High Yield Synthesis of Diverse Well-Defined End-Functionalized Polymers by Combination of Anionic Polymerization and "Click" Chemistry

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ABSTRACT: Well-defined poly(methyl methacrylate) (M_n = 3630 g mol^{-1}, PDI = 1.06) with a primary benzylic bromide prepared using anionic polymerization was successfully transformed into diverse end-functionalities (ω-carboxyl, ω-hydroxy, ω-methyl-vinyl, ω-trimethylsilane, and ω-glycidyl-ether) via "click" reaction. The bromine end-terminated poly(methyl methacrylate) was first substituted by an azide function and sequentially was reacted with various functional alkynes (propiolic acid, propargyl alcohol, 2-methyl-1-buten-3-yne, propargyl tri-methylsilane, and propargyl glycidylether). In all the cases, ^{1}H-NMR, ^{13}C NMR, FT-IR, and GPC measurements show qualitative and quantitative transformation of the chain-end poly(methyl methacrylate) into the desired functionalities with high conversion (above 99%). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1571–1580, 2009

Key words: anionic polymerization; click reaction; telechelics; poly(methyl methacrylate)

INTRODUCTION

The telechelic (end-functionalized) polymers, containing one or more end groups with the ability to interact with other organic, inorganic, and metal substances, are useful for many applications, for example, the synthesis of grafted polymers[1] and supramolecules that form stimuli-responsive bonds,[2] surface modifications of nanoparticles[3–5] and substrates,[6] fluorescently labeled chains,[7,8] and coupling reactions to form functional block copolymers.[9] However, because the substantial concentration of end groups is not high enough and side reactions with other functionalities within the polymer have the possibility to occur, the unexpected results can happen and the difficulty of postpurification can increase. Therefore, it is necessary to have reactions with high modularity and efficiency for successful and specific functionalizations of polymers

Sharpless and coworkers recently have optimized the Huisgen's 1,3-dipolar cycloaddition reaction of azides and alkynes by a copper(I) catalysis, resulting in highly specific and efficient preparation of 1,4-di-substituted 1,2,3-triazole products under mild reaction conditions.[10,11] This reaction, in general termed "click" chemistry, was demonstrated to be very powerful, because it can have high yield (above 95%) with great tolerance to various functional groups and solvents.[12,13] Moreover, the "click" reaction requires only a simple work-up procedure and thus formed 1,2,3-triazole which is chemically stable. Therefore, the technique has been applied in the field of polymer science.[14–16]

Recently, a wide range of controlled polymerization techniques such as nitroxide-mediated polymerization (NMP),[17] atom transfer radical polymerization (ATRP),[18] and reversible addition-fragmentation transfer polymerization (RAFT)[19] has been utilized to prepare various functional polymers. In particular, ATRP is highly versatile and most practical, because its terminal alkyl halide can be used for further nucleophilic substitutions or elimination reactions.[20] However, the chance of losing the halide functionality during ATRP polymerization is up to 20%[21,22] leading to the difficulty of subsequent modification for further applications. Matyjaszewski et al. have studied the transformation reaction from a halide end group to an azide of polystyrene[23] and poly(methyl acrylate).[24] The transformation reaction using various ATRP model initiators was also examined.[25] However, the efficiency of the S$_N$2 reaction transformation was limited by the inherent properties of monomers used in the ATRP.
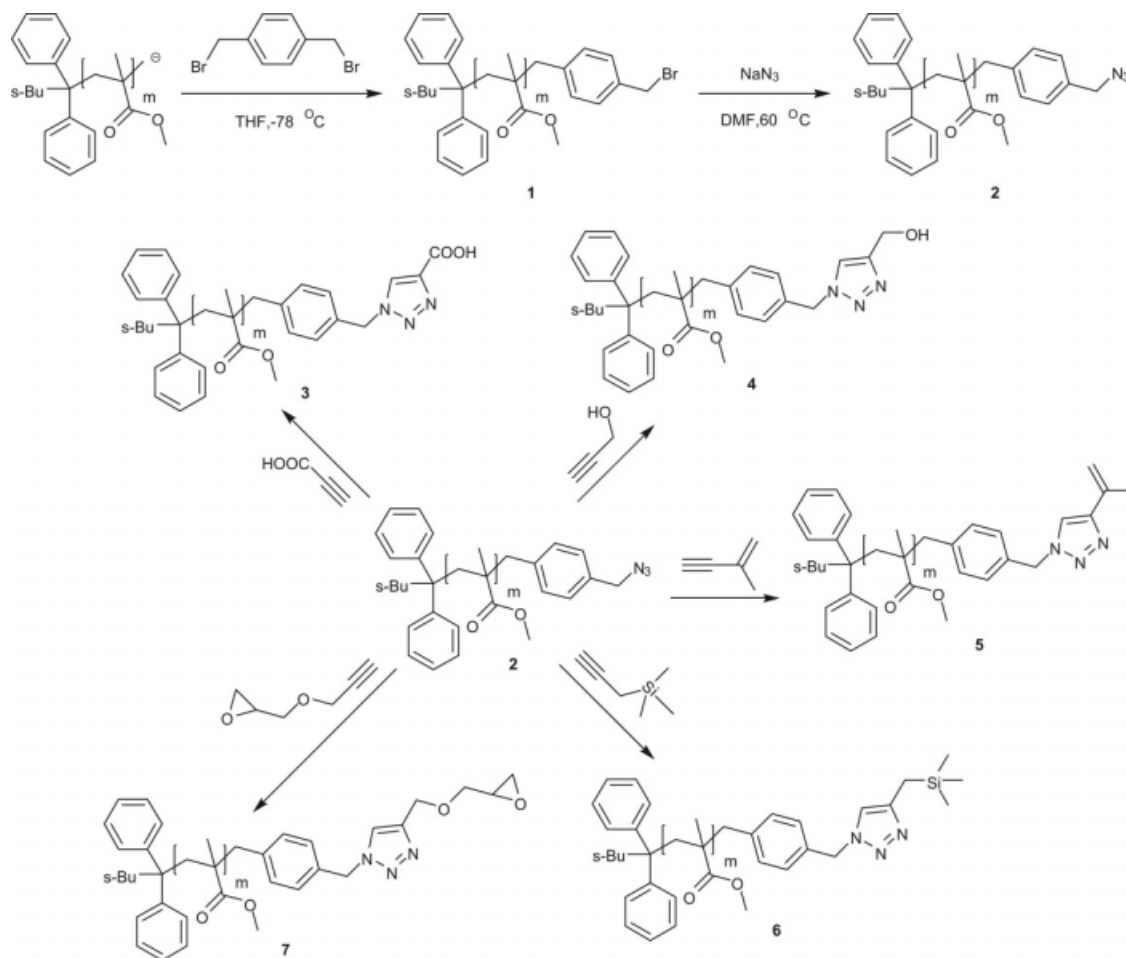
Scheme 1 Synthesis of well-defined functional polymers via the combination of anionic polymerization and "click" reaction.

If the polymer chain is ended with a tertiary carbon center then that will result in low transformation yield. Furthermore, prefunctionalized initiators of NMP,[26] ATRP,[9] and RAFT[27] are required to prepare telechelic polymers. The tedious synthesis of these initiators for various monomers is necessary to obtain good coordination among initiator, monomer, and catalyst system. The functional group of the initiator needs to be protected in advance to avoid the possibility of losing its reactivity and reacting to the functional group within the growing polymers.

These problems can be circumvented by using a synthesis method combining anionic polymerization and the "click" chemistry. Anionic polymerized living anion is readily to react with an electrophilic coupling agent, resulting in a transformation of the polymer with the primary benzylic halide chain-end. The high conversion of the primary benzylic halide chain-end can be obtained (above 98%) and subsequently transformed into an azide chain-end easily.[28] Furthermore, a myriad of functional alkynes for further modification of the azide terminated polymer is commercially available. Hence, we aimed the goal of

preparing diverse end-functionalized polymers with well-defined molecular weight, narrow molecular weight distribution, and stereospecificity in high yield (above 99%) by using the combination of anionic polymerization and "click" chemistry. In this study, we used poly(methyl methacrylate) as a model polymer which is ended up with a tertiary carbon center and prepared seven different chain-end functionalities, including ω-bromine, ω-azido, ω-carboxyl, ω-hydroxy, ω-methyl-vinyl, ω-trimethylsilane, and ω-glycidyl-ether (Scheme 1).

EXPERIMENTAL

Materials

α,α′-Dibromo-*p*-xylene (Fluka 98%), lithium chloride (LiCl, Acros 99%), sodium azide (NaN$_3$, Acros 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Fluka 99%), copper(I) iodide (RdH 99.5%), propiolic acid (Acros 98%), propargyl alcohol (Acros 99%), 2-methyl-1-buten-3-yne (Aldrich 99%), trimethyl(propargyl)silane (Acros 90%), and glycidyl propargyl ether

(Fluka 90%) were purchased from commercial suppliers and used without further purification. Methyl methacrylate (MMA, Acros 99%) and 1,1-diphenylethylene (DPE, Acros 99%) were dried over CaH_2 overnight, followed by freeze-and-thaw procedures and vacuum distilled. The reagents were stored under nitrogen atmosphere at $-4°C$. Tetrahydrofuran (THF, J.T.Backer) was purified by refluxing over fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). It was further dried with sec-butyllithium (s-BuLi, 1.3M in cyclohexane, Chemetall) dropwise immediately before use. N,N-Dimethylformamide (DMF, J.T. Backer) was dried over 4-Å molecular sieves.

Characterization

NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker Avance 400 MHz, and $CDCl_3$ was used as solvent. FTIR spectra were performed on a Bio-Rad Excalibur series FTS 3000. The molecular weight and molecular weight distribution were measured using a Waters GPC (Breeze system) in THF as an eluent at 35°C. The apparatus was equipped with two Waters Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414) and a dual-wavelength absorbance detector (Waters 2487). Poly(methyl methacrylate) standards (Polymer Laboratories) were used for calibration.

Synthesis of bromine end-functionalized poly(methyl methacrylate) [1]

Anionic polymerization was carried out in a flame dried glass reactor under dried nitrogen atmosphere. LiCl (1.1 g, 25.87 mmol) was first placed in a Schlenk flask which was equipped with a Ratoflo, evacuated and flame dried. THF (250 mL) and DPE (0.55 mL, 3.10 mmol) were introduced through a cannula and the reaction mixture was cooled at $-78°C$. Subsequently, s-BuLi (1.99 mL, 2.59 mmol) was injected using a gas-tight syringe to initiate DPE and the color of the solution turned to scarlet instantly. After 15 min, MMA (10 mL, 92.90 mmol) was added through a cannula and the reaction mixture immediately became colorless. The reaction was allowed to proceed at $-78°C$ for 30 min, and the living poly (methyl methacrylate) solution was introduced dropwise by a cannula into a α,α′-dibromo-p-xylene (6.83 g, 25.9 mmol) solution. Thirty minutes later, the reaction mixture was terminated with methanol. The corresponding polymer was purified over a basic alumina column and precipitated twice in hexane, yielding a white solid which was dried under vacuum. δ_H(400 MHz; $CDCl_3$), 0.12–0.24 (m, H_3C—CH_2, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH_2,

and CH_3), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 4.45 (s, Ph—CH_2—Br), and 6.96–7.25 (br m, arom. H); δ_C(400 MHz; $CDCl_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.6, 30.0, 30.5, 31.1, 33.1 (Ph—CH_2—Br), 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 54.1, 54.8, 125.5, 127.2, 128.5, 128.9, 130.3, 130.6, 136.0, 136.5, 147.0, 148.6, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 610 (C—Br), 703, 749, 810, 827, 841, 911, 966, 987, 1063, 1148, 1190, 1241, 1271, 1385, 1442, 1484, 1729, 2843, 2950, 2994, 3441, 3553, and 3628; SEC: M_n = 3.63 kg/mol, M_w/M_n = 1.06.

Synthesis of azide end-functionalized poly(methyl methacrylate) [2]

Bromine end-functionalized poly(methyl methacrylate) (8.0 g, 2.20 mmol) was dissolved in DMF (200 mL) and then sodium azide (1.43 g, 22.03 mmol) was added. The reaction mixture was stirred overnight at 60°C. The polymer was purified over a basic alumina column and precipitated twice in hexane, yielding a white solid. δ_H(400 MHz; $CDCl_3$), 0.12–0.24 (m, H_3C—CH_2, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH_2, CH_3), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 4.29 (s, Ph—CH_2—N$_3$), and 6.96–7.25 (br m, arom. H); δ_C(400 MHz; $CDCl_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.6, 30.0, 30.5, 31.1, 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 54.1, 54.3 (Ph—CH_2—N$_3$), 54.8, 125.6, 127.2, 127.7, 128.5, 128.9, 130.3, 130.6, 133.6, 136.3, 147.1, 148.5, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 703, 749, 810, 827, 841, 911, 967, 987, 1063, 1148, 1190, 1242, 1269, 1386, 1442, 1481, 1730, 2099 (—N$_3$), 2845, 2950, 2994, 3441, 3554, and 3620.

Typical procedures for the "click" reactions of the azide end-functionalized poly(methyl methacrylate) and the functional alkynes [3–7]

Azide end-functionalized poly(methyl methacrylate) (0.3 g, 0.08 mmol) and CuI (13.4 mg, 0.07 mmol) were placed in a Schlenk flask which was equipped with a Rotaflo, degassed, and recharged in the nitrogen atmosphere. DMF (6 mL) and DBU (1 mL, 6.69 mmol) were added and the functional alkyne (10 equiv) was subsequently injected by a gas-tight syringe. The reaction mixture was allowed to proceed at room temperature overnight. The reaction was terminated by precipitating it in hexane. The polymer was redissolved in dichloromethane and washed with an EDTA solution. The organic layer was dried with anhydrous magnesium sulfate and purified over a basic alumina column. The polymer was precipitated in hexane and yielded a white solid, which was dried under vacuum.

ω-carboxyl end-functionalized poly(methyl methacrylate) (3)

δ_H(400 MHz; CDCl$_3$), 0.12–0.24 (m, H_3C—CH$_2$, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH$_2$, CH$_3$), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 5.51 (s, Ph—CH$_2$—N), 6.96–7.25 (br m, arom. H), 7.46 (s, N—CH=C), and 7.69 (s, COOH); δ_C(400 MHz; CDCl$_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.6, 30.0, 30.5, 31.1, 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 53.4 (Ph—CH$_2$—N), 54.1, 54.8, 123.2 (N—CH=C), 125.6, 127.3, 127.7, 128.6, 129.0, 130.7, 133.1, 134.0 (CH=C(N)—COOH), 136.9, 147.1, 148.6, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 703, 749, 809, 827, 842, 911, 985, 1064, 1149, 1192, 1242, 1271, 1323, 1385, 1442, 1485, 1645 (—COOH), 1729, 2949, 2993, 3122 (—COOH), 3252 (—COOH), 3439.

ω-hydroxy end-functionalized poly(methyl methacrylate) (4)

δ_H(400 MHz; CDCl$_3$), 0.12–0.24 (m, H_3C—CH$_2$, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH$_2$, CH$_3$), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 4.76 (s, C—CH$_2$—OH), 5.47 (s, Ph—CH$_2$—N), 6.96–7.25 (br m, arom. H), and 7.43 (s, N—CH=C); δ_C(400 MHz; CDCl$_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.6, 30.0, 30.5, 31.1, 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 53.5 (Ph—CH$_2$—N), 54.1, 54.8, 56.3 (C—CH$_2$—OH), 121.5 (N—CH=C), 125.6, 127.2, 127.5, 128.5, 128.9, 132.9, 136.8, 147.0, 148.0 (CH=C(N)—CH$_2$), 148.5, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 483, 703, 749, 810, 827, 842, 911, 967, 985, 1063, 1149, 1192, 1242, 1272, 1385, 1444, 1481, 1645, 1730, 2846, 2950, 2995, 3442, 3547, 3615.

ω-methyl-vinyl end-functionalized poly(methyl methacrylate) (5)

δ_H(400 MHz; CDCl$_3$), 0.12–0.24 (m, H_3C—CH$_2$, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH$_2$, CH$_3$), 2.09 (s, H$_2$C=C—CH$_3$), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 4.76 (s, C—CH$_2$—OH), 5.07 (s, C=CH$_2$), 5.47 (s, Ph—CH$_2$—N), 5.67 (s, C=CH$_2$), 6.96–7.25 (br m, arom. H), and 7.39 (s, N—CH—C); δ_C(400 MHz; CDCl$_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.4 (CH$_3$—C(CH$_2$)—C), 20.6, 30.0, 30.5, 31.1, 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 53.5 (Ph—CH$_2$—N), 54.1, 54.8, 112.3 (CH$_2$=C(CH$_3$)—C), 119.4 (N—CH=C), 125.6, 127.2, 127.5, 128.5, 128.9, 130.6, 133.1 (CH=C(N)—CH$_2$), 133.3, 148.6, 148.9, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 702, 749, 802, 842, 911, 967, 985, 1065, 1149, 1192, 1242, 1271, 1321, 1385, 1442, 1483, 1645 (C=C), 1729, 2847, 2950, 2993, 3120, 3240, 3441.

ω-trimethylsilane end-functionalized poly(methyl methacrylate) (6)

δ_H(400 MHz; CDCl$_3$), −0.005 (s, CH$_2$—Si—(CH$_3$)$_3$), 0.12–0.24 (m, H_3C—CH$_2$, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH$_2$, CH$_3$), 2.07 (s, C—CH$_2$—Si), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 5.42 (s, Ph—CH$_2$—N), and 6.96–7.25 (br m, arom. H); δ_C(400 MHz; CDCl$_3$) −1.9 (CH$_2$—Si—(CH$_3$)), 10.8, 16.1, 17.4, 18.5, 19.8, 20.4 (CH$_3$—C(CH$_2$)—C), 20.6, 25.1 (C—CH$_2$—Si), 30.0, 30.5, 31.1, 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.8, 51.3, 51.6, 52.6, 53.3 (Ph—CH$_2$—N), 54.1, 54.8, 119.4 (N—CH=C), 125.6, 127.2, 127.3 (CH=C(N)—CH$_2$), 127.5, 128.5, 128.9, 130.6, 133.3, 147.1, 148.6, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 703, 749, 810, 827, 843, 911, 967, 987, 1064, 1149, 1190, 1242, 1273, 1385, 1444, 1481, 1639, 1730, 2849, 2950, 2994, 3441, 3556, 3627.

ω-glycidyl-ether end-functionalized poly(methyl methacrylate) (7)

δ_H(400 MHz; CDCl$_3$), 0.12–0.24 (m, H_3C—CH$_2$, and H_3C—CH), 0.45–3.32 (br m, backbone CH, CH$_2$, CH$_3$), 2.50–2.65, and 3.09–3.19 (m, epoxy H), 3.37–3.77 (br s, backbone H_3C—O$_2$C), 3.39–3.46, and 3.78–3.84 (m, O—CH$_2$—epoxide), 4.66 (q, C—CH$_2$—OCH$_2$), 5.46 (s, Ph—CH$_2$—N), 6.96–7.25 (br m, arom. H), and 7.46 (s, N—CH—C); δ_C(400 MHz; CDCl$_3$) 10.8, 16.1, 17.4, 18.5, 19.8, 20.6, 30.0, 30.5, 31.1, 44.0 (epoxide CH$_2$), 44.3, 44.6, 44.9, 46.4, 48.6, 49.8, 50.4 (epoxide CH), 50.8, 51.3, 51.6, 52.6, 53.6 (Ph—CH$_2$—N), 54.1, 54.8, 64.5 (C—CH$_2$—O), 71.0 (O—CH$_2$—epoxide), 122.4 (N—CH=C), 125.6, 127.2, 127.5, 128.5, 128.9, 130.6, 133.3, 144.9 (CH=C(N)—CH$_2$), 147.1, 148.6, 176.5, 176.7, 177.6, 177.9, and 178.2; ν_{max}(film)/cm^{-1} 482, 703, 749, 810, 827, 841, 912, 967, 982, 1063, 1149, 1192, 1242, 1274, 1384, 1448, 1485, 1621, 1730, 2846, 2950, 2994, 3436.

RESULTS AND DISCUSSION

The synthesis of a bromine terminated poly(methyl methacrylate) (1) was carried out in two sequential pathways. First, methyl methacrylate was initiated using s-BuLi in the presence of LiCl by ligated anionic polymerization method.[29] As the poly(methyl methacrylate) living anion was formed, the polymer anion was subsequently introduced into a solution containing an electrophilic coupling agent, α,α′-dibromo-p-xylene. This coupling agent was selected, because of its high coupling efficiency and the, thus, formed primary benzylic bromide is very favorable for the subsequent S$_N$2 reaction. To prevent the formation of the double-coupling through the other side of the coupling agent, the solution with excess coupling agent (5–10 equiv.) was prepared and the polymer anion was added dropwise slowly into this
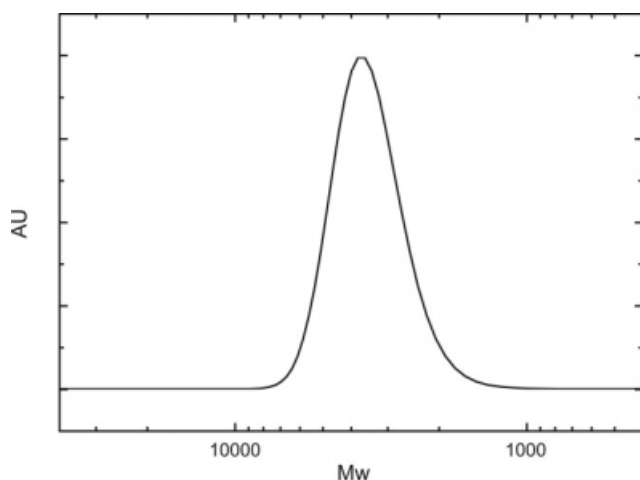
Figure 1 GPC traces of unfuntionalized, ω-bromine, ω-azido, ω-carboxyl, ω-hydroxy, ω-methyl-vinyl, ω-trimethyl-silane, and ω-glycidyl-ether terminated poly(methyl methacrylate)s [1–7]. Only one peak showed before and after functionalization indicates an efficient conversion reaction.

solution. The GPC was used to confirm whether double-coupling reaction occurred. The samples for GPC measurements were withdrawn before and after adding the polymer anion into the coupling agent solution. The GPC traces (Fig. 1) show that the curves of the samples were superimposed and only a unimodal peaks were observed, indicating no dou-

ble-coupling reaction occurred. The obtained polymer had well-defined number-average molecular weight (M_n = 3630 g mol^{-1}) and narrow molecular weight distribution (M_w/M_n = 1.06). The degree of the polymerization (n = 36) and syndiotacticity (above 80%) of the thus synthesized polymer was further examined using ^{1}H NMR, as shown in Figure 2. The number-average molecular weight was estimated by comparing the signal integration from the methylene protons (**H$_b$**, δ 4.45 ppm) bromine benzylic end group to the methyl ester protons (**H$_a$**, δ 3.42–3.74 ppm) of the PMMA repeating units. The integration of these proton peaks were tabulated in Table I. The result is in good agreement with the number-average molecular weight determined from the GPC (Table II). Thus, a complete conversion of the coupling reaction (above 99%) is obtained. Furthermore, an additional peak at 33.1 ppm was observed in ^{13}C NMR spectrum (Fig. 3) when compared with the nonfunctionalized polymer which gives a complementary evidence for the existence of bromine end-terminated group.

As afore-mentioned, for the purpose of performing the 1,3-dipolar cycloaddition of an azide and an alkyne, the bromine terminated poly(methyl methacrylate) (**1**) was transformed into an azido end-functionalized polymer (**2**) via nucleophilic substitution. This transformation reaction was performed in DMF
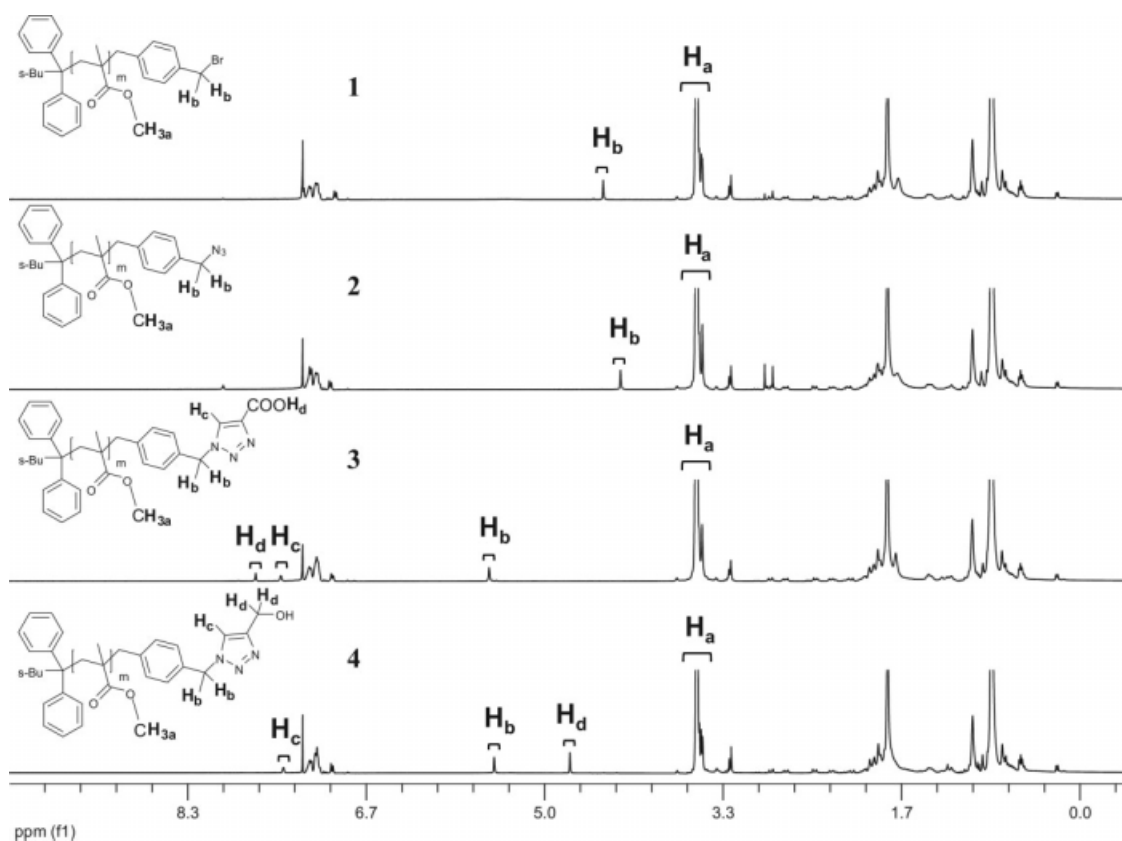

Figure 2 ^{1}H NMR spectra of ω-bromine, ω-azido, ω-carboxyl, and ω-hydroxy terminated poly(methyl methacrylate)s [1–4].

TABLE I
Proton Integrations of ω-Bromine, ω-Azido, ω-Carboxyl, ω-Hydroxy, ω-Methyl-Vinyl, ω-Trimethylsilane, and ω-Glycidyl-Ether Terminated Poly(Methyl Methacrylate)s [1–7]

Polymer	H_a	H_b	H_c	H_d	H_e	H_f
1	54.28	1.00				
2	53.98	1.00				
3	54.17	1.00	0.49	0.51		
4	53.99	1.00	0.48			
5	54.15	1.00	0.53	1.49	0.5	0.5
6	54.09	1.00		0.96	3.02	
7	54.97[a]	1.00	0.51	1.08	1.01	0.98, 1.02

[a] The integration is the sum of the methylene protons of the methylene ester protons of the PMMA repeating units and one of the methylene protons in the α position of the epoxide group.

with the excess amount of sodium azide. After the reaction finished, the obtained polymer **2** was examined using GPC. The chromatograms show the trace of **2** is consistent with that of **1**, as shown in Figure 1. In ¹H NMR spectra, the neighboring methylene protons (δ 4.45 ppm) to the bromine end group have been completely disappeared and a new methylene protons (δ 4.29 ppm) adjacent to the azido group appeared (Fig. 2). The ¹³C NMR spectra (Fig. 3) also show similar results that the carbon signal adjacent to the bromine end group all disappeared and a new peak (δ 54.3 ppm) neighboring to the azido group appeared. The appearance of a new signal in FTIR spectrum (2099 cm⁻¹) [Fig. 4(a)] demonstrates the formation of the azido group as well. Furthermore, signal integration of the new methylene protons in ¹H NMR, as tabulated in Table I, is compared with that from the methylene ester protons of the PMMA repeating units. The signal integration ratios between the methylene protons adjacent to the end-terminated functionalities and the methylene ester protons of the PMMA repeating units from the polymers, **1** and **2**, are quantatively close. The results suggest that the substitution reaction was complete (above 99%) and no other side reaction occurred.

Diverse functional alkynes, propiolic acid, propargyl alcohol, 2-methyl-1-buten-3-yne, trimethyl propargyl silane, and glycidyl propargyl ether functional groups, were respectively, reacted with the synthesized azide end-functionalized poly (methyl methacrylate) via the "click" reaction and a series of corresponding end-functionalized polymers **3–7** were obtained. The reactions were carried out using CuI and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a catalytic system.[30] DMF was used as a solvent to increase the solubility of the π-complex between Cuᴵ and alkyne in organic media. For Cuᴵ/propiolic acid system, the π-complex of the Cuᴵ/pro-

piolic acid became insoluble while THF was used as the solvent. It is important to note that a high polarity solvent and an efficient ligand, which is able to complex with Cuᴵ effectively in organic solvent,[22,31] can be used to improve the π-complex solubility in organic media and also improve the efficiency of the "click" reaction.[32,33]

The complete transformation of azide functionalities into the respective functional triazoles was determined using ¹H NMR, as shown in Figures 2 and 5. The total disappearance of the methylene protons adjacent to azide end group (δ 4.29 ppm) and the appearance of the methylene protons adjacent to the triazole (δ 5.42–5.52 ppm) are observed in all cases (**3–7**). As similar to ¹H NMR spectra, ¹³C NMR spectra (Figs. 3 and 6) show that the carbon signal adjacent to azide end group (δ 54.3 ppm) disappeared and the carbon signals adjacent to the nitrogen of the triazole ring (δ 53.3–53.6 ppm) in **3–7** appeared. Furthermore, a signal at δ 7.40–7.47 ppm in ¹H NMR spectra (Figs. 2 and 5) was observed in **3–5** and **7** but not in **6** (explain it later) and it is assigned to the proton signal of their triazole ring. In ¹³C NMR spectra (Figs. 3 and 6), two carbon signals at δ 119.4–122.4 ppm and δ 127.3–148.0 ppm were also appeared in those polymers. The first is attributed to the secondary carbon of the triazole ring, and the later is associated to the tertiary carbon of that triazol ring. The appearance of the new proton signal and the new carbon signals indicated the efficiency of the "click" reaction. The number-average molecular weight and PDI of the polymers **3–7** were determined by GPC, as tabulated in Table II. The chromatograms of these polymers (Fig. 1) show all traces are overlapping, suggesting no self-coupling and side reactions occurred in the sequential procedures.

In the case of **3**, a proton signal of presumably the carboxylic acid group (δ 7.69 ppm) was observed in its ¹H NMR spectrum and the signals at 1645 and 3439 cm⁻¹ [Fig. 4(b)] also appeared in the FTIR spectrum. Both the spectra indicated that **3** contain the carboxylic acid functional group. However, the

TABLE II
Molecular Weight and Conversion of ω-Bromine, ω-Azido, ω-Carboxyl, ω-Hydroxy, ω-Methyl-vinyl, ω-Trimethylsilane, and ω-Glycidyl-Ether Terminated Poly(Methyl Methacrylate)s [1-7]

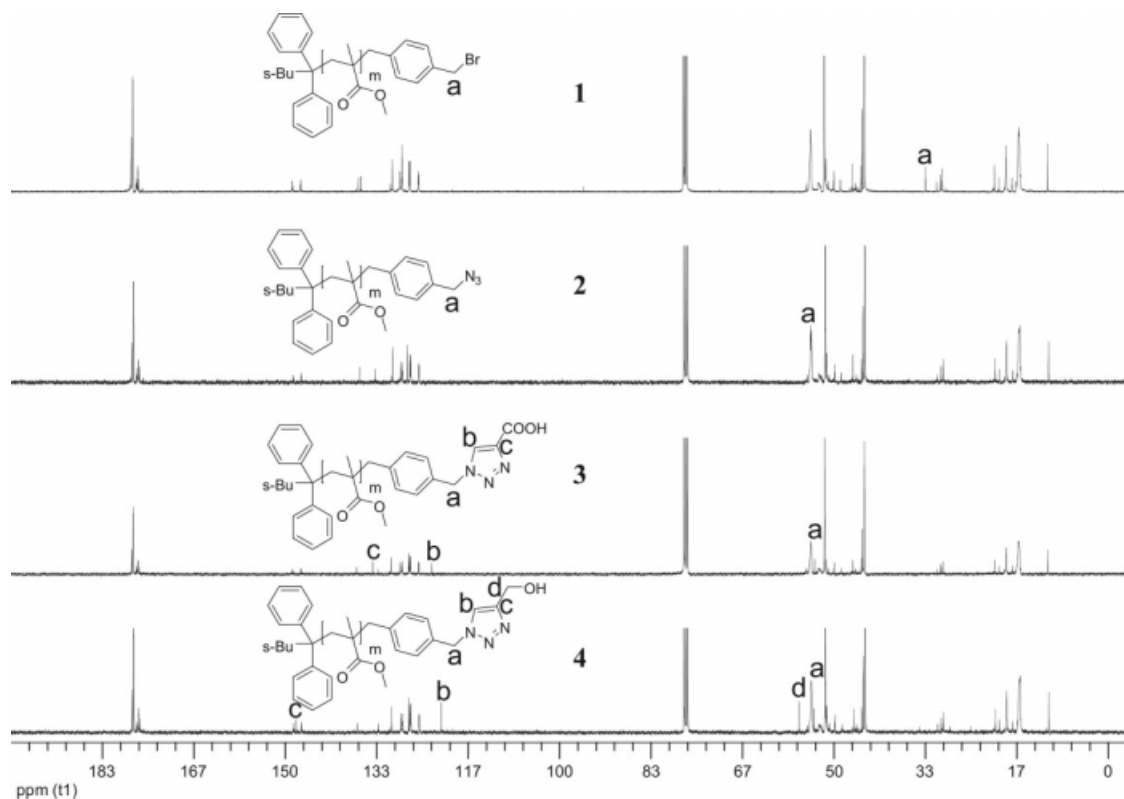| Polymer	Mn (GPC)	PDI	Mn (NMR)	Conversion (%)
1	3630	1.06	3623	>99
2	3630	1.06	3603	>99
3	3630	1.06	3615	>99
4	3630	1.06	3603	>99
5	3630	1.06	3614	>99
6	3630	1.06	3610	>99
7	3630	1.06	3602	>99

Figure 3 ^{13}C NMR spectra of ω-bromine, ω-azido, ω-carboxyl, and ω-hydroxy terminated poly(methyl methacrylate)s [1–4].

carbon signal of the carboxylic acid group was not observed in ^{13}C NMR spectrum. It can be attributed to the extremely small amount of carbon thirteen isotope from the carboxylic acid group and only one carboxylic acid group at each chain-end, resulting in difficult probing. As shown in Table I, the signal integration of the new methylene protons adjacent to the nitrogen of the triazole ring (δ 5.51 ppm) in ^{1}H NMR is compared with that from the methylene ester protons of the PMMA repeating units, the new methine proton of the triazole ring (δ 7.46 ppm), and the new proton of the carboxylic acid group (δ 7.69 ppm). These integration of the new proton peaks are in quantatively consistent with their stoichiometry and the number-average molecular weight (M_n). The M_n is estimated by calculating the number of repeating units of PMMA of ^{1}H NMR and by GPC. The results are in quantitatively agreement (Table II) which indicate that the "click" reaction for the transformation into the carboxylic acid functionality was complete (above 99%) and no other side reaction occurred.

In the case of **4**, one more signal was observed at δ 4.76 ppm in its ^{1}H NMR spectrum (Fig. 2) and this proton peak was assigned to the methylene protons adjacent to the hydroxyl. As analogous to the ^{1}H NMR spectrum, a new carbon signal in ^{13}C NMR adjacent to the hydroxyl group at δ 56.3 ppm was also observed. The signal integration of the new

methylene protons adjacent to the nitrogen of the triazole ring (δ 5.47 ppm) in ^{1}H NMR is compared with that from the methylene ester protons of the PMMA repeating units, the new methine proton of the triazole ring (δ 7.43 ppm) and the new methylene protons neighboring the hydroxyl group (δ 4.76 ppm), as tabulated in Table I. These integrations of the new proton peaks are in quantatively consistent
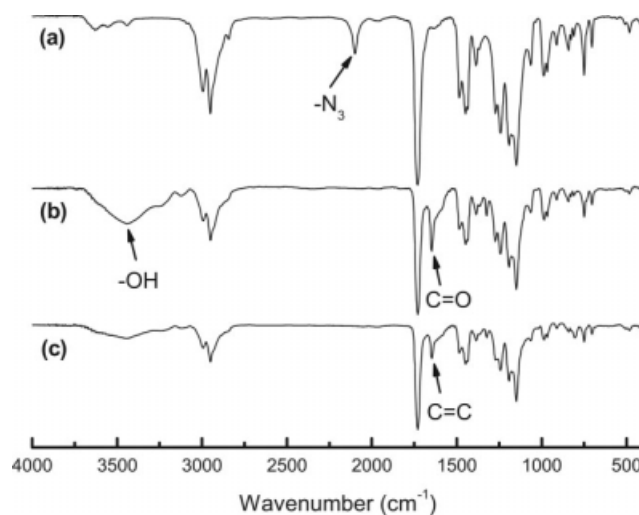

Figure 4 FT-IR spectra of poly(methyl methacrylate)s with end-functionalized group of (a) ω-azido, (b) ω-carboxyl, and (c) ω-methyl-vinyl.
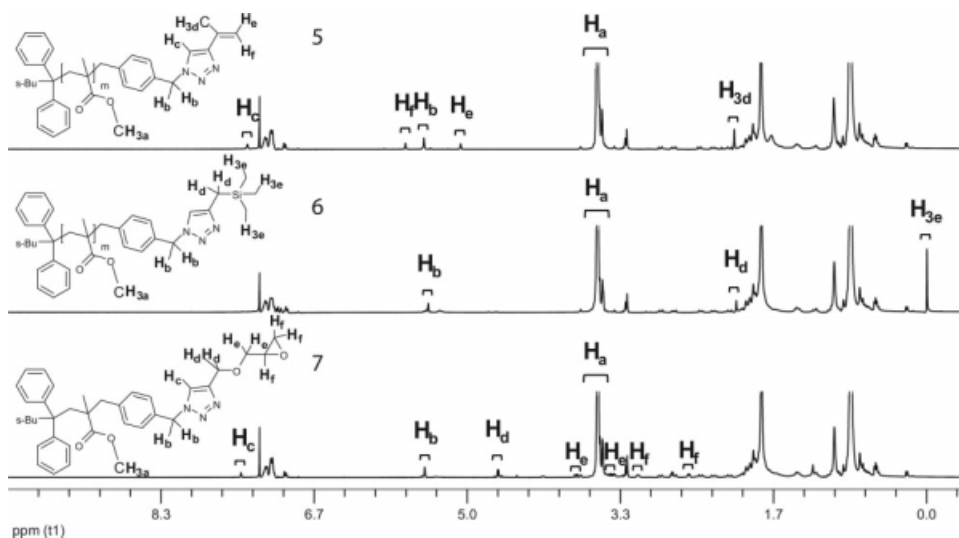
Figure 5 ^{1}H NMR spectra of ω-methyl-vinyl, ω-trimethylsilane, and ω-glycidyl-ether terminated poly(methyl methacrylate)s [**5–7**].

with their stoichiometry and the number-average molecular weight as shown in Table II. The results suggest that the "click" reaction for the transformation into the hydroxyl functionality was complete (above 99%) and no other side reaction occurred.

In the case of **5**, three more signals were observed at δ 2.09, 5.07, and 5.67 ppm in its ^{1}H NMR spectrum (Fig. 5). The first signal was attributed to the methyl protons in the α position of the vinyl group, whereas the other two signals were assigned to the ethylene protons of its chain end. ^{13}C NMR spectrum (Fig. 6) shows the characteristics of the vinyl

group as well. Carbon signals at δ 20.4 and 112.3 ppm were observed and these signals were ascribed to the methyl carbon and vinyl carbon, respectively. Moreover, the appearance of the signal at 1645 cm^{-1} [Fig. 4(c)] in the FTIR spectrum also demonstrated the presence of a vinyl. The signal integration of the new methylene protons adjacent to the nitrogen of the triazole ring (δ 5.47 ppm) in ^{1}H NMR is compared with that from the methylene ester protons of the PMMA repeating units, the new methine proton neighboring to the triazole ring (δ 7.39 ppm) and these new protons of the vinyl group (δ 2.09, 5.07,
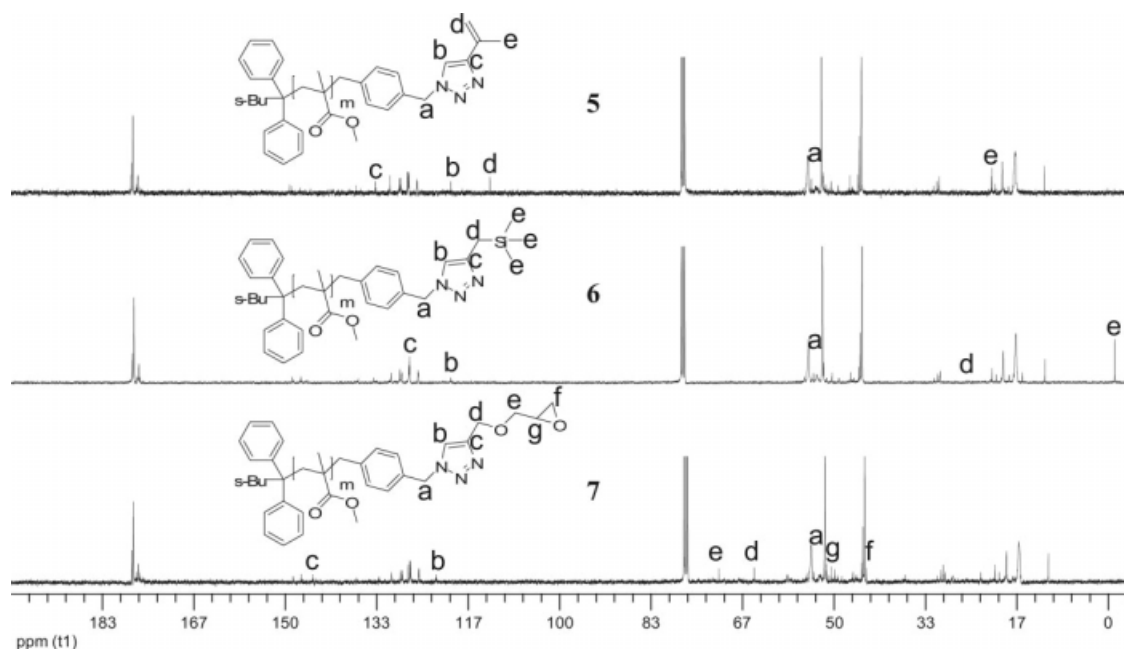

Figure 6 ^{13}C NMR spectra of ω-methyl-vinyl, ω-trimethylsilane, and ω-glycidyl-ether terminated poly(methyl methacrylate)s [**5–7**].

and 5.67 ppm), as tabulated in Table I. These integrations of the new proton peaks are in quantatively consistent with their stoichiometry and the number-average molecular weight (Table II). The results suggest that the "click" reaction for the transformation into the vinyl functionality was complete (above 99%) and no other side reaction occurred.

In the case of **6**, the proton of the triazole ring was shifted upfield and masked by a broad aromatic regions due to the shielding of the adjacent TMS group. However, ^{13}C NMR provided a complementary evidence: signals at δ 119.4 and δ 127.3 ppm were observed (Fig. 6) and it indicated the formation of a triazole ring, as above-mentioned. A trimethyl proton signal (δ –0.005 ppm) in the ^{1}H NMR spectrum (Fig. 2) and a trimethyl carbon signal (δ –1.9 ppm) in ^{13}C NMR spectrum (Fig. 6) revealed the characteristic of the silane functionality. Moreover, signal integration of the new methylene protons adjacent to the nitrogen of the triazole ring (δ 5.42 ppm) in ^{1}H NMR is compared with that from the methylene ester protons of the PMMA repeating units, the new methylene protons neighboring to the silane group (δ 2.07 ppm) and the new trimethyl protons (δ –0.005 ppm). The results are tabulated in Table I. These integration of the new proton peaks are in quantatively consistent with their stoichiometry and the number-average molecular weight. The results suggest that the "click" reaction for the transformation into the silane functionality was complete (above 99%) and no other side reaction occurred. It is important to note that the neutralization of acidity using sodium bicarbonate in CDCl$_3$ is necessary due to the hydrolysis of silane group can happen with a small amount of acid during NMR measurements.

In the case of **7**, several regions of signals were observed at δ 2.50–2.65, 3.09–3.19, 3.39–3.46, 3.78–3.84, and 4.61–4.72 ppm in its ^{1}H NMR spectrum. The first and the second regions of the signals were assigned to the methylene and methine protons of the epoxide. The third and the fourth regions of the signals were attributed to the methylene protons in the α position of the epoxide. The last region was ascribed to the methylene protons in the α position between ether and triazole groups. As analogous to its ^{1}H NMR spectrum, ^{13}C NMR spectrum also shows the features of the epoxide functionality at δ 44.0, 50.4, 64.5, and 71.0 ppm. The first and the second signals were also attributed to the carbons of the epoxide. The third was assigned to the carbon in the α position between the triazole ring and the ether groups. The last was attributed to the carbon in the α position of the epoxide. The signal integration of the new methylene protons adjacent to the nitrogen of the triazole ring (δ 5.46 ppm) in ^{1}H NMR is compared with that from the methylene ester protons of the PMMA repeating units, the new

methine proton neighboring to the triazole ring (δ 7.46 ppm) and these new protons of the epoxide group (δ 2.50–2.65, 3.09–3.19, 3.39–3.46, 3.78–3.84, and 4.61–4.72 ppm), as tabulated in Table I. In this case, one of the methylene protons (δ 3.39–3.46 ppm) in the α position of the epoxide group is superimposing with the methylene ester protons of the PMMA repeating units. However, the integration of the methylene ester protons of the PMMA repeating units still can be calculated by substracting the proton number of that methylene proton in the α position of the epoxide group. These integrations of the new proton peaks are in quantatively consistent with their stoichiometry and the number-average molecular weight (Table II). The results suggest that the "click" reaction for the transformation into the epoxide functionality was complete (above 99%) and no other side reaction occurred. It is important to note that the pKa of the DBU is about 24.13[34,35] and its basicity is relatively high, resulting in an increasing chance of losing the epoxide group during "click" reaction. Hence, the amount of DBU controlling and the order of reagent adding become crucial.

CONCLUSIONS

A bromine end-functionalized poly(methyl methacrylate) prepared by anionic polymerization was first transformed into an azide functionality and subsequently reacted with various functional alkynes (propiolic acid, propargyl alcohol, 2-methyl-1-buten-3-yne, trimethyl propargyl silane, and glycidyl propargyl ether). Solid evidence of the reaction efficiency, high conversion (above 99%), and the unambiguous functionalities has been obtained by ^{1}H NMR, ^{13}C NMR, FTIR, and GPC measurements. This promising method, hence, can be regarded as a "universal" technique for the preparation of macroinitiators and reactive polymers. Currently, we are extending this versatile method to the surface modifications of nanoparticles and substrates, and the synthesis of multifunctionalities block copolymers for optoelectronic and biomedical applications.

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