Mild Incorporation of CO_2 into Epoxides: Application to Nonisocyanate Synthesis of Poly(Hydroxyurethane) Containing Triazole Segment by Polyaddition of Novel Bifunctional Five-Membered Cyclic Carbonate and Diamines

Naoto Aoyagi,[1] Yoshio Furusho,[1,2] Takeshi Endo [1]
[1]Molecular Engineering Institute, Kindai University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan
[2]Department of Chemistry, Shiga University of Medical Science, Seta, Otsu 520-2192, Japan
Correspondence to: T. Endo (E-mail: tendo@moleng.fuk.kindai.ac.jp)

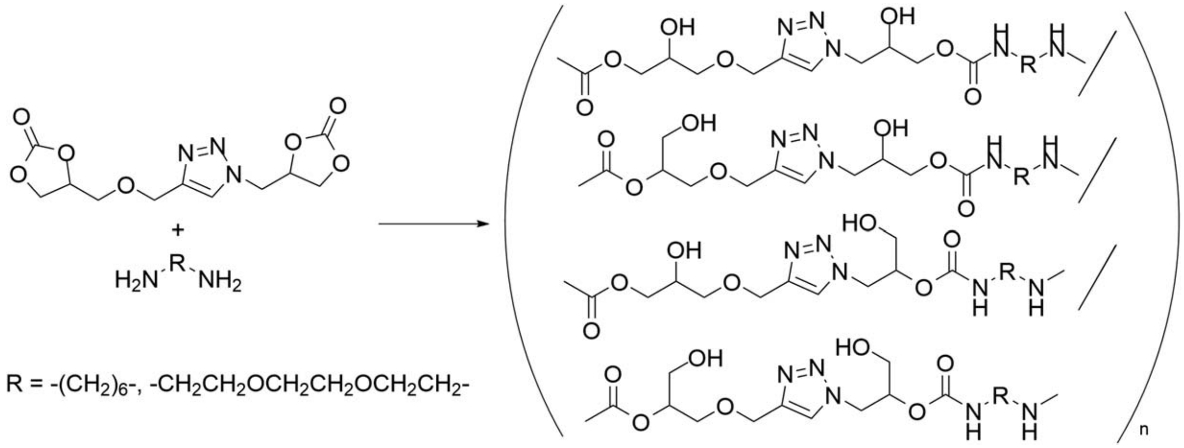
Received 27 November 2017; accepted 17 January 2018; published online 00 Month 2018
DOI: 10.1002/pola.28967

ABSTRACT: The cyclic amidinium iodide effectively catalyzed the ring-expansion addition of epoxides with carbon dioxide under ordinary pressure and mild conditions to obtain the corresponding five-membered cyclic carbonates in high yield. The novel triazole-linked bifunctional five-membered cyclic carbonate was synthesized successfully by the click reaction of the azide- and the alkyne-substituted five-membered cyclic carbonates under ambient temperature in high yield. The chemical structure of the novel bis(cyclic carbonate) was characterized by one- and two-dimensional nuclear magnetic resonance spectra. The obtained bis(cyclic carbonate) was converted with commercially available diamines to poly(hydroxyurethane) containing triazole segment without catalyst in high yield. Analyses of the resulting poly(hydroxyurethane)s were performed by proton nuclear magnetic resonance, size exclusion chromatography, thermogravimetric analysis, and differential scanning calorimetry. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

KEYWORDS: click reaction; CO_2; epoxide; five-membered cyclic carbonate; poly(hydroxyurethane)

INTRODUCTION Carbon dioxide (CO_2) is often accused of being a main culprit of global warming, while in synthetic chemistry it is regarded as an environmentally friendly reagent, which is useful especially for phosgene free processes.[1] Of particular importance is incorporation reaction of CO_2 into epoxides to give five-membered cyclic carbonates,[2] which are used in various areas, such as aprotic polar solvents,[3] electrolytes,[4–6] and lithium ion batteries.[7–9] Furthermore, bifunctional five-membered cyclic carbonates can be converted to poly(hydroxyurethane)s by polyaddition with α,ω-diamines, which provided an alternative route for the synthesis of polyurethanes without using toxic phosgene or isocyanates.[10–17] Hence, synthesis of functional poly(hydroxyurethane)s by nonisocyanate processes have recently attracted much attention from environmental concerns. For example, the hydroxyl groups of poly(hydroxyurethane)s can be utilized as crosslinking points to afford networked polymers.[18] Polarities of the networked polymers can be adjusted by judicious choice of the crosslinkers, which leads to control over the affinity toward various solvents. Incorporation of silicon backbones to poly(hydroxyurethane)s results in improved water resistance as well as flexibility, which suggest potential applications as soft adhesives and additives.[19] The ion gels that have hydroxyurethane crosslinking points show high ionic conductivities due to their high compatibility with ionic liquids.[20] Several other poly(hydroxyurethane)s are used as polymer/liquid crystal composite films,[21] amphiphilic antibacterial polymers,[22] and dye fixation agent.[23] Accordingly, synthetic chemists have developed a wide range of CO_2 incorporation reactions for the synthesis of cyclic carbonates.[2,24–28] However, most of these reactions require some pressure (~20 atm) and/or high temperature unless expensive metal catalysts are employed.[29] We have recently reported that the cyclic amidinium salts such as 1,8-diazabicyclo[5.4.0]-7-undecene hydroiodide (DBU•HI) effectively catalyzed the reaction of CO_2 and epoxides under mild conditions such as ordinary pressure and ambient temperature to obtain the corresponding five-membered cyclic carbonates in high yield.[30] As for bifunctional five-membered cyclic carbonates, they are prepared in general from commercially available bifunctional epoxides such as bisphenol A diglycidyl ether,[31] resorcinol diglycidyl

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Polyaddition of bifunctional five-membered cyclic carbonate and diamine.

ether,[32] ethylene glycol diglycidyl ether,[33] butanediol diglycidyl ether,[32] and so on. The thiol-ene "click" reactions of dithiol and vinyl-functionalized cyclic carbonate afford the bifunctional cyclic carbonates in moderate to high yield.[34,35] Although the azide-alkyne "click" cycloaddition is one of the most powerful methods for the synthesis of functional monomers and polymers,[36–41] they have not yet been employed for the synthesis of the bifunctional cyclic carbonates to the best of our knowledge.

Herein, we report the nonisocyanate synthesis of poly(hydroxyurethane) containing triazole segment using a novel bifunctional five-membered cyclic carbonate and commercially available α,ω-diamines (Scheme 1). The bifunctional cyclic carbonate bearing triazole linker was prepared from the copper(I) iodide-catalyzed azide-alkyne click reaction between cyclic carbonate with azide group and that with alkyne group, which were synthesized from epibromohydrin or epichlorohydrin via CO_2 insertion reaction in the presence of a catalytic amount of DBU•HI under ordinary pressure and mild conditions as a key step. Then, the obtained bifunctional cyclic carbonate was converted to poly(hydroxyurethane)s containing triazole segment in high yield by polyaddition with 1,6-diaminohexane or 1,2-bis(2-aminoethoxy)ethane without catalyst. We also investigated the solubility and thermal properties of the resulting poly(hydroxyurethane)s.

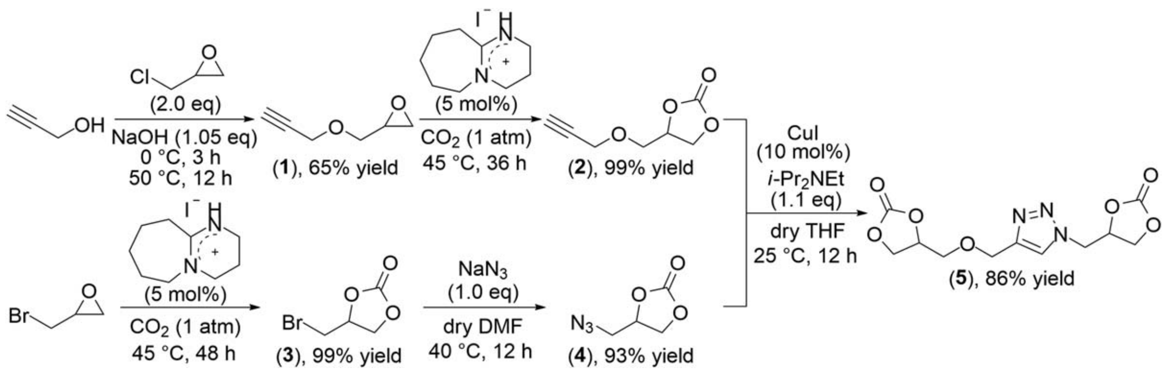
EXPERIMENTAL

Materials

CO_2 (>99.99%) was obtained from Fukuho Teisan. Epichlorohydrin (>99.0%), epibromohydrin (>97.0%), 2-propyn-1-ol (>98.0%), and 1-aminodecane (>98.0%) were obtained from Tokyo Kasei Kogyo. 1,6-Diaminohexane (>95.0%), 1,8-diazabicyclo[5.4.0]-7-undecene (>97.0%), *N*-ethyldiisopropylamine (>97.0%), sodium azide (>98.0%), sodium hydroxide (>97.0%), anhydrous *N,N*-dimethylformamide (>99.5%), anhydrous tetrahydrofuran (>99.5%), and anhydrous dimethyl sulfoxide (>99.0%) were obtained from Wako Pure Chemical Industries. Hydriodic acid (55.0%–58.0%), copper(I) iodide (>99.0%), 1,4-dioxane (>99.5%), sodium sulfate (>99.0%), spherical silica gel (63–210 μm, neutral), diethyl ether (>99.0%), hexane (>96.0%), ethyl acetate (>99.3%), acetone (>99.0%), chloroform (>99.0%), and acetonitrile (>99.0%) were obtained from Kanto Chemical. 1,2-Bis(2-aminoethoxy)ethane (98%) was obtained from Aldrich Chemical. 1,8-Diazabicyclo[5.4.0]-7-undecene and *N*-ethyldiisopropylamine were dried over CaH_2, and then distilled prior to use. All other reagents were used as received without further purification.

Characterizations

Proton (^{1}H, 400 MHz), carbon-13 (^{13}C, 100 MHz), distortionless enhancement by polarization transfer (DEPT), ^{1}H–^{1}H correlated spectroscopy (H-H COSY), heteronuclear multiple quantum coherence (HMQC), and heteronuclear multiple-bond correlation (HMBC) nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a JEOL ECS-400/SS instrument using tetramethylsilane or DMSO-d_6 as an internal standard at 25 °C. The melting points were measured using an SRS MPA100 automated melting point apparatus and were uncorrected. Mass spectroscopy was performed on a Shimadzu GCMS-QP5050A in electron ionization (EI) mode. Number average molecular weight (M_n) and polydispersity index (M_w/M_n) were estimated by size exclusion chromatography (SEC) using a TOSOH HLC-8220 GPC instrument equipped with three consecutive polystyrene gel columns [TSK-gels (particle size, exclusion limit); super AW4000 (6 μm, $>4 \times 10^5$), super AW3000 (4 μm, $>6 \times 10^4$), and super AW2500 (4 μm, $>2 \times 10^3$), 15 cm each], and a guard column [TSK-guard column Super AW-H, 3.5 cm] with DMF containing 0.01M LiBr as an eluent at a flow rate 0.5 mL/min at 40 °C after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed from 50 to 500 °C at a heating ratio of 10 °C/min under nitrogen atmosphere (flow rate: 200 mL/min) on a Seiko EXSTER6000 system with TGA-6200 instruments. Differential scanning calorimetry (DSC) was carried out from −20 to 100 °C at a heating ratio of 5 °C/min under nitrogen atmosphere (flow rate: 50 mL/min) on a Seiko EXSTER6000 system with DSC-6200 instruments.



SCHEME 2 Synthesis of bis(cyclic carbonate) monomer containing triazole group.

Synthesis of Catalyst for the Reaction of Epoxides with CO_2

Synthesis of 1,8-Diazabicyclo[5.4.0]-7-Undecene Hydroiodide (DBU•HI)

A solution of 55% aqueous hydroiodic acid (1 mL, ca. 7.3 mmol) was added dropwise for 1 min to a mixture of 1,8-diazabicyclo[5.4.0]-7-undecene (609 mg, 4 mmol) in dioxane (8 mL) at room temperature. After being stirred at room temperature for 12 h, the mixture was evaporated *in vacuo*. The residue was washed with ether, and the precipitate was dried in vacuo for 4 h at 60 °C to give DBU•HI (1.10 g, 98%) as a pale yellow powder. Mp 160.6–161.7 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.73–1.86 (m, 6H), 2.12 (quin, 2H, $J = 6.0$ Hz), 2.98–3.04 (m, 2H), 3.46–3.52 (m, 2H), 3.60–3.66 (m, 4H), 9.55 (brs, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 19.2, 23.7, 26.6, 28.8, 32.7, 37.7, 48.9, 54.8, 166.1.

Synthesis of Bis(Cyclic Carbonate) Monomer

Preparation of Glycidyl Propargyl Ether (1)

A mixture of epichlorohydrin (18.5 g, 200 mmol) and 2-propyn-1-ol (5.61 g, 100 mmol) was stirred at 0 °C, and then sodium hydroxide (4.20 g, 105 mmol) was added to the mixture over a period of 30 min. The resulting mixture was stirred at 0 °C for 3 h, then the ice bath was removed, and the reaction temperature was raised to 50 °C. After 12 h at 50 °C, the mixture was diluted with diethyl ether and filtered, and the residue was washed with diethyl ether. The combined filtrates were washed with water, dried over sodium sulfate, and the solvents were evaporated in vacuo. The residue was purified by silica gel column chromatography (hexane/chloroform = 1:1) to give **1** (7.28 g, 65%) as a colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.47 (t, 1H, $J = 2.4$ Hz), 2.64 (dd, 1H, $J = 5.2$, 2.8 Hz), 2.81 (t, 1H, $J = 4.6$ Hz),

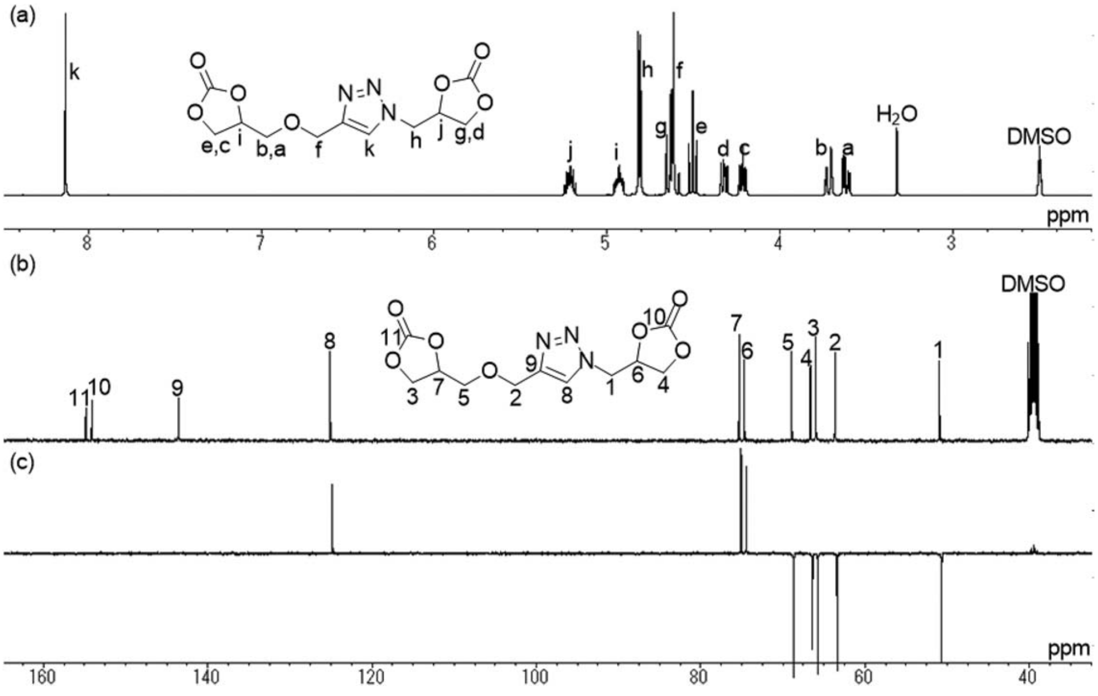


FIGURE 1 1D NMR spectra of a solution of **5** in DMSO-d_6 at 25 °C. (a) ^{1}H (400 MHz), (b) ^{13}C (100 MHz), and (c) DEPT-135 (100 MHz).

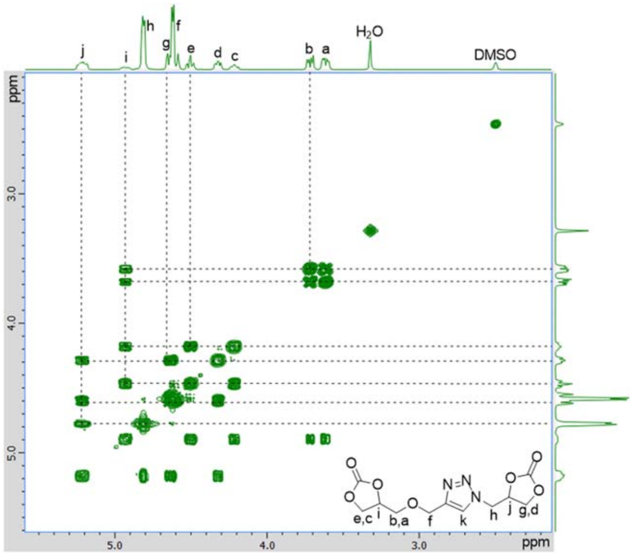


FIGURE 2 Partial H-H COSY NMR spectrum (400 MHz, 25 °C) of a solution of **5** in DMSO-d_6. [Color figure can be viewed at wileyonlinelibrary.com]

3.16–3.20 (m, 1H), 3.49 (dd, 1H, $J = 11.2$, 6.0 Hz), 3.84 (dd, 1H, $J = 11.2$, 3.2 Hz), 4.20 (dd, 1H, $J = 16.0$, 2.4 Hz), 4.25 (dd, 1H, $J = 16.0$, 2.4 Hz). ^{13}C NMR ($CDCl_3$, δ, ppm): 44.3, 50.5, 58.4, 70.3, 74.8, 79.2. MS (EI): $m/z = 112$ $[M]^+$.

Preparation of (Propargyloxymethyl)Ethylene Carbonate (2)

DBU•HI (280 mg, 1 mmol) was added to the epoxide **1** (2.24 g, 20 mmol) at room temperature. The atmosphere inside the flask was replaced with CO_2 (balloon, *ca.* 1 atm), and the reaction mixture was stirred at 45 °C. After 36 h, the mixture was purified by silica gel column chromatography (hexane/acetone = 3:1) to give **2** (3.10 g, >99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.50 (t, 1H, $J = 2.4$ Hz), 3.75 (dd, 1H, $J = 10.6$, 4.0 Hz), 3.80 (dd, 1H, $J = 10.4$, 4.0 Hz), 4.21 (dd, 1H, $J = 16.0$, 2.0 Hz), 4.28 (dd, 1H, $J = 16.2$, 2.4 Hz), 4.41 (dd, 1H, $J = 8.0$, 6.0 Hz), 4.52 (dd, 1H, $J = 8.4$, 8.4 Hz), 4.82–4.88 (m, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 58.8, 66.2, 68.4, 74.6, 75.6, 78.5, 154.7. MS (EI): $m/z = 156$ $[M]^+$.

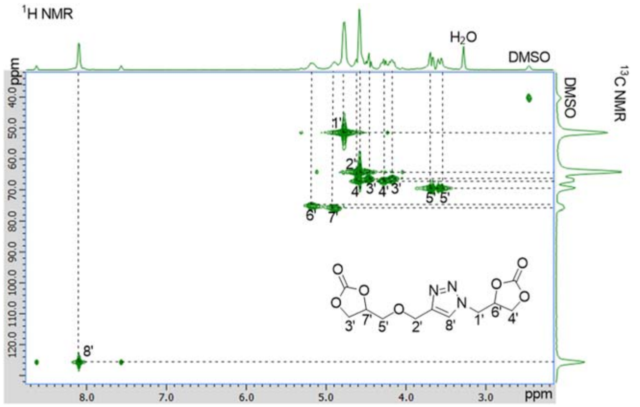


FIGURE 3 Partial HMQC NMR spectrum (^{1}H 400 MHz, ^{13}C 100 MHz, 25 °C) of a solution of **5** in DMSO-d_6. [Color figure can be viewed at wileyonlinelibrary.com]

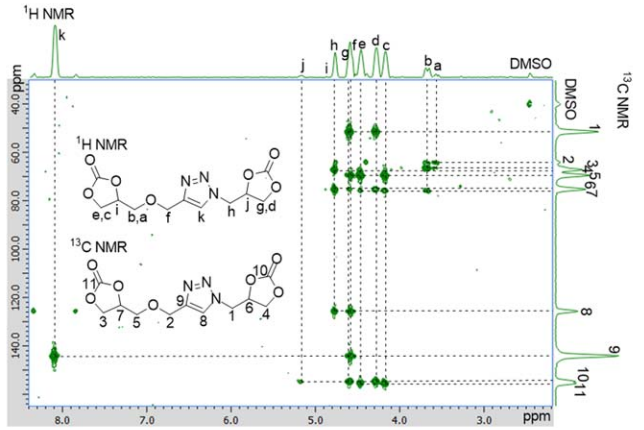


FIGURE 4 HMBC NMR spectrum (^{1}H 400 MHz, ^{13}C 100 MHz, 25 °C) of a solution of **5** in DMSO-d_6. [Color figure can be viewed at wileyonlinelibrary.com]

Preparation of (Bromomethyl)Ethylene Carbonate (3)

DBU•HI (280 mg, 1 mmol) was added to epibromohydrin (2.74 g, 20 mmol) at room temperature. The atmosphere inside the flask was replaced with CO_2 (balloon, *ca.* 1 atm), and the reaction mixture was stirred at 45 °C. After 48 h, the mixture was purified by silica gel column chromatography (hexane/acetone = 3:1) to give **3** (3.59 g, >99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.55–3.61 (m, 2H), 4.37 (dd, 1H, $J = 9.2$, 6.0 Hz), 4.61 (dd, 1H, $J = 8.4$, 8.4 Hz), 4.93–4.99 (m, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 31.2, 68.1, 73.9, 154.1. MS (EI): $m/z = 180$, 182 $[M]^+$.

Preparation of (Azidomethyl)Ethylene Carbonate (4)

Sodium azide (1.30 g, 20 mmol) was added to a solution of **3** (3.62 g, 20 mmol) in anhydrous *N,N*-dimethylformamide (20 mL) at room temperature. After being stirred at 25 °C for 12 h, the mixture was concentrated to one fourth of its original volume in vacuo at 30 °C. The residue was diluted with ethyl acetate and washed with water, and the aqueous

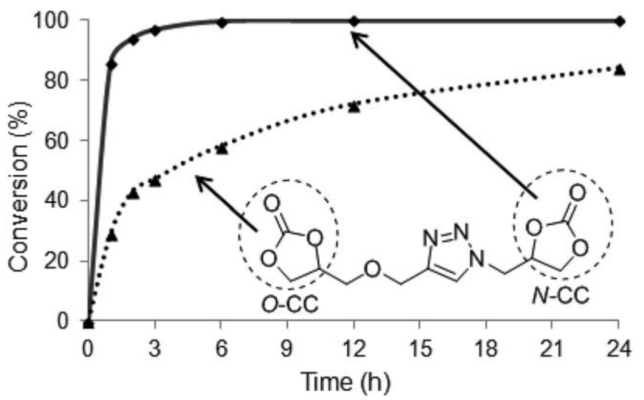
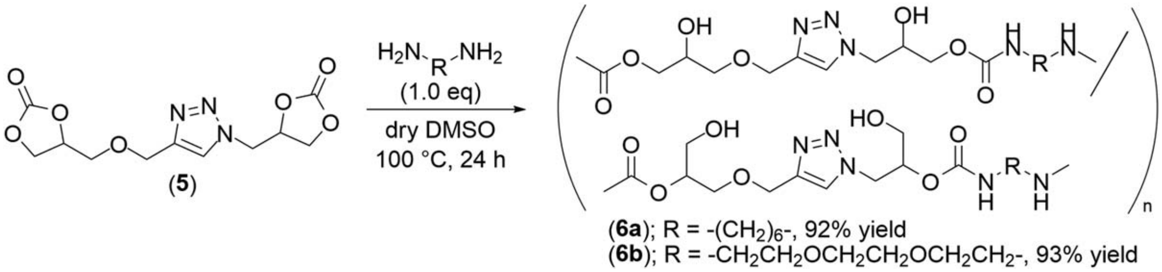


FIGURE 5 Time conversion curves of two cyclic carbonates of **5**. Reaction conditions: 0.5 mmol of **5**, 1 mmol of $CH_3(CH_2)_9NH_2$, 0.5 mL of anhydrous DMSO, and 80 °C for 24 h.



SCHEME 3 Synthesis of poly(hydroxyurethane)s containing triazole segment (secondary and primary hydroxyl groups exist randomly, but simplified as illustrated).

phase was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, and the solvents were evaporated in vacuo. The residue was purified by silica gel column chromatography (chloroform) to give **4** (2.67 g, 93%) as a colorless oil. ^{1}H NMR (CDCl$_3$, δ, ppm): 3.57 (dd, 1H, $J = 13.4$, 4.0 Hz), 3.72 (dd, 1H, $J = 13.4$, 4.0 Hz), 4.32 (dd, 1H, $J = 8.8$, 6.4 Hz), 4.53 (dd, 1H, $J = 8.4$, 8.4 Hz), 4.81-4.87 (m, 1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 52.0, 66.3, 74.0, 154.0. MS (EI): $m/z = 143$ [M]$^+$.

Synthesis of 4-[(1,3-Dioxolane-2-One-4-Ylmethoxy)Methyl]-1-(1,3-Dioxolane-2-One-4-Ylmethyl)-1H-[1,2,3]Triazole (5)

Copper(I) iodide (95 mg, 0.5 mmol) was added to a mixture of **2** (781 mg, 5 mmol), **4** (716 mg, 5 mmol) and *N*-ethyldiisopropylamine (711 mg, 5.5 mmol) in anhydrous tetrahydrofuran (50 mL) at room temperature. The resulting mixture was stirred at 25 °C for 12 h, and then the mixture was evaporated in vacuo. The residue was purified by silica gel column chromatography (chloroform/acetonitrile = 2:1) to give **5** (1.29 g, 86%) as a white solid. Mp 83.5–85.2 °C. ^{1}H NMR (DMSO-d_6, δ, ppm): 3.62 (ddd, 1H, $J = 12.8$, 4.2, 1.0 Hz), 3.72 (dd, 1H, $J = 11.2$, 2.4 Hz), 4.19–4.24 (m, 1H), 4.33 (ddd, 1H, $J = 9.0$, 6.0, 1.0 Hz), 4.51 (dd, 1H, $J = 8.6$, 8.6 Hz), 4.58–4.66 (m, 3H), 4.82 (d, 2H, $J = 5.2$ Hz), 4.90–4.96 (m, 1H), 5.18–5.25 (m, 1H), 8.14 (s, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm): 50.9, 63.7, 66.0, 66.6, 68.9, 74.7, 75.3, 125.1, 143.6, 154.2, 154.9. MS (EI): $m/z = 299$ [M]$^+$.

Synthesis of Poly(Hydroxyurethane)s

General Procedure for the Synthesis of Poly(Hydroxyurethane)s Containing Triazole Segment (6a,b)

A solution of 1,6-diaminohexane (232 mg, 2 mmol) or 1,2-bis(2-aminoethoxy)ethane (296 mg, 2 mmol) in anhydrous dimethyl sulfoxide (1 mL) was added to the mixture of **5** (598 mg, 2 mmol) in anhydrous dimethyl sulfoxide (1 mL) at room temperature, and was stirred at 100 °C. After 24 h, the mixture was cooled to rt, and was precipitated into acetone. The precipitate was washed with acetone and dried at 40 °C in vacuo to give **6a** (765 mg, 92%) or **6b** (835 mg, 93%) as a pale orange sticky solid. The obtained poly(hudroxyurethane)s were analyzed by ^{1}H NMR, SEC, TGA, and DSC.

RESULTS AND DISCUSSION

Synthesis of Triazole-Linked Bifunctional Five-Membered Cyclic Carbonate (5)

Scheme 2 shows the three-step convergent synthesis of **5** via click reaction. First, the glycidyl propargyl ether (**1**) was synthesized by ring-opening addition of propargyl alcohol to epichlorohydrin and subsequent ring-closing reaction in the presence of sodium hydroxide in moderate yield. Next, the ring-expansion addition of **1** and epibromohydrin with CO$_2$ were carried out in bulk using a catalytic amount of amidinium salt at ordinary pressure and 45 °C. Investigation of the catalytic effects of amidinium salts has been already reported in the literature.[30] The use of DBU•HI gave the corresponding five-membered cyclic carbonates **2** and **3** in high yields. The azide-substituted cyclic carbonate (**4**) was obtained by treatment of **3** with an equimolar amount of sodium azide in 93% yield. Finally, the copper (I)-catalyzed cycloaddition between the azide (**4**) and the alkyne (**2**) proceeded at ambient temperature to afford the desired bis (cyclic carbonate) monomer (**5**) in 86% yield. The characterization of **5** was achieved by 1D (^{1}H, ^{13}C and DEPT-135) and 2D (H-H COSY, HMQC, and HMBC) NMR spectra. As shown in Figure 1, the ^{1}H NMR spectrum showed a singlet at low

TABLE 1 Results of Polyaddition Reaction of 5 with Diamine

Polymer	Conv. (%)[a]	Yield (%)[b]	M_n (g mol^{-1})[c]	M_w (g mol^{-1})[c]	M_w/M_n (-)[c]	T_g (°C)[d]	T_{d5} (°C)[e]	T_{d10} (°C)[e]
6a	>99	92	14,500	54,700	3.77	35	244	263
6b	>99	93	7,400	15,900	2.15	19	241	266

[a] Determined by ^{1}H NMR.
[b] Isolated yield after precipitation with acetone.
[c] Estimated by SEC (DMF containing 10 mM LiBr, polystyrene standard).
[d] Measured by DSC.
[e] Measured by TGA.

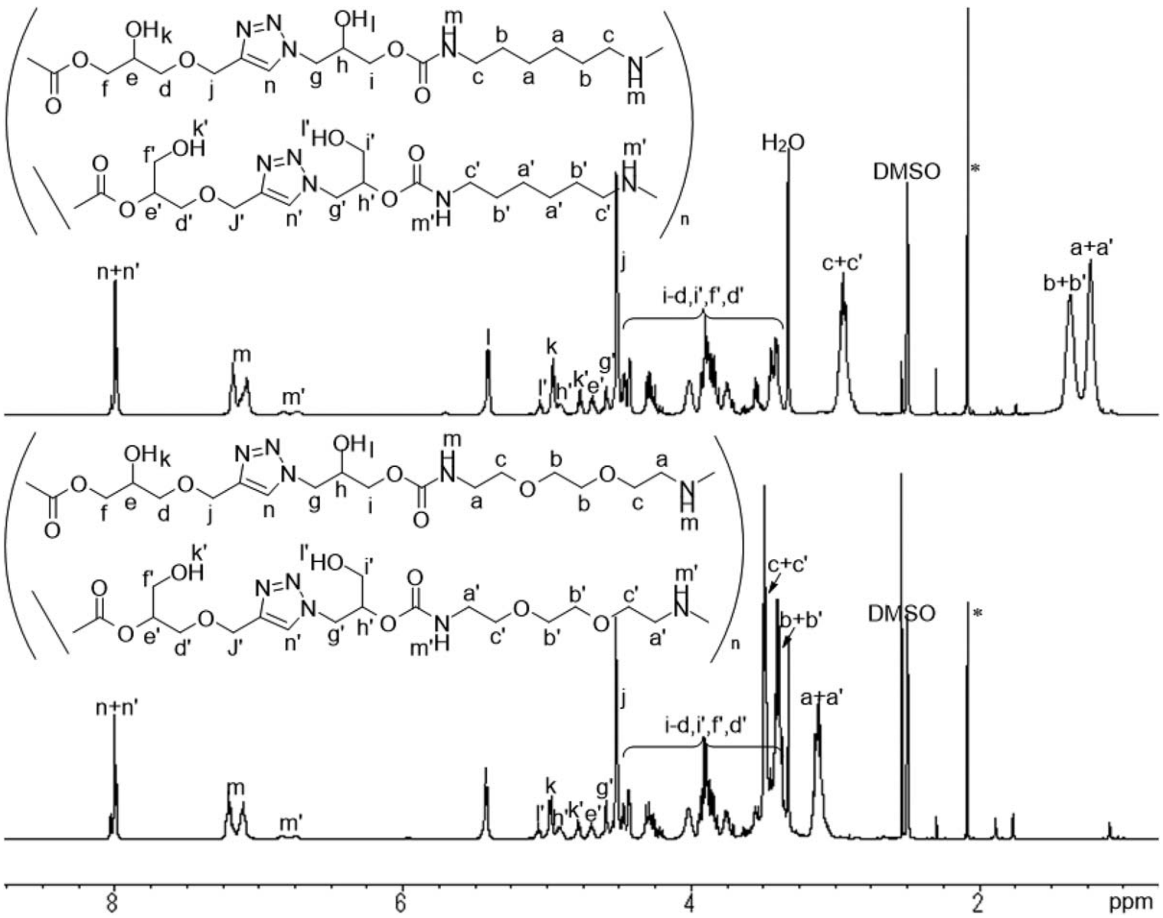


FIGURE 6 ^{1}H NMR spectra of a solution of **6a** or **6b** in DMSO-d_6 at 25 °C. Asterisks denote the remaining acetone used for purification.

magnetic field of 8.1 ppm assignable to the methine proton of the triazole ring. The signal of the methine carbon of the triazole ring was observed at *ca*. 125 ppm in the ^{13}C and DEPT-135 NMR spectra. The signal of the quaternary carbon of the triazole ring was observed at 143.6 ppm in the ^{13}C NMR spectrum, and two peaks assignable to the carbonyl groups of the two cyclic carbonate rings were shown at low magnetic field of 154.2 and 154.9 ppm. As shown in Figure 2, the proton signals of two different cyclic carbonate moieties were identified by H-HCOSY spectrum. The signal of the methylene proton at the 4-position of triazole ring and the carbon signals of two different cyclic carbonate moieties were assigned by HMQC and HMBC spectra (Figs. 3 and 4). All the signals could be reasonably assigned in accordance with the crosspeaks.

Synthesis and Characterizations of Poly(Hydroxyurethane)s (6a,b)

First, we investigated the reactivity of two different cyclic carbonate groups of **5** by aminolysis using monofunctional amine. As shown in Figure 5, the reaction of **5** was carried out with two equivalents of 1-aminodecane at 80 °C without catalyst. The conversion of two cyclic carbonate groups of **5** was calculated by the integration of ^{1}H NMR signals. The

TABLE 2 The Solubility of Poly(Hydroxyurethane)s

	H_2O	MeOH	EtOH	CH_3CN	DMAc	DMF	NMP	DMSO
6a	–	–	–	–	++	++	++	++
6b	++	+	–	–	++	++	++	++
	Hexane	Toluene	Et_2O	EtOAc	CH_2Cl_2	$CHCl_3$	THF	Acetone
6a	–	–	–	–	–	–	–	–
6b	–	–	–	–	–	–	–	–

++: soluble, +: partially soluble, –: insoluble. Conditions: 2 mg/mL, 150 rpm at 25 °C for 1 h.

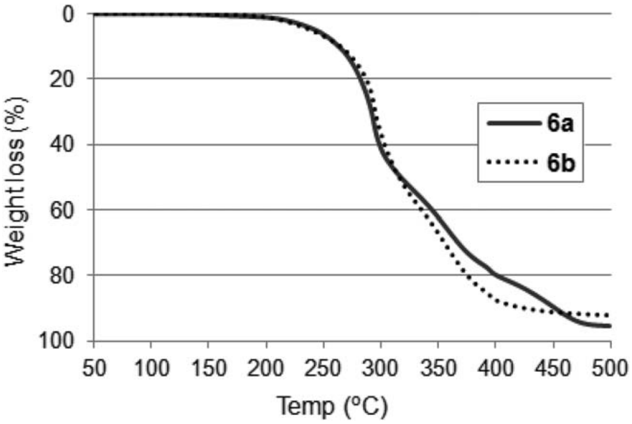


FIGURE 7 TGA curves of **6a** (solid line) and **6b** (dashed line) from 50 to 500 °C (10 °C/min) under N_2 atmosphere (200 mL/min).

cyclic carbonate at the side of triazole ring (*N*-CC) was more reactive than the other cyclic carbonate at the side of ether group (*O*-CC). The conversion of *N*-CC was more than 99% within 6 h, whereas the conversion of *O*-CC was not completed even after 24 h. Thus the reaction temperature needs more than 80 °C to complete the reaction within 24 h. The novel bis(cyclic carbonate) (**5**) could be applied to the synthesis of poly(hydroxyurethane)s by the polyaddition reaction with diamines. As shown in Scheme 3, the reaction of **5** was carried out with stoichiometric amount of 1,6-diaminohexane or 1,2-bis(2-aminoethoxy)ethane at 100 °C without catalyst. The results of the polyaddition reactions are summarized in Table 1. The conversion of **5** was calculated by the integration of ^{1}H NMR signals. The polymeric products (**6a**-**b**) were isolated as pale orange sticky solids simply by precipitation with acetone in high yield. The number average molecular weight of **6a** (M_n 14,500) estimated by SEC was 1.96 times higher than that of **6b** (M_n 7,400); however, the polydispersity index of **6a** (M_w/M_n 3.77) had a much broader distribution than that of **6b** (M_w/M_n 2.15). The ^{1}H NMR spectra of poly(hydroxyurethane)s are shown in Figure 6. The signals of the methine protons of the triazole rings were observed at *ca*. 8.0 ppm as in the case of the ^{1}H NMR spectrum of **5**. The assignment of the signals for the active hydrogen atoms such as amide groups (7.0–7.2 and 6.7–6.9 ppm), secondary hydroxyl groups (5.4 and 5.0 ppm), and primary hydroxyl groups (5.1 and 4.8 ppm) were confirmed by the disappearance of the signals by the addition of D_2O. The ratios of the secondary and the primary hydroxyl groups of **6a** and **6b** were estimated to 74:26 and 73:27, respectively, by the integration ratio of the triazole proton signal to the α-methine proton signals of the primary hydroxyl groups (Supporting Information, Fig. S1). The solubility of poly(hydroxyurethane)s (**6a**-**b**) are listed in Table 2. The polymer **6a** was soluble in highly polar aprotic solvents, such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), 1-methyl-2- pyrrolidone (NMP), and dimethyl sulfoxide (DMSO), but insoluble in nonpolar, low-polarity, and protic solvents. Poly(hydroxyurethane) containing ethylene glycol segment (**6b**) showed good solubility in water, whereas poly(hydroxyurethane) obtained from 1,6-diaminohexane (**6a**) was insoluble. This result clearly demonstrated that both the hydrophobic and the hydrophilic poly(hydroxyurethane)s containing triazole segment can be synthesized by using the choice of either alkyl moiety- or ether moiety-containing diamine. The thermal stabilities of **6a** and **6b** were studied by TGA. Figure 7 shows the TGA curves obtained at a heating rate of 10 °C/min under a nitrogen flow. The 5% and 10% weight loss temperatures (T_{d5} and T_{d10}) of **6a** and **6b** were shown in Table 1. The thermal degradation behaviors were almost identical, and the T_{d5} and T_{d10} were determined to be around 242 °C and 265 °C, respectively. The thermal phase transitions of **6a** and **6b** were examined by DSC. Figure 8 shows the DSC curves obtained at the second heating scan at a rate of 5 °C/min under a nitrogen flow. The value of glass transition temperature (T_g) of **6b** was observed at 19 °C, which is lower than that of **6a** observed at 35 °C. It seems that the T_g values were affected by molecular weights of **6a** and **6b**. The poly (hydroxyurethane)s (**6a**,**b**) can be applied to biopolymeric materials and electrolytes, because **6a** and **6b** have good T_g values around room temperature.

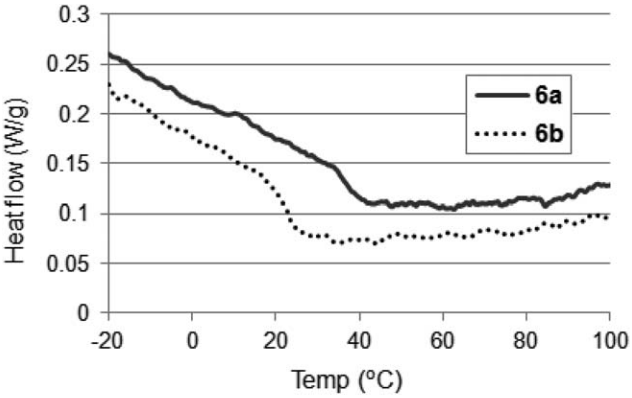


FIGURE 8 DSC curves of the second heating run of **6a** (solid line) and **6b** (dashed line) from −20 to 100 °C (5 °C/min) under N_2 atmosphere (50 mL/min).

CONCLUSIONS

The azide- and the alkyne-substituted five-membered cyclic carbonates were synthesized by two steps via ring-expansion addition of epoxides with CO_2, and the addition reaction proceeded under ordinary pressure in the presence of catalytic amount of DBU•HI in high yield. The click reaction of obtained cyclic carbonates was carried out to give the novel triazole-linked bifunctional five-membered cyclic carbonate in high yield. Both the hydrophobic and the hydrophilic poly(hydroxyurethane)s containing triazole segment were obtained in high yield by polyaddition of novel bis(cyclic carbonate) and diamines without catalyst. The thermal degradation behaviors of poly(hydroxyurethane)s were almost identical, and the T_{d5} were determined to be around 242 °C. It is envisioned that ionic conductive poly(hydroxyurethane)s can be designed and synthesized based on the cationic triazole segment, and such studies are ongoing in our laboratory.

REFERENCES AND NOTES

1 A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951.

2 M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514.

3 J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. Verevkin, A. Preetz, A. Börner, *Angew. Chem. Int. Ed.* **2007**, *46*, 5971.

4 K. Xu, Y. Lam, S. S. Zhang, T. R. Jow, T. B. Curtis, *J. Phys. Chem. C* **2007**, *111*, 7411.

5 T. Tsuda, K. Kondo, T. Tomioka, Y. Takahashi, H. Matsumoto, S. Kuwabata, C. L. Hussey, *Angew. Chem. Int. Ed.* **2011**, *50*, 1310.

6 J. Thielen, W. H. Meyer, K. Landfester, *Chem. Mater.* **2011**, *23*, 2120.

7 M. Inaba, Z. Siroma, A. Funabiki, Z. Ogumi, T. Abe, Y. Mizutani, M. Asano, *Langmuir* **1996**, *12*, 1535.

8 H. Tsutsumi, Y. Sumiyoshi, K. Onimura, T. Oishi, *Solid State Ionics* **2003**, *160*, 131.

9 H. Ota, X. Wang, E. Yasukawa, *J. Electrochem. Soc.* **2004**, *151*, A427.

10 N. Kihara, Y. Kushida, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 2173.

11 H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 851.

12 B. Ochiai, J. Nakayama, M. Mashiko, Y. Kaneko, T. Nagasawa, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5899.

13 B. Ochiai, S. Inoue, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 6282.

14 B. Ochiai, S. Inoue, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 6613.

15 B. Ochiai, Y. Satoh, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 4629.

16 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, *Chem. Rev.* **2015**, *115*, 12407.

17 A. Cornille, R. Auvergne, O. Figovsky, B. Boutevin, S. Caillol, *Eur. Polym. J.* **2017**, *87*, 535.

18 B. Ochiai, S. Sato, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3400.

19 B. Ochiai, H. Kojima, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 1113.

20 S. Jana, A. Parthiban, C. L. L. Chai, *Chem. Commun.* **2010**, *46*, 1488.

21 Y. H. Cho, B. K. Kim, *J. Appl. Polym. Sci.* **2001**, *81*, 2744.

22 Y. He, E. Heine, N. Keusgen, H. Keul, M. Möller, *Biomacromolecules* **2012**, *13*, 612.

23 S. Oprea, *Color. Technol.* **2007**, *123*, 329.

24 V. Besse, N. Illy, G. David, S. Caillol, B. Boutevin, *ChemSusChem* **2016**, *9*, 2167.

25 J. Wang, Y. Zhang, *ACS Catal.* **2016**, *6*, 4871.

26 K. R. Roshan, R. A. Palissery, A. C. Kathalikkattil, R. Babu, G. Mathai, H.-S. Lee, D.-W. Park, *Catal. Sci. Technol.* **2016**, *6*, 3997.

27 J. Steinbauer, T. Werner, *ChemSusChem* **2017**, *10*, 3025.

28 S. Sopeña, E. Martin, E. C. Escudero-Adań, A. W. Kleij, *ACS Catal.* **2017**, *7*, 3532.

29 A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, *49*, 9822.

30 N. Aoyagi, F. Furusho, T. Endo, *Chem. Lett.* **2012**, *41*, 240.

31 N. Aoyagi, F. Furusho, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1113230.

32 F. Camara, S. Benyahya, V. Besse, G. Boutevin, R. Auvergne, B. Boutevin, S. Caillol, *Eur. Polym. J.* **2014**, *55*, 17.

33 X. Sheng, G. Ren, Y. Qin, X. Chen, X. Wang, F. Wang, *Green Chem.* **2015**, *17*, 373.

34 H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 860.

35 C. N. Tang, H. B. Nulwala, K. Damodaran, P. Kaur, D. R. Luebke, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2024.

36 J. C. Barnes, D. J. C. Ehrlich, A. X. Gao, F. A. Leibfarth, Y. Jiang, E. Zhou, T. F. Jamison, J. A. Johnson, *Nat. Chem.* **2015**, *7*, 810.

37 J. Mindemark, T. Bowden, *Polym. Chem.* **2012**, *3*, 1399.

38 S. Andjouh, C. Bressy, Y. Blache, *RSC Adv.* **2016**, *6*, 14496.

39 M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952.

40 A. Qin, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2010**, *39*, 2522.

41 R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker, *Chem. Rev.* **2009**, *109*, 5620.