Macromol. Symp. ***150,*** *23–32 (2000)*

Controlled Radical Polymerization in Dispersed Media

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SUMMARY: Free radical degenerative transfer promoted by dithiocarbonate groups is the basis of a new method for controlled free radical polymerization (MADIX). Thus, certain alkyl xanthates are used to impart livingness to radical polymerization of styrene, acrylates and vinyl acetate. Among other analytical methods, MALDI-TOF mass spectrometry showed unambiguously the living character of the process. The MADIX technique was implemented in emulsion polymerization straightforwardly with no retardation effects and an excellent fit between experimental and theoretical molecular weights.

Introduction

Controlled Radical Polymerization (CRP) has been the subject of a large number of papers which demonstrate the industrial relevance of this fast expanding science. The ability to control radical polymerization to prepare polymers with narrow weight distribution and more importantly to produce new macromolecular architectures has been a dream for polymer chemists , now coming true. CRP is based upon a reversible deactivation reactions of macroradicals , which generates an equilibrium between the radicals and so-called dormant chains. When the rate of transformation [dormant chain ⇔ active chain] is high compared with the rate of propagation, the polymer chains grow in a controlled manner. To achieve this reversible radical deactivation, several routes have been developed since about half a dozen years : these include the use of radical traps such as nitroxides [1,2,3] , reversible addition-fragmentation reaction between macroradical and methacrylate-capped macromonomers [4] , metal-mediated halogen atom transfer *(ATRP)* [5]. Several of these CRP techniques were tentatively applied in dispersed media [6,7,8]. However stability problems are often encountered because of the high temperature conditions (Nitroxide-mediated CRP's) or because of the presence of multivalent metals (ATRP). Moreover the partition of the initiator (organic halide, metal catalyst or alkoxyamine) between the particle, monomer droplet and aqueous phases cause additional difficulties in the ultimate control of chain growth.

We present here a new approach in CRP (Scheme 1) which is based on a degenerative transfer reaction between a growing radical and a xanthate compound [9]:

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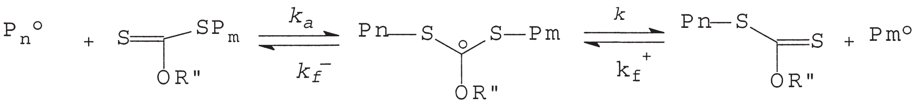
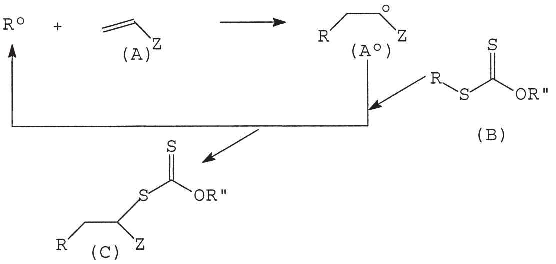


Scheme 1: Degenerative transfer reaction between active chain Pn° and xanthate-capped chains (dormant chains)

This new technique was coined MADIX for MAcromolecular Design *via* Interchange of Xanthate. The propagating macroradical $P_n°$ adds to the thiocarbonyl group leading to an adduct radical ; this transient radical undergoes a β-scission that produces $P_m°$ on one hand, and a dithiocarbonate end group on the other hand : this reaction is degenerate and comes down to an equilibrium between radical chains and dormants chains . At about the same time as this work was completed , Rizzardo *et al* reported a similar approach based on dithioesters that they named Reversible Addition Fragmentation Transfer [10].

Such a degenerative exchange of dithiocarbonyl groups (especially xanthates) has been exploited to generate and capture, even with unactivated olefins, a variety of radicals useful in traditional organic chemistry [11]. For synthetic purposes the reaction is designed in a way leading to mono-adduct ; thus in the following example (Scheme 2) an olefinic compound is reacted with an alkylxanthate B in a stoechiometric ratio together with a catalytic amount of a radical source (azo or peroxo compound).



Scheme 2 : Radical mono-addition of an alkyl xanthate on an olefinic compound

Radical A° reacts with the xanthate B to form the mono-adduct C and the expelled radical R°; the reverse reaction (regeneration of the A° radical from C) is unfavorable as R° is usually more stable than A°. R° can react on B, as well as A° does on C, but both reactions are degenerate giving back the original products so that the reaction is driven towards the C adduct. Of course this chain reaction is sustained by a radical flux provided by an initiator ; the rate of initiation is optimized in order to keep the radical coupling at a minimum but at the same time to maintain the reaction at a convenient rate. If the unsaturated compound is in large excess compared with the alkyl xanthate on one hand , and if on the other hand the radical derived from the olefin is stabilized (e.g. through π conjugation) and the olefin is activated towards radical addition, then the system meets the prerequisites for controlled radical polymerization. Typically a dithiocarbonate R”OCS$_2$R^1 , where R$^{1\circ}$ is a stabilized radical, is added to the monomer in a molar ratio 1:DPth , where DPth is the number average degree of polymerization to be reached. The actual number of growing chains is close to the number of xanthate groups as long as the number of chains produced by irreversible radical termination remain low. The polymerization obeys conventional kinetics except that the propagating radicals reversibly transfer the dithiocarbonate end-groups before they couple irreversibly forming dead polymer. In this paper preliminary results are shown in batch polymerization , either in bulk or in solution. Then this new CRP technique is applied to emulsion polymerization where the effect of radical segregation is thought to enhance the living character of the chain growth .

Results

Polymerization in bulk [12]

The dithiocarbonates studied in this work are listed in Table 1. Compounds ***1a*** to ***1d*** possess the same activating substituent (Ethyl) on the oxygen but differ in their leaving group. Thus the phenylethyl group in ***1a*** is known to be a poor leaving group whereas the radical fragment issued from ***1d*** , should be a good candidate for fragmentation because of its capto-dative structure. On the other hand both ***1b*** and ***2a*** have the 2-propionyl group as the leaving group, but different O-substituents (Et and R” respectively)

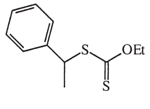
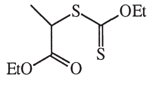
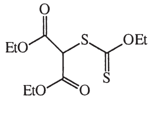
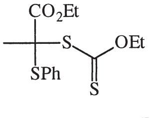
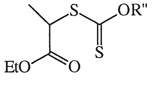
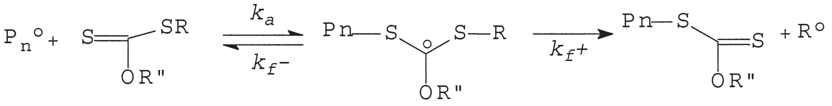
Compound	***1a***	***1b***	***1c***	***1d***	***2a***
Structure					

Table 1: Dithiocarbonate compounds tested in this work

As it is illustrated in Table 2, this selection of xanthates provides control in free radical polymerization of at least 3 important classes of monomer, i.e. acrylic esters, styrene and vinyl acetate, with the notable exception of methacrylates. The MALDI-TOF spectra [13] for polyethyl acrylate is given in Figure 2: Primary (most intense) series corresponds to the expected structure

$CH_3CH(CO_2CH_3)$-$[CH_2$-$CH(CO_2CH_2CH_3)]_n$-$SC(=S)OC_2H_5$. In contrast with what was obtained by Beyou *et al.*[14] on polystyrene terminated by diethyldithiocarbamyl group , in our hands no or few MALDI-induced fragmentation of the dithio moiety was observed. Chain functionality could be qualitatively estimated and appeared to be close to 1.



Scheme 3 : Transfer reaction between macroradicals Pn° and free xanthate groups

Vinyl acetate had been resistant to all the CRP methods reported so far and it is the first time to our knowledge that its polymerization exhibits a living character; this of course, opens up new directions in specialty polymers given the chemical versatility of polyvinylacetate. Looking at the first seven entries of Table 2 and the values of the polydispersity index, it becomes obvious that the more stable the leaving radical , the better the control for both styrene and methyl acrylate. This result is rationalized in writing the expression for the rate coefficient k_{tr} of the addition-fragmentation of the propagating radical on free xanthate, i.e. the "initiation rate" in the formalism of living polymerization (Scheme 3): $k_{tr} = k_a \frac{k_{f+}}{k_{f-} + k_{f+}}$. The relative stabilities of Pn° and R° dictate the ratio k_{f+} / k_{f-} and ultimately the rate of formation of dormant chains.

Table 2: Controlled Radical polymerization in bulk. See ref. [12] for experimental conditions.

Entry	Dithiocarbonate compound	Monomer	Mn theor. (g/mol)	Mn exp. (g/mol)	Mw/Mn (-)
1	***1a***	Styrene	3060	5200	2.1
2	***1b***	Id.	4220	3800	2.0
3	***1c***	Id.	3530	4300	1.9
4	***1d***	Id.	4200	3200	1.8
5	***1b***	Methyl acrylate	3460	3500	1.8
6	***1c***	Id.	3720	3900	1.5
7	***1d***	Id.	3790	3500	1.4
8	***1b***	Vinyl acetate	3080	3200	1.30
9	***1b***	Ethyl acrylate	6600	6950	1.74
10	***2a***	Id.	7630	7950	1.42

Independently of the nature of the leaving group the activating group located on the oxygen of the dithiocarbonate plays an important role as it is shown in Figure 1. Compound **2a** is more efficient than compound **1b** because of its higher transfer constant to polyacrylic radical (the rate of consumption of xanthate **2a** is about twice as much as that of **1b**) and also because of a higher rate of xanthate exchange between active and dormant chains. The rate of xanthate exchange in the degenerative transfer reaction governs the rate at which the system equilibrates (see scheme 1). But as the expelled macroradicals are undistinguishable (i.e. $k_{f+} = k_{f-}$) the addition on the C=S bond is now rate determining. In the case of compound **2a,** it is clear from Figure 1 that the chain growth is getting close to the theoretical value even if the rate of initiation is low. Thus by building in the xanthate structure the proper leaving and activating groups one obtains an excellent control as we shall describe in a forthcoming publication.

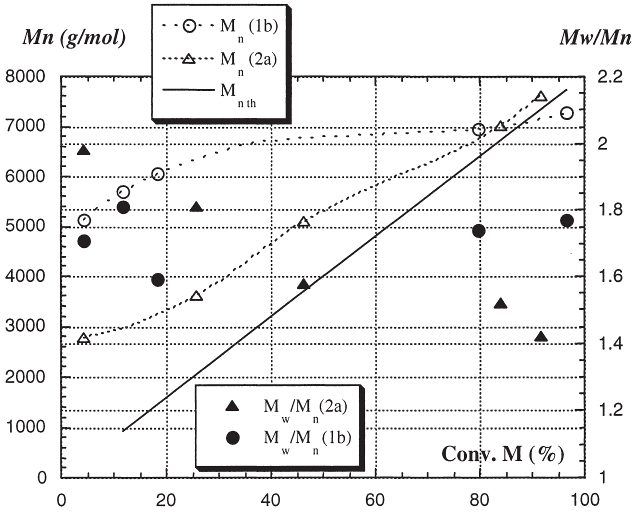


Figure 1 : Evolution of molecular weight and molecular weight distributions in polymerization of ethyl acrylate in the presence of xanthates bearing a propionyl leaving group. AIBN / Xanthate / Ethyl acrylate=0.03/1/80 (50% vol. in toluene). T=80°C.

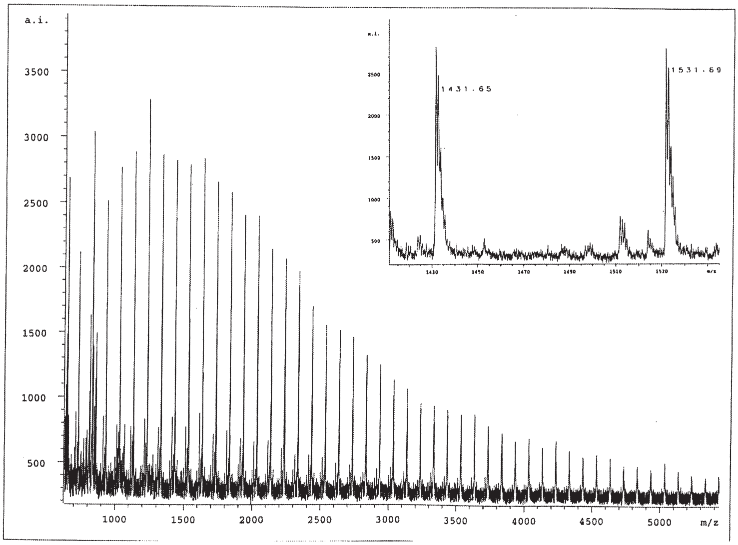


Figure 2: MALDI-TOF mass spectrum of Poly ethyl acrylate (Linear mode; no baseline correction). The theoretical mass value (1431.65) for structure CH3CHCO2CH3-[AET]$_{12}$-SCSOC2H5,Na^{+} fits perfectly the experimental mass value (1431.64).

Emulsion polymerization

Table 3)

Xanthate ***1b*** was purposely chosen as moderately efficient in order to visualize the effect of radical compartimentalization on the living features of MADIX. The latex were prepared *ab initio* with the xanthate ***1b*** introduced in the initial charge and the monomer fed over a period of 3 hours[15]. All the runs were carried out under identical conditions with the exception of the level of surfactant and persulfate which were varied in order to assess the impact of particle size and initiation rates on the molecular weight distribution (MWD). It is worth noting that no retardation was ever observed when dithiocarbonate ***1b*** was used : for the ***1b***/monomer ratios examined in this study, neither the rate of polymerization nor the particle size were changed when compared with the reference (not shown). Hence, such events as the re-initiation by the propionyl radical, or, more likely, the loss of the latter by particle desorption did not affect the kinetics. This is a definite advantage over the other techniques such as nitroxide-mediated CRP or ATRP where more demanding conditions in term of temperature or choice of polymerization aids are required.

Table 3: Results of emulsion polymerization (Homopolymers). Conditions: see ref.[1]. [a] based on monomer; [b] as polystyrene equivalents ; [c] S: styrene , BuA: butyl acrylate,

Entry	Monomer [c]	$Na_2S_2O_8$ (wt-%)[a]	D (nm)	Mn th. (g/mol)	Mn exp.[b] (g/mol)	Mw / Mn
X02	S	0.2	40	16800	17000	2.1
X03	S.	0.2	90	21000	16600	2.3
X04	S	0.2	112	21500	18400	2.3
X36	S	0.2	70	104000	58250	2.7
X39	S	0.04	60	104000	90600	3.3
X12	BuA	0.2	-	19700	20600	1.5
X17	BuA	0.2	-	30750	31100	1.4
X20	BuA	0.2	-	85000	81000	2.3

For styrene homopolymerization (X02 to X04) there was a reasonably good agreement between theoretical and experimental *Mn* , although the polydispersity index did not improve as expected. Interestingly enough, the level of control was not dependant upon the particle size.

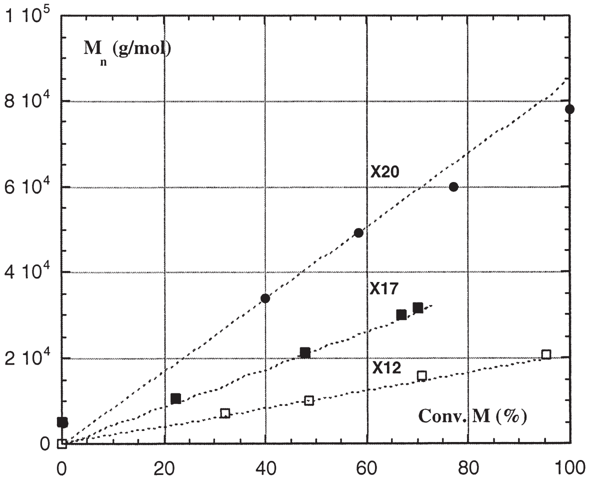


Figure 3 : Evolution of *Mn* vs. monomer conversion in *n*-butyl acrylate emulsion polymerization. Experimental conditions see [Ref.15]

When molecular weights in the range of 1.10^5 g/mol were targeted (X36, X39) the initiation rate had to be lowered in order to match theoretical *Mn* values, but at the expense of an increase in the polydispersity . Similar results were registered with butyl or 2-ethyl hexyl acrylates.

The excellent fit between experimental and theoretical *Mn*'s for all the tested monomers is striking ; this is illustrated for the polybutyl acrylates latexes in Figure 3 (To be compared with the Mn vs. conversion curve for the ethyl acrylate / ***1b*** system in bulk ; Figure 1) : this is a consequence of the rapid consumption of ***1b*** as witnessed by the disappearance of the xanthate peak in the UV trace as early as in the first 5 % conversion. This is also a good evidence of the absence of side reactions involving the xanthate which would have otherwise lead to a deviation of the *Mn* vs. conv. curve.

The features of emulsion polymerization when applied to controlled polymerization by reversible transfer can be rationalized further by developing some theoretical aspects : Thus the rate of dead polymer arising from the irreversible coupling of macroradicals can be predicted quite simply if we assume that the initiation step is completed , i.e. if all the xanthate groups are bound to the dormant chains; the instantaneous fraction of dead polymer, F, is defined as (P_d and P_l referring to dead and living polymer respectively) : $F = \dfrac{\partial P_d / \partial t}{\partial P_{d+l} / \partial t} = \dfrac{k_t Y_0 Y_1}{k_p M Y_0}$, with k_t and k_p termination and propagation constants respectively, M, the molar quantity of monomer, Y_i , the *i*th moment of the macroradicals (i.e $Y_i = \sum_{r=1}^{\infty} n(r) r^i$, $n(r)$ number of radical of length r). One can demonstrate [16] that a good approximation of Y_1 is given by : $Y_1 = (k_p M + k_{tr} Q_1)/(k_{tr} \dfrac{Q_0}{Y_0} + k_t)$, with Q_i, the *i*th moment of the dormant chains. This expression simplifies in $F = \dfrac{\beta}{\tau}(1 + DP_n \tau)/(1 + \beta/\tau)$, by using the adimensional variables β and τ with $\tau = \dfrac{k_{tr} Q_0}{k_p M}$ and $\beta = \dfrac{k_t Y_0}{k_p M}$; DP_n is the actual number average chain length of the dormant chains , $1/\beta$ represents the average chain length before radical termination (without transfer), and $1/\tau$ is the average number of monomer units added between two degenerative transfer events. By using typical values for τ , β and DP_n, it turns out that F can be simplified even further in $F = \beta DP_n$. The polydispersity of the dormant chains is mainly regulated by the τ value: As the reaction proceeds a re-equilibration between short and long chains should occur if the xanthate exchange is fast enough against propagation. These two simple expressions shed some light on the effect of reaction variables on the livingness of the process. Indeed emulsion polymerization is characterized by a low termination rate and a high polymer to monomer ratio P/M. F is minimized when the kinetic chain length $1/\beta$ is high , i.e. favored by a low radical flux and small particle size (in a 0-1 system); for instance a DPn of 5.10^2 will be achieved with a maximum of 5% of dead polymer provided $1/\beta$ exceeds 1.10^4 , a value currently met in emulsion polymerization. However F is bound to increase with P/M. The MWD of the dormant chains on the other hand will narrow as τ goes up , i.e when P/M is high . The numerical simulation based on the complete model [16] showed that increasing the P/M ratio lead to more narrow MWD of the total (dead + living) polymer while generating an increasing amount of dead polymer. Experimentally we were not able to see this improvement in the polydispersity index in the emulsion process as it is patent from the results in Table 3, whereas this trend was observable in bulk or solution polymerization. Further work is underway to try to reconcile theoretical predictions with experiment.

Conclusion

The MADIX technology hinges on the rapid interchange of xanthate groups at the polymer chain ends which then makes possible to control chain growth in free radical polymerization. The design of the dithiocarbonate compound is critical in the ultimate control of both molecular weight distribution and dead polymer : hence the proper selection of the leaving radical and the activating substituent is essential to achieve fast fragmentation of the living radical and a high rate of addition of the propagating radical on the thiocarbonyl. Xanthate compounds are exceedingly cheap materials derived from now well established organic synthesis routes; they offer a large variety of chemical structures and functionalities . For the first time, the living free radical polymerization of notoriously difficult monomers such as vinyl acetate is reported, the same xanthates being also active in the CRP of styrene and acrylate derivatives, with the exception of methacrylates. The extension of MADIX to emulsion polymerization is straightforward and comes down to a simple utilization of a (reversible) chain transfer agent in a latex recipe : regular surfactant such as alkyl sulfate, and initiator , such as persulfate can be used, and more importantly reaction cycles and temperatures remain within the usual range , since the kinetics are not affected by the xanthate exchange reaction. The emulsion process, when implemented semi-batch wise, brings additional advantages over the homogeneous one: as opposed to the batch process, the xanthate is consumed at the very beginning of the reaction yielding 100% dormant chains early in the process: this in turn leads to a linear increase of Mn's versus conversion lying exactly on the theoretical curves. The few elements of kinetic modeling presented here show that high polymer / monomer ratio usually met in emulsion polymerization should improve polydispersity , but at the same time should favor the formation of dead polymer. Work is underway to validate these trends experimentally as well as to expand the MADIX to produce multiblock copolymers latexes.

Acknowledgments

The authors wished to thank C.T. Vuong and M.Pennavaire for their contribution in polymer synthesis, M.Sarraf for the MALDI-TOF experiments, M.Destarac for helpful discussions and Rhodia for permission to publish this work.

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[12] Dithiocarbonates were prepared as described in ref.9. Bulk polymerization were performed in glass tubes sealed after the oxygen had been removed by repeated freeze thaw cycles. After the tubes were broken and their content retrieved , monomer conversion was determined gravimetrically and molecular weights measured by GPC (Eluent THF, *Mw, Mn* expressed in polystyrene equivalents.

[13] MALDI data were collected using a Bruker Biflex III equipped with N_2 laser ($\lambda = 337$ nm).. All spectra obtained in linear mode and a short delay extraction, averaged over 100 laser shots. PAET solutions (10^{-3} M) were prepared in THF and doped with NaCl (0.01M in ETOH/H_2O (90:10)) in a 1:5 ratio of PAET/salt. PAET and salt solution were mixed in a 1:1 volumetric ratio with a 0.4 M solution of *trans*-3-indole acrylic acid

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[15] Emulsion polymerization was carried out in 2L glass reactor equipped with temperature control and monomer feed. Monomer and recipe ingredients were used as received ; there was no oxygen purging but nitrogen blanketing. The xanthate was first mixed with a few wt-% of the monomer charge and introduced with the water, surfactant (Sodium lauryl sulfate) and buffer ($NaHCO_3$). Temperature was allowed to rise to 85°C in 15 mn , sodium persulfate was then added in one shot then continuously fed over a period of 3 hours together with the rest of the monomer charge. The final dry content was about 30 wt-% in all cases ; particles sizes were measured by quasielastic light scattering

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