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A highly active Fe(I) catalyst for radical polymerisation and taming the polymerisation with iodine

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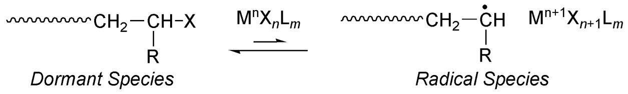
A fast and controlled radical polymerisation of acrylates and acrylamides can be achieved with a combination of a highly active metal catalyst, $Fe_2Cp_2(CO)_4$, and a mild radical scavenger, iodine, in the presence of an iodide initiator.

Recent years have witnessed dramatic advances in controlling radical polymerisation *via* various methods, most of which are based on dormant species that can reversibly generate growing radicals at low concentrations.[1] Such an equilibrium offers an almost equal opportunity of growth to all polymer chains and minimises side reactions between the growing radical polymer chains. However, this often leads to a slow polymerisation in return for the control. The advent of new, faster controlled or living radical polymerisations is awaited, in part from the viewpoint of industrial applications.

Metal-catalysed living radical polymerisation is one of the most promising ways in terms of the controllability and owes such controlled formation of radical species to reversible and homolytic cleavage of the dormant carbon–halogen bond through one-electron redox reaction of the metal centre (Scheme 1).[1a,b,2–6] A strategy for the control thus seems a use of mild catalysts that do not induce uncontrolled radical formation. However, for a faster polymerisation, a highly active catalyst should be needed, although this may in turn lead to poor control.



Scheme 1

This study reports on a highly active complex for a fast radical polymerisation and shows control of the reaction with a new additive.

We thus employed a dinuclear iron(I) complex, $Fe_2Cp_2(CO)_4$,[7,8] which has a lower redox potential than a mononuclear iron(II) counterpart, Fe(Cp)I$(CO)_2$, in conjunction with an iodide initiator (**1**; ethyl 2-iodoisobutyrate) (Fig. 1) for polymerisation of methyl acrylate (MA) in toluene at 60 °C.†

The polymerisation proceeded rapidly to reach a 89% conversion in 1 h (Fig. 2), which is in a remarkable contrast to the absence of activity of Fe(Cp)I$(CO)_2$ under the same conditions.[9] The molecular weight distributions (MWDs) of the polymers were not very narrow although the number-average molecular weights (M_n) were close to the calculated values. In contrast, $Fe_2Cp_2(CO)_4$ alone did not induce polymerisation without **1** at least for 30 days. Thus, the Fe(I)-catalysed polymerisation most probably proceeded *via* activation of the C–I covalent bond originating from **1**.‡

For controlling the polymerisation, molecular iodine (I_2) was added to the reaction mixture, where the additive may not only serve as a radical scavenger to trap the growing radicals[10] but may regenerate the carbon–iodine dormant terminal. On addition of a small amount (10 mM) of iodine, the polymerisation was slightly retarded but reached a high conversion (86%) in 1 h. The MWDs of the polymers became much narrower (M_w/M_n = 1.34). A similarly fast (93% in 5 h) and controlled (M_w/M_n = 1.28) polymerisation was also achieved with a larger amount (20 mM) of iodine. However, further addition of iodine, to over a half equivalent to the Fe(I) catalyst, inhibited the polymerisation.

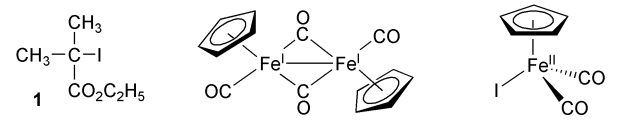


Fig. 1

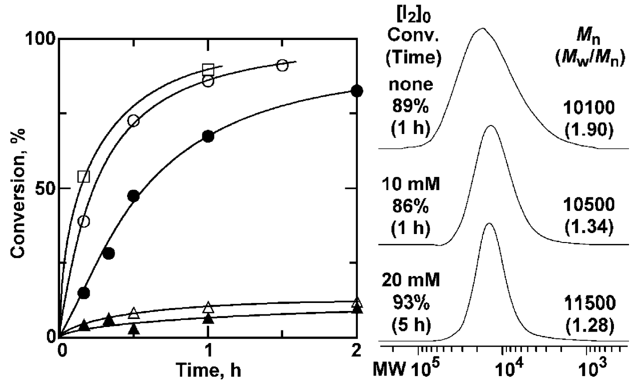


Fig. 2 Polymerisation of MA with $1/Fe_2Cp_2(CO)_4$ in toluene at 60 °C; $[MA]_0$ = 4.0 M, $[1]_0$ = 40 mM, $[Fe_2Cp_2(CO)_4]_0$ = 40 mM, $[I_2]_0$ = 0 (□), 10 (○), 20 (●), 30 (△), 40 (▲) mM.

The M_n obtained with 20 mM of iodine increased in direct proportion to monomer conversion (Fig. 3) and close to the calculated values (dotted the diagonal line) assuming that one molecule of **1** generates one polymer chain. ^1H NMR analysis of the polymers showed the presence of the ethyl methacrylate group from **1** at the α-end. This indicates that the polymerisation was initiated by the radical species from **1**. The added iodine reacts with the growing carbon radical species to give an iodine radical, which may add to monomer to generate a new polymer chain. However, this can be neglected due to the low reactivity of the iodine radical toward carbon–carbon double

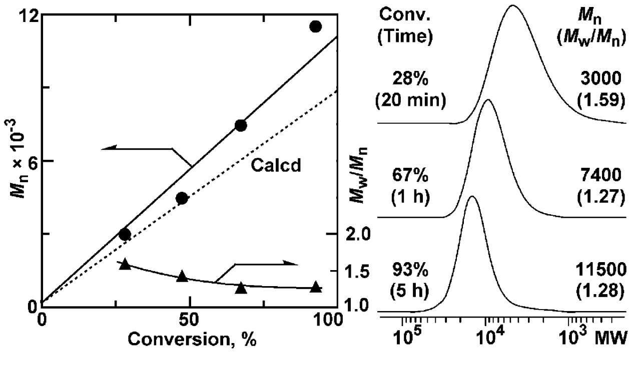


Fig. 3 M_n, M_w/M_n and size-exclusion chromatograms of poly(MA) obtained with $1/Fe_2Cp_2(CO)_4/I_2$ in toluene at 60 °C; $[MA]_0$ = 4.0 M, $[1]_0$ = 40 mM, $[Fe_2Cp_2(CO)_4]_0$ = 40 mM, $[I_2]_0$ = 20 mM.

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bonds,[11] although it can rapidly react with another iodine radical or a carbon radical species at a diffusion controlled rate.[12] The virtual absence of initiation by iodine radicals was also supported by ^{1}H NMR analysis.

Another possible working mechanism of the iodine additive is to convert the iron(I) complex into an iron(II) counterpart, $Fe(Cp)I(CO)_2$. The latter can be synthesised from $Fe_2Cp_2(CO)_4$ and I_2,[13] where iodine oxidises $Fe_2Cp_2(CO)_4$ into $Fe(Cp)I(CO)_2$. Addition of $Fe(Cp)I(CO)_2$ similarly slowed the polymerisation [94% conversion in 5 h with 40 mM of $Fe(Cp)I(CO)_2$; equimolar to $Fe_2Cp_2(CO)_4$]. The polymers had relatively narrow MWDs (M_w/M_n = 1.54) although the controllability was inferior to that with iodine. The added $Fe(Cp)I(CO)_2$ may react with the growing carbon radicals to generate a C–I covalent linkage and an active iron(I) species. The added Fe(II) complex may work similarly to copper(II) halides in Cu(I)-catalysed radical polymerisation.[14] The role of the added iodine still awaits further characterisation.

The Fe(I)/I_2-based system also enables a fast and controlled radical polymerisation of an acrylamide monomer, the control of which has been difficult with metal catalysts. The polymerisation of *N*,*N*-dimethylacrylamide (DMAA), for example, was almost quantitative within 2 h. As shown in Fig. 4, the M_n increased in direct proportion to monomer conversion and was close to the calculated values. The MWDs were narrow (M_w/M_n = 1.22). The system is one of the best suited for acrylamides in terms of the controllability and the maximum conversion, in comparison to other metal catalysts such as ruthenium[15] and copper.[16] A narrower MWD (M_w/M_n = 1.18) was attained with a copper catalyst while the polymerisation seemed to stop below 80% conversion.[16b]

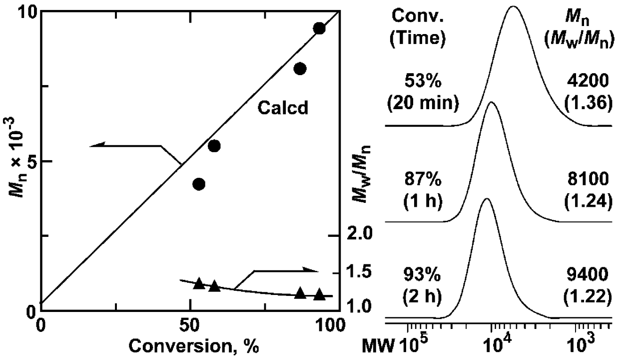

Fig. 4 M_n, M_w/M_n and size-exclusion chromatograms of poly(DMAA) obtained with **1**/$Fe_2Cp_2(CO)_4$/I_2 in toluene at 60 °C; $[DMAA]_0$ = 4.0 M, $[\mathbf{1}]_0$ = 40 mM, $[Fe_2Cp_2(CO)_4]_0$ = 40 mM, $[I_2]_0$ = 20 mM.

In conclusion, the Fe(I)/I_2-based system is effective in controlling radical polymerisations of acrylates[17] and acrylamides. This system can be regarded as new, consisting of a highly active metal catalyst that can generate a relatively high concentration of radical species and a weak radical scavenger that can regenerate the dormant species. The Fe(I)/iodine pair may therefore be regarded as a combined system of metal-catalysed, stable radical-mediated, and degenerative iodide-transfer radical polymerisations.[1,18]

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Notes and references

† *Materials* MA (Tokyo Kasei; > 99%) and DMAA (Wako Chemicals; > 98%) were dried over calcium chloride and distilled over calcium hydride under reduced pressure before use. $Fe_2Cp_2(CO)_4$ and $Fe(Cp)I(CO)_2$ (both Aldrich; > 97%) were used as received and handled in a glove-box (M. Braun Labmaster 130) under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm; O_2 < 1 ppm). Ethyl 2-iodoisobutyrate (**1**) was prepared according to the litereture.[19] Toluene (solvent) and *n*-octane (an internal standard for gas chromatographic analysis) were dried overnight over calcium chloride, distilled twice over sodium benzophenone ketyl (for toluene) or calcium hydride (for *n*-octane), and bubbled with dry nitrogen for 15 min immediately before use. *Polymerisations.* Polymerisation was carried out by the syringe technique under dry nitrogen in oven-dried glass tubes equipped with a three-way stopcock. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-octane as an internal standard. *Measurements.* The M_n and M_w/M_n of polymers were measured by size-exclusion chromatography in chloroform [for poly(MA)] or in DMF containing 10 mM LiBr [for poly(DMAA)] at 40 °C on three polystyrene gel columns [Shodex K-805L or KF-805L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL min^{-1}] connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; M_n = 630–220000; M_w/M_n = 1.06–1.22) as well as the monomer.

‡ Two working mechanisms of $Fe_2Cp_2(CO)_4$ in radical addition reactions have been suggested.[20] In one,[20a] the dinuclear complex reversibly activates the C–X bond while in the other[20b] it decomposes into an Fe(I) radical species [$\cdot FeCp(CO)_2$] under UV-irradiation and abstracts a halogen atom from a halide to generate a carbon radical species. In our case, the iodide compound (**1**) alone induced a very slow and incomplete consumption of MA probably due to thermal initiation to give polymers with broad MWDs (38% conversion in 41 days, M_n = 2800, M_w/M_n = 5.6). Addition of Fe(II) [$Fe(Cp)I(CO)_2$] inhibited the polymerisation completely. Futhermore, our polymerisation with **1**/$Fe_2Cp_2(CO)_4$ was carried out without irradiation. These results may support Scheme 1 but may not completely rule out a degenerative chain transfer mechanism.[1,18]

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