Polymerization

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Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid**

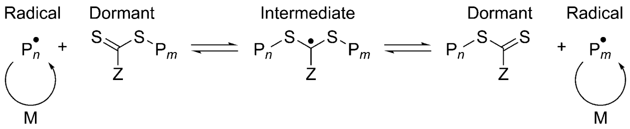
Mineto Uchiyama, Kotaro Satoh, and Masami Kamigaito**

Abstract: *A metal-free, cationic, reversible addition–fragmentation chain-transfer (RAFT) polymerization was proposed and realized. A series of thiocarbonylthio compounds were used in the presence of a small amount of triflic acid for isobutyl vinyl ether to give polymers with controlled molecular weight of up to* 1×10^5 *and narrow molecular-weight distributions* ($M_w/M_n < 1.1$). *This "living" or controlled cationic polymerization is applicable to various electron-rich monomers including vinyl ethers, p-methoxystyrene, and even p-hydroxystyrene that possesses an unprotected phenol group. A transformation from cationic to radical RAFT polymerization enables the synthesis of block copolymers between cationically and radically polymerizable monomers, such as vinyl ether and vinyl acetate or methyl acrylate.*

The development of controlled/"living" polymerizations that enable precision synthesis of macromolecules had a tremendous impact not only on polymer chemistry but also on other related fields such as organic and materials chemistry.[1] The methodologies for these "living" polymerizations were developed synergistically for various polymerizations proceeding via anionic, cationic, coordination, and radical species. Most of these recently developed "living" or controlled polymerizations are based on the reversible activation of dormant species into active ones. The key for controlling these polymerizations is developing an efficient reversible activation–deactivation process, which is of course governed by an organic reaction.[2]

Living cationic polymerization of vinyl monomers was first discovered for vinyl ether[3] and isobutene[4] in the 1980s and has now been achieved for various cationically polymerizable monomers mainly through reversible and transient activation of dormant carbon–halogen or oxygen–ester bonds (C–X; X = I, Cl, OC(O)R, etc.) to carbocationic species using metal-based Lewis acid catalysts (MX_n).[5–8] In this polymerization, one polymer chain is generated from one molecule of initiator possessing the dormant bond, which is mostly generated from protonic acid (HX) with a nucleophilic anion and the monomer, whereas the Lewis acid works as a catalyst for the polymer chain. This development led to further discoveries of metal-catalyzed living radical polymerization[9] or atom-transfer radical polymerization (ATRP),[10] which is based on a transition-metal-catalyzed reversible activation of carbon–halogen bonds into radical species and is now widely used to prepare various precisely controlled polymers.[11–15]

Another widely used "living" or controlled radical polymerization is reversible addition–fragmentation chain-transfer (RAFT)[16] or macromolecular design through the interchange of xanthate (MADIX) polymerization.[17] It is based on the chemistry of a radical species adding to the thiocarbonylthio compound to cleave the carbon–heteroatom bond, which is widely used in organic reactions such as the Barton–McCombie reaction.[18,19] This polymerization proceeds through the reversible addition–fragmentation mechanism, in which a small amount of initiating or growing carbon radical species attack the C=S double bonds in the dormant species originating from the RAFT agent to pass through the stabilized radical intermediate and then to fragment into another growing radical species through β-scission (Scheme 1).[20–25] Under optimized conditions, most polymer chains originate from the RAFT agents, whereas a small amount of the propagating radical species catalytically activates the dormant RAFT terminals through a degenerative chain-transfer mechanism. Several specific features of RAFT radical polymerization include versatility due to the designed RAFT agents, simplicity of the radical initiator and RAFT agent, and a metal-free system. Although the RAFT methodology has only been limited to radical chemistry, it is presumably applicable to cationic chemistry.



Scheme 1. Mechanism for RAFT radical polymerization.

Here, we propose cationic RAFT polymerization, proceeding through a similar degenerative but cationic chain-transfer mechanism, as a novel method for controlling cationic polymerization based on the high affinity of the carbocationic species for sulfur atoms (Scheme 2).[26] No such

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[*] M. Uchiyama, Prof. Dr. K. Satoh, Prof. Dr. M. Kamigaito
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603 (Japan)
E-mail: satoh@apchem.nagoya-u.ac.jp
kamigait@apchem.nagoya-u.ac.jp
Prof. Dr. K. Satoh
Precursory Research for Embryonic Science and Technology
Japan Science and Technology Agency
4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)

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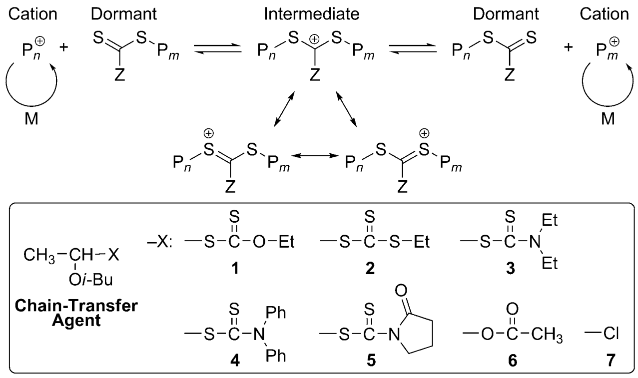

Scheme 2. Proposed mechanism for RAFT cationic polymerization.

sulfur-based cationic RAFT chemistry has been reported for polymerizations or organic reactions, although there are many examples in radical chemistry.[16–25]

A series of thiocarbonylthio compounds were thus synthesized from the hydrogen chloride adduct of isobutyl vinyl ether (IBVE) and the sodium salt of the corresponding thiocarbonylthio acid.[27,28] These compounds were then used as possible RAFT agents in conventional free cationic polymerizations of IBVE initiated by a small amount of triflic acid (CF_3SO_3H or TfOH) ($[TfOH]_0 = 0.05$ mM), which proceeded very quickly (Figure S1 in the Supporting Information, SI), resulting in polymers with uncontrolled molecular weights ($M_n > 2\times10^4$, $M_w/M_n > 3$; Figure 1). The addition of the thiocarbonylthio compounds (**1**–**3**) slightly retarded the polymerization, lowered the molecular weights efficiently, and narrowed the molecular-weight distributions (MWDs). The narrowest MWDs were attained ($M_w/M_n < 1.1$) for the dithiocarbamate (**3**). The M_n values increased in direct proportion to the monomer conversion and agreed well with the calculated values assuming that one polymer chain is generated from one molecule of the thiocarbonylthio compounds. This result suggests that these thioesters work as efficient reversible chain-transfer agents in the cationic polymerization. Another dithiocarbamate (**4**) with diphenyl substituents also gave narrow MWDs ($M_w/M_n < 1.1$), whereas a pyrolidinone-substituted one (**5**) resulted in broader MWDs ($M_w/M_n > 1.8$; Figure S2). Thus, trithiocarbonate (**2**) and dithiocarbamate (**3** and **4**) with electron-donating nitrogen atoms are most effective at controlling the molecular weights, most likely through the formation of a more stabilized cationic intermediate. In contrast to these thioesters, an oxygen ester (**6**) and a chloride (**7**), which are effective initiators for living cationic polymerizations mediated by Lewis acids,[5–8] are not efficient in this system, suggesting a mechanism that differs from that of the Lewis acid-catalyzed systems.

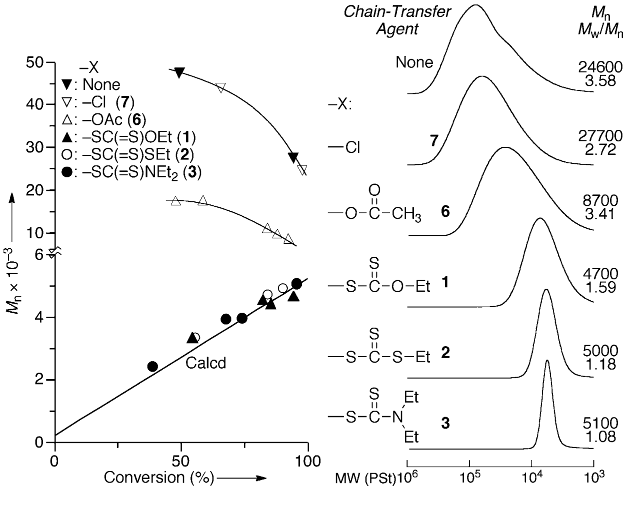

Figure 1. M_n and size-exclusion chromatography curves of the polymers obtained in cationic polymerization of IBVE with TfOH in the absence or presence of various chain-transfer agents in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10 vol%) at −40°C. $[M]_0$/[chain-transfer agent]$_0$/$[TfOH]_0 = 500/10/0.05$ mM.

The chain-end structures of the polymers obtained from **1**–**5** were analyzed using ^1H NMR spectroscopy (Figure S3). All of the spectra show the characteristic methine protons (b') adjacent to the thioesters at the growing or ω-chain ends. Furthermore, the M_n values calculated from the chain-end (b') to main-chain (e) protons are close to those obtained from size-exclusion chromatography (SEC) measurements. Therefore, almost all of the polymer chains possess thiocarbonylthio moieties with high end-group fidelity.

To further confirm the “living” or controlled nature of the polymerization, a fresh feed of IBVE was added to the polymerization mixture when the initial feed of monomer was nearly consumed (conversion > 95%). Even after the addition, the polymerization continued to induce further linear increases in M_n with narrow unimodal MWDs ($M_w/M_n < 1.1$) (Figure S4). Furthermore, controlled high-molecular-weight polymers were successfully obtained by changing the feed ratios of IBVE to the RAFT agent ($[M]_0/[\mathbf{2}]_0$) while keeping the concentration of the initiator constant. The M_n linearly increased in direct proportion to ($[M]_0/[\mathbf{2}]_0$) × conversion, reaching 1×10^5 (Figure 2). These results show that this cationic polymerization is very well controlled and that the polymer molecular weight is determined not by the protonic acid but by the thiocarbonylthio compound under the condition that the acid concentration is very low. It is

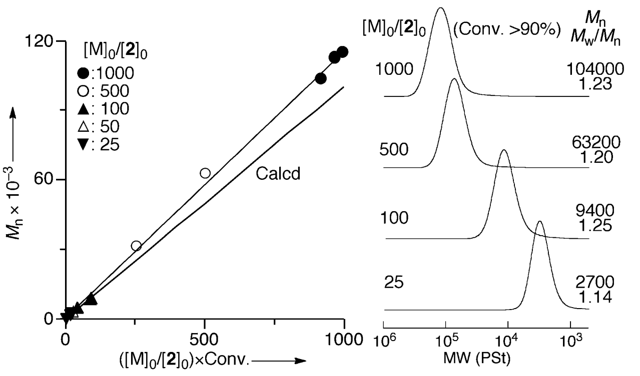

Figure 2. Synthesis of high-molecular-weight polymers by changing the feed ratio of monomer to RAFT agent. $[M]_0/[\mathbf{2}]_0/[TfOH]_0 = 500$ or 1000/1, 5, 10, or 20/0.05 mM in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10 vol%) at −40°C ($[M]_0/[\mathbf{2}]_0 = 25, 50, 100$) or −78°C ($[M]_0/[\mathbf{2}]_0 = 500, 1000$).

different from the results observed in the living cationic polymerization using HX/MX_n, in which the protonic acid determines the molecular weight through the formation of stable dormant C–X species.[5–8,29] Additionally, a low concentration of TfOH ($[TfOH]_0 = 0.05$ mM or ca. 8 ppm in the solution; $[TfOH]_0/[M]_0 = 1 \times 10^{-4}$; $[TfOH]_0/[\mathbf{2}]_0 = 5 \times 10^{-3}$) efficiently induces the metal-free "living" or controlled cationic polymerization.[3,29,30]

To further clarify the polymerization mechanism, the effects of TfOH were investigated, because it was already reported that the C–S bonds in thiocarbonylthio compounds can also be activated by Lewis acids.[27] The TfOH concentration was thus changed between 0.05 and 5.0 mM, while the concentrations of the monomer and RAFT agent were held constant ($[M]_0/[\mathbf{3}]_0 = 500/10$ mM). As the $[TfOH]_0$ increased, the polymerization became faster (e.g., $[TfOH]_0$, time, conversion = 0.05 mM, 90 min, 96%; 5.0 mM, 2 s, >99%) (Figure S5), and M_n gradually decreased, whereas the MWDs remained narrow ($M_w/M_n \leq 1.1$) (Figure 3a). Figure 3b shows the ratio of the molecular weight measured using SEC [M_n(obs)] to the calculated one [M_n(calcd)] assuming the formation of one polymer chain per molecule of **3**. As $[TfOH]_0$ increased, the ratio decreased to below 1, indicating that more chains were formed. Furthermore, in the ^{1}H NMR spectrum of the obtained polymer (Figure 3c), a new peak (*h*) appeared at 4.6 ppm, which can be attributed to another ω-chain end, i.e., an acetal proton originating from methanol quenching the polymerization. As indicated by the filled circles in Figure 3b, the acetal-chain-end content from all ω-ends [$-OCH_3/(-SC(S)Z) + (-OCH_3)$] nearly agrees with the TfOH content ($[TfOH]_0/([\mathbf{3}]_0 + [TfOH]_0)$). This result indicates that the growing carbocationic species exists at the same concentration as that of the initial TfOH and is terminated by methanol, whereas the dormant thioester terminal is intact upon quenching, and that the cationic polymerization proceeds not through a Lewis acid-catalyzed mechanism, which has already been reported for the thiocarbonylthio compounds,[27,28] but through a RAFT mechanism. Thus, the growing carbocationic species undergoes propagation without significant irreversible side reactions and reversibly interchanges with the dormant thioester terminal, resulting in a control of the molecular weight as in radical RAFT polymerizations.[31]

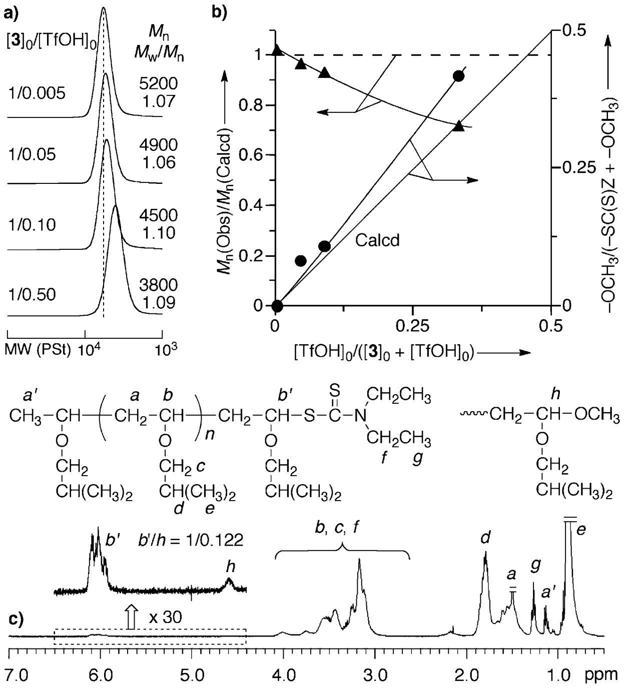

Figure 3. Effects of $[TfOH]_0$ on a) SEC curves of the polymers obtained at conversion >95% and b) M_n observed by SEC and terminal acetal groups by ^{1}H NMR spectroscopy in the polymerization of IBVE at $[M]_0/[\mathbf{3}]_0/[TfOH]_0 = 500/10/0.05–5.0$ mM in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10 vol%) at −40 °C; c) typical ^{1}H NMR spectrum of the polymers (M_n(SEC) = 2000, M_n(NMR) = 1800, $M_w/M_n = 1.07$) obtained at $[M]_0/[\mathbf{3}]_0/[TfOH]_0 = 500/10/0.10$ mM (conversion = 34%).

The cationic RAFT mechanism was further confirmed by ^{1}H NMR spectroscopy of the model reaction, in which an equimolar mixture of two RAFT agents (R–SC(S)Z) with different R and Z moieties (**3**: $R = CH_3CH(O\textit{i}Bu)$, $Z = NEt_2$, **8**: $R = CH_3CH(OEt)$, $Z = OEt$) were treated with a small amount of TfOH ($[\mathbf{3}]_0/[\mathbf{8}]_0/[TfOH]_0 = 30/30/0.15$ mM) in the absence of monomer at −40 °C (Figure S6). Even after 24 h, no exchange reaction occurred between the two RAFT agents (Figure S6C), indicating that TfOH does not work as a Lewis acid catalyst for the thiocarbonylthio compounds. In contrast, when the mixture was treated with $ZnCl_2$, a typical Lewis acid catalyst for the living cationic polymerization, the exchange reaction occurred to result in the exchanged products at least within 30 min (Figure S6D).[32] These results clearly demonstrate that the cationic polymerization with R–SC(S)Z/TfOH proceeds through the RAFT mechanism.

The choice of protonic acid is also important for inducing the controlled cationic polymerization. A series of protonic acids with different acidity or different nucleophilicity of their anions were used in conjunction with **2** for IBVE (Figure S7). A stronger acid, triflylimide (Tf_2NH), induced a faster polymerization to give polymers with controlled molecular weights. However, when using a weaker acid, such as TfOH·Py, CH_3SO_3H, or CF_3CO_2H, no polymers were obtained, most likely due to the formation of stable adducts of IBVE cation and a more nucleophilic counteranion.

The versatility of the RAFT cationic polymerization was then examined for other vinyl ethers (EVE: ethyl vinyl ether, CEVE: 2-chloroethyl vinyl ether) and *p*-methoxystyrene (pMOS). Although the conditions were optimized depending on the reactivity of the monomers, all of these monomers were successfully polymerized in a controlled fashion to give polymers with controlled molecular weights (Figure S8). In addition, *p*-hydroxystyrene (pHS) or *p*-vinylphenol, which usually cannot be polymerized with a Lewis acid due to the phenolic functional groups, were also successfully polymerized without protection of the hydroxy group, to give polymers with controlled molecular weights (Figure S9).[33,34]

Another notable feature of the cationic RAFT polymerization is its good compatibility with the radical RAFT polymerization, which would enable a more direct synthesis of block copolymers between cationically and radically polymerizable monomers. The transformation of cationic polymerization of IBVE into radical polymerization of vinyl acetate (VAc) was investigated using xanthate (**1**), which possesses a suitable Z group (Z = OR) in the RAFT agent (R−SC(S)Z) for VAc.[20–25,35] The homopolymer of IBVE prepared using **1** was isolated and used as a macro-RAFT agent for the radical polymerization of VAc in the presence of 2,2′-azobisisobutyronitrile (AIBN). The SEC curve shifted to higher molecular weights but kept its unimodal distribution, suggesting the formation of block copolymers of IBVE and VAc (Figure 4 a).

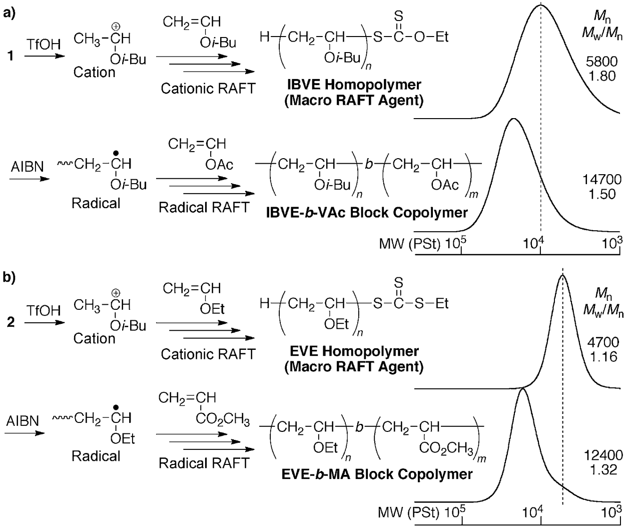

Figure 4. SEC curves a) IBVE homopolymer and IBVE-*b*-VAc block copolymer and b) EVE homopolymer and EVE-*b*-MA block copolymer by transformation of cationic to radical RAFT polymerization: $[\mathrm{IBVE\ or\ EVE}]_0/[\mathbf{1}\ \mathrm{or}\ \mathbf{2}]_0/[\mathrm{TfOH}]_0 = 500/10/0.50$ mM in *n*-hexane/CH_2Cl_2/Et_2O (80/10/10 vol%) at −78 °C; $[\mathrm{VAc}]_0/[\mathrm{macroRAFT}]_0/[\mathrm{AIBN}]_0 = 6000/60/30$ mM in bulk at 60 °C; $[\mathrm{MA}]_0/[\mathrm{macroRAFT}]_0/[\mathrm{AIBN}]_0 = 6400/64/8.0$ mM in toluene at 60 °C.

The formation of block copolymers was also confirmed using ^{1}H NMR spectroscopy, for which the observed unit ratio of IBVE to VAc was in good agreement with the calculated value (Figure S11). In addition, the terminal methine proton of the IBVE unit completely disappeared after the block copolymerization. The block copolymer was then saponified to prepare a block copolymer of vinyl ether and vinyl alcohol, which is difficult to synthesize directly using other reported methods. The saponification of VAc units results in the complete disappearance of the acetyl group and the appearance of hydroxy and methine protons of poly(vinyl alcohol) units (Figure S12). Each peak of both units was broad in [D$_6$]DMSO, suggesting that the block copolymers form micelles due to the amphiphilic nature of the resultant copolymers.

Another block copolymer between EVE and methyl acrylate (MA) was synthesized using trithiocarbonate (**2**), which is effective for controlling the radical polymerization of acrylate.[27] The formation of block copolymers was similarly confirmed using SEC (Figure 4 b) and ^{1}H NMR (Figure S13) analysis. These results indicate that the combination of the cationic and radical RAFT polymerizations is very effective for the synthesis of various block copolymers consisting of cationically and radically polymerizable monomers.

In conclusion, a novel, metal-free cationic RAFT polymerization was proposed and realized using thiocarbonylthio compounds in the presence of a small amount of a strong Brønsted acid, even at the ppm level. This polymerization proceeds through a reversible chain transfer of the growing carbocationic species to the dormant thioester bond. It is versatile for various electron-rich monomers, such as vinyl ether and alkoxy- and hydroxystyrene, and directly applicable to block copolymer synthesis by a transformation from cationic to radical RAFT polymerization. This discovery will open new cationic RAFT chemistry, which can be used in organic reactions as well as for preparing molecules or materials that cannot be accessed by radical RAFT chemistry.

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Keywords: block copolymers · cationic polymerization · living polymerization · organocatalysis · RAFT polymerization

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[32] The exchange reaction with $ZnCl_2$ suggests that the RAFT mechanism concurrently occurs in the Lewis acid-catalyzed living cationic polymerization through activation of the thioester bond.
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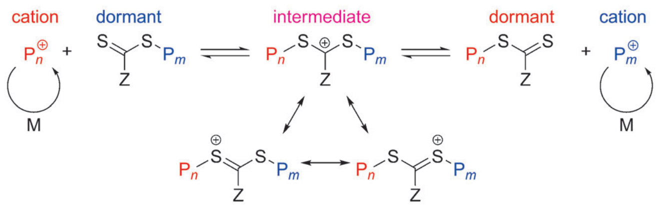
Communications

Polymerization

M. Uchiyama, K. Satoh,*
M. Kamigaito* ______ ■■■■–■■■■

Cationic RAFT Polymerization Using ppm Concentrations of Organic Acid



Cationic RAFTing: A cationic reversible addition–fragmentation chain-transfer (RAFT) polymerization with thiocarbonylthio compounds proceeds in the presence of a small amount of CF_3SO_3H. Various monomers including vinyl ethers as well as alkoxy- and hydroxystyrene can be used. A transformation from cationic to radical RAFT polymerization enables the synthesis of block copolymers between cationically and radically polymerizable monomers.