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Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes

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Atom transfer radical addition, ATRA, is an efficient method for carbon−carbon bond formation in organic synthesis, and many benefits of this method are now well recognized.[1] In some of these reactions, a transition-metal catalyst acts as a carrier of the halogen atom in a reversible redox process.[2] Initially, the transition-metal species, $M_t{}^n$, abstracts halogen atom X from the organic halide, RX, to form the oxidized species, $M_t{}^{n+1}X$, and the carbon-centered radical $R^{\bullet}$. In the subsequent step, the radical $R^{\bullet}$ participates in an inter- or intramolecular radical addition to alkene, Y, with the formation of the intermediate radical species, $RY^{\bullet}$. The reaction between $M_t{}^{n+1}X$ and $RY^{\bullet}$ results in a target product, RYX, and regenerates the reduced transition-metal species, $M_t{}^n$, which further promotes a new redox process. The fast reaction between $RY^{\bullet}$ and $M_t{}^{n+1}X$ apparently suppresses bimolecular termination between alkyl radicals and efficiently introduces a halogen functional group X into the final product in good to excellent yields.[2c−e]

This communication reports that the aforementioned transition-metal-catalyzed ATRA can be successfully used to control radical polymerization. An alkyl chloride, 1-phenylethyl chloride, 1-PECl, is an efficient initiator, and a transition-metal halide, CuCl, complexed by 2,2′-bipyridine, bpy, an efficient chlorine atom transfer promoter. This initiating system affords controlled polymers with predetermined molecular weight and narrower molecular weight distribution, $M_w/M_n < 1.5$, than obtained by conventional free radical polymerization. Recently, several methods for controlled/"living" radical polymerization have been reported.[3]

A typical polymerization was carried out by heating a reddish brown styrene, St, solution[4] of 1-PECl (0.01 molar equiv relative to monomer), CuCl (1 molar equiv relative to 1-PECl), and bpy (3 molar equiv relative to CuCl) in a glass tube sealed under vacuum, at 130 °C. A linear increase of number average molecular weight, $M_{n,SEC}$,[5] versus monomer conversions up to 95% was found after ca. 3 h (Figure 1).

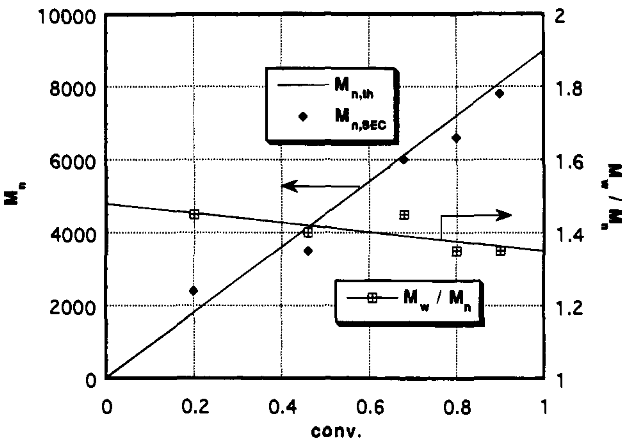

Figure 1. Dependence of molecular weights and polydispersities on conversion in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0 = 0.1$ mol/L, $[\mathrm{CuCl}]_0 = 0.1$ mol/L, $[\mathrm{bpy}]_0 = 0.3$ mol/L.

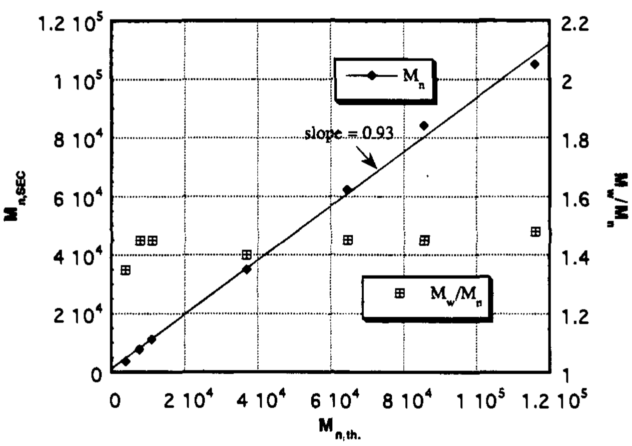

Figure 2. Correlation of experimental and theoretical (eq 1) molecular weights and polydispersities in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0/[\mathrm{CuCl}]_0/[\mathrm{bpy}]_0 = 1{:}1{:}3$.

The $M_{n,SEC}$ is very close to the theoretical one, $M_{n,th}$, calculated by means of eq 1.[6]

$$M_{nn,th} = ([M]_0/[1 - \mathrm{PECl}]_0) \times (MW)_0 \times \text{conversion} \quad (1)$$

This indicates that 1-PECl acts as an efficient initiator and the number of chains is constant. The molecular weight distribution is fairly narrow ($M_w/M_n = 1.3{-}1.45$). A linear plot of $\ln([M]_0/[M])$ versus polymerization time indicates that the concentration of growing radicals remains constant during propagation and termination is not significant. Both of these results suggest a "living" polymerization process with a negligible amount of irreversible transfer and termination.

Additionally, a series of experiments has been carried out at 130 °C, using various $[M]_0/[1\text{-PECl}]_0$ ratios and a constant $[1\text{-PECl}]_0/[\mathrm{CuCl}]_0/[\mathrm{bpy}]_0$ ratio of 1/1/3. Figure 2 compares the $M_{n,SEC}$ and $M_{n,th}$ calculated based on eq 1.

A linear plot is observed in a molecular weight range from 3.8×10^3 to 1.05×10^5. The slope of the straight line is 0.93, indicating a high initiator efficiency. The polydispersities of all polymers obtained also remain low and are smaller than in a conventional radical polymerization, i.e., $M_w/M_n < 1.5$.

Table 1 summarizes the results of styrene polymerization under various experimental conditions. When neither 1-PECl,

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(1) For reviews of atom transfer methods in organic synthesis, see: (a) Curran, D. P. *Synthesis* **1988**, 489. (b) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 715.

(2) For recent references to the formation of carbon−carbon bonds by transition metal-catalyzed chlorine atom transfer radical reactions, see: (a) Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827. (b) Hayes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 5533. (c) Nagashima, H.; Wakamatsu, H.; Ozaki, N., Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 1682. (d) Nagashima, H.; Ozaki, N., Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, *58*, 464. (e) Udding, J. H.; Tuijp, K. J. M.; van Zanden, M. N. A.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1994**, *59*, 1993.

(3) (a) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127, 133. (b) Solomon, D. H.; Waverly, G.; Rizzardo, E.; Hill, W.; Cacioli, P. U.S. Pat. 4,581,429, 1986. (c) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. (d) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943. (e) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638. (f) Matyjaszewski, K.; Gaynor, S.; Wang, J. S. *Macromolecules* **1995**, *28*, 2093.

(4) The reddish brown color of a slightly heterogeneous solution was formed within 30 s at 130 °C, irrespective of the mixing order of the components.

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

(6) $[M]_0$ and $[1\text{-PECl}]_0$ represent the initial concentrations of monomer, St, and 1-PECl, respectively, and $(MW)_0$ is the molecular weight of monomer.

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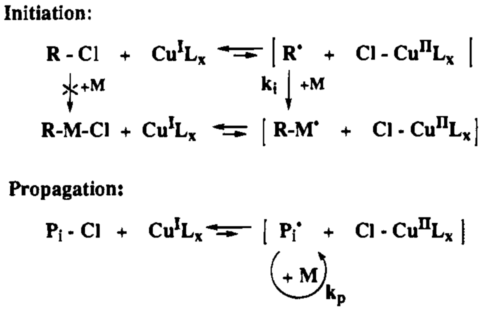
Table 1. Results of Styrene Bulk Polymerization at 130 °C

$[St]_0$ (mmol)	conv (%)	$[1\text{-PECl}]_0$ (mmol)	$[CuCl]_0$ (mmol)	$[bpy]_0$ (mmol)	$M_{n,th}$[a]	$M_{n,SEC}$	M_w/M_n
4.375	15	0	0	0		132100	1.76
4.375	52	0	0.182	0.54		134700	1.95
4.375	40	0.0528	0.0455		3400	68700	3.10
4.40	45	0.0528		0.135	4100	76500	2.10

[a] Calculated on the basis of eq 1.

Scheme 1



CuCl, nor bpy is used, the polymers have ill-controlled molecular weight and broader molecular weight distribution.

Furthermore, similar initiating systems based on various alkyl halides/transition metal species/coordinative ligands can be successfully used for the controlled polymerization of various vinyl monomers, such as acrylics, styrenics, and dienes.[7] Moreover, block copolymers of St and (meth)acrylates have been produced using the same technique as described for homopolymerization of styrene. Heating of chlorine atom end-capped polystyrene[8] (0.5g, $M_n = 4000$, $M_w/M_n = 1.45$) and 2-fold excess MA (1.0 g) in the presence of 1 molar equiv of CuCl and 3 molar equiv of bpy (both relative to polystyrene) at 130 °C results in MA block polymerization to form a desired PSt-*b*-PMA block copolymer (yield: 95%, $M_n = 13\,000$, $M_w/M_n = 1.35$).

By analogy with transition-metal-catalyzed ATRA[2c–e,9] the present results can be explained by the plausible mechanism shown in Scheme 1. It constitutes a number of ATRA processes and therefore can be called atom transfer radical polymerization, ATRP.

The catalyst Cu^I acts as a carrier of the chlorine atom in a redox reaction between Cu^I and Cu^{II}.[2c–e,9] The coordination of the bidentate nitrogen ligand to Cu^I increases the solubility of the inorganic salt and can also affect the position of the redox equilibrium to facilitate the abstraction of a chlorine from the initiator, 1-PECl, and the dormant species, P_i–Cl, with the formation of initiating and growing radicals, respectively. The reversible conversion of alkyl radical, R• and P_i•, to alkyl halide, R–Cl and P_i–Cl, may involve a direct atom transfer reaction[9,10] or oxidative addition/reductive elimination with the formation of the organocopper(III) intermediates.[9,11] If the concentration of growing radicals is low and the redox reaction is fast compared to bimolecular reactions of the radicals, the extent of the termination reactions is minimized, resulting in a "living" process. Moreover, if the rate of *reversible* conversion of P_i• to P_i–Cl is comparable to that of propagation, the molecular weight should be defined by eq 1 and the molecular weight distribution remains narrow.

Two observations support the participation of free radicals in ATRP. First, the tacticity of the polymers is similar to the tacticity of polymers synthesized by typical radical initiators.[12] Therefore, the organocuprate(III) species, if it exists, should not react directly with monomer; otherwise some effect on tacticity would be expected. Second, addition of 1.5 molar equiv of galvinoxyl relative to 1-PECl effectively inhibits the polymerization, and no styrene polymerization was found within 18 h.

It must be stressed that the present transition-metal-promoted ATRP, in which the molecular weight linearly increases with monomer conversion, is very different from typical redox radical telomerization promoted by transition-metal species,[13,14] in which the molecular weight does not increase with conversion.

In conclusion, we have shown that, when an alkyl chloride, 1-PECl, and a CuCl/bpy complex were used as an initiator and a catalyst, respectively, styrene polymerized by repetitive atom transfer radical additions to yield well-defined high molecular weight polymers with narrow molecular weight distributions. Compared to other "living" radical systems,[3] ATRP represents a simple, inexpensive, and more general method for controlled radical polymerization.[7]

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[7] Matyjaszewski, K.; Wang, J. S. U.S. pat. pending.

[8] Polystyrene was prepared as follows: heating of styrene (52.5 mmol), 1-PECl (1.66 mmol), CuCl (1.66 mmol), and bpy (4.98 mmol) in a sealed tube with stirring at 130 °C for 5 h. It was then dissolved in THF and precipitated in MeOH (three times), filtered, and finally dried at 60 °C under vacuum for 48 h. Yield: 95%.

[9] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978 and references therein.

[10] (a) Asscher, M.; Vofsi, D. *J. Chem. Soc., Phys. Org.* **1968**, 947. (b) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

[11] (a) Orochov, A.; Asscher, M.; Vofsi, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1000. (b) Mitani, M.; Kato, I.; Koyama, K. *J. Am. Chem. Soc.* **1983**, *105*, 6719.

[12] For example, the tacticity of poly(methyl methacrylate) ($M_n = 35\,400$, $M_w/M_n = 1.40$) synthesized using 1-PECl/CuCl/Bpy (1/1/3 molar ratio) initiator system at 130 °C is *rr/mr(rm)/mm*: 53/38/9. These values are very close to the one prepared using a typical radical initiator, BPO, at the same temperature.

[13] Boutevin, B.; Pietrasanta, Y. In *Comprehensive Polymer Science*; Allen, G., Aggarwal, S. L., Russo, S., Eds.; Pergamon: Oxford, 1991; Vol. 3, p 185.

[14] Bamford, C. H. In *Comprehensive Polymer Science (First Supplement)*; Allen, G., Aggarwal, S. L., Russo, S., Eds.; Pergamon: Oxford, 1991; p 1.