‘‘Click Polyester’’: Synthesis of Polyesters Containing Triazole Units in the Main Chain via Safe and Rapid ‘‘Click’’ Chemistry and Their Properties

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ABSTRACT: Click Cu(I)-catalyzed polymerizations of diynes that contained ester linkages and diazides were performed to produce polyesters (click polyesters) of large molecular weights [($\sim$1.0–7.0) $\times$ 10^4], that contained main-chain 1,4-disubstitued triazoles in excellent yields. Incorporation of triazole improved the thermal properties and magnified the even-odd effect of the methylene chain length. We also found that, by changing the positions of the triazole rings, the thermal properties of the polyesters could be controlled. The use of *in situ* azidation was a safe reaction, as explosive diazides are not used. In addition, the microwave heating was found to accelerate the polymerization rates. This is the first study that has applied click chemistry for the synthesis of a series of polyesters. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4207–4218, 2010

KEYWORDS: click reaction; functionalization of polymers; polyesters; step-growth polymerization; thermal properties

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INTRODUCTION Even though many different kinds of polymers have been synthesized, their properties characterized, and used in commercial applications, polyesters still constitute a useful class of polymers. Specifically, aliphatic polyesters are expected to soon replace conventional plastics, because they are biodegradable and are mechanically strong.[1] However, the syntheses of high molecular weight ($M_n > 1.0 \times 10^4$) aliphatic polyesters obtained via polycondensations of dicarboxylic acids and diols require severe conditions (>250 °C and a greatly reduced pressure).[2] Recently, we published reports concerning the “room-temperature polycondensations” of dicarboxylic acids with diols that were catalyzed by the Lewis acids, scandium trifluoromethanesulfonate [$Sc(OTf)_3$],[3(a)] and scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$].[3(b)] These polycondensations directly afforded aliphatic polyesters with M_ns $> 1.0 \times 10^4$. Although identifying new Lewis acids has been a difficult task,[4] we focused on scandium catalysts, because they are insensitive to protic compounds.[5] After the polycondensations, the catalysts could be recovered and then subsequently reused.[3(a,b,e)] Another way to simplify the recovery process, is to covalently couple the scandium catalyst to a polystyrene resin support.[3(c)] These so-called “room-temperature polycondensations” not only save energy by not requiring high temperatures, but increase the types of monomers that can be used. We have published reports concerning room-temperature polycondensations of diols with dicarboxylic acids that contained a C=C double bond,[3(c)] bromo substituents,[3(c)] hydroxyl groups (chemoselective dehydration polycondensation),[3(f,g)] or chirality.[3(e)] Using atom-transfer radical polymerization (ATRP) in combination with poly(butylene bromoadipate) as the macroinitiator, it was possible to synthesize polyesters that had poly(methyl methacrylate) side chains.[3(c)]

It is still unusual to find examples of work that report new synthetic strategies and catalysts[3(h)] for the synthesis of aliphatic polyesters under environmentally benign conditions. Click chemistry, introduced by Sharpless and coworkers,[6] is used to efficiently prepare many different types of organic compounds. The Cu(I)-catalyzed click 1,3-dipolar cycloadditions between azides and alkynes[7(a)] proceed readily under mild conditions, without producing by-products, and with great chemoselectivities. In addition, these Cu(I)-catalyzed azide-alkyne cycloadditions (CuAAC) are usually highly regioselective, for example, the formation of 1,4-disubstituted 1,2,3-triazoles. Although there have been many reports concerning the improvement of reaction conditions for click-type syntheses,[7(b)] and click reactions have been used to synthesize biologically active substances,[8] its application to polymer synthesis (click polymerization) has been limited.[9] Polyesters are a major class of polymeric materials, nevertheless click chemistry has not been used to synthesize polyesters instead of condensation reactions.

For industrial processes and applications, control of the thermal properties of polymeric materials is necessary. Polymer

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Additional Supporting Information may be found in the online version of this article. Correspondence to: A. Takasu (E-mail: takasu.akinori@nitech.ac.jp)

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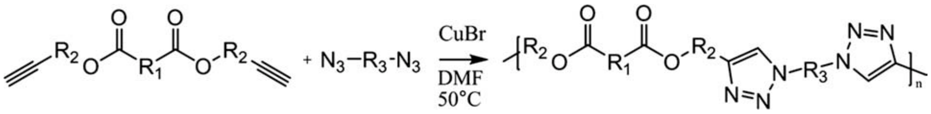


SCHEME 1 Synthesis of click polyesters.

blends have been used to achieve the desired thermal properties, however, for the production of nanomaterials, the microscale molecular design must be considered. Therefore, we need to be able to control the physical and chemical properties of the targeted polymer by changing the type(s) of monomer(s) incorporated and/or the type(s) of synthetic reaction(s). Click polymerization should enable the synthesis of polyesters from diyne monomers containing ester linkages and diazido monomers. Click polymerizations are polyaddition reactions, by which we can design a large number of different molecular architectures by changing the type(s) of monomer(s) incorporated. In addition, the polymerization may be accompanied by the formation of main-chain 1,4-disubstituted triazoles. Therefore, production of main-chain 1,4,-disubstitured triazole polyesters will substantially increase the types of "next-generation" polyesters available (Scheme 1).

On the other hand, the small molecular weight, organic azides that are used for CuAAC are dangerous compounds. A small azide molecule is considered to have less than six carbon and one oxygen atoms per azide functionality. This definition is an empirically derived rule and does not guarantee that a particular azide-containing compound is stable. Handling purified azides is not a safe practice, and they, therefore, should not be purified. To improve the safety of CuAACs for polyester, we developed a practical reaction that uses azide reactants that are generated *in situ* from their corresponding halides[10] and that then react immediately with Cu(I) acetylides, to form the corresponding 1,4-disubstituted-1,2,3-triazoles.

Rapid syntheses induced by microwave irradiation to control the temperature have attracted considerable attention recently, because such procedures are more convenient and economical than the corresponding traditional syntheses that use alternative heat sources, for example, an oil bath. Almost 4000 articles have been published concerning microwave-assisted organic synthesis since Gedye et al.[11] first reported the use of microwave heating to accelerate organic chemical transformations. Microwave heating reduces reaction times from hours to minutes, reduces the amounts of by-products produced, increase yields, and improves reproducibility.[11(c)] Therefore, many academic and industrial research groups are already using microwave-assisted reactions for the rapid optimization of reactions, for the efficient synthesis of new chemical entities, and for the discovery and characterization of new chemistries.[11(c)] Fokin and coworkers[10(b)] have developed a microwave-enhanced, fast, completely regioselective, and efficient three-component reaction that uses small compounds for the generation of 1,4-disubstituted-1,2,3-triazoles. Furthermore, as reported by Liskamp and coworkers,[12] microwave-assisted CuAAC can be used to polymerize peptide-based polymers from amino acids derivatives. To broaden the scope of microwave-assisted CuAAc reactions, we report herein the application of microwave heating to safely form polyesters via *in situ* azidation. With the use of microwave irradiation and *in situ* azidation, we reduced the reaction times needed and eliminated the danger incurred when handling small azide compounds.

Herein, we report the use of click chemistry to synthesize polyesters. These reactions were accompanied by the formation of main-chain 1,4-disubstituted triazoles. We found that the triazole backbone improved the thermal properties of the polyesters. We also found that, in conjunction with *in situ* azidation, microwave irradiation accelerated the polymerization rates. To the best of our knowledge this is the first time click chemistry has been used to synthesize a series of polyesters.[13]

EXPERIMENTAL

Materials and Methods

Chemicals were obtained from commercial sources and were used without further purification. A MWO-1000S synthesizer (EYELA, Tokyo, Japan) was used for microwave irradiation. ^{1}H-NMR spectra were acquired at 27 °C using Bruker Analytik DPX200 and DPX600 spectrometers (200 and 600 MHz, respectively). The chemical shift of tetramethylsilane (TMS) was taken as zero ppm. Number average molecular weights (M_n) and the polydispersity indexes (PDI; M_w/M_n) of the polyesters were estimated using a size exclusion chromatography (SEC) system consisting of a Tosoh DP8020 pump system, a Tosoh RI-8020 differential refractometer, and Tosoh TSK-gel α-3000 and α-5000 columns (Tosoh, Tokyo, Japan). The eluent was 0.05% LiBr, 100 mM of tetramethylethylenediamine in DMF. The flow rate was 0.5 mL/min, and the temperature was 40 °C. Differential scanning calorimetry (DSC), using a DSC6220S calorimeter (Seiko Instruments Inc., Chiba, Japan) was performed from −80 to 180 °C, with the temperature increased or decreased at a rate of 10 °C/min. The instrument was calibrated using indium and tin samples. For all experimental samples, a complete temperature, heating cycle from −80 to 180 °C and back to −80 °C, was obtained. Each sample weighted between 4 and 6 mg and was placed into an aluminum pan that was covered with a lid within the calorimeter. The glass transition temperature (T_g) was taken as the inflection point of the corresponding heat capacity jump of the DSC trace. The melting temperature (T_m) was defined as the minimum point of the endothermic trough. Thermogravimetric analyses (TGA) were performed under nitrogen, at rates of 10 °C/min between 20 and 600 °C (TG/DTA 220U; Seiko Instruments, Chiba, Japan).

Preparation of Diazido Monomers

As an example, the preparation of 1,4-diazidobutane is described. Into a 20-mL round-bottom flask were added 1,4-dibromobutane (1.51 g, 7.0 mmol) and sodium azide (1.24 g, 19.0 mmol) both of which had been dissolved in 10 mL of DMF. After stirring the mixture at room temperature for 24 h, 5 mL of water was added to quench the reaction. After having been cooled to room temperature, the solution was extracted with 30 mL of diethyl ether. The organic phases were combined, washed twice with 10-mL volumes of 50% $NaHCO_{3(aq)}$, and then dried over $MgSO_4$. After filtration and solvent evaporation, 1,4-diazidobutane was obtained in 90% yield (881 mg) as a white liquid. The other diazido-alkanes, 1,5-diazidopentane (91% yield), 1,6-diazidohexane (82% yield), 1,7-diazidoheptane (50% yield), and 1,3-diazidopropane (32% yield), were prepared using similar procedures and were isolated as syrups. *m*-Diazidoxylene (79% yield) and *p*-diazidoxylene (64% yield), which were used as aromatic, monomeric diazido reactants, were prepared using similar procedures and were obtained as white liquids. The diazides used for this report were not purified and were stored in ethyl acetate.

1,3-diazidopropane: ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.42 (t, 4H, 6.5 Hz), 1.84 (2H, quintet, 6.5 Hz).

1,4-diazidobutane: ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.33 (t, 4H, 6.2 Hz), 1.71–1.65 (m, 4H).

1,5-diazidopentane: ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.39 (t, 4H, 6.6 Hz), 1.70–1.57 (m, 4H), 1.54–1.40 (m, 2H).

1,6-diazidohexane: ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.28 (t, 4H, 6.6 Hz), 1.69–1.58 (m, 4H), 1.48–1.35 (m, 4H).

1,7-diazidoheptane: ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.27 (t, 4H, 6.7 Hz), 1.68–1.58 (m, 4H,), 1.46–1.33 (br, 6H).

m-diazidoxylene: ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.42 (t, 1H, 6.6 Hz), 7.30 (d, 2H, 3.2 Hz), 7.26 (s, 1H), 4.38 (s, 4H).

p-diazidoxylene: ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.34 (s, 4H), 4.36 (s, 4H).

Preparation of Diyne Monomers

As an example, the preparation of bis(butynyl) methylsuccinate is described. Into a 50-mL round-bottom flask were added methylsuccinic acid (633 mg, 4.80 mmol), $Sc(OTf)_3$ (49 mg, 9.95 mmol), and 3-butyn-1-ol (1.36 g, 19.4 mmol). The reaction mixture was stirred at 60 °C for 6 h under reduced pressure (25 mmHg). After the reaction mixture had been diluted with 30 mL chloroform, the solution was washed with 10 mL of water saturated with $NaHCO_3$ and then dried over $MgSO_4$. After filtration and solvent evaporation, bis(butynyl) methylsuccinate was obtained as an auburn liquid in 71% yield (803 mg). Bis(butynyl) succinate (62% yield, white solid), bis(butynyl) adipate (87% yield, white solid), bis(isobutynyl) succinate (43% yield, auburn liquid), bis(isobutynyl) malonate (15% yield, auburn liquid), bis(butynyl) phthalate (10% yield, white solid), and bis (propynyl) methylsuccinate (92% yield, auburn liquid) were prepared using similar procedures.

bis(butynyl) succinate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.21 (t, 4H, 6.8 Hz), 2.67 (s, 4H), 2.54 (dt, 4H, 2.7 and 6.8 Hz), 2.01 (t, 2H, 2.7 Hz).

bis(butynyl) methylsuccinate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.19 (t, 4H, 6.7 Hz), 2.93 (quintet, 1H, 6.6 Hz), 2.78 (dd, 1H, 8.1 and 16 Hz), 2.57–2.50 (m, 4H), 2.45 (dd, 1H, 6.0 and 16 Hz), 2.00 (t, 2H, 2.5 Hz), 1.24 (d, 3H, 7.1 Hz).

bis(butynyl) adipate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.19 (t, 4H, 6.8 Hz), 2.57–2.49 (m, 4H), 2.36 (t, 4H, 6.4 Hz), 2.01 (t, 2H, 2.6 Hz), 1.71–1.65 (m, 4H).

bis(isobutynyl) succinate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.45 and 5.44 (2H, 2xq, 6.7 Hz), 2.67 (s, 4H), 2.45 and 2.44 (2xs, 2H), 1.51 (d, 6H, 2.9 Hz).

bis(isobutynyl) malonate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.50 and 5.49 (2H, 2xq, 6.7 Hz), 3.43 (s, 2H), 2.49 and 2.48 (2xs, 2H), 1.54 (d, 6H, 3.5 Hz).

bis(butynyl) phthalate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.78–7.71 (m, 2H), 7.60–7.53 (m, 2H), 4.43 (t, 4H, 6.8 Hz), 2.70–2.62 (m, 4H), 2.03 (t, 2H, 2.6 Hz).

bis(propynyl) methylsuccinate: ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.70 (s, 2H), 2.98 (m, 1H), 2.82 (dd, 1H, 4.0 and 16Hz), 2.48 (t,2H, 2.2 Hz), 2.49 (dd, 1H, 3.0 and 16 Hz), 1.26 (d, 3H, 3.6 Hz).

Model Reactions

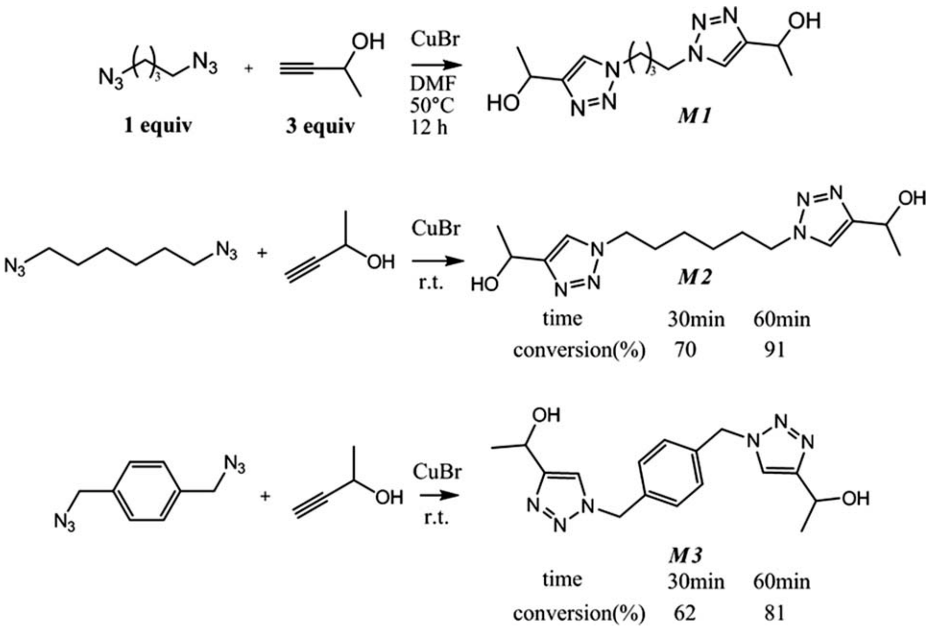
The model compounds ***M1***, ***M2***, and ***M3*** (Scheme 2) were prepared by click reactions of 1,6-diazidohexane or *p*-diazidoxylene, respectively, with 3-butyn-2-ol. As an example of the procedure used, into a 10-mL round-bottom flask were added 1,6-diazidohexane (137 mg, 0.8 mmol) and three equivalents of 3-butyn-2-ol both dissolved in 0.5 mL of DMF. The mixture was stirred at room temperature for 1 h. The products were characterized using ^{1}H-NMR spectroscopy and were not purified so that the extent of conversion could be determined.

Polymer Syntheses: Click Polyesters Synthesized Using an Oil Bath for Temperature Control

The structures and chracterizations of all click polyesters synthesized for this report are summarized in Figure 1 and Table 1. As an example of the procedure used (run 4, Table 1), bis(butynyl) methylsuccinate, which served as the diyne (236 mg, 1.0 mmol), and 1,4-diazidobutane (140 mg, 1.0 mmol), which served as the diazide were added into a 10-mL round-bottom flask that contained 0.5 mL DMF. Next, with the contents of the flask contained under a nitrogen atmosphere, 10 mg of CuBr was added. After stirring the mixture at 50 °C for 30 h, it was diluted with 5-mL volumes of DMF. A green solid was obtained in 99% yield after twice being precipitated from the DMF solution with 90 mL volumes of diethyl ether.

For runs 1 and 2 the yields could not be calculated, and their ^{1}H-NMR spectra could not be acquired, because the products were insoluble in all organic solvents tested.

run 3 (yield: 99%): ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.93 (2H, brs), 4.34 (4H, t, 6.9Hz), 4.20 (4H, brs), 2.95–2.89 (5H, br), 2.74



SCHEME 2 Model click reactions of model reaction that used 1,4-diazidobutane, 3-butyn-2-ol, and Cu(I)Br as the catalyst in DMF at 50 °C (M1). 1,6-diazidohexane (M2) and p-diazidoxylene (M3) with 3-butyn-2-ol. (solvent, DMF; catalyst, Cu(I)Br, room temperature, 1 h reaction time).

(1H, dd, 6.6 and 15 Hz), 2.38 (1H, dd, 7.3 and 15 Hz), 2.36–2.29 (2H, br), 1.02 (3H, d, 6.8 Hz).

run 4 (yield: 89%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.50 (2H, brs), 4.37 (8H, br), 3.05 (4H, brs), 2.91–2.81 (1H, m), 2.68 (1H, dd, 8.8 and 16 Hz), 2.38 (1H, dd, 5.1 and 16 Hz), 1.92 (4H, brs), 1.17 (3H, d, 7.1 Hz).

run 5 (yield: 99%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.44 (1H, s), 7.43 (1H, s), 4.32 (4H, t, 6.4 Hz), 3.05 (4H, brs), 2.91–2.85 (1H, m), 2.69 (1H, dd, 8.6 and 16 Hz)), 2.40 (1H, dd, 5.4 and 16Hz), 1.94 (4H, brs), 1.34 (2H, brs), 1.17 (3H, d, 7.2 Hz).

run 6 (yield: 99%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.89 (2H, s), 4.30–4.17 (8H, br), 2.94–2.87 (5H, br), 2.73 (1H, dd, 6.8 and 14 Hz), 2.39 (1H, dd, 6.0 and 17 Hz), 1.74 (4H, brs), 1.21 (4H, brs), 1.02 (3H, d, 7.0 Hz).

run 7 (yield: 84%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.87 (2H, s), 4.30–4.22 (4H, br), 4.22–4.17 (4H, br), 2.93–2.87 (5H, br), 2.74 (1H, dd, 7.1 and 14 Hz), 2.40 (1H, dd, 6.0 and 17 Hz), 1.81–1.67 (4H, br, 5.9 Hz), 1.29–1.13 (4H, br), 1.02 (3H, d, 7.0 Hz).

run 8 (yield: 64%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.93 (1H, s), 7.92 (1H, s) 7.25 (4H, s), 5.51 (4H, brs), 4.19 (4H, brt, 6.4 Hz), 2.89 (4H, brt, 6.9 Hz), 2.73 (1H, m), 2.70 (1H, dd, 6.7 and 13 Hz), 2.34 (1H, dd, 6.0 and 16 Hz), 0.96 (3H, brd, 7.0 Hz).

run 9 (yield: 70%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.94 (1H, s), 7.93 (1H, s), 7.35–7.16 (4H, br), 5.52 (4H, brs), 4.20 (4H, t, 6.4 Hz), 2.90 (4H, t, 6.4 Hz), 2.73 (1H, m), 2.70 (1H, dd, 6.7 and 16 Hz), 2.37 (1H, dd, 5.9 and 17 Hz), 0.98 (3H, brd, 7.1 Hz).

run 10 (yield: 53%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.96 (2H, s), 7.34–7.17 (4H, br), 5.53 (4H, s), 4.21 (4H, t, 6.4 Hz), 2.94–2.90 (4H, br), 2.82 (4H, d, 32Hz).

run 11 (yield: 95%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 8.02 (2H, s), 7.66 (2H, brs), 7.52 (2H, brs), 4.51–4.40 (4H, br), 4.37–4.30 (4H, br), 3.18–3.10 (4H, br), 2.05–1.50 (6H, br).

run 12 (yield: 99%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.57 (2H, brs), 6.05–6.00 (2H, br), 4.37 (4H, brs), 2.63 (4H, brs), 1.92 (4H, brs), 1.64 (6H, brs).

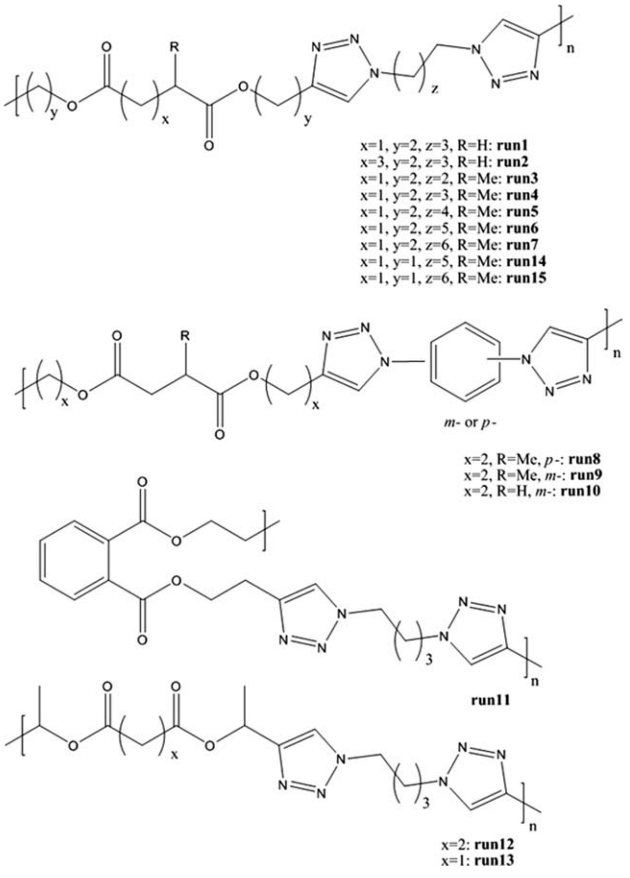
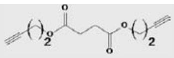
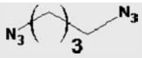
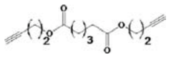
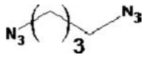
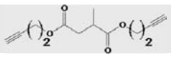
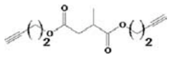
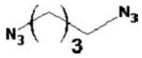
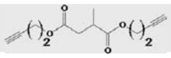
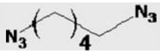
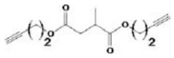
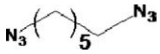
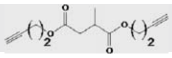
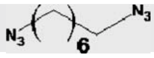
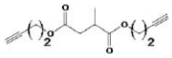
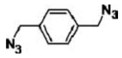
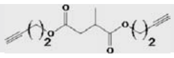
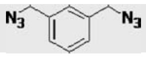
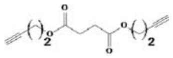
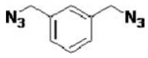
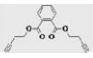
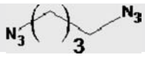
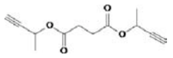
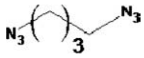
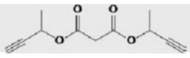
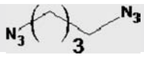
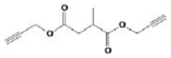
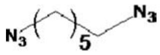
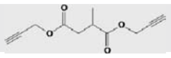


FIGURE 1 The click polyesters synthesized in Table 1.

TABLE 1 Click Polymerizations of Dialkynes and Diazides[a]

Run	Diyne	Diazide	Yield[b] (%)	M_n[c] × 10^{-4}	M_w/M_n[c]	T_g[d] (°C)	T_m[d] (°C)
1			–[e]	Insoluble	Insoluble	–[e]	–[e]
2			–[e]	Insoluble	Insoluble	–[e]	–[e]
3			99	0.88	2.08	17	76
4			89	1.37	2.49	14	125
5			99	1.36	2.85	−4	52
6			99	5.08	2.46	6	76
7			84	1.13	2.90	−3	72
8			64	5.93	2.26	51	137
9			70	0.84	1.70	29	Not detected
10			53	6.69	2.53	50	78
11			95	0.19	1.40	–[e]	–[e]
12			99	0.89	3.24	–[e]	–[e]
13			85	0.59	5.83	–[e]	–[e]
14			99	1.33	2.72	14	84
15			73	1.14	2.52	1	68

[a] All runs were performed on a 1 mmol scale in 0.5 mL (DMF), at 50 °C, for 30 h, with 10 mg CuBr as the catalyst.

[b] After reprecipitation from DMF with diethyl ether.

[c] Determined by SEC with DMF as the eluent and relative to poly(stylene) standards.

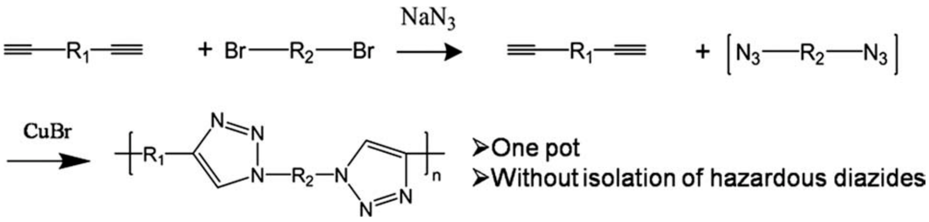
[d] T_m was determined from the first heating DSC scan and T_g from the second scan (heating and cooling rates: 10 °C/min).

[e] Not measured.

run 13 (yield: 85%): ^{1}H-NMR (DMSO-d_6) δ (ppm): 8.10 (2H, brs), 5.95 (2H, brs), 4.36 (4H, brs), 3.49 (2H, brs), 1.77 (4H, brs), 1.51 (6H, brs).

run 14 (yield: 99%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.63 (2H, brs), 5.19 (4H, brs), 4.35 (4H, brs), 2.93–2.79 (1H, m), 2.72 (1H, dd, 7.7 and 17 Hz), 2.44 (1H, dd, 4.6 and 16 Hz), 1.90 (4H, brs), 1.36 (4H, brs), 1.19 (3H, d, 6.5 Hz).

run 15 (yield: 73%): ^{1}H-NMR (CDCl$_3$) δ (ppm): 7.60 (1H, s), 7.58 (1H. s), 5.19 (4H, d, 5.6 Hz), 4.34 (4H, t, 7.2 Hz), 2.98–2.86 (1H, m), 2.73 (1H, dd, 8.4 and 17 Hz), 2.45 (1H, dd, 5.8



SCHEME 3 One pot *in-situ* click polymerization.

and 17 Hz), 1.89 (4H, brt, 6.4 Hz), 1.38–1.28 (6H, br), 1.30 (3H, d, 7.0 Hz).

Safe Syntheses of Click Polyesters via *In Situ* Azidation Using an Oil Bath for Temperature Control

The reactants and the properties of the products for the click polyester syntheses via *in situ* azidation, using an oil bath for temperature control, are given in Scheme 3 and Table 2. As an example of the experimental procedure (run 2, Table 2), bis(butynyl) methyl succinate, which served as the diyne (236 mg, 1.0 mmol), 1,4-dibromobutane (216 mg, 1.0 mmol), and sodium azide (130 mg, 2.0 mmol) were added into a 10-mL round-bottom flask that contained 1.0 mL of DMF. Then, with the contents of the flask under nitrogen, 30 mg (0.20 mmol) of CuBr was added. After stirring at 50 °C for 24 h, the reaction mixture was diluted with 5-mL volumes of DMF and the product was precipitated from the DMF solution with two 90-mL volumes of diethyl ether, washed with water, and dried *in vacuo*. A brown solid was obtained in a 99% yield.

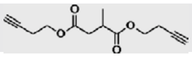
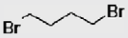
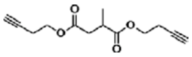
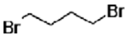
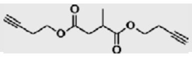
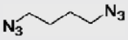
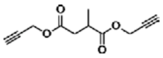
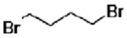
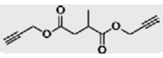
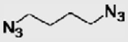
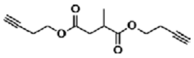
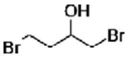
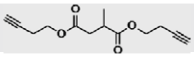
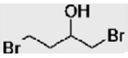
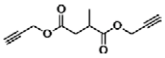
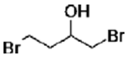
runs 1–3: ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.88 (2H, brs), 4.32 (4H, brs), 4.21 (4H, brt, 6.4 Hz), 2.93–2.87 (5H, br), 2.72 (1H, dd, 7.1 and 15 Hz), 2.40 (1H, dd, 6.1 and 16 Hz), 1.74 (4H, brs), 1.02 (3H, brd, 7.0 Hz).

runs 4–5: ^{1}H-NMR (DMSO-d_6) δ (ppm): 8.10 (1H, brs), 8.03 (1H, brs), 5.38–5.34 (1H, m), 5.09 (4H, brs), 4.39–4.31 (4H, br), 3.82 (1H, brs), 2.88-2,68 (2H, m), 2.60–2.50 (1H, m), 2.16–1.78 (2H, m), 1.08 (3H, d, 6.9 Hz).

runs 6–7: ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.88 (1H, brs), 7.82 (1H, brs), 5.35–5.33 (1H, m), 4.44–4.19 (6H, m), 3.80 (brs, 1H), 2.94–2.85 (5H, m), 2.81–2.64 (1H, m), 2.55–2.36 (1H, m), 1.92–1.74 (2H, m), 1.05 (3H, d, 6.8 Hz).

run 8: ^{1}H-NMR (DMSO-d_6) δ (ppm): 8.12 (1H, s), 8.04 (1H, s), 5.39 (1H, m), 5.10 (4H, brs), 4.48–4.31 (4H, m), 3.80 (brs,

TABLE 2 Safe Syntheses of Click Polyesters via *In Situ* Azidation that Used an Oil Bath for Temperature Control[a]

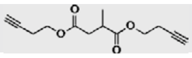
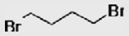
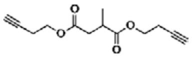
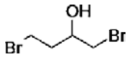
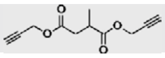
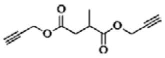
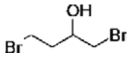
Run	Diyne	Dibromo or Diazide Compound		DMF (mL)	Yield[b] (%)	M_n[c]$\times 10^{-4}$	M_w/M_n[c]
1			NaN_3	0.5	99	0.3	1.9
2			NaN_3	1.0	98	0.6	3.1
3				1.0	99	3.7	2.8
4			NaN_3	1.0	98	0.3	2.2
5				1.0	99	0.7	2.4
6			NaN_3	0.5	98	0.1	2.1
7			NaN_3	1.0	99	0.3	2.2
8			NaN_3	1.0	99	0.2	2.3

[a] All runs are performed on a 1 mmol scale in DMF at 50 °C, for 24 h, with 30 mg of CuBr as the catalyst, and 1.0 equiv each of sodium azide and the halide.

[b] After reprecipitation from DMF using diethyl ether.

[c] Determined by SEC measurement in DMF relative to poly(stylene) standards.

TABLE 3 Safe Synthesis of Click Polyesters via *In Situ* Azidation that Used Microwave Irradiation for Temperature Control[a]

Run	Diyne	Dibromo Compound	Yield[b] (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c
1			99	0.9	2.4
2			99	0.2	1.9
3			98	0.4	2.4
4			99	0.2	2.1

[a] All runs are performed on a 1 mmol scale in 1 mL DMF, for 24 h, at 50 °C that was maintained by modulating the irradiation power between 0 and 50 W; with 30 mg CuBr as the catalyst; and 1.0 equiv of sodium azide and 1.0 equiv. of the halide.

[b] After reprecipitation from DMF using diethyl ether.

[c] Determined by SEC with DMF as the eluent relative to poly(stylene) standards.

1H), 2.85–2.69 (2H, m), 2.61–2.56 (1H, m), 2.04–1.79 (2H, m), 1.05 (3H, d, 6.8 Hz).

Safe Syntheses of Click Polyesters via *In Situ* Azidation Using Microwave Irradiation for Temperature Control

The reactants and properties of the polyester products are given in Table 3. As an example of the experimental procedure (run 1), bis(butynyl) methyl succinate as the diyne (236 mg, 1.0 mmol), 1,4-dibromobutane (216 mg, 1.0 mmol), and sodium azide (130 mg, 2.0 mmol) were added into a test tube that contained 1.0 mL of DMF. Next, with the contents of the tube under a nitrogen atmosphere 30 mg of CuBr was added. After stirring for 24 h in the microwave synthesizer (with the microwave power varied between 0 and 50 W, so that the temperature remained at 50 °C), the reaction mixture was diluted with 5-mL volumes of DMF, precipitated from the DMF solution with two 90 mL volumes of diethyl ether, washed with water, and dried *in vacuo*. A brown solid was obtained in 99% yield.

Instant Click Polymerization via *In Situ* Azidation

The reactants and properties of the polyester products are given in Table 4. As an example of the experimental procedure (run 1), bis(butynyl) methylsuccinate as the diyne (236 mg, 1.0 mmol), 1,4-dibromobutane (216 mg, 1.0 mmol), and sodium azide (130 mg, 2.0 mmol) were added into a test tube containing 2.0 mL of DMF. Next, with the contents of the tube under a nitrogen atmosphere, 30 mg of CuBr was added. After stirring the reaction mixture for 30 min in the microwave synthesizer (irradiation power at 50 W, 153 °C, which is the boiling point for DMF), the reaction mixture was diluted with 5-mL volumes of DMF, precipitated from the DMF solution with two 90-mL volumes of diethyl ether, washed with water, and dried *in vacuo*. A brown solid was obtained in 99% yield.

Semiempirical Molecular Orbital Calculation

The repeat units of the click polyesters, that is, Me-[OCOCH$(CH_3)CH_2COO(CH_2)_2$-triazole-$(CH_2)_4$-trialzole-$(CH_2)_2]_2$-Me and Me-$[OCOCH(CH_3)CH_2COO(CH_2)_2$-triazole-$(CH_2)_5$-trialzole-$(CH_2)_2]_2$-Me using semiempirical molecular orbital calculations by AM1 molecular orbital (MO) method[14] in MOPAC 2000 (MOPAC 2000 version 1.0, Fujitsu, Tokyo, Japan, 1999) to investigate the conformations of the corresponding click polyesters (runs 4 and 5 in Table 1), in which planar zigzag structure of the polyester main chain is programmed for the starting conformation.

Biodegradation Test

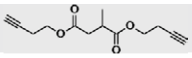
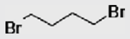
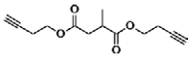
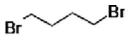
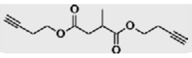
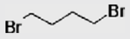
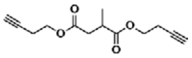
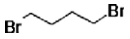
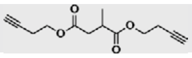
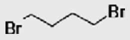
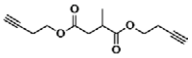
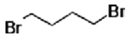
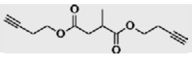
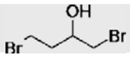
Using a biodegradation (BOD) tester (Model 200F; Taitec, Koshigaya-shi, Japan) in accordance with the ISO standard guidelines (ISO 14851), BOD was assessed as the amount of oxygen consumed at 25 °C during a 40-day period. The biodegradability was calculated as the percentage of the amount of consumed oxygen and normalized to that of a blank test sample to the theoretical amount of oxygen required for complete oxidation of the sample. The BOD values are reported as the means of three measurements. Activated sludge was obtained from a sewage plant in Naka-ku, Nagoya, Aichi Prefecture, Japan. After filtration of the sludge samples, the supernatants (15 mL) were added to the incubation medium (150 mL) that contained (mg/L): K_2HPO_4, 217; KH_2PO_4, 85; Na_2HPO_4, 447; NH_4Cl, 5; $CaCl_2$, 27; $MgSO_4 \cdot 7H_2O$, 23; and $FeCl_3 \cdot 6H_2O$, 0.25. The sample (10 mg/L) was coated onto the bottle, and $NaOH_{(aq)}$ (11 mol/L) was placed within to absorb the CO_2 produced.

RESULTS AND DISCUSSION

Model Reactions

We first investigated a Cu(I)-catalyzed, Huigen-type, 1,3-dipolar cycloaddition that used 1,4-diazidobutane as the azide and 3-butyn-2-ol as the alkyne with Cu(I) (CuBr) as the

TABLE 4 Instant "Click Polymerization" via *In Situ* Azidation Using Microwave Irradiation for Temperature Control[a]

Run	Diyne	Dibromo Compound	DMF (mL)	Time (min)	Yield[b] (%)	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$
1			2.0	30	99	2.5	4.8
2			2.0	15	99	1.8	3.7
3			1.5	30	99	1.3	4.5
4			1.5	15	99	1.1	4.0
5			1.0	30	99	0.8	2.3
6			1.0	15	99	0.7	2.7
7			1.0	15	99	0.5	2.4

[a] All runs are performed with 50 W irradiation power, with 30 mg CuBr as the catalyst, 2.0 equiv of sodium azide, and 2.0 equiv of the halide.

[b] After reprecipitation from DMF using diethyl ether.

[c] Determined by SEC with DMF as the eluent and relative to poly(styrene) standards.

catalyst. We heated a mixture of 1,4-diazidobutane (1.3 mmol) and 3-butyn-2-ol (3.9 mmol) to 50 °C, then added 10 mg CuBr in 1-mL volumes of DMF, and then stirred the mixture at 50 °C for 12 h (Scheme 2). The reaction proceeded smoothly and gave the expected product (***M1***), the 1,4-disubstituted 1,2,3-triazole isomer, in high yield (~100%), and its structure and yield were confirmed by characterization of the ^{1}H-NMR spectrum of the unpurified product.

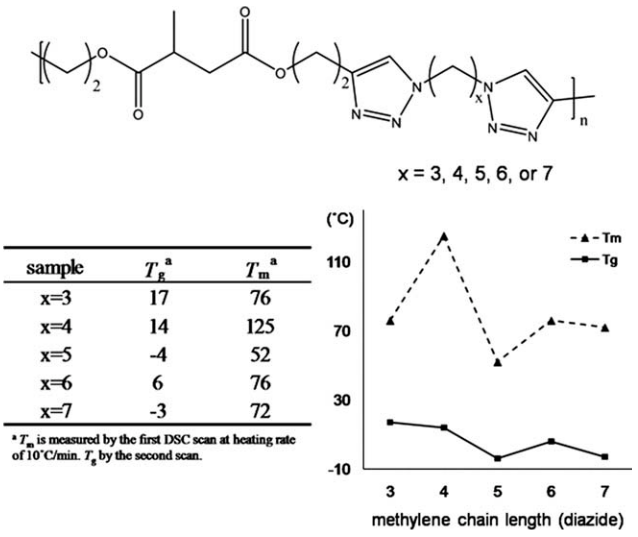
The model reaction to synthesize ***M3*** using the aromatic *p*-diazidoxylene and 3-butyn-2-ol was also carried out at 25 °C for 1 h with a yield of 81% (Scheme 2). However, under the same reaction conditions, with the substitution of 1,6-diazidohexane for *p*-diazidoxylene, 91% conversion to ***M2*** was achieved in the same amount of time. Therefore, we could not confirm the higher conversion based on the reactive nature of benzyl azide and lower conversion compared to alkyl azide was obtained in the ^{1}H-NMR spectrua. This is ascribed to steric hindrance by the aromatic ring.

Polymer Syntheses

Because the model 1,3-dipolar cycloaddition reactions proved to be regioselective, it appeared possible to use the click reaction to synthesize polyesters (Scheme 1). The diyne monomers, bis(butynyl) succinate, bis(butynyl) adipate, bis (butynyl) methylsuccinate, bis(butynyl) phthalate, bis(isobutynyl) succinate, bis(isobutynyl) malonate, bis(propynyl) methylsuccinate, and the diazide monomers, 1,3-diazidopropane, 1,4-diazidobutane, 1,5-diazidopentane, 1,6-diazidohexane, 1,7-diazidoheptane, *p*-diazidoxylene, *m*-diazidoxylene, were prepared according to published methods.[13]

The click polymerizations were catalyzed by Cu(I) (as CuBr) without an *N*-substituted Cu(I)-stabilizing ligand that might have reduced the product yield by base cleavage of the ester bonds.[15] The click polymerizations were run in DMF at 50 °C for 30 h, and the products were obtained in excellent yields (85–99%, Table 1). The number averaged molecular weights (M_n) and the molecular weight distributions (M_w/M_n) of the click polyesters were determined using SEC. The measurements were performed in the presence of 100 mM tetramethylethylenediamine to eliminate the possibility that Cu would promote the Cu(I)-mediated crosslinking of a newly formed triazole pair.[9(d)]

Using bis(butynyl) methylsuccinate as the diyne monomer and different alkane diazides (runs 3–7), the click polymerizations proceeded smoothly to give the corresponding polyesters with M_ns between ~1.0 × 10^4 and 5.0 × 10^4. For each of their size exclusion chromatograms, only a single, symmetrical peak was recorded. The click polymerizations that used a diazide derivative of *p*-xylene in conjunction with bis(butynyl) methylsuccinate also proceeded smoothly to give the corresponding polyesters. When *p*-diazidoxylene was used as the monomer, a high molecular weight polyester ($M_n = 5.9 \times 10^4$) was obtained. It seems that the high molecular weight was ascribed to the conformation of the obtain "click polyester" not to reactivity of benzylic azide (see model reaction), as *m*-diazidoxylene as the monomer did not afford much higher molecular weight polyester ($M_n = 0.8 \times 10^4$, run 9).



sample	T_g [a]	T_m [a]
x=3	17	76
x=4	14	125
x=5	-4	52
x=6	6	76
x=7	-3	72

[a] T_m is measured by the first DSC scan at heating rate of 10°C/min. T_g by the second scan.

FIGURE 2 Plots of the T_m and T_g values of click polyesters as a function of the main-chain number of methylene units.

Safe Synthesis of Click Polyesters via *In Situ* Azidation

We performed click polymerizations of diynes and dibromo compounds in the presence of sodium azide to synthesize click polyesters via *in situ* azidation. These reactions were benign, as purified diazide compounds, which might explode, were not involved (Scheme 3).

We first investigated Cu(I)-mediated safe click reactions with the reaction temperatures controlled by an oil-bath (Table 2). The reactions were performed at 50 °C for 24 h. For all synthesizes, the polyesters obtained via *in situ* azidation had M_n values molecular weights (0.59×10^4, run 2; 0.33×10^4, run 4; Table 2) that were smaller than the corresponding click polyesters that had been synthesized using ioslated diazido monomers (3.79×10^4, run 3; 0.68×10^4, run 5; Table 2). The high yield and ^{1}H-NMR spectra indicated that the *in situ* azidation proceeded completely and no side reaction occurred under the employed conditions. We also performed click polymerizations with the hydroxyldibromide, 1,4-dibromo-2-butanol, in the presence of sodium azide, to synthesize click polyesters containing pendent hydroxyl groups (runs 6–8). However, only polyesters of relatively low molecular weight were recovered ($M_n = (0.14–0.26) \times 10^4$).

Next, we attempted click polymerizations, with the temperature (50 °C) controlled by modulating the power of the microwave irradiation between 0 and 50 W and reaction times of 24 h (Table 3). In contrast to the results obtained when the temperature was controlled by an oil bath ($M_n = 0.59 \times 10^4$, run 2; 0.33×10^4, run 4; Table 2), controlling the temperature using microwave irradiation produced higher molecular weight click polyesters ($M_n = 0.94 \times 10^4$, run 1; 0.42×10^4, run 3; Table 3). The polymerizations were completed in shorter periods of time when microwave irradiation was used than when an oil bath was used and that microwave radiation provides the effective driving force for the click polymerizations.[9(c),10(b),12,16] However, microwave irradiation did not improve the incorporation of monomers that contained hydroxyl groups (runs 3 and 4). This lack of improvement might be ascribed to absorbance of microwave by the pendent hydroxyls during the polyaddtion.

Finally, the irradiation power was set to 50 W (Table 4). Remarkable increases in the molecular weights of the polyesters were achieved to attain a more effective microwave-assisted polymerization. For example, the polyester of run 1 ($M_n = 2.5 \times 10^4$) was prepared in only 30 min and that of run 2 in 15 min ($M_n = 1.8 \times 10^4$). We also found that the molecular weight of the polyester that incorporated 1,4-dibromo-2-butanol increased (run 7). As expected, the molecular weights of the polyesters tended to decrease with increasing monomer concentration, perhaps because transesterification was favored at the high temperature used, which was the boiling point of DMF.

This microwave-assisted polymerization is a simple technique, requiring only the mixing of reagents and microwave irradiation. It avoids the need to isolate and handle potentially unstable small organic azides and shortens the reaction time from hours to a minutes.

Themal Properties of "Click Polyester"s

Polymerization shown in this study was accompanied by the formation of main-chain 1,4-disubstituted triazoles. We found that the presence of main-chain triazole rings improved the thermal properties of the polyesters *per se* and magnified the even-odd effect of the methylene chain length

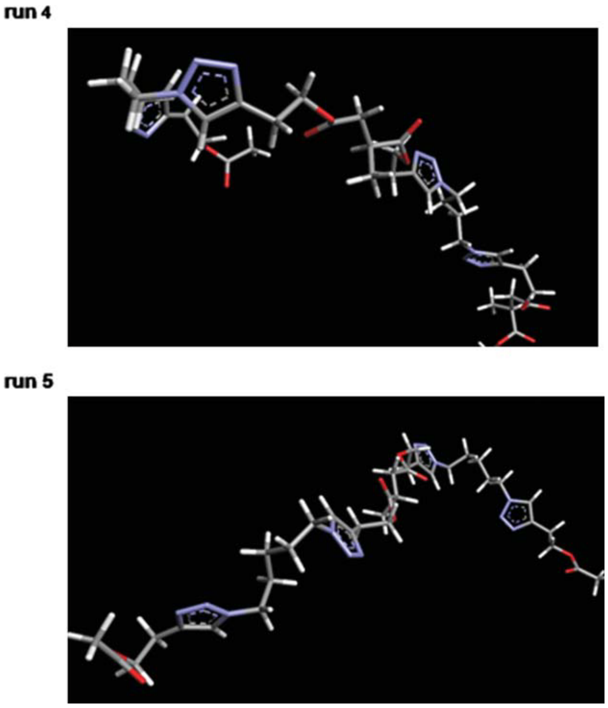


FIGURE 3 Semiempirical molecular orbital calculations to model the conformations of the corresponding click polyesters (runs 4 and 5 in Table 1).

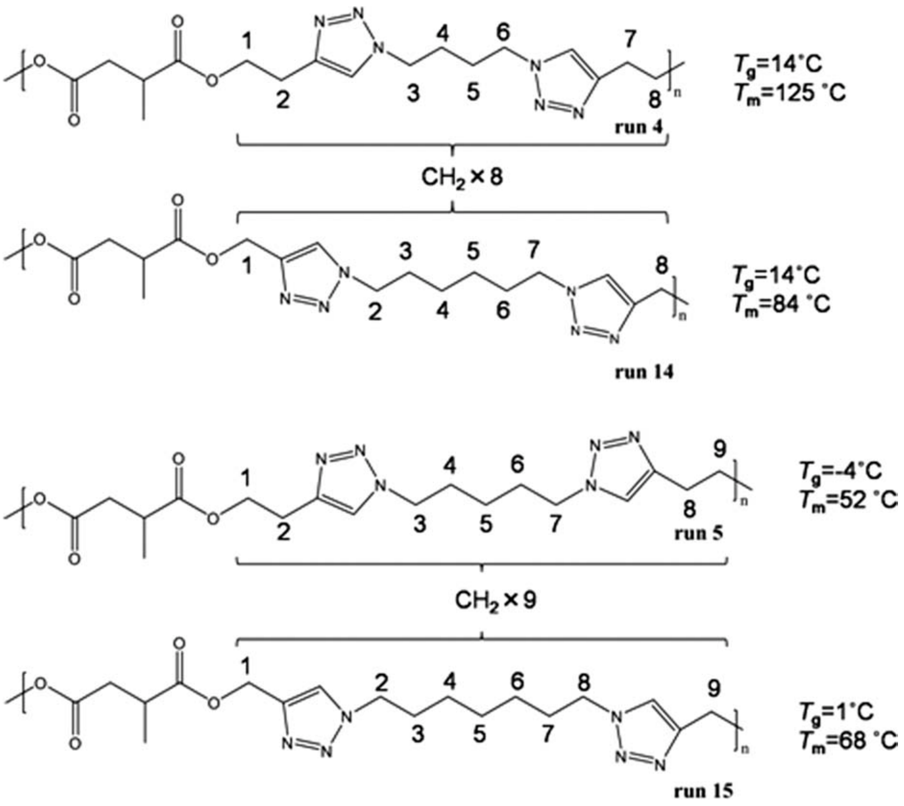


FIGURE 4 Changes in the positioning of the triazole rings.

on the thermal properties. For example, the polyester synthesized from bis(butynyl) methylsuccinate and 1,4-diazidobutane ($x = 4$, where x is the number of methylene groups) had higher T_g and T_m values ($M_n = 1.37 \times 10^4$, $T_g = 14$ °C, $T_m = 125$ °C, run 4, in Table 1) compared with poly(octamethylene methylsuccinate), which did not have a main-chain triazole ring ($M_n = 2.2 \times 10^4$, $T_g = -53$ °C, T_m was not observable). In contrast, the polyester synthesized from 1,5-diazidopentane ($x = 5$, run 5 in Table 1) had values for its thermal properties that were much smaller ($T_g = -4$ °C, $T_m = 52$ °C).

The differences for ΔT_g (18 °C) and ΔT_m (73 °C) (runs 4 and 5) were greater than those usually effected by the even-odd effect for T_gs [e.g., for poly(nonamethylene methylsuccinate), $T_g = -61$ °C, ΔT_g (8 °C)].[17] The click polyester synthesized from 1,6-diazidohexane ($x = 6$, run 6) had larger T_g (6 °C) and T_m (76 °C) values than did that synthesized from 1,5-diazidopentane ($x = 5$). Zigzag curves with zigzag shapes were observed for plots of T_g and T_m versus the methylene chain length of the diazides (Fig. 2). Although an even-odd effect is usually observed for the thermal properties of polyesters,[2,17] the height difference between the highest and lowest points is usually small for the zigzag plots of aliphatic polyesters. Therefore, the introduction of main-chain triazole rings enhanced the even-odd effect.

Energy minimizations were performed for the repeat units of the click polyesters, that is, Me-[OCOCH(CH$_3$)CH$_2$COO(CH$_2$)$_2$-triazole-(CH$_2$)$_4$-trialzole-(CH$_2$)$_2$]$_2$-Me and Me-[OCOCH(CH$_3$)CH$_2$-COO(CH$_2$)$_2$-triazole-(CH$_2$)$_5$-trialzole-(CH$_2$)$_2$]$_2$-Me using semi-empirical molecular orbital calculations[14] to model the conformations of the corresponding click polyesters (runs 4 and 5). The three-dimensional structures of the energy-minimized models (Fig. 3), indicate that the value of the main-chain torsion angle is larger for the click polyester synthesized from 1,5-diazidopentane (run 5), which produces a larger overall free volume and inhibits intramolecular stacking.

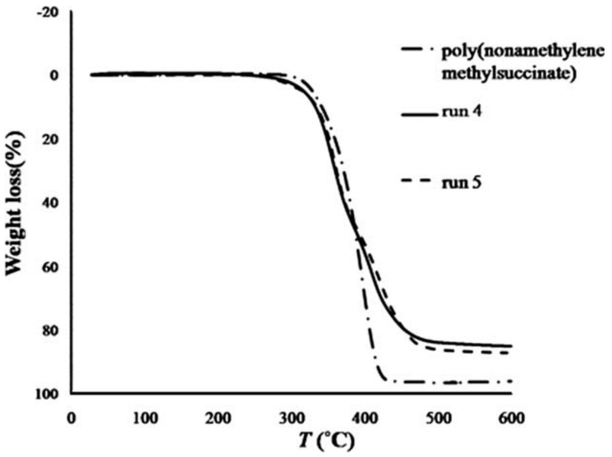


FIGURE 5 Thermogravimetric analysis under nitrogen flow, with a heating rate of 10 °C min^{-1}.

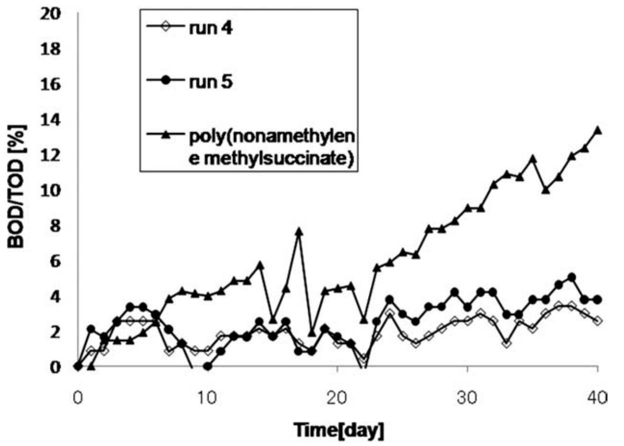


FIGURE 6 BOD curves for of poly(nonamethylene methylsuccinate), and the polyesters of runs 4 and 5, each mixed with activated sludge (pH, 7.5, 25 °C).

Interestingly, when the number of intervening methylenes between the triazole rings was an even value, for example, run 4 (number of intervening methylenes: 4) and 14 (number of intervening methylenes: 6) (Table 1), a decrease in the T_m value was found ($\Delta T_{m(\text{run 14-run 4})} = -41$ °C) with increase of the methylene number; whereas, when the number of intervening methylenes was an odd value, for example, runs 5 (number of intervening methylenes: 5) and 15 (number of intervening methylenes: 7), an increase in the T_m value was found ($\Delta T_{\mathrm{m}\ (\text{run 15-run 5})} = 16$ °C); although the corresponding T_g values were not affected (Fig. 4). Therefore, it is revealed that we can control the thermal properties of the click polyesters by changing the methylene chain length of the monomer and/or the positioning of the triazole rings, which should allow us to control their thermal properties.

Thermal Degradability

For the thermal gravimetric measurements of the click polyesters (runs 4 and 5 in Table 1) produced by oil bath heating, although the thermal stabilities of the click polyesters are slight improved compared with poly(nonamethylene methylsuccinate), remarkable even-odd effect were not confirmed (Fig. 5).

Biodegradability

Biodegradation of the click polyesters of runs 4 and 5 (Table 1) and poly(nonamethylene methylsuccinate), that had been mixed with activated sludge (pH 7.4, 25 °C) was monitored using a BOD tester. The amount of a polymer degraded was calculated from its BOD value and the theoretical oxygen demand (TOD) value, and reported as a percentage (Fig. 6), as defined in the Experimental Section. All three BOD values were reproducible. The click polyesters were not biodegraded within 40 days as shown their BOD/TOD values of ~2–4%; whereas the value for poly(nonamethylene methylsuccinate) was 14% by day 40. Therefore, the main-chain triazoles of the click polyesters suppressed biodegradation.

CONCLUSIONS

In this article, we used dialkynes containing ester linkages and diazides to synthesize, via click polymerization catalyzed by Cu(I), polyesters with high $M_\mathrm{n}s$ [(1.0–7.0) $\times$ 10^4] in excellent yields. These polymers contained main-chain 1,4-disubtituted triazoles. We found that the presence of the main-chain triazoles improved the thermal properties of the polyesters and magnified the even-odd effect caused by the of methylene chain length on the thermal properties of the polyesters. In addition, we could fine tune the thermal properties of the polyesters by changing the positions of triazoles. We also demonstrated that it is possible produce the click polymers via microwave irradiation and that, when used in conjunction with *in situ* azidation, the synthesis of a click polyester is a safe and effective procedure that should find industrial use. Our work is the first time that click chemistry has been used to synthesize polyesters and our results should provide the foundation for the synthesis of novel polyester-based materials.

This article is dedicated to the 2 years memory of the late Tadamichi Hirabayashi (Nagoya Institute of technology). We acknowledge the Nagoya Institute of Technology's Research Promotion Program.

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