Monte Carlo simulation on the kinetics and molecular weight distribution in RAFT polymerization: The effect of the concentration of RAFT agent .

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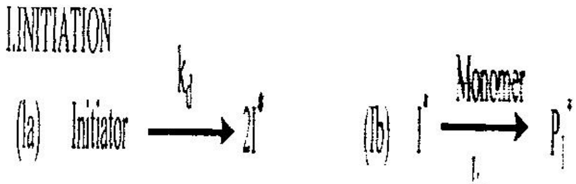
ABSTRACT

The effect of the concentration of RAFT agent of Styrene in RAFT polymerization are the subject of discussion. The kinetics and molecular weight distribution (MWD) occurring in RAFT polymerizations were simulated by using a completely Stochastic Monte Carlo algorithm (SMCA). The simulation results have shown that the polymerization rate (R_p) is strongly retarded by adding the RAFT agent and the higher initial concentration of RAFT agent will cause stronger retardation although it results in narrower MWD. All of theses findings basically agree with the experimental observations quite well.

INTRODUCTION

Reversible addition fragmentation chain transfer (RAFT) polymerization is a versatile technique for the preparation of polymers with both low polydispersity and functionalized groups[1-4]. In the RAFT polymerization[5-7], Molecular weight (MW) control is established via fast, reversible chain transfer to the RAFT agents, such as a dithioester [8,9], trithiocarboonate [10],or dithiocarbamate [11],...etc., as polymer end groups.

Scheme 1 shows the widely accepted mechanism for reversible addition fragmentation chain transfer (RAFT) polymerization. The effectiveness of the process in terms of molecular weight control and polydispersity is governed by the nature of the groups Z and R. In cumyl dithiobenzoate, the Z group is given by phenyl, whereas R is represented by cumyl. The Scheme consists of (I) the initiation processes, (II) a preequilibrium involving the initial RAFT agent, (III) propagation and re-initiation processes, (IV) the addition–fragmentation equilibrium, and (V) bimolecular termination reactions for simple program we take in account only this termination. During a particular transfer event, the propagating end of a chain is converted to a polymeric transfer agent, which can then undergo transfer itself, re-releasing the propagating radical. Through this equilibrium, chains convert from propagating radicals to polymeric transfer agents, meaning that they all grow incrementally with conversion. This process results in living radical behavior, characterized by a predictable, linear evolution of molecular weight with conversion, narrow molecular weight distribution, and pseudo-first order kinetics.



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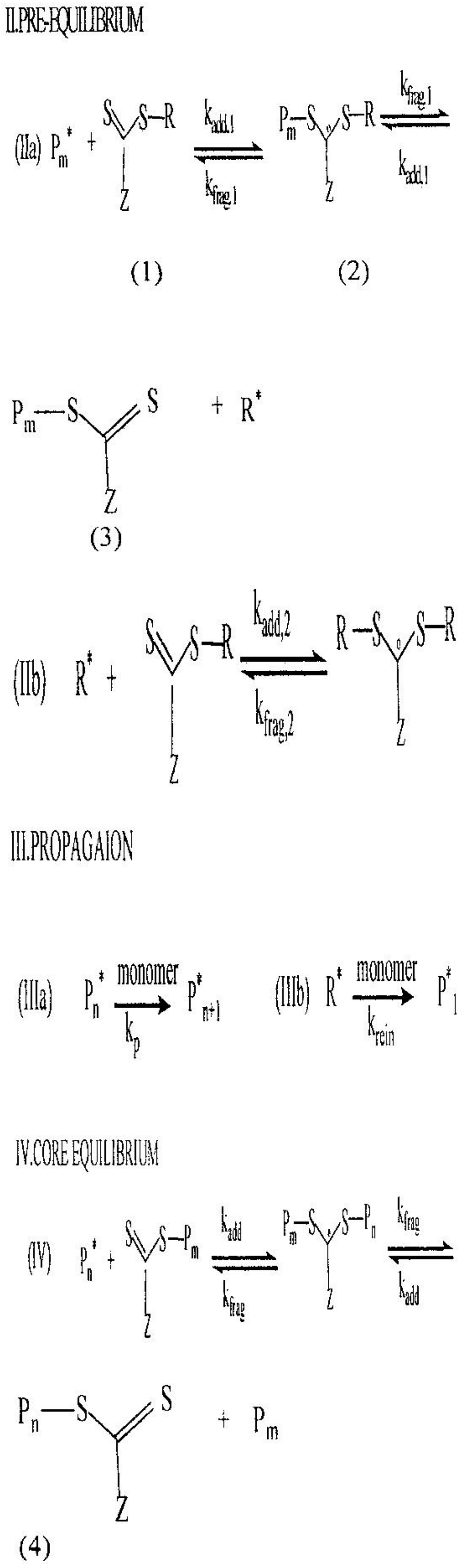

V.TERMINATION

$$(V)\quad P_n + P_m \xrightarrow{k_t} P_{n+m}$$

, were I=AIBN,R=C(CH$_3$)$_2$ph,Z=ph, P=Dead polymer, p$_n$, p$_m$=chains growth polymer

Scheme1. Reactions scheme for the free radical reversible addition fragmentation chain transfer polymerization.

Results And Discussion

The time-dependent chain-length distribution at time t can be calculated according to the following expressions:

$$f(i) = \frac{P(i)}{\sum_{i=1}^{i_{\max}} P(i)} \quad ....(1)$$

number averaged chain length distribution

$$W(i) = \frac{iP(i)}{\sum_{i=1}^{i_{\max}} iP(i)} \quad ....(2)$$

weight averaged chain length distribution

Thus, also the polydispersity index can be readily calculated

$$d(t) = X_w(t)/X_n(t) \quad ....(3)$$

where X_w and X_n are the weight and number-averages of polymerization, respectively.

To assess our simulations, we change the values of initial concentration of RAFT agent from .10^{-3} to 7.10^{-3} mol L^{-1}. and the rate constants and the initial concentrations of various species used in this work are shown in **Table 1** which set basically according to the polymerization of Styrene initiated by AIBN at the temperature of 60C°[12].

Table 1. The fixed input parameters for all simulations

$[M]_0$=6.8 molL^{-1}	$[I]_0$=3.99×10^{-3}mol.L^{-1}
k_{add}=5.0×10^{5} Lmol^{-1}s^{-1}	K_{frag}=3.0×10^{-2} Lmol^{-1}s^{-1}
k_p=275 Lmol^{-1}s^{-1}	k_i =1.8×10^{3} Lmol^{-1}s^{-1}
k_d=5.1×10^{-6} s^{-1}	k_t =4.0×10^{8} Lmol^{-1}s^{-1}

We study the effect of initial concentration of RAFT agent $[RS]_0$ on the kinetics and MW as well as MWD of RAFT polymerization by using the parameters listed in **Table 1**. Fig.1 shows the monomer conversion profiles of four polymerizations with different concentrations of $[RS]_0$. It is seen from fig.1 that the increase of $[RS]_0$ results in the decrease of the polymerization rate due to the reduction of the concentration of propagating radicals. In addition to that, the linearity of the conversion curve increased with increasing of $[RS]_0$.

The living character is confirmed by the fact that chain lengths almost linearly growing with monomer conversion shown in fig.2. It can be seen from fig.2 that, at the same monomer conversion, chain lengths (*Mn*) decreases with increasing of $[RS]_0$.

This is due to the fact that, instead of propagation reactions, the growing radicals spent much more time on the addition and fragmentation reactions when $[RS]_0$ is high.

Fig.3 shows the $[RS]_0$ dependence of the polydispersity index (PDI). As it is expected from the living nature of RAFT polymerization, the PDIs are much lower than the conventional free radical polymerization and it decreases with increasing $[RS]_0$.

The MWD profiles during the polymerization are shown in fig.4. It is seen from fig.4 that the RAFT polymerization do produce narrow MWD. It is also found that reduce $[RS]_0$ will broaden the MWD and increase *Mn*.

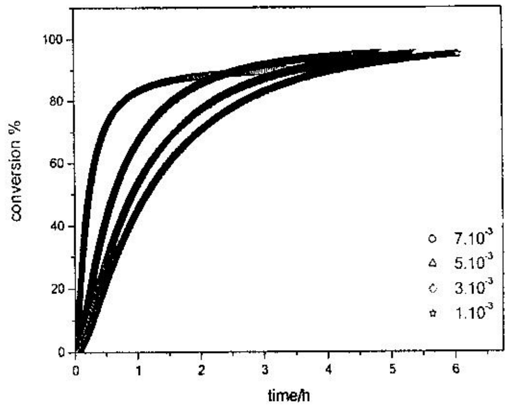

Fig.1. Monomer conversion as a function of reaction time for RAFT agent mediated polymerization of styrene at 60 ^{0}C with with initial concentration of initiator ranging from 1.10^{-3} to 7.10^{-3} mol L^{-1}.

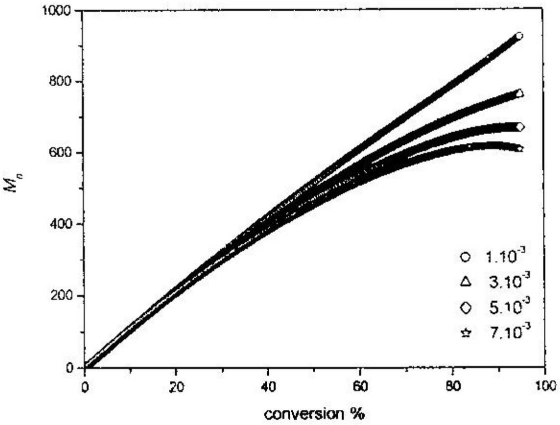

Fig. 2. Average molar mass M_n as a function of monomer conversion for RAFT agent mediated polymerization of styrene at 60 ^{0}C with initial concentration of initiator ranging from 1.10^{-3} to 7.10^{-3} mol L^{-1}.

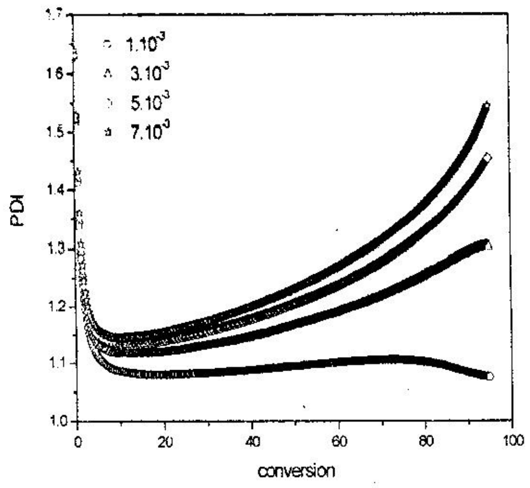

Fig. 3. Polydispersity index PDI as a function of monomer conversion for RAFT agent mediated polymerization of styrene at 60 ^{0}C with initial concentration of initiator ranging from 1.10^{-3} to 7.10^{-3} mol L^{-1}.

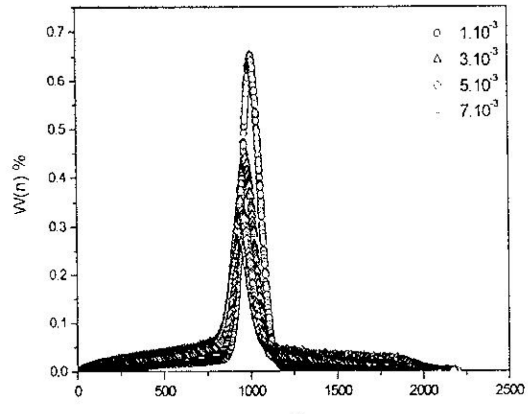

Fig. 4. Weight fraction distributions for different of initiator concentration ranging from 1.10^{-3} to 7.10^{-3} mol L^{-1} at 90% monomer conversion .

CONCLUSIONS

The universal applicability of the SMCA to the RAFT polymerization has been demonstrated in this work. It is demonstrated that the SMCA has the most important advantage that it provides detailed information about the kinetics and MWDs of both living, dead and intermediate chains varying with reaction time or monomer conversion in RAFT polymerization.

The R_p retardation has been observed when the initial concentration of RAFT agent is high. Therefore, although the higher concentration of RAFT agent can result much narrower MWD, we have to pay the cost of low polymerization rate and low MW

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استخدام طريقة المماكاة (مونت كارلو) في دراسة الحركية وتوزيع الوزن الجزيئي لبلمرة الجذور الحرة (RAFT): تأثير تراكيز معامل (RAFT).

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الخلاصة:

تم دراسة تاثير التركيز الابتدائي لعامل البلمرة العكوسة(الاضافة والتفكك)لبوليمرالستايرين على الحركيه وتوزيع الوزن الجزيئي في بلمرة الجذور الحرة العكسية(الأضافة والتفكك) . لقد اجريت الدراسة باستخدام المحاكاة وذلك باستعمال طريقة مونت كارلو الضمنية.وكانت النتائج تشير الى ان زيادة التركيز الابتدائي لعامل البلمرةالعكوسة يؤدي الئ زيادةاعاقة سرعة البلمرة وبالتالي امكانية السيطرة علئ الوزن الجزيئي للبوليمر . وكانت النتائج المستحصلة على تطابق تام مع النتائج العملية الموجودة في الادبيات.