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"Living"/Controlled Radical Polymerization. Transition-Metal-Catalyzed Atom Transfer Radical Polymerization in the Presence of a Conventional Radical Initiator

Jin-Shan Wang and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie-Mellon University, 4400 5th Avenue, Pittsburgh, Pennsylvania 15213

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The transition-metal-catalyzed atom transfer radical addition, ATRA, paves a unique and efficient way for carbon−carbon bond formation in organic synthesis.[1] Recently, we have successfully introduced this method into polymer chemistry as a novel "living"/controlled radical polymerization process, i.e., atom transfer radical polymerization, ATRP.[2,3] Using a simple alkyl halide, R−X, as an initiator and a transition-metal species complexed with suitable ligand(s), M_t^n/L_x, as a catalyst, ATRP of alkenes proceeds with a negligible amount of irreversible termination and transfer reactions, leading to polymers with predetermined molecular weight up to M_n ~10^5 and narrow molecular weight distribution, M_w/M_n down to ~1.10.[2,3] Compared with other "living"/controlled radical polymerization systems reported,[4] ATRP works well with a broader class of monomers and offers a more general and efficient way toward various tailor-made polymers.[2,3]

In this communication, we report that in addition to a typical ATRP initiating system ($R-X/M_t^n/L_x$, bulk radical polymerization of vinyl monomers, such as styrene, St, and methyl acrylate, MA, at 100 ± 30 °C), a "living"/controlled process is observed using a conventional radical initiator, AIBN, and a transition-metal compound at higher oxidation state, e.g., $Cu^{II}Cl_2$, complexed with suitable ligand(s), e.g., 2.2′-bipyridine, bpy, as a catalyst.

Table 1 reports the characterization data of St bulk polymerization at 130 °C initiated by AIBN combined with or without $Cu^{II}Cl_2$ complexed by bpy. The molar ratio of $Cu^{II}Cl_2$ versus AIBN represents a critical parameter for the controlled polymerization while keeping constant $[bpy]_0/[Cu^{II}Cl_2]_0$ of 2/1. In the absence of $Cu^{II}Cl_2$, the polymerization is an ill-controlled process, as evidenced by a much higher molecular weight than expected and broader molecular weight distribution,[5] M_w/M_n ~ 3.0. However, the polymerization becomes much better controlled when only 2 molar equiv of $Cu^{II}Cl_2$ versus initiator is added. The initiator efficiency, *f*,[6] was increased from 22 to 65% and M_w/M_n reduced from 3.0 to 1.8. An increase in $[Cu^{II}Cl_2]_0/[AIBN]_0$ ratio further improves the degree of the control of the polymerization. A 10-fold molar excess of $Cu^{II}Cl_2$ results in a well-controlled radical polymerization with 95% initiator efficiency and the polydispersity as low as $M_w/M_n \approx 1.30$. It must be pointed out here that 1 molar equiv of Cu^{II} species versus growing radicals should be sufficient to promote a "living"/controlled ATRP of St.[2] The present results thus suggest that in these heterogeneous polymerization systems the real concentration of Cu^{II} species in the solution is much lower than $Cu^{II}Cl_2$ added, due to its low solubility in the system, and the rate of solubilization is lower than that of decomposition of AIBN.

Table 1. Characterization Data of Styrene Bulk Polymerization Initiated with AIBN/CuCl₂/bpy at 130 °C

$[AIBN]_0$ (mol/L)	$[CuCl_2]_0$ (mol/L)	$[bpy]_0$ (mol/L)	time (h)	conv,[a] (%)	$M_{n,th}$[b]	$M_{n,SEC}$	M_w/M_n
0.023	0	0	1.5	85	16 800	75 600	3.00
0.034	0.068	0.135	21	90	12 000	18 500	1.80[c]
0.025	0.10	0.20	41.5	90	16 300	21 300	1.55
0.018	0.18	0.36	70	92	23 300	24 600	1.30
0.0091	0.09	0.18	110	91	45 300	41 200	1.45
0.0065	0.060	0.12	119	88	59 500	56 900	1.45

[a] Detected by GC using THF as an internal reference. [b] Calculated based on eq 1. [c] Bimodal.

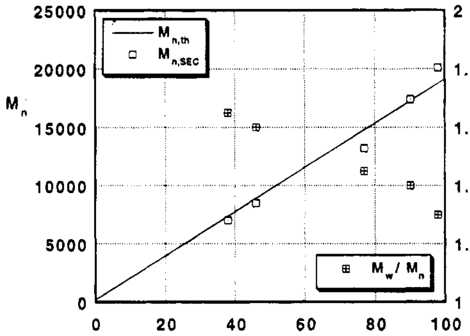

Figure 1. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk polymerization of styrene initiated with AIBN/$Cu^{II}Cl_2$/bpy at 130 °C. $[St]_0 = 8.75$ M, $[AIBN]_0 = 0.025$ M, $[Cu^{II}Cl_2]_0 = 0.25$ M, $[bpy]_0 = 0.50$ M.

Figure 1 shows that the experimental molecular weight linearly increases with monomer conversion up to 95% and matches the theoretical one calculated from eq 1 for bulk St polymerization initiated with AIBN and in the presence of 10 molar equiv of $Cu^{II}Cl_2$ and 20 molar equiv of bpy at 130 °C. This suggests the presence of minimal irreversible chain transfer reactions. Moreover, there appears a linear semilogarithmic plot of $\ln([M]_0/[M])$ vs polymerization time, indicative of a constant concentration of growing radicals during the polymerization. These results point toward a "living"/controlled process in St bulk polymerization initiated with the AIBN/$Cu^{II}Cl_2$/bpy system. Furthermore, a very good correlation of the theoretical molecular weight with the experimental one was found up to at least 5 × 10^4 with $M_w/M_n \leq 1.45$ (also see Table 1), indicating a high initiation efficiency of AIBN at 130 °C.[7]

$$M_{n,th} = 104 \times \{\Delta[M]/(2[AIBN]_0)\} \times conv \qquad (1)$$

It is known that $Cu^{II}Cl_2$ is a strong and efficient inhibitor/retarder for radical polymerization under usual conditions.[8] However, at high temperatures and in the presence of a coordinative ligand such as bpy, a reversible activation of the resulting alkyl chlorides occurs.[2] By analogy to ATRP initiated with the $R-X/M_t^n/L_x$ system,[2] the present results can be interpreted in terms of an alternative ATRP cycle (Scheme 1). Initially, the highly oxidized transition-metal species, $M_t^{n+1}X$, donates the halogen atom X to the initiating or propagating radicals, $I^\bullet$ or $I-P_i^\bullet$, with the formation of the reduced transition-metal species, M_t^n, and the dormant species, I−X and P_i-X. In the subsequent steps, the transition-metal species, M_t^n, promotes exactly the same ATRP process as the one initiated by $R-X/M_t^n/L_x$ as described previously.[2] The only difference between these two ATRPs is the following. In the case of using the $R-X/M_t^n/L_x$ initiating system, ATRP is first promoted by the activation of a dormant species, R−X, with M_t^n.[2] On the other hand, using $I-I/M_t^{n+1}X/L_x$, ATRP

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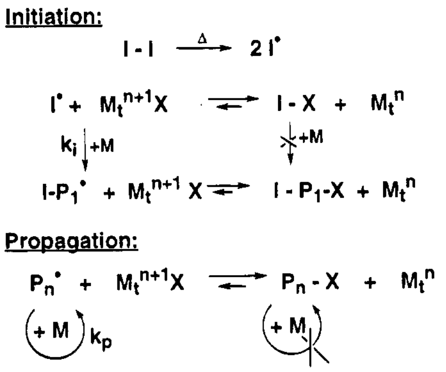
Scheme 1



originates from the deactivation reaction between radicals, I• or P_i–I•, and $Mt^{n+1}X$.

The involvement of an atom transfer pathway in AIBN/Cu^{II}/bpy-catalyzed ATRP of St is supported by the analysis of the end groups in the resulting products. Figure 2 presents the ^1H NMR spectrum of PSt produced using [AIBN]$_0$/[Cu^{II}Cl$_2$]$_0$/[bpy]$_0$ (1/10/20) at 130 °C. Two broad triplets at ca 4.4 ppm are attributed to the end group *c*-CH$_2$-C(Ph)*H*-Cl of two different stereoisomers (*m*/*r*) in Cl-end-capped PSt. Moreover, comparison of the integration of the signals of end group *c* with those of group *a* or *b* in the main chain of PSt gives a molecular weight, $M_{n,NMR} \approx 2950$, close to the one from SEC based on PSt standards, $M_{n,SEC} \approx 3140$ ($M_w/M_n \approx 1.30$). This strongly suggests that the PSt radicals are efficiently deactivated by Cu^{II}Cl$_2$.

However, an extension of the AIBN/Cu^{II}/bpy-catalyzed ATRP to other monomers reveals some interesting phenomena. For instance, by using the same initiating system, AIBN/Cu^{II}Cl$_2$/bpy (1/10/20), and the same experimental conditions, in bulk and at 130 °C, as ATRP of St, the MA polymerization is not a controlled process. The polymerization was very fast and led to gelation at ca. 40% monomer conversion. SEC analysis of the THF-soluble portion gave a much higher molecular weight than calculated according to eq 1, $M_{n,SEC} \approx 23\,500$ against $M_{n,SEC} \approx 6800$, and a very broad multimodal molecular weight distribution, $M_w/M_n \sim 3.7$. This suggests that the deactivation of growing radicals by Cu^{II}Cl$_2$ is much less efficient in MA polymerization than in St polymerization initiated with AIBN/Cu^{II}Cl$_2$/bpy (1/10/20) at 130 °C, leading to a very high concentration of growing radicals. This is consistent with the fact that electrophilic PMA radicals are less efficiently scavenged by electrophilic Cu^{II}X$_2$ than nucleophilic PSt radicals, due to the different polar properties of the transition states in these reactions.[8] Moreover, it is also well known that the rate constant of radical propagation for MA is ca. 15 times higher than that for St.[9] Therefore, the ratio of the deactivation rate of the growing radicals to the dormant species to the propagation rate must be higher in St ATRP than in MA ATRP. This, in addition to differences in solubilities of Cu^{II}X$_2$, may be responsible for the broader molecular weight distribution observed in MA ATRP.

To cope with such a problem, among the methods so far tried we found that the easiest and most practical way is to use a catalytic amount of AIBN as radical source in order to maintain the low concentration of growing radicals and a suitable alkyl halide, e.g., 2-chloropropionitrile, 2-PNCl, as a co-initiator to control the molecular weight of the final product. In this respect, it was observed that 1% molar equiv of AIBN relative to 2-PNCl is sufficient to promote a controlled ATRP of MA under otherwise the same [Cu^{II}Cl$_2$]$_0$, temperature, and [2-PNCl]$_0$/[Cu^{II}Cl$_2$]$_0$/[bpy]$_0$ of 1/1/2, resulting in a high initiator efficiency ($f \approx 94\%$) and a symmetrical molecular weight distribution with a lower polydispersity, $M_w/M_n \approx 1.25$. Thus, even 1–2 molar % of the catalyst (Cu^I species generated from Cu^{II} species and AIBN) is sufficient to catalyze the ATRP process.

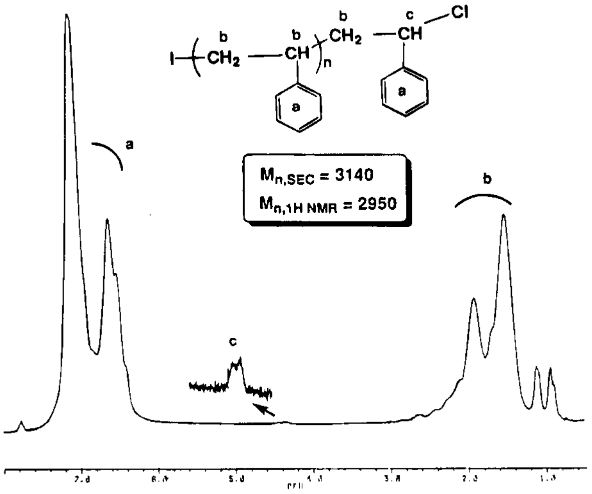


Figure 2. ^1H NMR of polystyrene initiated with AIBN/Cu^{II}Cl$_2$/bpy (1/10/20) at 130 °C.

In conclusion, the present work again suggests that our recently developed ATRP process offers a versatile route toward the "living"/controlled radical polymerization of alkenes with radical stabilizing substituents such as styrenes and (meth)acrylates. The presence of a catalytic amount of growing radicals and a fast equilibration between growing radicals and dormant species are mandatory for a successful ATRP.

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(5) $M_{n,SEC}$ values were determined by size exclusion chromatography calibrated using polystyrene standards.

(6) Initiator efficiency, $f = M_{n,th}/M_{n,SEC}$.

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