

A novel strategy for synthesis of multiblock copolymers

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Received (in Cambridge, UK) 21st August 2002, Accepted 9th October 2002

First published as an Advance Article on the web 25th October 2002

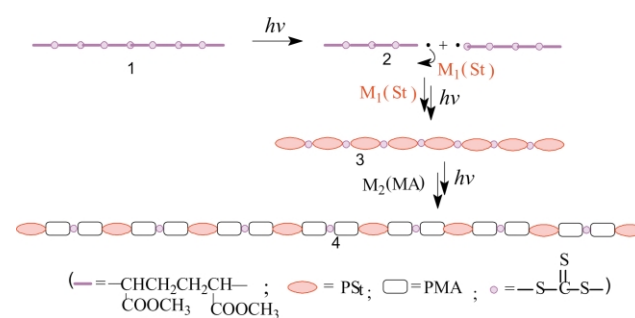
Multi-block copolymers with well-controlled numbers of blocks and block chain length are synthesized for the first time using a 'polyinitiator'.

It has very long been a dream in polymer science to synthesize long multi-block copolymers with an ordered chain sequence and controllable block length due to the expected special properties.^{1,2} Although living polymerizations have been developed,³ it is still a challenge to find a method to prepare *n*-block copolymers.¹ In theory, *n*-block copolymers can be prepared by alternatively adding different types of monomer into a living polymerization system. However, in the experiment, each addition of new monomer will introduce impurities, resulting in the terminations of some living sites. So until now, the greatest number of blocks in copolymers prepared by living polymerization method is 7.^{1,2} In principle, *n*-block copolymers can also be prepared by joining the narrowly distributed copolymer blocks together. However, such a reaction will practically stop as soon as a few copolymer blocks are coupled together because the concentration of end groups is too low. As a result, the number of blocks in the copolymers obtained is low.^{1,4} Therefore, it is of value to find an easy and new polymerization method to prepare *n*-block copolymers.

One of the earliest attempts to control molecular weight and end functional groups of the resulting polymers is to use disulfide compounds as photochemical iniferters as introduced by Otsu *et al.*^{5a,b} Although it can be used successfully to prepare block polymers, their structure and molecular weight distribution cannot be controlled due to fact that the sulfur-centered radical can initiate polymerization.^{5c} In our previous work,^{5d} we investigated living radical polymerization using dibenzyl trithiocarbonate as a photoinitiator and found that the trithiocarbonate radical is stable towards monomers. Based on these results, if we connect *n* photo-initiating groups by alkyl groups together to form a 'polyinitiator', *n*-triblock copolymers could be prepared by using this polyinitiator to initiate the polymerizations of different kinds of monomers as shown in Scheme 1. Under 310 nm UV irradiation, the weak S–C bond is cleaved into an active radical and a resonance-stabilized inactive radical. The former can initiate polymerization of monomer,

whereas the latter could scavenge the growing chain radical to form a dormant chain (**3**), which has *n* trithiocarbonate groups embedded in the long polymer chain. If we then use **3** as polyinitiator in the copolymerization, *n*-triblock copolymer (**4**) would be formed, which has *n*-triblock copolymer segments. In this communication, we report the preparation of *n*-triblock copolymers using a polyinitiator.

To test this idea, the polymerization of styrene (St) was performed under 310 nm UV irradiation for 48 h at 18 °C in the presence of **1** (DP = 8 $M_w/M_n = 2.0$ or DP = 27 $M_w/M_n = 1.9$), PSt with 8 or 27 trithiocarbonate groups embedded in the long chain was obtained, and the results are listed in Table 1. The GPC curve (for DP = 8) is shown in Fig. 1B and Fig. 2B shows its ¹H NMR spectrum. Comparison with the ¹H NMR spectrum of **1** in Fig. 2A, shows that besides the characteristic peaks of PSt, a new peak at δ 4.7 corresponding to the methine proton in the St unit next to trithiocarbonate function appears in Fig. 2B, while the peak at δ 4.8 in Fig. 2A belonging to the methine proton adjacent to trithiocarbonate group is absent, indicating the cleavage of the C–S bond in **1**, and the formation of a new C–S bond between the methine group of the St unit and a trithiocarbonate group, which indicates the successful insertion of St at these trithiocarbonate sites. No cage effect was observed since initiation efficiency is close to unity (obtained by comparing the moles of trithiocarbonate group in the polymer obtained with that of **1** added).



Scheme 1

Table 1 The results of *n*-triblock copolymers prepared using a 'polyinitiator' under UV irradiation^a

Sample	M	Conv. (%)	Long polymer chain		After cleavage at trithiocarbonate sites		
			$M_n (\times 10^{-4})^d$	M_w/M_n^d	$M_n (\times 10^{-4})^d$	M_w/M_n^d	<i>n</i>
3	(–S–C(=S)–S–PSt–) _{<i>n</i>} ^b	—	1.54	1.82	0.196	1.37	8
4a	MA	13.1	2.31	1.71	0.326	1.41	7.1
4b	MA	28.6	3.26	1.66	0.44	1.29	7.3
3	(–S–C(=S)–S–PSt–) _{<i>n</i>} ^c	—	3.69	1.86	—	—	27
4a	MA	11.0	5.08	1.71	0.153	1.35	32
4b	MA	23.2	7.30	1.76	0.292	1.21	25

^a Polymerization conditions: [MA]/(–S–C(=S)–S–PSt–)_{*n*} = 0.50 g/0.10 g; THF: 1.0 mL; Temp: 18 °C. ^b (–S–C(=S)–S–PSt–)_{*n*} prepared by the polymerization of St (1.0 g) under 310 nm UV irradiation in the presence of polytrithiocarbonate (50.0 mg) with DP = 8 for 48 h at 18 °C. ^c As for footnote *b* but with DP = 27. ^d Measured on a Waters 150C gel permeation chromatograph (GPC) equipped with 10³, 10⁴ and 10⁵ Å columns, narrow polydispersity polystyrene samples as standards, THF as eluent at a flow rate of 1.0 mL min^{–1}.

For preparing the n -triblock copolymer ([PMA- b -PSt- b -PMA] $_n$), **3** was used in the polymerization of MA under UV irradiation at 18 °C, and the results are listed in Table 1. The ^1H NMR spectrum and GPC curve of the n -triblock copolymer, [PMA- b -PSt- b -PMA] $_n$ are shown in Fig. 2C and Fig. 1C, respectively. Besides the characteristics of PSt and PMA, a new peak at $\delta = 4.8$ representative of the methine proton in the MA unit next to trithiocarbonate group appears in Fig. 2C, while the peak at $\delta = 4.7$ in Fig. 2B is absent in Fig. 2C, demonstrating that C-S bonds in **3** are completely cleaved, and that the block copolymerization of MA occurred at these trithiocarbonate sites, forming (PMA- b -PSt- b -PMA) $_n$. A way to further confirm this is to cleave the copolymer chains at the trithiocarbonate

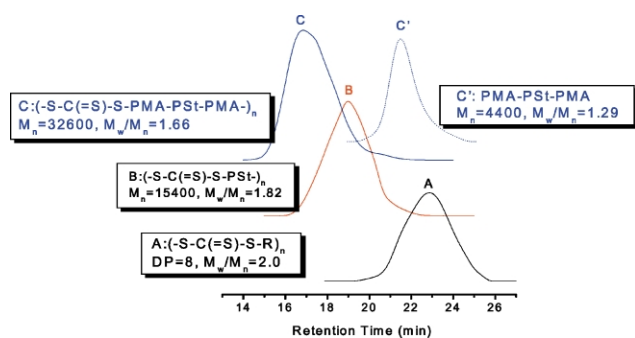


Fig. 1 GPC traces of (A) poly[thio(thiocarbonyl)thio-1,4-bis(methoxycarbonyl)-1,4-tetramethylene] (**1**); (B) $(-\text{S}-\text{C}(=\text{S})-\text{S}-\text{PSt}-)_n$; (C) $(-\text{S}-\text{C}(=\text{S})-\text{S}-\text{PMA}-b-\text{PSt}-b-\text{PMA}-)_n$ and (C') PMA- b -PSt- b -PMA.

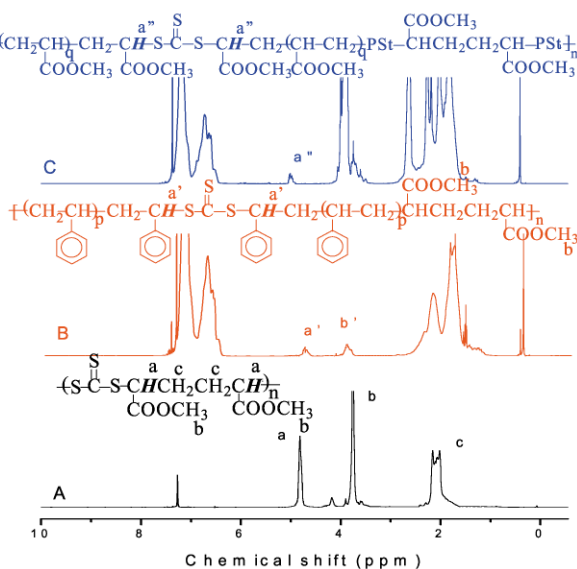


Fig. 2 ^1H NMR spectra of (A) poly[thio(thiocarbonyl)thio-1,4-bis(methoxycarbonyl)-1,4-tetramethylene] (**1**), (B) sample **3** in Table 1 and (C) sample **4b**.

sites. This can be achieved readily by aminolysis of the copolymers in THF solution of ethylenediamine, and PMA- b -PSt- b -PMA with two thiol end groups was obtained,⁶ whose structure was confirmed by ^1H NMR spectroscopy. GPC curves of **4** and its aminolysis product are shown in Fig. 1C and 1C', respectively. In Table 1, it can be seen that $M_n(\text{GPC})$ of **4** is much larger than that of its aminolysis product. The narrow polydispersity for the aminolysis product demonstrates that each triblock, PMA- b -PSt- b -PMA, has a similar chain length.

From the molecular weights of **4** and its aminolysis product, we estimated the average number (n) of triblocks in the copolymers obtained according to eqn. (1).

$$n = (M_4 - (44 \times \text{DP}_{\text{PI}}))/M_{4c} \quad (1)$$

where M_4 and M_{4c} are the molecular weights of **4** and its aminolysis product, respectively. DP_{PI} is the average degree of polymerization of the polytrithiocarbonate **1** used and 44 is the 'molecular weight' of $-\text{C}(=\text{S})-$. The n values calculated are listed in Table 1, and are close to the DP of **1** used, indicating that the n -triblock copolymer can be prepared in two steps by using the polyinitiator, and the number of triblocks in the copolymers obtained can be controlled by the sample of **1** used.

In summary, a novel method for preparing n -triblock copolymers consisting of n triblock copolymer chains is successfully designed by using a polyinitiator and its average number of triblocks is controlled by the degree of polymerization of **1** used. ^1H NMR and GPC results show that the n -triblock copolymer has an ordered chain sequence and controllable block lengths.

Authors thank for the financial support of National Natural Science Foundation of China under contact No. 50173025.

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