Macromol. Symp. ***150,*** *33–38 (2000)*

Reversible Addition Fragmentation Transfer (RAFT) Polymerization in Emulsion

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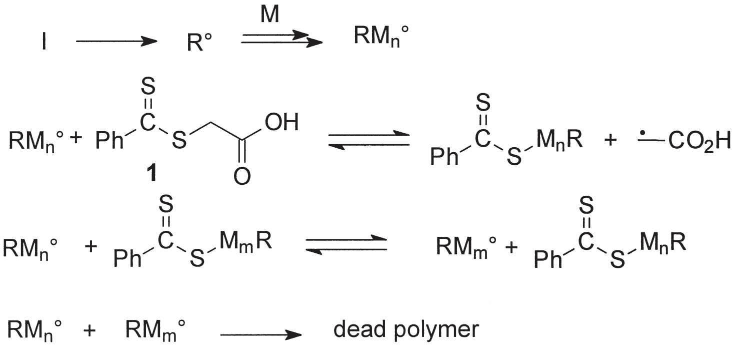
SUMMARY : RAFT polymerization of styrene, methyl methacrylate (MMA) and vinyl acetate has been effected in emulsion polymerization. A commercial chain transfer agent, **1**, was used for starting the reversible transfer reaction. Usually, low chain transfer constants were found with this compound, but transfer could be improved by generating *in situ* a suitable chain transfer agent. Controlled behavior was then observed under emulsion conditions.

Introduction

RAFT[1] is a recently disclosed radical polymerization in which a dithio chain transfer agent (CTA, **1**) is introduced in the reaction medium, in addition to monomer (M) and radical initiator (I).



(1)

(2)

(3)

(4)

At very low conversion, initiator decomposition generates propagating radicals (equation 1) that react with the CTA, to give transferred chains (equation 2). The length of these chains is equal to C_{tr}^{-1} $[MON]_0/[CTA]_0$, where C_{tr} is the chain transfer constant, k_{tr}/k_p (Figure 1).[2] Thus, the molecular weight of the polymer extrapolated at zero conversion gives

CCC 1022-1360/00/$ 17.50+.50/0

direct access to C_{tr}. Rizzardo *et al* have reported C_{tr} in the range of 200, and initial molecular weights near 0.[1]

After sufficient amount of time, the proportion of transferred (dormant) chains is high enough so that chain transfer occurs between propagating radicals and dormant chains (equation 3). Due to this very fast reversible transfer reaction, all polymer chains are growing at the same speed, giving a very narrow molecular weight distribution. Ideally, as transfer does not change the overall radical concentration, [R°], the rate of propagation is not changed by the presence of a reversible transfer. All along the process, new chains are created, in a proportion which is negligible if [I] << [CTA]. Accordingly, the number of dead chains that are terminated (by radical coupling) exactly corresponds to the amount of decomposed initiator. Therefore, living polymerization features are observed if [I] << [CTA].

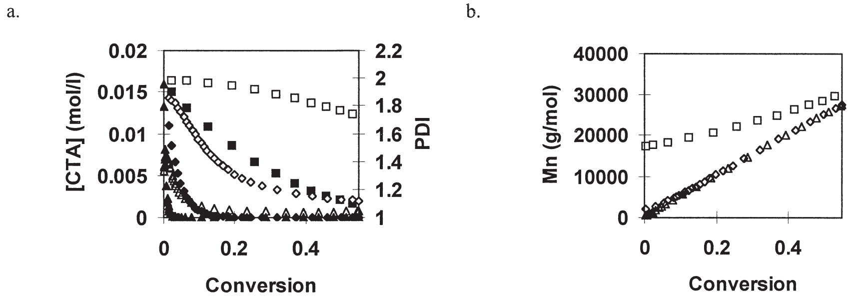


Figure 1. Simulated kinetics of a RAFT polymerization. 1.a (left). Concentration of the chain transfer agent (left, plain symbols) and PDI (right, open symbols) for a RAFT polymerization, when C_{tr} is respectively 3 (square), 30 (losange) and 300 (triangle). 1.b (right). Number average molecular weight versus conversion, when C_{tr} is respectively 3 (square), 30 (losange) and 300 (triangle). [M]:[CTA]:[INIT] = 500 : 1 : 0.005, $k_p = 850$ l/mol/s, $k_t = 10^8$ l/mol/s, $k_i = 10^{-5}$ /s, $[M]_0 = 8$ mol/l. Conversion is limited to 55% corresponding to 34 hours of polymerization.

RAFT in bulk

Using commercial S-thiobenzoyl-thioglycolic acid, **1**, for CTA, we have effected the RAFT polymerization of styrene in bulk at 110 °C. The evolution of number average molecular weight with conversion is linear (Figure 2), but does not go through origin, thus indicating a low chain transfer constant. Using the Mayo equation ($C_{tr} = 1/X_n$ $[MON]_0/[CTA]_0$), C_{tr} is calculated to be 6 for this system.[1] This behavior is easily explained by the fact that reaction 2 is thermodynamically unfavorable as it converts a phenyl stabilized radical into a less stabilized radical. Using the thermochemical data compiled by Benson,[3] it is possible to estimate that the free energy for this equilibrium is $\Delta G° = +2$ kCal/mol (K =

0.0067 at 110 °C). Thus, initial transfer will be much less efficient ($C_{tr} = 6$) than subsequent transfers ($C_{tr} = 200$).

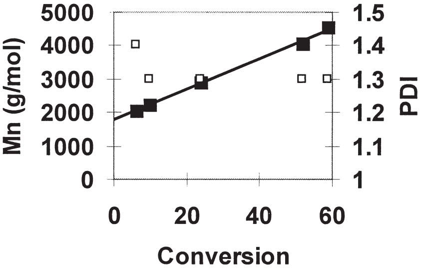


Figure 2 Average number molecular weight (full square) and PDI (open square) for the bulk polymerization of styrene, using [Styrene] : [**1**] : [AIBN] = 100 : 1 : 0.02.

RAFT polymerization in emulsion

Diffusion of CTA through aqueous phase

Emulsion polymerization was carried out using the CTA dissolved in styrene, and the organic red solution was suspended in water/sodium dodecyl sulfate (SDS) and potassium persulfate (KPS). As pH was below 7, the CTA was very insoluble in water. A slow polymerization was observed, with living characteristics, but accompanied with massive amount of floc (up to 40%) due to precipitation of unreacted CTA. In addition, an apparent chain transfer constant of 5 could be found for this system. Overall, most of the reaction occurred in a similar fashion to bulk polymerization.

Diffusion in the aqueous phase of the chain transfer agent can be greatly improved by using the anionic form of the CTA (sodium salt generated at pH = 9.5). In addition, the ratio of [MON]/[CTA] (in the aqueous phase) is much lower than when CTA is dissolved in styrene, forcing the initial transfer reaction. In the water phase, we found that the CTA salts are readily oxidized by persulfates, to yield CO_2, CS_2 and organic products. Thus, all the subsequent work has been carried out using 2,2'-azobis(2-methylpropionamidine) dihydrochloride, V50, a water soluble diazo initiator. Using the sodium salt of CTA leads only to uncontrolled behavior. As CTA **1** is a poor chain transfer agent, radicals can enter particles or micelles without undergoing transfer, followed by uncontrolled polymerization in the particles. We thus rendered the CTA both water and oil soluble by preparing its triethyl amine salt. This salt is slightly water soluble compound, and it readily dissociates to give back oil soluble CTA and triethyl amine.

Ratio of initiator to CTA

The molecular weight evolution with conversion has been followed for different amounts of initiator (Figure 3). Contrary to what we expected, we found that high amounts of initiator are necessary for the molecular weight to grow linearly with conversion. A very high chain transfer constant is found for the system (around 100), as shown by the fact that initial molecular weight is close to zero. Yet, the system is not living due to the excess of radical initiator (PDI = 3 at 94% conversion). We believe that, as CTA is intrinsically a poor chain transfer agent, numerous initiator derived radicals must be generated before the first transfer occurs. When monomer is present, the radicals will not only transfer, but also propagate in an uncontrolled fashion.

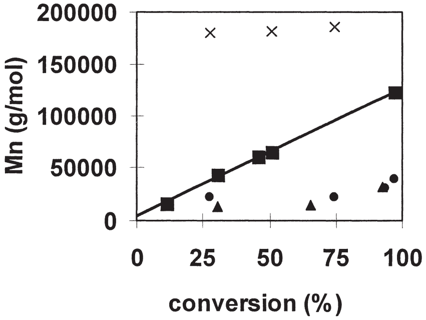
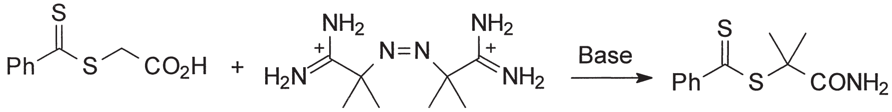


Figure 3. Molecular weight versus conversion for different amount of radical initiator, in emulsion polymerization of styrene ([M] = 190 g/l, [M]/[**1**] = 500, $[NEt_3]/[\mathbf{1}]$ = 1, cationic surfactant [CTAB] = 3 g/l). x : [**1**]/[V50] = 1/0.25, ▲ : [**1**]/[V50] = 1/1, ● : [**1**]/[V50] 1/3, ■ : [**1**]/[V50] = 1/20.

Preparation of CTA 2

In order to prevent uncontrolled polymerization, a new transfer agent can be generated *in situ* by heating a large excess of initiator relative to CTA (typically 10:1) at 95°C for 2 to 8 hours in the absence of monomer. At this temperature, the initiator rapidly decomposes into radicals that transfer to CTA **1**. As the medium is slightly basic, due to the presence of triethylamine, hydrolysis of the amidine moiety into amide can be observed. In general we do not isolate the CTA **2**, but add it directly to the other components of the emulsion recipe. Residual amounts of V50 in mixture with CTA **2** are usually sufficient to initiate the polymerization.



Using **2**, the polymerization seems to be controlled, as shown by linear increase of the molecular weight with conversion, and low polydispersity indices (Figure 4). Moreover, there is a satisfactory match between theoretical (line) and experimental (squares) molecular weights. At the end of the reaction, a 17% solids latex is obtained with no floc. The final particle size is 339 nm +/- 90 nm.

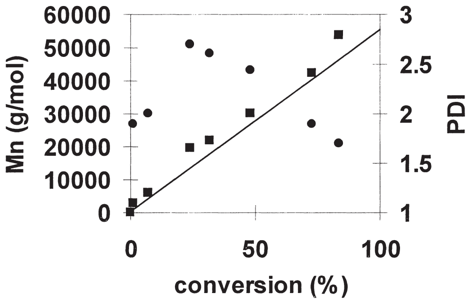


Figure 4. Molecular weight (square) and PDI (circles) versus conversion for styrene polymerization ([M] = 190 g/l, [M]/[**1**] = 500, cationic surfactant [CTAB] = 3 g/l, water = 200 ml). The CTA **2** was prepared by reacting 1 equivalent of **1** with 8 equivalents of V50 at 95 °C for 8 hours in 20 ml of water prior adding other components.

RAFT of other monomers in emulsion

RAFT of MMA (Figure 5 a) using the new CTA gives linear increase of the molecular weight with conversion, yet with higher PDI than expected. In one hour, 18% solids latex is obtained, with particle size distribution centered around 120 nm +/- 36 nm. Within experimental errors, the molecular weight goes through origin, indicating that the initial C_{tr} is very high. The large PDI might come from the very low radical mobility in the PMMA particle, lowering the rate of transfer reaction between propagating and dormant chain. It is also possible that decomposition of the dormant chain occurs through β-hydrogen elimination, as for nitroxide, although this reaction has not been reported for this type of systems.

RAFT of vinyl acetate (Figure 5 b) in emulsion is possible up to 40% conversion, after which the particles are gelled. The molecular weight increases linearly with conversion, but an initial molecular weight of 9000 g/mol is found (corresponding to C_{tr} = 4). Surprisingly, very long reaction times are necessary for this polymerization, unlike a conventional emulsion polymerization of vinyl acetate.

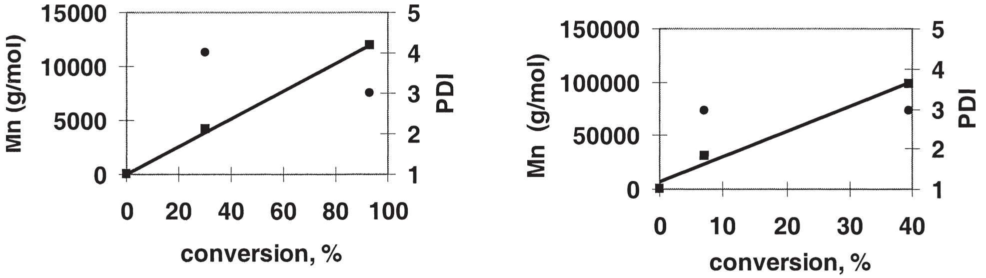


Figure 5 Molecular weight (square) and PDI (circles) versus conversion for MMA (left) and VAc (right) emulsion polymerization ([M] = 190 g/l, [M]/[**1**] = 500, cationic surfactant [CTAB] = 3 g/l). The initiator was prepared by reacting 1 equivalent of **1** with 8 equivalents of V50 at 95 °C for 8 hours.

Conclusions

RAFT is a powerful technique to control radical polymerization in emulsion. As it is suitable for more than one class of monomer (acrylic, styrenic and vinylic), this process should allow block-copolymer synthesis. Further work in this direction is under progress.

References

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