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Stereoregular poly(methyl methacrylate) with double-clickable ω-end: Synthesis and click reaction

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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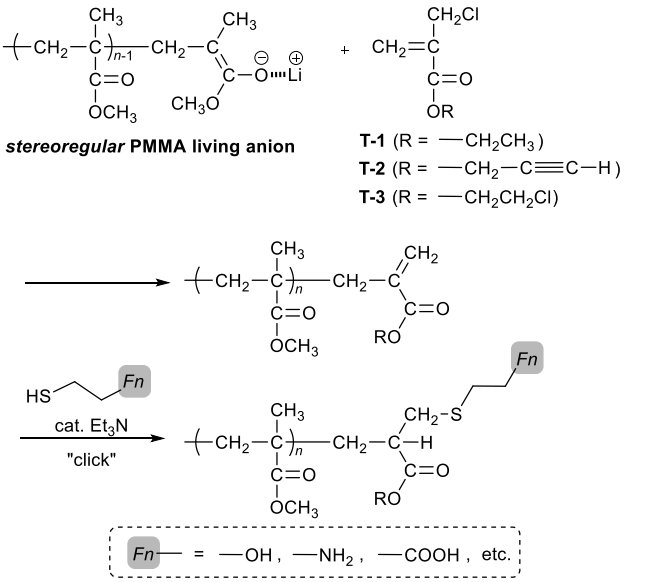
Isotactic and syndiotactic poly(methyl methacrylate)s with orthogonally double-clickable terminal ends, that is, α,β-unsaturated ester for Michael addition-type thiol-ene reaction and azide or alkynyl groups for azide-alkyne click reaction, were prepared via terminating reaction of stereospecific anionic polymerization with propargyl and 2-chloroethyl α-(chloromethyl)acrylates. The subsequent polymer modification via double click reaction proceeded quantitatively in one-pot system under ambient conditions. The facile and almost quantitative double-end-functionalization would open a new material design based on stereoregular PMMAs with controlled molecular weights.

Introduction

Since the concept of 'click chemistry', an approach to build up molecules through a series of reactions with high selectivity and quantitative yields under mild conditions, has been proposed by Sharpless *et al.*,[1] it has gained a mighty position in synthetic chemistry, including application field such as pharmaceutical chemistry[2] and material science.[3-5] From the viewpoint of polymer synthesis, to say nothing of the polyaddition via click chemistry,[6-11] polymers possessing clickable pendant groups[12, 13] and/or end-functionalities[14-16] have attracted researchers' attention, as such polymers can be used as 'building blocks' for syntheses of highly functionalized polymers,[17, 18] construction of sophisticated topology,[19,20] and surface modification[21, 22].

In this decade, a further advanced concept called double click chemistry has been suggested, where two 'orthogonal' click reactions proceeding in chemically and mechanistically different manners are used for macromolecular conjugation.[3, 23] The concept inspires polymer chemists to synthesize interesting new classes of topological polymers, such as 'star block polymer',[23-25] 'hetero-graft copolymer',[26] H-shaped polymer,[27] P-, Q-, 8-, and α-shaped polymers,[28] and tandem cyclic copolymer.[29] However, the research has still remained fundamental, and facile method to incorporate two different clickable ends is desired. In particular, polymers possessing two orthogonally clickable functionalities at ω-end are important to synthesize multi end-functionalized polymers and to incorporate branching junction in macromolecular chain-ends, although such polymers have not been reported.

On the other hand, historically, polymer synthetic chemistry has focused on the control of primary structures of macromolecules, *i.e.* molecular weight and stereoregularity, as they strongly affect the macromolecular properties. Stereospecific anionic polymerization of methyl methacrylate (MMA) is one of the successful examples, which affords isotactic (*it*-),[30] syndiotactic (*st*-),[31, 32] and heterotactic (*ht*-)[32] poly(methyl methacrylate) (PMMA) with narrow molecular weight distribution. Recently, we have reported the synthesis and end-functionalization of stereoregular PMMA by the combination of stereospecific living anionic polymerizations and thiol-ene click reaction (Scheme 1);[15] stereoregular PMMA living anions were reacted with ethyl α-(chloromethyl)acrylate (**T-1**) as a terminating agent, affording α,β-unsaturated terminal end through addition-elimination (S_N2') mechanism. Further



Scheme 1. End-functionalization of stereoregular PMMA via terminating reaction and thiol-ene click reaction.

base-catalyzed addition of thiols with various functional groups to the C=C group allowed quantitative end-functionalization of the stereoregular PMMAs. It should be noted that the activation of the allylic C=C bond of **T-1** by the carbonyl group is necessary for effective termination, as simple allyl halide could not functioned as a terminating agent in these stereospecific polymerization systems, where the PMMA living anions are stabilized by counter cation and/or additives for the control of stereoregularity.[33, 34] If the terminating agent like **T-1** carries a functional group in its ester substituent, the terminal unit should have two kinds of reaction sites, the C=C bond and the ester substituent as long as the introduced functions do not interfere the terminating reaction. According to this idea, we designed novel terminating agents, propargyl α-(chloromethyl)acrylates (**T-2**), and 2-chloroethyl α-(chloromethyl)acrylates (**T-3**); the former straightforwardly allows copper catalyzed azide-alkyne cycloaddition (CuAAC) click reaction, and the latter is also accessible for CuAAC after the azidation of the chloroethyl group. Herein, we reports the synthesis and double click reaction of stereoregular PMMAs utilizing **T-2** and **T-3**.

Experiment

Materials

CH_2Cl_2 (Wako, super dehydrated grade) was dried over CaH_2 and distilled under high vacuum just before use. Toluene (Aldrich, anhydrous grade) dehydrated with red colored adduct of butyllithium (*n*-BuLi) and 1,1-diphenylethene, and distilled under high vacuum just before use. Ethylaluminum bis(2,6-di-*tert*-butylphenoxide) [EtAl(ODBP)$_2$] was prepared according to our previous report[32] and stored as toluene solution under N_2 atmosphere. MMA (Nacalai Tesque) was fractionally distilled and stored over CaH_2. The monomer was distilled over CaH_2 under reduced pressure just before use. Me_3SiOLi (Aldrich) was dried *in vacuo* at 100 °C for several hours and used as dry toluene or CH_2Cl_2 solution. The received reagent contains a significant amount of insoluble material, and thus the supernatant solution was used for polymerization. Isopropyl α-lithioisobutyrate (Li-*i*PrIB) was prepared and recrystallized in toluene according to our previous report.[30] Ethyl α-(chloromethyl)acrylate (**T-1**) was synthesized from ethyl α-(hydroxymethyl)acrylate, a kind gift from Nippon Shokubai Co., Ltd, according to our previous reports.[15] **T-1** (44.3–45.0 °C per 2.5 mmHg) was distilled under reduced pressure and stored under N_2 atmosphere in the presence of Molecular Sieves 4A (MS4A) at –20 °C. Other reagents were used as purchased.

Instruments

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Aldrich) on a Unity Inova 500 (Varian) spectrometer or an ECS-400 spectrometer (JEOL). Chemical shifts in ^1H NMR spectra were referred to the signal of tetramethylsilane (TMS). Molecular weights and its distributions of the polymers were determined at 40 °C by size-exclusion chromatography (SEC) using a GPC-900 chromatograph (JASCO) equipped with two SEC columns [Polymer Laboratories, PL-gel, Mixed C (300 mm × 7.5 mm)] and a differential refractometer installed in the system, using tetrahydrofuran (THF) as an eluent, and calibrated against standard PMMA samples (Shodex, MW: 1.25×10^6, 6.59×10^5, 1.95×10^5, 4.96×10^4, 2.06×10^4, 6.82×10^3, 2.00×10^3). Samples were loaded as THF solutions (1 g L^{-1}, 100 μL). IR spectra were recorded on a FT/IR-410 spectrometer (JASCO). Purities of terminating agents were determined from the gas chromatogram (GC) recorded on a GC-2014 (Shimadzu) equipped with a HP-5 capillary column (Hewlett-Packard).

Synthesis of propargyl α-(chloromethyl)acrylate (T-2) (*cf.* Scheme 2)

To a solution of methyl α-(hydroxymethyl)acrylate (**1**, 34.8 g, 0.300 mol) in tetrahydrofuran (THF, 150 mL) was added a solution of LiOH (8.62 g, 0.360 mol) in water (150 mL). The reaction mixture was refluxed for 9 h and acidified with *sat*. $KHSO_4$ aq. After concentration, the product was extracted from the residue with CH_3OH (200 mL) and concentrated in 300 mL recovery flask. The residual sticky colorless solid was dried *in vacuo* to give a mixture (33.3 g) containing α-(hydroxymethyl)acrylic acid (**2**).

The recovery flask was then connected to a distillation head; the top of the distillation head was equipped to a pressure equalizing dropping funnel, while the side was jointed to a glass branch tube leading to a NaOH aq (200 g / 800 mL) for acidic gas trap. To this mixture, $SOCl_2$ (109 mL, 1.50 mol) was added dropwise from the dropping funnel over 90 min, and then a catalytic amount of *N*,*N*-dimethylformamide (DMF, ca. 0.30 mL) was added. The reaction mixture was warmed to 40 °C, and stood for 15 h. The distillation head was replaced with a condenser, and the reaction mixture was refluxed for 1 h. DMF (1 mL) was added, and the mixture was refluxed for further 1 h. DMF (1 mL) and Et_3N (1 mL) was added, and it was refluxed for further 1 h. The residual $SOCl_2$ was removed by concentration, and the product was distilled under reduced pressure (53.0–55.0 °C/ 18 mmHg) to give α-(chloromethyl)acryloyl chloride (**3**) as a colorless oil (19.7 g, 47.6%).

To a solution of propargyl alcohol (3.50 mL, 60.6 mmol) and *i*Pr_2NEt (10.3 mL, 60.6 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added dropwise **3** (7.06 g, 50.8 mmol). The reaction mixture was stirred for 1 h at ambient temperature, and propargyl alcohol (0.480 mL, 8.31 mmol) was added. After 1 h, the reaction mixture was poured into hexane (450 mL), and the precipitated salt was removed by filtration on Celite No.535 (Wako Pure Chemical). After concentration, the filtrate was distilled under reduced pressure (59.0–60.0 °C/ 1.3–1.4 mmHg) to afford **T-2** (2.38 g) as a colorless oil. It was stored at −20 °C under dried N_2 atmosphere.

T-2: Total yield (3 steps): 14.0%; purity 95.5%; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.46 (s, 1H, CH*H*=), 6.06 (d, *J* = 0.9 Hz, 1H, C*H*H=), 4.81 (d, *J* = 2.3 Hz, 2H, OCH_2), 4.30 (d, *J* = 0.9 Hz, 2H, CH_2Cl), 2.50 (t, *J* = 2.3 Hz, 1H, C≡CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 164.1, 136.3, 129.6, 77.2, 75.2, 52.6, 42.2 ppm.

Synthesis of 2-chloroethyl α-(chloromethyl)acrylate (T-3)

T-3 was prepared from **3** in a similar manner to **T-2** using 2-chloroethanol (4.10 mL, 61.0 mmol). The product was purified by distillation under reduced pressure (55.0-57.0 °C/ 0.35-0.40 mmHg) to give **T-3** (3.19 g) as a colorless oil.

T-3: Total yield (3 steps): 16.4%; purity 96.7%; ^{1}H NMR (400 MHz, 30 °C, $CDCl_3$) δ 6.45 (s, 1H, CH*H*=), 6.04 (d, *J* = 0.9 Hz, 1H, C*H*H=), 4.46 (t, *J* = 5.5 Hz, 2H, -OCH_2-), 4.30 (d, *J* = 0.9 Hz, 2H, α-CH_2), 3.74 (t, *J* = 5.5 Hz, 2H, CH_2CH_2Cl) ppm, ^{13}C NMR (100 MHz, 30 °C, $CDCl_3$) δ 164.6, 136.5, 129.5, 64.6, 42.3, 41.3 ppm.

Polymerization

A typical procedure (Table 1, Run 2): To a glass ampoule filled in dried N_2 gas passed through MS4A cooled at –78 °C, CH_2Cl_2 (5.0 mL), MeAl(ODBP)$_2$ (2.5 mmol), and Li-iPrIB (0.25 mmol) were added at room temperature using hypodermic syringes. The reaction mixture was cooled to –78 °C, and the polymerization was started by adding MMA (5.0 mmol). After 1 h, **T-2** (1.25 mmol) was added and reacted for 1 h, and the reaction was finally quenched with 5 M HCl aq—MeOH solution. Then the polymer was recovered by precipitation with hexane, filtered and washed with hexane, acidic water and water, successively, and dried *in vacuo* at 40 ˚C.

CuAAC reaction of PMMA

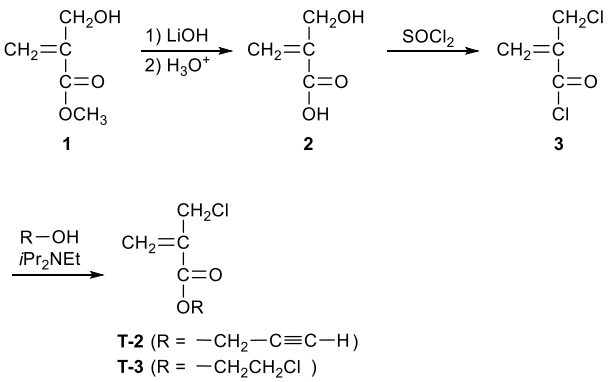
A typical example: To a solution of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 2 μL, 10 μmol), CuBr (6.3 mg, 43 μmol), **S-Pg** (250 mg, 49 μmol /chain) in THF (0.60 mL) was added benzyl azide (9 μL, 70 μmol). The reaction mixture was stirred at ambient temperature for 24 h and diluted with $CHCl_3$ (30 mL). The reaction mixture was washed successively with aqueous disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA·2Na·2H_2O) (0.26 M, 45 mL), *sat*. NH_4Cl aq (30 mL) and water (30 mL). The organic phase was poured into hexane (220 mL), and the precipitate was collected and dried *in vacuo* to give the polymer (257 mg, 99.8%).

Azidation of PMMA terminated with T-3

S-Cl (50 mg, 12 μmol/chain) was dissolved in dimethyl sulfoxide (DMSO, 1.0 mL), and NaN_3 (77 mg, 1.20 mmol) was added. The reaction mixture was stirred at 50 °C for 24 h, and CH_3OH (25 mL) - H_2O (25 mL) cosolvent was added into the reaction mixture. The precipitate was collected by centrifugation and dried *in vacuo* to afford the polymer **S-N_3** (23 mg, 46%).

Base-catalyzed thiol-ene reaction of PMMA

A typical example: **S-N_3** (M_n 4760, 35 mg, 7.4 μmol/chin) was dissolved in CH_3CN (0.190 mL) with a catalytic amount of Et_3N (*ca.* 0.1 mL) and benzyl mercaptan (90 μL, 0.77 mol). The reaction mixture was stood for 20 h, and poured into hexane (30 mL). The precipitate was collected and dried *in vacuo* to afford the polymeric product (36 mg, 94%).



Scheme 2. Syntheses of terminating agents.

Results and Discussion

Preparation of terminating agent

In our first attempt, **T-2** and **T-3** were prepared through the ester exchange reaction of methyl α-(chloromethyl)acrylate with propargyl alcohol and 2-chloroethanol, respectively. Although the reaction proceeds in ca. 70% conversion, however, the purification of **T-2** and **T-3** from the resulting product mixture by distillation was found very troublesome to reduce the total yields (13% for **T-2**, 3.4% for **T-3**). Thus, the alternative synthetic route described in Scheme 2 was investigated.

1 was hydrolysed in THF-H_2O with LiOH, and both carboxyl and hydroxyl groups in the acid **2** were chlorinated with $SOCl_2$. Then the obtained carbonyl chloride **3** was reacted with 2-chloroethanol in the presence of *i*Pr_2NEt, a non-nucleophilic weak base to trap the liberated HCl with preventing the attack of amine to the vinyl group. Although the overall yield was not so high (14.0%), the facile purification by distillation afforded **T-2** (purity: 95.5%). In a similar way, **T-3** was prepared (overall yield: 16.4%, purity 96.7%).

Synthesis of double end-clickable stereoregular PMMA

Isotactic-specific living anionic polymerization of MMA was initiated by Li-*i*PrIB in the presence of Me_3SiOLi in CH_2Cl_2 at − 78 °C according to our previous reports,[15,30] and the terminating agent, **T-1** was added (Scheme 1, Table 2, Run 1). In similar ways, the polymerization was terminated with **T-2** (Run 2) and **T-3** (Run 3).

Figure 1 shows the ^{1}H NMR spectra of the obtained polymers, **I-Et**, **I-Pg**, and **I-Cl** from Runs 1-3, respectively. In any case, as the CH_2 signals **a** of the main chains at 1.54 and 2.16 ppm were observed as an AB quartet, isotactic configurations were apparent. In fact, the isotacticities (*mm* triad content) determined from the CH_3 signals were ~98%. Further, the terminal unit signals labelled **ω1-ω4** were clearly observed in the magnified spectra, indicating that the termination through S_N2' mechanism to give the unsaturated terminal unit. The end-functionality (*F*), determined from the intensity ratio of **ω1** against CH signals **α** of isopropyl ester group in α-ends were 91-92%. It should be noted that the

Table 1. Synthesis of stereoregular PMMA with double-clickable ω-end.

Run[a]	Additive (equiv.)[b]	$[MMA]_0$ /$[Li\text{-}i\text{PrIB}]_0$	M_n[c]	M_w/M_n[c]	Tacticity/%[d] *mm*	*mr*	*rr*	Terminating agent	*F* /%[d,e]	Polymer code
1	Me_3SiOLi	25/1	6600	1.23	98	2	~0	**T-1**	91	**I-Et**
2	(10)	25/1	9900	1.45	97	2	~0	**T-2**	91	**I-Pg**
3		25/1	7800	1.38	98	3	~0	**T-3**	92	**I-Cl**
4	$EtAl(ODBP)_2$	50/1	5900	1.06	~0	9	91	**T-1**	96	**S-Et**
5	(5.0)	50/1	5200	1.07	~0	11	89	**T-2**	97	**S-Pg**
6		50/1	4200	1.08	~0	9	91	**T-3**	96	**S-Cl**

[a] Polymerization of MMA (5.0 mmol) was carried out in CH_2Cl_2 (5.0 mL) at −78 °C for 1 h (Runs 1-3) or 24 h (Runs 4-6). [b] Equivalent to Li-*i*PrIB. [c] Determined from SEC (THF, 40 °C , PMMA standards). [d] Determined from ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$, 55 °C). [e] End functionality.

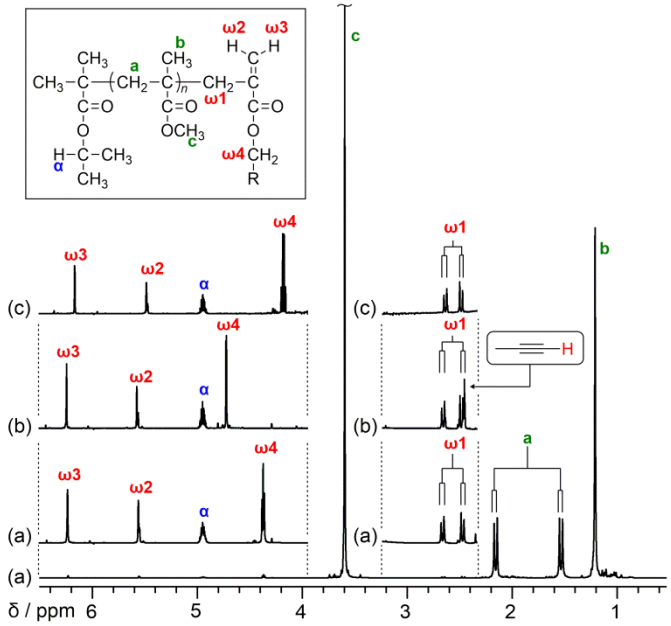


Figure 1. ^{1}H NMR spectra of (a) **I-Cl**, (b) **I-Pg**, and (c) **I-Et** (500 MHz, $CDCl_3$, 55 °C).

termination with **T-2** proceeded efficiently as in the case of **T-1**, though **T-2** has an acidic alkynyl hydrogen. As well known, propargyl group is normally protected with trialkylsilyl group in the anionic polymerization to prevent the proton abstraction.[12] However, the terminating agent **T-2** with non-protected propargyl group reacted with the living anion at C=C bond exclusively. The high reactivity of the vinylidene group of α-(chloromethyl)acrylate has been evidenced for **T-1**, which terminates the living PMMA anion even in the presence of an excess amount of unreacted MMA. The intensity of alkynyl proton (2.45 ppm) agreed with that of vinylidene signals, **ω2** and **ω3**.

Syndiotactic-specific living anionic polymerizations of MMA were also conducted in the presence of $EtAl(ODBP)_2$ for 24 h and terminated with **T-1** (Run 4), **T-2** (Run 5) and **T-3** (Run 6) to give **S-Et**, **S-Pg** and **S-Cl**, respectively. In any case, high syndiotacticities (*rr* content ~ 91%) and almost quantitative termination (*F* ~ 97%) were confirmed by ^{1}H NMR spectroscopy.

Double click reaction of propargyl-terminated PMMAs

Double click reactions of **S-Pg** through CuAAC and base-catalyzed thiol-ene reaction were carried out according to Scheme 3. Although a variety of functional azides and thiols are reported to be applicable,[3-5,15,35] benzyl azide and 2-mercaptoethanol were selected for the current model reactions in order to facilitate ^{1}H NMR observation of the proceeding of each reaction without any signal overlaps of the original and resulting polymers.

Figure 2 shows the ^{1}H NMR spectra of the polymers in each step. After the CuAAC reaction (1st click reaction), signal **ω5** assignable to alkynyl proton of **S-Pg** (Figure 2a, 2.45 ppm) completely disappeared and a new peak assignable to the triazolyl hydrogen was observed at 7.54 ppm in Figure 2b. The signal **ω4** assignable to *O*-CH_2 (4.71 ppm) shifted to 5.24 ppm reflecting the aromatic nature of the triazole ring. Besides, signals originating from the benzyl azide moieties, **ω6** at 5.51 ppm and **Ph** (phenyl group) at 7.35-7.28 ppm, are also observed. Other signals of **S-Pg** such as **ω2** (5.52 ppm) and **ω3** (6.26 ppm) showed slight shifts upon the CuAAC reaction but their intensities were kept unchanged, confirming that the CuAAC reaction proceeded selectively and quantitatively without any side reactions. After the subsequent base-catalyzed thiol-ene reaction (2nd click reaction), signals **ω2** (5.46 ppm) and **ω3** (6.20 ppm) disappeared completely and the new peaks were observed in aliphatic region (2.72-2.42 ppm) as multiplets, overlapping with **ω7** (*S*-CH_2) and **ω8** (*O*-CH_2) originating from the 2-mercaptoethanol moiety. These spectral changes confirm the quantitative 2nd click reaction. Hence, double click reactions in the terminal end were successful with high

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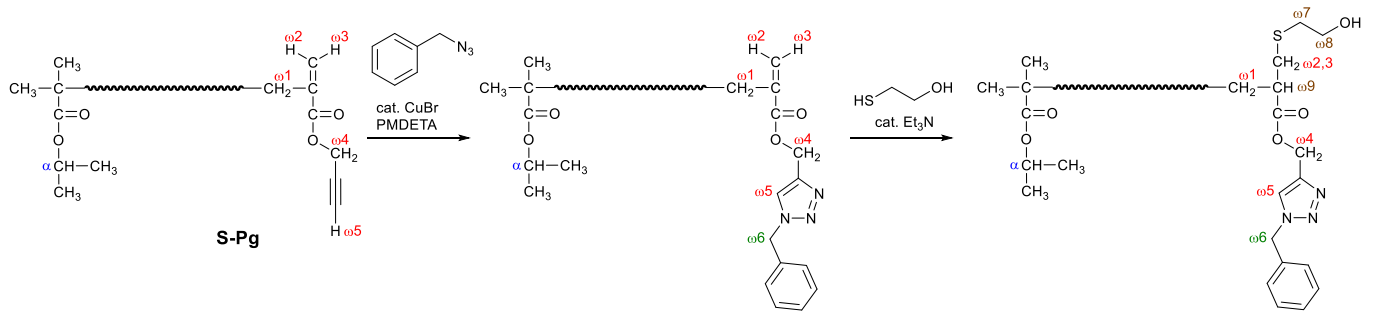


Scheme 3. Double click reaction of **S-Pg**.

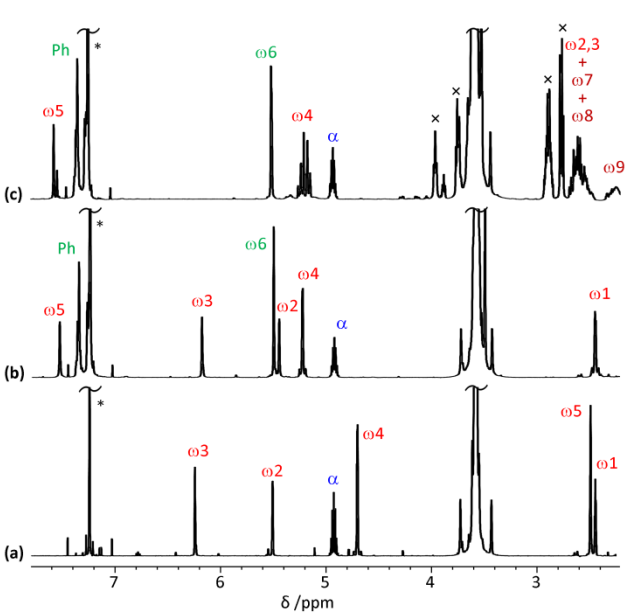


Figure 2. ^{1}H NMR spectra of (a) **S-Pg** and the products after (b) CuAAC reaction (1st click) and (c) thiol-ene reaction (2nd click) (500 MHz, $CDCl_3$, 55 °C). Labels on signals correspond to those in Scheme 3. *: $CHCl_3$, ×: unreacted 2-mercaptoethanol.

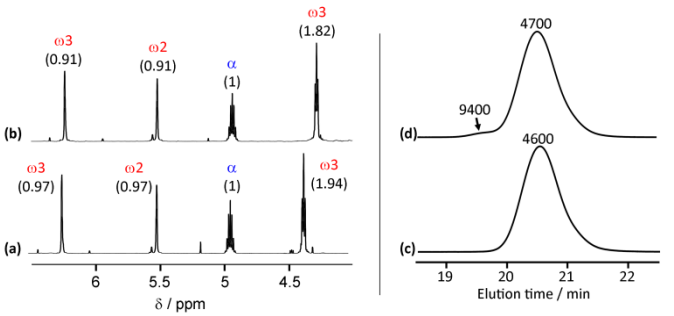


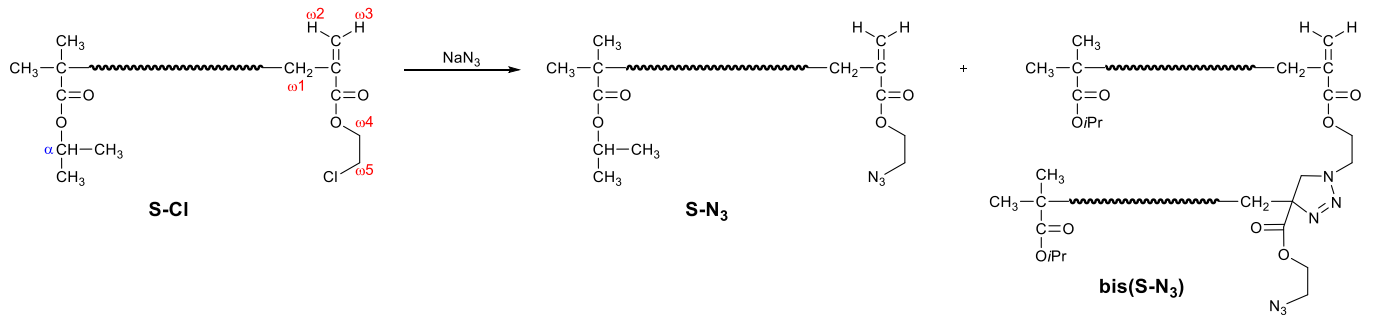
Figure 3. ^{1}H NMR spectra (a, b) (500 MHz, $CDCl_3$, 55 °C) and SEC traces (c, d) (THF, 40 °C) of **I-Cl** before (a, c) and after (b, d) azidation. Labels of ^{1}H NMR signals are corresponding to those in Figure 1, while numerals in brackets are integral ratio of each signals against to signal α. Numerals on the top of SEC peaks shows molecular weight calibrated against PMMA standards.

efficiency. Notably, the double click reaction could proceed in one-pot without the isolation of the intermediate. Thus, this strategy could be regarded very efficient and convenient methodology to synthesize doubly end-functionalized stereoregular PMMA.

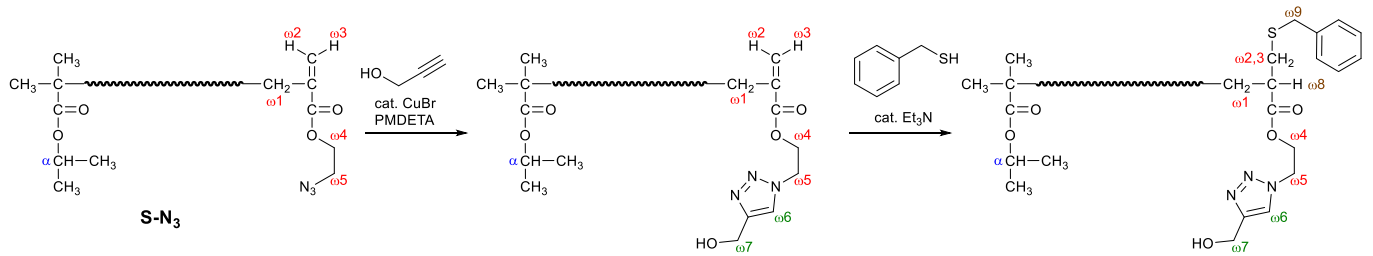
Azidation and double click reaction of 2-chloroethyl-terminated PMMA

Recently, anionic polymerization of ω-chloroalkyl methacrylate and the subsequent azidation with NaN_3 have been reported as an efficient route to afford poly(ω-azidoalkyl methacrylate).[36-38]

In a similar way, **S-Cl** was treated with an excess amount of NaN_3 to give the corresponding azide-terminated PMMA (Scheme 4); the reaction was carried out in DMSO-d_6 at 50 °C for 24 h with monitoring the reaction by ^{1}H NMR spectroscopy. Figure 3 shows the ^{1}H NMR spectra of the precursor (**S-Cl**) and the isolated product (**S-N$_3$**). The chemical shift change of signal **ω3** from 4.36 ppm to 4.29 ppm indicates the complete azidation. The incorporation of azide group was also confirmed by the appearance of azide vibration (2106 cm^{-1}) in the IR spectrum. However, it was also found that the intensities of ^{1}H NMR signals assignable to the terminal structure, **ω1-ω3**, decreased as indicated in Figure 3; end-functionality of **S-Cl** (F = 97%) decreased to 91% after azidation. Moreover, the SEC curve of the product (Figure 3d) exhibited a shoulder at high molecular weight region after azidation, whose peak top (M_p = 9400) is about twice molecular weight of the precursor (M_p = 4700). Thus, a possible side reaction might be dimerization of **S-N$_3$** (Scheme 4). As the vinylidene group at ω-end of **S-N$_3$** has similar structure to MMA, it may accept the azide group of



Scheme 4. Azidation and dimerization of **S-Cl**.



Scheme 5. Double click reaction of **S-N_3**.

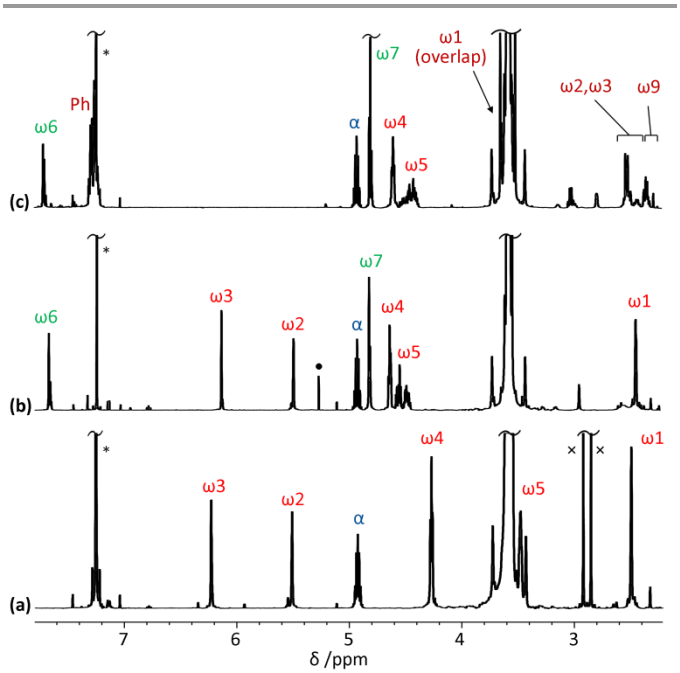


Figure 4. ^{1}H NMR spectra of (a) **S-N_3** and the products after (b) CuAAC reaction (1st click) and (c) thiol-ene reaction (2nd click) (500 MHz, $CDCl_3$, 55 °C). Labels on signals correspond to those in Scheme 4. *: $CHCl_3$, ×: DMF, •: CH_2Cl_2.

other macromolecular chain to afford the dimerized product, **bis(S-N_3)**. In fact, the addition of azide group to MMA has been reported.[39] In order to avoid this side reaction, azidation was conducted at ambient temperature with long reaction time (24 days). Although the product still included a small amount of **bis(S-N_3),** its fraction was suppressed to less than 3% of total macromolecular chains as estimated from the change of *F* value after azidation. Then the double click reactions were carried out without removal of **bis(S-N_3)** from the crude product.

CuAAC reaction (1st click) of **S-N_3** with propargyl alcohol conducted in a similar manner to that of **S-Pg** described before (Scheme 5). Figure 4 shows the ^{1}H NMR spectra of the polymers before and after the reaction. The appearances of new signals, **ω6** (7.68 ppm) of triazole-ring hydrogen and **ω7** (4.83 ppm) of *O*-CH_2, clearly indicate the complete proceeding of CuAAC. Subsequently, benzyl mercaptan was reacted in the presence of a base catalyst (2nd click). The shifts of vinylidene signals (**ω2**: 5.50 ppm, **ω3**: 6.14 ppm) to aliphatic region (2.59-2.42 ppm) and appearance of phenyl signal (7.30-7.27 ppm) revealed the quantitative thiol-ene reaction. Notably, these azidation and double click reaction could be conducted in one-pot without isolation of the intermediate as in the case of **S-Pg**.

Conclusions

Isotactic and syndiotactic PMMAs with double-clickable terminal ends were synthesized via the terminating reaction of stereospecific anionic polymerization of MMA with **T-2** and **T-3**. Even though **T-2** has propargyl group with an acidic alkynyl proton, the termination reaction proceeded efficiently as in the case of a simple alkyl ester, **T-1**. Although the azidation of PMMA terminated with **T-3** slightly caused dimerization through the addition of azide group to α,β-unsaturated ester in the terminal unit, the azide- and propargyl-terminated PMMAs allowed the orthogonal double-click reactions, that is, CuAAC and base-catalyzed thiol-ene reactions. It should be emphasized that the double click reaction described above can be conducted in one-pot system at ambient conditions to achieve quantitative efficiency.

Recently, end-clickable polymers have attracted researchers in diverse fields of material science, since they allow the incorporation of macromolecular chains onto various molecules and substances as a 'macromolecular building-block'. The present results present a synthetic basis for new material designs based on multiply functionalized polymethacrylates with well-defined stereoregularity and molecular weight.

Acknowledgement

The authors appreciate Nippon Shokubai Co., Ltd. for a kind gift of methyl α-(hydroxymethyl)acrylate. This work was supported by JSPS KAKENHI Grant Number 26620105.

Notes and references

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