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# One-pot synthesis of star polymer by ATRP of bismaleimide and an excess of styrene with a conventional initiator

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## Abstract

A pragmatic one-pot approach to the synthesis of star polymers is reported using atom transfer radical copolymerization (ATRcP) of a bismaleimide and an excess of styrene (St) initiated with a conventional ATRP initiator.

*Keywords:* Polystyrene; Star polymer; Atom transfer radical polymerization

One-pot approach is a more convenient way to synthesize star-branched polymers than the 'core-first' or the 'arm-first' approches [1,2]. In the one-pot photopolymerization system reported by Ishizu and coworkers [1], (*N*,*N*-diethyldithiocarbamyl) methyl-styrene (DTCS), 4,4′-bismaleimidediphenylmethane (BMIM) and methyl methacrylate were employed. DTCS acted as an inimer and BMIM was a cross-linking agent. The in situ formed microgel became the core of the star polymer-to-be. In our previous work [2], star polystyrene (polySt) was synthesized in one-pot by copolymerization of *N*-[2-(2-bromoisobutyryloxy) ethyl]maleimide (BiBEMI) with an excess of styrene (St) under atom transfer radical polymerization (ATRP) condition. It was based on preferential consumption of BiBEMI, as an inimer, through its copolymerization with St, to form a branched intermediate in situ as a multifunctional core, which initiated homopolymerization of the excessive St to produce a star polymer. Such one-pot approach is different from another facile way to prepare branched vinyl polymers which involve conventional radical polymerization of a vinyl monomer in the presence of a multifunction comonomer like divinyl benzene (DVB) [3–5]. Though the polymers are soluble, the structures of the branched polymers obtained by the latter approach are randomly branched and slightly crosslinked instead of star branched. In order to prevent crosslinking and gelation, a controlled amount of chain transfer agent and optimized feed ratio of vinyl monomer to multifunctional comonomer are necessary. ATRP or group transfer polymerization has also been applied to prepare branched polymer by this method [6]. In the one-pot approach to star polymers [1,2], the inimers were needed, but their syntheses were tedious. Herein, we report a more pragmatic one-pot approach to prepare star-branched polymers by an ATRP system containing 4-(2-bromo-isobutyryloxy)anisole (BiBA), 1,6-bismaleimide-hexane (BMIH) and a large excess of St. Different from the random copolymerization of vinyl monomer and multifunctional comonomer (DVB), BMIH tends to form CTC (charge transfer complex) with St and can be preferentially consumed to give a cross-linked microgel in situ through a controlled radical polymerization. Owing to the presence of active groups (Br) of the polymerization on the microgel originated from BiBA, an excess of St was further initiated and polySt arms were grafted from the microgel, i.e. star polymers were produced. The principle of this approach is shown in Scheme 1.

ATRcP of BMIH and excess St initiated by BiBA was carried out in dioxane at 80 °C catalyzed by CuBr and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). The feed molar ratio of BMIH/St/BiBA/CuBr/PMDETA was 1/60/1/1/1, and the volume of dioxane to that of St was

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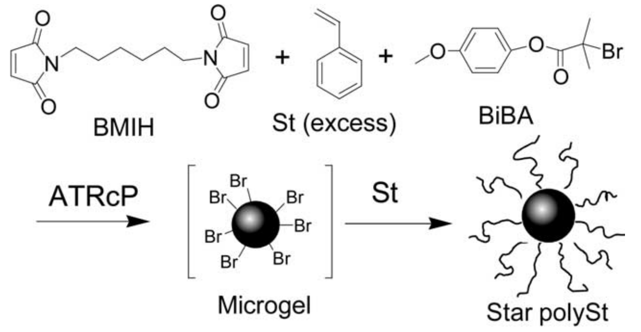

Scheme 1.

7–3.9. All the reagents were commercially available or prepared easily from commercial reagents. Conversion of St during the polymerization was tracked by gas chromatography (GC) using dioxane as internal standard. Kinetic data for the ATRP are shown in Fig. 1.

The plot of ln([$M$]$_0$/[$M$]) against time is linear for styrene conversion below 40%, but deviates from linearity at higher conversion. This result indicates that the polymerization followed the first order kinetic but radical termination appeared gradually. The change of the molecular weight of the polymer was monitored by GPC against linear polySt standards using those samples for kinetic studies. The results are shown in Fig. 2. One may note that the polymer contained two fractions: Pl with low polydispersity (PDI = 1.05) at the low molecular weight region and a portion with relatively high polydispersity (PDI = 2.05) at the high molecular weight region. This kind of GPC curves was similar to the results reported previously from the inimer [2]. The content of Pl in the whole polymer was 31% by comparing the area of the Pl with that of the whole curve, and it also kept consistent during the polymerization process. The peak molecular weight of Pl increased linearly with the rise of conversion of St (Fig. 3, left), indicating constant radical concentration during the reaction. It was of note that no gel formed during the polymerization, which is remarkable.

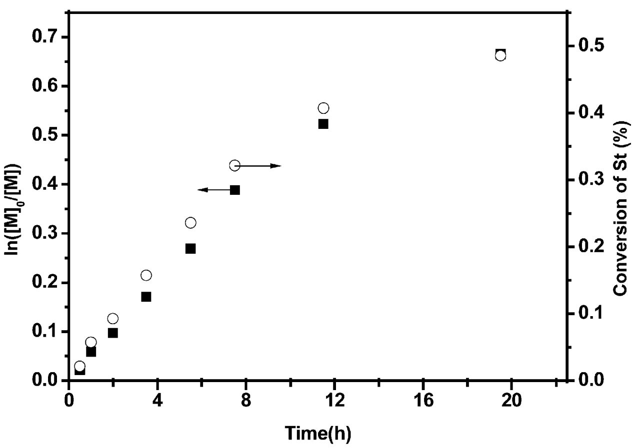

Fig. 1. Kinetic plot of the copolymerization of BMIH, BiBA with St by ATRP. [BiBA]$_0$:[St]$_0$:[BMIH]$_0$:[CuBr]:[PMDETA] = 1:60:1:1:1, at 80 °C in dioxane, $V_{\text{dioxane}}$:$V_{\text{St}}$ = 7:3.9.

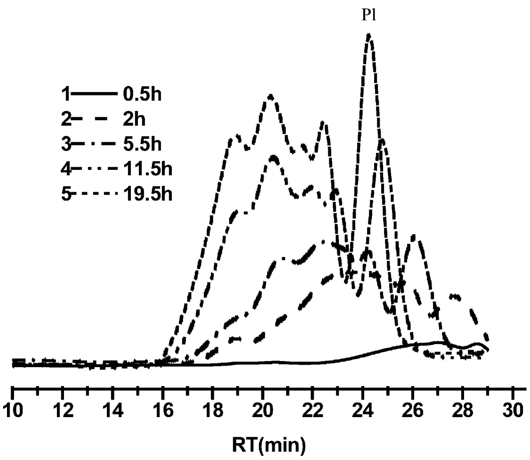

Fig. 2. GPC traces of the copolymerization of BMIH, BiBA with St by ATRP. Condition: see caption of Fig. 1.

In order to identify the structure of Pl, the product from another run under the same reaction conditions as shown in Fig. 1 at reaction time of 6 h was fractionated to get the Pl fraction (Fig. 3, right), which was then analyzed by MALDI-TOF-MS. The mass spectrum (Fig. 4) showed that Pl was a linear polySt initiated by one BiBA molecule with the formula depicted in Fig. 4, and no BMIH unit existed in Pl. Therefore, some chains were homopolySt produced by homopolymerization of St besides the copolymerization.

The Pl fraction (Fig. 3, right) and the high molecular weight part from the same polymer were analyzed by $^1$H NMR spectroscopy, respectively, and the spectra are shown in Fig. 5. Both spectra revealed typical peaks of polySt. The signal a at about 3.75 ppm ascribed to the –OCH$_3$ group, and b at 0.89 and 1.10 ppm ascribed to the two –CH$_3$ groups from the initiator were found in both $^1$H NMR spectra of Pl and the fraction with high molecular weight. But the broad peak, c attributed to the two methene groups adjacent to the nitrogen atom in the BMIH unit only appeared on the $^1$H NMR spectrum of the fraction with high molecular weight at 2.70–3.50 ppm. The small and broadened peak c was due to the cross-linked microgel structure and low content of the core in the product. This fact also supported the MALDI-TOF-MS analysis results that Pl contained no BMIH unit and the high molecular weigh fraction might possess a star-branched structure deriving from the BMIH as the cross-linker in the core.

By comparing the area of peak a and the area from the phenyl protons (from 6.30 to 7.20 ppm) on the $^1$H NMR spectrum of Pl (Fig. 5, down), the number average molecular weight ($M_{\text{n,NMR}}$) of Pl was estimated to be 2800. This value is close to the $M_{\text{n,MS}}$ = 2700 (Fig. 4), $M_{\text{n,GPC}}$ = 2100 (Fig. 3, right) and $M_{\text{n,conv.}}$ = 2000 (conv. = 27%). By comparing the same two areas on the $^1$H NMR spectrum of the high molecular weight fraction (Fig. 5, up),

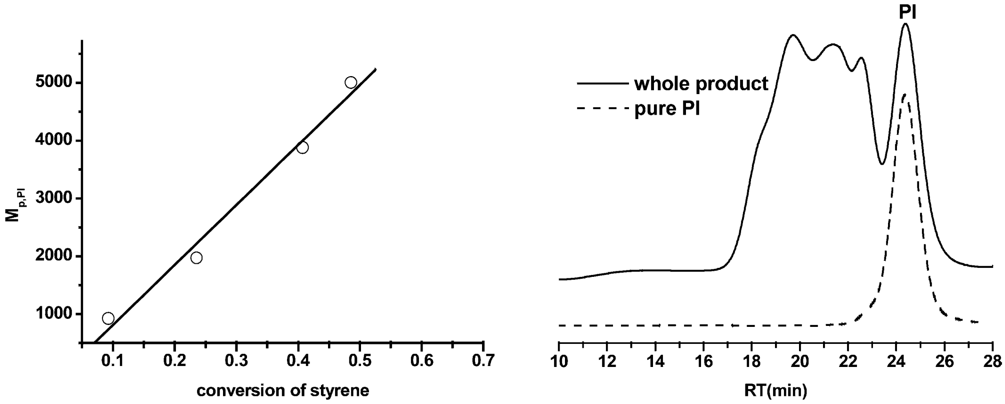

Fig. 3. Left: peak molecular weight of Pl against conversion of St in the copolymerization. Condition: see caption of Fig. 1. Right: Pl fraction from the polymerization product at a reaction time of 6 h.

Table 1
Characterization of the fractionated star polySt produced by one-pot

| $M_{w,GPC}$ (PDI) | $M_{w,SLS}$ | $[\eta]$[a] | $g'$[b] | $M_{w,GPC}$ of Pl | Average arm number[c] |
|---|---|---|---|---|---|
| 65,700 (2.15) | 172,000 | 0.13 | 0.19 | 12,000 | 14 |

[a] Measured by an Ubbelohde-type capillary viscometer in toluene at 35 °C.

[b] $g'=[\eta]/[\eta]_L$, $[\eta]_L=1.26\times10^{-4}$, $M_{w,SLS}^{0.71}=0.66$ [2,7].

[c] $M_{w,SLS}/M_{n,Pl}$.

the ratio of St units to BiBA in the star ploymer was determined to be 29, close to the value of the same ratio of Pl, 24. This outcome indicates that the length of the arm in the star polymer was close to the length of Pl chain.

The copolymerization was also carried out at 50 °C for 48 h with a feed molar ratio of BMIH/St/BiBA/CuBr/PMDETA = 1/100/1/1/1, but the product has similar GPC shape as those shown in Fig. 2. The content of Pl and the polydispersity of the two parts had no difference comparing to the polymerization under different condition. The result reveals that polymerization conditions applied had no obvious effect on the composition of the polymer. This phenomenon is different from the results reported previously [2] in which linear polymer content was dependent on polymerization conditions and the feed ratio of St to the inimer BiBEMI. The product obtained at 50 °C for 48 h was fractionated to eliminate most of Pl and the resulted high molecular weight fraction was characterized by GPC, static light scattering (SLS) and viscosity tests to get its compact factor ($g'$) and the results are shown in Table 1. The $g'$ value (0.19) demonstrates the compact nature of the fractionated polymer, proving that it possessed typical star-branched structure [2,7]. Since the molecular weight of the arm was roughly the same with that of linear Pl, the average arm

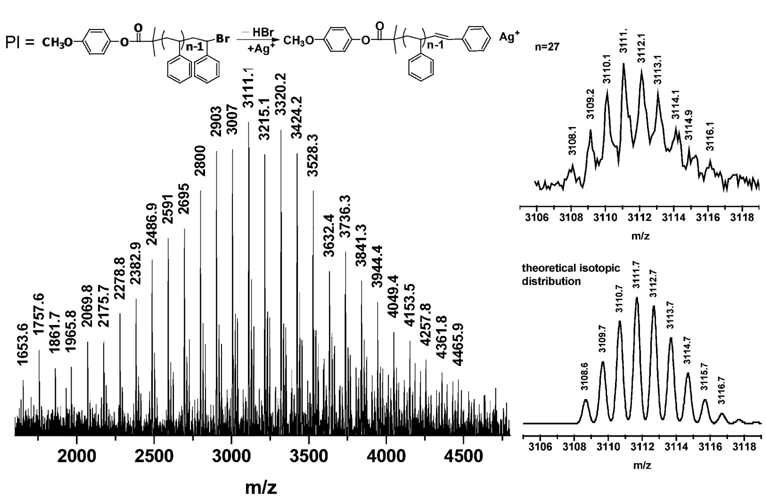

Fig. 4. MALDI-TOF-MS spectra of Pl fraction (Fig. 3, right) and its formula. Inlet: detected isotropic distribution when $n=27$ (right up); theoretical isotropic distribution (right down). The spectra were obtained by using the same instrument and parameters as reported in the literature [2] but the matrix CCA was replace by $AgOOCCF_3$.

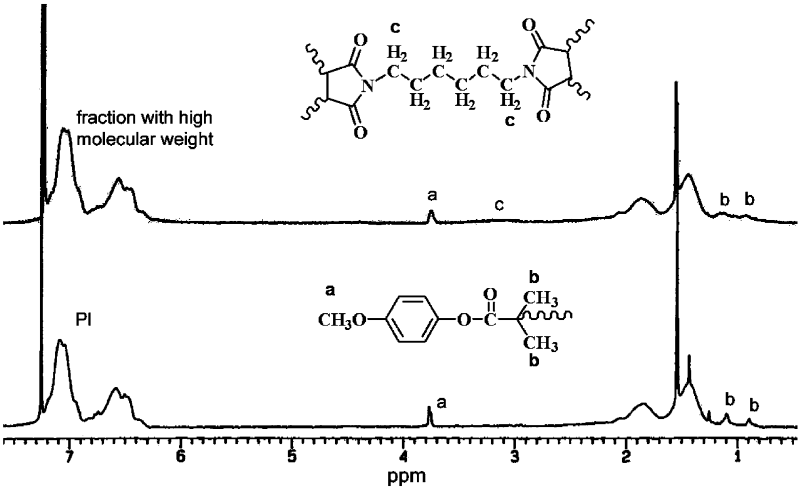

Fig. 5. $^1$H NMR spectra of PI (down) and the fraction with high molecular weight (up) after fractionation from the polymer shown in Fig. 3 (right).

number was estimated to be 14 by comparing $M_{w,SLS}$ of the star polymer and $M_{w,GPC}$ of PI.

In conclusion, star-branched polySt was prepared by ATRcP of a bismaleimide with an excess of St initiated by an ordinary ATRP initiator. Though there is linear polymer coexisted, it is a more pragmatic and convenient one-pot approach than those reported in the literatures which inimers were needed. Further investigation of this novel system is ongoing.

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## References

[1] Ishizu K, Park J, Shibuya T, Sogabe A. Macromolecules 2003;36: 2990–3.
[2] Deng GH, Chen YM. Macromolecules 2004;37:18–27.
[3] Isaure F, Cormack PAG, Sherrington DC. Macromolecules 2004;37: 2096–105.
[4] Isaure F, Cormack PAG, Sherrington DC. J Mater Chem 2003;13: 2701–10.
[5] Slark AT, Sherrington DC, Titterton A, Martin IK. J Mater Chem 2003; 13:2711–20.
[6] Isaure F, Cormack PAG, Graham S, Sherrington DC, Armes SP, Bütün V. Chem Commun 2004;1138–9.
[7] Nakata M. Makromol Chem 1971;149:99–115.