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A unique synthesis of a well-defined block copolymer having alternating segments constituted by maleic anhydride and styrene and the self-assembly aggregating behavior thereof

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A unique synthesis of a well-defined block copolymer having alternating maleic anhydride(MAn)/styrene(St) segments and PSt segments was achieved *via* radical addition–fragmentation chain transfer (RAFT) copolymerization and the self-assembly aggregating behavior of its hydrolyzed amphiphilic product in water was demonstrated.

One of the extensively studied CTC (charge transfer complex) forming monomer pairs is the combination of maleic anhydride (MAn) and styrene (St),[1] which can be alternately copolymerized under ordinary free radical initiating techniques to give a functional copolymer by further modification. However, the molecular weight and molecular weight distribution (M_w/M_n) of the copolymer thus obtained are not well-defined.

Recently developed 'living' free radical polymerization has received rapidly increasing interest, since it not only furnishes control over the resulting polymers with narrow M_w/M_n but also can be performed under ordinary radical polymerization procedures avoiding the stringent conditions needed for living ionic polymerization. The preparative technique for well-defined polymers of vinyl monomers *via* precision free radical polymerization has witnessed explosive growth in nitroxide-mediated polymerization,[2] atom transfer radical polymerization (ATRP),[3] and consequently developed radical reversible addition–fragmentation chain transfer (RAFT) polymerization.[4] They are marked with their respective features and limitations. A RAFT polymerization can be achieved by using thiocarbonylthio compounds as a reversible capping agent to produce 'living' polymer chains *via* a free radical mechanism.[4] The 'living' controlled radical copolymerization of electron-deficient and electron-rich monomer pairs is an elusive target, but the works are scarce.[5,6] The challenge associated with ATRP is to obtain an alternating copolymer of MAn, which destroys the ATRP catalytic system. Recently, Hawker *et al.* reported a one-step controlled copolymerization of MAn with St by nitroxide-mediated polymerization, giving a P(St-*co*-MAn)-*b*-PSt block copolymer,[2] and the same polymerization system was also reported for the copolymerization of St with MAn.[7] However, there is no alternating structure observed in the MAn-St copolymer. More recently, there was a report on a copolymerization of MAn and St *via* the RAFT process in which a dithiobenzoate residue was linked to a polyolefine chain end affording a block copolymer.[8] Here we describe a copolymerization of MAn with an excess amount of St in molar feed *via* the RAFT technique affording a well-defined block copolymer, P(MAn-*alt*-St)-*b*-PSt and the self-assembly aggregating behavior of its hydrolyzed amphiphilic product in water.

A typical RAFT initiating system used is the combination of (*S*)-benzyl dithiobenzoate (BTBA) with AIBN. The copolymerization of MAn with St takes place readily at 80 °C and the results are listed in Table 1. During the polymerization, both monomer conversion and number average molecular weight (M_n) increase with polymerization time. The copolymers obtained possess narrow $M_w/M_n(\sim 1.2)$, and the composition of P(MAn-*co*-St) is approximately 1:1 in molar ratio. The M_n determined by GPC method increases linearly with the monomer conversion, and matches well with the theoretical value. A thermal copolymerization of MAn with St at 80 °C in the absence of BTBA was demonstrated as a comparison. It can be seen that the copolymer obtained by using AIBN as an initiator possesses a higher M_n up to 6.3×10^4, with a broader M_w/M_n of 2.96. This firmly supports the conclusion that the RAFT copolymerization of MAn and St is of a controlled polymerization nature.

To further reveal the alternating nature of the MAn-St copolymer, a RAFT copolymerization of MAn and St with a molar feed of 1:9 was demonstrated at 60 °C. The conversions of both MAn and St were determined by GC. As can be seen from Fig. 1, the conversion of MAn apparently increases faster than that of St, but the absolute consumption of MAn and St are approximately the same until 80% of MAn was consumed. This indicates that the copolymer obtained possesses a predominantly alternating character at any monomer conversion before MAn has been exhausted. After MAn was completely consumed, the alternating copolymer chain subsequently continued to propagate forming a block copolymer with St sequence. Thus, the copolymerization basically involves: the simultaneous incorporating of MAn and St resulting in an alternating copolymer (Stage I), and the consumption of essentially pure St to continue chain propagation affording a block copolymer with a PSt segment (Stage II). At both stages, Mn increases linearly

Table 1 Molecular weight, molecular weight distribution and composition of MAn-St copolymers obtained *via* RAFT polymerization[a]

Copolymer	Time/h	Conversion (%)[b]	M_n[f] (theory)	M_n[c] (found)	M_w/M_n[c]	St in copolymer (mol%)[e]
MAn-St-1	0.1	17.4	1 580	2 450	1.19	45.9
MAn-St-2	0.3	64.1	5 820	6 180	1.24	48.6
MAn-St-3	1.0	93.3	8 480	7 250	1.22	47.9
MAn-St-4[d]	0.5	96.5	—	63 000	2.96	50.2

[a] $[MAn]_0:[St]_0:[BTBA]_0:[AIBN]_0 = 90:90:2:1$ in molar ratio, $[MAn]_0 = 2.0$ mol L^{-1}, dioxane, 80 °C. [b] Determined by gas chromatography (GC) method. [c] Determined by GPC, THF as an eluent, 35 °C. [d] Thermal polymerization, the monomer feed was 1:1 in molar ratio, 80 °C; [e] Calculated by ^{1}H-NMR analysis (200 MHz); [f] Mn (theory) = $[\mathrm{MW\ (MAn)} + \mathrm{MW\ (St)}] \times [MAn]_0 \times \mathrm{conversion} / [BTBA]_0$.

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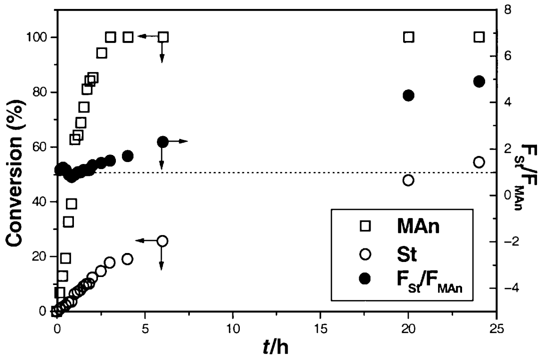


Fig. 1 Evolution of monomer conversions for St and MAn and their consumed molar ratio (F_{St}/F_{MAn}) with the polymerization time *via* RAFT polymerization. $[MAn]_0:[St]_0:[BTBA]:[AIBN] = 100:900:2:1$ in molar ratio, $[MAn] = 0.2$ mol L^{-1}, 60 °C.

with the conversion and M_w/M_n lies in the range of 1.2–1.4. It is thus concluded that, under RAFT polymerization conditions, the consuming rate of MAn is approximately equal to that of St during Stage I regardless of the large excess of St presented in the monomer feed. A well-defined block copolymer, P(MAn-*alt*-St)-*b*-PSt, composed of P(MAn-*alt*-St) and PSt sequences can thus be obtained by RAFT polymerization. Similar results were also manifested by the RAFT copolymerization of *N*-phenylmaleimide with St conducted at 60 °C.

It should be pointed out that the composition and sequence of the copolymer in the present work were different from the nitroxide-mediated ones reported by Hawker *et al.*[2] and Yoon *et al.*[7] There was no alternating character in the copolymer of MAn-St observed during the early stage of nitroxide-mediated polymerization performed at above 120 °C. In this work, the RAFT polymerization was carried out at 60 °C, where the CTC formation of MAn and St plays an important role in the copolymerization. On the contrary, the nitroxide-mediated copolymerization is always conducted at 120 °C or higher, which would destroy the CTC formed by MAn and St, hence the copolymerization of St or MAn favorably takes place in a 'free' monomer manner. In this regard, Seymour and Garner[1] reported that there is a change of the copolymer sequential distributions from alternating to random structure when the polymerization temperature increased from 80 to 130 °C for the MAn/St comonomer pair. Obviously, the polymerization temperature of 120 °C or higher and the large excess of St would lead to the tendency of homopolymerization of St.

DSC profile can provide valuable information about the block copolymer. The final copolymer possessed two distinct glass transition temperatures (T_g) at 104 and 167 °C, while the copolymer from Stage I showed only one T_g at 164 °C. This also strongly supports the conclusion that the final product is a block copolymer.

The P(MAn-*alt*-St) segment in the block copolymer can easily be hydrolyzed resulting in an amphiphilic block copolymer which can form uniform nanoscale particles by self-assembly. Fig. 2 shows the AFM (atomic force microscopy) image of the amphiphilic block copolymer in water obtained by hydrolyzing P(MAn-*alt*-St)$_{50}$-*b*-PSt$_{80}$ as illustrated in Scheme 1. The particles possess a uniform size with an average diameter of 63 nm and height of 30 nm. In addition, P(MAn-*alt*-St)-*b*-PSt can also form similar micelles in polar solvents such as propan-2-ol. These architectural particles in nanoscale size constructed by PSt segment as a core, and P(MAn-*alt*-St) or P(MA-*alt*-St) segment as a corona, which provides reactive anhydride or carboxylic groups on the surface of particles, are of interest in further chemical or biological modification. The surface modification of the copolymer micelle and the morphology of their derivatives in selective solvents are underway.

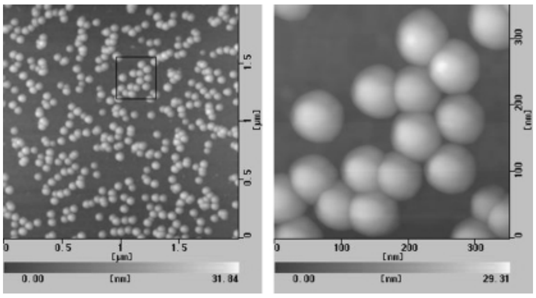
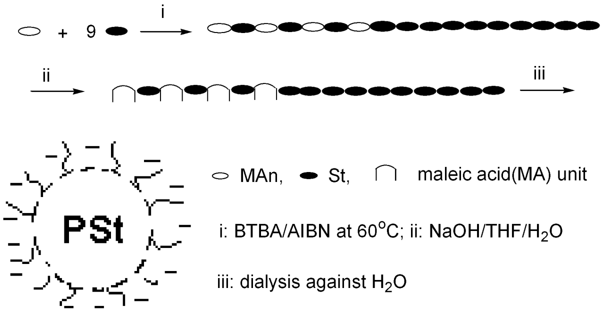


Fig. 2 AFM images of the hydrolyzed product of P(MAn-*alt*-St)$_{50}$-*b*-PSt$_{80}$ (M_n = 18,000, M_w/M_n = 1.34) by spin-coating 5.0×10^{-4} wt% aqueous solution (pH = 9.7) on mica. (a) 2 × 2 μm region; (b) 350 × 350 nm area from (a).



Scheme 1

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