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Controlled Radical Copolymerization of Styrene and the Macromonomer of PEO with a Methacryloyl End Group

Yunbing Wang and Junlian Huang*

The Open Laboratory of Molecular Engineering of Polymer, Department of Macromolecular Science, Fudan University, State Education Commission of China, Shanghai 200433, People's Republic of China

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ABSTRACT: The amphiphilic copolymer with uniform poly(ethylene oxide) as side chains was prepared by initiating of AIBN polymerization of methacryloyl-terminated PEO macromonomer (PEO_M) and styrene (St) in the presence of 4-hydroxyl-2,2,6,6-tetramethylpiperidine-1-oxy (HTEMPO). The copolymerization is controllable, the molecular weight of the copolymer and the conversion of the monomer increase with the polymerization time, and the distribution is rather narrow and is in the range 1.23−1.33. It was confirmed that the relative reactivity of PEO_M macromonomer decreases with an increase in its molecular weight, and the variation of concentration of HTEMPO and AIBN can affect the copolymerization greatly.

Introduction

Macromonomers, as a new kind of polymerizable intermediate, have been widely used in the molecular design of polymers.[1−4] A variety of comb polymers with uniform graft chain and different structure and properties, such as hard/soft,[5] crystalline/noncrystalline, hydrophilic/hydrophobic, and polar/inpolar[6] were prepared by it, which overcame the shortcoming of inhomogeneity of graft chains obtained by common methods. Therefore polymer scientists pay the greatest attention to the synthesis and polymerization of macromonomers, which has been taken as an independent research field called "macromolecule technology".

However the copolymerization of macromonomers with small monomers and macromonomers with macromonomers are generally carried out by a radical method, in which molecular weight and distribution of the copolymers are difficult to control. This is also one of the most difficult problems that needs to be resolved in polymer chemistry.

Nevertheless a lot of people have tried their best to find some methods to control the radical polymerization. It is a generally acceptable view that one of the main causes of uncontrollability of radical polymerization lies in the very high termination rate due to the high reactivity of common radicals. Therefore many nice papers have been published to postulate the idea of using reversible termination of growing polymer chain in a radical polymerization to give a pseudoliving polymer that is capable of stepwise chain growth. The molecular weight distribution of ca. 1.3 or less of polystyrene by using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)[7] and polymethyl methacrylate with a molecular weight distribution of ca. 1.4 or less formed by atom transfer radical polymerization[8] have been reported. However no successful example of controllable copolymerization of a small monomer with a macromonomer has been published up to now.

In this presentation, the copolymerization of macromonomer PEO with an acryloyl end group (M_1) with styrene (M_2) in the presence of HTEMPO is described; the copolymerization evidenced by us is controllable.

Experimental Section

Materials. EO, St, and *tert*-butyl alcohol were dried by calcium hydride and then distilled under N_2 before use. Methacrylic acid was dried with 3A molecular sieves and then distilled under reduced pressure; the fraction at 42 °C/6 mmHg was collected. PCl_3 (Shanghai Tingxin Chemical Factory) was distilled before use. AIBN was purified by recrystallization with absolute ethanol. Absolute $SnCl_4$ was prepared as in ref 9 by the reaction of $SnCl_4 \cdot 5H_2O$ (Rugao Chemical Reagent Factory, Jiangsu, China) with thionyl chloride. Methacryloyl chloride was obtained by the reaction of methacrylic acid with PCl_3 using $SnCl_4$ as catalyst,[10] and the product was dried with

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* To whom all correspondence should be addressed.

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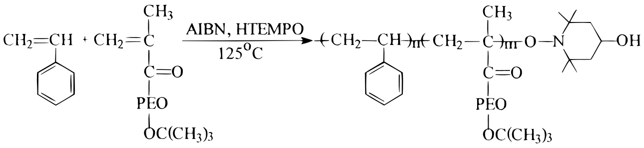
calcium hydride and distilled under reduced pressure to collect the fraction at 35 °C/70 mmHg. HTEMPO was prepared by oxidization of 4-hydroxy-2,2,6,6,-tetramethylpiperidine (Beijing ChaoYang HuaShan Auxiliary Factory) with hydrogen peroxide using sodium tungstate as catalyst:[11] mp 71−72 °C. All other solvents were purified by common methods.

Preparation of PEO$_M$. PEO$_M$ was prepared by initiating the *tert*-butyl alcohol potassium opening-polymerization of EO and then terminated by using excess methacryloyl chloride.[12] Characterization: IR(cm^{-1}) 1718 (C═O), 1636 (C═C), and 1114(−OCH$_2$CH$_2$); ^{1}H NMR (δ: ppm) 6.2 and 5.6 (CH$_2$═C), 4.4−3.0 (−CH$_2$CH$_2$O−), 2.0 (−CH$_3$ connected with double bond), and 1.2 (−CH$_3$ of *tert*-butyl). The Double bond content is about 93%, which is calculated by NMR using the peak areas ratio of the protons of double bond at 6.2−5.6 vs the protons of *tert*-butyl at 1.2 and then multiplying by a factor of $^9/_2$.

Copolymerization of PEO$_M$ with Styrene. A typical copolymerization



is described as follows: to a 100 mL ampule were added 10 mL of St (87.1 mmol), 3.18 g of PEO$_M$ (M_n 3400; 0.871 mmol), 26.0 mg of HTEMPO (0.151 mmol), 13.8 mg of AIBN (0.084 mmol) and 10 mL of xylene. After three cycles of freeze−pump−thaw, the ampule was sealed and placed into an oil bath at 90° C, then the temperature was quickly raised to 125 °C after 3 h. To control the reaction accurately, the system was frizzed with liquid nitrogen after the end of the copolymerization, and then the resulting product was dissolved in xylene and precipitated in petroleum ether. The copolymer could be purified by successive extraction of cold water and cyclohexane to remove the unreacted PEO$_M$ macromonomer and possible leftover polystyrene (PS) homopolymer. However we did not find any trace of PS homopolymer. Characterization: IR (cm^{-1}) 1720 (C═O), 1110 (−CH$_2$CH$_2$O−), and 1450, 750, and 700 (benzene ring); ^{1}H NMR (δ: ppm) 7.3−6.3 (benzene ring), 3.3−4.1 (−CH$_2$CH$_2$O−), and 1.2−2.4 (−CH$_2$−CH−).

Instruments. IR spectra were scanned on a Nicolet Magna-550 IR spectrometer. ^{1}H NMR was recorded on a Bruker MSL-300 spectrometer with TMS as internal standard and CDCl$_3$ as solvent. The number-average molecular weight of the copolymers was derived with a Shimadzu LC-3A gel permeation chromatograph (GPC) with computer using refractive index as detector: column length, 1.2 m; filler, cross-linking polystyrene gel (1250 mesh), injection volume, 1 mL (concentration: 0.1 g/mL); solvent and eluent, chloroform; flow rate, 1.0 mL/min; pump pressure, 40 kg/cm^2 (3.99 × 10^{6}Pa). Monodistribution PS was used as a standard sample.

Results and Discussion

Controllability of Copolymerization. Table 1 gives the data for the copolymerization in the presence of HTEMPO. The molecular weight of the copolymers increases with the polymerization time, which shows the basic properties of the “living” radical polymerization. It was found that in the preliminary stage the conversion increased rapidly with the time due to the higher monomer concentration, and then the increase of the conversion slowed, especially for the macromonomer PEO$_M$, where the increase of the conversion was much slower than that of the styrene. It may be caused by the high viscosity of the system in the later stage of the reaction leading to the difficulty of diffusing PEO$_M$. This phenomenon is more serious for PEO$_M$ than styrene.

Figure 1 gives the molecular weight−total conversion plot for copolymerization of PEO$_M$ and styrene. A nice linear relationship was obtained, which is quite different from the common radical copolymerization in which the molecular weight of the copolymer is independent of the conversion. We also found that in the entire course of copolymerization, the molecular weight distributions of all the copolymers are rather narrow. Therefore this kind of copolymerization is controllable.

Hawker[13] has reported that the copolymerization of MMA and St in the presence of TEMPO is a “living” free-radical polymerization, and we derived a similar conclusion from this system. However in this copolymerization system of PEO macromonomer and St, the molecular weight distribution is narrower that of the former case, so the PEO chain may play a role in the copolymerization.

We also found that the homopolymerization of PEO macromonomers in the presence of TEMPO is quite

Table 1. Copolymerization Data for PEO$_M$ (M$_1$) with St (M$_2$)[a]

reaction time (h)	M_n (×10^{-4})	M_w/M_n	% conversion M$_1$ (R_{M_1})	% conversion M$_2$ (R_{M_2})	R_t[b]	N_g[c]
2	0.4	1.32	5.5	5.0	5.1	0.3
4	1.7	1.32	25.8	22.6	23.4	1.4
8	2.3	1.24	36.8	33.2	34.1	1.8
12	3.0	1.28	47.9	44.8	45.6	2.3
16	3.5	1.28	57.1	51.5	53.0	2.7
24	3.9	1.29	62.6	57.4	58.7	3.0
36	4.3	1.29	63.7	61.8	62.3	3.2
48	4.5	1.33	64.4	64.2	64.2	3.3

[a] [St] = 4.36 mol/L, [PEO$_M$] = 4.36 × 10^{-2} mol/L, [HTEMPO] = 7.55 × 10^{-3} mol/L, and [AIBN] = 4.2 × 10^{-3} mol/L. [b] Total conversion [R_t = (weight of M$_1$ in copolymer + weight of M$_2$ in copolymer)/($W_{1,0}$ + $W_{2,0}$)] ($W_{1,0}$ and $W_{2,0}$ are the initial weights of M$_1$ and M$_2$, respectively). [c] Average side chain number (N_g = $M_n W_g/M_{M_1}$: M_n, molecular weight of copolymer; W_g, weight percent of M$_1$ in copolymer; M_{M_1}, molecular weight of M$_1$).

Table 2. Effect of HTEMPO Concentration on the Copolymerization[a]

[HTEMPO]/[AIBN]	M_n (×10^{-4})	M_w/M_n	R_{M_1} (%)	R_{M_2} (%)	R_t (%)	N_g
3.0/1	0.4	1.16	5.5	4.3	4.6	0.3
1.8/1	3.0	1.28	47.9	44.8	45.6	2.3
0.8/1	5.8	1.43	60.6	60.0	60.1	4.2
0/1	6.1	1.78	58.1	63.0	61.8	4.2

[a] [St] = 4.36 mol/L, [PEO$_M$] = 4.36 × 10^{-2} mol/L, [AIBN] = 4.2 × 10^{-3} mol/L, and time = 12 h. R_{M_1}, R_{M_2}, R_t, and N_g have the same meaning as in Table 1.

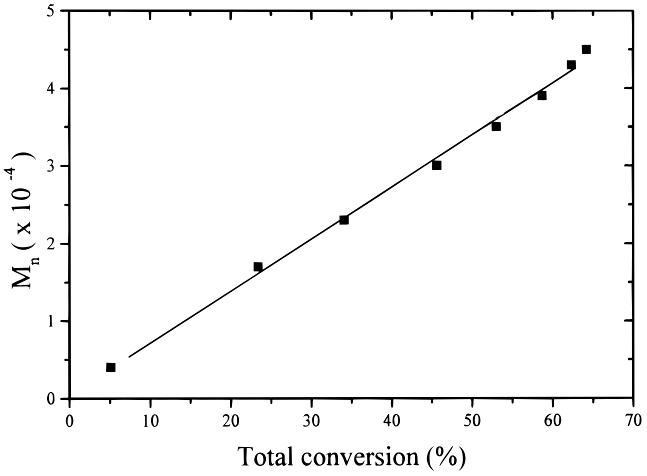


Figure 1. M_n as a function of total conversion.

Table 3. Effect of Simultaneous Change of HTEMPO and AIBN Concentrations on the Copolymerization for a Constant Ratio of [HTEMPO]/[AIBN][a]

[HTEMPO] (mol/L)	[AIBN] (mol/L)	reaction time (h)	M_n ($\times 10^{-4}$)	M_w/M_n	R_{M_1} (%)	R_{M_2} (%)	R_t (%)	N_g
1.51×10^{-2}	8.4×10^{-3}	8	0.8	1.24	21.2	15.1	16.6	0.7
		12	1.7	1.22	46.3	33.8	36.9	1.6
		16	2.5	1.23	52.4	41.9	44.5	2.1
		24	2.9	1.23	62.5	53.5	55.7	2.4
		36	3.5	1.29	63.1	56.9	58.5	2.7
7.55×10^{-3}	4.2×10^{-3}	8	2.3	1.24	36.8	33.2	34.1	1.8
		12	3.0	1.28	47.9	44.8	45.6	2.3
		16	3.5	1.28	57.1	51.5	53.0	2.7
		24	3.9	1.29	62.6	57.4	58.7	3.0
		36	4.3	1.29	63.7	61.8	62.3	3.2

[a] [St] = 4.36 mol/L, and [PEO$_M$] = 4.36×10^{-2} mol/L. R_{M_1}, R_{M_2}, R_t, and N_g have the same meaning as in Table 1.

difficult to carry out; only a little homopolymer was obtained after 24 h at 125 °C, and the molecular weight distribution is greater than 1.5 and the molecular weight is independent of the polymerization time. Therefore the homopolymerization of PEO macromonomer with methacryloyl end group, as for MMA, is not a "living" process.

Effect of the Concentration of HTEMPO on the Copolymerization. Table 2 shows the data which illustrated the influence of the HTEMPO concentration on copolymerization in the conditions of constant reaction time and constant concentration of PEO$_M$, St, and AIBN. We found that in the higher concentrations of HTEMPO, the molecular weight of the copolymer is rather low and the distribution is much narrower. On the other hand, for the lower HTEMPO concentration, the molecular weight of the copolymer is higher and the distribution is widened.

It is well-known in the radical polymerization in the presence of HTEMPO following equilibrium should occur:[14]

$$P^\bullet + \text{HTEMPO}^\bullet \rightleftharpoons P{-}\text{HTEMPO} \qquad (1)$$

Here P$^\bullet$ is the propagation macromolecule active species, HTEMPO$^\bullet$ is the free radical, and P−HTEMPO represents the dormant compound. For the low concentration of HTEMPO, it is not possible for the HTEMPO to form the dormant compound with all P$^\bullet$, as excessive propagation reactive species can still initiate the copolymerization of PEO$_M$ and St with the common radical mechanism, so the distribution is widened and the molecular weight is high. When the concentration of HTEMPO increases, the exchange rate between radicals and dormant compound rises; the propagation of PEO$_M$ and St is restricted by this process, so the distribution is narrow. As for the molecular weight in this case, which could be expressed by $X_n = [M]_t/[P{-}\text{HTEMPO}]$[15] ($X_n$, number average polymerization degree; $[M]_t$, total concentration of PEO$_M$ and St; [P−HTEMPO], concentration of dormant compound) decreases with the increase of HTEMPO concentration due to the increase of the dormant compound concentration. We also found that even the ratio of [HTEMPO]/[AIBN] was kept constant, if the [HTEMPO] and [AIBN] increase or decrease in the same multiples simultaneously, which also exerts an effect on the copolymerization. Table 3 gives the experimental results, from which it could be derived that when the [HTEMPO] and [AIBN] increase in the same multiples, the molecular weight of the copolymer and the total conversion of PEO$_M$ and St obviously decreased in the primary stage of the reaction and the molecular weight distribution is narrower than before, which are shown in Table 1 and Figure 2. If the ratio of the concentration of AIBN and HTEMPO preserves the constant, for example, [HTEMPO]/[AIBN] = 1.8/1, and their concentrations are increased in the same multiples, the concentration of P$^\bullet$ in eq 1 also increased, so the molecular weight of copolymer decreases because the concentration of PEO$_M$ and St is still unchangeable in this case. On the other hand when the [HTEMPO] and [AIBN] increase in the same multiples, the [HTEMPO$^\bullet$] should increase much more than P$^\bullet$ due to a higher [HTEMPO] in the initial ratio, so the exchange rate in eq 1 is much faster than before, the copolymerization is controlled more strictly, and the distribution is much narrower.

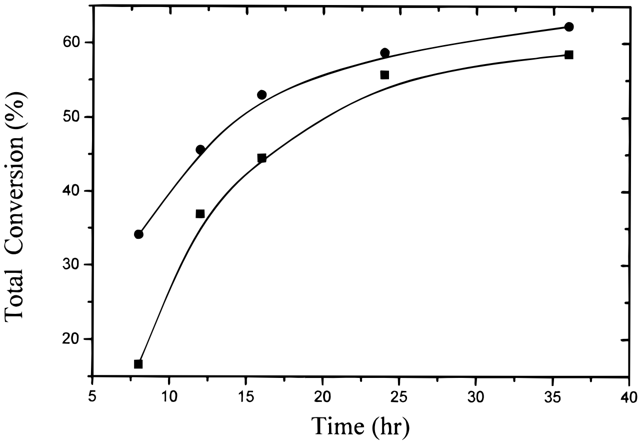


Figure 2. Total conversion as a function of polymerization time. [HTEMPO]/[AIBN] = 1.8:1: (■) [HTEMPO], 1.51×10^{-2} mol/L, [AIBN] = 0.84×10^{-2} mol/L; (●) [HTEMPO] = 7.55×10^{-3}mol/L, [AIBN] = 4.20×10^{-3}mol/L.

Effect of Molecular Weight of PEO$_M$ on Copolymerization. Table 4 shows the copolymerization data in the different PEO$_M$. The effect of molecular weight of PEO$_M$ on copolymerization is remarkable; the N_g, R_{M_1}, R_{M_2}, and R_t values are decreased with an increase in the molecular weight of PEO$_M$.

When the PEO$_M$ with different molecular weights copolymerized with St, the monomer reactivity ratios could be derived from the Mayo−Lewis formula.[16] If St(M$_2$) is in great excess, that is $[M_2] \gg [M_1]$, the Mayo−Lewis equation, eq 2, could be rewritten as eq 3 (here

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (2)$$

$$\frac{d[M_1]}{[M_1]} = \frac{1}{r_2}\,\frac{d[M_2]}{[M_2]} \qquad (3)$$

Table 4. Effect of PEO_M Molecular Weight on the Copolymerization[a]

MW of PEO_M ($\times 10^{-3}$)	reaction time (h)	M_n ($\times 10^{-4}$)	M_w/M_n	R_{M_1} (%)	R_{M_2} (%)	R_t (%)	N_g
6.2	4	0.9	1.35	11.1	11.0	11.0	0.6
	8	2.6	1.24	30.5	30.0	30.2	1.6
	12	3.6	1.24	40.6	40.0	40.2	2.2
	16	4.0	1.25	45.6	45.1	45.3	2.4
	24	4.3	1.28	52.5	52.0	52.2	2.6
	36	4.8	1.30	58.5	58.4	58.4	2.9
	48	5.0	1.32	61.4	62.0	61.8	3.0
3.4	4	1.7	1.32	25.8	22.6	23.4	1.4
	8	2.3	1.24	36.8	33.2	34.1	1.8
	12	3.0	1.28	47.9	44.8	45.6	2.3
	16	3.5	1.28	57.1	51.5	53.0	2.7
	24	3.9	1.29	62.6	57.4	58.7	3.0
	36	4.3	1.29	63.7	61.8	62.3	3.2
	48	4.5	1.32	64.4	64.2	64.2	3.3

[a] $[St] = 4.36$ mol/L, $[PEO_M] = 4.36 \times 10^{-2}$ mol/L, $[HTEMPO] = 7.55 \times 10^{-3}$ mol/L, and $[AIBN] = 4.20 \times 10^{-3}$ mol/L. R_{M_1}, R_{M_2}, R_t, and N_g have the same meaning as in Table 1.

$d[M_1]$ and $d[M_2]$ are the instant compositions of M_1 and M_2 in the copolymer, $[M_1]$ and $[M_2]$ are the concentrations of M_1 and M_2 in the system at a given time, and r_1 and r_2 are the monomer reactivity ratio of M_1 and M_2 respectively). Then, when both sides are integrated from time 0 to time t, the formula in (4) is obtained.

$$\ln\frac{[M_1]_t}{[M_1]_0} = \frac{1}{r_2}\ln\frac{[M_2]_t}{[M_2]_0} \tag{4}$$

(here $[M_1]_0$ and $[M_2]_0$ are the initial concentrations and $[M_1]_t$ and $[M_2]_t$ are the concentrations at time t.) If the conversions of M_1 and M_2 at time t are defined as R_{M1} and R_{M2}, respectively, (4) could be rewritten again as (5), and then the plot shown in Figure 3 could be derived

$$\ln(1 - R_{M_1}) = \frac{1}{r_2}\ln(1 - R_{M_2}) \tag{5}$$

by $\ln(1 - R_{M_1})$ vs $\ln(1 - R_{M_2})$; the slope is $1/r_2$. For the PEO_M with molecular weight 3400, $1/r_2$ is 1.16, and for 6200 PEO_M, $1/r_2$ is 1.01. Therefore the PEO_M with the low molecular weight is more reactive than PEO_M with the high molecular weight in the copolymerization because of the more difficult diffusion of the latter than the former in the system.

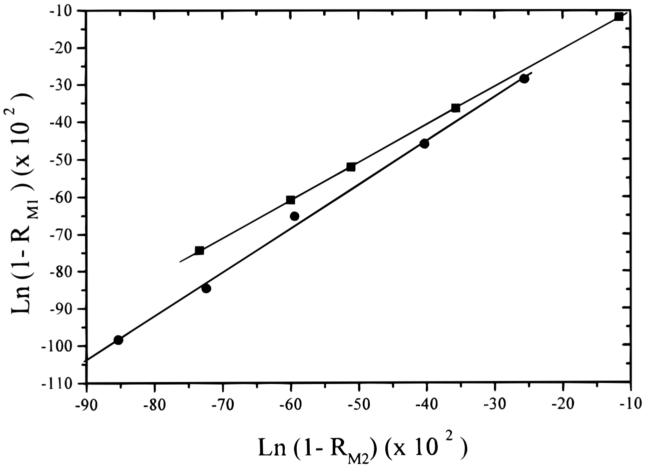


Figure 3. Plot of $\ln(1 - R_{M1})$ as a function of $\ln(1 - R_{M2})$: (■) M_n of PEO_M, 6200; (●) M_n of PEO_{M2}, 3400.

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