Ru(II)-Mediated Living Radical Polymerization: Block and Random Copolymerizations of *N*,*N*-Dimethylacrylamide and Methyl Methacrylate

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SUMMARY: $RuCl_2(PPh_3)_3$ led to living radical copolymerization of *N*,*N*-dimethylacrylamide (DMAA) and methyl methacrylate (MMA) in conjunction with a halide-initiator (R–X; $CHCl_2COPh$, CCl_3Br) and $Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C. Both the monomers were polymerized at almost the same rate into random copolymers, where the number-average molecular weights (M_n) increased in direct proportion to weight of the obtained polymers, and the molecular weight distributions (MWDs) were narrow throughout the reactions (M_w/M_n = 1.2–1.6). MMA was consumed faster in the copolymerization than in the homopolymerization, which was due to the interaction of DMAA with the ruthenium complex. The Ru(II)-based initiating system was also effective in block copolymerization of DMAA and MMA.

Introduction

Extensive efforts have been directed towards developing living polymerizations[1]. Although it is increasingly important to develop such precision processes applicable to polar functional monomers, not many living polymerizations are tolerant to polar groups. One of the most significant features of radical polymerizations is their versatility, as indicated by the wide variety of applicable monomers and their facile copolymerizability, in contrast to ionic counterparts, where polar functional groups often deactivate ionic growing species and the monomer reactivity greatly changes with electronic nature of their substituents.

We have developed living radical polymerizations of methacrylates and styrenes catalyzed by transition metal complexes such as ruthenium[3], iron[4], nickel[5], and rhenium[6] (Eq. 1). These living polymerizations proceed via the metal-assisted reversible activation of carbon–halogen terminals derived from a halide initiator, where the metal center undergoes one-electron redox reaction. A key to these living polymerizations is an equilibrium between the dormant and

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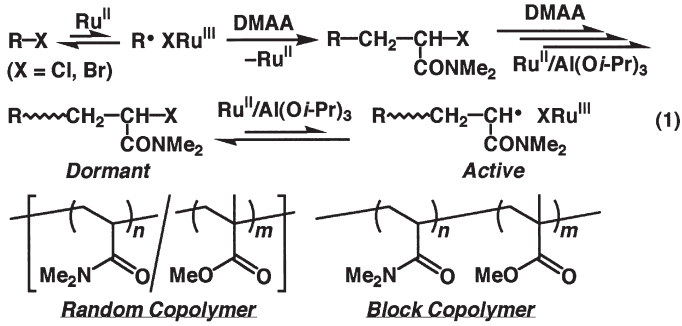
the active species, where the equilibrium is shifted to the former[2f, 2g]. This methodology has proved effective because the growing radical species is kept at low concentrations to diminish bimolecular termination reactions[2], the most serious chain breaking processes in free radical polymerization.



More recently, we have found that a ruthenium(II)-complex, $RuCl_2(PPh_3)_3$, induced living radical polymerization of a polar monomer, *N*,*N*-dimethylacrylamide (DMAA), in conjunction with a halide initiator (R–X) and $Al(O\textit{i}\text{-}Pr)_3$ to give polymers of controlled molecular weights and narrow molecular weight distributions (MWDs)[7]. This study deals with the living radical, statistic (or random) copolymerization of DMAA and methyl methacrylate (MMA) with the Ru(II)-based initiating system and the synthesis of their block copolymers by sequential living polymerization.

Living Random Copolymerization of MMA and DMAA

An equimolar mixture of MMA and DMAA was polymerized with $CHCl_2COPh$/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C. As shown in Fig. 1, both monomers were polymerized almost simultaneously. MMA was consumed much faster than in the homopolymerization where it takes over 4 days to reach 90% conversion under the same conditions[8], while such a dramatic acceleration was not seen for DMMA in its homo- and copolymerizations. The fast consumption of MMA is due to some interaction between $RuCl_2(PPh_3)_3$ and the amide group of DMAA or of the DMAA unit in the polymers, similarly to added amines, which also accelerate the Ru(II)-catalyzed polymerization of MMA[9]. A bromide-initiator, CCl_3Br, also induced random copolymerization of the two monomers in conjunction with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}\text{-}Pr)_3$.

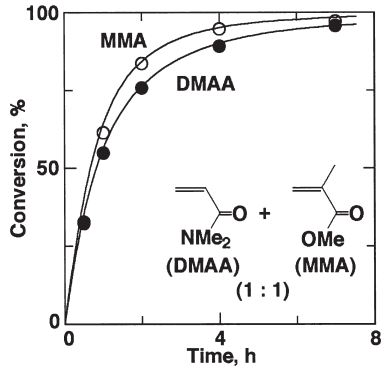


Fig. 1: Polymerization of mixture of DMAA (●) and MMA (○) with $CHCl_2COPh$/$RuCl_2(PPh_3)_3$/$Al(Oi\text{-}Pr)_3$ in toluene at 80°C: $[DMAA]_0 = [MMA]_0 = 1.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

Fig. 2 plots the number-average molecular weights (M_n) and MWDs of the polymers. Irrespective of the halogens in the initiators, the size-exclusion chromatograph (SEC) curves shifted to higher molecular weights as the reaction proceeds, keeping unimodal and narrow MWDs. With CCl_3Br, the M_n increased with polymer yield and was very close to the calculated value assuming that one molecule of the initiator generates one living polymer chain. The M_n were higher with $CHCl_2COPh$ similarly to the homopolymerization[7]. These are due to the low reactivity of the C–Cl bonds relative to C–Br, which results in slower initiation as well as slower interconversion between the dormant and the radical species (cf. Eq. 1).

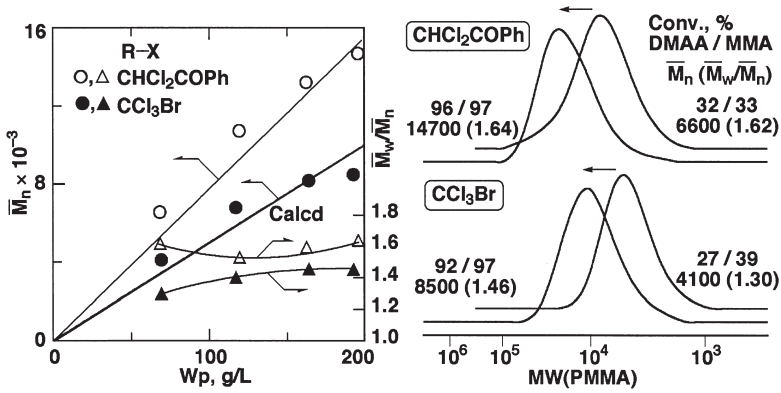


Fig. 2: M_n, M_w/M_n, and SEC curves of copolymers of DMAA and MMA obtained with R–X/$RuCl_2(PPh_3)_3$/$Al(Oi\text{-}Pr)_3$ in toluene at 80°C: $[DMAA]_0 = [MMA]_0 = 1.0$ M; $[R\text{–}X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: (○, △) $CHCl_2COPh$; (●, ▲) CCl_3Br.

Another copolymerization at a feed ratio DMAA/MMA = 1/9 also gave similar results; both monomers were polymerized almost simultaneously to give polymers whose molecular weights increased with conversion (Fig. 3). The MWDs were unimodal throughout the reactions and narrower than those obtained in the copolymerization of the equimolar mixture. This is due to the lower content of DMAA, which results in broader MWDs when polymerized with the Ru(II)-based system.

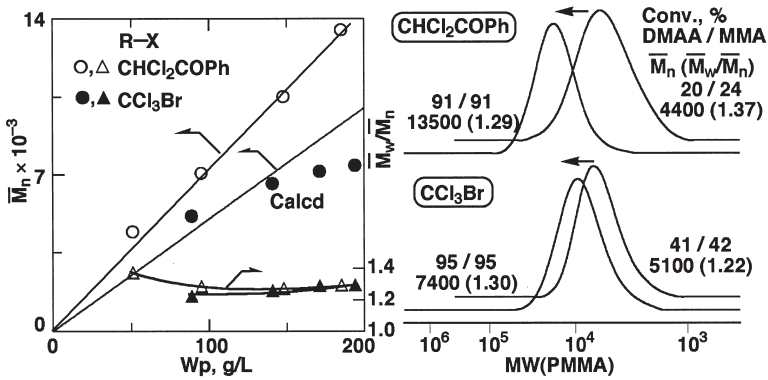


Fig. 3: M_n, M_w/M_n, and SEC curves of copolymers of DMAA and MMA obtained with R–X/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ in toluene at 80°C: $[DMAA]_0$ = 0.20 M; $[MMA]_0$ = 1.8 M; $[R–X]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(Oi\text{-}Pr)_3]_0$ = 40 mM. R–X: (○, △) $CHCl_2COPh$; (●, ▲) CCl_3Br.

The ^{1}H NMR spectrum (Fig. 4C) of the products obtained from the equimolar mixture is different from a simple sum of those of homopolymers (Fig. 4A and 4B). The signals (d) of the methyl ester protons of MMA units in Fig. 4C are not single, unlike that of the homopoly(MMA) (Fig. 4B), and the methyl protons of DMAA units (signal a) were broadened in comparison with the homoply(DMAA) (Fig. 4A). Similar changes were also observed for other absorptions. These show that the products are not mixtures of the homopolymers but statistical or random copolymers. This is also the case for the products from the 1/9-mixture of DMAA and MMA (Fig. 4D). The number-average degrees of polymerization (DP_n) of each monomer, calculated from the peak intensity ratios of the main-chain units to the phenyl groups originated from $CHCl_2COPh$, were slightly higher than the calculated values based on the feed ratio and the gas-chromatographic conversions. However, the unit ratios were close to the calculated values.

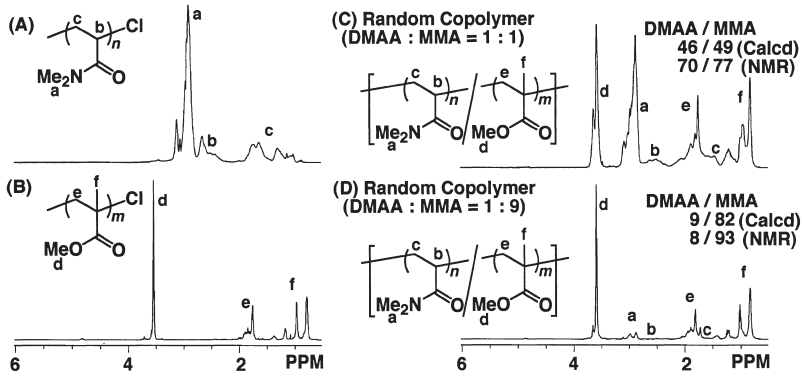


Fig. 4: ^{1}H NMR spectra of poly(DMAA) (A), poly(MMA) (B), copolymers of DMAA and MMA at 1/1 (C) and 1/9 (D) feed ratio obtained with $CHCl_2COPh/RuCl_2(PPh_3)_3/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C.

These results indicate that the R–X/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ initiating system induced living random copolymerization of DMAA and MMA.

Acceleration of Polymerization by DMAA

As described above, the consumption of MMA was much faster than that in the homopolymerization. This indicates a fast cross propagation between the two monomers or due to some interaction of DMAA with the Ru(II)-catalyst, which increases the catalytic activity.

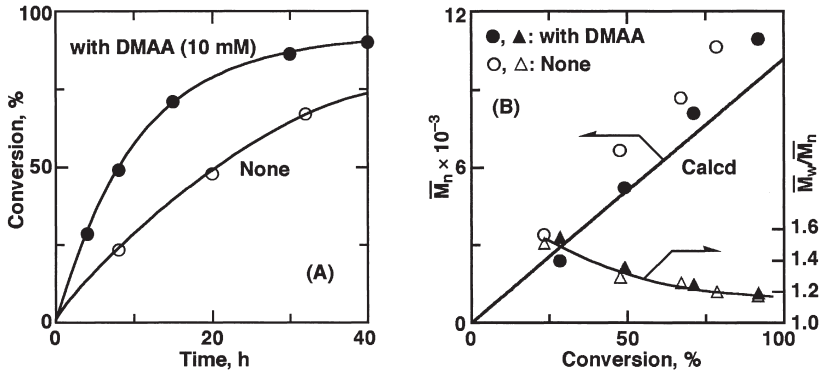


Fig. 5: Polymerization of MMA with $CHCl_2COPh/RuCl_2(PPh_3)_3/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C in the presence (●) and the absence (○) of DMAA: $[MMA]_0$ = 2.0 M; $[CHCl_2COPh]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(O\textit{i}\text{-}Pr)_3]_0$ = 40 mM; $[DMAA]_0$ = 10 mM.

To investigate this, homopolymerization of MMA was carried out in the presence of small amount (10 mM) of DMAA, equimolar to $RuCl_2(PPh_3)_3$ or only 0.5 mol% of MMA. As shown in Fig. 5A, a small amount of DMAA accelerated the MMA polymerization almost 2.5 times. Such a large increase in rate by a small amount of added DMAA indicates that it is mainly due to some interaction between DMAA or the repeat unit in the polymer chain and the Ru(II) complex. Interestingly, a similar acceleration also occurs on addition of nitrogen compounds like butyl amines[9]. The M_n increased in direct proportion to monomer conversion and agreed well with the calculated, as with that obtained without DMAA (Fig. 5B).

Block Copolymers of MMA and DMAA

We also investigated the synthesis of AB-type block copolymers of MMA and DMAA with the Ru(II)-based initiating system. MMA was thus polymerized with a monofunctional chloride initiator, H–$(MMA)_2$–Cl[10], coupled with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}\text{-}Pr)_3$ to give living homopoly(MMA) with M_n = 11000 and M_w/M_n = 1.32, into which was added an equimolar amount of DMAA (Fig. 6). Added DMAA was smoothly polymerized to increase the molecular weights with keeping monomodal MWDs (M_n = 23900, M_w/M_n = 1.80). This shows the formation of block copolymers of MMA and DMAA.

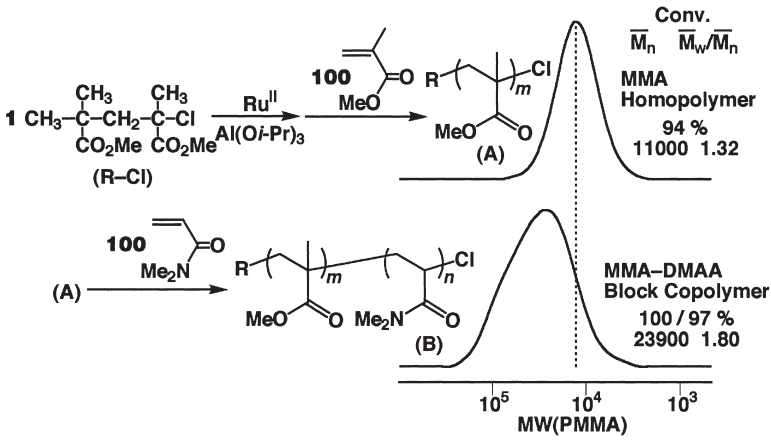


Fig. 6: SEC curves of poly(MMA) (A) and MMA–DMAA block copolymers (B) obtained with **1**/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80°C: $[MMA]_0$ = 2.0 M; $[\mathbf{1}]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(O\textit{i}\text{-}Pr)_3]_0$ = 40 mM; DMAA/MMA = 1/1.

Fig. 7 also supports the formation of block copolymers. As shown in Fig. 7B, the spectrum showed absorptions (d–f) due to DMMA repeat units in addition to those of MMA units. The absorptions of MMA units remain sharp, unlike the spectra of the random copolymers (cf. Fig. 4C). The methyl ester protons adjacent to the PMMA ω-end chloride (a') completely disappeared in Fig. 4D, which suggests that the polymerization of DMAA was initiated from the living PMMA to form AB-type block copolymers. The unit ratio of MMA to DMAA measured by their peak intensity ratios was 0.90 close to that from the calculated value (1.02). The copolymer was soluble in methanol whereas the prepolymer of MMA was insoluble. These results indicate that the R–Cl/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ initiating system is effective in the synthesis of block copolymers of DMAA and MMA.

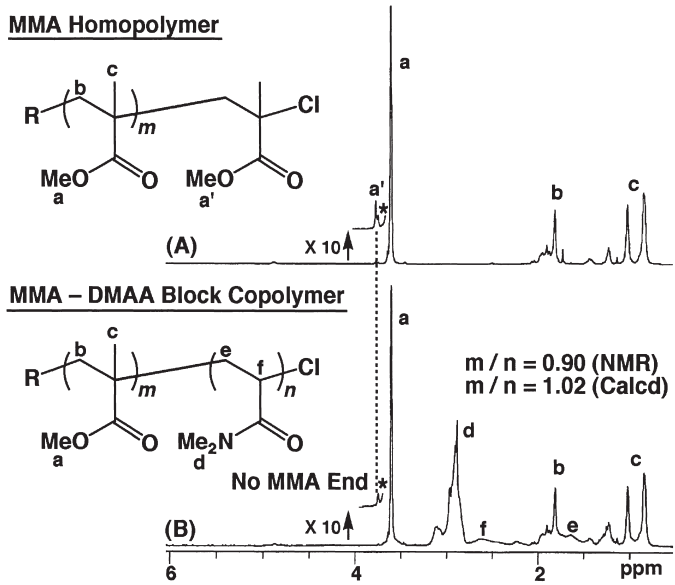


Fig. 7: ^{1}H NMR spectra of poly(MMA) (A) and MMA–DMAA block copolymers (B) obtained with **1**/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ in toluene at 80°C. The lines marked by * are ascribed to satellite lines.

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