

# Synthesis of Two-End-Functionalized Copolymer of Styrene and Methyl Methacrylate Via Living Radical Polymerization

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**ABSTRACT:** The random copolymers (HO-P(St-*r*-MMA)-COOH) of styrene (St) and methyl methacrylate (MMA) with hydroxyl group at one end and carboxyl group at another end were synthesized by nitroxide-mediated living radical polymerization initiated by 4,4'-azobis(4-cyanovaleic acid) (ACVA) and 4-hydroxyl-2,2,6,6-tetramethylpiperidineoxyl (TEMPO-OH). The experimental results have shown that all synthesized copolymers have narrow molecular weight distribution. The conversion of monomers and the molecular weight of copolymer increase with polymerization time. Thus, a copolymerization mechanism containing living radical polymerization is suggested. The use of this method permits the copolymer with two functional

chain ends and controllable molecular weight as well as low molecular weight distribution. X-ray photoelectron spectroscopy result shows that the synthesized copolymers can be tethered on the surface of silicon wafer through the reaction between the hydroxyl end of the copolymer and native oxide layer on the wafer. In addition, an organic/inorganic hybrid surface has achieved by treating copolymer tethered Si-substrates with SiCl<sub>4</sub> vapor. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3118–3122, 2006

**Key words:** nitroxide-mediated living radical polymerization; copolymers of styrene and methyl methacrylate; chain end functionalization

## INTRODUCTION

Accurate control of polymerization processes to give well-defined molecular weight, narrow polydispersity, and end-functionalized polymers has always been a highlight of polymer chemistry since these end-functionalized polymers can produce various types of block copolymers,<sup>1</sup> form networks,<sup>2</sup> and anchor to a solid surface to adjust the surface characteristics of a substrate.<sup>3</sup> Until recently, ionic polymerizations were the only "living" techniques available that efficiently controlled the structure and architecture of vinyl polymers. Although these techniques ensure low polydispersity materials and controlled molecular weight, they are not useful for the polymerization of a wide range of functionalized vinylic monomers. This limitation is due to the incompatibility of the growing polymer chain end with numerous functional groups and certain monomer families. In addition, these polymerization techniques require stringent reaction conditions including the use of ultrapure reagents and the total

exclusion of water and oxygen. Free-radical polymerization requires less rigorous synthetic condition, and in some cases, can offer end-functionalized polymers.<sup>4</sup> However, the drawback of free-radical processes is that they cannot accurately control the molecular weight, polydispersity of products, and more important, the number of chain ends.<sup>5</sup>

In 1993, Georges et al. first reported the pseudo-living free radical polymerization in the synthesis of polystyrene (PS) by nitroxide-mediated radical polymerization.<sup>6</sup> Then, a number of homopolymers, random copolymers, and block copolymers with narrow polydispersity were prepared by a living free radical polymerization technique by using a nitroxide initiator based on 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and benzoyl peroxide (BPO).<sup>7–9</sup> However, the synthesis of random copolymers of styrene and methyl methacrylate (MMA) with narrow polydispersity, controllable molecular weight and two functional end groups has not been reported.

In this article, we report the direct synthesis of hydroxyl- and carboxyl-terminated copolymers of styrene (St) and MMA with low polydispersity by nitroxide-mediated radical polymerization initiated by TEMPO-OH and ACVA. Also, the end-functional copolymers can modify silicon surface properties by grafting to the wafer directly.

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## EXPERIMENTAL

### Materials

Styrene (St, Shanghai 1st Factory of Chemicals), MMA (Shanghai 1st Factory of Chemicals), calcium hydride (Shanghai 1st Factory of Chemicals), 4-hydroxyl-2,2,6,6-tetramethyl-piperidine (Beijing Huashan Auxiliary Factory), 4,4'-azobis(4-cyanovaleric acid) (ACVA, Acros), 30% hydrogen peroxide (Shanghai Chemistry and Chemical Engineering Factory, People's Republic of China), sodium tungstate (Guangdong Liushan Chemistry and Chemical Engineering Factory, People's Republic of China), ethylenediaminetetraacetic acid (Chemical Factory, Jiangsu Huakang Science and Technology Company, People's Republic of China),  $\text{SiCl}_4$  (Aldrich) were purchased. St and MMA were dried with calcium hydride and distilled under reduced pressure before use. TEMPO-OH was prepared by oxidization of 4-hydroxyl-2,2,6,6-tetramethyl piperidine with 30% hydrogen peroxide using sodium tungstate and ethylenediaminetetraacetic acid as catalyst.<sup>10</sup> All unspecified chemicals were obtained from the Shanghai Chemical Reagent, Shanghai, People's Republic of China.

### Synthesis

Copolymers of styrene and MMA with hydroxyl group at one end and carboxyl group at another end were synthesized. The typical synthesis procedure is described as follows: after a 25 mL polymerization tube was treated with three freeze-pump-thaw cycles, 5.20 g St (0.05 mol), 5.01 g MMA (0.05 mol), 56.0 mg ACVA (0.2 mmol), 67.4 mg (0.36 mmol) TEMPO-OH and a magnetic stirrer were added into the tube and sealed with flame under vacuum, then the tube was put into an airtight steel chamber filled with oil. The chamber was placed into an oil bath at 100°C for 2 h to allow the decomposition of ACVA, and then was heated up to 130°C. The polymerization was stopped by quenching the reaction system to -20°C. The copolymer was purified through dissolving it in toluene, and precipitating in ethanol. This purification procedure was repeated three times. Finally, the obtained copolymers of styrene and MMA with hydroxyl at one end and carboxyl at another end were dried in a vacuum oven and the copolymer was named as HO-P(St-*r*-MMA)-COOH.

### Grafting reaction on silicon wafer

The hydroxyl group in copolymer end was used to graft copolymer to the surface of silicon wafer covered with native oxide layer based on the method reported.<sup>11</sup> Briefly, the silicon wafers were cleaned in advance by immersing them in a solution of sulfuric acid (98%) and hydrogen peroxide (30%) (7:3 ratio

by volume) at 90°C for 2 h, then immersing in distilled water for several times.<sup>12</sup> The thin copolymer film of HO-P(St-*r*-MMA)-COOH on silicon wafer was prepared by spin-coating. The copolymer-coated substrates were heated under vacuum at 125°C for 48 h, to permit the hydroxyl and carboxyl end groups diffuse to and react with the native oxide layer. Then, the substrate were taken out of the oven and cooled to room temperature. The ungrafted copolymers were removed by repeatedly washing copolymer-coated substrates with toluene. AFM observation was performed before and after the grafting procedure.

### Reaction with $\text{SiCl}_4$ vapor

Both the copolymer-grafted wafers and bare silicon wafers were immersed in pure water for 2 h prior to the reaction with  $\text{SiCl}_4$  vapor.  $\text{SiCl}_4$  was cooled to -46°C and its vapor was transferred to the reaction vessel containing a substrate. The reaction was performed for 1 min at 25°C and under 75 mmHg.<sup>13</sup>

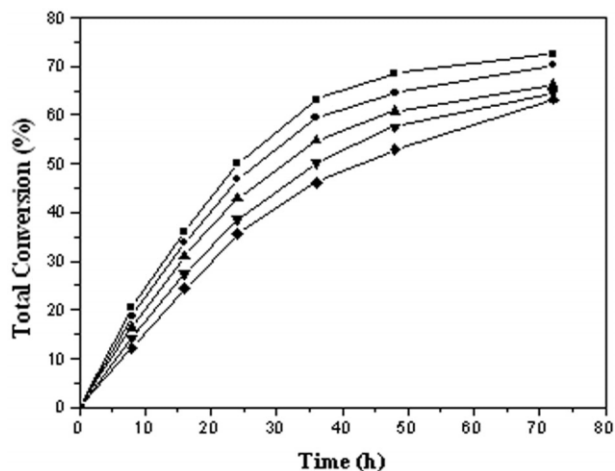
### Measurements

The conversion of copolymerization was determined by FTIR spectra measurement on Nicolet 170SX FTIR spectrometer. From IR spectra, the conversion of total monomer at different polymerization time can be calculated based on the variation of adsorption intensity of vinyl group at 1630  $\text{cm}^{-1}$ .  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) measurement was performed on a Bruker MSL-300 spectrometer with  $\text{CDCl}_3$  as the solvent. The molecular weight ( $M_n$ ,  $M_w$ ) and distribution index ( $M_w/M_n$ ) were determined with a Waters 244 gel permeation chromatograph employed with ultraviolet detector using tetrahydrofuran as an elution solvent. Monodisperse PS samples were used as standards for calibration. X-ray photoelectron spectroscopy (XPS) measurement was carried out on an ESCALab MK II (V. G. Scientific, UK) equipped with Mg  $\text{K}_\alpha$  radiation source at 12 kV and 20 mA at the anode. AFM images were obtained by SPI3800N scanning force microscopy (Seiko Instruments) in the tapping mode. The SI-DF-20 cantilevers (Seiko Instruments) were used (spring constant is about 12 N/m, resonance frequency ranging from 90 to 150 kHz).

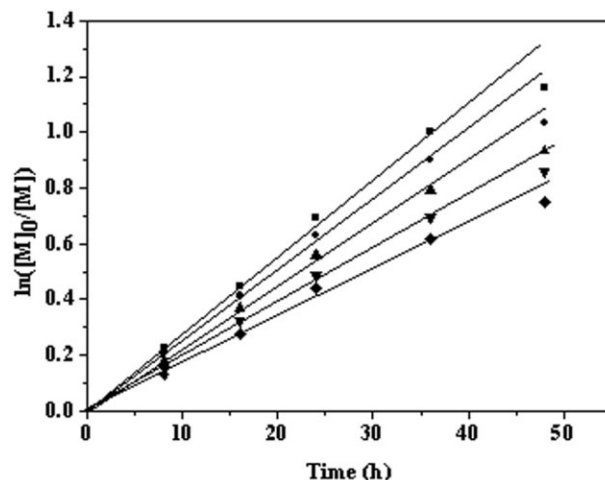
## RESULTS AND DISCUSSION

### Synthesis of HO-P(St-*r*-MMA)-COOH

To investigate the copolymerization of St and MMA initiated by ACVA and TEMPO-OH, the FTIR spectra of the samples at various polymerization times were measured and the monomer conversion was monitored. Figure 1 gives the plot of conversion versus



**Figure 1** Total conversion as a function of polymerization time in different feed ratios of St to MMA. (■), 9/1; (●), 7/3; (▲), 5/5; (▼), 3/7; (◆): 1/9.



**Figure 2**  $\ln([M]_0/[M])$  as a function of polymerization time in different feed ratios of St to MMA. (■), 9/1; (●), 7/3; (▲), 5/5; (▼), 3/7; (◆), 1/9.

time of the copolymerization. The molar ratio of TEMPO to ACVA is 1.8 : 1.<sup>14,15</sup> It shows that the conversion of monomers increases with polymerization time in different feed ratios of St to MMA. In the initial stage, the conversion increased rapidly with the polymerization time because of the higher monomer concentration and lower viscosity of the reaction system, the increased rates of conversion then slows down with the increase in viscosity and the decrease in monomer concentration. In addition, with a decrease in feed ratios of St to MMA, the rates of copolymerization decrease.

Table I summarizes the data related to the total conversion of monomers, molecular weights and poly-

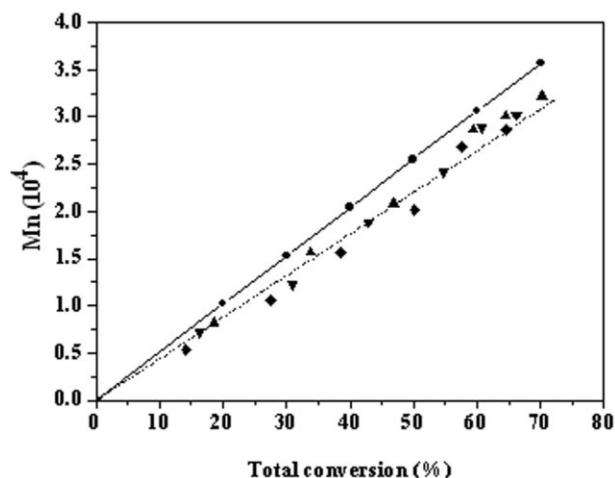
**TABLE I**  
Copolymerization Data of St and MMA

Reaction time (h)	Total conversion (%)	$M_n$ ( $10^{-4}$ )	$M_w$ ( $10^{-4}$ )	$M_w/M_n$	St/MMA (feed mole ratio)
8	18.6	0.95	1.06	1.12	7/3
16	33.8	1.72	1.98	1.15	
24	46.8	2.39	2.82	1.18	
36	59.4	3.03	3.67	1.20	
48	64.5	3.29	3.85	1.17	
72	70.2	3.58	4.33	1.21	
8	16.4	0.83	0.94	1.13	5/5
16	30.9	1.58	1.85	1.17	
24	42.9	2.19	2.74	1.25	
36	54.7	2.79	3.29	1.18	
48	60.8	3.09	3.77	1.22	
72	66.2	3.38	4.33	1.28	
8	14.2	0.72	0.83	1.15	3/7
16	27.5	1.40	1.64	1.17	
24	38.6	1.97	2.49	1.26	
36	50.2	2.56	3.10	1.21	
48	57.6	2.93	3.72	1.27	
72	64.5	3.28	4.24	1.29	

dispersities of samples obtained using TEMPO-OH-mediated living radical polymerization at different reaction time. As expected, the polydispersity was in the range of 1.1 to 1.3, which suggested a mechanism of living radical polymerization. Also, the molecular weights of copolymers somewhat increased with increasing styrene concentration in system.

Figure 2 shows  $\ln([M]_0/[M])$  as a function of polymerization time for the copolymerization system with the feed molar ratios of St and MMA of 9/1, 7/3, 5/5, 3/7, and 1/9, respectively. The linear dependence of  $\ln([M]_0/[M])$  on polymerization time suggests first-order kinetics with respect to the total monomer concentration, which is according with Baumann and Schmidt-Naake's result.<sup>16</sup> Comparing the slope of these lines, it is obvious that the polymerization rate of MMA is lower than that of St, and the copolymerization rate of system increases with the increase of St concentration.

Figure 3 gives the plot of number average molecular weight ( $M_n$ ) versus conversion for polymerization. The theoretical values are calculated based on the assumption that the number of growing chains equals to the concentration of TEMPO-OH and the equation:<sup>16</sup>  $M_n = 0.01C \times [M] \times M_M/[PN]$ , where  $C$  is the conversion [%],  $[M]$  the monomer concentration,  $M_M$  the molecular weight of the monomer, and  $[PN]$  the TEMPO-OH concentration. Obviously, the molecular weight of the copolymers increases with the conversion. And, a nice linear relationship between  $M_n$  and conversion is observed, exhibiting the basic character of living radical polymerization. The theoretical values are somewhat larger than the experiment values by the reason of a small quantity of monomer taking a free radical polymerization mechanism. Comparing the similar polymerization initiated by TEMPO and

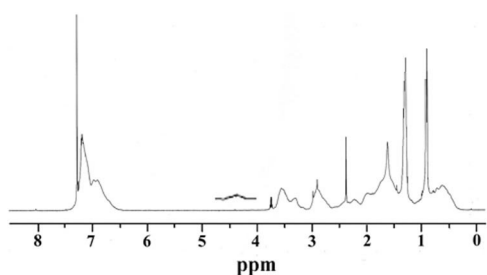


**Figure 3**  $M_n$  as a function of total conversion at different feed ratios of St to MMA. ( $\blacktriangle$ ), 7/3; ( $\blacktriangledown$ ), 5/5; ( $\blacklozenge$ ), 3/7; ( $\bullet$ ) and solid line: theoretical values.

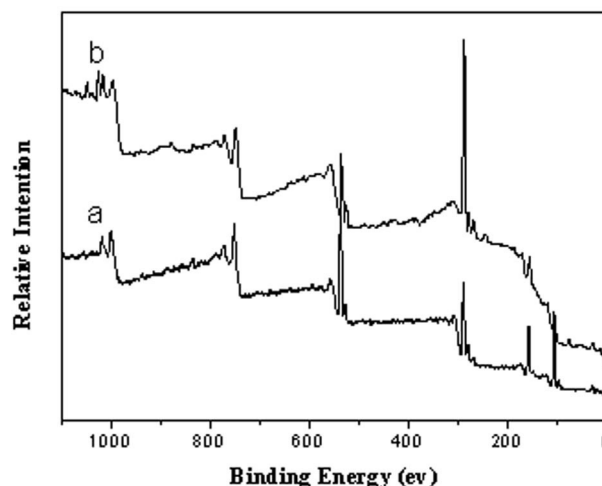
BPO system,<sup>17,18</sup> although a much longer reaction time is needed, a high molecular weight and low polydispersity copolymers with hydroxy and carboxyl end were get easily in our system.

#### $^1\text{H}$ NMR spectrum of copolymer

Figure 4 shows the typical  $^1\text{H}$  NMR spectra of copolymer with a feed molar ratio of 7/3 (St/MMA) and number-average molecular weight of 23.9 kDa. As seen in Figure 4, the broad peaks near  $\delta 6.9$  and  $\delta 7.2$  are ascribed to the aromatic protons of PS;<sup>19</sup> the small peak near  $\delta 4.4$  is attributed to the methine proton in neighborhood to the TEMPO-OH group.<sup>20</sup> The peak near  $\delta 3.6$  belongs to the methoxyl protons of PMMA. The peak near  $\delta 1.9$ – $2.3$  is attributed to the methylene protons of PMMA, while the sharp peaks near  $\delta 0.9$  and  $\delta 1.3$  correspond mainly to the methylene protons from PS and the  $\alpha$ -methyl protons of PMMA. These results indicate that the chemical structure of synthesized copolymer is consistent with that of the random copolymer of St and MMA.



**Figure 4**  $^1\text{H}$  NMR spectra of copolymer of styrene and methyl methacrylate with feed ratio of 7/3 and  $M_n$  23.9 kg/mol.

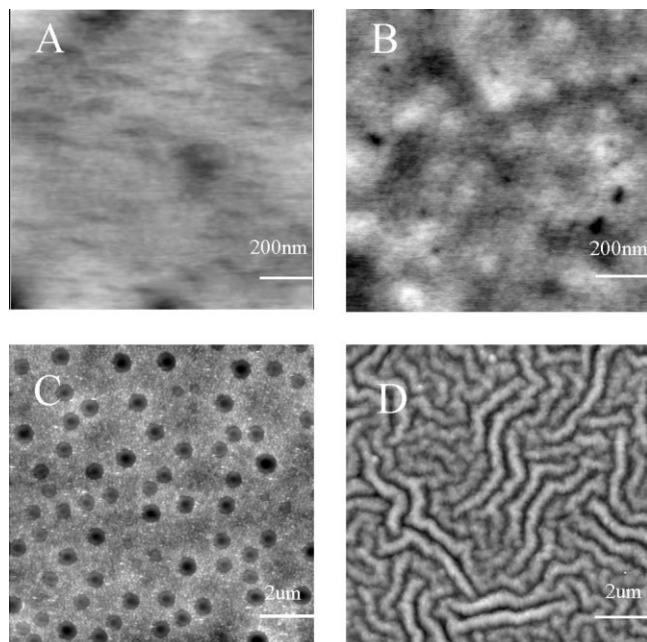


**Figure 5** The XPS spectrum of bare silicon substrate (a) and copolymer (St/MMA feed ratio 5/5,  $M_n$  27.9 kDa) grafted substrate (b).

#### Grafted copolymer of St and MMA on silicon substrate

To investigate the grafting ability of the copolymer with carboxyl and hydroxyl end groups on silicon wafer, the solution of copolymer in toluene was spin coated onto treated silicon wafers. The grafting reaction was carried out in a vacuum oven at 125°C for 48 h. Unattached copolymer was removed by rinsing with toluene for six times. Figure 5 shows the XPS spectra of the copolymer (St/MMA feed ratio 5/5,  $M_n$  27.9 kDa) grafted to silicon substrate recorded at the emission angle of 45°. The analytical depth (about 6.8 nm) was calculated by using the value of the inelastic mean free path evaluated from Ashley's equation.<sup>21</sup> From Figure 5, it can be seen that the characteristic peaks corresponding to  $\text{O}_{1s}$  (532 eV),  $\text{C}_{1s}$  (285 eV) are detected for copolymer-grafted substrate. Compared to the XPS spectrum of bare silicon substrate, the relative intensity of  $\text{C}_{1s}$  peak is much stronger, the ratio of  $\text{C}_{1s}$  to  $\text{O}_{1s}$  greatly increases from 0.52 to 3.35, and the  $\text{Si}_{2s}$  and  $\text{Si}_{1s}$  peaks at the binding energies of 150 eV and 100 eV, respectively, almost disappear. It is obvious that the hydroxyl ended copolymer has been chemically attached to the silicon wafer and the grafted layer densely covered the silicon substrate as we demonstrated in TEMPO-OH terminated poly(styrene-*co*-4-vinyl pyridine) system.<sup>11</sup>

Figure 6 gives the typical morphologies, obtained by AFM, of bare silicon wafers, copolymer-grafted (St/MMA feed ratio 5/5,  $M_n$  27.9 kDa) wafers, and the wafers (bare and grafted) treated with  $\text{SiCl}_4$  vapor. Comparing the AFM images of A and B, the roughness slightly increases after the copolymer has been attached to the silicon wafers, which reveals the grafted layer densely and homogeneously covered the silicon substrate. Although the grafted and ungrafted



**Figure 6** The AFM image of the substrate before and after the reaction with  $\text{SiCl}_4$  vapor. (A), (C) silicon substrate, (B), (D) copolymer grafted substrate.

wafers have similar uniform surface [Fig. 6(A, B)], they show totally different surface properties that led to different morphologies after they were treated with  $\text{SiCl}_4$  vapor [Fig. 6(C, D)]. We believe this phenomenon is related to the different hydrophilicity between bare silicon wafers and copolymer-grafted wafers. Bare silicon substrate is more hydrophilic than copolymer-grafted one because plentiful Si—OH bonding with  $\text{H}_2\text{O}$ , and a large number of microdrop water remained at the surface. The reaction between  $\text{SiCl}_4$  vapor and the residual water on surface is exothermic. The reaction heat accelerates the residual water drop evaporation, which leads to the convection with the deposition of  $\text{SiCl}_4$  vapor. This convection process causes the deposition follow the template function of microdrop water, which induces the formation of “hole” morphologies [Fig. 6(C)] after the deposition. When  $\text{SiCl}_4$  vapor deposits on copolymer grafted substrate, because few water drops remained on the surface, the main deposition process is the condensing of water together with  $\text{SiCl}_4$  vapor. This process is somewhat like sediment growth on the surface, which cause the “stripe” morphologies [Fig. 6(D)] after the deposition. This AFM observation result demonstrates graphically that the surface property of substrate can be manipulated by grafting end-functionalized copolymers to target substrates and an organic/inorganic hybrid surface can be obtained.

## CONCLUSIONS

The random copolymerization of St and MMA initiated by ACVA and TEMPO-OH in bulk was investigated. It shows that two-end-functionalized copolymers of styrene and MMA, with hydroxyl group at one end and carboxyl group at another end, can be obtained by nitroxide-mediated radical polymerization. The polymerization shows a mechanism of living radical polymerization. The synthesized copolymers have controllable molecular weight and narrow molecular weight distribution. XPS and AFM results show that the copolymers can be tethered on the silicon wafers to modify the surface properties.

Although we have focused on the synthesis of two-end-functionalized copolymers in this paper, the potential application of this method is broader; for example, these copolymers can initiate the ring-opening polymerization of caprolactone and lactide. Thus, the synthesis of the block copolymers becomes simple.

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