ICAR ATRP of Styrene and Methyl Methacrylate with Ru(Cp*)Cl(PPh$_3$)$_2$

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Atom transfer radical polymerization (ATRP)[1,2] is a robust and facile method for the controlled radical polymerization of various vinyl monomers.[3] ATRP employs dynamic equilibrium between free radicals (R$^\bullet$ or P$^\bullet$) and dormant species (R−X or P−X), which is strongly shifted toward the latter species. The equilibrium relies on a redox process between a transition metal complex catalyst (Mt^z/L$_n$) and an organic halide to reversibly form X−Mt^{z+1}/L$_n$ and a propagating radical. One of the limitations of ATRP is the relatively large amount of catalyst needed to mediate polymerization and compensate for radical termination. This limitation has been recently alleviated by using catalyst recycling[4−6] and also regeneration via activators regenerated by electron transfer (ARGET) and initiators for continuous activator regeneration (ICAR).[7−15] These processes carried out with ppm amounts of the most active ATRP catalyst also tolerate some air and inhibitors in the reaction mixtures[16,17] (Scheme 1).

The most commonly used transition metal for ATRP catalyst is copper;[18,19] however, other transition metal complexes have been also used successfully.[2,20−33] Some active ATRP catalysts contain a half-sandwich organometallic complex with transition metals such as Mo^{III},[34] Fe^{II},[30] and Ru^{II}.[35−38] It was reported that ATRP of methyl methacrylate (MMA) with Ru(Cp*)Cl(PPh$_3$)$_2$ catalyst proceeded rapidly in the early stage but leveled off around monomer conversion of 50%.[35] Probably, the high activity of this catalyst could be related to electron-donating pentamethylcyclopentadienyl (Cp*) ligand. It leads to a high concentration of the growing radicals at the very early stages of the polymerization, resulting in excessive radical termination. Although this catalyst seems to be too active for normal ATRP, it could be a good candidate for ARGET or ICAR ATRP. For example, although CuBr/Me$_6$TREN catalysts is too active in normal ATRP of MMA,[39,40] it is an excellent catalyst in ARGET ATRP for MMA and styrene (S) with a few ppm of Cu.[8,41] Ru(Cp*)Cl$_2$(PPh$_3$) activated by AIBN was previously applied for atom transfer radical addition of CCl$_4$ and *p*-tosyl chloride to alkenes, e.g., S (50−1000 ppm Ru) and MMA (2000 ppm Ru).[42] However, polymerization of these monomers catalyzed by 100 ppm or less of Ru complex has not been reported.

In this Communication, we present results of ICAR ATRP of S and MMA catalyzed by 100 ppm or less of Ru(Cp*)Cl(PPh$_3$)$_2$. Thermal radical initiators, V-40 [1,1′-azobis(1-cyclohexanecarbonitrile)] and AIBN (2,2′- azobis(isobutyronitrile)), were used to continuously regenerate the Ru^{II} activator from the Ru^{III} deactivator, which resulted from the radical termination process. Table 1 presents typical conditions for ICAR ATRP of S and MMA.

Scheme 1. ICAR ATRP Catalyzed by Ru(Cp*)Cl(PPh$_3$)$_2$

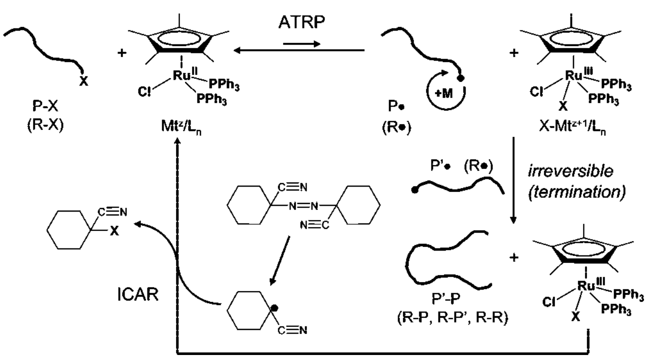

Table 1. Conditions for ICAR ATRP of S and MMA in the Presence of Ru^{II} (Cp*)Cl(PPh$_3$)$_2$ Catalyst[a]

expt	M	solvent	temp (°C)	I	[I]/[RX]	[RX]	[Ru] (ppm)
1	S	A	85	V-40	0.1	EBiB	100
2	S	A	85	V-40	0.1	EBiB	30
3	S	A	85	V-40	0.1	EBiB	10
4	MMA	A/D	80	V-40	0.2	BPN	100
5	MMA	A	60	AIBN	0.1	BPN	100

[a] Monomers (M): styrene (S) and methyl methacrylate (MMA). General conditions: 25 vol % of solvent: anisole (A) or anisole/*N,N*-dimethylacetamide (D) 3:7 by volume (A/D), targeted M_n = 30 000: [S]:[RX] = 286:1 and [MMA]:[RX] = 298:1. Thermal initiators (I): V-40 ($T_{1/2,10\,h}$ 88 °C), AIBN, ($T_{1/2,10\,h}$ 65 °C). ATRP initiators (RX): ethyl 2-bromoisobutyrate (EBiB), 2-bromopropionitrile (BPN). Concentration of Ru in mol ppm related to monomer.

ICAR ATRP of S was carried out at 85 °C using V-40 and EBiB as the initiator (Table 1, experiments 1−3). The molar ratio of [V-40]/[EBiB] was 0.1. The targeted M_n was 30 000 (DP = 286), and the concentration of the catalyst was progressively decreased from 100 to 10 ppm. Semilogarithmic plots of ln([M]$_0$/[M]) vs time (Figure 1a) show some deviation from the first-order kinetics with respect to monomer due to a significant decomposition of the initiator at long reaction times. The slowest polymerization was at the highest concentration of catalyst, since a significant portion of V-40 was plausibly consumed to reduce Ru^{III} species. Figure 1b shows evolution of M_n and polydispersity (PDI = M_w/M_n) as a function of styrene conversion. Number-average molecular weights in all cases (10, 30, and 100 ppm Ru) were slightly lower than those calculated for quantitative initiation, and the discrepancy increased with monomer conversion. This could be caused by generation of new chains not only by RX but also by concurrent initiation with thermal initiator (I) and thermal self-initiation of S, as previously observed for an ICAR process.[43] PDI values for polymerizations carried out with 100 and 30 ppm of catalyst were below 1.2. However, for the reaction carried out with 10 ppm of ruthenium, the PDI reached a value of 2 at 40% styrene conversion and then decreased to 1.5 at 75% conversion. This could be due to slow deactivation because of too low concentration of Ru^{III} in the system. Nevertheless, polystyrene obtained in the presence of 10 and 100 ppm of Ru was successfully chain extended with methyl acrylate (MA) under CuCl/CuCl$_2$/PMDETA-catalyzed ATRP conditions (anisole, 60 °C).

Copolymers of S and MA were analyzed by means of GPC and liquid chromatography under critical conditions (LCCC), and the traces are shown in parts c and d of Figure 1, respectively. GPC traces show a clear shift of molecular weight toward higher values in both cases ($M_{n,10Ru,PS}$ = 22 000 → $M_{n,PS\text{-}b\text{-}PMA}$ = 34 200; $M_{n,100Ru,PS}$ = 15 300 → $M_{n,PS\text{-}b\text{-}PMA}$ = 23 800). PDI decreased after chain extension of the PS macroinitiator obtained with 10

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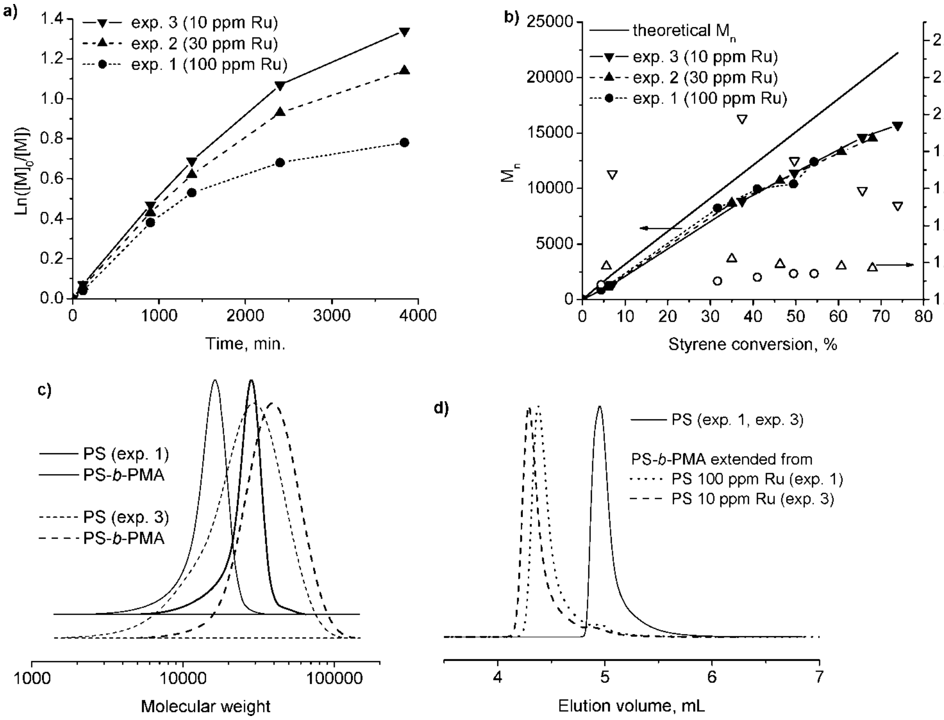

Figure 1. Results of ICAR ATRP of styrene: (a) kinetic plot; (b) evolution of M_n (filled symbols) and PDI (empty symbols) as a function of monomer conversion. Results of chain extension with MA of PS obtained in the presence of 10 and 100 ppm of Ru catalyst: (c) GPC and (d) LCCC traces.

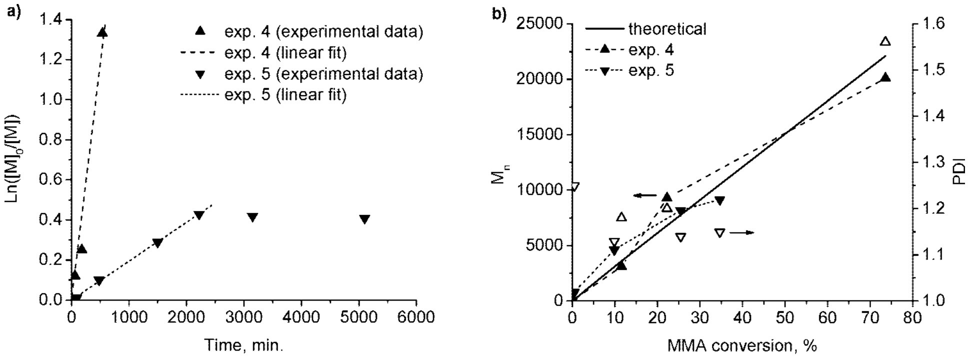

Figure 2. Results of ICAR ATRP of methyl methacrylate: (a) kinetic plot; (b) evolution of M_n (filled symbols) and PDI (empty symbols) as a function of monomer conversion.

ppm (1.48 → 1.21) or 100 ppm of Ru (1.13 → 1.11). LCCC analysis of both samples showed less than 5% of residual PS chains. This means that ICAR ATRP of styrene catalyzed even in the presence of small amounts of ruthenium provides polymers with high retention of chain-end functionality.

MMA was also successfully polymerized by ICAR ATRP with 100 ppm of Ru catalyst complex in different solvents. Reaction conditions are listed in Table 1 (experiments 4 and 5). The targeted M_n was 30 000 (DP = 298). Experiment 4 was carried out in a mixture of DMA and anisole at 80 °C. The rate of polymerization was much faster than in experiment 5, which was carried out in anisole at 60 °C (Figure 2a). In experiment 5, the reaction stopped when monomer conversion was ~35%. The molecular weights were close to those calculated for quantitative initiation. PDI was below 1.2 in the range of monomer conversion of 10–35% for experiment 5. For experiment 4 the PDI value was higher and reached 1.5 at ~75% MMA conversion (Figure 2b). Thus, for MMA polymerization more Ru catalyst is needed than for S to reach a comparable control. This may be mostly attributed to slower deactivation of tertiary MMA radicals.[39,44]

In conclusion, $Ru(Cp^*)Cl(PPh_3)_2$ was successfully employed in ICAR ATRP of styrene and methyl methacrylate in combination with V-40 and AIBN as thermal initiators. A low amount of Ru catalyst (30 ppm) was needed to obtain polystyrene with PDI < 1.2. Nevertheless, high degree of chain-end functionality was found even with 10 ppm Ru complex. These results indicate that not only Cu but also Ru catalysts could be used in very small amounts to control ATRP of S and MMA under ICAR conditions.

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