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# Preparation of Azido Polycarbonates and Their Functionalization via Click Chemistry

Xiaojin Zhang, Zhenlin Zhong,* and Renxi Zhuo*

Key Laboratory of Biomedical Polymers of Ministry of Education, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

S *Supporting Information*

In the past decades, increasing attention has been paid to biocompatible, biodegradable, or bioresorbable polymers because of their potential uses in biomedical and environmental applications, such as medical implants and drug-delivery systems.[1] As a kind of surface erosion biodegradable materials, aliphatic polycarbonates are usually derived from ring-opening polymerization (ROP) of six-membered cyclic carbonate monomers and have gained increasing interest for their potential use in biomedical and pharmaceutical applications due to their favorable biocompatibility, biodegradability, and nontoxicity.[2] To improve hydrophilicity, degradation rate, and mechanical properties of polycarbonates, various functional groups such as carboxyl,[3−5] amino,[6−8] hydroxyl,[9−12] etc., were introduced through copolymerization with functional carbonate monomers.

Click chemistry is a chemical philosophy proposed by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together,[13] which has some advantages of fast, effective, reliable, selective, etc., and is widely used in new drug research and biochemistry.[14−16] One of the most popular reactions within the click chemistry philosophy is the Huisgen 1,3-dipolar cycloaddition reaction of azide and alkyne using a Cu(I) catalyst at room temperature, which has attracted more and more attention because of simple reaction conditions, high yields (no byproducts), easy purification, etc.[17,18] Since the first report by Emrick et al. on the chemical modification of a biodegradable aliphatic polyester by Huisgen's cycloaddition,[19] a steadily increasing number of works have been devoted to the macromolecular engineering of biodegradable polyesters by ROP and click chemistry.[20−23] In contrast, examples of modification on polycarbonates by click chemistry are relatively rare. Lactide−carbonate copolymers with pendant alkynyl groups were prepared by ring-opening copolymerization of lactide and 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one.[24] Sugars[24] and proteins[25,26] were readily immobilized on the copolymers via Huisgen's click reaction. In the present work, we report polycarbonates with pendant azido groups that could be feasibly functionalized by the click reaction.

The synthetic route is shown in Scheme 1. First, a novel six-membered cyclic carbonate monomer with azido groups, 2,2-bis(azidomethyl)trimethylene carbonate (ADTC), was synthesized by cyclization of 2,2-bis(azidomethyl)propane-1,3-diol[27] with ethyl chloroformate using triethylamine as a base in dry THF at room temperature in 80% yield. Then, azido polycarbonates PADTC and PADTC-*co*-PDTC were gained via ROP of ADTC and 2,2-dimethyltrimethylene carbonate (DTC) with 1,6-hexanediol as an initiator and $Sn(Oct)_2$ as a catalyst. Finally, azido copolycarbonates PADTC-*co*-PDTC were reacted with various alkynyl compounds, i.e., alkynyl-terminated poly(ethylene glycol) monomethyl ether (propargyl-PEG),[28,29] propargyl alcohol, dimethylpropargylamine, and propargyl methacrylate, via click chemistry catalyzed by CuBr−$Et_3N$ in THF at 35 °C to afford the polycarbonates with pendant groups or chains. The experimental details could be found in the Supporting Information.

The composition and molecular weight of the polycarbonates were characterized by $^1H$ NMR and GPC with the results listed in Table 1. As an example, the $^1H$ NMR spectrum of copolycarbonate $PADTC_5$-*co*-$PDTC_{45}$ (the subscript numbers represent degree of polymerization) in $CDCl_3$ is shown in Figure 1. The degree of polymerization (DP) of each monomer unit was calculated by comparing the integration of signals at 3.50−3.45 ($CH_2N_3$ of ADTC) and 1.12−0.95 ($CH_3$ of DTC) with the signals of initiator residue at 1.75−1.61 ($CH_2CH_2CH_2CH_2$-$CH_2CH_2O$). The composition and DP of PADTC-*co*-PDTC copolycarbonates calculated from $^1H$ NMR spectra were very close to those predicted on the basis of the feed ratios. GPC analyses showed the polycarbonates PADTC and PADTC-*co*-PDTC had a narrow unimodal molecular weight distribution (PDI = 1.20−1.41). The molecular weights determined by GPC were in good agreement with those by $^1H$ NMR (Table 1). The results suggest that the azido content and molecular weight of the polycarbonates could be well controlled by adjusting the feed.

To investigate the limit of molecular weight of the azido polycarbonate could reach, bulk polymerization of ADTC with 0.1 mol % of $Sn(Oct)_2$ as a catalyst was carried out in the absence of an initiator. GPC analysis showed the PADTC product had a $M_n$ of 57 900 and a PDI of 1.41.

Because azido group is a highly energetic group, organic azides with a (C + O)/N atom ratio of <3 could decompose violently upon exposing to mechanical energy or heat.[30] 2,2-Bis(azidomethyl)-propane-1,3-diol and 2,2-bis(azidomethyl)trimethylene carbonate (ADTC) have a (C + O)/N ratio of 1.2 and 1.5, respectively. According to the literature,[30] these kind of compounds would be manipulable during synthesis and characterization. However, their explosion risk should not be neglected. Before the ROP of ADTC, we had evaluated the potential of explosion risk by impact sensitivity testing and thermoanalytical measurements of the azides.[31] Impact sensitivity testing was performed using the fall hammer apparatus developed by the German Federal

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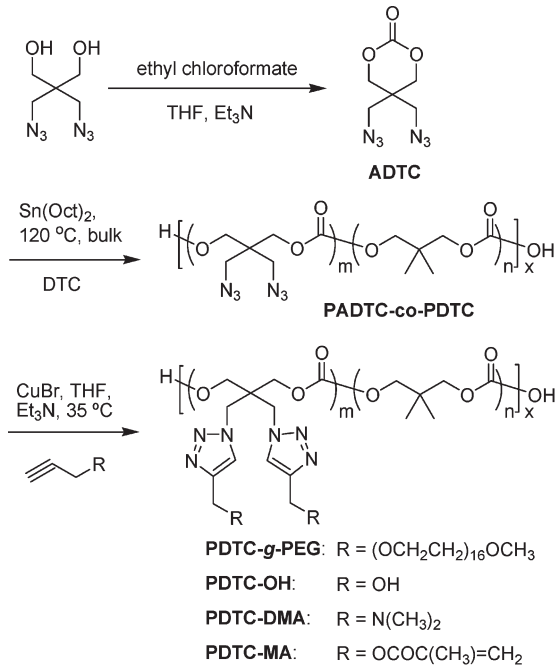
Institute for Materials Testing (BAM) as described by Keicher et al.[31] Briefly, a 40 mm$^3$ sample was placed between two steel cylinders that are fixed by a steel ring. The cylinders have a diameter and a height of 10 mm. Impact energy was imparted to the sample by means of falling a 10 kg steel hummer from a definite height to determine the lowest energy at which a flash, flame, or explosion could be observed. To our surprise, the samples of both 2,2-bis(azidomethyl)propane-1,3-diol and monomer ADTC did not explode or even decompose at an impact of 100 J, which is the higher limit of the apparatus we used. This result suggests that the two azido compounds are less sensitive to impact in comparison with other common explosives such as trinitrotoluene and nitroglycerine whose BAM impact sensitivity is 15 and 0.2 J, respectively. For its good stability to shock, trinitrotoluene is used as a standard for measurement of figure of insensitivity of explosives. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate thermal and caloric properties of the azido compounds. As shown in Figures S1 and S2 in the Supporting Information, 2,2-bis(azidomethyl)propane-1,3-diol has an onset decomposition temperature of 208 °C, a peak decomposition temperature of 238 °C, a decomposition mass loss of 87%, and a decomposition enthalpy of 702 J g$^{-1}$ (131 kJ mol$^{-1}$); ADTC has an onset decomposition temperature of 218 °C, a peak decomposition temperature of 238 °C, a decomposition mass loss of 73%, and a decomposition enthalpy of 1399 J g$^{-1}$ (297 kJ mol$^{-1}$) under the experimental conditions. These results suggest that the explosion tendency of the two azido compounds is low under conventional laboratory operations.

An alternate route for preparation of azido polycarbonates via azidation of bromo polycarbonates was proposed and tried

**Scheme 1. Synthesis of Azido Copolycarbonates PADTC-*co*-PDTC and Their Functionalization via the the Click Reaction**



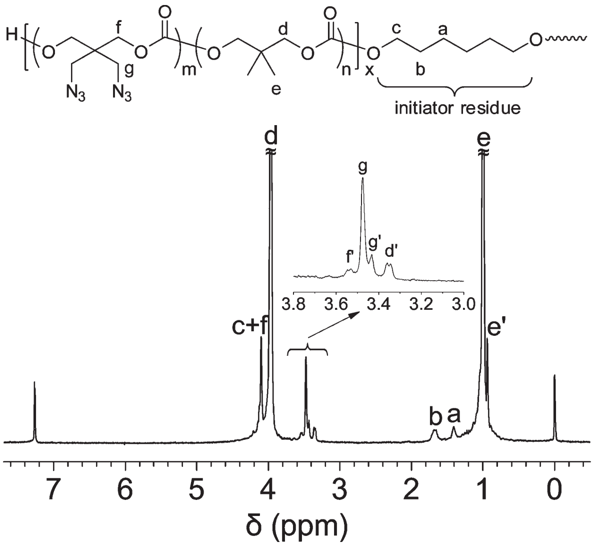


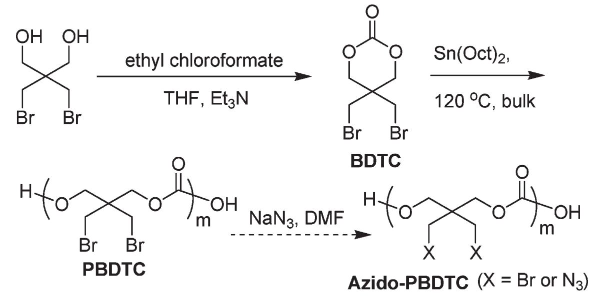
**Figure 1.** $^1$H NMR spectrum of azido copolycarbonate PADTC$_5$-*co*-PDTC$_{45}$ (300 MHz, CDCl$_3$). The signals for end groups are labeled with prime-marked letters d′, f′, and g′.

**Table 1. Synthetic Results of Azido Homopolycarbonate PADTC,[a] Azido Copolycarbonates PADTC-*co*-PDTC,[a] and Functionalization via the Click Reaction[b]**

| | | | | $^1$H NMR | | GPC | |
|---|---|---|---|---|---|---|---|
| sample[c] | feed ratio | yield (%) | $M_n$(theory) | molar composition | $M_n$ | $M_n$ | PDI |
| PADTC$_{43}$ | 45:1[d] | 95 | 9600 | 43:1[d] | 9200 | 10700 | 1.20 |
| PADTC$_{273}$ | n.a.[e] | 92 | | | | 57900 | 1.41 |
| PADTC$_5$-*co*-PDTC$_{20}$ | 6:24:1[f] | 86 | 4500 | 5:20:1[f] | 3800 | 4300 | 1.26 |
| PADTC$_5$-*co*-PDTC$_{45}$ | 5:50:1[f] | 90 | 7700 | 5:45:1[f] | 7000 | 7400 | 1.23 |
| PDTC$_{25}$-*g*-(PEG)$_{10}$ | 2.4:1[g] | 69 | 11300 | 2.0[h] | 11300 | 12200 | 1.35 |
| PDTC$_{50}$-*g*-(PEG)$_{10}$ | 2.4:1[g] | 72 | 14500 | 2.0[h] | 14500 | 15000 | 1.33 |
| PDTC$_{50}$-(OH)$_{10}$ | 2.4:1[g] | 86 | 7600 | 2.0[h] | 7600 | 8000 | 1.30 |
| PDTC$_{50}$-(DMA)$_{10}$ | 2.4:1[g] | 89 | 7800 | 2.0[h] | 7800 | 8100 | 1.27 |
| PDTC$_{50}$-(MA)$_{10}$ | 2.4:1[g] | 85 | 8200 | 2.0[h] | 8200 | 8600 | 1.29 |

[a] Polymerization conditions: [monomer]/[Sn(Oct)$_2$] = 1000, 120 °C, 24 h, in bulk. [b] CuBr, Et$_3$N, THF, 35 °C, 3 h. [c] The subscripted numbers at the lower right corner of a monomer unit represent the degree of polymerization calculated on the basis of $^1$H NMR except that in PADTC$_{273}$ which was based on GPC analysis. The subscripted numbers outside of the parentheses, however, represent the number of the pendant chains or functional groups in the parentheses. [d] ADTC/1,6-hexanediol. [e] Homopolymerization of ADTC in the absence of an initiator. [f] ADTC/DTC/1,6-hexanediol. [g] Alkyne/ADTC units in PADTC-*co*-PDTC. [h] Number of pendant functional groups or PEG chains attached on each ADTC unit via the click reaction.

**Scheme 2. Synthesis and Attempted Azidation of Bromo Polycarbonate PBDTC**



(Scheme 2). Bromo polycarbonate PBDTC was prepared successfully by the ROP of 2,2-bis(bromomethyl)trimethylene carbonate (BDTC) with $Sn(Oct)_2$ as a catalyst. Transforming the bromo groups of the polycarbonate into azido groups were performed by the reaction with sodium azide in DMF at various combinations of temperature and reaction time. $^1H$ NMR and FT-IR spectra of the azido-PBDTC products showed, however, that the azidation did not give satisfiable results. Figure 2 shows the $^1H$ NMR and FT-IR spectra of PBDTC and the azido-PBDTC products of the azidation of PBDTC at 25 °C for 24 h and at 75 °C for 24 h, respectively. By comparing with the spectra of azido polycarbonate PADTC, the spectra of azido-PBDTC products could be partially assigned to give an estimation of the azidation ratio. In the $^1H$ NMR spectrum of azido-PBDTC prepared at 25 °C for 24 h, new signals emerged at 4.21 and 3.47 ppm. These signals are assignable to $OCH_2C(CH_2Br)(CH_2N_3)\mathit{CH_2}O$ and $OCH_2C(CH_2Br)(\mathit{CH_2}N_3)CH_2O$ of the partially azidated structure unit. The azidation ratio was calculated to be about 7% at 25 °C for 24 h by comparing the integration of the signal at 4.21 ppm with the signal at 4.27 ppm ($O\mathit{CH_2}$ of BDTC units). Though the azidation ratio increased slowly with the increase of reaction time, it was still less than 25% after 96 h. In the FT-IR spectrum of azido-PBDTC, a characteristic absorbance peak at 2108 $cm^{-1}$ of azide group could be observed. The peak, however, is not strong, implying a low azidation ratio as well. For the azido-PBDTC prepared at 75 °C for 24 h, the $^1H$ NMR signals became very sharp and complicated, and the peak at 1748 $cm^{-1}$ for $\nu_{C=O}$ of polycarbonates disappeared in the FT-IR spectrum. These results implied a complete destruction of the polycarbonate backbone and indicated the existence of small molecular byproducts of degradation at an elevated temperature of 75 °C. A similar phenomenon of degradation of the polycarbonate backbone was reported in the literature.[32] In short, transforming the bromo groups of PBDTC into azido groups has problems of very low conversion rate at ambient temperature and severe degradation at elevated temperatures. In comparison with this functional group transforming route, the direct route of ROP of azido monomer is much superior for preparation of azido polycarbonates.

The copolycarbonates PADTC-*co*-PDTC with pendant azido groups could be used to introduce various functional groups on the side chains of polycarbonates via azide−alkyne click reaction. The feasibility was demonstrated by quantitatively PEG-grafting on the polymers. Using CuBr/$Et_3N$ as a catalyst, the reaction of propargyl-PEG with azido polycarbonates PADTC-*co*-PDTC in THF yielded PEG-grafted polycarbonates PDTC-*g*-PEG. 20% excess of propargyl-PEG was added to accomplish complete click reaction of the pendant azido groups. The PEG-grafted polycarbonates PDTC-*g*-PEG were purified by dialysis against deionized water to remove the excess propargyl-PEG and other byproducts. The $^1H$ NMR spectrum of PEG-grafted polycarbonate $PDTC_{50}$-*g*-$(PEG)_{10}$ (the subscript number 50 represents DP of PDTC and the subscript number 10 outside the parentheses represents number of grafted PEG chains) is shown in Figure 3. The new signals presented at 7.85 ppm ($N\mathit{CH}{=}C$), 4.70 ppm ($CH{=}C\mathit{CH_2}O$), and 4.57−4.46 ppm ($\mathit{CH_2}N$) are evident for formation of the triazole ring. FT-IR spectra of the copolycarbonates PADTC-*co*-PDTC and PEG-grafted polycarbonates PDTC-*g*-PEG were recorded using carefully dried samples using a Pekin Elmer-2 Fourier transform infrared spectroscopy (Figure 4A). The peak of $\nu_{azide}$ at 2108 $cm^{-1}$ completely disappeared, and a new peak of $\nu_{triazole}$ at 1641 $cm^{-1}$ appeared in the IR spectrum of $PDTC_{50}$-*g*-$(PEG)_{10}$, proving the complete reaction of the azido groups with alkynyl groups. Figure 4B presents normalized GPC curves of the copolycarbonate $PADTC_5$-*co*-$PDTC_{45}$ and PEG-grafted polycarbonate $PDTC_{50}$-*g*-$(PEG)_{10}$. The polymers were in unimodal molecular weight distributions and moderate polydispersities. The molecular weight increases, $PADTC_5$-*co*-$PDTC_{45}$ ($M_n$ 7400) to $PDTC_{50}$-*g*-$(PEG)_{10}$ ($M_n$ 15000), and $PADTC_5$-*co*-$PDTC_{20}$ ($M_n$ 4300) to $PDTC_{25}$-*g*-$(PEG)_{10}$

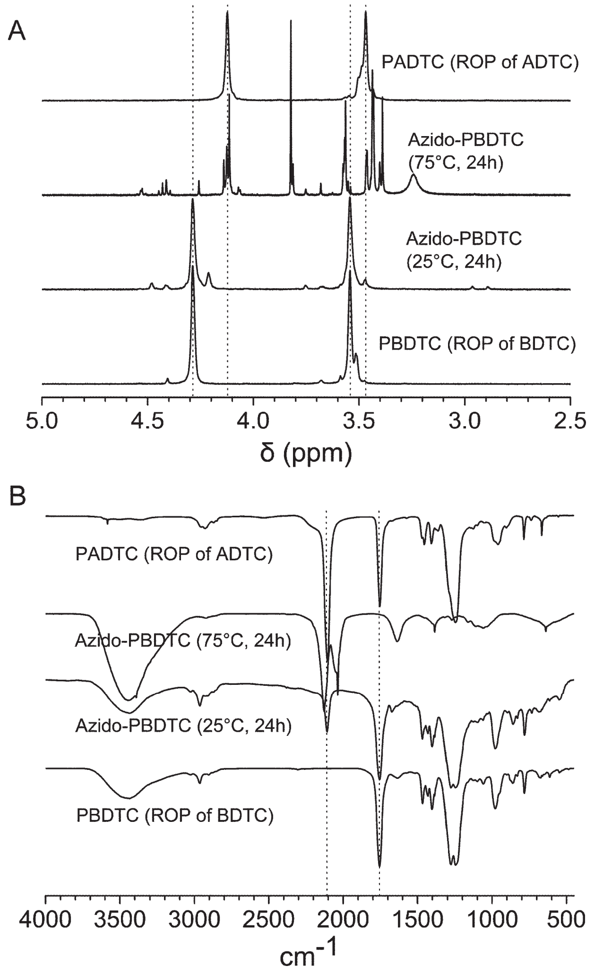


**Figure 2.** $^1H$ NMR (A) and FT-IR (B) spectra of PBDTC (ROP product of BDTC) and the azido-PBDTC products of the azidation of PBDTC at 25 °C for 24 h and at 75 °C for 24 h, respectively. For comparison, the spectra of azido polycarbonate PADTC prepared by ROP of ADTC are also shown.

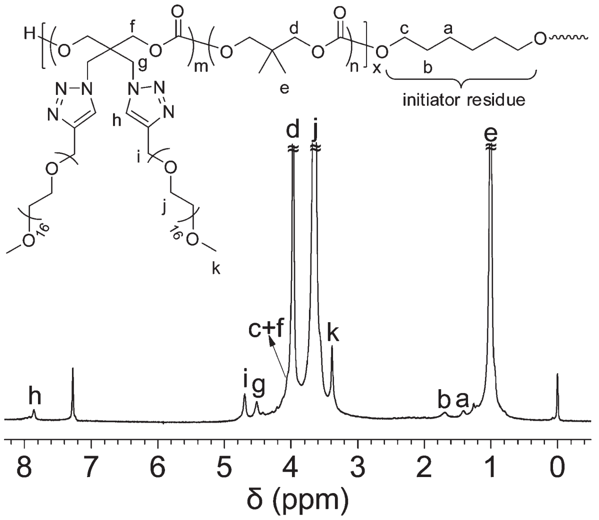


**Figure 3.** $^1$H NMR spectrum of PEG-grafted polycarbonate PDTC$_{50}$-*g*-(PEG)$_{10}$ (300 MHz, CDCl$_3$).

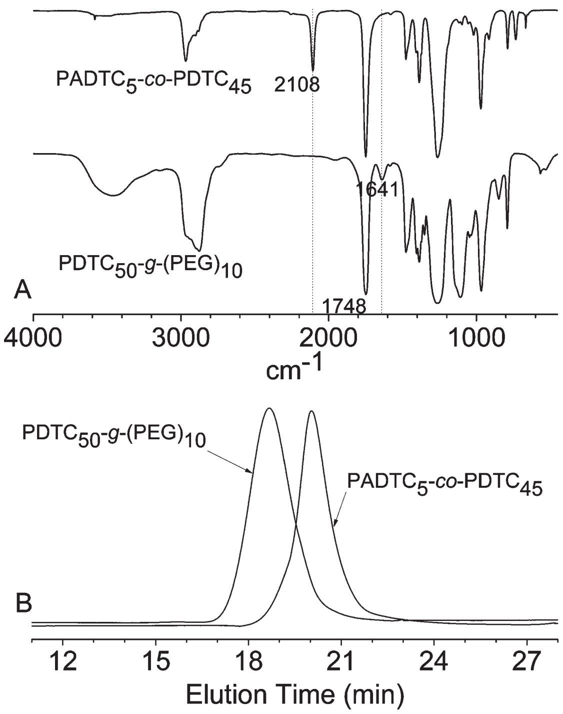


**Figure 4.** FT-IR spectra (A) and normalized GPC curves (B) of azido copolycarbonate PADTC$_5$-*co*-PDTC$_{45}$ and PEG-grafted polycarbonate PDTC$_{50}$-*g*-(PEG)$_{10}$.

($M_n$ 12200), are in accordance with the number of PEG chains grafted onto the PDTC backbones. These results suggest complete click reaction of azido groups and intact polycarbonate backbones during the reaction.

It was found that the type of basic cocatalyst is critical for the click chemistry reaction of the azido polycarbonates. Using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) instead of Et$_3$N as the ligand, the reaction did not work properly. The obtained product was in a low yield. Moreover, the FT-IR spectrum indicated that the polymer had a very serious degradation (Figure S3 in Supporting Information). Though the peak of $\nu_{\text{azide}}$ at 2108 cm$^{-1}$ disappeared, the peak of $\nu_{\text{C=O}}$ of polycarbonates at 1748 cm$^{-1}$ also disappeared, implying a complete destruction of the polycarbonate backbone. Contrastively, no degradation had been observed with Et$_3$N as a base, as evidenced by the results of FT-IR, GPC, and $^1$H NMR analyses.

To demonstrate the capability of the azido polycarbonate as a platform starting material for the preparation of functionalized polycarbonates, propargyl alcohol, dimethylpropargylamine, and propargyl methacrylate were allowed to react with PADTC$_5$-*co*-PDTC$_{45}$ via the click reaction catalyzed by CuBr-Et$_3$N in THF at 35 °C to afford polycarbonates PDTC$_{50}$-(OH)$_{10}$, PDTC$_{50}$-(DMA)$_{10}$, and PDTC$_{50}$-(MA)$_{10}$ with pendant groups of hydroxyl, dimethylamino, and methacrylate, respectively (Scheme 1). The products were characterized by $^1$H NMR, FT-IR, and GPC (Table 1). $^1$H NMR and FT-IR spectra revealed the complete reaction of the azido groups with alkynyl groups. The GPC analysis results suggested the stability of the polycarbonate main chain during the click reaction.

The obtained PDTC-*g*-PEG with polycarbonates as the main chains and PEG as the side chains are amphiphilic copolymers, which could form micelles by self-assembly in a selective solvent. Micelles were prepared from PDTC$_{50}$-*g*-(PEG)$_{10}$ by dialysis of a 0.5 wt % THF solution of the polymer against deionized water. The size and morphology of the micelles were characterized by DLS and TEM (Figure S4 in the Supporting Information). As determined by DLS, the micelles have an average size of 100 nm and a polydispersity index of 0.138. Nanosized particles with spherical shape and similar sizes could be observed in the TEM images. With well-recognized biocompatibility and biodegradability of the PDTC backbone and PEG side chains, the PDTC-*g*-PEG micelle particles might be applicable as drug delivery carriers.

In summary, this Communication presents a convenient route for the preparation of azido polycarbonates via direct ROP of azido cyclic carbonate monomer. The molecular weight and azido content are controllable by adjusting the amount of initiator and comonomer. The feasibility of azide−alkyne click reaction on the pendant azido groups was demonstrated by the reactions with propargyl-PEG and other functional alkynyl compounds. With CuBr/Et$_3$N as a catalyst, the click reaction took place quantitatively without causing byreactions on the main chain. Therefore, it provides a platform for preparation of various functionalized carbonate polymers.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental details for preparation and characterization of the monomers and polymers; experimental details for impact sensitivity testing and thermoanalytical measurements of azido monomer ADTC and its diazido diol precursor. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Tel +86 27 6875 4061; Fax +86 27 6875 4509; e-mail zlzhong@whu.edu.cn (Z.Z.), bmp@whu.edu.cn (R.Z.).

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