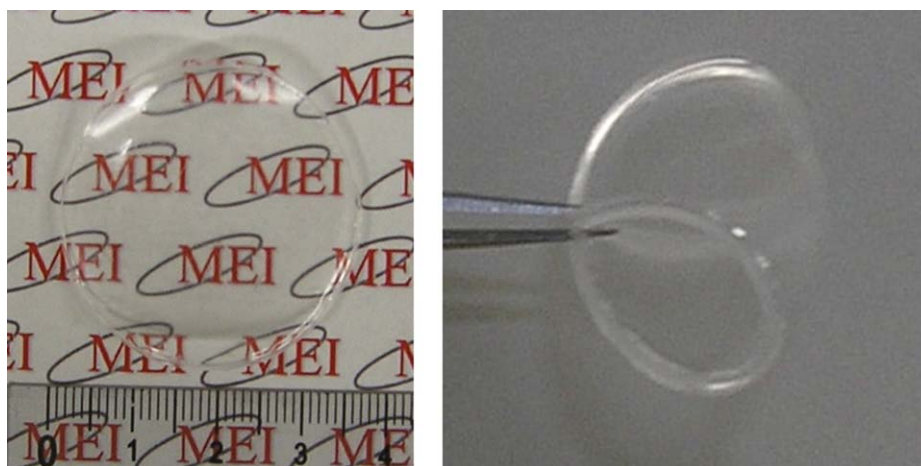
Figure 8. Photographs of networked polycarbonate film prepared by the anionic ROP of a THF solution containing NPG and DTMPC with a NPG/DTMPC feed ratio of 4 at 60°C for 12 h. Left: Top view. Right: image of the film bend by a tweezers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DTMPC with respect to $[M]_0$ to THF solutions containing NPGC and 2 mol % of DBU and then the mixture was stirred at 60°C for 18 h under nitrogen atmosphere. After precipitation by methanol, the resulting copolymer p(NPGC-*co*-DTMPC) was characterized by SEC and ^{1}H NMR spectroscopy and the results are shown in Figures 7(b) and S8, Supporting Information, respectively. The SEC trace shows a broad peak at an elution time of 3.5–5.0 min. M_n and M_w/M_n were calculated to be 16,400 g mol^{-1} and 6.25, respectively. These indicate the generation of higher molecular weight species, implying the construction of networked structures. The amount of DTMPC in the copolymer was evaluated by ^{1}H NMR spectrum and proved to be about 1 mol %, suggesting that the polymerization properties of DTMPC is similar to that of NPGC.

It is expected that an increase in the amount of DTMPC more than 1 mol % gives well-developed polycarbonate films. To pur-

pose of this aim, we added 10 mol % of DTMPC with respect to $[M]_0$ to THF solution of NPG (90 mol %) containing 5 mol % of DBU and the solution was filled in a PTFE petri-dish and the ROP was carried out in the dish by simply aging at 60°C for 12 h. During this treatment, THF was removed gradually and concentration of the monomers became increased, which is favorable for the construction of well-developed networked structures. The resulting film was shown in Figure 8. The film shows excellent transparency and is enough flexible to be bend.

Networked polycarbonate films were also fabricated from THF solutions of NPGC and DTMPC at different NPGC/DTMPC feed ratios. The resulting films showed to some extent the transparency in near-UV to near-infrared regions (Figures S9 and S10, Supporting Information). Mechanical properties were measured and stress–strain curves and the parameters obtained are shown in Figure S11 and Table S1, Supporting Information, respectively. The film prepared with 10 mol % of DTMPC showed a yield point and the values of stress and strain at maximum point were 10.4 MPa and 12.7%, respectively [Figure S11(a)]. On the other hands, the films prepared with 20 or 30 mol % of DTMPC exhibited about 25 MPa of stress and about 5% of strain [Figure S11(b)]. A larger amount of DTMPC gave harder and more fragile films, which is due to an increase in the crosslink points. The film prepared with 50 mol % of DTMPC showed lower stress and strain values, which might be caused by the generation of heterogeneous domains in the polymer networks. The thermal degradability of these films were evaluated by TG measurements and the TG curves were shown in Figure 9. Without DTMPC, the pure pNPGC showed the drastic weight loss at 260–340°C. The film prepared with 10 mol % of DTMPC showed a weight loss at 280–360°C, which is slightly higher than that of the pure pNPGC. While, the further increase in the feed ratios led to the weight loss at broader ranges. The start of the weight loss was decreased down to 150°C, which could be caused by an increase in chain ends of polycarbonates and/or generation of heterogeneous regions of the polymer networks. While the end of the degradation reached up to 420°C. In the case of pure pDTMPC, the thermal degradation proceeded gradually from 160°C and mainly
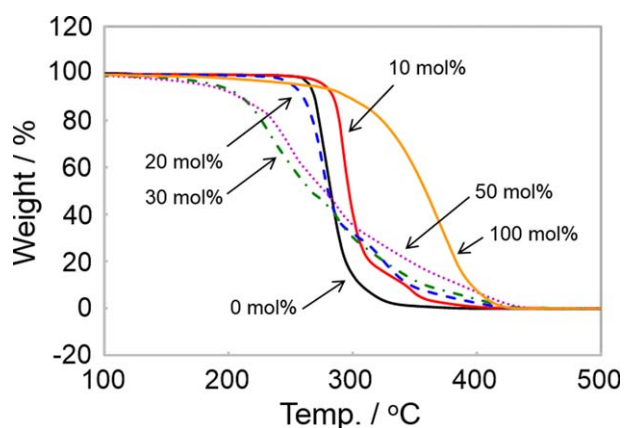

Figure 9. TG curves of networked polycarbonate solids or films prepared by the anionic ROP of NPG/DTMPC THF solution with different NPG/DTMPC feed ratios at 60°C for 12 h. The mole fraction of DTMPC with respect to $[M]_0$ were 0 (black lines), 10 (red lines), 20 (blue broken lines), 30 (green dotted and chain lines), 50 (purple dotted lines), or 100 mol % (orange lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

occurred at 300–430°C. Therefore, the weight loss at 340–430°C of these films would be attributed to the formation of well-developed pDTMPC network domains.

CONCLUSIONS

In this article, we focused on the facile synthesis of six-membered cyclic carbonates utilizing DPC as a transesterification agent and then explored an application of these carbonates to the facile fabrication of networked polycarbonate films. DPC is less toxic and highly stable as compared to the conventional chlorocarbonate esters. In the DPC system, bases such as triethylamine, which are generally added to trap the leaving Cl ion, are not needed and DPC also serve as a solvent at above its melting point. Besides, DPC can be synthesized from the route that involves neither phosgene nor phosgene derivatives. Therefore, it is obvious that the synthesis of six-membered cyclic carbonates from the corresponding diols with DPC is definitely the phosgene-free route. Actually, from NPG and 4 equiv. of DPC, we synthesized and isolated a six-membered cyclic carbonate NPGC with a yield of 74%. Although the efficient synthesis of NPGC needs thermal energy, the addition of nonexpensive magnesium salts makes it possible to synthesize NPGC with a good conversion and selectivity at lower temperature than 140°C. Especially, NPGC was obtained with a selectivity of 68% by the reaction of NPG with 5 equiv. of DPC at 85°C for 94 h. Similarly, we reacted DTMP with 10 equiv. of DPC to synthesize and isolate the bifunctional carbonate DTMPC with a yield of 82%. The monofunctional carbonate NPG can be polymerized efficiently by the anionic ROP at high monomer concentration. The copolymerization of the NPGC with a small amount of DTMPC easily formed networked structures to give higher molecular weight structures, which can be confirmed by ^{1}H NMR spectroscopy and SEC measurements. The ROP of a THF solution containing NPGC with DTMPC at 60°C coupled with the gradual evaporation of solvents easily give polycarbonate films with good transparency and flexibility. The fabrication of functionalized polycarbonate films using six-membered cyclic carbonates bearing functional groups is in progress.

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