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Controlled alternating copolymerization of St with MAh in the presence of DBTTC

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Abstract

The copolymerization of styrene (St) with maleic anhydride (MAh) performed at 22 °C in the presence of dibenzyl trithiocarbonate exhibits controlled nature evidenced by: narrow molecular weight distribution, controlled molecular weight and first-order polymerization kinetics. The composition analysis of the copolymers obtained by ^{13}C NMR spectra shows the molar fraction of St in obtained copolymers is almost equal to 0.5 throughout the copolymerization. The sequence structure of the copolymer was obtained from DEPT experiments by recording the spectra at $\pi/4$ and $3\pi/4$, and then combining them together, the results showed that the copolymers obtained possessed well-defined alternating structure. The experiment shows that charge-transfer-complex formed from St and MAh participates in both initiation and chain growth throughout the copolymerization.

Keywords: Alternating copolymerization; Controlled polymerization; Sequence structure; Styrene; Maleic anhydride; Benzyl trithiocarbonate

1. Introduction

Recent years, considerable attention has been paid to the preparation of alternating copolymers from which special materials with different functionalities could be designed and manufactured [1,2]. In addition, the well-defined alternating copolymers (such as styrene-alt-maleic anhydride (St-alt-MAh), St-alt-Maleimide, etc.) exhibit unique properties such as superior thermal stabilities [3,4], fire resistances [5], photo-, X-ray and E-beam sensitivities [4,6,7], catalytic and chiroptical activities [8–10], and extremely low band gap materials [11]. These copolymers prepared by general free radical method behave a strong compositional drift, the molar fraction of St increases as the polymer chain size increases [12]. Thus, the structure of copolymer obtained is complex. Therefore, studies on preparation of well-defined alternating copolymers, such as alternating copolymer of St and MAh or N-substituted maleimide with controlled molecular weight and narrow molecular weight distribution are of academic and industrial values.

Recently, controlled free radical polymerization has undergone tremendous progress, particularly in the areas of nitroxide-mediated free radical polymerization, [13–17] atom transfer radical polymerization (ATRP) using various transition-metal complexes [18–22] and reversible addition fragmentation chain transfer (RAFT) process [23–26]. Several research groups have tried to extend these methods to the copolymerization of St and MAh. Li and coworkers studied the copolymerization of MAh with St using ATRP method [27], but the polymerization did not take place due to the reaction of MAh with one component of the ATRP initiator system, such as Cu(I) or/and 2,2′-pyridine; Hawker reported that the copolymerization of St and MAh can proceed in a controlled fashion at 120 °C with a specially designed alkoxyamine nitroxide-mediated polymerization [28]; and Brouwer and Li have employed RAFT method in this copolymerization of St and MAh [29,30]. However, they are all unsuccessful to prepare strictly

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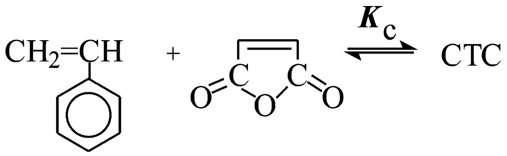


Scheme 1.

alternating copolymer of St and MAh although the copolymerizations are of living nature.

It was reported that there is an equilibrium between CTC (charge-transfer-complex) and St, MAh (see Scheme 1), and the equilibrium constant (K_c) determines the manner of copolymerization [32]. $K_c < 0.01$ L/mol, no alternating copolymerization occurs and the copolymerization proceeds randomly rather than in alternating manner; $K_c > 0.1$ L/mol, free radical alternating copolymerization can occur easily; while $1 < K_c < 5$ L/mol, spontaneous ionic polymerization happens [31]. In addition, K_c is determined by temperature, and decreases with the increase of temperature, ranging from 0.34 at 22 °C to 0 at 80 °C by UV and NMR measurements [32,33]. The thermal initiated controlled free radical polymerization methods employed in copolymerization were generally performed at high temperature, such as 80 °C, even higher. At this temperature, St-MAh CT complexes cannot be formed, the copolymerization proceeds randomly rather than in alternating manner. Therefore, a key point of preparing strictly alternating copolymers of St and MAh with well-controlled molecular weight and narrow molecular weight distribution (MWD) is to perform the copolymerization of St and MAh at low temperature.

Recently, it has been reported that RAFT process could offer exceptional versatility in providing polymers with well-controlled molecular weight and very narrow molecular weight distribution with the temperatures ranging from −20 to 200 °C during the polymerization [23–26]. In this study, we employ RAFT method in performing copolymerization of St with MAh at 22 °C without adding initiator. This method has two advantages: alternating copolymerization can occur easily (K_c around 0.34 L/mol), and the possibility of homopolymerization of St decreases without initiator.

2. Experiments

2.1. Materials

St (Shanghai Chem. Co.) was distilled at reduced pressure before use. MAh (Shanghai Chem. Co.) was sublimed at 50 °C/2.5 kPa, and then stored at −20 °C prior to use. Tetrahydrofuran (THF) (Shanghai Chem. Co.) was refluxed for 20 h over sodium, and then distilled. All other reagents were of analytical grade, and used as received.

2.2. Synthesis of dibenzyl trithiocarbonate (DBTTC)

DBTTC was prepared in 80% of yield according to Ref. [34]. ^{1}H–NMR(500 MHz, $CDCl_3$:δ 4.67(s, 4H, 2 –CH_2–), 7.15–7.25 (m, 10 H, 2 aromatic H) IR: $\nu = 1062.6$ cm^{-1} (C=S).

2.3. Copolymerization

The general procedure is as follows: DBTTC, St and MAh in THF were added in a polymerization tube. The mixture was immediately degassed by three freeze-evacuate-thaw cycles, and sealed under vacuum. Then it was kept at 22 °C for a prescribed time, the polymerization tube was open, and the reaction mixture was diluted with THF. The polymer was precipitated by adding polymer solution into a 10-fold excess of chloroform or absolute ether, collected by filtration, and dried in a vacuum oven at 60 °C. Conversions were determined by gravimetric method and calculated according to Eq. (1)

$$\text{Conversion}(\%) = \frac{W_p - W_{DBTTC}}{W_m} 100\%, \tag{1}$$

where W_p, W_{DBTTC} and W_m are the weights of the copolymer obtained, DBTTC and monomers added, respectively.

2.4. Characterization of copolymer

2.4.1. GPC Measurement

The molecular weight, M_n (GPC), molecular weight distribution were measured on a Waters 515 gel permeation chromatography (GPC) equipped with 10^3, 10^4, 10^5 Å waters ultrastyragel columns, and using THF as eluent at a flow rate of 1.0 mL/min. Monodisperse polystyrene was used as calibration standards.

2.4.2. NMR Measurement

^{13}C NMR analyses were performed on a Bruker DMX-500 nuclear magnetic resonance instrument with acetone-d_6 as solvent, and tetramethylsilane (TMS) as internal standard at ambient. During the measurements of ^{13}C NMR spectra, pulse recycle times were sufficiently long to allow recovery of all polymer carbon, and NOE was removed using gated decoupling. DEPT subspectra were generated using the combination of the $\pi/4$ and $3\pi/4$ experiments: $CH_2 = (\pi/4) + 1.15(3\pi/4)$ [35].

3. Results and discussion

3.1. Living polymerization characters

It was reported that there are some experimental criteria to diagnose a living free radical polymerization [36]. Among these criteria, some are crucial: narrow MWD, a linear evolution of molecular weight with monomer conversion, and constant concentration of active centers. To identify whether the copolymerization of St with MAh is of living nature, the copolymerizations of St with MAh were carried out in sealed tubes in the presence of DBTTC at 22 °C. Typical GPC curves of copolymerization of St with MAh throughout the polymerization are shown in Fig. 1. The MWDs of the polymers obtained remain narrow throughout the copolymerization of St with MAh, and range from 1.19 to 1.31 upon various conversions.

Fig. 2 shows the relationships of the number-average molecular weight, M_n (GPC) and polydispersity index, M_w/M_n with monomer conversion. Linear growth of the molecular weight with increase of conversion shown in Fig. 2 is one evidence of "living" polymerization. With the similar phenomenon observed in SFRP [13–17], ATRP [18–22] and RAFT [23–26], M_w/M_ns became slightly narrower as the monomer conversion increased.

Fig. 3 is the result of studying the relationship between $\ln([M]_0/[M]_t)$ and polymerization time. An induction period of about 4 h for the copolymerization of St and MAh with 1.0 molar feed ratio of St to MAh at 22 °C in the presence of DBTTC was observed. A probable reason for this phenomenon is due to slow formation rate of primary radical from CTC of St and MAh at 22 °C or a small amount of oxygen can not be excluded from the polymerization tube. However, after the induction period, plotting $\ln([M]_0/[M]_t)$ versus polymerization time affords a straight line (see Fig. 3), indicating that the chain radical concentration remains constant during the copolymerization of St with MAh after the induction period.

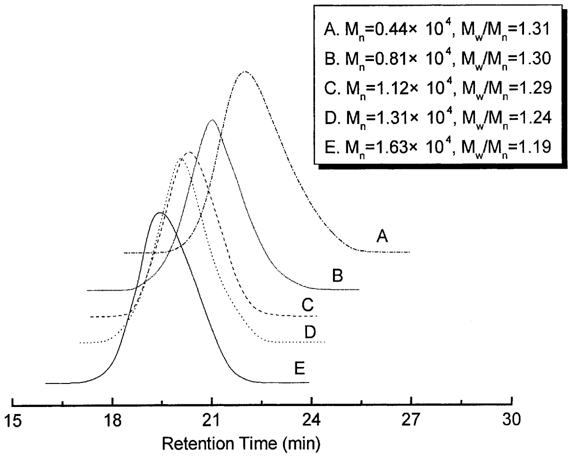


Fig. 1. GPC traces of copolymerization of St (1.550 g) with MAh (1.450 g) in 1 ml THF in the presence of DBTTC (0.10 mmol).

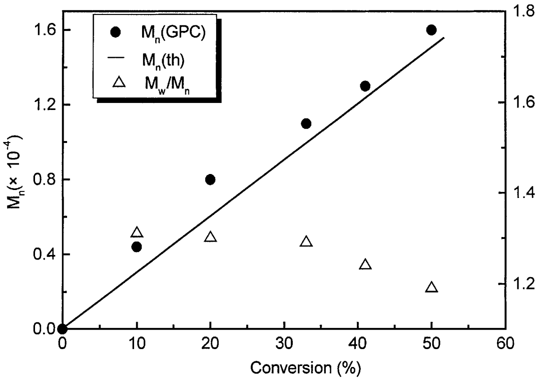


Fig. 2. Variation of M_n and M_w/M_n with conversion for the copolymerization of St (1.550 g) with MAh (1.450 g) in 1 ml THF at 22 ° C in the presence of DBTTC (0.10 mmol).

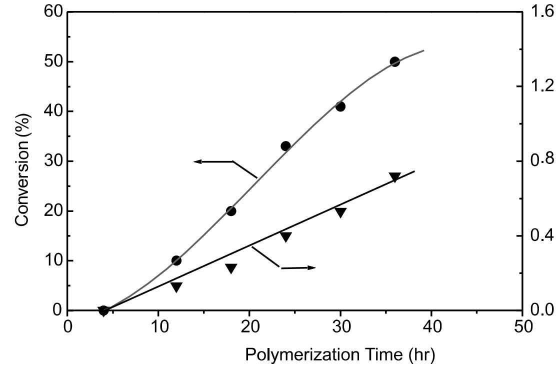


Fig. 3. Kinetic curves for the copolymerization of St (1.550 g) with MAh (1.450 g) in 1 ml THF at 22 °C in the presence of DBTTC (0.10 mmol).

Due to the overlap of the peaks in ^{1}H NMR spectra for methylene and benzene ring originated from DBTTC with those of backbone methine groups from MAh and benzene group from St unit, we characterized the copolymer by ^{13}C NMR spectra as shown in Fig. 4. Besides the characteristic peaks of PSt and PMAh, a new peak around 222 ppm ascribed to C=S carbon in trithiocarbonate group appeared in Fig. 4, which reveals that trithiocarbonate group remained in the copolymer, DBTTC participated in the chain transfer reaction with propagating radical. The IR and UV/Visible spectra results also demonstrated that trithiocarbonate group remained in the copolymer of St and MAh.

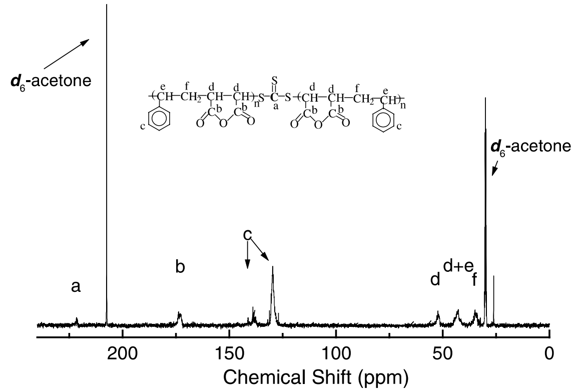


Fig. 4. ^{13}C NMR spectrum (500 MHz, d$_6$-acetone) of MAh-alt-St (Sample A).

If each macromolecule contains one trithiocarbonate group, M_n(th) could be calculated according to Eq. (2)

$$M_n(\mathrm{th}) = \frac{W_m M_{\mathrm{DBTTC}}}{W_{\mathrm{DBTTC}}}\mathrm{Conv} + M_{\mathrm{DBTTC}}, \tag{2}$$

where W_m and W_{DBTTC} are the weights of monomer and DBTTC respectively, and M_{DBTTC} is the molecular weight of DBTTC. M_n (GPC) is slightly larger than M_n (th) (see Fig. 2). The deviation between M_n (GPC) and M_n (th) may result from the different dynamic volumes of St/MAh copolymers and PSt standards, or low transfer efficiency of DBTTC with chain radical at 22 °C, or both.

3.2. Alternating copolymerization

There are several methods to analyze the composition of St unit in St/MAh copolymer: (1) elemental analysis of C% and H%; (2) non-aqueous microtitration in acetone using sodium methoxide as titrant; (3) the relative intensities of the aromatic (S unit), methylene and methine (MAh+S units) proton signals in ^{1}H NMR spectra; (4) relative areas of the carbonyl carbon peak to the total aromatic carbon peaks from ^{13}C NMR spectrum with gated decoupling to remove NOE; (5) triad fractions according to Eq. (3) [32,35]

$$\frac{F_s}{F_{\mathrm{MAh}}} = 1 + \frac{2A_{\mathrm{SSS}} + A_{\mathrm{SSM+MSS}}}{2A_{\mathrm{MSM}} + A_{\mathrm{SSM+MSS}}}, \tag{3}$$

where F_s and F_{MAh} are the molar fractions of St and MAh in copolymer respectively, and A_{SSS}, A_{MSM} and $A_{\mathrm{SSM+MSS}}$ are the integral values for SSS, MSM, MSS and SSM sequence units in St/MAh copolymer respectively.

Among these methods, ^{13}C NMR spectroscopy has advantage over elemental analysis, non-aqueous titration and ^{1}H NMR spectroscopy due to that it is not affected by the presence of water, which is very difficult to exclude from the copolymer [37]. Fig. 5 shows the molar fraction of St (F_s) in St/MAh copolymers calculated from ^{13}C NMR spectra and the value (F_s) almost remained 0.5 throughout the copolymerization.

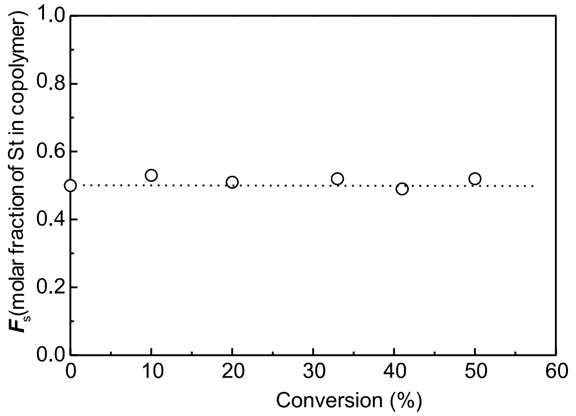


Fig. 5. The relationship between molar fraction of St in copolymers obtained and conversion for the copolymerization of St (1.550 g) with MAh (1.450 g) at 22 °C in the presence of DBTTC (0.10 mmol).

The ^{13}C NMR spectrum as shown in Fig. 4 does not give sequence information because the signals due to methine and methylene carbons are partially overlapped [35]. However, sequence information can be obtained from DEPT experiments, by recording the spectra at $\pi/4$ and $3\pi/4$, and then combining them together [12,35]. Barron and Montaudo reported that three distinct CH$_2$ regions (S: St unit; M: MAh unit): 33–37 (MSM), 37–42 (SSM+MSS) and 42–47 ppm (SSS) were observed in the ^{13}C NMR DEPT spectrum of 78% St/22% MAh copolymer [12,35]. Fig. 6(a) and (b) are the ^{13}C NMR sequence structure of St/MAh copolymer prepared by the copolymerization of St and MAh at 41% and 50% conversion with 1.0 molar feed ratio of St to MAh. From Fig. 6(a) and (b), it can be seen that the signals at 37–42 (SSM+MSS) and 42–47 ppm (SSS) are completely

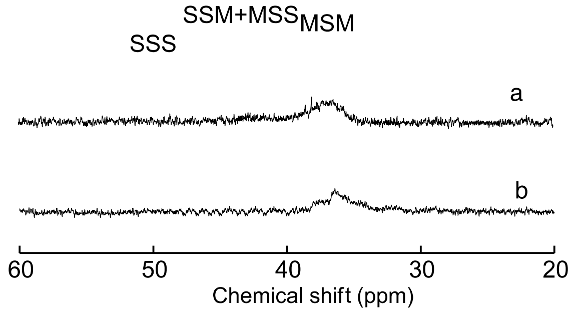


Fig. 6. Combination of DEPT NMR spectra of the obtained copolymers (Samples D, E).

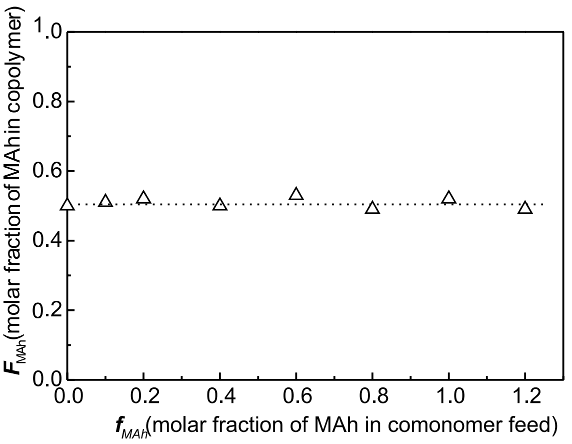


Fig. 7. The relationship between molar fraction of MAh in copolymers obtained with molar fraction of MAh in comonomer (5.200 g) feed St and MAh in 2 ml THF in the presence of DBTTC (0.10 mmol) at 22 °C.

absent, demonstrating that in the presence of DBTTC at 22 °C, the copolymerization of St with MAh proceeds via strictly alternating reaction to form PSt-alt-PMAh with MSM sequence structure. Conversion and chain size have no effect on composition content and sequence structure. This result agrees well with the calculated molar fraction (F_s) of St in St/MAh copolymer as shown in Fig. 5.

To investigate the copolymerization of St with MAh mechanism at 22 °C in the presence of DBTTC, the copolymerization of St with MAh with different monomer feed ratios was performed at 22 °C in the presence of DBTTC. Fig. 7 shows the relationship between the molar fraction (F_{MAh}) of MAh unit in the St/MAh copolymer obtained after four days and molar fraction (f_{MAh}) of MAh monomer in the comonomer feed, which shows that all the copolymers obtained exhibit alternating structure although the monomer feeds are different very much. On the other hand, it is interesting to find that the polymerization almost cannot continue when the MAh is consumed, that is when CTC comonomer is consumed, the homopolymerization of St cannot continue at 22 °C in the presence of DBTTC. Fig. 8 is the relationship of conversion with time at 0.1 of feed molar ratio of MAh to St, and the conversion remains almost constant after the overall conversion reached 18%, indicating that almost no homopolymerization of St occurred at 22 °C in the presence of DBTTC.

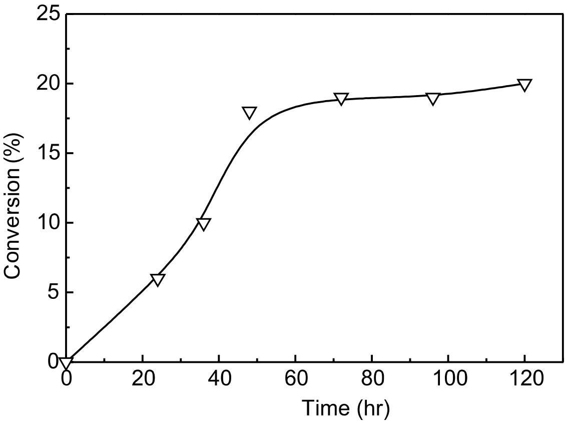


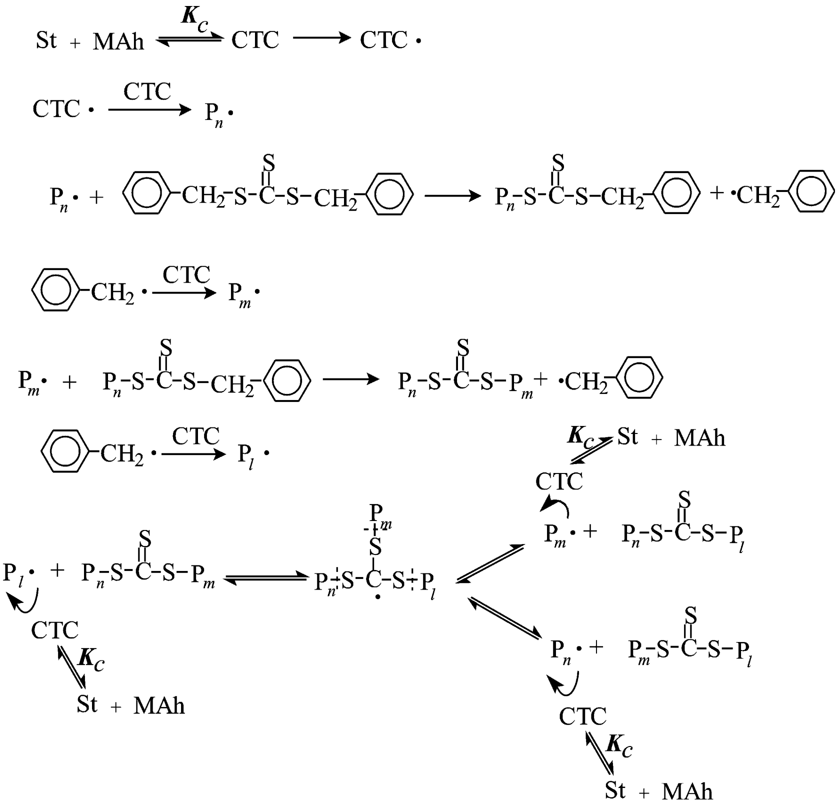
Fig. 8. Variation of conversion with polymerization time for the copolymerization of St (5.200 g) with MAh (0.490 g) in 2 ml THF in the presence of DBTTC (0.10 mmol) at 22 °C.

4. Mechanism

It was reported that free radical polymerization of St with MAh or N-maleimide is dominated by alternating copolymerization with the participation of comonomer CTC in both initiation and chain growth when $K_c > 0.1$ L/mol [38]. Based on this finding and the experiment discussed above, a mechanism was proposed as shown in Scheme 2. At 22 °C, CTC comonomer can produce CT complex-radicals (CTC$^\bullet$) [38].The complex-radical initiates the polymerization of CTC comonomer to form a propagating radical ($P_n^\bullet$). In succession, the transfer reaction of propagating radical ($P_n^\bullet$) with DBTTC may occur, while the benzyl radical liberated reacts with CTC comonomer complex formed from St and MAh to generate a new propagating radical ($P_m^\bullet$ or $P_l^\bullet$). A rapid equilibrium between chain radical and dormant chain containing trithiocarbonate group is established, thus, the copolymerization of St with MAh occurs via RAFT process. On the other hand, CTC comonomer has a large π-electron system, making the system highly polarizable as a whole, and the activation energy is therefore reduced [38,39]. As such, it can interact much more readily with an approaching radical of the correct polarity than an individual monomer St or MAh can [39]. Thus almost no homopolymerization of St occurs at this temperature in the presence of DBTTC. As a result, there is no SSS, SSM or MSS sequence structure unit observed in the DEPT ^{13}C NMR spectra, and a strictly alternating copolymer of St and MAh with narrow MWD and controlled molecular weight has been successfully prepared.

5. Conclusion

Controlled copolymerization of St with MAh has been successfully performed at 22 °C in the presence of DBTTC. The copolymerization of St with MAh followed by GPC measurement shows that the St/MAh copolymers with controlled molecular weight and narrow



Scheme 2.

MWD are successfully prepared. By analyzing the molar fraction of St and MAh in the copolymers obtained from ^{13}C spectra, the copolymers obtained are proved to be alternating in structure, and sequence information obtained from DEPT experiments also verifies the copolymers with MSM sequence.

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