Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

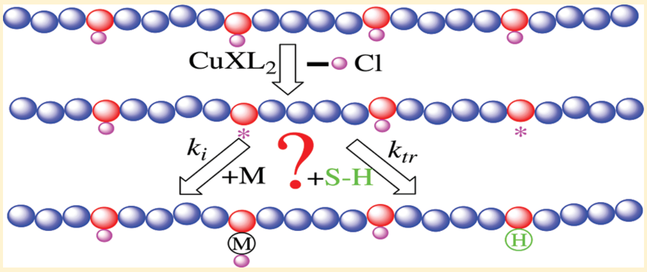
Study of Chain Transfer Reaction to Solvents in the Initiation Stage of Atom Transfer Radical Polymerization

Shaobo Tan,[†] Junjie Li,[†] and Zhicheng Zhang*[,†,‡]

[†]Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an, P. R. China

[‡]MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an, P. R. China, 710049

S *Supporting Information*



ABSTRACT: ATRP has been recognized as a powerful tool to synthesize polymers with well-defined structures, narrow polydispersity, and controlled molecular weight in the past decades. Usually, it is believed that the typical side reactions (such as termination and chain transfer reactions) in typical radical polymerizations could be inhibited in ATRP for the persistent radical effect. More recently, some researchers did notice that some chain transfer reaction to N containing ligands happens in ATRP. However, the chain transfer constant (k_{tr}/k_p) in ATRP has never been able to be measured experimentally due to the difficulty of determining the precise composition of the resultant polymer. Therefore, the influence of chain transfer reaction onto ATRP has rarely been discussed. In this work, we provide a novel method to determine the competition between chain transfer reaction and initiation reaction of free radicals (k_{tr}/k_i) by analyzing the structure of grafting copolymers from poly(vinylidene fluoride-*co*-trichlorofluoride ethylene) P(VDF-*co*-CTFE). The perfect coincidence of experimental results with theoretical ones indicates that the method may help to understand the chain transfer reaction in ATRP as well as its influence on the chain end of resultant polymer.

INTRODUCTION

Living/controlled radical polymerization (CRP) has achieved significant accomplishments for the synthesis of polymers with controlled architecture, molecular weight, and narrow polydispersity in the last two decades.[1,2] Atom transfer radical polymerization (ATRP), invented by both Matyjaszewski and Sawamoto in 1995[3,4] adapted from the concept of continuous atom transfer radical addiction (ATRA),[5,6] is one of the most representative examples among all the CRP methods. It has been successfully utilized to polymerize a series of vinyl monomers such as styrene as well as its derivative, (meth)acrylate and acrylonitrile[7−17] as well as synthesize corresponding polymers with very narrow molecular weight distribution ($M_w/M_n < 1.1$) and well-defined polymer architectures such as graft copolymers, block copolymers, and (hyper) branched polymers.[18−22]

In ATRP, dormant halogenated chain-ends (R−X) are reversibly activated (k_{act}) by a copper(I) complex, CuX/L_n (X = Cl or Br, L = ligand, n = 1 or 2), via halogen atom transfer reaction leading to free radicals (R*) and Cu^{II} complexes in a fast, dynamic equilibrium. R* can then initiate (k_i) and propagate (k_p) with vinyl monomer, terminate (k_t) as in conventional free radical polymerization by either coupling or disproportionation, or be reversibly deactivated (k_{deact}) in this equilibrium by $Cu^{II}X_2/L_n$ to form a halide-capped dormant polymer chain. The bimolecular coupling terminations, always occur in radicals involved polymerization system, are recognized to be insignificant and negligible due to the persistent radical effect (PRE) in ATRP and other CRPs.[9,23,24]

However, some researchers has reported that a chain transfer reaction (which involves the transfer of hydrogen radicals from some species to the active chain) exists in the ATRP of alkyl acrylate monomers using the *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) ligand, which could not be explained by the conventional four-component (i.e., initiation, equilibrium, propagation, and termination) ATRP reaction mechanism.[25−28] The excess PMDETA ligand has eventually been identified to be involved in the chain transfer reaction (k_{tr}) by GPC and MALDI−TOF. The excess PMDETA has also been utilized as chain transfer reagent to synthesize halogen-free poly(butyl acrylate) by ATRP process.[29] That indicates the hydrogen radical involved chain transfer reaction does occur in ATRP, although the transfer constant (k_{tr}/k_p) could not be determined since it is a complicated function of monomer concentration and conversion. Also, it is due to the difficulty to identify the molecular structure and the precise amount of transferred and propagated polymer chains.[26] More recently, we presented a facile method to prepare trifluoroethylene (TrFE) containing fluoro-copolymer from poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-*co*-CTFE)) via a controlled hydrogenation process.[30] In this method, P(VDF-*co*-CTFE) is first converted into macromolecular radicals by a typical ATRP activation system (CuX/BPy)

Received: August 25, 2011
Revised: September 9, 2011
Published: September 21, 2011

© 2011 American Chemical Society

followed by radical chain transfer reaction to polar solvents in absence of monomers subsequently. Fortunately, chain transfer reaction occurred onto CTFE units of P(VDF-*co*-CTFE) macroinitiator generates new units (TrFEs) and shows an obvious multipeak at 5.5 ppm on ^{1}H NMR, which allows us to precisely identify the chain transfer reaction from the active sites. Additionally, the unreacted CTFE could be precisely isolated either from ^{1}H NMR or ^{19}F NMR. Thus, the initiation reaction occur from the active sites could be calculated accordingly if the overall Cl content is fixed. That promotes us to report a facile kinetic method to determine the competition between the chain transfer reaction and initiation reaction of free radicals (k_{tr}/k_i) in ATRP via analyzing the detailed structure of various grafted copolymers from P(VDF-*co*-CTFE) under varied ATRP reaction conditions in this work.

■ EXPERIMENTAL SECTION

Materials. P(VDF-*co*-CTFE) (31508) with 9 mol % CTFE was purchased from Solvay Solexis. CuCl (99.99% from Sigma-Aldrich) and CuBr (99.999% from Sigma-Aldrich) were stored in N_2 atmosphere and used as received. Methyl methacrylate (MMA), methyl acrylate (MA), butyl methacrylate (BMA), and styrene (St) were washed twice with aqueous 5% NaOH and twice with water, dried overnight with $MgSO_4$, distilled under reduced pressure, and stored under N_2 at −20 °C. All the other chemicals were commercially available and used as received.

Synthesis of P(VDF-*co*-CTFE) Grafted Copolymers. A typical synthesis procedure of P(VDF-*co*-CTFE) grafted copolymers is following the typical ATRP procedure as reported.[31] Into a N_2 purged 250 mL three-necked glass bottle, 2 g of P(VDF-*co*-CTFE) (VDF/CTFE = 91/9 mol %) (containing 2.6 mmol Cl atom), 60 mL of *N*-methyl pyrrolidone (NMP), 2.6 mmol of CuCl, and 5.2 mmol of 2,2′-bipyridine (BPy) are introduced and heated at required temperatures in N_2 atmosphere with vigorous stirring. Samples were taken at regular time intervals followed by precipitating in H_2O/CH_3OH (1:1 in volume) mixture, washing five times with methanol and drying for 8 h at 60 °C under reduced pressure. ^{1}H and ^{19}F NMR are applied to determine the exact composition of the grafted copolymers.

Characterization. ^{1}H and ^{19}F NMR spectra were obtained using a Bruker (Advance II) 400 M Hz spectrometer with acetone-d_6 as solvent and tetramethylsilane as an internal standard.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of P(VDF-*co*-CTFE) Grafted Copolymers. A series of grafted copolymers from P(VDF-*co*-CTFE) have been synthesized under varied reaction conditions including reaction temperature, reaction time, monomers, solvents and copper salt as listed in Table 1S, Supporting Information. The structure and composition of the resultant copolymers were characterized with ^{1}H NMR as shown in Figure 1 and Figures 1S−3S (Supporting Information). P(VDF-*co*-CTFE)-*g*-PMMA (entry 3) is selected as an instance to show how the exact structure and composition of copolymers are determined. As shown in Figure 1, the two multiple peaks appear at 2.2−2.4 ppm (I_1) and 2.7−3.2 ppm (I_2) are related to the typical head−head and head−tail connection of VDF units in P(VDF-*co*-CTFE). The peak at 3.3−3.5 ppm (I_3) is attributed to the proton on VDF adjacent to CTFE ($-CF_2-CH_2-CFCl-CF_2-$). New peaks emerge at 0.7−2.0 ppm (I_4), 3.6−3.9 ppm (I_5), 5.0−5.5 ppm (I_6), and 6.0−6.5 ppm (I_7) are identified as the proton on the backbone of MMA grafted ($-CH-CH_2-$), methyl group on MMA ($-COOCH_3$), TrFE ($-CFH-CF_2-$) converted from CTFE, and a few double bonds ($-CH{=}CF-$) generated from the elimination reaction catalyzed by *N* containing compounds, respectively. Therefore, the main chain composition of the grafted copolymers, including unreacted CTFE ($[CTFE]_t$), TrFE or hydrogenated CTFE ($[tr]_t$), grafted CTFE ($[g]_t$) and elimination involved CTFE ($[e]_t$) could be calculated by eqs 1−4, and listed in Table 1S of the Supporting Information.

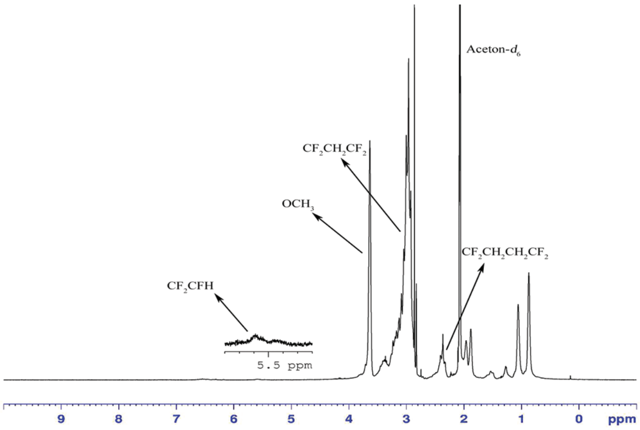


Figure 1. ^{1}H NMR spectra of P(VDF-*co*-CTFE)-*g*-PMMA.

$$[CTFE]_t = \frac{I_3}{(I_1 + I_2 + 2 \times I_7)} \times 91 \text{ mol } \% \tag{1}$$

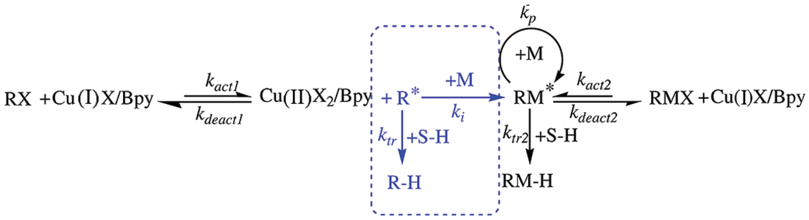
$$[tr]_t = \frac{2 \times I_6}{(I_1 + I_2 + 2 \times I_7)} \times 91 \text{ mol } \% \tag{2}$$

$$[e]_t = \frac{2 \times I_7}{(I_1 + I_2 + 2 \times I_7)} \times 91 \text{ mol } \% \tag{3}$$

$$\begin{aligned}[g]_t &= [CTFE]_0 - ([CTFE]_t + [tr]_t + [e]_t) \\ &= 9 \text{ mol } \% - \frac{(I_3 + 2 \times I_6 + 2 \times I_7)}{(I_1 + I_2 + 2 \times I_7)} \times 91 \text{ mol } \%\end{aligned} \tag{4}$$

As shown in Table 1S (entry 1−5), Supporting Information, the molar content of hydrogenated CTFE is increasing gradually with respect to the reaction time, while the content of unreacted CTFE is decreasing correspondingly. Chain transfer reaction in NMP (entry 4) is much higher than that observed in DMF (entry 21) and DMSO (entry 25), although the chain propagation reactions in these three solvents are close. Additionally, higher reaction temperature favors both the chain transfer and propagation reactions as shown in entry 30−33 due to the endothermic character of both reactions. Also, more monomer in feed leads to continuous increase of chain propagation reaction as well as drop of chain transfer reaction as shown in entry 34−38 because of the enhanced monomer concentration. Compared to CuCl (entry 4), CuBr (entry 42) is less favorable for chain transfer reaction, which may be explained by the halogen exchange effect.[32] About 1−2 mol % of CTFE units are involved in the HCl elimination reaction between the H on VDF and Cl on adjacent CTFE unit catalyzed by the *N* containing compounds in all the entries, which will be discussed more detailed in the other work. Different monomers result into varied chain

Scheme 1. Chain Initiation, Propagation, and Transfer Reaction in ATRP



transfer and propagation reaction rate as well, but they could hardly be compared fairly since the reaction temperature is also varied.

Kinetic Analysis of ATRP Reaction Combined with Chain Transfer Reaction to Solvents. The first step of the reaction (Scheme 1) is the same as typical ATRP including the activation reaction (or formation of R*) together with the deactivation reaction (or formation of RX). Two kinds of initiators, RX (X bonded on the main chain of P(VDF-*co*-CTFE)) and RMX (X bonded onto the inserted monomer), would be generated as soon as monomer is inserted. The chemical condition of these two kinds of initiators is different, which may lead to varied transfer and propagation reaction rate. Meanwhile, the Cl bonded onto RMCl could hardly to be tracked on NMR, so does H on RMH generated by the chain transfer reaction occurred onto the RMX. Therefore, the chain transfer constant (k_{tr}/k_p) could hardly be obtained directly. However, if only RX involved (R*) chain transfer and initiation reactions are took into account as indicated in Scheme 1, the rate constant ratio of chain transfer reaction to initiation reaction (k_{tr}/k_i) could be determined. The ratio could show the competition between the chain transfer reaction to solvents and addition reaction to monomers of the initiator, which may help to understand the influence of chain transfer reaction on ATRP as well as the chain end structure of the resultant products.

$[\mathrm{g}]_t$ calculated from ^{1}H NMR in Table 1S, Supporting Information, refers to the overall molar percentage of initiation reaction occurred from CTFE in time t, which may be described as the integral of initiation rate v_i in t and expressed as eq 5.

$$[\mathrm{g}]_t = \int_0^t v_i \, \mathrm{d}t \tag{5}$$

where v_i=k_i[R*][M], and $[R^*] = (k_{act1}[RX][CuX/L_n])/(k_{deact1}[CuX_2/L_n])$ could be obtained from the equilibrium of ATRP as shown in Scheme 1. [M] could be calculated from the chain propagation rate of ATRP as follows,

$$\ln\frac{[M]_0}{[M]_t} = (k_i[R^*] + k_p[RM^*])t, \quad \text{thus } [M]_t = [M]_0 \mathrm{e}^{-(k_i[R^*] + k_p[RM^*])t} \tag{6}$$

Then, eq 5 could be expressed as

$$\begin{aligned}[\mathrm{g}]_t &= \int_0^t v_i \, \mathrm{d}t = \int_0^t k_i[\mathrm{R}^*][\mathrm{M}]_0 \mathrm{e}^{-(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t} \, \mathrm{d}t \\ &= [\mathrm{M}]_0 \frac{k_i k_{act1}}{k_{deact1}} \frac{[\mathrm{RX}][\mathrm{CuX/L}_n]}{[\mathrm{CuX_2/L}_n]} \frac{1 - \mathrm{e}^{-(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t}}{(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])}\end{aligned} \tag{7}$$

Similarly, $[\mathrm{tr}]_t$ in Table 1S, Supporting Information, referring to the overall molar percentage of chain transfer reaction occurred on CTFE in time t, could be simplified as eq 8.

$$\begin{aligned}[\mathrm{tr}]_t &= \int_0^t v_{tr} \, \mathrm{d}t = \int_0^t k_{tr}[\mathrm{R}^*][\mathrm{S}] \, \mathrm{d}t \\ &= \frac{k_{tr} k_{act1}}{k_{deact1}} \frac{[\mathrm{RX}][\mathrm{CuX/L}_n]}{[\mathrm{CuX_2/L}_n]} \int_0^t [\mathrm{S}] \, \mathrm{d}t\end{aligned} \tag{8}$$

The concentration of solvent ([S]) could be simplified as a constant ($[\mathrm{S}]_0$) with respect to time (t), since it is usually much higher and would not change significantly comparing to [M]. Then the above eq 8 could be described as

$$[\mathrm{tr}]_t = \frac{k_{tr} k_{act1}}{k_{deact1}} \frac{[\mathrm{RX}][\mathrm{CuX/L}_n]}{[\mathrm{CuX_2/L}_n]} [\mathrm{S}]_0 t \tag{9}$$

The function of $[\mathrm{g}]_t/[\mathrm{tr}]_t$ with respect to t could be obtained by dividing eq 7 with eq 9 and simplified as eq 10.

$$\begin{aligned}\frac{[\mathrm{g}]_t}{[\mathrm{tr}]_t} &= \frac{[\mathrm{M}]_0 \dfrac{k_i k_{act1}}{k_{deact1}} \dfrac{[\mathrm{RX}][\mathrm{CuX/L}_n]}{[\mathrm{CuX_2/L}_n]} \dfrac{1 - \mathrm{e}^{-(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t}}{(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])}}{\dfrac{k_{tr} k_{act1}}{k_{deact1}} \dfrac{[\mathrm{RX}][\mathrm{CuX/L}_n]}{[\mathrm{CuX_2/L}_n]} [\mathrm{S}]_0 t} \\ &= \frac{[\mathrm{M}]_0 k_i}{[\mathrm{S}]_0 k_{tr}} \frac{1 - \mathrm{e}^{-(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t}}{(k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t}\end{aligned} \tag{10}$$

When t is taken the limit to zero, namely the right beginning of reaction, eq 10 could be rewritten as

$$\lim_{t \to 0} \frac{[\mathrm{g}]_t}{[\mathrm{tr}]_t} = \frac{[\mathrm{M}]_0 k_i}{[\mathrm{S}]_0 k_{tr}} \tag{11}$$

since $\lim_{t\to 0}(1 - \mathrm{e}^{-(k_i[\mathrm{R}^*]+k_p[\mathrm{RM}^*])t})/((k_i[\mathrm{R}^*] + k_p[\mathrm{RM}^*])t) = 1$.

As a result, the ratio of rate constant between the chain transfer reaction and addition reaction (k_{tr}/k_i) could be obtained from eq 11 as

$$\frac{k_{tr}}{k_i} = \frac{[\mathrm{M}]_0/[\mathrm{S}]_0}{\lim\limits_{t \to 0}([\mathrm{g}]_t/[\mathrm{tr}]_t)} \tag{12}$$

Determination of the Ratio of Rate Constant between the Chain Transfer Reaction and Initiation Reaction (k_{tr}/k_i) in ATRP. Since the original concentrations of solvent ($[\mathrm{S}]_0$) and monomer ($[\mathrm{M}]_0$) are known, the only unknown part in eq 12 is the molar ratio of initiation and transfer reaction at the right beginning of the reaction ($[\mathrm{g}]_t/[\mathrm{tr}]_t$ at $t \to 0$). Apparently, it could hardly be observed from analyzing the structure and composition of grafted copolymers prepared in very small t since the trace content of $[\mathrm{g}]_t$ and $[\mathrm{tr}]_t$ could hardly be measured precisely even on ^{1}H NMR. However, the function of $[\mathrm{g}]_t/[\mathrm{tr}]_t$ with respect to t could be obtained by correlating the structure

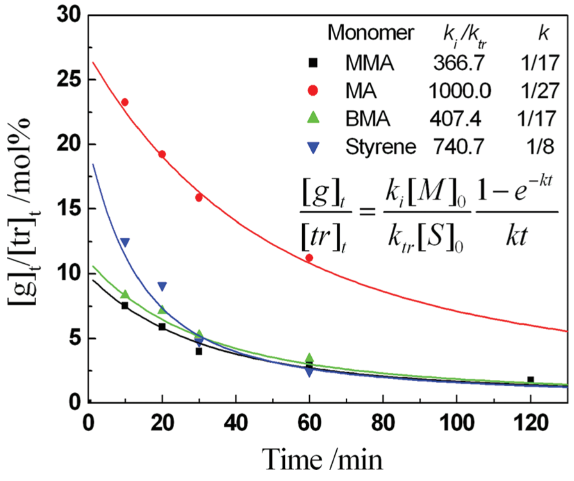


Figure 2. Function of $[g]_t/[tr]_t$ with respect to t measured with varied monomers.

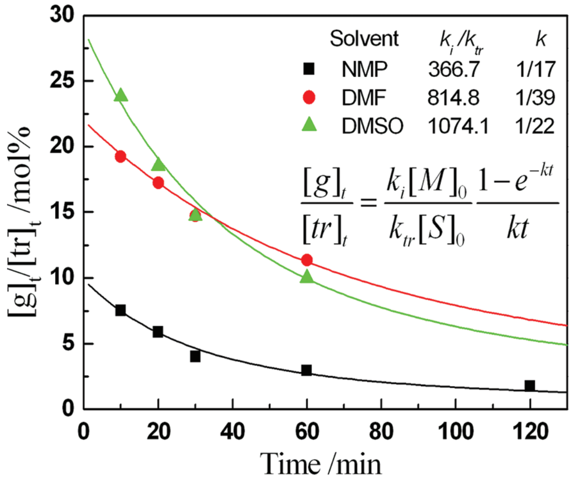


Figure 3. Function of $[g]_t/[tr]_t$ with respect to t in different solvents.

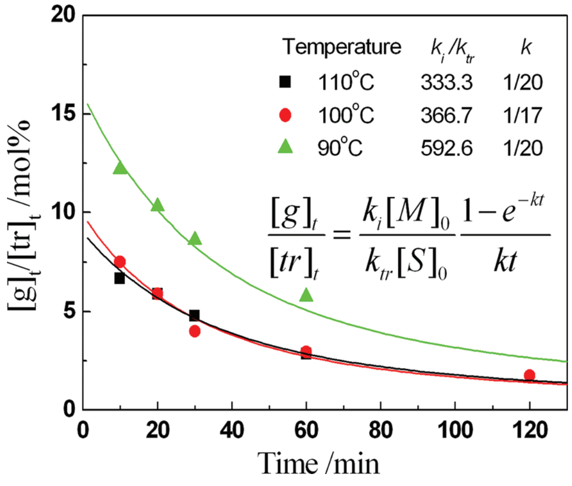


Figure 4. Function of $[g]_t/[tr]_t$ with respect to t measured with MMA as monomer at different temperature.

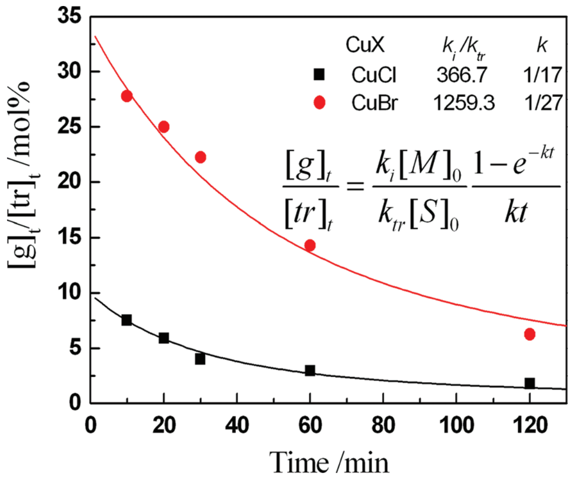


Figure 5. Function of $[g]_t/[tr]_t$ with respect to t measured with different CuX/BPy complex.

and composition of samples taken at designed time intervals. For example, $[g]_t/[tr]_t$ of entry 1−17 calculated from ^{1}H NMR with respect to time t is presented in Figure 2.

At the initial stage, $[g]_t/[tr]_t$ drops rapidly as reaction time increases, and becomes flat after 1 h as shown in Figure 2. It has been demonstrated above that $[g]_t/[tr]_t$ *vs* t is following the function described in eq 10, which allows us to find a function of $y = a(1 - e^{-bt})/bt$ and simply adjust a and b to match all the isolated points obtained in Figure 2. The perfectly matched a and b correspond to $\lim_{t\to 0}([g]_t/[tr]_t)$ and $(k_i[R^*]+k_p[RM^*])$, respectively. For instance, in synthesis of P(VDF-*co*-CTFE)-*g*-PMMA with CuCl/BPy/MMA/NMP=2.6/5.2/28.3/1035 in mmol at 100 °C, a and b are found to be 366.7 and 1/17, respectively. Therefore, the rate constant ratio of chain transfer reaction to initiation reaction (k_{tr}/k_i) could be calculated as 2.73×10^{-3} by eq 12.

k_{tr}/k_i Measured under Varied Reaction Conditions. Following the method discussed above, the ratios of rate constant between the chain transfer reaction and initiation reaction (k_{tr}/k_i) are obtained under altered reaction conditions (Figure 3−5) and listed in Table 1. Solvents, monomers, reaction temperature and CuX salt exhibit significant influence on the chain transfer constant. As shown in entry 1−3 in Table 1, k_{tr}/k_i measured in NMP is 2−3 times of that obtained in DMF and DMSO under the consistent conditions, which indicates that it is more difficult for the macromolecular radical to abstract a hydrogen radical from DMF or DMSO than from NMP. That coincides very well with the 2 times higher chain transfer efficiency in ATRCT observed in NMP than DMF published by our group recently.[30] In addition, the elevated reaction temperature shows positive influence on the chain transfer constant under the consistent conditions (entry 7 and 8 in Table 1). According to Arrhenius equation, elevated temperature favors most of the reactions in a certain degree since their activation energy is usually positive. It seems that the higher temperature is more desirable for chain transfer reaction. Monomer shows significant influence on k_{tr}/k_i as well (entry 1−4 in Table 1), although it could hardly compare with each other fairly since the reaction temperature is also varied. In NMP at 100 °C, k_{tr}/k_i measured with BMA as monomer is slightly lower than MMA indicating the higher chain propagation constant of BMA than MMA, which confirms the data obtained in the literature.[33] The fact that k_{tr}/k_i obtained from MA at 85 °C is comparable with that of MMA at 90 °C

Table 1. k_{tr}/k_i Measured under Varied Reaction Conditions

entry	CuX (mmol)	ligand (mmol)	solvent (mL)	monomer (mmol)	temperature, °C	$k_{tr}/k_i \times 10^{-3}$
1	CuCl (2.6)	Bpy (5.2)	NMP (100)	MMA (28.3)	100	2.73
2	CuCl (2.6)	Bpy (5.2)	NMP (100)	BMA (28.3)	100	2.45
3	CuCl (2.6)	Bpy (5.2)	NMP (100)	MA (33.1)	85	1.00
4	CuCl (2.6)	Bpy (5.2)	NMP (100)	St (26.1)	120	1.35
5	CuCl (2.6)	Bpy (5.2)	DMF (100)	MMA (28.3)	100	1.23
6	CuCl (2.6)	Bpy (5.2)	DMSO (100)	MMA (28.3)	100	0.93
7	CuCl (2.6)	Bpy (5.2)	NMP (100)	MMA (28.3)	90	1.69
8	CuCl (2.6)	Bpy (5.2)	NMP (100)	MMA (28.3)	110	3.00
9	CuBr (2.6)	Bpy (5.2)	NMP (100)	MMA (28.3)	100	0.79

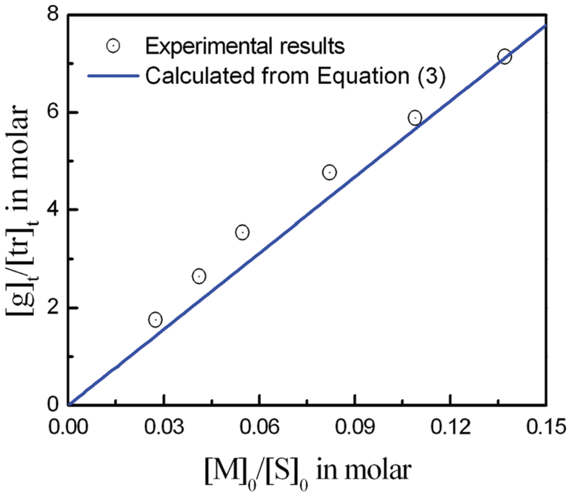


Figure 6. Dependence of $[g]_t/[tr]_t$ with respect to $[M]_0/[S]_0$ in P(VDF-*co*-CTFE)-*g*-PMMA synthesized in NMP at 100 °C.

means these monomers possess similar structure and close chain propagation properties. However, k_{tr}/k_i obtained from styrene at 120 °C is even lower than that from MMA at 100 °C indicates that the propagation of styrene at 120 °C is much higher than MMA at 100 °C. The switch of CuCl to CuBr under the same other conditions leads to dramatically drop of k_{tr}/k_i from 2.73×10^{-3} to 0.79×10^{-3} as shown in entry 1 and 9, which may be related to the halogen exchange effect well discussed in ATRP.[32]

It seems that the chain transfer reaction could be omitted in ATRP since the rate constant ratios of chain transfer reaction to addition reaction (k_{tr}/k_i) of ATRP under presented conditions are only about 1/1000−3/1000 as shown in Table 1. However, even that small value of k_{tr}/k_i may lead to huge influence on the end of growing polymer chain if the original molar ratio of monomer to solvent ($[M]_0/[S]_0$) and the rapid vanishing of $[M]_t/[S]_t$ against *t* are taken into account. As shown in Figure 2, taking MA for instance, $[g]_t/[tr]_t$ is obtained as about 27/1 at the right beginning of the reaction with $[M]_0/[S]_0$ of 0.032, which indicates that about 3−4 mol % starting free radicals ($-CF_2-CF^*-$) would be terminated with H instead of monomers. The situation is getting worse with the consumption of monomer or the quick decrease of $[M]_t/[S]_t$ as indicated in eq 10. In 1 h, $[g]_t/[tr]_t$ quickly drops to about 12/1, indicating nearly 8 mol % of the growing chain is ended with H. Also, $[M]_0/[S]_0$ may affect the chain transfer reaction as indicated in eq 10. In fixed 2 h reaction, $[g]_t/[tr]_t$ of P(VDF-*co*-CTFE)-*g*-PMMA increases in linear against $[M]_0/[S]_0$ as presented in Figure 6, which coincides perfectly with that calculated from eq 10. Equation 10 also strongly suggests that keeping a high initial monomer concentration (high $[M]_0/[S]_0$), terminating the reaction at the initial stage (small *t*) and low temperature (low k_{tr}/k_i) are effective ways to minimize the solvent involved chain transfer reaction in ATRP.

■ CONCLUSIONS

In summary, a series of rate constant ratios of chain transfer reaction to initiation reaction (k_{tr}/k_i) in ATRP are obtained with a facile method via simply analyzing the structure and composition of a series P(VDF-*co*-CTFE) grafted copolymers synthesized under altered conditions. The perfect coincidence between the experimental and the theoretical results indicates the high reliability of this method. Besides the type of monomer and solvent, three other factors, including the higher initial monomer concentration in one shot reaction ($[M]_0/[S]_0$), lower reaction temperature and short reaction time (*t*), are desirable for minimizing the overall chain transfer reaction rate in ATRP conducted in solution. This method may also be helpful to understand the influence of chain transfer reaction on ATRP as well as the chain end structure of the resultant products, which is particularly important for the synthesis of copolymers with well-defined structure (such as block, comb- and star-like copolymers) by ATRP process in more than one step.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed reaction condidtions, ^{1}H NMR spectra, and assignment of all the grafted copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhichengzhang@mail.xjtu.edu.cn.

■ ACKNOWLEDGMENT

This work was financial supported by NSF of China (50903065), SRF for ROCS, SEM, Program for New Century Excellent Talents in University, and the Fundamental Research Funds for the Central Universities.

■ REFERENCES

(1) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101* (12), 3661–3688.

(2) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101* (9), 2921–2990.

(3) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117* (20), 5614–5615.

(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28* (5), 1721–1723.

(5) Kharasch, M. S.; Englemann, H.; Mayo, F. R. *J. Org. Chem.* **1938**, *2*, 288–302.

(6) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102* (2640), 128.

(7) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28* (23), 7901–7910.

(8) Patten, T. E.; Xia, J. H.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272* (5263), 866–868.

(9) Matyjaszewski, K.; Patten, T. E.; Xia, J. H. *J. Am. Chem. Soc.* **1997**, *119* (4), 674–680.

(10) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28* (23), 7970–7972.

(11) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, H. *Macromolecules* **1996**, *29* (10), 3665–3668.

(12) Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30* (7), 2216–2218.

(13) Granel, C.; Dubois, P. h.; Jerome, R.; Teyssie, P. h. *Macromolecules* **1996**, *29* (27), 8576–8582.

(14) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30* (8), 2244–2248.

(15) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30* (8), 2249–2253.

(16) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Shipp, D. A. *Macromolecules* **1999**, *32* (20), 6431–6438.

(17) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Gaynor, S. G. *Macromolecules* **1997**, *30* (20), 6398–6400.

(18) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30* (17), 5192–5194.

(19) Matyjaszewski, K.; Gaynor, S. G.; Muller, A. H. E. *Macromolecules* **1997**, *30* (23), 7034–7041.

(20) Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* **1997**, *30* (23), 7042–7049.

(21) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29* (3), 1079–1081.

(22) Matyjaszewski, K.; Pyun, J.; Gaynor, S. G. *Macromol. Rapid Commun.* **1998**, *19* (12), 665–670.

(23) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581–3610.

(24) Tang, W.; Tsarevsky, N. V.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 1598–1604.

(25) Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol. Rapid Commun.* **1999**, *20*, 59–65.

(26) Roos, S. G.; Muller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 864–867.

(27) Bednarek, M.; Biedron, T.; Kubisa, P. *Macromol. Chem. Phys.* **2000**, *201*, 58–66.

(28) Huang, J.; Pintauer, T.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3285–3292.

(29) Schon, F.; Hartenstein, M.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 5394–5397.

(30) Tan, S. B.; Liu, E. Q.; Zhang, Q. P.; Zhang, Z. C. *Chem. Commun.* **2011**, *47* (15), 4544–4546.

(31) Zhang, M. F.; Russell, T. P. *Macromolecules* **2006**, *39*, 3531–3539.

(32) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.

(33) Beuermann, S.; Buback, M. *Prog. Polym. Sci.* **2002**, *27*, 191–254.