Metal-catalyzed radical polyaddition as a novel polymer synthetic route†

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A new class of polymerizations was developed *via* metal-catalyzed C–C bond forming radical polyaddition; the monomers were designed to have a reactive C–Cl bond, which can be activated by the metal catalysts to generate a carbon radical species, along with a C=C double bond, to which the carbon radical generated from another molecule adds to form a C–C backbone polymer with an inactive C–Cl pendant.

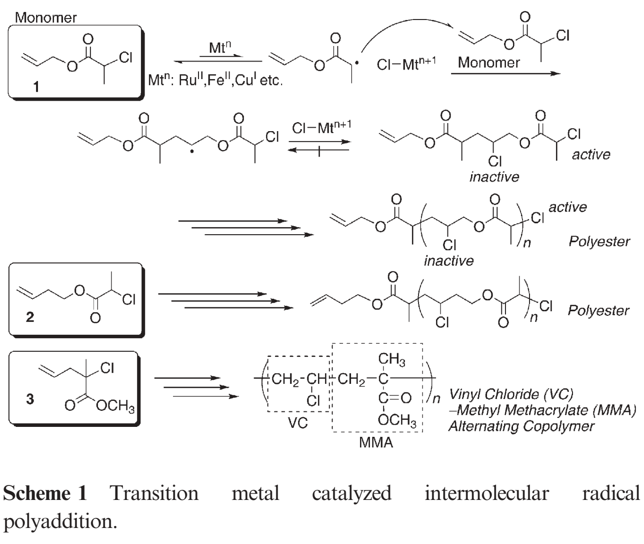
The metal-catalyzed atom transfer radical addition (ATRA) is one of the highly efficient carbon–carbon bond forming radical reactions, in which the radical species is generated through the metal-catalyzed cleavage of a carbon–halogen (C–X) bond and adds to an olefin to form the 1 : 1 adduct of the halide and olefin.[1] This chemistry has been effectively and widely applied to radical addition polymerizations of vinyl monomers that developed into the metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP) and to open a new era of precision polymer synthesis.[2–6] The radical addition polymerization proceeds *via* the metal-catalyzed reversible formation of the growing radical species from the dormant polymer terminal with a C–X bond, which originates from the halide initiator, and the addition of the growing radical species to the vinyl monomers.

In this communication, novel radical polyaddition reactions are developed for a designed monomer that possesses an active C–X bond and an unconjugated carbon–carbon double bond *via* metal-catalyzed carbon–carbon bond forming radical reactions (Scheme 1). Namely, the active or dormant C–X bond in the monomer is activated by the metal catalysts to form a radical species, which adds to the C=C double bond of another monomer molecule to generate a C–C bond as the main chain, along with an inactive C–X bond as the pendant. The original C–X bond in the monomer or the resulting oligomer or polymer is active in the catalysis due to the adjacent carbonyl group while the resulting C–X bond is inactive due to the absence of the adjacent carbonyl moiety.[7] These conceptually new polyaddition reactions can provide new types of linear polymers, such as the equivalents for the sequence-regulated vinyl polymers, as shown below. While monomers with a C–X bond and a conjugated C=C double bond were used in the metal-catalyzed radical addition polymerizations, the monomers served as an "ini-mer" to produce highly branched polymers *via* the activation of both the original and the resulting C–X bonds.[8]

Herein, we designed ester-linked monomers (**1** and **2**), which would afford aliphatic polyesters, and another monomer (**3**), which could apparently produce the equivalent structure of the alternating copolymer of vinyl chloride (VC) and methyl methacrylate (MMA). All these monomers were designed to have unconjugated double bonds, and the activated C–Cl bond adjacent to the carbonyl group.

For the first attempts to show the new radical polyaddition reactions, **1**, which can be easily obtained from allyl alcohol and 2-chloropropionyl chloride, was examined in conjunction with various transition metal complexes, such as Ru^{II}, Fe^{II}, and Cu^{I}, in toluene at 100 °C (Fig. 1). The reactions were carried out by the appropriate combinations of the metals and the ligands, all of which are effective for the metal-catalyzed living radical polymerizations; *i.e.*, the $RuCl_2(PPh_3)_3$ complex with an amine additive, $FeCl_2$ with 4 equiv. of P*n*-Bu$_3$ or *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and CuCl with 4 equiv. of PMDETA were used.[2,3,9–11] The monomer was smoothly consumed and the conversion reached over 90% to afford polymers in high yield with the $RuCl_2(PPh_3)_3$, $FeCl_2$–P*n*-Bu$_3$, and CuCl–PMDETA systems.

Fig. 2 shows the size-exclusion chromatography (SEC) curves of the polymers obtained using $FeCl_2$–P*n*-Bu$_3$ and CuCl–PMDETA. The peaks of the SEC curves shifted to a higher molecular weight and the peak areas of the lower molecular weight regions decreased as the polymerization proceeded. Similar to the conventional step polymerizations, the molecular weight of the



Scheme 1 Transition metal catalyzed intermolecular radical polyaddition.

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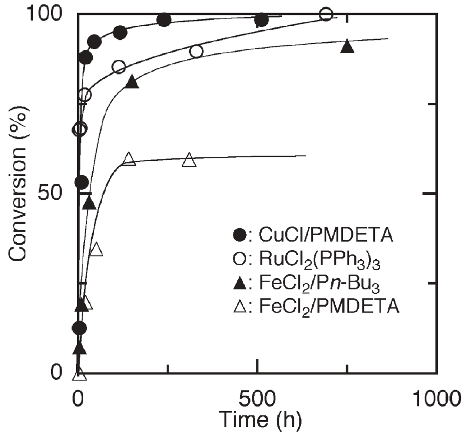

Fig. 1 Time–conversion curves for the polyaddition of allyl 2-chloropropanoate (**1**) with various metal complexes: $[\mathbf{1}]_0$ = 4.0 M; $[\mathrm{Mt}]_0$ = 100 mM; $[\mathrm{ligand}]_0$ = 400 mM in toluene at 100 °C. $[n\text{-}\mathrm{Bu}_3\mathrm{N}]_0$ = 400 mM (for $\mathrm{Ru^{II}}$).

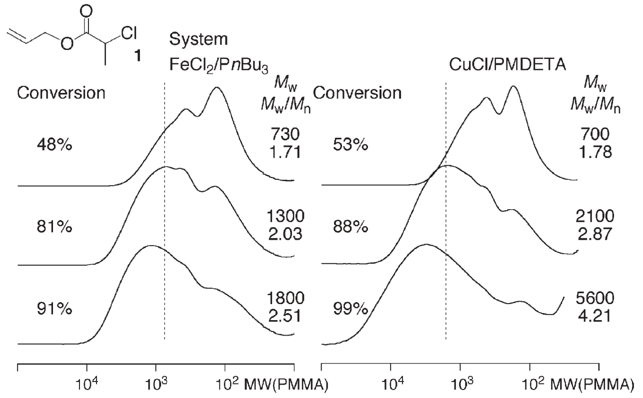

Fig. 2 Size-exclusion chromatograms of poly(**1**) obtained with the $\mathrm{FeCl_2}$–Pn-$\mathrm{Bu_3}$ (left) and CuCl–PMDETA (right) systems: $[\mathbf{1}]_0$ = 4.0 M; $[\mathrm{Mt}]_0$ = 100 mM; $[\mathrm{P}n\text{-}\mathrm{Bu}_3]_0$ = 200 mM (for Fe); $[\mathrm{PMDETA}]_0$ = 400 mM (for Cu) in toluene at 100 °C.

polymers increased exponentially at the later stage of the polymerizations. These results indicated that the step-growth polyaddition reactions effectively took place without unwanted ring-closing processes.[12]

Table 1 summarizes the polymerizations of **1–3** with a series of the catalysts under various conditions. The reactions proceeded in all cases to produce the polymers, although the molecular weights of some polymers were relatively low. For **1** and **2**, the reaction rates and the molecular weights of the polymers were dramatically changed by a combination of the central metals and the ligands. Among them, higher molecular weights were attained with the $\mathrm{FeCl_2}$–Pn-$\mathrm{Bu_3}$ and CuCl–PMDETA systems that reached M_w $\sim 5 \times 10^3$. Furthermore, upon the addition of tin 2-ethylhexanoate $[\mathrm{Sn(EH)_2}]$, which recently proved effective as a reducing agent for the oxidized catalyst in the Cu-mediated ATRP,[13] the reactions of **2** with the Cu and Fe systems were accelerated and the molecular weights of the polymers became the highest (ESI†). These indicate that the polyaddition proceeded *via* a one-electron redox reaction of the metal center and that this polyaddition reaction also suffered from the formation of small amounts of inactive catalysts during the metal-catalyzed radical reactions. For **3**, which possesses a C–Cl bond similar to that derived from methacrylate, the $\mathrm{RuCl_2(PPh_3)_3}$ system was more effective, giving a higher monomer conversion than the others. These results are consistent with the fact that the $\mathrm{Ru^{II}}$-based systems are more suitable for methacrylates in terms of the control of the polymerizations.[2,9] The addition of $\mathrm{Sn(EH)_2}$ also accelerated the polyaddition of **3** with $\mathrm{FeCl_2}$–Pn-$\mathrm{Bu_3}$, though the effects on the polymer molecular weight increase were smaller than those for **2**.

The structures of the obtained polymers were then analyzed by ^{1}H NMR and matrix-assisted laser-desorption-ionization time-of-flight mass (MALDI-TOF-MS) spectroscopy. Fig. 3 shows the ^{1}H NMR spectra of monomer **2** and typical samples of poly(**2**), which were obtained using $\mathrm{FeCl_2}$–Pn-$\mathrm{Bu_3}$ and CuCl–PMDETA and purified by preparative SEC to remove the residual monomer and the catalysts. In both spectra of the polymers, a series of sharp peaks (*1′–6′*) were observed, similar to those in the monomer (*1–6*), which indicates the presence of the double bond

Table 1 Transition metal catalyzed radical polyaddition of **1–3**[a]

Monomer	Metal	Ligand	$[\mathrm{Ligand}]_0$	Additive	Temperature/°C	Time/h	Conversion (%)[e]	M_n[f]	M_w[f]	$M_\mathrm{w}/M_\mathrm{n}$[f]
1	$\mathrm{RuCl_2(PPh_3)_3}$[b]	—	—	n-$\mathrm{Bu_3N}$[c]	100	330	90	410	820	2.01
1	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	400 mM	None	100	1180	94	460	1000	2.28
1	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	200 mM	None	100	750	91	710	1800	2.51
1	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	200 mM	$\mathrm{Sn(EH)_2}$[d]	100	750	87	630	1500	2.35
1	$\mathrm{FeCl_2}$	PMDETA	400 mM	None	100	310	60	1100	4000	3.70
1	CuCl	PMDETA	400 mM	None	100	240	99	1300	5600	4.21
2	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	200 mM	None	100	250	91	620	1200	1.95
2	$\mathrm{FeCl_2}$	$\mathrm{PPh_3}$	400 mM	None	100	300	47	400	610	1.52
2	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	200 mM	$\mathrm{Sn(EH)_2}$[d]	100	480	>99	1500	3500	2.32
2	CuCl	PMDETA	400 mM	None	100	460	97	1100	3000	2.74
2	CuCl	PMDETA	400 mM	None	80	240	97	1700	5500	3.30
2	CuCl	PMDETA	400 mM	None	60	1350	99	2600	11 000	4.12
2	CuCl	PMDETA	400 mM	$\mathrm{Sn(EH)_2}$[d]	60	500	>99	4600	21 000	4.60
3	$\mathrm{RuCl_2(PPh_3)_3}$[b]	—	—	n-$\mathrm{Bu_3N}$[c]	100	700	92	540	910	1.68
3	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	200 mM	None	100	1500	75	470	660	1.42
3	$\mathrm{FeCl_2}$	Pn-$\mathrm{Bu_3}$	400 mM	$\mathrm{Sn(EH)_2}$[d]	100	480	79	490	770	1.57
3	CuCl	PMDETA	400 mM	None	100	540	62	570	980	1.73

[a] Polymerization conditions: $[\mathrm{M}]_0$ = 4.0 M; $[\mathrm{Metal}]_0$ = 100 mM in toluene. [b] $\mathrm{RuCl_2(PPh_3)_3}$ was used as purchased. [c] $[n\text{-}\mathrm{Bu_3N}]_0$ = 400 mM. [d] $[\mathrm{Sn(EH)_2}]_0$ = 45 mM; EH: 2-ethylhexanoate. [e] Determined by gas chromatography. [f] The number-average and weight-average molecular weight (M_n and M_w, respectively) and polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) were determined by size-exclusion chromatography.

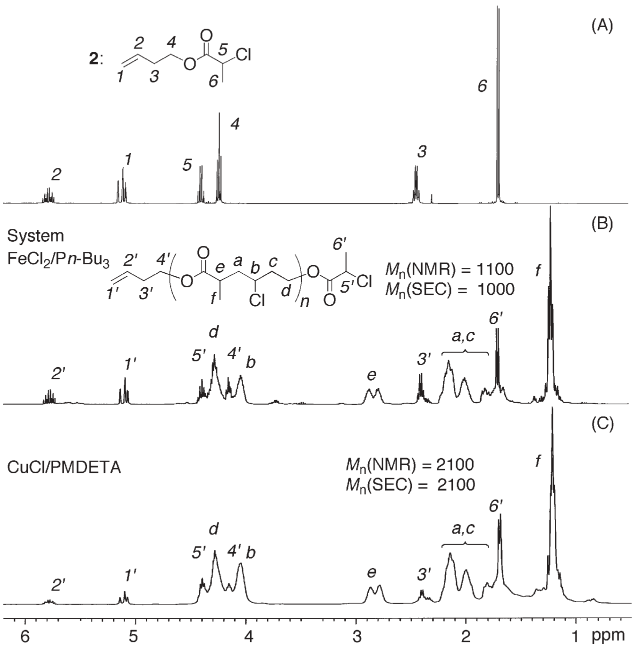

Fig. 3 ^{1}H NMR spectra of (A) 3-butenyl 2-chloropropionate (**2**) and poly(**2**) obtained in toluene with (B) $FeCl_2$–P*n*-Bu_3 at 100 °C or (C) CuCl–PMDETA at 80 °C.

and the active C–Cl bonds at the chain ends of the polymers. In addition to these signals, broad and relatively large peaks (*a*–*f*) appeared, assignable to the main chain protons of the repeating units of the aliphatic polyester that should be generated *via* the expected polyaddition reactions. No unsaturated protons, possibly caused by chlorine elimination, were detected other than those of the original terminal C=C bond, further indicating that the effective polyaddition reactions proceeded without any significant side reactions under the appropriate conditions. The molecular weights determined from the relative peak areas of the main-chain repeat units (*e*) to the end-group moiety (*1′* and *2′*) were close to those determined by SEC. These results show that the polymers were produced *via* the expected intermolecular polyaddition.

Fig. 4 shows the MALDI-TOF-MS spectra of poly(**1**) and poly(**2**) obtained using the CuCl–PMDETA system. The spectra consist of a series of peaks each separated by 148.3 and 161.8 Da intervals, which correspond to the formula weight of monomers **1** and **2**, respectively. The molecular weights of each individual peak were very close to the calculated values; *i.e.*, multiples of the formula weight of **1** or **2** plus the sodium ion from the salt for the MS analysis. This again indicates that the polymerizations proceed *via* intermolecular polyaddition. Both spectra exhibited a minor series of peaks, shifted by *ca.* 35 Da from the major series, which most probably suggests some loss of the reactive Cl atom at the chain end during the laser-induced ionization. Similar Cl-capped polymers synthesized *via* the living radical polymerization also lose the halogen at the ω-end during the MS analysis.[14] In contrast, the resulting C–Cl bonds in the main chain are more stable even toward the laser ionization.

In conclusion, metal-catalyzed intermolecular radical polyadditions successfully proceeded for the designed monomers and proved a novel polymer synthetic method. Further studies are now in progress to explore the systems for designing the equivalents to the sequence-regulated vinyl polymers.

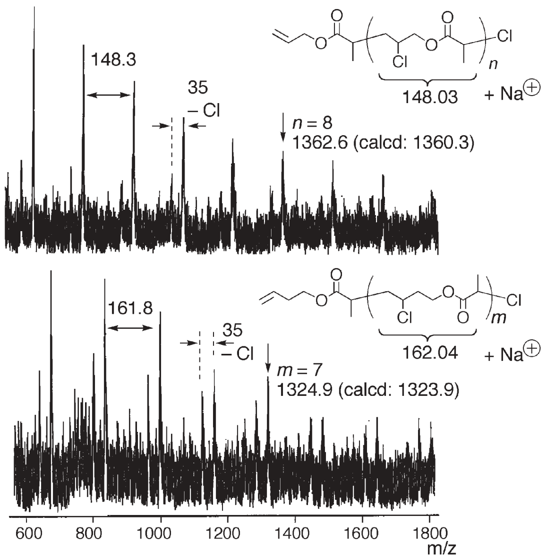

Fig. 4 MALDI-TOF-MS spectra of poly(**1**) (M_n = 1600, M_w/M_n = 2.51) and poly(**2**) (M_n = 1300, M_w/M_n = 3.07) obtained with CuCl–PMDETA: $[M]_0$ = 4.0 M; $[CuCl]_0$ = 100 mM; $[PMDETA]_0$ = 400 mM in toluene at 100 °C.

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