

RAPID COMMUNICATION

One-Pot Preparation of 3-Miktoarm Star Terpolymers via “Click Chemistry” and Atom Transfer Nitroxide Radical Coupling Reaction

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INTRODUCTION

The ABC 3-miktoarm star terpolymers are a kind of nonlinear polymers, which consists of three different polymeric chains emanating from a central junction point.^{1,2} Increasing attention is paid nowadays to star terpolymers^{1,3–6} because of their asymmetric structure leading to different properties, such as crystallinity, mechanical, and viscoelastic properties, in comparison with their corresponding linear analogues.⁷ However, the investigation of 3-miktoarm star terpolymer is limited by the difficulties in synthetic techniques. The living anionic polymerization is an accomplished technique for synthesis of 3-miktoarm star terpolymers.^{7–10} Focusing on which, the linking agent approach are applied broadly using chlorosilane^{9,11} or 1,1-diphenylethylene derivatives.^{3,12} However, the monomers suited for anionic polymerization are limited and polymerization conditions are strict. Recently, a new strategy to combine the different polymerization methods together was suggested to synthesize star terpolymers.¹³ Tunca and coworkers reported new strategies for preparing stars via combinations of radical polymerization with Huisgen 1,3-dipolar cycloaddition,¹⁴ or Diels–Alder reaction (DA).¹⁵ This [3 + 2] or DA [4 + 2] cycloaddition

using CuBr/ligand as catalyst is termed as “click chemistry,”¹⁶ which has showed some important features including high yields, functional group tolerance and selectivity. Nowadays, click chemistry is a mature technique and applied in many fields.^{17–22}

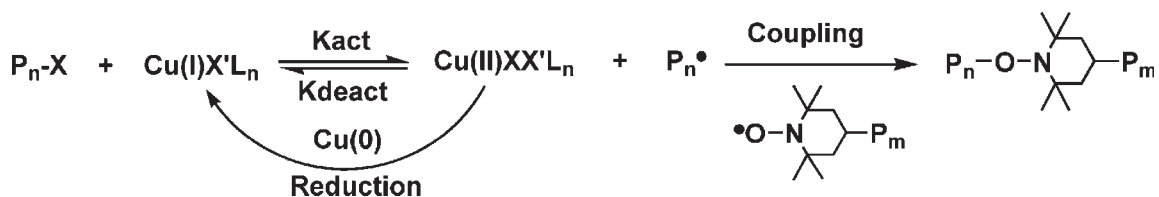
Recently, our group reported a new coupling reaction: “atom transfer nitroxide radical coupling” (ATNRC) reaction.²³ In which the bromine end-functional group of one polymer served as oxidant is reduced to bromine anion and carbon radical is formed. The Cu¹⁺ is oxidized to Cu²⁺ in the presence of CuBr/ligand. Then polymeric radical is immediately captured by another 2,2,6,6-tetramethyl-piperidiny-1-oxyl (TEMPO) end-functional polymer, and alkoxyamine is formed between the two polymers²⁴ (Scheme 1). Since the bromine and TEMPO are the typical groups for ATRP and nitroxide-mediated polymerization (NMP), ATNRC reaction can be widely used in synthesis of polymers with various structures.

Herein, we report a new strategy for synthesis of 3-miktoarm star terpolymer without any protection of initiating sites or tedious purification steps. The fully-defined precursors PtBA-N₃ (poly(*tert*-butyl acrylate) with azide end group), TEMPO-PEO or TEMPO-PCL (poly(ethylene oxide) or poly(ϵ -caprolactone) with TEMPO end group) and PS-alkyne/Br (polystyrene with ω -propargyl and ω' -(2-bromoiso butyryl) groups) are designed and prepared first, then the star terpolymers composed of PtBA, PS, and PEO (PCL) chains could be prepared via combination of click chemistry and ATNRC reaction using a one-pot (Scheme 2).

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Mechanism of the “ATNRC” reaction.

RESULTS AND DISCUSSION

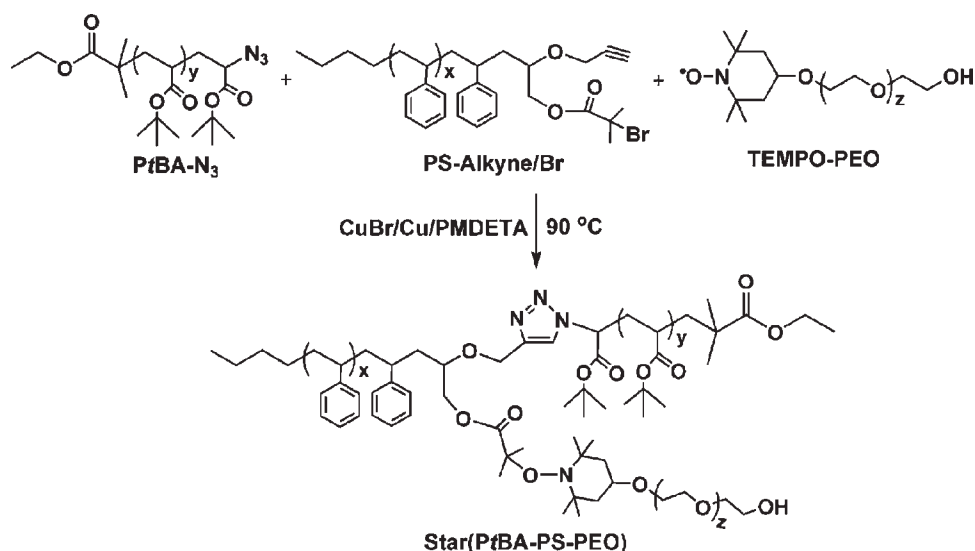
The key precursors PS-alkyne/Br,²⁵ PtBA-N₃,²⁶ and TEMPO-PEO^{27,28} or TEMPO-PCL²⁹ were prepared according to previous literatures, and characterized fully by GPC, ¹H NMR, MALDI-TOF, and FT-IR (see Supp. Info.). Figure 1 shows the GPC traces of all the precursors with nice Gaussian distribution and low molecular weight distribution (M_w/M_n), except PEO1 with a little tail. The molecular weights (M_n) of all precursors by GPC were almost the same as which derived from ¹H NMR, except PCL because of the quite difference of the chain structure of PCL from PS standard. The more reliable M_n of PCL measured by GPC can be calculated by a correction formula³⁰: $M_{n\text{ modify}} = 0.259 M_{n\text{GPC}}^{1.073}$, and the calibrated value was then consistent with that calculated by ¹H NMR data and obtained by MALDI-TOF MS. Other details can be obtained in supporting information.

The one-pot procedure was carried out in presence of CuBr/Cu/PMDETA at 70 °C for 24 h, the click chemistry between azide group and alkyne functional group, and ATNRC reaction between TEMPO group and bromine group were realized simultaneously.²⁴ The GPC

traces of star terpolymers composed of PS, PtBA, and PEO or PCL arms were shown in Figure 1.

In the one-pot process, the feeding PtBA-N₃ and TEMPO-PEO were slightly excessive comparing with PS-alkyne/Br, the molar ratio was about 1.2/1.2/1. Because PtBA-N₃ and TEMPO-PEO can dissolve in methanol completely, after reaction, the excessive PtBA or PEO can be easily removed from the mixture by precipitation in methanol. The GPC traces of star(PtBA1-PS1-PEO1) and star(PtBA2-PS2-PEO2) were smooth, and no signs represented PtBA or PEO were detected. In the case of star(PtBA2-PS1-PCL), the feeding PtBA-N₃ and TEMPO-PCL were slightly deficient, the molar ratio of them to PS-alkyne/Br was about 1/1/1.2. After precipitating in methanol, the crude products were dissolved in toluene and then passed through column chromatography. After front running of excess PS eluted out of the column by toluene, THF was used to washing out star(PtBA2-PS1-PCL) in a yield of 55.8%. Figure 1(C) showed the GPC trace of star(PtBA2-PS1-PCL) with narrow M_w/M_n , and tailing was not observed in the molecular weight region of the precursors.

This procedure was supported by ¹H NMR spectra. Comparing the ¹H NMR spectrum of PtBA-N₃ [Supp.



Scheme 2. One-pot synthesis of 3-miktoarm star terpolymer star(PtBA-PS-PEO) via combination of “click chemistry” and ATNRC reaction.

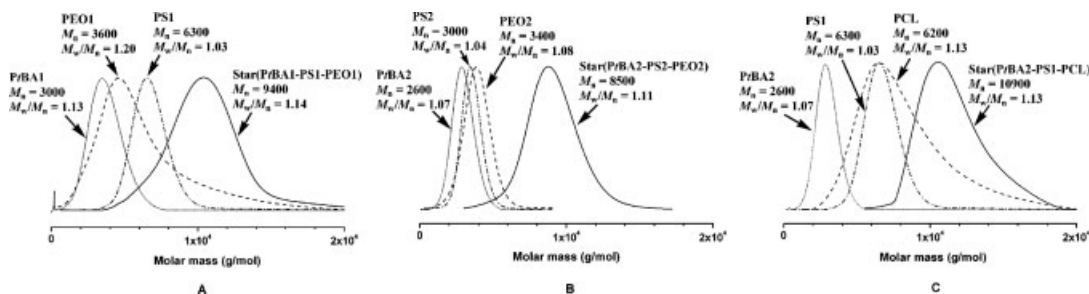


Figure 1. The GPC curves of 3-miktoarm star terpolymers and their precursors.

Info. Fig. 3(A)] with that of star(*Pt*BA1-PS1-PEO1) [Fig. 2(A)], the resonance occurred at 3.6–3.8 ppm for methine group proton ($-\text{CH}_2\text{CH}-\text{N}_3$, “*f*”) disappeared and the new signal at 3.63 ppm for the methine group proton ($-\text{CH}_2\text{CH}$ -triazole, “*c*”) can be seen; in the case of star(*Pt*BA2-PS1-PCL) [Fig. 2(B)], the signal at 3.6 ppm obviously intensified compared with that in supporting information Figure 3(C). Since the resonance of methine group proton ($-\text{CH}_2\text{CH}$ -triazole, “*c*”) overlapped the original one belong to methylene group pro-

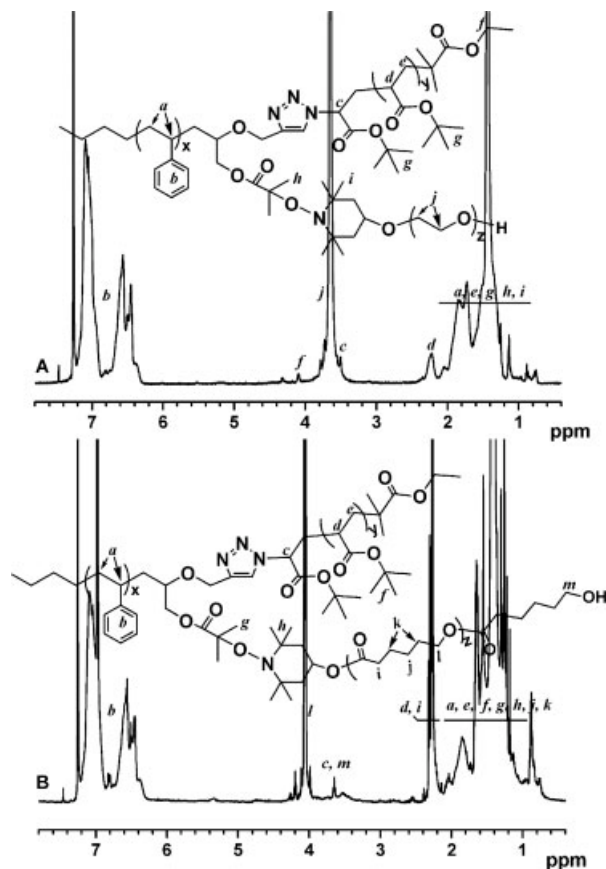


Figure 2. ^1H NMR spectra of (A) star(*Pt*BA1-PS1-PEO1) and (B) star(*Pt*BA2-PS1-PCL) in CDCl_3 .

ton of PCL ($-\text{CH}_2-\text{OH}$, “*m*”). Moreover, intensity of original resonance occurred at 1.94 ppm for methyl group protons [$-\text{C}(\text{CH}_3)_2-\text{Br}$, “*h*” in Fig. S-1(D)] was weakened (original integral area for aromatic ring protons $-\text{C}_6\text{H}_5$ “*A_b*”) was used as standard). Because the methyl group protons moved to the upfield when the bromine atom was removed from ω -end of PS and new C—O bond generated. Further evidence for the formation of star terpolymer can be seen in the FTIR spectrum in supporting information Figure 2(D). The characteristic bands of PS arms $\text{C}=\text{C}_{\text{aromatic}}$ stretching at $1450\text{--}1600\text{ cm}^{-1}$, $\text{C}-\text{H}_{\text{aromatic}}$ stretching at $3000\text{--}3100\text{ cm}^{-1}$ and the characteristic bands of PEO arms $\text{C}-\text{O}-\text{C}$ stretching at $1100\text{--}1200\text{ cm}^{-1}$ could be detected easily. The characteristic bands of *Pt*BA arms $\text{C}=\text{O}$ stretching at 1735 cm^{-1} obviously intensified compared with that in supporting information Figure 2(C). These results indicated the occurrences of click chemistry and ATNRC reaction, and the formation of star terpolymers.

The characteristic peak of aromatic ring $-\text{C}_6\text{H}_5$ (“*b*” in both spectrum A and B, repeating unit of PS), the peak of $-\text{CH}_2\text{CH}-$ (“*d*” in both spectrum A and B, repeating unit of *Pt*BA) at 2.1–2.4 ppm, the peak of $-\text{CH}_2\text{CH}_2\text{O}-$ (“*j*” in spectrum A, repeating unit of PEO) at 3.5–3.8 ppm, and the peak of $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ (“*l*” in spectrum B, repeating unit of PCL) at 3.95–4.18 ppm were used to determine the ratio of the integration of PS arm to *Pt*BA and PEO (PCL) arms using eqs 1 and 2 and then to calculate the actual molecular weight ($M_{n,\text{NMR}}(\text{star})$) of star terpolymers.

$$M_{n,\text{NMR}}(\text{star}_{\text{PtBA-PS-PEO}}) = \frac{5A_d}{A_b} \times \frac{M_{n,\text{NMR}}(\text{PS})}{104} \times 128 + \frac{5A_j}{4A_b} \times \frac{M_{n,\text{NMR}}(\text{PS})}{104} \times 44 + M_{n,\text{NMR}}(\text{PS}) \quad (1)$$

Here as Figure 2(A) showed, A_d represents the integral area of the peaks at “*d*” for $-\text{CH}_2\text{CH}-$ methine group proton on *Pt*BA arm, A_b represents the integral area of the peaks at “*b*” for aromatic ring protons on PS arm, and A_j represents the integral area of the peaks at “*j*” for $-\text{CH}_2\text{CH}_2\text{O}-$ methylene group protons on PEO

Table 1. One-Pot Synthesis of 3-Miktoarm Terpolymers

Exp.	M_n GPC ^a (g/mol)	M_w/M_n ^a	M_n NMR ^b (g/mol)	M_n theo ^c (g/mol)	E.F. (%) ^d		
					Formation	ATNRC	Click
Star(<i>Pt</i> BA1-PS1-PEO1)	9400	1.14	12,900	14,200	90.8	83.4	85.3
Star(<i>Pt</i> BA2-PS2-PEO2)	8500	1.11	9100	10,100	90.4	83.9	86.5
Star(<i>Pt</i> BA2-PS1-PCL)	10,900	1.13	11,700	12,800	91.3	82.8	84.3

^a Determined by GPC in THF, calibration with linear PS as standard.

^b Calculated from ¹H NMR data.

^c The theoretical molecular weight, calculated by eq 3.

^d Efficiencies of the formation of terpolymers and the “ATNRC” reaction or “click chemistry,” calculated from ¹H NMR data.

arm; the values 104, 128, and 44 were the molecular weights of monomer St, *t*BA, and EO, respectively.

$$M_{n,NMR}(\text{star}_{PtBA-PS-PCL}) = \frac{5(A_{d+i} - A_l)}{A_b} \times \frac{M_{n,NMR}(PS)}{104} \\ \times 128 + \frac{5A_l}{2A_b} \times \frac{M_{n,NMR}(PS)}{104} \times 114 + M_{n,NMR}(PS) \quad (2)$$

Here as Figure 2(B) showed, A_{d+i} represents the integral area of the peaks at “d” and “i” for the $-\text{CH}_2\text{CH}-$ methine group proton on *Pt*BA and $-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ first methylene group connected to carbonyl on PCL; A_l represents the integral area of the peaks at “l” for $-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ fifth methylene group protons connected to carbonyl on PCL, the value 114 is the molecular weight of repeating unit of PCL, and others were defined as eq 1.

Theoretical molecular weight ($M_{n,theo}(\text{star})$) can be calculated by the sum of the separate molecular weight resulted from ¹H NMR ($M_{n,NMR}$) of precursors, using eq 3.

$$M_{n,theo}(\text{star}) = M_{n,NMR}(PtBA) + M_{n,NMR}(PS) \\ + [M_{n,NMR}(PEO) \text{ or } M_{n,NMR}(PCL)] - 80 \quad (3)$$

Here, $M_{n,NMR}(PtBA)$, $M_{n,NMR}(PS)$, $M_{n,NMR}(PEO)$, and $M_{n,NMR}(PCL)$ represented the M_n s obtained from ¹H NMR data of the precursors (see Supp. Info.); the value 80 was the molecular weight of bromine atom.

In ATNRC reaction, CuBr served as reactant, and an improvement can be realized by taking advantage of the ability of Cu(0) powder to reduce Cu^{2+} to Cu^{1+} when there are stabilizing ligands present. This approach can be adapted to allow for the efficient synthesis of alkoxyamine through the continuous regeneration of the Cu^{+1} complexes by the reduction of the resulting $\text{CuBr}_2/\text{ligand}$ complexes by Cu(0) powder.³¹ The formation efficiencies of star terpolymers were found to be 90.8, 90.4, and 91.3% from a ratio of $M_{n,NMR}(\text{star})$ to $M_{n,theo}(\text{star})$ of star(*Pt*BA1-PS1-PEO1), star(*Pt*BA2-PS2-PEO2), and star(*Pt*BA2-PS1-PCL),

respectively. The efficiencies of the ATNRC and click reaction were calculated by the ratio of PEO (PCL) and *Pt*BA arms to PS arm in ¹H NMR spectra (Table 1). It seemed that the values of click chemistry (85.3, 86.5, and 84.3%) were slightly higher than that of ATNRC reaction (83.4, 83.9 and 82.8%). However, the coupling efficiency no matter click chemistry or ATNRC can not be improved by decreasing the M_n s of precursors. It may attribute that the efficiency of coupling reaction was mainly influenced by the steric hindrance of junction centre.

Thermal transitions of the 3-miktoarm star terpolymer and its corresponding linear analogue were determined by DSC, and the results of the second heating run were discussed (Fig. 3). In the case of linear triblock copolymer *Pt*BA-PS-PEO (a),²⁹ three transitions were observed at -51 °C (T_g for PEO segment), 38 °C (T_g for *Pt*BA segment), and 70 °C (T_g for PS segment). However, in the case of 3-miktoarm star terpolymer

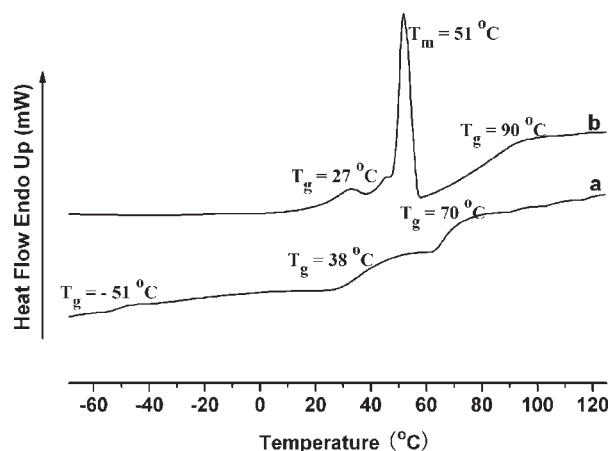


Figure 3. DSC spectra of (a) linear triblock copolymer *Pt*BA-PS-PEO and (b) star terpolymer star(*Pt*BA1-PS1-PEO1). (Heating rate: 10 °C/min, a nitrogen atmosphere; the glass transition (T_g) and the melting temperatures (T_m) were calculated as a midpoint and a peak apex of thermograms, respectively).

star(*Pt*BA1-PS1-PEO1) (b), there were only two T_g s can be observed at 27 °C (T_g for *Pt*BA segment)³² and 90 °C (T_g for PS segment),³³ and one melting transition (T_m) was detected at 51 °C for PEO segment.³⁴ It means that the space arrangement of polymer chains may exert great effect on the interaction between segments. The further investigation is undergoing.

In summary, 3-miktoarm star terpolymers composed of *Pt*BA, PS, PEO, or PCL arms were successfully synthesized by one-pot method via combination of click chemistry with ATNRC reaction. Moreover, the efficiency of ATNRC is as high as click chemistry, and the molecular weight of precursor polymers did not exert great effect on the coupling efficiency.

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