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

Atsushi Goto, Koichi Sato, Yoshinobu Tsujii and Takeshi Fukuda

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 $P^{\bullet}$, 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 $[P^{\bullet}]$, indicating that reversible addition-fragmentation chain transfer (RAFT) is the only important mechanism of activation. The magnitude of the exchange rate constant k_{ex} ($= k_{act}/[P^{\bullet}]$) 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 $P^{\bullet}$ by, e.g., thermal and chemical stimuli. In the presence of monomer M, $P^{\bullet}$ 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.[1] The mechanism of activation is supposed to involve a **r**eversible **a**ddition-**f**ragmentation chain **t**ransfer (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)-$SCSCH_3$

ORGANIC MATERIALS CHEMISTRY — Polymeric Materials —

Scope of research

Kinetic and mechanistic analyses are made for better understandings and systematization of the chemical and physicochemical reactions occurring in polymerization systems and for the development of better routes to the synthesis of well-defined polymers. By the application of various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed for new polymer-based materials of practical importance. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization. (2) Synthesis of new polymeric materials by living polymerizations and polymer reactions and their structure/properties studies. (3) Synthesis, properties, and applications of high-density polymer brushes.

Prof
FUKUDA, Takeshi
(D Eng)

Instr
TSUJII, Yoshinobu
(D Eng)

Students:
YAMAMOTO, Shinpei (PD)
EJAZ, Muhammad (DC)
GOTO, Atsushi (DC)
MIWA, Nobuhiro (MC)
SATO, Koichi (MC)
HIROSE, Yuichi (MC)
YOSHIKAWA, Chiaki (MC)
MARUTANI, Eizo (UG)
KOH, Kyungmoo (RS)
KWAK, Yungwan (RS)

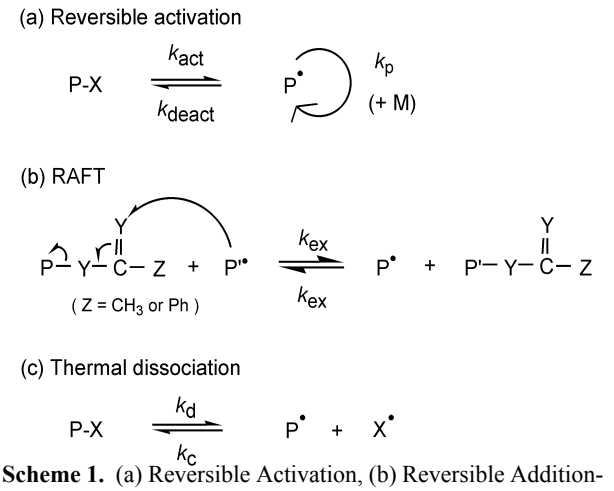
(0.45 mM) as a probe P_0-X and variable amounts of benzoyl peroxide (BPO: 0–10 mM) as a radical initiator. For all the examined values of $[BPO]_0$, the mean polymerization rate $R_p/[M]$ (= $k_p[P^\bullet]$, where k_p is the propagation rate constant) was found to be constant. The plot of $(R_p/[M])^2$ 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 P_0-X. When P_0-X is activated, the released $P_0^\bullet$ will propagate until it is deactivated to give a new adduct P_1-X. Since P_0-X and P_1-X are generally different in chain length and its distribution, they may be distinguished by GPC. By following the change in [P_0-X], k_{act} will be determined. A lower $[P_0\text{-X}]_0$ leads to a larger number of monomer units added to $P_0^\bullet$ during an activation-deactivation cycle. In fact, with a sufficiently low $[P_0\text{-X}]_0$ (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 [P_0-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

$$k_{act} = k_d + k_{ex}[P^\bullet] \quad (1)$$

Figure 2 shows the plot of k_{act} against $R_p/[M]$ (= $k_p[P^\bullet]$). 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}), k_{ex} is estimated to be



Scheme 1. (a) Reversible Activation, (b) Reversible Addition-Fragmentation Chain Transfer (RAFT), and (c) Thermal Dissociation.

Table 1. Comparison of C_{ex} (60 °C)

P-X	C_{ex}
PS-$SCSCH_3$	180
PS-SCSPh	6000 ± 2000[a]
PMMA-SCSPh	140
PS-I[2]	4.0
PMMA-macromonomer[3]	0.20

[a] Preliminary result at 40 °C.

61000 M^{-1} s^{-1}. The temperature dependence of C_{ex} was found to be given by

$$C_{ex} = 3.1 \exp(+11.5 \text{ kJ mol}^{-1}/RT) \quad (2)$$

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-iodide[2] and PMMA-macromonomer[3] 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.

References

(1) Chiefari, J. et al. *Macromolecules* **1998**, *31*, 5559.
(2) Goto, A. et al. *Macromolecules* **1998**, *31*, 2809.
(3) Moad, C. L. et al. *Macromolecules* **1996**, *29*, 7717.

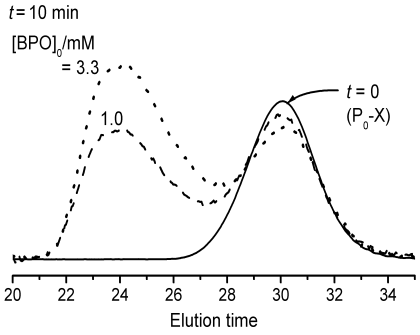


Figure 1. Examples of GPC chromatograms in the styrene/PS-$SCSCH_3$(P_0-X) system (60 °C): $[P_0\text{-X}]_0$ = 0.45 mM; $[BPO]_0$ as indicated in the figure.

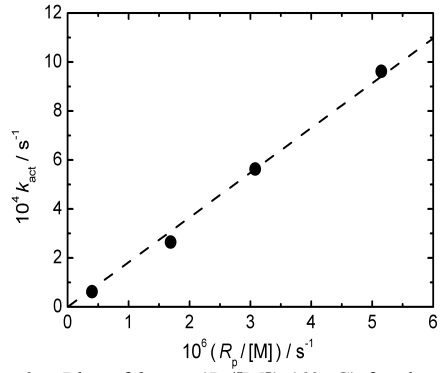


Figure 2. Plot of k_{act} vs $(R_p/[M])$ (60 °C) for the styrene/PS-$SCSCH_3$ system.