

CONTROLLED RADICAL COPOLYMERIZATION OF STYRENE AND MALEIC ANHYDRIDE UNDER GAMMA RADIATION IN THE PRESENCE OF BENZYL DITHIOBENZOATE

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Abstract The copolymerization of styrene (St) with maleic anhydride (MAh) under gamma radiation at room temperature in the presence of benzyl dithiobenzoate (BDTB) was found to display “living” nature evidenced by constant concentration of chain radicals during the copolymerization, linear evolution of molecular weights with conversion and narrow molecular weight distribution ($M_w/M_n = 1.23\text{--}1.35$). The compositional analysis and the sequence structural information of the copolymers obtained from DEPT (Distortionless Enhancement by Polarization Transfer) experiments demonstrate that the copolymers obtained also possess strictly alternating structure.

Keywords Controlled radical polymerization, Alternating copolymer, Maleic anhydride, Styrene

INTRODUCTION

The well-defined alternating copolymers (such as St-*alt*-MAh, St-*alt*-Maleimide, *etc.*) exhibit unique properties such as superior thermal stabilities, fire resistance, photo-, X-ray and E-beam sensitivities, catalytic and chiroptical activities, and are extremely low band gap materials^[1, 2], they have been studied widely^[3, 4]. These copolymers prepared by conventional free radical methods show a strong compositional drift; the molar fraction of St unit in the polymer increases as the polymer chain size increases^[5], causing the copolymer to have a complex structure. Therefore, studies on the 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 value. Recently, the thermo-initiated free radical polymerization system has been extensively employed in the radical copolymerization of St and MAh. Li^[6–8], Hawker^[9] and Brouwer^[10] have used living free radical polymerization methods but they were all unable to obtain strictly alternating copolymer of St and MAh although these copolymerizations exhibit living characters.

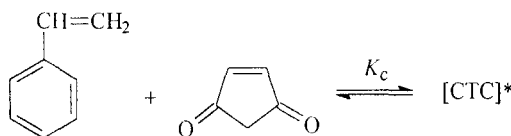
In the copolymerization of MAh with St, the equilibrium constant (K_c , see Scheme 1) determines the manner of copolymerization^[11]. When $K_c > 0.1$ L/mol, free radical alternating copolymerization can occur easily. In addition, K_c is determined by temperature, and decreases with the increase of temperature, ranging from 0.34 at 22 °C to 0 at 80 °C^[12, 13]. The thermally initiated and controlled free radical polymerization methods employed in the copolymerization were generally performed at high temperature, *e.g.*, 80 °C, and even higher. At this temperature range, St-MAh charge transfer complexes (CTC) cannot be formed, the copolymerization proceeds randomly rather than in alternating manner^[13]. Therefore, strictly alternating copolymers of St and MAh with well-controlled molecular weight and narrow molecular weight distribution may be prepared by performing the copolymerization of St and MAh at low temperature, *i.e.*, ambient temperature.

In our previous research^[14–16], we have studied the living free radical polymerization of various vinyl monomers in the presence of dibenzyl trithiocarbonate (DBTTC) under γ -ray irradiation at room temperature,

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and found that the weakest $\text{PhCH}_2\text{-S}$ bond in DBTTC underwent facile homolytic cleavage to form an active benzyl radical and a stable sulfur radical. The former can initiate the polymerization of monomer, while the latter has a strong affinity to propagating radical to form dormant polymer chain, leading to a living polymerization. Here, we study the copolymerization of St with MAh under γ -ray irradiation using benzyl dithiobenzoate (BDTB) as the initiator for two reasons. Firstly at room temperature, alternating copolymerization can occur easily (K_c around 0.34 L/mol). Secondly, the homopolymerization of St under γ -ray irradiation at low dose rate is very slow, thus the possibility of homopolymerization of St during the copolymerization of St and MAh under γ -ray irradiation in the presence of BDTB may be greatly reduced.



Scheme 1

EXPERIMENTS

Materials

St (AR, The First Shanghai Chemicals Co.) was distilled under reduced pressure. MAh (AR, The First Shanghai Chemicals Co.) was recrystallized from benzene. Tetrahydrofuran (AR, The First Shanghai Chemicals Co.) was distilled from a constant deep-green solution of sodium-benzophenone under nitrogen atmosphere, and other reagents were used as received.

Synthesis of BDTB

A typical procedure for preparing BDTB is as follows. Phenyl magnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g, 0.04 mol) in dry THF (30 mL). The solution was warmed to 40°C and carbon disulfide (3.05 g, 0.04 mol) was added over 15 min at 40°C. To the resultant dark brown solution, benzyl bromide (7.7 g, 0.036 mol) was added. The reaction temperature was raised to 50°C, and maintained at this temperature for further 45 min. Ice water (150 mL) was added, and the reaction mixture was extracted with diethyl ether (4 × 50 mL). The ether extracts were combined, and then washed with water (100 mL), brine (50 mL) and dried over anhydrous magnesium sulfate. After the removal of solvent under vacuum, BDTB was obtained as a red oil (3.55 g, 36.4% yield). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 4.60 (s, 2H); 7.30–7.60 (m, 8H) and 7.95 (m, 2H)

Radiation-induced Polymerization

The solution polymerization of St with MAh in THF was conducted in a sealed glass tube. A representative feed molar ratio was BDTB: St : MAh = 1:100:100, and the ratio of THF to monomer = 0.75 (V/W). After the mixture was degassed three times, the tube was sealed under vacuum, and then exposed to γ -rays from a ^{60}Co source at a dose rate of 80 Gy/min at room temperature. After the polymerization had proceeded for a prescribed time, polymer was obtained as a light red fine powder by precipitation from dichloromethane, and dried in a vacuum oven at 40°C. Conversion was calculated based on Eq. (1):

$$\text{Conversion (\%)} = [(W_p - W_{\text{BDTB}}) / (W_{\text{St}} + W_{\text{MAh}})] \times 100\% \quad (1)$$

Where W_p , W_{BDTB} , W_{St} and W_{MAh} are the weights of the polymer obtained, BDTB, St and MAh added, respectively.

Characterization

The polymerization kinetics was obtained by a gravimetric method. The molecular weight (MW) and molecular weight distribution (MWD) were measured at room temperature on a Waters 150C gel permeation chromatograph (GPC) equipped with three ultrastayragel columns (HR1, HR3, HR4), using monodispersed

polystyrenes as calibration standards. THF was used as eluent at a flow rate of 1 mL/min. ^1H and ^{13}C -NMR spectra of the polymers were performed on a Bruker-500 NMR spectrometer using acetone- d_6 as solvent and tetramethylsilane (TMS) as internal reference. Pulse recycle times were sufficiently long to allow recovery of all polymer carbon, and NOE (Nuclear Overhauser Effect) was removed using gated decoupling. DEPT (Distortionless Enhancement by Polarization Transfer) subspectra were generated using the following combination of the $\pi/4$ and $3\pi/4$ experiments: $\text{CH}_2 = (\pi/4) + 1.15 (3\pi/4)$.

RESULTS AND DISCUSSION

Living Polymerization Characters

The results and conditions for the copolymerization of MAh with St are listed in Table 1. The results show that MW increased with polymerization time, and copolymers with narrow MWD (1.23–1.35) were obtained. Typical GPC curves of the copolymers obtained are shown in Fig. 1. A symmetric peak and narrow MWD are evidence for living polymerization^[17].

Table 1. Controlled radical alternating copolymerization of MAh and St under γ irradiation in the presence of BDTB^a

Sample no.	St : MAh : BDTB (molar ratio)	Time (h)	Conv. (%) ^b	$M_n(\text{th})^c$ ($\times 10^{-3}$)	$M_n(\text{NMR})^d$ ($\times 10^{-3}$)	$M_n(\text{GPC})$ ($\times 10^{-3}$)	M_w/M_n	MAh (%) ^e
1	100:100:1	3	24.8	5.3	4.9	5.5	1.33	49.3
2	100:100:1	5.5	38.1	7.9	7.6	7.8	1.23	49.1
3	200:100:1	5.5	30.5	4.9	4.4	4.3	1.30	49.0
4	200:100:1	10	63.4	9.9	9.7	10.3	1.35	48.9

^a γ -Ray irradiation with 80 Gy/min at room temperature

^b Calculated based on Eq. (1)

^c Calculated based on Eq. (3)

^d Calculated based on Eq. (2)

^e Calculated based on Eq. (4)

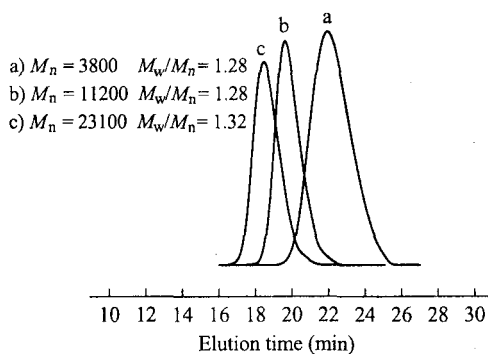


Fig. 1 GPC curves of poly(St-*alt*-MAh) prepared by γ -ray irradiated solution polymerization of St and MAh in THF using BDTB as initiator at room temperature. a, b and c are the samples obtained at different conversions $[\text{St}]:[\text{MAh}]:[\text{BDTB}] = 100:100:1$ (molar ratio); St: 2.08 g

Figure 2 shows the dependence of M_n and M_w/M_n on monomer conversion. A linear increase of M_n with conversion demonstrates that the MW of the copolymers obtained could be controlled by the molar ratio of monomer consumed to BDTB added or polymerization time. Plotting $\ln([M]_0/[M])$ against polymerization time affords a straight line (see Fig. 3), indicating that the copolymerization is of first-order kinetics, and radical concentration remains constant during the copolymerization.

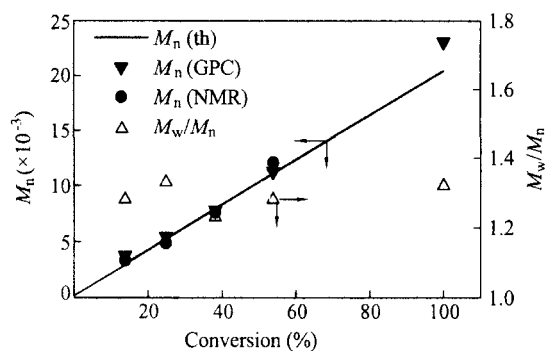


Fig. 2 M_n and M_w/M_n versus total conversion of two monomers' profiles for the copolymerization of MAh with St under γ -ray irradiation at room temperature [St]:[MAh]:[BDTB] = 100:100:1 (molar ratio); St: 2.08 g

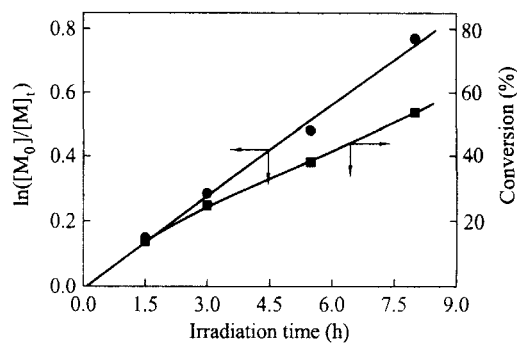


Fig. 3 Kinetics of the copolymerization of MAh with St under γ -ray irradiation at room temperature [St]:[MAh]:[BDTB] = 100:100:1 (molar ratio); St: 2.08 g

Figure 4 shows a typical ^1H -NMR spectrum of poly(St-*alt*-MAh) prepared by polymerization of St and MAh in THF under γ -ray irradiation using BDTB (see No. 1 in Table 1) as initiator. The signals at $\delta = 3.0$ – 3.8 , 6.0 – 7.7 , 7.95 correspond to the protons of two methine groups in MAh unit, the aromatic protons of the St unit and *ortho*-ArH of dithiobenzoate at the end of polymer chain, respectively. Assuming that each macromolecule contains a dithiobenzoate residue, M_n (NMR), can be calculated according to Eq. (1)

$$M_n(\text{NMR}) = [(2 \times I_{7.0}) / (5 \times I_{7.9})] \times M_{\text{St}} + (I_{3.4} / I_{7.9}) \times M_{\text{MAh}} + M_{\text{BDTB}} \quad (2)$$

Where, $I_{3.4}$, $I_{7.0}$ and $I_{7.9}$ are integral values of the peaks at $\delta = 3.0$ – 3.8 , 6.0 – 7.7 and 7.9 , respectively; M_{St} , M_{MAh} and M_{BDTB} are the MW of St, MAh and BDTB, respectively. With the same assumption in calculation of $M_n(\text{NMR})$, the theoretical number-average MW, $M_n(\text{th})$, could be calculated according to Eq. (3):

$$M_n(\text{th}) = [(W_{\text{St}} + W_{\text{MAh}}) / (W_{\text{BDTB}} / M_{\text{BDTB}})] \times \text{Conversion} + M_{\text{BDTB}} \quad (3)$$

Where, W_{St} , W_{MAh} and W_{BDTB} are the initial weights of St, MAh and BDTB, respectively. The agreement of $M_n(\text{NMR})$ with $M_n(\text{th})$ is a further evidence of the living nature for the copolymerization of St and MAh.

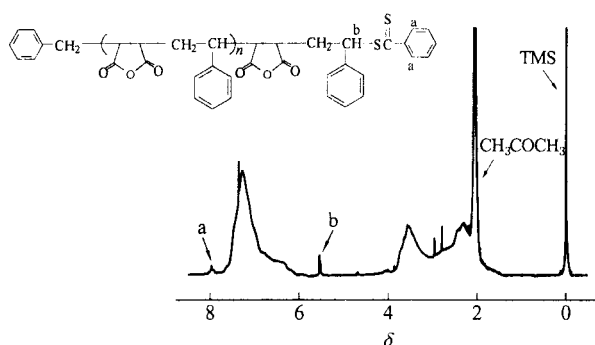


Fig. 4 ^1H -NMR spectrum of poly(St-*alt*-MAh) prepared by copolymerization of MAh and St under γ -ray irradiation at room temperature (No. 1 in Table 1)

Alternating Copolymerization

Generally, homopolymerization of St cannot be excluded during the copolymerization of St and MAh. In our experiment, it was found that the homopolymerization of St under irradiation at low dose rate is very slow^[14], thus the possibility of homopolymerization of St during the copolymerization of St and MAh under irradiation in

the presence of BDTB may be greatly reduced. On the other hand, at room temperature, CTC can be formed easily from St and MAh. CTC comonomer has a large π -electron system, making the system highly polarizable as a whole, and the activation energy is thus reduced^[18, 19]. Therefore, it can interact with an approaching radical more readily than an individual monomer St or MAh can. As a result, almost no homopolymerization of St occurs at this temperature in the presence of BDTB.

Generally, the methylene peak of PSt appears at $\delta = 1.16$ – 1.63 . In this range, there is almost no peak appearing in Fig. 4 due to the fact that all methylene groups are connected with MAh, and the peak of methylene protons moves to high chemical shift. The peaks at $\delta = 1.63$ – 3.0 correspond to the methylene and methine protons of St units in the copolymer. This implies that a strictly alternating copolymer of MAh and St was formed by the copolymerization of MAh and St at room temperature in the presence of BDTB under γ -irradiation. On the other hand, the compositions of the copolymers prepared from different feed ratios were calculated based on Eq. (4).

$$\text{MAh}\% = 5 \times I_{3.4} / (2 \times I_{7.0} + 5 \times I_{3.4}) \quad (4)$$

where MAh% is the molar percentage of MAh in the copolymer. All values of MAh% are close to 50% irrespective of the feed molar ratio of St/MAh = 1:1 or 2:1 (see Table 1). Therefore, an alternating structure of the copolymer was suggested.

In order to understand precisely the sequence distribution and strictly alternating characters of poly(MAh-*alt*-St) prepared, we use ^{13}C -NMR spectroscopy to analyze the St-MAh copolymers. Although the ^{13}C 500 MHz spectrum can not provide sufficient sequence information because the signals due to methine and methylene carbons are partially overlapped, sequence information can be obtained from DEPT experiments, by recording the spectra at $\pi/4$ and $3\pi/4$, and then combining them together^[20, 21]. For St-MAh copolymers, the chemical shift of the CH_2 in SSS, MSS, SSM and MSM sequences is different by around 5: SSS, $\delta = 42$ – 47 ; SSM, MSS, $\delta = 37$ – 42 ; MSM, $\delta = 33$ – 37 ^[18, 19]. Figure 5 shows the resulting combination of NMR spectra for the St-MAh copolymer (Table 1, No. 1). Only one broad signal at $\delta = 33$ – 38 is observed, indicating the existence of only the MSM sequence in the copolymer. The result shows the St-MAh copolymers prepared under γ -ray irradiation possess the strictly alternating sequence structure.

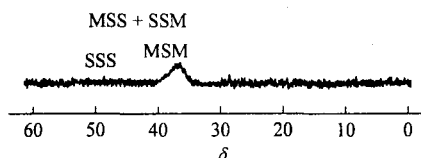


Fig. 5 Methylene subspectra of poly(MAh-*alt*-St) (No.1 in Table 1)

CONCLUSION

The copolymerization of St and MAh in the presence of BDTB under γ -ray irradiation at room temperature is of “living” nature, evidenced by constant concentration of chain radicals during the copolymerization, linear relationship between M_n and conversion, and narrow MWD ($M_w/M_n = 1.23$ – 1.35). The microstructure analysis indicates that the copolymer with strictly alternating structure (MSM) was produced via polymerization of St-MAh CTC.

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