A Simple Way for Synthesis of Alkyne-Telechelic Poly(methyl methacrylate) via Single Electron Transfer Radical Coupling Reaction

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The telechelic *α,ω*-alkyne-poly(methyl methacrylate) (alkyne-PMMA-alkyne) was synthesized by single electron transfer radical coupling (SETRC) reaction of *α*-alkyne, *ω*-bromine-poly(methyl methacrylate) (alkyne-PMMA-Br). The propargyl 2-bomoisobutyrate (PgBiB) was first prepared to initiate atom transfer radical polymerization (ATRP) of methyl methacrylate at 45 ℃ using CuCl/1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA) as homogeneous catalytic system. Then the SETRC reaction was conducted at room temperature in the presence of nascent Cu(0) and *N,N,N′,N″,N″*-pentamethyldiethyllenetriamine (PMDETA). The precursor alkyne-PMMA-Br and coupled product alkyne-PMMA-alkyne were characterized by GPC and ^{1}H NMR in detail.

Keywords radical reactions, polymerization, poly(methyl methacrylate) (PMMA), single electron transfer radical coupling (SETRC), atom transfer radical polymerization (ATRP)

Introduction

The *α,ω*-telechelic polymers are of enormous use in preparing block copolymers for the construction of various polymer materials[1] and the investigation of self-assembly morphologies.[2] Many *α,ω*-telechelic polymers with reactive end groups such as hydroxyl, carboxyl, ester or amino are synthesized by traditional techniques including living ionic polymerization,[3] polymer oxidative cleavage,[4] poly-condensation[5] and atom transfer radical coupling (ATRC) reaction[6] using styrene, methacrylate and butadiene *etc.* as monomers.

Specially, the ATRC has been proved to be a feasible and facile pathway, in which macro-radicals generated *in situ* by atom transfer radical equilibrium take part in bimolecular radical termination in the presence of a reducing agent. Furthermore, by means of designation of initiator, a wide range of functional groups may be introduced into polymer chains by ATRP and then ATRC. For example, Matyjaszewski *et al.* synthesized *α,ω*-telechelic polystyrene (PS) with trimethylsilyl, hydroxytehyl, phenylacetic acid end groups and *α,ω*-telechelic poly(methyl acrylate) (PMA) with hydroxyl end groups via ATRC using the *ω*-bromine PS and *ω*-bromine PMA as precursors.[6] Boutevin *et al.* extended the ATRC reaction for *α,ω*-telechelic poly(butyl acrylate) (P*n*BA) and poly(*tert*-butyl acrylate) (P*t*BA).[7] However, the *α,ω*-telechelic PMMA has not yet been synthesized by the above ATRC strategy due to the serious *β*-hydrogen transfer of generated PMMA macro-radicals at elevated temperature.[8-12]

Recently, Percec *et al.* reported that single electron transfer living radical polymerization (SET-LRP) was a powerful tool for ultrafast synthesis of ultrahigh-molecular-weight polymers from various monomers with well-controlled manner. Specially, the SET-LRP can be conducted at ambient temperature, which is convenient and useful for many applications.[13] For example, by combining the SET-LRP and nitroxide mediated polymerization (NMP) mechanism, Fu *et al.* provided a new coupling strategy of single electron transfer-nitroxide radical coupling (SET-NRC), in which the PMMA macroradicals could be easily captured by 2,2,6,6-tetramethylpiperidinyl-1-oxy(TEMPO)-contained polymers at ambient temperature condition.[14]

In this article, we try to carry the radical coupling reaction at ambient temperature based on the SET-LRP mechanism, and this new strategy is termed as Single Electron Transfer Radical Coupling (SETRC) reaction (Scheme 1). In order to testify its versatility, *α*-alkyne-*ω*-bromine-poly(methyl methacrylate) (alkyne-PMMA-Br) prepared by ATRP is used as precursors for SETRC reaction, and nascent Cu(0) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) are used as catalysis system at room temperature (25 ± 5 ℃). The bimolecular radical coupling takes place between secondary carbon radicals of alkyne-PMMA generated by single electron transfer mechanism.

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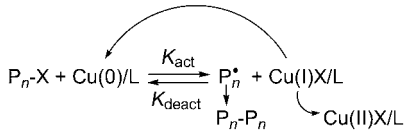
Scheme 1 The mechanism of single transfer radical coupling (SETRC) reaction



Experimental

Materials

Methyl methacrylate (MMA, 99%, SCR), anisole (99%, SCR) and toluene (99%, SCR) were dried over CaH_2 and distilled under reduced pressure. Tetrahydrofuran (THF, 99%, SCR) was refluxed and distilled from sodium naphthalenide solution. Methanol (99%, SCR), heptane (99%, SCR) and copper powder (99%, Aldrich) were used as received. CuCl (95%, SCR) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. PMDETA (99%, Aldrich) and HMTETA (99%, Aldrich) were used directly without further purification. Propargyl 2-bomoisobutyrate (PgBiB) was synthesized according to our previous work.[15]

Synthesis of *α*-alkyne-*ω*-bromine-poly(methyl methacrylate) (alkyne-PMMA-Br) The ATRP of MMA was carried out as follows: CuCl (0.18 g, 1.8 mmol), PgBiB (0.15 mL, 1.0 mmol), HMTETA (0.49 mL, 1.8 mmol), anisole (15 mL) and methyl methacrylate (15 mL, 0.15 mol) were added into a 100 mL ampoule. After three cycles of freezing-pumping-thawing, the ampoule was immersed in oil bath and stirred at 45 ℃ for 25 min, then taken from the oil bath and dipped in liquid nitrogen to terminate the polymerization. The products were diluted with THF and the solution was passed through a column chromatograph filled with neutral alumina to remove the residual copper complex, and then precipitated in heptane. The precipitate was collected and purified by dissolution/precipitation with THF/heptane twice, and then dried at 40 ℃ *in vacuo* overnight. A series of PMMA with various molecular weights were synthesized by varying the feeding monomer/initiator ratios and the reaction time: $M_{n,GPC}$: 2500 g/mol, M_w/M_n: 1.12; $M_{n,GPC}$: 3500 g/mol, M_w/M_n: 1.19; $M_{n,GPC}$: 4900 g/mol, M_w/M_n: 1.21.

Synthesis of telechelic *α*,*ω*-alkyne-poly(methyl methacrylate) (alkyne-PMMA-alkyne) by SETRC of alkyne-PMMA-Br The SETRC reaction was carried out using precursor alkyne-PMMA-Br ($M_{n,GPC}$=4900 g/mol) as example: each of the four 50 mL ampoules was charged with alkyne-PMMA-Br ($M_{n,GPC}$=4900 g/mol, 0.20 g, 0.041 mmol), PMDETA (8.2 μL, 0.041 mmol), THF (2.0 mL) and copper powder (2.6 mg, 0.041 mmol) under magnetic stirring, respectively. After three freeze-pump-thaw cycles, the ampoules were immersed in an oil bath at 25 ℃ for a predetermined time (2, 4, 12, 24 h), then withdrawn from the oil bath in turn and dipped in liquid nitrogen. Each sample was diluted with THF and passed through a column chromatograph filled with neutral alumina to remove the copper complex, and then precipitated in heptane. The precipitate was dried at 40 ℃ in vacuum oven overnight.

Measurements

Gel Permeation Chromatography (GPC) was performed on an Agilent 1100 with a G1310A pump, a G1362A refractive-index detector, and a G1314A variable-wavelength detector with THF as the eluent at a flow rate of 1.0 mL/min at 35 ℃. One 5 μm LP gel column (500 E, molecular range 500—2×104 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200—3×106 g/mol). PS was used as the calibration standard (molecular range of the standards is 580—3.39×106 g/mol). ^{1}H NMR spectra were recorded at room temperature by a Bruker (500 MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as solvent.

Results and discussion

Synthesis and characterization of precursor alkyne-PMMA-Br

The synthesis of alkyne-PMMA-Br by ATRP of MMA and the following SETRC process are illustrated in Scheme 2.

A series of alkyne-PMMA-Br with different molecular weight ($M_{n,GPC}$) and narrow molecular weight distribution (M_w/M_n) were synthesized by ATRP using PgBiB as an initiator and CuCl/HMTETA as catalyst at 45 ℃. HMTETA was chosen as ligand of the ATRP for methyl methacrylate because it could ensure high preservation of halogen chain end and well-controlled polymerization.[16] Table 1 listed the sample information of precursors alkyne-PMMA-Br obtained by ATRP.

Figure 1 shows the structure information of precursor alkyne-PMMA-Br (Entry 1, $M_{n,GPC}$=2500, M_w/M_n=1.12). The resonance signals for protons of

Scheme 2 Synthesis of alkyne-PMMA-Br by ATRP and the following alkyne-PMMA-alkyne by SETRC

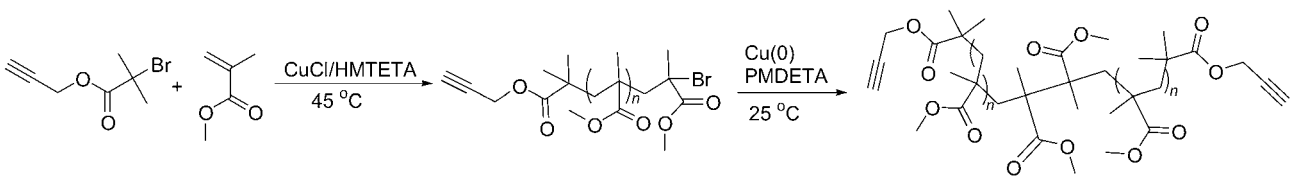


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Table 1 The data of the precursors alkyne-PMMA-Br by ATRP and coupling products alkyne-PMMA-alkyne by SETRC

Entry	Alkyne-PMMA-Br		Alkyne-PMMA-alkyne			
	$M_{n,GPC}$[a]/(g•mol^{-1})	M_w/M_n[a]	Time/h	$M_{n,GPC}$[a]/(g•mol^{-1})	M_w/M_n[a]	x[b]
1	2500	1.12	24	4400	1.20	0.86
			2	3800	1.32	0.16
			4	4600	1.26	0.48
2	3500	1.19	12	5300	1.38	0.65
			24	6400	1.22	0.91
			2	5700	1.31	0.28
			4	6800	1.38	0.56
3	4900	1.21	12	7600	1.33	0.71
			24	9100	1.23	0.92

[a] The molecular weight of precursors and coupling products was measured by GPC in THF using PS as standard. [b] The extent of coupling (x) was calculated according to formula 1.

alkyne ("a") and the methylene groups ("b") of initiator PgBiB residual could be observed at δ 2.48 and δ 4.65 (2H, integral value$=I_{4.65}=1$) respectively. The resonance signal at δ 3.40—3.82 ("e", "f") was assigned to the protons on methoxyls of MMA repeat units (3H, integral value$=I_{3.82}=33.87$).

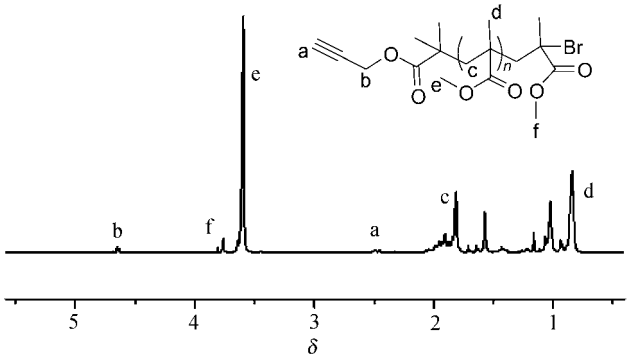

Figure 1 The ^{1}H NMR spectrum of akyne-PMMA-Br ($M_{n,GPC}$ $=$2500 g/mol, $M_w/M_n=1.12$, solvent: $CDCl_3$).

Clearly, the GPC and ^{1}H NMR showed that the precursors of alkyne-PMMA-Br were successfully synthesized.

Synthesis and characterization of coupling product alkyne-PMMA-alkyne by SETRC

For the SETRC reaction of alkyne-PMMA-alkyne (Scheme 1), the Cu(0) and PMDETA were used as catalytical system. According to a successful precedent,[14] the THF was chosen as solvent for PMMA and the quantity of Cu(0) was nearly equal to that of bromine end groups. In this case, no disproportionation of Cu(I)X could be found in THF solvent, and the concentration of alkyne-PMMA-Br was maintained at 0.10 g/mL to enhance bimolecular encountering probability.

Figure 2 shows all the GPC curves of three precursors and their corresponding SETRC products. For

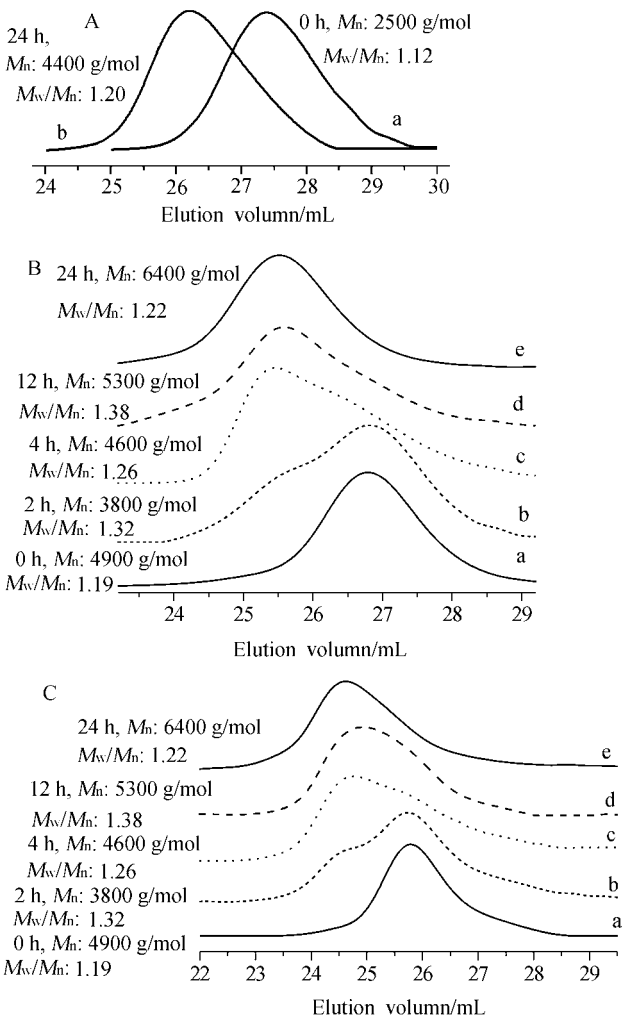

Figure 2 Dependence of $M_{n,GPC}$ and M_w/M_n of the reaction system upon time during SETRC of alkyne-PMMA-Br. (A) The SETRC based on precursor alkyne-PMMA-Br (Entry 1, $M_{n,GPC}=$ 2500 g/mol, $M_w/M_n=1.12$). (B) The SETRC based on precursor alkyne-PMMA-Br (Entry 2, $M_{n,GPC}=3500$ g/mol, $M_w/M_n=1.19$). (C) The SETRC based on precursor alkyne-PMMA-Br (Entry 3, $M_{n,GPC}=4900$ g/mol, $M_w/M_n=1.21$).

alkyne-PMMA-Br (Entry 1, $M_{n,GPC}=2500$ g/mol) (Figure 2A), the GPC curves before and after SETRC indicate an obvious shift, which proved that the SETRC was a well-controlled and successful procedure.

In order to observe the SETRC process further, the coupling products obtained at different reaction time were measured by GPC for alkyne-PMMA-Br precursors ($M_{n,GPC}=3500$ g/mol and $M_{n,GPC}=4900$ g/mol). Take precursor alkyne-PMMA-Br (Entry 3, $M_{n,GPC}=$ 4900 g/mol) as an example. The peak at higher elution volume (25.80 mL) was attributed to alkyne-PMMA-Br precursors and peak at lower elution volume (24.60 mL) was attributed to coupling products alkyne-PMMA-alkyne with twofold molecular weight. As the SETRC reaction was going, peaks at 24.60 mL were more and more weaker [curves (b), (c), (d)], the peaks at 25.80 mL were more and more stronger. In these cases, GPC

data showed that the apparent molecular weight of the mixed product was lower than the actual molecular weight of coupling product due to the overlapping of the molecular weight of precursors and coupling products. As time extended to 24 h, only the peak attributed to the products of twofold molecular weight existed [curves (a)], while the peak attributed to the precursor disappeared, which meant the coupling process was finished and alkyne-PMMA-Br was effectively transformed to alkyne-PMMA-alkyne.

Likewise, the GPC curves of SETRC reaction for alkyne-PMMA-Br precursor (Entry 2, $M_{n,GPC}=3500$) showed a similar phenomenon as shown in Figure 2C.

Based on the GPC data, the contents of coupling products by SETRC process (0.17—0.92, Table 1) were calculated from the following formula:

$$\chi_c=2(1-M_{n,o}/M_{n,c}) \quad (1)$$

where $M_{n,0}$ and $M_{n,c}$ were the molecular weights of precursor alkyne-PMMA-Br and coupling product alkyne-PMMA-alkyne, respectively.[17]

Thus, all these results indicated that alkyne-PMMA-alkyne with alkyne end groups was successfully synthesized with high efficiency via SETRC.

Conclusion

The telechelic alkyne-PMMA-alkyne was successfully prepared with high efficiency through a facile SETRC reaction by using alkyne-PMMA-Br as precursor. The reaction could be carried out at ambient temperature, which provides a promising strategy for preparing more well-defined α,ω-telechelic polymers with various functional groups.

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