KINETIC APPROACH TO MODELING RAFT POLYMERIZATION UNDER EXTERNALLY APPLIED MAGNETIC FIELD

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Abstract- Based on Stationary State Model of reversible addition-fragmentation chain transfer (RAFT) radical polymerization, a kinetic approach via externally applied magnetic field is established in this work. The kinetic parameters, including \( k_{\text{cross}} \) and \( k_{\text{self}} \) as well as \( k_{\text{add}} \) are estimated through the simulation of the curve between apparent polymerization and concentration of RAFT agent. The importance of cross termination and self termination in rate retardation is discussed. The effective reduction of \( k_{\text{cross}} \) under 0.2T EAMF can explain the effect of EAMF on RAFTP at a quantitative and kinetic level. The results demonstrate a new tool to modeling kinetics of RAFT polymerization, and shed a light on the research of mechanism of the rate retardation effect during RAFT process.

Keywords- Reversible Addition-Fragmentation chain Transfer (RAFT), MagneticField, Kinetics.

I. INTRODUCTION

The development of reversible addition-fragmentation chain transfer (RAFT) radical polymerization since its invention in 1998 has proved it most versatile and widely used polymerization process in facile synthesis of diverse functional polymers with controllable molecular weight, narrow molecular weight distribution and well-defined sequence and architecture. The general mechanism of RAFT polymerization (RAFTP) can be outlined as Scheme 1. Propagating radical reacts with RAFT agent, resulting in carbon-centered intermediate radical, which cannot participate in chain propagation. The adduct radical in turn releases propagating radicals and dormant macro RAFT agent. The individual reactions of these equilibriums are described kinetically via so-called addition rate coefficient, \( k_{\text{add}} \), and fragmentation rate coefficient, \( k_{\text{frag}} \) (see Scheme 1). Equilibrium between dormant and living chains established by recurring RAFT process ensures the living/controlled characteristic of RAFT polymerization. Though the main equilibrium cannot explain the rate retardation effect in RAFT compared to conventional free radical polymerization (FRP). Besides the elementary steps of conventional radical polymerization: initiation, propagation termination, and main equilibriums of chain transfer, cross termination and self termination are depicted in Scheme 1, trying to explain the main cause of rate retardation.

Various models were promoted to explain rate retardation, the essence of major difference between these models is the difference in orders of magnitude of rate coefficients for individual reaction in RAFT polymerization, specifically addition rate coefficient, \( k_{\text{add}} \), fragmentation rate coefficient, \( k_{\text{frag}} \), cross termination rate coefficient \( k_{\text{cross}} \), and self termination coefficient \( k_{\text{self}} \). At this time, detailed knowledge of the kinetics of all the reactions during RAFT process is necessary for analysis of the mechanism of RAFTP, and has been studied through the methods of computational chemistry and analysis through experimental facts such as ESR (electron spin resonance) spectroscopy, NMR(nuclear magnetic resonance) spectroscopy, etc. ESR and NMR spectroscopy as well as product analysis need substantial work and specific design, thus there is a demand of more convenient ways for further exploration. In 2006, the then current situation was critically reviewed by the IUPAC task group, and a particular focus on processes and kinetics involving retardation of RAFT polymerization was stated. A new way to estimate such rate coefficients and modeling kinetics of RAFT polymerization is introduced. Mathematical simulation of the experimental kinetic data is presented, the valuations of rate coefficients are discussed and a more clear kinetics mechanism picture can be acquired.

II. DETAILS EXPERIMENTAL

2.1. Materials

Styrene monomer (CP, Sinopharm Chemical Reagent Co., Ltd) was distilled under reduced pressure after being washed three times with 15% sodium hydroxide aqueous solution and then distilled water. Benzoyl peroxide (BPO) (CP, Sinopharm Chemical Reagent Co., Ltd) was used after recrystallization in methanol. Trithiocarbonate chain transfer agent, S-1-dodecyl-S’-(α, \( \alpha’ \)-dimethyl-\( \alpha” \) -acetic acid) trithiocarbonate (DDMAT) was synthesized according to the literature procedure. The purity of DDMAT was verified by 1H NMR.

2.2. Dilatometry

The dilatometry experiments were carried out under externally applied magnetic field (EAMF). The mixture of St, BPO and RAFT agent was charged into...
dilatometer, degassed, sealed and polymerized in bulk under 70°C. The details of procedure can be found in our earlier work.\textsuperscript{26,27}

III. RESULTS AND DISCUSSION

A series of RAFT bulk polymerization of St mediated with different concentration of trithiocarbonate DDMAT were conducted under EAMF under 70°C. Pseudo-first-order kinetics of FRP and RAFTP are shown in Figure 1A. The rate of the polymerization is found to decrease along with increase of the concentration of DDMAT, showing a sensible dependence of rate retardation on the concentration of RAFT agent. The fact that 0.2T EAMF can effectively reduce the rate retardation effect of RAFT polymerization was confirmed in our previous work. In this work, corresponding $R_M$ under the same condition is calculated as Equation 1, to evaluate the extent of rate retardation bought by cross termination,

$$R_M = \frac{R(\text{RAFT})_{\text{MF}} - R(\text{RAFT})_0}{R(\text{FRP})_{\text{MF}} - R(\text{RAFT})_0} \quad (1)$$

where $R(\text{RAFT})_{\text{MF}}$ is apparent polymerization rate for the bulk FRP with EAMF, $R(\text{RAFT})_0$ is for bulk RAFT polymerization without EAMF and $R(\text{RAFT})_{\text{MF}}$ is for bulk RAFT polymerization under EAMF with the same strength as that in the bulk FRP, respectively.

Fig.1. Pseudo-first-order kinetics (A) and corresponding $R_M$ of FRP and DDMAT-mediated bulk RAFT polymerization of St under EAMF with [St]= 8.70 mol·L$^{-1}$, [BPO]= 0.00870 mol·L$^{-1}$, 70°C. As we can see in Figure 1B, $R_M$ does not vary along the concentration of RAFT agent linearly, instead, it has a peak. At some certain concentration of RAFT agent, EAMF can effectively promote the rate of RAFT polymerization by restraining cross termination, making RAFT polymerization faster. The possible reason can be deduced in terms of the mechanism of RAFT polymerization as shown in Scheme 1. More intermediate radicals brought by higher concentration of RAFT agent, however more propagating radicals are consumed, leaving less to react with intermediate radicals at the same time. This explanation to the special phenomenon is not precise, further work needs to be done in the future work. It needs to be stressed the fact that rate retardation cannot be fully eliminated by EAMF, which means cross termination is not the only factor causing retardation of RAFT polymerization.\textsuperscript{27}
According to the mechanism of EAMF working on rate retardation of RAFTP, rate coefficients of all the reactions during RAFT process in Scheme 1 will not be changed by EAMF except cross termination rate coefficient $k_{\text{cross}}$. $B$ can be considered to be constant under different density of EAMF since self termination is between two radicals with same structure and is not in the influence of EAMF. The simulation according to Equation 3 based on the experimental data of RAFTP with low concentration of DDMAT ([DDMAT] < 0.04mol/L) turns out to be a little different, A=100, B=10 (see Figure3), which indicates that EAMF effectively restrains rate retardation by reducing the cross termination rate coefficient by one half. Moreover, considering K is bigger than 10 in all models involving cross termination or slow fragmentation, the fact that $k_{\text{cross}}$ is much bigger than $k_{\text{self}}$ can be got from the comparison between A and B, meaning cross termination causes more rate retardation than self termination in St/DDMAT system. Results for the same RAFTP with a high concentration of DDMAT ([DDMAT] > 0.05mol/L) turns out to be a little different, A=100, B=2.5 under 0T EAMF, A=100, B=2.5 under 0.2T EAMF. Compared with the former situation, the cross termination rate coefficient is also reduced but with a smaller degree. It is obvious that the concentration RAFT agent has a significant influence on the kinetic parameters in RAFTP, besides the extent of cross termination, equilibrium constant, K, also changes. The change of cross termination has been discussed above. Possible reason for the change of equilibrium constant lies in the difference between the pre-and main-equilibrium. In this work, the simulation is proceeded based on the fact that main-equilibrium is established rapidly enough to ignore the difference of K between the pre-and main-equilibrium, while with larger amount of RAFT agent, more time is needed to establish pre-equilibrium in St polymerization. One interesting prediction from the theoretical simulation of apparent polymerization rate of DDMAT-mediated bulk RAFT polymerization of St under 0T or 0.2T EAMF is that rate coefficients of all RAFTP under 0T or 0.2T EAMF to concentration of RAFT agent, [St]= 8.70 mol·L$^{-1}$, [BPO]= 0.00870 mol·L$^{-1}$, 70°C.

In Stationary State Model, all reactions in Scheme 1 are reversible and in quasiequilibrium and the concentrations of all radicals are approximately invariant with time.$^{12,28-30}$ Stationary State Model is proposed to simplified kinetics of complicated reactions in RAFT polymerization, and is chosen in our work, trying to give a quantitative explanation to the influence of EAMF on kinetics of RAFT polymerization. In this case, the RAFT polymerization rate can be got through mathematical calculation as Equation 2.$^{29}$

$$R_p = \frac{R_{p,0}}{\sqrt{1 + 2k_{\text{cross}}K[RAFT]+k_{\text{self}}K^2[RAFT]^2}}$$

(2), where $R_{p,0}$ is the polymerization rate of the conventional FRP, K is the equilibrium constant of main equilibrium, equals $k_{\text{add}}/k_{\text{add}}+k_{\text{cross}}$ and $k_{\text{self}}$ are the polymerization rate constants of the cross termination and the self termination respectively, and [RAFT] is the concentration of RAFT agents. The expression can be simplified as follows,

$$\frac{R_p ^{-2}}{R_{p,0} ^{-2}} = 1 + A[RAFT] + B[RAFT]^2$$

(3), where

$$A=2Kk_{\text{cross}}/k_b, B=K^2k_{\text{self}}/k_c, R_p, R_{p,0}$$ of all RAFTP under 0T/0.2T EAMF is acquired through dilatometry experiments. The apparent polymerization rate of DDMAT-mediated bulk RAFT polymer decreases along with the increase of concentration of DDMAT, which is found to be one of the features of RAFTP, rate retardation in proportion to concentration of RAFT agent. If just one termination involving intermediate radicals takes place, $(R_p/R_{p,0}) ^{-2}$ will be linear with respect to [RAFT] or [RAFT]$ ^2$. It turns out to be the curve is not linear, so both cross termination and self termination exist in St/DDMAT system.
In conjunction with K value detected with ESR spectroscopy in Stationary State Model with trithiocarbonate as RAFT agent (about 50-100 at 70°C), the value of \( k_{\text{cross}} / k_s \) is estimated to be 0.25-0.5, \( k_{\text{self}} / k_s \) is estimated to be 10^3, yielding \( k_{\text{cross}} \) and \( k_s \) are of the same order of magnitude, \( k_{\text{self}} \) is three orders of magnitude lower. Thus in conclusion, cross termination plays an important role in rate retardation of DDMAT-mediated RAFTp of St, and self termination is little but not ignorable.

It should be noted that the estimate of the kinetic parameter of the DDMAT-mediated RAFTP of St obtained herein is based on several assumptions, so not precise, However, this kinetic analysis satisfactorily describes the experimental data of our work and offers an effective explanation to the retardation reduction under EAMF at the qualitative level.

**CONCLUSIONS**

In this work, DDMAT-mediated bulk RAFT polymerizations of St were performed under EAMF and apparent polymerization rates were calculated within 5% monomer conversion. The dependence of \( R_m \) on concentration of RAFT agent is examined. Based on Stationary State Model, a kinetic approach based on EAMF is established, the kinetic parameters are estimated through the simulation of the curve between apparent polymerization and concentration of RAFT agent. Both cross termination and self termination are proved to exist in DDMAT-mediated RAFTP of St, and \( k_{\text{cross}} \) and \( k_{\text{self}} \) are of the same order of magnitude, \( k_{\text{cross}} \) is much smaller, that is, cross termination causes more rate retardation than self termination. The effective reduction of \( k_{\text{cross}} \) under 0.2T EAMF can explain the effect of EAMF on RAFTP at a quantitative and kinetic level. The results demonstrate a new tool to modeling kinetics of RAFTP, and shed a light on the research of mechanism of the rate retardation effect during RAFT process.

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**REFERENCES**


