Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization of Vinyl Monomers Initiated by Poly(methyl methacrylate) Peroxide

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Abstract: Poly(methyl methacrylate) peroxide (PMMAP) was synthesized and used as the initiator in the reversible addition-fragmentation chain transfer (RAFT) polymerization. Methyl methacrylate (MMA) as the monomer and 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as the chain transfer agent was used in the polymerization system. The polymerization was successfully initiated by PMMAP while maintaining features of “living”/controlled radical polymerization such as the number-average molecular weights ($M_n$) increasing linearly with the monomer conversions and low polydispersity index (PDI) values. The results of $^1$H NMR and IR spectra confirmed that a small quantity of polymer chains were derived from the PMMAP moieties. The PMMAP can also initiate the RAFT polymerization of styrene (St) and methyl acrylate (MA), and the polymerization proceeded in a “living”/controlled fashion.

Introduction

The “living”/controlled radical polymerization (CRP) techniques, such as nitroxide mediated polymerization (NMP) [1], atom transfer radical polymerization (ATRP) [2], and the reversible addition-fragmentation chain transfer (RAFT) polymerization [3] have been well studied over the past decade. These techniques have enabled the synthesis of a wide range of polymers with well-defined architectures, compositions, and functionalities [4]. Among these techniques, the RAFT process has received much attention and became one of the most convenient and versatile methodologies for the synthesis of well-designed polymers. The initiator plays a very important role in RAFT polymerization since the radicals produced by initiator at the very start of the polymerization is the trigger for the reversible chain transfer reactions [5]. Usually, radicals in RAFT polymerization could be generated by the following three means: (i) decomposition of thermal initiators, such as benzoyl peroxide (BPO) [6], 2,2’-azobisisobutyronitrile (AIBN) [7]; (ii) an external source (UV-vis [8], γ-ray [9] or plasma initiation [10]); (iii) thermal self-initiation (usually for styrene). According to RAFT polymerization mechanism, the mole ratio of RAFT agent to initiator ([RAFT agent]$_0$/[initiator]$_0$) should be kept high to reduce the probability of termination reactions. The majority of the polymers obtained from the RAFT polymerization contained R group of the RAFT agent at the chain-ends, only a small fraction of polymer chains were derived from the initiator [11]. As a consequence, the initiator-derived chains were not always readily discernable [12-15]. Several groups tried to use the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [16-19] and electrospray-ionization-quadrupole time-of-flight mass spectrometry (ESI-TOF-MS) [11] to identify the chain end structures of the RAFT
polymers. The results did show signals corresponding to polymers with initiator-derived end groups. However, a significant extent of fragmentation may occur for MALDI-generated ions [20-21], and MALDI (ESI)-TOF-MS analysis was more difficult for the polymers with higher molecular weights. Therefore, it was beneficial for the RAFT-mechanism-understanding to easily distinguish the chain end structures of RAFT polymer with few limitations.

A novel finding in our lab [22] demonstrated that the rate of thermal polymerization of MMA via a RAFT process was remarkably enhanced in the presence of oxygen compared with that without oxygen, and the rate of polymerization increased with an increase of oxygen concentration. We concluded that the polymeric peroxide, PMMA peroxide (PMMAP) generated in situ, was probably responsible for the initiation behavior [22]. The PMMAP is an alternate copolymer of MMA and oxygen with molecular weight from 3000 to 5000 [23-26], and it has been reported as a thermal initiator for the styrene polymerization [27, 28]. The structure of PMMAP is given in Scheme 1.

![Scheme 1](image)

**Scheme 1.** The structure of MMA peroxide.

To the best of our knowledge, the polymeric peroxide has not been used in the field of living radical polymerizations. This work first investigated the feasibilities of the PMMAP as a thermal initiator in the RAFT polymerization. At the same time, it can go deep into the mechanism of the oxygen-accelerated RAFT polymerization of MMA introduced in our published work [22]. Furthermore, since the PMMAP was polymeric in structure, its characteristic signals at the chain-ends of the RAFT polymers were expected to be discerned. 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) was used as the RAFT agent in this work, which was an efficient RAFT agent for the polymerization of alkyl (meth)acrylates [29, 30].

**Results and Discussion**

**RAFT polymerization of MMA in the presence of PMMAP**

Fig. 1 shows the results of RAFT polymerization of MMA in the presence of various concentrations of PMMAP (0-0.0114 M) and a constant concentration of CPDN (0.019 M) at 80 °C. It was found that the polymerization rates increased dramatically with PMMAP concentrations increasing from 0 M to 0.0019 M. The explanation may be that the PMMAP was involved the initiating process [27, 28]. An initialization period [31-33], especially at non-or-low concentration of PMMAP, was observed in Fig. 1. The prolonged initialization period in the presence of non-or-low concentration of PMMAP was due to the low initiation rate which induced the low rate of the consumption of RAFT agent [31-33].

Fig. 2 exhibits the evolution of $M_n$ and PDI values with monomer conversions at various concentration of PMMAP. The $M_{n,GPC}$ increased linearly with monomer
conversion; at the same time, the $M_{n,GPC}$ was close to the predicted value ($M_{n,th}$) and PDI value of the obtained polymer was less than 1.51. All the evidences indicated “living” natures of RAFT polymerization in the presence of PMMAP.

Fig. 1. Dependence of ln($[M]_0/[M]$) on polymerization time at various concentrations of PMMAP, $[MMA]_0 = 9.40 \text{ M}$, $[CPDN]_0 = 0.019 \text{ M}$, $80 ^\circ \text{C}$.

Fig. 2. Dependence of $M_n$ and PDI on conversion for thermal polymerization of MMA, same reaction conditions as in Figure 1. $M_{n,th} = ([MMA]_0/[CPDN]_0) \times MW_{MMA} \times \text{conversion} + MW_{CPDN}$.

Unlike benzoperoxide, the peroxide bonds in PMMAP can not decompose completely [27, 28]. If the polymerization was initiated by the PMMAP, the polymer chain would contain some of the incomplete-decomposed PMMAP moieties that can be detected. The structure of obtained PMMA was characterized by $^1H$ NMR spectroscopy and is shown in Fig. 3. The signals at $\delta = 7.4 \sim 8.1 \text{ ppm}$ were attributed to the aromatic protons of the naphthylene units in CPDN which revealed that the polymer chain was end-capped by CPDN moiety. A weak peak at $\delta = 4.34 \text{ ppm}$ corresponding to the –
OCH₂ protons (e) of PMMAP was found in the spectrum. The appearances of –OCH₂ of PMMAP indicated that a fraction of the polymer chains were stemmed from the incomplete-decomposed PMMAP segments. The FT-IR spectra of PMMAP and obtained PMMA is shown in Fig. 4. The spectra unanimously showed broad absorption at 3200-3500 cm⁻¹, which was ascribed to the vibration of –OH or –OOH at the end of PMMAP [34, 35]. The results from ¹H NMR and FT-IR confirmed sufficiently the initiating behavior of PMMAP in the polymerization.

**Fig. 3.** ¹H NMR spectrum of PMMA with CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. PMMA, $M_n$ GPC = 12500, PDI = 1.26.

**Fig. 4.** FT-IR spectra of PMMAP ($M_n$ GPC = 4000, PDI = 1.65) and PMMA ($M_n$ GPC = 12500, PDI = 1.26).

The DSC and TGA traces of PMMAP and PMMA are shown in Fig. 5. The distinct exotherm of PMMAP and weight loss observed at around 145 °C were ascribed to the decomposition of the PMMAP segments [27], however, the exothermic peak and
weight loss of PMMA were not found. In a well-designed RAFT polymerization, the majority of the polymers contains R group of the RAFT agent at the chain-ends, only a small fraction of polymer chains were derived from the initiator [11-15]. As a consequence, the amount of the PMMAP-derived chains was too low to be detected by DSC and TGA.

![DSC-TGA thermogram of PMMAP (M\textsubscript{n,GPC} = 4000, PDI = 1.65) and PMMA (M\textsubscript{n,GPC} = 12500, PDI = 1.26) under nitrogen atmosphere with heat rate of 10 °C/min.](image)

Fig. 5. DSC-TGA thermogram of PMMAP (M\textsubscript{n,GPC} = 4000, PDI = 1.65) and PMMA (M\textsubscript{n,GPC} = 12500, PDI = 1.26) under nitrogen atmosphere with heat rate of 10 °C/min.

All the above evidences supported the idea that the PMMAP could act as the thermal initiator in the polymerizations of MMA with CPDN as RAFT agent, the polymerization was well controlled and consistent with the RAFT mechanism. It was worthy to be noted that the polymer chains derived from PMMAP can be detected by \(^1\)H NMR and FT-IR. Whereas, the signals of the polymer chains derived from low-molecular-weight initiators in RAFT polymerization were not readily detected [12-15].

For a comprehensive understanding of the RAFT polymerization of MMA in the presence of PMMAP, a series of experiments were then conducted. The results are presented in Table 1. From the entries 1 and 5, it can be found that increasing the ratio of [MMA]\textsubscript{0}/[CPDN]\textsubscript{0} while fixing the ratio of [CPDN]\textsubscript{0}/[PMMAP]\textsubscript{0}, the polymerization rate decreased due to the lower concentration of PMMAP. These results complied with the RAFT polymerization with AIBN as initiator [29]. When PMMAP was in a low concentration ([MMA]\textsubscript{0}/[CPDN]\textsubscript{0}/[PMMAP]\textsubscript{0} = 1500/1/0.30), the M\textsubscript{n,GPC} was much higher than the M\textsubscript{n,th} and the PDI value was 1.46, indicating some loss of control during the polymerization. The low rate of initiation and low concentration of CPDN may be responsible for the poor controlled polymerization. From the entries 2-4 and 6-7, it can be found that the polymerization rate increased with the PMMAP concentration. When the ratio of [MMA]\textsubscript{0}/[CPDN]\textsubscript{0} changed from 500 : 1 (entries 4, 5) to 500 : 2 (entries 8, 9), an obvious induction period was observed and polymerization rate was remarkably retarded. Similar retardation effects were reported in the literature [36-41], and there is currently some controversy surrounding the causes of the retardation effect. In order to investigate the true role of PMMAP in
the polymerization system, tin(II) 2-ethylhexanoate (Sn(EH)₂) was chosen as the reducing agent and added into the polymerization system. Since Sn(EH)₂ can reduce the peroxide to alcohol derivatives that cannot initiate the radical polymerization, the polymerization rate was thus expected to be depressed. From entries 6, 10 and 11 in Tab. 1, it can be found that the polymerization rate was slower than that in the absence of Sn(EH)₂. Furthermore, the polymerization rate decreased with the increasing of the concentration of Sn(EH)₂. The result was a supplementary proof that it was PMMAP which initiated the RAFT polymerization.

The decomposing of PMMAP depended mightily on the temperature. From the entries 5, 12-14, it can be found that when the polymerization temperature decreased from 80 °C to 60 °C and 40 °C, there were no products within 3 hours; however, the conversion reached to 99% at the elevated temperature (100 °C) after the same reaction time. It should be noted that the high polymerization rate at elevated temperature was not only owing to the fast initiation of the PMMAP, but also owing to the fast propagation of the free radicals, fast addition and fragmentation reactions of RAFT agent.

Tab. 1. The comparison of experimental results of the polymerization of MMA.

<table>
<thead>
<tr>
<th>entry</th>
<th>[MMA]₀/[CPDN]₀/[PMMAP]₀</th>
<th>time (h)</th>
<th>con (%)</th>
<th>(M_{n,th}^d)</th>
<th>(M_{n,GPC})</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500:1:0.3</td>
<td>3</td>
<td>5.7</td>
<td>8790</td>
<td>48300</td>
<td>1.46</td>
</tr>
<tr>
<td>2</td>
<td>500:1:0</td>
<td>3</td>
<td>0</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>3</td>
<td>500:1:0.03</td>
<td>5</td>
<td>4.8</td>
<td>2700</td>
<td>15710</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>500:1:0.1</td>
<td>3</td>
<td>23.1</td>
<td>11800</td>
<td>22300</td>
<td>1.19</td>
</tr>
<tr>
<td>5</td>
<td>500:1:0.1</td>
<td>12</td>
<td>86.6</td>
<td>43600</td>
<td>53500</td>
<td>1.20</td>
</tr>
<tr>
<td>6</td>
<td>500:1:0.3</td>
<td>3</td>
<td>43.8</td>
<td>22200</td>
<td>23000</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>500:1:0.6</td>
<td>3</td>
<td>52.4</td>
<td>26500</td>
<td>33300</td>
<td>1.08</td>
</tr>
<tr>
<td>8</td>
<td>500:2:0.1</td>
<td>4</td>
<td>0</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>9</td>
<td>500:2:0.1</td>
<td>12</td>
<td>47.0</td>
<td>12050</td>
<td>19900</td>
<td>1.07</td>
</tr>
<tr>
<td>10</td>
<td>500:1:0.3 (^b)</td>
<td>3</td>
<td>29.0</td>
<td>14800</td>
<td>21100</td>
<td>1.12</td>
</tr>
<tr>
<td>11</td>
<td>500:1:0.3 (^c)</td>
<td>3</td>
<td>15.5</td>
<td>8000</td>
<td>19400</td>
<td>1.15</td>
</tr>
<tr>
<td>12</td>
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<td>3</td>
<td>0</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td>13</td>
<td>500:1:0.1</td>
<td>3</td>
<td>0</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>14</td>
<td>500:1:0.1</td>
<td>3</td>
<td>99.0</td>
<td>49800</td>
<td>53500</td>
<td>1.17</td>
</tr>
</tbody>
</table>

\(^a\): entry 1-11, temperature = 80 °C; temperature of entry 12, 13 and 14 was 40 °C, 60 °C and 100 °C, respectively.
\(^b\): Sn(EH)₂ = 0.0019 M.
\(^c\): Sn(EH)₂ = 0.019 M.
\(^d\): \(M_{n,th} = ([MMA]₀/[CPDN]₀) \times MW_{MMA} \times \) conversion + MW_{CPDN}
RAFT polymerization of St and MA in the presence of PMMAP

To examine the initiation capability of the PMMAP on other monomers, the polymerizations of St and MA were then conducted in the presence of PMMAP with CPDN as RAFT agent. The kinetic plots of the polymerization of St in the presence and absence of PMMAP are shown in Fig. 6. The polymerization rate in the presence of PMMAP was remarkably enhanced in comparison with that without PMMAP. The plots of $M_n$ and PDI value versus monomer conversion of St are presented in Fig. 7.

**Fig. 6.** Dependence of $\ln([M]_0/[M])$ on polymerization time at various concentrations of PMMAP, $[St]_0 = 8.74$ M, $[CPDN]_0 = 0.017$ M, 80 °C.

**Fig. 7.** Dependence of $M_n$ and PDI on monomer conversion for RAFT polymerization of St, same reaction condition as that in Figure 3. $M_{n,\text{th}} = ([St]_0/[CPDN]_0) \times MW_{St} \times \text{conversion} + MW_{CPDN}$.

$M_{n,GPC}$ values increased linearly with monomer conversions, and polymers with low PDI values (PDI < 1.20) were obtained. The $M_{n,GPC}$ values agreed well with the
theoretical values. All the above-mentioned evidences demonstrated “living”/controlled features of the polymerization of St initiated by PMMAP.

The chain end analysis of the PS by $^1$H NMR is showed in Fig. 8. The signals at $\delta =$ 7.8 ~ 8.0 ppm were attributed to the aromatic protons (b) of the naphthalene units in CPDN. The signals of other protons (a, c and d) of the naphthalene units could not be distinguished because they were overlapped by the signals of the St units (e).

**Fig. 8.** $^1$H NMR spectra of PS with CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. CPDN end-capped PS, $M_{n,GPC} =$ 5500, PDI = 1.07.

Furthermore, the RAFT polymerization of MA in the presence of various amounts of PMMAP was also carried out. The results are listed in Table 2. It was found that the polymerization rate increased with an increase of the PMMAP concentration, which indicated that the PMMAP could also serve as a thermal initiator in the RAFT polymerization of MA.

**Tab. 2.** RAFT polymerization of MA in the presence of various amount of PMMAP.

<table>
<thead>
<tr>
<th>entry $^a$</th>
<th>[MA]$_0$/[CPDN]$_0$/[PMMAP]$_0$</th>
<th>con (%)</th>
<th>$M_{n,th}$ $^b$</th>
<th>$M_{n,GPC}$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>500/1/0</td>
<td>0</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>16</td>
<td>500/1/0.03</td>
<td>7.3</td>
<td>3400</td>
<td>18970</td>
<td>1.12</td>
</tr>
<tr>
<td>17</td>
<td>500/1/0.1</td>
<td>32.8</td>
<td>14350</td>
<td>28900</td>
<td>1.06</td>
</tr>
<tr>
<td>18</td>
<td>500/1/0.3</td>
<td>66.8</td>
<td>29000</td>
<td>34700</td>
<td>1.43</td>
</tr>
<tr>
<td>19</td>
<td>500/1/0.6</td>
<td>76.9</td>
<td>33350</td>
<td>35500</td>
<td>1.52</td>
</tr>
</tbody>
</table>

$a$: entry 15-19, temperature = 80 °C, time = 9 h.

$b$: $M_{n,th} = ([MA]$_0$/[CPDN]$_0$) × MW$_{MA}$ × conversion + MW$_{CPDN}$. 

Unauthenticated
Conclusions

PMMAP was successfully used as the initiator in the RAFT polymerizations of MMA, St and MA. The polymerizations were well controlled and complied with the RAFT mechanism. This work extended the scope of initiators used in RAFT polymerization. The results, as a compensatory proof, validated the initiation mechanism of the oxygen-accelerated RAFT polymerization reported previously by our group. Furthermore, the chain-end structure of polymer chains derived from PMMAP was easily discerned by $^1$H NMR and FT-IR, which was not so facile to do with low-molecular-weight initiators before.

Experimental Part

Materials

The monomers, MMA (> 99 %), MA (> 99%) and St (> 99%) were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and were washed three times with aqueous solution of sodium hydroxide (5 wt%), followed by deionized water until neutralization, then dried over anhydrous magnesium sulfate. They were distilled twice under reduced pressure and stored at -18 °C. CPDN was synthesized according to the method reported in literature [29] with the purity greater than 94% by HPLC. PMMAP ($M_n, GPC = 4000$, PDI = 1.65) was prepared according to literatures [25, 42-43].

RAFT Polymerization of MMA, MA and St in the presence of PMMAP

A typical polymerization procedure was as follows: A solution of monomer, PMMAP and CPDN (prescribed molar ratio) was added to a dried ampoule, the content was bubbled with argon for 20 min, then the ampoule was flame sealed, placed in an oil bath held by a thermostat at the desired temperature to polymerize. After the desired polymerization time, the ampoule was cooled by immersing it into ice water. Afterwards, it was opened and the contents were dissolved in THF, and then precipitated into a large amount of methanol. The resulting polymer after filtration was dried under vacuum at room temperature until constant weight. The monomer conversion was determined gravimetrically.

Characterization

The number-average molecular weights ($M_n$) and polydispersities indices (PDI) of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector, using HR 1, HR 2, and HR 4 columns with molecular weights ranged $10^2 \sim 5 \times 10^5$. The columns were calibrated with PMMA standard samples. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min and 30 °C.

$^1$H NMR spectra of the precipitated polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl$_3$ as solvent and tetramethyldisilane (TMS) as an internal standard.

TGA-DSC was measured by 2960 SDT V3.0F (TA Co.).

The FT-IR spectra of PMMAP and PMMA were recorded on a Fourier Transform MagNa-IR550 (Nicolet) spectrophotometer.
All the samples for the analysis of $^1$H NMR, TGA-DSC and FT-IR were purified twice by dissolving them in THF followed by precipitation in methanol and dried in vacuum oven below 40 °C.

Acknowledgements

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