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Controlled/"Living" Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process

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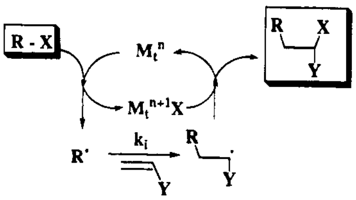
ABSTRACT: An extension of atom transfer radical addition, ATRA, to atom transfer radical polymerization, ATRP, provided a new and efficient way to conduct controlled/"living" radical polymerization. By using a simple alkyl halide, R−X (X = Cl and Br), as an initiator and a transition metal species complexed by suitable ligand(s), M_t^n/L_x, e.g., CuX/2,2′-bipyridine, as a catalyst, ATRP of vinyl monomers such as styrenes and (meth)acrylates proceeded in a living fashion, yielding polymers with degrees of polymerization predetermined by $\Delta[M]/[I]_0$ up to $M_n \approx 10^5$ and low polydispersities, $1.1 < M_w/M_n < 1.5$. The participation of free radical intermediates was supported by analysis of the end groups and the stereochemistry of the polymerization. The general principle and the mechanism of ATRP are elucidated. Various factors affecting the ATRP process are discussed.

Introduction

Atom transfer radical addition, ATRA, is a well-known method for carbon−carbon bond formation in organic synthesis.[1] Two types of atom transfer methods have been developed. One of them is also called atom abstraction or homolytic substitution,[2] in which a univalent atom, typically a halogen, or a group, such as SAr, SeAr, is transferred from a neutral molecule to a radical to form a new σ-bond and a new radical. In this respect, the use of an iodine atom or a SePh group was successful, due to the presence of weak C−I and C−SePh bonds toward the reactive radicals.[2] Indeed, we have recently demonstrated that alkyl iodides may also induce a degenerative transfer process in radical polymerization, leading to a controlled radical polymerization of several alkenes. This is consistent with the fact that alkyl iodides with groups stabilizing radicals can undergo a fast transfer in the initiation step and *degenerative* transfer in the propagation step.[3]

Another atom transfer method is promoted by a transition metal species.[4−9] In these reactions, the catalytic amount of transition metal compound acts as a carrier of the halogen atom in a redox process, Scheme 1.

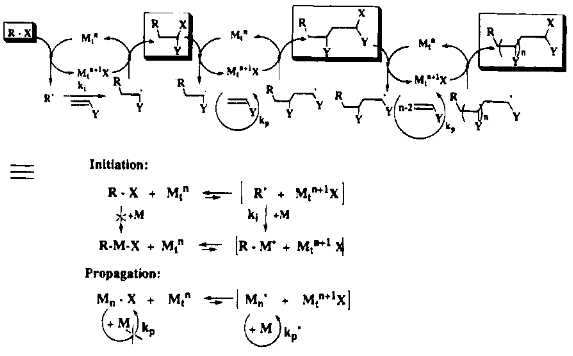
Scheme 1. Atom Transfer Radical Addition, ATRA[5,6]



Initially, the transition metal species, M_t^n, abstracts the halogen atom X from the organic halide, R−X, to form the oxidized species, $M_t^{n+1}X$, and the carbon-centered radical R•. In the subsequent step, the radical, R•, reacts with alkene, M, with the formation of the intermediate radical species, R−M•. The reaction between $M_t^{n+1}X$ and R−M• results in the target product, R−M−X, and regenerates the reduced transition metal species, M_t^n, which further reacts with R−X and promotes a new redox cycle.

The high efficiency of the transition metal catalyzed atom transfer reaction in producing the target product, R−M−X, in good to excellent yields, often >90%,[4−9] suggests that the presence of such a M_t^n/M_t^{n+1} redox process can effectively induce a low concentration of free radicals, resulting in less significant termination reactions between radicals.[1] If polymeric halides, R−M_i−X, are reactive enough toward M_t^n and the monomer is in excess, a number of atom transfer radical additions, i.e., a possible "living"/controlled radical polymerization, may occur, Scheme 2.

Scheme 2. From ATRA[5,6] to Atom Transfer Radical Polymerization, ATRP[10]



In a preliminary communication,[10] we reported that, using 1-phenylethyl chloride, 1-(PE)Cl, as an initiator, CuCl as a catalyst, and 2,2′-bipyridine, bpy, as a complexing ligand, a living radical bulk polymerization of styrene at 130 °C yielded polymers with molecular weights predetermined by the ratio $\Delta[M]/[I]_0$ up to $M_n \approx 10^5$ and with molecular weight distribution, $M_w/M_n < 1.5$, narrower than in conventional radical systems, which at high conversion are $M_w/M_n > 2$. By analogy with ATRA, we called this process *atom transfer radical polymerization*, ATRP,[10] which describes the involvement of the *atom transfer* pathway and the *radical* intermediates.

In this paper, we report that a number of commercially available alkyl halides, R−X, combined with Cu^IX/bpy, X = Cl and Br, can be used as efficient initiating systems for the ATRP of styrene and (meth)acrylates. The effects of various parameters on ATRP are also discussed.

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Table 1. ATRP of Styrene and Various (Meth)acrylates Initiated with RX/CuX/bpy[a]

monomer	RX[b]/CuX	T, °C	$M_{n,th}$[c]	$M_{n,SEC}$	M_w/M_n
St	1-(PE)Cl/CuCl	130	120 000	110 500	1.45
	1-(PE)Cl/CuCl	100	97 000	93 300	1.50
	1-(PE)Br/CuBr	80	8 300	8 000	1.25
	1-(PE)Br/CuBr	110	8 500	8 750	1.10
	α,α′-DBr-xylene/CuBr	110	12 500	12 000	1.12
MA	2-(EPN)Cl/CuCl	130	30 500	31 000	1.40
	2-(EPN)Br/CuBr	80	19 100	21 500	1.25
	2-(MPN)Br/CuBr	100	27 500	29 000	1.15
	α,α′-DBr-xylene/CuBr	100	29 500	31 000	1.25
BuA[d]	2-(MPN)Br/CuBr	130	15 000	13 500	1.50
MMA[d]	2-(EiB)Br/CuBr	100	10 000	9 800	1.40

[a] Molar ratio of RX/CuX/bpy, 1/1/3, monomer conversions, 85–100%. [b] Abbreviations: 1-(PE)Cl, 1-phenylethyl chloride; 1-(PE)Br, 1-phenylethyl bromide; 2-(EPN)Cl, 2-ethyl chloropropionate; 2-(EPN)Br, 2-ethyl bromopropionate; 2-(MPN)Br, 2-methyl bromopropionate; α,α′-DBr-xylene, α,α′-dibromoxylene; 2-(EiB)Br, 2-ethyl bromoisobutyrate. [c] Calculated according to eq 1. [d] In EAc solution, 50% in volume.

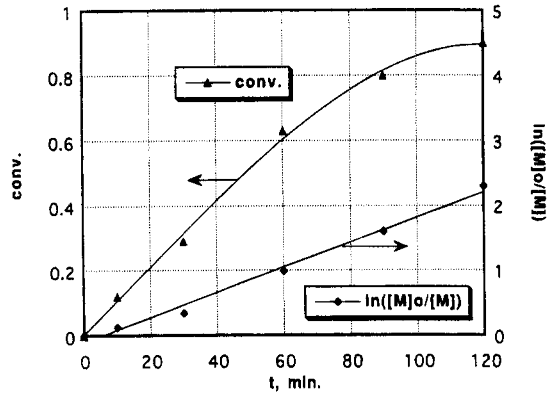


Figure 1. Kinetics of the bulk polymerization of methyl acrylate at 130 °C: $[MA]_0$ = 11.1 M; $[1\text{-(PE)Cl}]_0$ = $[CuCl]_0$ = 0.1 M; $[bpy]_0$ = 0.3 M.

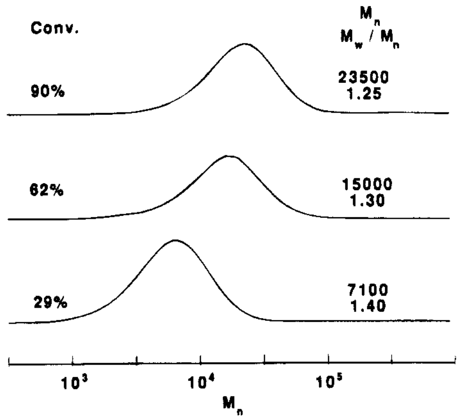


Figure 2. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk polymerization of methyl acrylate at 130 °C: $[MA]_0$ = 11.1 M; $[1\text{-(PE)Cl}]_0$ = $[CuCl]_0$ = 0.038 M; $[bpy]_0$ = 0.11 M.

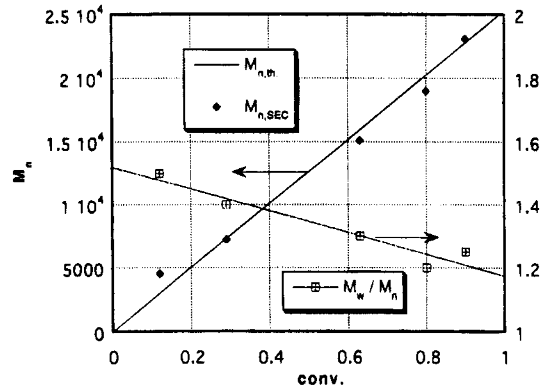


Figure 3. Molecular weight, M_n, and molecular weight distribution, M_w/M_n, dependence on monomer conversion for the bulk polymerization of methyl acrylate at 130 °C: $[MA]_0$ = 11.1 M; $[1\text{-(PE)Cl}]_0$ = $[CuCl]_0$ = 0.038 M; $[bpy]_0$ = 0.11 M.

Results

Atom Transfer Radical Polymerization of Styrene and (Meth)acrylates Initiated with Alkyl Halide, R–X, and in the Presence of CuX Complexed by 2,2′-Bipyridine. As reported previously,[10] using 1-PECl as an initiator, 1 molar equiv of Cu^ICl as a catalyst, and 3 molar equiv of 2,2′-bipyridine, bpy, as a ligand (both relative to 1-(PECl), the ATRP of styrene, St, provides controlled polymerization at 130 °C. Moreover, the desired block copolymers of PSt–*b*– PMA have also been successfully prepared using the same technique.[10]

Similarly, using various R–X/CuX/bpy (1/1/3) initiating systems, the atom transfer radical polymerization of styrene and various (meth)acrylates at different temperatures also afforded the polymers with the predetermined molecular weights up to $M_n \approx 10^5$ and polydispersities as low as 1.10, Table 1.

Figure 1 presents the kinetics of the bulk polymerization of methyl acrylate, MA, at 130 °C initiated by 1-(PE)Cl in the presence of Cu^ICl (1 equiv) and bpy (3 equiv). The straight semilogarithmic kinetic plot of ln($[M]_0/[M]$) vs time, t, indicates that the concentration of growing radicals is constant.

Moreover, the experimental molecular weight, $M_{n,SEC}$, increases with monomer conversion, Figure 2, and matches the theoretical one, $M_{n,th}$, Figure 3, calculated from eq 1, where $\Delta[M]$, $[R-X]_0$, and $(MW)_0$ represent

$$M_n = (\Delta[M]/[R-X]_0)(MW)_0 \qquad (1)$$

the concentration of consumed monomer MA, the initial concentration of 1-(PE)Cl, and the molecular weight of MA, respectively. This provides evidence that 1-(PE)Cl acts as an efficient initiator and the number of active chains remains constant during the polymerization. Both of these results suggest a living process of ATRP of MA with fast initiation and negligible irreversible transfer and termination reactions.

Furthermore, a series of bulk ATRP of MA have been carried out at 130 °C, using various monomer/initiator molar ratios, $[MA]_0/[1\text{-(PE)Cl}]_0$, and a constant complexing ligand/catalyst/initiator molar ratio of 3/1/1. Figure 4 shows the correlation of the experimental molecular weights, $M_{n,SEC}$, with the theoretical ones, $M_{n,th.}$, calculated by eq 1. A linear plot is obtained in a molecular weight range from 1.5×10^3 to 1.35×10^5. The slope of the straight line is 0.95, indicating a high initiator efficiency and small contribution of irreversible transfer, supporting a living process of MA polymerization initiated with 1-(PE)Cl/CuCl/bpy.

End Group of Polymers Obtained by Atom Transfer Radical Polymerization. The structure of the chain ends of low molecular weight poly (methyl acrylate), PMA, synthesized by the ATRP technique was analyzed by ^1H NMR spectroscopy. Figure 5 presents the ^1H NMR spectra of PMA which was prepared at 130 °C using 1-phenylethyl chloride as an initiator and in the presence of 1 molar equiv of CuCl and 3 molar equiv of bpy. The broad triplet at ca. 4.2 ppm is assigned to the $-CH$(COOMe)Cl end group *e*. Another two broad bands at 7.1 and 7.4 ppm in Figure 5 represent the end group *a*. Methyl group *f* resonates at ca. 1.15 ppm.

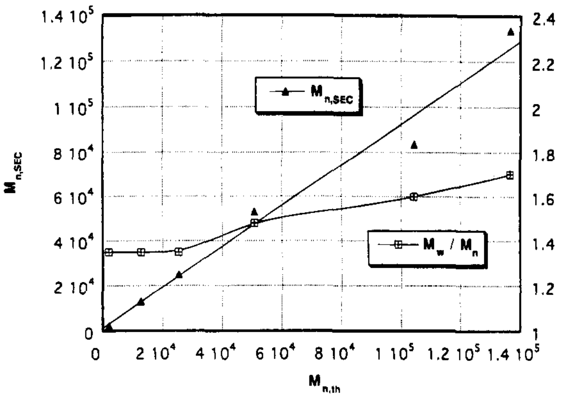


Figure 4. Comparison of theoretical molecular weight, $M_{n,th}$, calculated on the basis of eq 1 and experimental molecular weight, $M_{n,SEC}$, determined by SEC for the bulk polymerization of methyl acrylate at 130 °C: $[MA]_0 = 11.1$ M; $[1\text{-(PE)Cl}]_0$:$[CuCl]_0$:$[bpy]_0$ = 1:1:3.

Comparison of the integration values for two end group resonances in the spectrum, Figure 5, shows a 5/1 ratio of *a* and *e*. This suggests that the MA polymerization was initiated with 1-phenylethyl radicals and efficiently deactivated with an equimolar amount of chlorine atom (relative to 1-phenylethyl group).[11] Comparison of the integration of the end groups with the methoxy group, *d*, at ca. 3.5 ppm, or other groups in backbone, *b* and *c*, at 1.2–2.6 ppm, in the PMA chain provides a molecular weight similar to the one obtained from SEC, i.e., $M_{n,NMR} \approx 1450$ against $M_{n,SEC} \approx 1500$, indicating a quantitative initiation by 1-phenylethyl chloride.

Stereochemistry of Atom Transfer Radical Polymerization. To better understand the mechanism of ATRP, the stereochemistry of MMA polymerization was investigated.

The tacticity of PMMA was calculated from the ^{13}C NMR of the C═O group and the quaternary carbon group and/or the ^{1}H NMR of the α-methyl group. The ^{13}C NMR of the C═O group and the quaternary carbon group resonate in the regions 175–179 and 44–46.5 ppm, respectively. The assignment of the ^{13}C signals was performed according to Peat and Reynolds.[12,13]

Figure 6 compares the ^{13}C NMR spectra of the C═O group and the quaternary carbon group of PMMA prepared at 100 °C using methyl 2-bromoisobutyrate/CuBr/bpy (1/1/3) as the initiating system, Figure 6A, and a classic radical initiator, AIBN, Figure 6B, respectively. Both spectra are almost identical. Indeed, up to the pentad sequence, PMMA prepared using AIBN or BPO and various ATRP initiator systems have the same composition within experimental error, Table 2. The stereochemistry for ATRP of MMA also appears to be consistent with a Bernoullian process as indicated by $\rho \sim 1$. These results indicate the presence of the same type of active species in the Cu^{I}X catalyzed polymerization and the classic free radical polymerization. The similarities in stereochemistry and regiochemistry in the AIBN/Bu_3SnH mediated radical cyclizations and Cu(I) catalyzed chlorine transfer cyclizations have already been reported by several groups as evidence for radical intermediates.[5,6]

Effect of the Structure of Alkyl Halide, R–X, on Atom Transfer Radical Polymerization. Table 3 reports the data for the ATRP of styrene at 130 °C using various commercially available alkyl chlorides, R–Cl, Cu^{I}Cl (1 molar equiv), and bpy (3 molar equiv) as initiator, catalyst, and ligand, respectively. Alkyl chlorides with either inductive or resonance stabilizing substituents are efficient mono- or bifunctional initiators and lead to polymers with narrow molecular weight distribution, i.e., $M_w/M_n \sim 1.25$–1.5.

In contrast, such simple alkyl chlorides as butyl chloride, C_4H_9Cl, and dichloromethane, CH_2Cl_2, are less efficient, giving uncontrolled polymers with much higher molecular weights than expected and broader molecular weight distributions. These results are very similar to that obtained without any alkyl chlorides under similar conditions, Table 3. This indicates very poor efficiency of C_4H_9Cl and CH_2Cl_2 at the initiating step of ATRP of St.

The results shown in Table 3 may be correlated with the bond strength of carbon–halide, i.e., bond dissociation energy, BDE, in alkyl chlorides. For alkyl chlorides with a high BDE, such as in the case of C_4H_9Cl and CH_2Cl_2,[14] the chloride atom transfer from R–Cl to Cu^{I}Cl

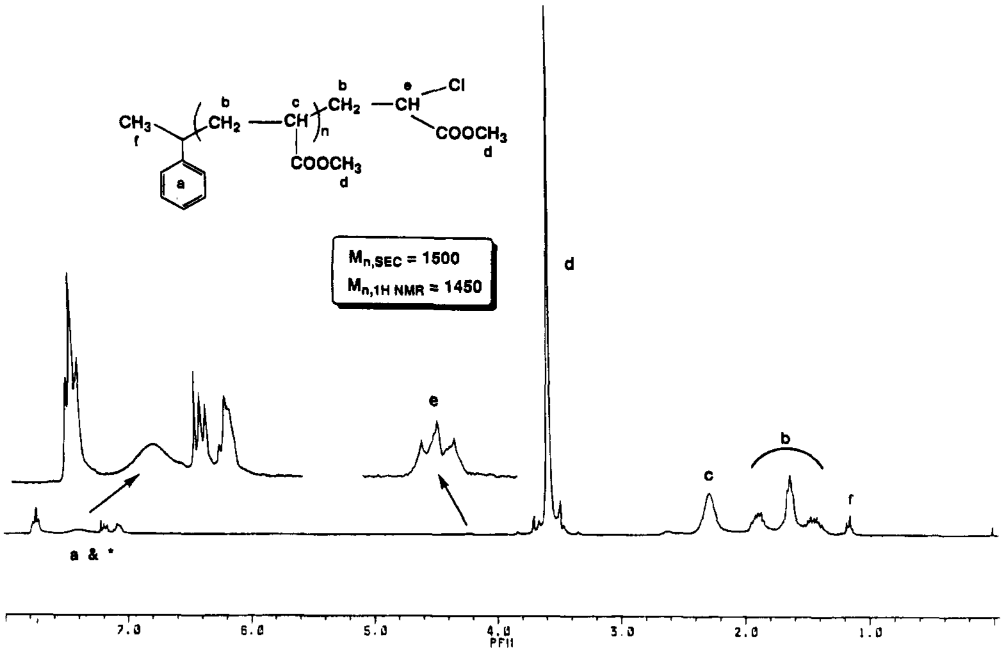


Figure 5. ^{1}H NMR of ATR PMA initiated with 1-(PE)Cl/CuCl/bpy (1/1/3) at 130 °C: *, resonances of residual bpy.

Table 2. Comparison of Fractions of Pentads, Tetrads, Triads, and Diads in Poly(methyl methacrylate) (PMMA) Prepared Using BPO, AIBN, and Various ATRP Initiator Systems

T,°C	Initiator system	mmmm	mmmr	rmmr	rmrm + mmrm	rmrr + mmrr	mrrm	mrrr	rrrr	mm	mr	rr	m	r	ρ^a
130	1-(PE)Cl/CuCl/bpy[b]									0.06	0.38	0.56	0.25	0.75	0.99
	BPO[c]									0.06	0.37	0.55	0.245	0.755	1.00
100	(EiB)Br/CuBr/bpy[d]	0.01	0.03	0.04	0.11	0.26	0.06	0.22	0.27	0.05	0.36	0.59	0.23	0.77	1.04
	AIBN[e]	0.02	0.03	0.04	0.11	0.27	0.04	0.21	0.28	0.06	0.34	0.60	0.23	0.77	1.04
60	(EiB)Br/CuBr/bpy[d]									0.04	0.33	0.63	0.205	0.795	0.99
	AIBN[f]									0.03	0.35	0.62	0.205	0.795	0.94

[a] The persistence ratio, $\rho = 2(\mathrm{m})(\mathrm{r})/(\mathrm{mr})$. [b] Polymerization conditions: $[\mathrm{MMA}]_o = 9.36$ M; $[1\text{-(PE)Cl}]_o = 0.11$ M; $[1\text{-(PE)Cl}]_o/[\mathrm{CuCl}]_o/[\mathrm{bpy}]_o = 1/1/3$. [c] Polymerization conditions: $[\mathrm{MMA}]_o = 9.36$ M; [BPO] = 0.1 M. [d] $[\mathrm{(EiB)Br}]_o = 0.055$ M; $[1\text{-(PE)Cl}]_o/[\mathrm{CuCl}]_o/[\mathrm{bpy}]_o = 1/1/3$. [e] Polymerization conditions: $[\mathrm{MMA}]_o = 9.36$ M; [AIBN] = 0.1 M. [f] Hatada, K.; et al. *Polym. J.* **1987**, *19*, 413.

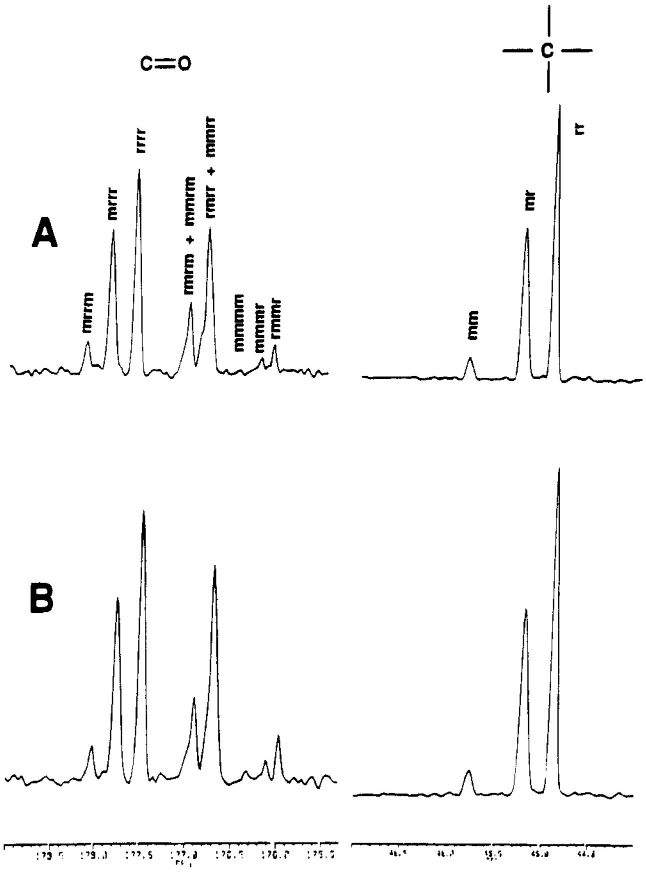


Figure 6. Comparison of ^{13}C NMR of PMMA prepared at 100 °C with the 2-methyl 2-bromoisobutyrate/CuBr/bpy (1/1/3) initiating system, A, and a conventional radical initiator, AIBN, B, respectively.

Table 3. Styrene ATRP Using Various R−Cl as Initiator in the Presence of CuCl (1 molar equiv) and bpy (3 molar equiv)[a]

R−Cl	$[\mathrm{R{-}Cl}]_o$ mol/L	$M_{n,th}$[b]	$M_{n,SEC}$	M_w/M_n
			134 700	1.95
C_4H_9Cl	0.082	10 000	111 500	1.75
CH_2Cl_2	0.085	9 700	129 000	2.20
$CHCl_3$	0.040	20 500	21 900	1.45
CCl_4	0.047	17 600	15 500	1.30
$CH_3CH(Cl)CN$	0.037	22 300	22 400	1.35
$CH_3CH(Cl)CN$	0.35	2 280	2 100	1.25
$CH_3CH(Cl)COOC_2H_5$	0.038	21 500	20 000	1.45
$CH_3CH(Cl)COOC_2H_5$	0.65	1 210	1 290	1.35
$C_6H_5CH_2Cl$	0.075	11 000	10 600	1.45
$ClCH_2C_6H_4CH_2Cl$	0.12	6890	6 600	1.45

[a] Conversion of the polymerization: 90−100%. [b] $M_{n,th} = M_0(\Delta[\mathrm{M}]/[\mathrm{R{-}Cl}]_o)$.

with the formation of R$^\bullet$ and Cu^{II}Cl is very difficult because of the strong carbon−chlorine bond. Introduction of the inductive or resonance stabilizing substituent into the R group reduces the BDE of the R−Cl bond,[14] and the generation of initiating radicals by chlorine atom transfer becomes more facile,[5,6] resulting in higher initiator efficiency and narrower MWD.

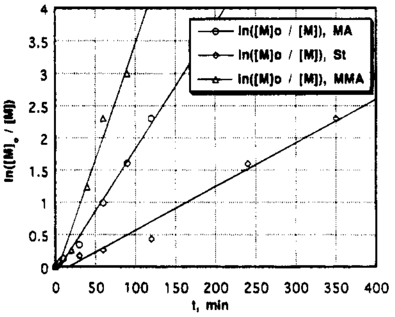


Figure 7. Kinetics of the bulk polymerization of methyl acrylate, styrene, and methyl methacrylate at 130 °C: $[1\text{-(PE)Cl}]_0 = [\mathrm{CuCl}]_0 = 0.038$ M; $[\mathrm{bpy}]_0 = 0.11$ M.

Effect of the Structure of Monomer on Atom Transfer Radical Polymerization. Figure 7 illustrates the kinetic plots of ATRP of three typical monomers, St, MA, and MMA, using the same initiator system, 1-(PE)Cl/CuCl/bpy (1/1/3), and under the same experimental conditions, in bulk, at 130 °C.

The slopes of the straight kinetic plots in Figure 7 allow for the calculation of the apparent propagation rate constants of ATRP of St, MA, and MMA, k_p^{app}. Assuming propagation occurs via "normal" free radicals, the stationary concentration of radicals, $[\mathrm{P}^\bullet]_{st}$, can be estimated from the ratio of the apparent rate constant, k_p^{app}, and the rate constant of radical propagation available, $k_p^\bullet$.

$$R_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p^\bullet[\mathrm{M}][\mathrm{P}^\bullet]_{st} \approx k_p^{app}[\mathrm{M}] \qquad (2)$$

$$\ln([\mathrm{M}]_0/[\mathrm{M}]) = k_p^{app}t \qquad (3)$$

$$[\mathrm{P}^\bullet]_{st} = k_p^{app}/k_p^\bullet \qquad (4)$$

Table 4 shows the kinetic data and estimated concentrations of growing radicals in bulk ATRP of St, MMA, and MA initiated with 1-(PE)Cl/CuCl/bpy (1/1/3) at 130 °C. The concentration of growing radicals decreases in the order $[\mathrm{P}^\bullet_{i,\mathrm{MMA}}] > [\mathrm{P}^\bullet_{i,\mathrm{St}}] \approx [\mathrm{P}^\bullet_{i,\mathrm{MA}}]$.

Effect of the Leaving Group, X, on Atom Transfer Radical Polymerization. Since the atom transfer process reflects the strength of the bond breaking and forming in M_n−X,[1] it is expected that the leaving group, X, will also strongly affect the atom transfer radical polymerization.

From Table 5, it can be noted that ATRP with bromine as a ligand is faster than with chlorine. This can be explained by the enhanced contribution of

Table 4. Kinetic Data and Estimated Concentration of Growing radicals, [P$^•$], for Bulk ATRP of Monomers St, MA, and MMA Initiated with 1-(PE)Cl/CuCl/Bpy (1/1/3) at 130 °C[a]

	MA	MMA	St
$[M]_o$, mol/L	11.1	9.36	8.7
$k_p^•$, (130 °C), 10^3 M^{-1} s^{-1}	14.1[b]	3.17[c]	2.3[d]
k_p 10^{-4} s^{-1}	3.14	5.83	1.35
$[P^•]$ 10^{-7}M	0.22	1.90	0.58

[a] $[1\text{-(PE)Cl}]_o$ = 0.038 mol/L. [b] $\ln(k_{p,MA}) = 18.42 - 3574/T$; see: Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1991. [c] $\ln(k_{p,MMA}) = 14.685 - 2669/T$, see: Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410. [d] Value extrapolated from the 30 to 90 °C range to 130 °C; see: Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410.

Table 5. Effect of the Leaving Group, X, on the Kinetics of ATRP at Different Temperatures[a]

monomer	T, °C	ATRP	k_p^{app}, 10^{-5} s^{-1}	kp•, 10^3 M^{-1} s^{-1}	[P•], 10^{-9} mol/L
MMA	80	Cl ATRP	~1.71	1.24	13.8
		Br ATRP	~3.52	1.24	28.4
MA	80	Cl ATRP	*b*	4.01	
		Br ATRP	~1.28	4.01	3.19
	100	Cl ATRP	1.45	6.89	2.10
		Br ATRP	3.47	6.89	5.02
St	80	Cl ATRP	*b*	0.64	
		Br ATRP	~1.45	0.64	22.6

[a] 1-(PE)Cl and 1-(PE)Br were used as initiators for Cl and Br ATRP, respectively: $[1\text{-PEX}]_o$ = 0.1 M, and $[1\text{-PEX}]_o/[CuX]_o/[Bpy]_o$ = 1/1/3. [b] No polymer can be detected in ca. 40 h.

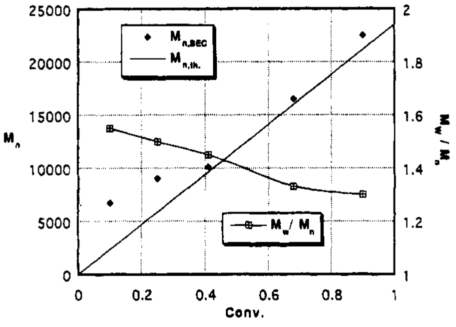


Figure 8. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk ATRP of methyl acrylate at 100 °C: $[MA]_0$ = 11.1 M; [2-ethyl chloropropionate]$_0$ = $[CuCl]_0$ = 0.040 M; $[bpy]_0$ = 0.12 M.

growing radicals in the former polymerization process than in the latter one, Table 5.

The effect of the leaving group, X, on the degree of the control of polymerization is significant. For instance, in the cases of MA polymerization at 100 °C using the same molar ratio of R–X/CuX/bpy of 1/1/3 and the same initiating radical, ethyl propionate, the molecular weight is better controlled in Br ATRP than in Cl ATRP, Figures 8 and 9. Polydispersities of resulting polymers obtained with Br are lower than those with Cl, Figures 8 and 9, e.g., M_w/M_n = 1.15–1.35 against 1.30–1.55.

Effect of the Concentrations of the Components in the Initiator System, R–X/CuX/Bpy, on Atom Transfer Radical Polymerization. In order to gain a better understanding of the ATRP mechanism, we have studied the effect of the ratio of the components in the initiating system on the kinetics and the level of the control of polymerization.

As discussed in the previous sections, the slope of the kinetic semilogarithmic anamorphoses allows the calculation of k_p^{app}, and thus the external orders in the initiator, catalyst, and ligand, can be determined:

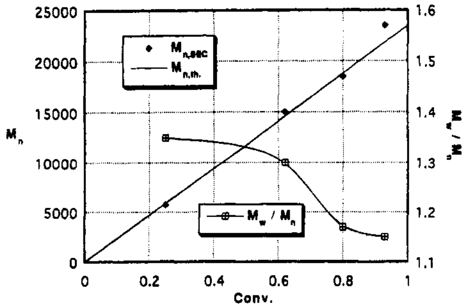


Figure 9. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk ATRP of methyl acrylate at 100 °C: $[MA]_0$ = 11.1 M; [2-ethyl bromopropionate]$_0$ = $[CuBr]_0$ = 0.040 M; $[bpy]_0$ = 0.12 M.

$$k_p^{app} = d(\ln[M])/dt = k[RX]_0^x[CuX]_0^y[bpy]_0^z \quad (5)$$

$$\ln(k_p^{app}) = \ln(k) + x\ln([RX]_0) + y\ln([CuX]_0) + z\ln([bpy]_0) \quad (6)$$

The plots of $\ln(k_p^{app})$ *vs* $\ln([1\text{-(PE)Cl}]_o)$, $\ln(k_p^{app})$ *vs* $\ln([CuCl]_0)$, and $\ln(k_p^{app})$ *vs* $\ln([bpy]_0)$ for St ATRP in bulk at 130 °C are given in Figure 10A–C. The fractional orders observed in these graphs are approximately 1, 0.4, and 0.6 for $[1\text{-(PE)Cl}]_0$, $[CuCl]_0$, and $[bpy]_o$, respectively. The first order of k_p^{app} in initiator, $[1\text{-(PE)Cl}]_0$, is as expected. However, since the systems which we studied were not completely homogenous, it is difficult to explain the precise physical meanings for 0.4 and 0.6 orders in $[CuCl]_0$ and $[bpy]_0$, respectively.

The effect of the compositions of the components in the initiator system on the degree of control of ATRP of St reveals several important features. As seen from Figure 11, there appears to be no significant effect of $[CuCl]_0$ on the initiator efficiency and the molecular weight distribution. Indeed, even in the presence of 0.3 molar equiv of CuCl relative to 1-(PE)Cl, $M_{n,SEC}$ still increases linearly with monomer conversion and is close to $M_{n,th.}$, obtained by means of eq 1. The similar results were also found for the ATRP of MA, Figures 3 and 12. These findings suggest that, in the ATRP, the CuX acts as a catalyst and the addition of a catalytic amount of CuX complexed by bpy is sufficient for promoting a controlled ATRP, even in these heterogeneous systems.

Discussion

Transition Metal Catalyzed Atom Transfer Radical Addition and Transition Metal Catalyzed Atom Transfer Radical Polymerization. As described in the Introduction ATRP can be considered as a sequence of consecutive ATRAs. The prerequisite for a successful transformation of transition metal catalyzed ATRA to transition metal catalyzed ATRP is that the macromolecular halides, R–M_n–X, can be effectively activated by M_t^n, Scheme 2. The present work demonstrates that the Cu(I)/Cu(II) based redox process in the presence of bpy can achieve that goal.

Indeed, to prevent possible polymerization and to obtain the monomeric adduct, R–M–X, in good to excellent yields in the ATRA process, organic chemists often use the activated organic halides as radical sources and the alkenes without resonance stabilizing substitutes.[4-9] Under such conditions, the further genera-

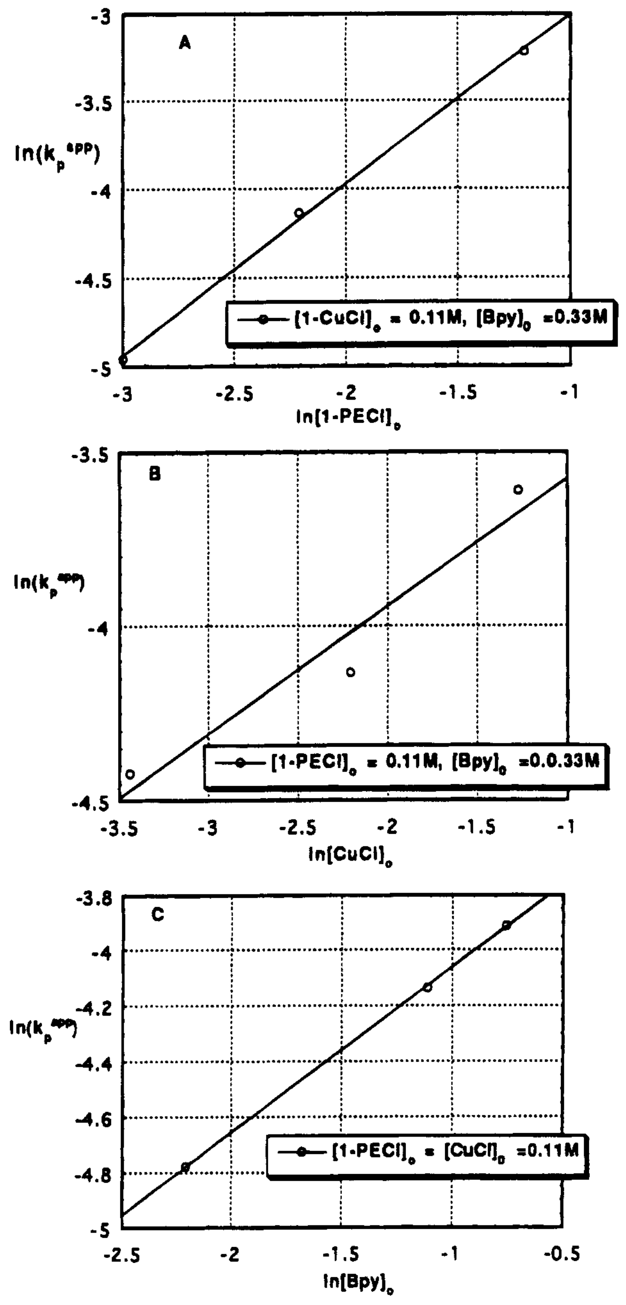


Figure 10. Plots of $\ln(k_p^{app})$ *vs* $\ln([1\text{-(PE)Cl}]_0)$ (**A**), $\ln(k_p^{app})$ *vs* $\ln([\text{CuCl}]_0)$ (**B**), and $\ln(k_p^{app})$ *vs* $\ln([\text{bpy}]_0)$ (**C**) for bulk ATRP of St at 130 °C

tion of free radicals, R−M•, is kinetically less favorable, since R−M−X is much less reactive than R−X towards the transition metal species, Mt^n (Scheme 2).[4-9]

From the results described in the preceding sections and in a previous paper,[10] the following parameters are important for promoting the successful transformation of ATRA to ATRP. First, it seems that the use of suitable ligands, e.g., bpy, in the present work, not only increases the solubility of the inorganic salt by coordination to CuX but can also facilitate the abstraction of a halogen atom from the initiator, R−X, and from the dormant polymeric halide, $\text{R}-\text{M}_n-\text{X}$, with the formation of initiating and growing radicals, Scheme 2, respectively.[5,6] Second, as demonstrated in Table 3, the presence of either inductive or resonance stabilizing substituent in the initiator, R−X, is critical for the quantitative generation of initiating radicals, R•. Finally, the use of a high temperature is necessary to complete the polymerization in a reasonable time, especially for Cl ATRP, Table 5. Higher temperatures also provide a better k_p/k_t ratio, since $E_p > E_t$ for radical polymerization.

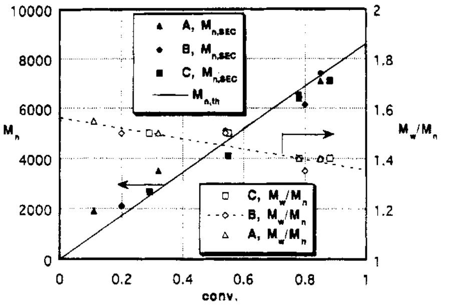


Figure 11. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk ATRP of styrene at 130 °C using the 1-(PE)Cl/CuCl/bpy initiating system with different molar ratios: (**A**) $[1\text{-(PE)Cl}]_0 = 0.11$ M, $[\text{CuCl}]_0 = 0.032$ M, and $[\text{bpy}]_0 = 0.33$ M; (**B**) $[1\text{-(PE)Cl}]_0 = [\text{CuCl}]_0 = 0.11$ M and $[\text{bpy}]_0 = 0.33$ M; (**C**) $[1\text{-(PE)Cl}]_0 = [\text{CuCl}]_0 = [\text{bpy}]_0 = 0.11$ M.

Very recently, it has been reported that although $\text{RuCl}_2(\text{PPh}_3)_3$ itself can only promote the monomeric addition of CCl_4 to alkenes, the addition of a suitable activator, methylaluminium bis(2,4-di-*tert*-butylphenoxide), induced the controlled radical polymerization of MMA at 60 °C.[15] However, we have found that, at a higher polymerization temperatures, e.g., 130 °C, without using any activators, several monomers also undergo ATRP with $\text{RuCl}_2(\text{PPh}_3)_3$ under otherwise the same experimental conditions.[16] This indicates that, instead of using an activator, increasing the polymerization temperature can alternatively enhance the reactivity of less reactive monomeric or polymeric halides, $\text{R}-\text{M}_i-\text{X}$, towards transition metal species with the formation of propagation radicals.

Radical Addition vs Insertion. Regarding the mechanism of ATRP, the important question is whether the ATRP really involves radical intermediates during polymerization.

The generation of radical intermediates by reacting some transition metal species,[17] including salts and/or complexes of copper,[4,5] ruthenium,[6,7] iron,[7] vanadium,[8] niobium,[7] and others,[9] with R−X is well documented. Moreover, it is also known that several redox initiators based on R−X/transition metal compounds, such as $\text{Mo(CO)}_6/\text{CHCl}_3$, $\text{Cr(CO)}_6/\text{CCl}_4$, $\text{Co}_4(\text{CO})_{12}/\text{CCl}_4$, and $\text{Ni}\{\text{P(OPh)}_3\}_4/\text{CCl}_4$, promote radical polymerization.[18] The participation of free radicals in these redox initiator promoted polymerization was supported by end group analysis and direct observation of radicals by ESR spectroscopy.[19]

However, various transition metal species may act differently. They may induce an atom transfer reaction, or provide a source of metal complexed radicals, or even initiate a catalytic cycle that does not involve radical intermediates.[1]

In fact, using additives such as CuX, several examples reported previously showed that the reactions between some poly(haloalkanes), e.g., CCl_4, and alkenes lead exclusively to 1/1 adducts in many cases.[4] Thus, it is possible that $\text{Cu}^{\text{I}}\text{Cl}$ cleaves the carbon−halogen bond by an atom transfer process to generate a carbon radical and Cu(II) species, Scheme 2, or by an overall two-electron change to generate a Cu(III) species **2**, Scheme 3, followed by insertion of the alkene into the carbon−copper(III) σ-bond of **2** and halogen ligand transfer, reductive elimination, within the new Cu(III) species **3** formed.

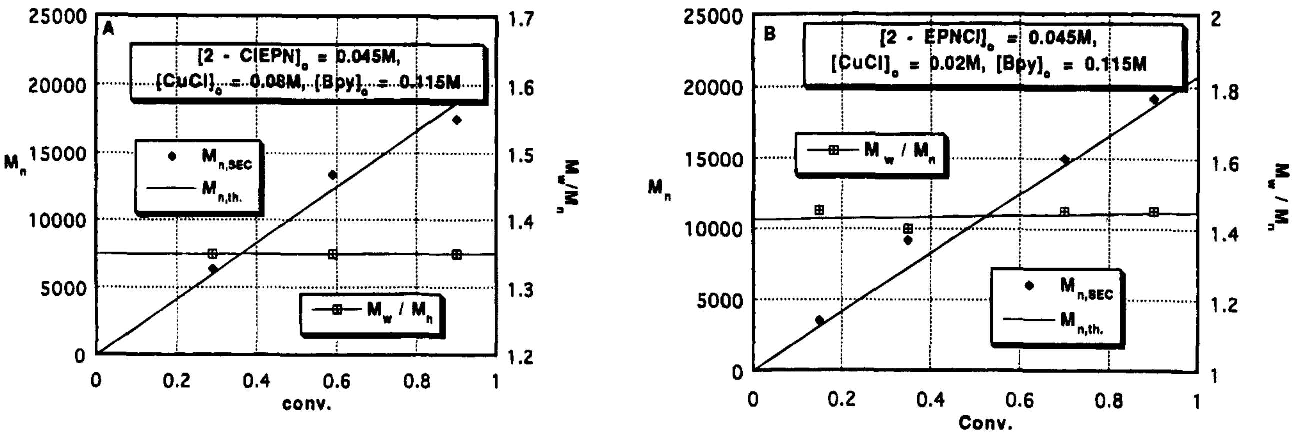
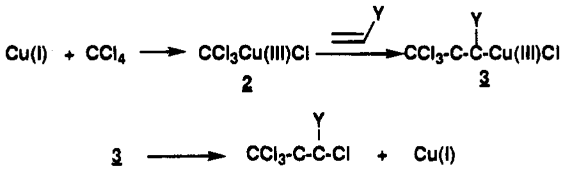
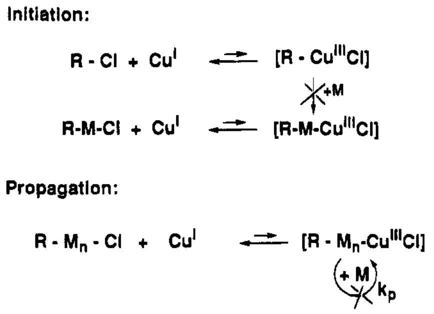


Figure 12. Evolution of molecular weight, M_n, and molecular weight distribution, M_w/M_n, with monomer conversion for the bulk ATRP of methyl acrylate at 130 °C using 2-EPNCl/CuCl/bpy initiating system with different molar ratios.

Scheme 3



Scheme 4

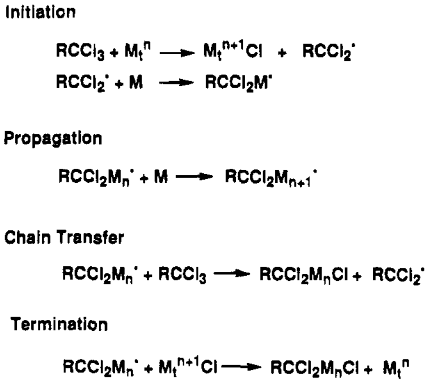


In contrast to earlier observations, we have already shown in previous sections that the polymerization of several alkenes does occur, when alkyl halides including CCl_4 are used as initiators and CuX, complexed by bpy, as the catalyst. The uncomplexed CuX species does not abstract the halogen atom from the 1/1 monomeric adduct to promote the possible atom transfer radical polymerization. As reported previously, the polymerization of St initiated with 1-(PE)Cl/CuCl, but without bpy, was an ill-controlled thermally self-initiated polymerization.[10a] Bpy increases the solubility of CuX and may also affect the equilibrium between Cu(I) and Cu(II).

Moreover, the similarities in stereochemistry of the polymerizations of MMA initiated with classic radical initiators and various R–X/CuX/bpy initiating systems, Table 2, suggest that the insertion process, Scheme 4, is not involved in the polymerizations of alkenes initiated with the R–X/CuX/bpy system, where a radical process is most probable, Scheme 2.

The participation of radical intermediates was also supported by the observation that addition of 1.5 molar equiv of galvinoxyl relative to 1-(PE)Cl effectively inhibits the polymerization and no styrene polymerization initiated with 1-(PE)Cl/CuCl/bpy (1/1/3) was found within 18 h.[10] The possibility of propagation of radicals reversibly coordinated to copper exists. However, the tacticity of the resulting polymers indicates very weak interactions.

Scheme 5



Atom Transfer Radical Polymerization vs Redox Radical Telomerization. It is well-known that the radical telomerization can be initiated by transition metal species based redox catalysts.[20] The mechanism is generally described as in Scheme 5.

The fundamental differences between ATRP and redox radical telomerization are the following. In ATRP, the polymeric halides, $R-M_n-X$, behave as *dormant* species, Scheme 2. They can be repeatedly activated by transition metal species, M_t^n, to form the growing radicals, $R-M_n^\bullet$, and oxidized transition metal species, M_t^{n+1}, which can further react with $R-M_n^\bullet$ to regenerate $R-M_n$-X and M_t^n, i.e., a *reversible* transfer process. Contrary to ATRP, the redox radical telomerization represents a *degradative* transfer process, in which the resulting polymeric halides, $R-M_n-X$, are *dead* chains, Scheme 5. Consequently, the molecular weight of the obtained polymers does not increase with monomer conversion in the redox radical telomerization,[20] whereas the molecular weight increases linearly with increasing monomer conversion in ATRP (present work and ref 10).

Factors Affecting the Atom Transfer Radical Polymerization. (a) "Living"/Controlled Radical Polymerization. To better understand the controlled ATRP, we first recall some general properties for living/controlled radical polymerization.

Free radicals, which are the growing species in radical polymerization, are highly reactive species. Unlike anions or cations, they recombine and/or disproportionate at rates approaching the diffusion controlled limit, i.e., $k_t \approx 10^{8\pm1}$ $M^{-1}\cdot s^{-1}$, which is much higher than the corresponding propagation rate constant, i.e., $k_p \approx 10^{3\pm1}$ $M^{-1}\cdot s^{-1}$. Moreover, in conventional systems, initiation

Scheme 6

$$M_n^\bullet + X \rightleftharpoons M_n-X$$

is incomplete due to slow decomposition of a classic radical initiator, i.e., $k_d \approx 10^{-4}-10^{-6}$ s^{-1}. These are the kinetic reasons why conventional radical polymerization yields ill-defined polymers with unpredicted molecular weight, broad molecular weight distribution, and uncontrolled structures.

Moreover, due to the same kinetic reasons, it is impossible to entirely suppress the irreversible termination reactions and to obtain a *living* radical polymerization process, in which any chain breaking (termination) reactions are absent.[21] Thus, for the sake of accuracy, we proposed the term *controlled* or "*living*" radical polymerization to describe the process, in which the side reactions are not significant and consequently several structural parameters, such as molecular dimension, molecular weight distribution, composition, topology, and functionality, can be controlled to a large extent.

The preparation of the polymers in a "living" radical process requires a low stationary concentration of growing radicals, $M_n^\bullet$, which are in a fast dynamic equilibrium with the dormant species, M_n-X, where X are usually species with an odd number of electrons, Scheme 6.[22]

Because termination is second order and propagation is first order with respect to growing radicals (eqs 7 and 8), at a low concentration of free radicals, the proportion

$$R_p = -d([M])/dt = k_p^\bullet[M][P^\bullet]_{st} \tag{7}$$

$$R_t = -d[P^\bullet]/dt = k_t[P^\bullet]_{st}^2 \tag{8}$$

of termination versus propagation reaction is reduced. If the *reversible* exchange between growing radicals, $M_n^\bullet$, and dormant species, M_n-X, is fast, the degree of polymerization can be predetermined by the ratio of the concentration of the consumed monomer to that of the dormant chains, eq 9, and the molecular weight distribution may remain narrow.

$$DP_n = \Delta[M]/[M_n-X] = \Delta[M]/[I]_0 \tag{9}$$

Recent progress in the controlled/"living" radical polymerization can be indeed related to the approach illustrated in Scheme 6, in which growing radicals, $M_n^\bullet$, react reversibly with species X which may be carbon-, sulfur-, and oxygen-centered radicals,[23-26] alkyl aluminum complexes,[27] and organocobalt porphyrin complexes[28] in a reversible, deactivated process. Another approach is based on using alkyl iodides in a degenerative transfer process.[3] Compared to the aforementioned approaches based on the homolytic cleavage of M_n-X with the formation of 1/1 $M_n^\bullet$/X, one of the main advantages of ATRP is that the concentration of $M_n^\bullet$ can be adjusted simply by changing the amount and the nature of the metal(s), M_t, atom(s)/group(s), X, and coordinative ligand(s).

Table 6. Estimated [P$^\bullet$], $t_{0.9}$, $[P]_{self,0.9}$, $[P]_{d,0.9}$, and UC for Bulk ATRP of St and MA Initiated with 1-PECl/CuCl/Bpy (1/1/3) at 130 °C[a]

	MA	MMA	St
$[M]_o$, (mol / l)	11.1	9.36	8.7
$k_p^\bullet$, (130 °C),[b] (M^{-1} s^{-1})[b]	14100	3170	2330
k_t, (130 °C),[c] (10^7 M^{-1} s^{-1})[c]	1.98	0.31	2.4[d]
k_p^{app} (130 °C), (10^{-4} s^{-1})	3.14	5.83	1.35
$[P^\bullet]_{st}$, (10^{-7} M)[b]	0.22	1.84	0.58
$t_{0.90}$, (s^{-1})	7300	4000	17100
$[P]_{t,0.90}$, (10^{-4} mol/L)	0.7	4.20	14.4
$[P]_{self,0.90}$, (10^{-4} mol/L)			~17
UC, %	0.2	1.1	8.2

[a] $[1\text{-(PE)Cl}]_o = 0.038$ mol/L. [b] See Table 4. [c] Data from: Odian, G. *Principles of Polymerization*; Wiley-Interscience New York, 1991. $\ln(k_{t,MA}) = 23.43-2671/T$, $\ln(k_{t,MMA}) = 18.5-1432/T$; $\ln(k_{t,St} = 17.87-962/T$. [d] Because a value of $k_t = 0.5 \times 10^7$ M^{-1} s^{-1} at 130 °C, estimated from the activation parameters cited above, was lower than measured directly from the ESR spectroscopy ($k_t = 1.7 \times 10^7$ M^{-1} s^{-1} at 70 °C; Yamada, B.; Kageoka, M.; Otsu, T. *Macromolecules* **1991**, *24*, 5236), the value of $k_t = 2.4 \times 10^7$ M^{-1} s^{-1} was calculated from the latter value and $E_t = 8$ kJ/mol.

(b) Significance of the Presence of the Low Concentration of Growing Radicals in Maintaining "Living" ATRP. Since ATRP promoted by the Cu(I)/Cu(II) redox process resembles a conventional radical polymerization, the termination reactions, which are second order with respect to growing radicals (eq 8), cannot be completely eliminated. However, if the concentration of growing radicals is kept low enough, and a fast and reversible equilibrium between growing radicals and dormant species is established, Scheme 6, the proportion of termination in comparison to propagation can be minimized, resulting in predicted molecular weight and narrow molecular weight distribution. Indeed, this is the case for living ATRP.

Table 6 lists the estimated polymerization time for 90% monomer conversion, $t_{0.9}$, concentration of the dead polymer chains due to the spontaneous termination reactions at that time, $[P]_{t,0.9}$, concentration of the polymer chains due to the self-initiation, $[P]_{self,0.9}$, and percentage of uncontrolled polymer chains generated by side reactions, "UC", in the bulk ATRPs of St, MMA, and MA initiated with 1-PECl/CuCl/bpy of 1/1/3 at 130 °C:

$$\ln([M]_0/[M]) = \ln(10) = k_p^{app}t_{0.9} \tag{10}$$

$$[P]_{t,0.9} = k_t[P^\bullet]_{st}^2 t_{0.9} \tag{11}$$

$$[P]_{self,0.9} = R_{i,self}t_{0.9} \tag{12}$$

$$UC = ([P]_{self,0.9} + [P]_{t,0.9})/[R-X]_0 \tag{13}$$

As shown in Table 6, at 90% monomer conversion the concentrations of uncontrolled polymer chains, UC, are all less than 10% in ATRPs of St, MMA, and MA, when 1-(PE)Cl/CuCl/bpy (1/1/3) is used as the initiating system at 130 °C. Reactions are quite fast. During polymerization only a very small proportion of chains can be generated by self-initiation of styrene. Moreover, these chains are efficiently scavanged by Cu$^{(II)}$ species. The proportion of chains generated by self-initiation is probably overestimated because self-initiation slows down considerably with conversion. Because the proportion of uncontrolled chains is so low, ATRPs promoted by Cu(I)/Cu(II) redox process proceed in a living manner.

(c) Significance of the Presence of Fast Exchange between $R-M_n-X$ and $R-M_n^\bullet$ in Inducing Low Polydispersity in ATRP. At such a low concentration of radicals, Table 6, i.e., $[M_n^\bullet] \sim 10^{-7}-10^{-8}$ mol/L, polymers with very high and unpredicted molecular weight are usually found. To cope with this problem, a reversible equilibrium between a minute amount of growing radicals and a large amount of the dormant species needs to be established, Scheme 6. Moreover, only if the exchange reaction between the growing radicals, $M_n^\bullet$, and the dormant species, $M_n{-}X$, is fast in comparison with propagation, the molecular weight of the resulting polymers can be predetermined by means of eq 9 and low polydispersity polymers can be obtained.

The polydispersity of the resulting polymers in the reversibly deactivating system largely depends on the ratio of the deactivation rate to the propagation rate.[29] On the other hand, it has already been demonstrated that many transition metal species, e.g., $Cu^{II}X_2$, can be used as efficient retarders or even inhibitors in radical polymerization.[30] Therefore, the existence of fast deactivation or scavenging reaction of the growing radicals by CuX_2 (X = Cl and Br) can be considered as a reasonable explanation for the low polydispersity obtained by ATRP. It seems that a small amount (≈1%) of CuX_2 or a trace of oxygen in the initial reaction mixture is beneficial for the control of the polymerization.

(d) Factors Affecting the Concentrations of the Growing Radicals and the Exchange Rate between $R{-}M_n{-}X$ and $R{-}M_n^\bullet$ in ATRP. As discussed previously, two important parameters, the concentrations of the growing radicals and the exchange rate between $R{-}M_n{-}X$ and $R{-}M_n^\bullet$, control the livingness of ATRP. The factors affecting these two parameters are now qualitatively discussed.

The stationary concentration of growing (initiating) radicals can be expressed as in eq 16.

$$R{-}M_n{-}X + Cu^{I} \underset{k_{\mathrm{deact.}}}{\overset{k_{\mathrm{act.}}}{\rightleftharpoons}} R{-}M_n^\bullet + X{-}Cu^{II} \qquad (14)$$

$$K = k_{\mathrm{act.}}/k_{\mathrm{deact.}} = ([R{-}M_n^\bullet][X{-}Cu^{II}])/([R{-}M_n{-}X][Cu^{I}]) \qquad (15)$$

$$[R{-}M_n^\bullet] = (k_{\mathrm{act.}}/k_{\mathrm{deact.}})([R{-}X]_0[Cu^{I}])/([X{-}Cu^{II}]) \qquad (16)$$

An increase in $[R{-}X]_0$ and $[Cu^{I}]_0$ results in an increase in the concentration of growing radicals and subsequently in higher polymerization rates, Figure 10.

As also deduced from eq 16, the concentration of growing radicals is proportional and inversely proportional to the activation and deactivation rate constants, respectively. This is related to the energetics of the bond breaking and making in $R{-}M_n{-}X$ and $X{-}Cu^{II}$, which strongly depends on the structural factors of alkyl groups in $R{-}M_n{-}X$, the leaving group, X, the nature of the metal and complexing ligands, and the polymerization temperature, as confirmed by the results presented previously[10] and in Tables 3−5, as well as in Figure 7.

Since the energetics of the bond breaking and making in $R{-}M_n{-}X$ and $X{-}Cu^{II}$ determines the activation and deactivation rate constants in the Cu(I)/Cu(II) based ATRP, Scheme 2, the described structural factors may strongly affect the polydispersity of the polymers obtained by ATRP.

Further investigations are in progress in order to shed light on the quantitative relationships between the structural factors of the components, the energetics of the bond breaking and making in $R{-}M_n{-}X$ and $X{-}Cu^{II}$, and the livingness of the polymerization.

Conclusions

This paper demonstrates a successful extension of atom transfer radical addition to atom transfer radical polymerization based on the Cu(I)/Cu(II) redox process. It opens a new pathway to conduct the living/controlled radical polymerization of alkenes. The living process found in ATRP results from two phenomena: (i) the presence of the low stationary concentration of growing radicals; (ii) the fast and reversible equilibration between the growing radicals and the dormant species. Several parameters, such as the nature of the transition metal, the structure and property of ligands, the polymerization conditions, etc., may strongly affect the course of living ATRP.

Experimental Section

Reagents and Solvent. Styrene, (meth)acrylates, and ethyl acetate, (Aldrich) were vacuum distilled over CaH_2 just before polymerization.

Initiator. All alkyl halides, except for 1-phenylethyl chloride, which was prepared according to a literature method,[31] were used as received from Aldrich without purification.

Catalyst. CuCl and CuBr (98%, Aldrich) were used as received without purification.

Ligand. 2,2′-Bipyridine (Aldrich) was used as received without purification.

Polymerization. The general procedure was as follows: to a glass tube, catalyst, ligand, initiator, monomer, and solvent were added. The heterogeneous mixture was first degassed (3 times), then sealed under vacuum, and finally immersed in an oil bath and heated at the desired temperature. After a certain time, the tube was opened and THF or $CDCl_3$ was added to the sample to dissolve the polymer.

Polymer Characterization. The monomer conversion was determined gravimetrically and/or by GC using THF as an internal standard or NMR using $CDCl_3$ as a solvent. The three different methods gave comparable results.

Molecular weight and molecular weight distribution were obtained using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å, and 100 Å. Polystyrene and poly(methyl methacrylate) standards were used to determine PSt, polyacrylates and PMMA molecular weights and molecular weight distributions, respectively.

The end groups and the tacticity of the polymers were analyzed by ^{13}C and/or ^{1}H NMR spectroscopy using a Bruker AM 300. To perform a quantitative analysis of ^{13}C NMR spectra, an inverse-gated proton decoupling technique was applied.

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