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Mechanism and Kinetics of RAFT-Based Living Radical Polymerizations of Styrene and Methyl Methacrylate

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The bulk polymerizations of styrene and methyl methacrylate in the presence of model polymer-dithiocarbonate adducts as mediators and benzoyl peroxide (BPO) as a conventional initiator were kinetically studied. The polymerization rate, hence the concentration of polymer radical $P^*$, was proportional to $[BPO]^{1/2}$. The pseudo-first-order activation rate constants $k_{act}$ were determined by the GPC peak-resolution method. The results showed that $k_{act}$ is directly proportional to $[P^*]$, indicating that reversible addition-fragmentation chain transfer (RAFT) is the only important mechanism of activation. The magnitude of the exchange rate constant $k_{ex} (= k_{act}/[P^*])$ was strongly dependent on both the structures of the dithiocarbonate group and the polymer. The $k_{ex}$ values for the three RAFT systems examined in this work were all very large, explaining why these systems can provide low-polydispersity polymers from an early stage of polymerization.

Keywords: RAFT / Reversible activation / Activation rate constant / Living radical polymerization

There has recently been a surge of interest in living radical polymerization (LRP) techniques as new and facile synthetic routes to well-defined, low-polydispersity polymers. Mechanistically, these techniques are based on the common concept of alternating activation-deactivation processes (Scheme 1a), in which a potentially active (dormant) species $P-X$ is reversibly activated to the active radical $P^*$ by, e.g., thermal and chemical stimuli. In the presence of monomer $M$, $P^*$ propagates until it is deactivated by a capping agent X. A number of activation-deactivation cycles allow all the chains to have an almost equal opportunity to grow, resulting in low-polydispersity polymers. This means that the frequency of such cycles, i.e., the magnitude of the activation rate constant $k_{act}$, fundamentally characterizes the performance of a given LRP.

Recently, a novel LRP using dithio compounds (Scheme 1b: e.g., $X = –SCSCH_3$ and $–SCSPh$) has been developed. The mechanism of activation is supposed to involve a reversible addition-fragmentation chain transfer (RAFT: Scheme 1b) process. The low polydispersity polymers ($M_w/M_n < 1.1$, where $M_w$ and $M_n$ are weight- and number-average molecular weights, respectively) produced in this polymerization even at an early stage of polymerization indicate that these RAFT processes are extremely fast. In this work, we have determined the $k_{act}$ for the RAFT-based polymerizations of styrene and methyl methacrylate (MMA) as a function of polymerization rate $R_p$ and temperature $T$. In this way, we were able to evaluate the fundamental abilities of these systems, and also experimentally confirm the supposed activation mechanism.

We first examined the polymerization of styrene including a fixed amount of polystyrene (PS)-SCSCH$_3$...
(0.45 mM) as a probe P₀-X and variable amounts of benzoyl peroxide (BPO: 0–10 mM) as a radical initiator. For all the examined values of [BPO]₀, the mean polymerization rate $R_p/[M] = k_p/[P^*]$, where $k_p$ is the propagation rate constant) was found to be constant. The plot of $(R_p/[M])^2$ vs [BPO]₀ was almost linear, which is relevant with the conventional (RAFT agent-free) system.

The $k_{act}$ was determined by the gel permeation chromatographic (GPC) peak-resolution method, which focuses on an early stage of the polymerization containing P₀-X. When P₀-X is activated, the released P₀ will propagate until it is deactivated to give a new adduct P₁-X. Since P₀-X and P₁-X are generally different in chain length and its distribution, they may be distinguished by GPC. By following the change in [P₀-X], $k_{act}$ will be determined. A lower [P₀-X] leads to a larger number of monomer units added to P₀ during an activation-deactivation cycle. In fact, with a sufficiently low [P₀-X] (0.45 mM), the GPC curves were composed of two definite peaks such as shown in Figure 1, which allowed accurate resolution. Thus, we could unequivocally follow the [P₀-X] and obtain well-defined values of $k_{act}$.

The mechanism of activation, i.e., the cleavage of the C-S bond, is supposed to be RAFT (rate constant = $k_{ex}$: Scheme 1b). However, thermal homolysis (rate constant = $k_d$: Scheme 1c) might contribute as well. When both processes are involved, $k_{act}$ takes the form

$$k_{act} = k_d + k_{ex}[P^*]$$

Figure 2 shows the plot of $k_{act}$ against $R_p/[M] (= k_p[P^*])$. Evidently, the data points form a straight line passing through the origin, showing that $k_d = 0$ and the slope of the curve gives $C_{ex} (= k_{ex}/k_p) = 180$. This result suggests that the main mechanism of activation in this system is the RAFT process rather than thermal dissociation. With the known value of $k_p$ (340 M⁻¹ s⁻¹), $C_{ex}$ is estimated to be 3.1 exp(+11.5 kJ mol⁻¹/RT) (2)

We also determined $k_{act}$ in the styrene/PS-SCSPh system and the MMA/PMMA-SCSPh system. The corresponding $C_{ex}$ values are summarized in Table 1. The results clearly show that $C_{ex}$ is strongly dependent on both the structures of carbonate and polymer (alkyl) moiety. In comparison with the $C_{ex}$ values for other exchanging chain transfer-type LRP systems (PS-iodide² and PMMA-macromonomer³ systems), those for the examined RAFT systems are exceptionally large. This explains why these RAFT systems can yield low-polydispersity polymers from an early stage of polymerization.

<table>
<thead>
<tr>
<th>$P-X$</th>
<th>$C_{ex}$</th>
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</thead>
<tbody>
<tr>
<td>PS-SCSCH₃</td>
<td>180</td>
</tr>
<tr>
<td>PS-SCSPh</td>
<td>6000 ± 2000²</td>
</tr>
<tr>
<td>PMMA-SCSPh</td>
<td>140</td>
</tr>
<tr>
<td>PS-I²</td>
<td>4.0</td>
</tr>
<tr>
<td>PMMA-macromonomer³</td>
<td>0.20</td>
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</tbody>
</table>

* Preliminary result at 40 °C.

References