Synthesis of Well-Defined Multigraft Copolymers by a Two-Step Living Radical Polymerization with Nitroxyl-Functionalized Poly(methyl methacrylate)

F. J. HUA,1 B. LIU,2 C. P. HU,2 Y. L. YANG3

1Max-Plank Institute of Polymer Research, Ackermannweg 10, Mainz D-55128, Germany
2Institute of Material Science and Technology, the East China University of Science and Technology, Shanghai, 200237
3The Key Laboratory of Molecular Engineering of Polymer, Fudan University, Shanghai 200433, China

Received 16 March 2001; accepted 8 March 2002

ABSTRACT: Novel multigraft copolymers of poly(methyl methacrylate-graft-polystyrene) (PMMA-g-PS) in which the number of graft PS side chains was varied were prepared by a subsequent two-step living radical copolymerization approach. A polymerizable 4-vinylbezenyl 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) monomer (STEMPO), which functioned as both a monomer and a radical trapper, was placed in a low-temperature atom transfer radical polymerization (60°C) process of methyl methacrylate with ethyl 2-bromopronionate (EPNBr) as an initiator to gain ethyl pronionate-capped prepolymers with TEMPO moieties, PMMA-STEMPOs. The number of TEMPO moieties grafted on the PMMA backbone could be designed by varying STEMPO/EPNBr, for example, the ratios of 1/2, 2/3, or 3/4 gained one, two, or three graft TEMPO moieties, respectively. The resulting prepolymers either as a macromolecular initiator or a trapper copolymerized with styrene in the control of stable free-radical polymerization at an elevated temperature (120 °C), producing the corresponding multigraft copolymers, PMMA-g-PSs. The nitroxyl-functionalized PMMA prepolymers produced a relatively high initiation efficiency (>0.8) as a result of the sterohindrance and slow diffusion of TEMPO moieties connected on the long PMMA backbone. The polymerization kinetics in two processes showed a living radical polymerization characteristic. The molecular structures of these prepolymers and graft copolymers were well characterized by combining Fourier transform infrared spectroscopy, gel permeation chromatography, chemical element analysis, and 1H NMR. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 1876–1884, 2002

Keywords: living polymerization; graft copolymers; synthesis; kinetics (polym.)

INTRODUCTION

Radical polymerization with living characteristics has attracted much attention in the polymer synthesis field, considering they can offer numerous benefits over conventional free-radical polymerization approaches. Many articles concerning living radical polymerization have been published in recent years1–8 in which three kinds of polymerization methods have been reported—nitroxide-mediated or alkoxyamine-initiated polymerization, called stable free-radical polymerization (SFRP), atom transfer radical polymerization (ATRP),...
(ATRP), and reversible addition–fragmentation chain transfer, which have been developed and investigated as effective synthetic routes to well-defined copolymers, such as block, graft, or star copolymers with special architectures.10–19 However, every living free polymerization method has shown a monomer limitation when carrying out precise control. For example, methyl (methyl)acrylate-type monomer is difficult to perform a stepwise propagation according to an SFRP mechanism with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or its derivative as a radical trapper because of the strong hydrogen-abstracting reaction between the growing radical and TEMPO.6,11 Recently, Grubbs et al.17 reported a multistep approach by combining two living radical polymerization approaches to synthesize a multibranch polystyrene-graft-poly(methyl methacrylate) copolymer (PS-g-PMMA). The nitroxide-mediated SFRP of a mixture composed of 1-phenylethyl chloride, p-(4′-chloromethylbenzyloxymethyl) styrene, and styrene (St) to form PS main backbone with dendritic graft benzenyl halides was followed by subsequent ATRP of methyl methacrylate (MMA) with these halide groups as initiators. However, a low initiation efficiency of benzenyl halogen20,21 and a competing propagation reaction of growing radicals, respectively, from alkoxyamines and organic halides at high temperature (>100 °C) could easily make the stepwise propagation out of control.

We have performed the study on improving the SFRP rate by varying the initiators and the addition procedure.22–24 Chen and coworkers25–30 found a new kind of Cu-bipyridine (bpy) complex system that carried ATRP of MMA out at low temperatures (≤80 °C). In this study, a subsequent two-step free-radical polymerization approach is advanced to synthesize various well-defined PMMA-g-PS multigraft copolymers. By a low-temperature ATRP of MMA in the presence of polymerizable nitroxide radical, 4-vinylbenzenyl-TEMPO (STEMPO), as presented in Scheme 1,31 that acted as both a stable radical and polymerizable monomer, PMMA prepolymers with dendritic graft TEMPO moieties was synthesized. The prepolymers copolymerized with St in SFRP in the second step led to multigraft copolymers, PMMA-g-PS, in contrast with that reported by Grubbs et al.,17 as outlined in Schemes 2(a,b). These prepolymers and multigraft copolymers were characterized in detail. The polymerization kinetics was investigated.

**EXPERIMENTAL**

**Materials**

MMA and St (AR, provided from Shanghai Reagent Co.) were used after distillation in vacuum. Ethyl 2-bromopropionate (EPNBr) and 4-vinylbenzyl chloride were directly used after being obtained from Aldrich. 4-Hydroxyl-2,2,6,6-tetramethyl-1-piperidinyloxy (HTEMPO) received from BASF was recrystallized in n-hexane before use. Other chemicals of analysis purity purchased from various manufacturers were purified according to standard methods.32

**Polymerization**

PMMA prepolymers with various graft TEMPO moieties were synthesized through polymerization of MMA and polymerizable STEMPO in ATRP at low temperature (60 °C). The schematic synthetic pathway is presented in Scheme 2(a). Into a 100-mL medical salt-water glass bottle carrying a magnetic stirrer of 0.5 mmol of Cu, 0.5 mmol of CuBr, 2 mmol of bpy, 1 mmol of EPNBr, 35 mmol of MMA, and 0.5 mmol of STEMPO in 10 mL acetonitrile solution were added, and the mixture was strongly stirred at room temperature for 10 min. The bottle was evacuated by three freeze-pump-thaw cycles, purged by purified argon for 15 min, and then sealed with a rubber tip before being placed in preheated oil at 60 °C. The crude prepolymer solution was first purified by passing through an alumina column (neutral) with tetrahydrofuran (THF) as a mobile phase. The THF solution was distilled to remove solvent, yielding the grafted prepolymer (PMMA-STEMPO). The further purification was made through dissolution in chloroform and precipitation in methanol. The number of grafted TEMPO moieties can be

![Scheme 1](attachment:image.png)
designed by varying the molar ratio of STEMPO to EPNBr, for example, if the ratio of [STEMPO]/[EPNBr] is 1/2, 2/3, or 3/4, the number of the nitroxyl-grafted chains is expected to be 1, 2, and 3, respectively.

The multigraft copolymers, such as PMMA-g-PS were synthesized through a subsequent SFRP process of St and the prepolymers at high temperature [120 °C; see Scheme 2(b)]. Briefly, a solution of St and the previously mentioned prepolymer (molar ratio = 150/1) was added into a glass flask, degassed with three pump-thaw cycles, and heated at 120 °C for 18 h. The reaction was stopped through precipitation in methanol. These multigraft copolymers were further purified by extraction of n-hexane to remove possible PS homopolymer. The elution residue was checked by gel permeation chromatography (GPC), and in all cases the PS homopolymer was not detected.

Instrumentation

The molecular structures of the prepolymers and multigraft copolymers were characterized by a combination of Fourier transform infrared spectroscopy (Magenic 550), chemical element analysis (PerkinElmer 2400, SeriesII CHNS/O Analyzer), and $^1$H NMR (Bruker, 300 MHz). The radical characteristics of STEMPO were determined by electronic spin resonance (ESR, Bruker ER200D-SRC). Molecular weight and its distribution of the prepolymers and the multigraft copolymers were determined by GPC on a Waters instrument equipped with two Waters Styragel columns (pore sizes: $10^2$ and $10^4$ Å) in sequence (eluent, THF, 1 mL/min, 38 °C, PS as standard samples). Netzsch TGA 304 was used to perform measurements of monomer conversion.24,33

RESULTS AND DISCUSSION

Synthesis of PMMA Prepolymers with Varied Graft TEMPO Moieties, PMMA-STEMPO

MMA was polymerized in the presence of a polymerizable TEMPO, STEMPO at low temperature (60 °C) as presented in Scheme 2(a). The resulting prepolymers, PMMA prepolymers grafted with various nitroxide moieties end capped with ethyl propionate, PMMA-STEMPOs, were characterized as follows. IR spectra of the PS-MTEMPOs exhibited the characteristic vibration presence assigned to the MMA unit (carboxyl stretching vibration at 1740 cm$^{-1}$) and STEMPO moiety (double-substituted benzene, $\equiv$C–H swing vibration at 750 cm$^{-1}$). GPC curves of the prepoly-
mers showed a single peak, and the molecular weight distributions were in the narrow range of 1.3–1.5 as shown in Table 1. Elemental analysis for these prepolymers was performed. The number of grafted TEMPO moieties, $N_e$, was conveniently calculated from the relative content ratio between halide ($C_1$) and nitrogen ($C_2$), for example, $N_e = (C_2/14.0)/(C_1/35.5)$, because halide and nitrogen atoms are ascribed to the end group in the PMMA main backbone and side group in the dendritric TEMPO moiety. The average graft numbers obtained from elemental analysis methods are close to the designed value as listed in Table 1.

The prepolymers were further characterized by $^1$H NMR [taking a typical sample such as PMMA-STEMPO-1 (feed ratio of [STEMPO]/[EPNBr] = 1/2)]. In Figure 1, some characteristic signals at 6.93–7.13 and 3.60 ppm are, respectively, ascribed to two substituted aromatic protons of STEMPO moieties and the methyl proton of OCH$_3$ in PMMA. The average graft number ($N_H$), was obtained through calculation of the integral peak area ratio between the aromatic proton of STEMPO moiety and the OCH$_3$ proton of MMA units of the PMMA chain as follows

$$N_H = \frac{M_{n,\text{GPC}}}{M_{n,\text{theo}}}$$ (1)

$$M_{n,\text{theo}} = n \times \frac{1/3A_{1.6}}{1/4A_{7.0}} \times M_{n,\text{MMA}} \times \text{conv\%}$$ (2)

where $n$ is 1, 1/2, or 1/3 when [STEMPO]/[EPNBr] is 1/2, 2/3, or 3/4, respectively. The results from the NMR spectra agree with the elemental analysis method, and the average graft efficiency, $N(N_H/N_{\text{theo}})$, are all above 0.85 as listed in Table 1. This indicates that the PMMA-STEMPOs with varied TEMPO moiety have been well synthesized according to Scheme 2(a).

Figure 2 demonstrates the linear dependence of ln($M_n/M$) on the reaction time for various MMA/STEMPO polymerization systems by varying the [STEMPO]/[EPNBr] ratios with EPNBr as the initiator. This means that polymerization of MMA follows a first-order kinetics. Taking the [STEMPO]/[EPNBr] = 1/2 system as an example, molecular weight linearly increases with an increase of monomer conversion in accordance with the theoretical expectation (dotted line) for the ATRP system (see Fig. 3), whereas their molecular weight distributions are in a narrow range from 1.1 to 1.4. This indicates that this kind of polymerization system is of a living characteristic and follows an ATRP mechanism. As a strictly parallel comparison, the MMA homopolymerization system without HTEMPO was performed by ATRP at a low temperature of 60 °C. The three MMA/STEMPO polymerization systems showed a somewhat induction period of about 40 min because of the inhibition effect of STEMPO containing a nitroxide radical. Furthermore, the reaction rates for these systems are lower than that for MMA homopolymerizations and decrease in the order of the [STEMPO]/[EPNBr] ratio of 1/2 > 2/3 > 3/4 in Figure 2. The unusual kinetics can be related to the complicated polymerization mechanism in the ATRP process with STEMPO. In a general ATRP redox cycle as described by Wang and Matyjazewski, bromide atom transfer between EPNBr and bpy-Cu(I) complexes yielded bpy-copper(II) complexes and primary radicals that were quickly trapped by STEMPO nitroxide radicals, leading to an ethyl propionate-terminated styrenic alkoxyamine, a dead compound. Homolytical fission from thermally labile NO-C linkage could be suppressed possibly at a lower reaction temperature (60 °C). The primary radicals were consumed quickly once they were released through a bromide-transfer reaction in a redox cycle. After STEMPO consumed the sto-

Table 1. Physical Parameters for Ethyl Propionate-Capped PMMA-STEMPO Prepolymers

<table>
<thead>
<tr>
<th>Prepolymers</th>
<th>[STEMPO]/[EPNBr]</th>
<th>Temperature (°C)</th>
<th>$M_{n,\text{GPC}}$</th>
<th>MWD</th>
<th>$N_e$</th>
<th>$N_H$</th>
<th>$N^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-STEMPO-1</td>
<td>1/2</td>
<td>60</td>
<td>6200</td>
<td>1.40</td>
<td>0.94</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>PMMA-STEMPO-2</td>
<td>2/3</td>
<td>60</td>
<td>6700</td>
<td>1.38</td>
<td>1.83</td>
<td>1.7</td>
<td>0.85</td>
</tr>
<tr>
<td>PMMA-STEMPO-3</td>
<td>3/4</td>
<td>60</td>
<td>7800</td>
<td>1.54</td>
<td>2.87</td>
<td>2.76</td>
<td>0.92</td>
</tr>
</tbody>
</table>

$^a N_e = (C_2/14.0)/(C_1/35.5)$, where $C_1$ and $C_2$ were the weight percentages of halide and nitrogen, respectively, measured by chemical element analysis.

$^b N = N_H/N_{\text{theo}}$. 

MUL Ti GRAFT COPOLYMERS 1879
ichemical amount of EPNBr, the remaining part of EPNBr prompted copolymerization of MMA as a true initiator according to the ATRP mechanism. Thus, for the [STEMPO]/[EPNBr] system with a lower ratio (<1), the greater amount of EPNBr residual took part in initiation leading to a higher propagation rate.

**Synthesis of Multigraft Copolymers, PMMA-g-PS**

Various multigraft copolymers, PMMA-g-PSs, with a varied number of graft side chains were obtained by copolymerization of St in the presence of the PMMA prepolymers mentioned previously at high temperature (120 °C) as outlined in Scheme 2(b). The IR spectrum of PMMA-g-PS exhibited a combined characteristic of the PMMA and PS homopolymers. The GPC traces for the

Figure 1. $^1$H NMR spectra of PMMA-STEMPO-1; reaction conditions: 60 °C, [MMA] = 4 M, [EPNBr]/[Cu]/[CuCl]/[bpy]/[STEMPO] = 2:1:1:4:1.

Figure 2. ln(M₀/M) versus reaction time in ATRP process, feed ratio identical to Figure 1: (a) without STEMPO and (b), (c), and (d) [STEMPO]/[EPNBr] = 1/2, 2/3, and 3/4, respectively.
multigraft copolymers revealed a single peak, and the polydispersities were in the narrow range of 1.5–1.7 (as listed in Table 2). The PMMA-g-PS multigraft copolymers were further characterized by both $^1$H NMR and elemental analysis. In Figure 4 of the $^1$H NMR spectrum of a typical PMMA-g-PS-1 from PMMA-STEMPO-1 (one TEMPO moiety), two big signals appear at 6.5–7.1 and 3.64 ppm as compared with PMMA-STEMPO-1 in Figure 2 as a result of monosubstitution of the benzene proton of the PS side chain and the $^\text{O}_3\text{OCH}_3$ proton in PMMA.

Figure 5 portrays some GPC traces of the samples directly taken out in the different reaction periods for a typical St/PMMA-STEMPO-1 system. In the initial period before 1.5 h, the curves illustrate clearly bimodal shapes in which a low molecular weight peak strength decreases and a high molecular weight peak strength increases and shifts forward gradually. The small peak obviously originated from the macromolecular PMMA-STEMPO-1 fragment. With additional increases of reaction time, a combined big peak shifts gradually to high molecular weight, whereas for these St/PMMA-STEMPO systems, linear dependence of ln($M_0/M$) on reaction time and a linear increase of molecular weight with monomer conversion (shown in Figs. 6 and 7) demonstrate that polymerization of St is a typical living polymerization process. It is obvious that in the polymerization process of St, the PMMA prepolymer played two roles of either an initiator or a radical trapper. The graft side group on the PMMA backbone, ethyl propionate-capped TEMPO moieties, were decomposed at high temperature resulting in a nitroxide radical connected on the PMMA backbone and an ethyl propionate radical in a dynamic equilibrium. The latter initiated St, whereas the former functioned as a macromolecular trapper to control a stepwise propagation according to an SFRP mechanism as typically described by Georges et al.\textsuperscript{3} The resulting multigraft copolymers with different graft numbers of PS side chains were prepared from the corresponding PMMA prepolymer with varied TEMPO moieties.

The St/PMMA-STEMPO-2 system with two TEMPO moieties reveals a higher reaction rate and faster increase of molecular weight as compared with the St/PMMA-STEMPO-1 system with one TEMPO moiety, as shown in Figures 6 and 7, because PMMA-STEMPO-2 in the former system was decomposed to produce two times higher the possibility of the ethyl propionate primary radicals as compared with the latter. The initiation efficiency ($M_{n,GPC}/M_{n,\text{theo}}$) for multigraft copolymers are especially high over 80%, more than that reported in the literature.\textsuperscript{6,20,21} For a general initiator/TEMPO system, the initiator was decomposed quickly at high temperature to give excessive primary radicals that tended to take place the bimolecular termination reaction.

![Figure 3](image-url). Dependence of molecular weight and polydispersity on monomer conversion in ATRP process of MMA system at 60 °C, reaction conditions identical to Figure 1(a): (a) experimental points and (b) theoretical expectation.

### Table 2. Physical Parameters for the Multigraft Copolymers of PMMA-g-PS

<table>
<thead>
<tr>
<th>Type of Products</th>
<th>Temperature (°C)</th>
<th>$M_{n,GPC}$</th>
<th>$M_{n,\text{theo}}$</th>
<th>MWD</th>
<th>$N$</th>
<th>Initiation Efficiency\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-g-PS-1</td>
<td>120</td>
<td>14,170</td>
<td>12,300</td>
<td>1.57</td>
<td>0.92</td>
<td>0.87</td>
</tr>
<tr>
<td>PMMA-g-PS-2</td>
<td>120</td>
<td>24,560</td>
<td>19,890</td>
<td>1.62</td>
<td>0.85</td>
<td>0.81</td>
</tr>
<tr>
<td>PMMA-g-PS-3</td>
<td>120</td>
<td>36,780</td>
<td>29,410</td>
<td>1.70</td>
<td>0.92</td>
<td>0.80</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $M_{n,\text{theo}} = M_{n,\text{prepolymer}} + \{\text{St}\}^\text{Conv\%}\cdot M_{n,\text{St}}\cdot N/\text{[prepolymer]}$.

\textsuperscript{b} From Table 1.

\textsuperscript{c} Initiation efficiency = $M_{n,\text{theo}}/M_{n,GPC}$. 

MULTIGRAFT COPOLYMERS 1881
The initiation efficiency was lower even below 60%. In our case, the released TEMPO radical connected on the PMMA backbone from decomposition of the PMMA-STEMPO prepolymer can lower the effectiveness of the trap of the ethyl propionate radical because of the high stereoregularity and slow diffusion rate of the long backbone. This can increase the effectiveness of the initiation and step propagation of St molecules on the free ethyl propionate radicals.

To afford further evidence for the designed graft structure of PMMA-g-PS, the GPC traces were checked after the graft copolymer (taking PMMA-g-PS-1 as an example) was heated with ascorbic acid in THF, as shown in Figure 8. Because ascorbic acid can easily get TEMPO reduced to the corresponding hydroxylamine as following reaction in Scheme 3.24,33,34

The labile NO-C linkage in the dendritric TEMPO moiety between the PS side chain and...
PMMA was decomposed at high temperature and gave a nitroxide radical connected on the PMMA backbone and styrenic radical connected on the PS side chain in the thermoreversible equilibrium. The nitroxide radical was quickly consumed by ascorbic acid as presented in Scheme 3. As a result, the graft copolymer gradually degraded to form two monochains of PS and PMMA as the treatment time increased. The GPC traces during the degradation process illustrate a peak-shape variation from a single peak before treatment to form double peaks after treatment, as shown in Figure 8, whereas the molecular weights decreased, and molecular weight distributions of two small peaks slightly became narrower. It is obvious that two peaks originated from PMMA and PS chains in a multigraft copolymer. The similar reversible decomposition behavior for the PMMA-\(g\)-PS with various graft chain numbers can be observed. This suggests that these synthesized multigraft copolymers with different chemical distinct arms can gain a special rheological property at high temperatures and indicate potential in the polymer-blending process in industry.

CONCLUSION

A new kind of multigraft copolymer, PMMA-\(g\)-PS, with a varied number of graft side chains was prepared by a subsequent two-step living radical copolymerization method, for example, a combination of ATRP and SFRP as a result of different reaction characteristics. In the ATRP process of MMA, a polymerizable TEMPO, STEMPO, was first copolymerized at lower temperature (60 °C) with EPNBr as the initiator, producing the prepolymers, PMMA-STEMPOs, with different grafted TEMPO moieties. The resulting prepolymers that functioned either as a macromolecular initiator or trapper subsequently copolymerized with St in the subsequent SFRP process at elevated temperature (120 °C) to gain the corresponding multigraft copolymers. The number of graft chains was designed by varying the STEMPO/EPNBr ratios, for example, the ratios of 1/2, 2/3, and 3/4 gained one, two, and three graft side chains, respectively. The polymerization kinetics for the two polymerizations was of a living radical polymerization characteristic. However, these well-controlled multigraft copolymers show an interesting thermoreversible behavior at high temperature, and its special rheological behavior is noteworthy to investigate further.
This project was supported by the Open Fund from the Key Laboratory of Molecular Engineering of Polymer in China.

REFERENCES AND NOTES

31. STEMPO was prepared through the reverse-phase substitution reaction between HTEMPO and 4-vinylbenzyl chloride with (Bu)4HSO4 as a phase-transfer catalyst in aqueous solution at room temperature. The detailed procedure is described as follows. Into a round-bottom flask (100 mL) with a magnetic stirrer, 1 mmol of (Bu)4HSO4 and 0.4 mol of 4-vinylbenzyl chloride in 50 mL of 50% NaOH solution were added. The mixture was strongly stirred for 10 min at room temperature. About 0.1 mol of HTEMPO was added in four parts (0.025 mol per part) within 2 h, and the mixture was kept under strong stirring at room temperature for 24 h. Then, unreacted 4-vinylbenzyl chloride was removed by the excess addition of triethyl amine (1 mol). The crude product was dissolved in 30 mL of chloroform and washed with a lot of deionic water for some time to remove the remainder of HTEMPO and triethyl amine or its salt. STEMPO-chloroform solution was dried with MgSO4, and a dot could be detected on a thin-layer chromatographer (Merck) (mobile phase: ethyl acetate). The solution was distilled at low temperature under vacuum to remove solvent. The purified STEMPO was obtained and showed red viscous liquid. MS [molecular ionic peaks (m/z)]: 288, C18H26NO2. Caled. C, 75%; H, 9.03%; N, 4.86%; O, 11.11%. Found: 74.62%, C, 75%; H, 9.01%, N, 4.89%, O, 11.48%. ESR spectrum of the STEMPO exhibits a typical three-peak signal, assigned to nitroxide radical. This means that the nitroxide radical on a molecule is not destroyed in the synthetic process.