Polymer 51 (2010) 2947–2953

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

RAFT polymerization of N,N-diethylacrylamide: Influence of chain transfer agent and solvent on kinetics and induction period

Xuewei Zhang, Olivia Giani, Sophie Monge*, Jean-Jacques Robin

Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II cc1702, Place Eugène Bataillon. 34095 Montpellier Cedex 5, France

ARTICLE INFO

Article history:
Received 7 February 2010
Received in revised form
29 March 2010
Accepted 30 April 2010
Available online 10 May 2010

Keywords:
Dithiobenzoates
Induction period
Living radical polymerization

ABSTRACT

RAFT polymerization of N,N-diethylacrylamide was achieved using three different chain transfer agents bringing cyanoisopropyl, cumyl, or tert-butyl R groups, in different solvents (dioxane, toluene), or in bulk. Reactions were controlled and allowed the synthesis of poly(N,N-diethylacrylamide) with targeted molecular weights. Best results were obtained with cyanoisopropyl dithiobenzoate at 80 °C in toluene. This chain transfer agent (CTA) led to the highest efficiency with a very short induction period. On the reverse, cumyl and tert-butyl dithiobenzoates led to relatively high induction periods which were explained by the slow fragmentation of the intermediate radicals and/or the presence of irreversible termination reactions. Initialization process was also discussed. Cumyl dithiobenzoate surprisingly gave the highest induction in comparison with other CTAs and the slowest polymerization rate in all reactional media. Finally, we demonstrated that the induction period was influenced by the solvent.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

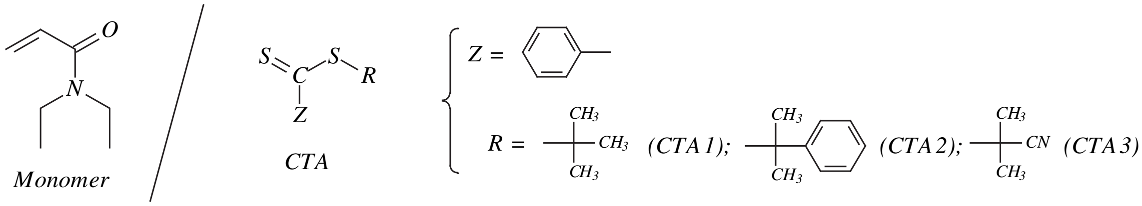
In the last ten years, new materials based on reversible supramolecular organization have become increasingly important. For instance, some polymers show critical phenomena such as phase transition [1] that can be induced by external stimuli: changes in temperature, pH, solvent, ionic composition, electric or magnetic fields, light, etc.... Water soluble polymers that undergo phase transition in response to the temperature were notably investigated for drug delivery with the use of poly(N-isopropylacrylamide) (PNIPAM) [2,3] which showed a lower critical solution temperature (LCST) at 32 °C, close to the human body temperature. As phase transition value depends on the molecular weight and on structural factors, controlled radical polymerization methods, especially reversible addition-fragmentation transfer (RAFT) polymerization, appeared to be useful to control the LCST. RAFT polymerization permitted the synthesis of polymers with well-known architectures [4–6], and proved to be an efficient method to polymerize acrylamide derivatives. In this context, N,N-diethylacrylamide monomer was quite interesting to study as the LCST of the resulting poly(N,N-diethylacrylamide) (PDEAm) was similar to the PNIPAM one [7,8]. As a consequence, PDEAm could be used for biomedical applications. To date, the homopolymerization of DEAm has only been briefly reported. To our knowledge, the only examples described in the literature deal with the synthesis of poly(N,N-diethylacrylamide) under RAFT conditions using 1-cyano-1-methylethyldithiobenzoate as RAFT agent in dimethylformamide [9,10] or in bulk [11]. The PDEAm was characterized by different techniques but no information was given about the influence of the experimental conditions such as the effect of solvent or the choice of chain transfer agent (CTA) on kinetics.

Solvent effects on the propagation and termination rate constants have been the subject of intensive research [12,13] in radical polymerization. In most cases, it was proved that the presence of a solvent affected the reactivity of the propagating radicals [14] and many theories were developed tempting explaining experimental results notably via polarity effects, and the formation of monomer-solvent or radical-solvent complexes. On the other hand, little papers were published dealing with solvent effects on controlled/living radical polymerization and were mainly focused on atom transfer radical polymerization (ATRP) [15,16]. Concerning RAFT process, polymerization of methyl methacrylate was achieved using different experimental conditions [17], and the influence of dithioester substituents, solvent, and temperature was studied. Investigation of the experimental factors affecting the trithiocarbonate-mediated RAFT polymerization of methyl acrylate was also carried out [18]. In both studies, solvents effects were relatively minor on the rate of polymerization and over the control of the molecular weight distribution.

---

* Corresponding author. Fax: +33 467144028.
E-mail address: Sophie.Monge-Darcos@univ-montp2.fr (S. Monge).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.04.073



Scheme 1. Chemical structures of the monomer and the different chain transfer agents (CTAs) used in this study.

Kinetic mechanisms of RAFT polymerization were also deeply studied by many researchers [5,19–21]. It was notably shown that chain-length dependent behavior at short chain lengths affected addition, fragmentation, propagation, and termination kinetics [22,23]. As a consequence, many variables were able to fit different models. Two predominant theories were developed, giving conflicting predictions. Barner-Kowollik et al. [24] assumed that the intermediate radical formed during the RAFT process was relatively stable and long-lived (slow fragmentation model) whereas Monteiro et al. [25] assumed that there was cross-termination of the intermediate radical with other free radicals present in solution (intermediate radical termination model). Recently, Perrier et al. [26,27] proposed a unifying model which took elements of both the slow fragmentation and the intermediate termination model, achieving good results. In this kinetic model, the authors assumed that the rate of cross-termination of short or oligomer radicals with the RAFT intermediate was large, while the rate of cross-termination of long chain polymeric radicals with the RAFT intermediate was low. Results were consistent with all experimental data observed, fitted available quantum calculations, and demonstrated that the two conflicting models proposed so far could coexist.

We report here the first evaluation of experimental parameters on RAFT polymerization of N,N-diethylacrylamide using different chain transfer agents: tert-butyl dithiobenzoate, cumyl dithiobenzoate, and cyanoisopropyl dithiobenzoate, with dioxane, toluene as solvents or in bulk. To our knowledge, this is the first example of comparison of the reactivities of these chain transfer agents for the polymerization of acrylamides. We showed that both chain transfer agent and solvent had an influence on RAFT kinetics and on the induction period.

2. Experimental section

2.1. Materials

2,2-Azobis(2-methylpropionitrile) (AIBN, Acros 98%) was purified twice by recrystallization from methanol. N,N-diethylacrylamide (Polysciences 97%) was used as received. Dioxane and toluene were dried with CaH_2, and with 4A molecular sieves, respectively, and then distilled.

2.2. Instrumentation

Average molecular weights and molecular weight distributions of the different poly(N,N-diethylacrylamides) were measured using size exclusion chromatography (SEC) on a system equipped with a guard column and PLgel 500, 10^3, 10^4 columns (Polymer Laboratories) and a differential refractive-index detector (Waters). The eluent used was tetrahydrofuran at a flow rate of 1 mL min^{-1} at 30 °C. Polystyrene standards (Polymer Laboratories) ranging from 1400 to 1300.10^3 g mol^{-1} were used to calibrate the SEC. We assumed that the PS calibration was suitable for the determination of the molecular weight as it had already been used in the literature, notably in the case of the RAFT polymerization of the N,N-diethylacrylamide to produce thermo-responsive 4-arm star-shaped porphyrin-centered PDEAm [28]. ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer (Bruker) with chloroform as solvent, using tetramethylsilane (TMS) as internal standard.

2.3. Synthesis

2.3.1. Synthesis of chain transfer agents

The tert-butyl dithiobenzoate (CTA1), the cumyl dithiobenzoate (CTA2), and the cyanoisopropyl dithiobenzoate (CTA3) were synthesized as reported in the literature [29,30]. All CTAs were purified by several chromatographies on silica gel and proved to be pure (checking by ^{1}H NMR and mass spectroscopy).

2.3.2. Typical procedure for the RAFT polymerization of N,N-diethylacrylamide

N,N-diethylacrylamide (3 g, 23.69 mmol), cyanoisopropyl dithiobenzoate (CTA3) (0.093 g, 0.42 mmol), AIBN (0.01 g, 70.10^{-3} mmol), and dioxane (14 mL) were introduced in a Schlenk tube. The solution was degassed by five freeze pump thaw cycles, and then heated under nitrogen in a thermostated oil bath at the reaction temperature for appropriate time. The polymer was purified by precipitation in a large volume of cold hexane. Samples for analysis of the molar mass distribution and monomer conversion were taken at different intervals throughout the reaction. Conversion was determined by ^{1}H NMR comparing acrylic protons of the double bond and methylene of N-ethyl groups. Polymerizations were stopped at about 70% conversion.

3. Results and discussion

3.1. Polymerization of N,N-diethylacrylamide using CTA1, 2 and 3 in dioxane, toluene or in bulk.

The N,N-diethylacrylamide was first polymerized using three different chain transfer agents, namely the tert-butyl dithiobenzoate

Table 1
Conversion and molecular weight data for the polymerization of N,N-diethylacrylamide with different chain transfer agents using AIBN as initiator and dioxane or toluene as solvent or in bulk.

Entry	Solvent	CTA[a]	Temp. (°C)	Time (mins)	Conv. (%)	$M_{n,th}$[b] (g mol^{-1})	$M_{n,exp}$[c] (g.mol^{-1})	PDI[c]
1	dioxane	CTA1	80	300	67	4800	3900	1.06
2	toluene	CTA1	80	210	73	5240	5000	1.08
3	bulk	CTA1	80	360	61	4360	3600	1.07
4	dioxane	CTA2	80	480	55	3930	4500	1.06
5	toluene	CTA2	80	330	64	4570	3900	1.09
6	bulk	CTA2	80	360	67	4800	4100	1.07
7	dioxane	CTA3	80	300	86	6140	6300	1.05
8	toluene	CTA3	80	270	84	6000	5800	1.10
9	bulk	CTA3	80	180	71	5090	4400	1.06

[a] CTA1: tert-butyl dithiobenzoate; CTA2: cumyl dithiobenzoate; CTA3: cyanoisopropyl dithiobenzoate.
[b] $M_{n,th} = ([M]_0/[CTA]_0 \times M_w \text{ of monomer} \times \text{conv})/100$.
[c] Estimated by PS-calibrated size exclusion chromatography (SEC).

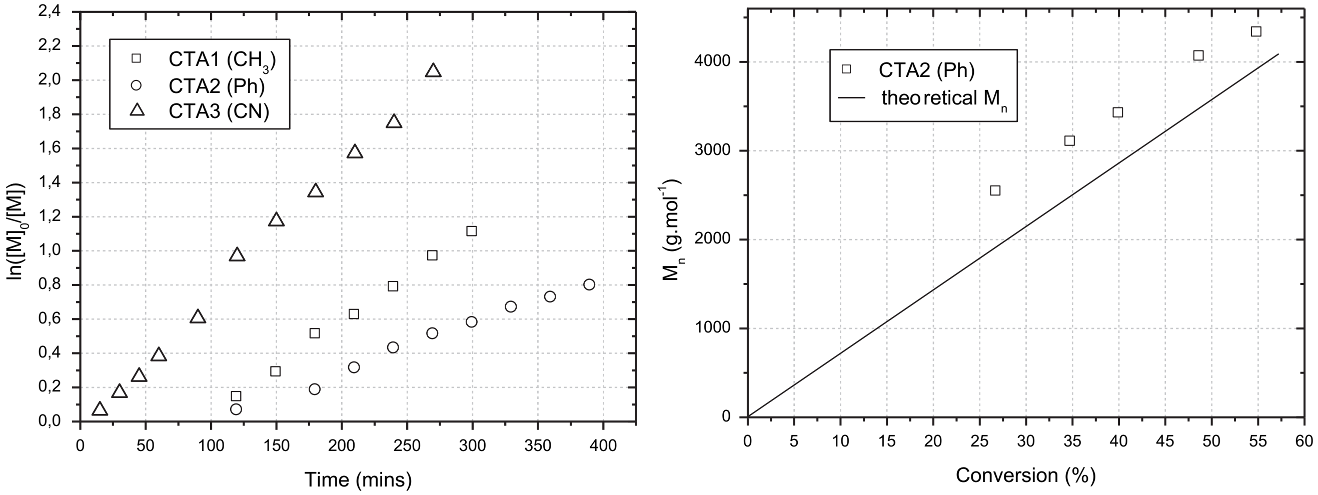


Fig. 1. (Left) Pseudo-first order kinetic plots for the RAFT polymerization of N,N-diethylacrylamide in dioxane at 80 °C using CTA1, 2, and 3 and AIBN as initiator; (Right) Number-average molecular weight (M_n), determined by SEC, vs conversion plot for the polymerization of N,N-diethylacrylamide in dioxane at 80 °C using CTA2 and AIBN as initiator. [Monomer]/[CTA]/[AIBN] = 56/6/1. [Monomer] = 1.37 M.

(CTA1), the cumyl dithiobenzoate (CTA2), and the cyanoisopropyl dithiobenzoate (CTA3) (Scheme 1). Chain transfer agent is an important parameter in RAFT methodology and polymerization reaction depends on its chemical structure (*Z* and R groups). Dithiobenzoate derivatives (*Z* = phenyl) led to good chain transfer coefficients [31] and were able to activate the double bond to radical addition and to provide stability for the adduct radical.

Polymerization of the N,N-diethylacrylamide was first achieved in dioxane at 80 °C (Table 1, Entries 1, 4, 7) and gave first order kinetic plots for all CTAs, indicating that the number of active species remained constant. Unwanted termination processes were minimized because of the rapid transfer of the growing polymeric radicals between their free and dormant forms.

The number-average molecular weights determined by size exclusion chromatography (SEC) using THF as eluent and PS standards showed a relative good agreement with those expected from the corresponding monomer/chain transfer agent ratio (Fig. 1). The observed difference between theoretical and experimental M_n values could be attributed to the PS calibration or to some RAFT agent not being consumed. The polydispersities were quite narrow as obtained M_w/M_n was 1.06 or 1.05. The highest efficiency was obtained for CTA3 whereas CTA2 was the less reactive, which was quite surprising as electron-withdrawing effects on the *R* groups were similar for CTA3 and CTA2.

To study the influence of the solvent, polymerization of N,N-diethylacrylamide was also carried out at 80 °C in toluene and in bulk (Table 1). All polymerization reactions were controlled with first order kinetic plots (Figs. 2 and 3). Experimental molecular weights, determined by ^{1}H NMR for CTA1 and CTA3 in bulk, were close to theoretical ones. Once again, CTA3 was the most efficient chain transfer agent and CTA2 the less reactive. Polymerization also occurred faster in toluene than in bulk. As propagation rate is dependent on monomer and radical concentrations, one would expect slower kinetics for diluted system. This was surprisingly not the case as polymerizations were more rapid in concentrated medium as shown by the apparent rate constants which were higher when toluene was used as solvent. Our experimental results were reproducible and could be explained by a better solubility of the CTAs in the organic medium. Toluene apparently allowed a better solubility of the chain transfer agents than dioxane or the bulk medium. Finally, we also concluded from these results that polarity did not improve the rate of polymerization, as already previously reported [18].

An entire concentration range was also studied to assess the influence of the RAFT agent concentrations in each solvent (Fig. 4), using CTA3 as it proved to be the most efficient chain transfer agent, also giving a very low induction period. Polymerization went on faster with higher RAFT chain transfer agent concentration. Nevertheless, the influence of CTA3 concentration appeared to be less significant above 0.028 M in both dioxane and toluene. Experimental molecular weights determined by size exclusion chromatography showed a linear behavior as a function of the conversion and low polydispersity indexes indicating that polymerizations were controlled in all cases. It was also interesting to notice that the CTA concentration had no influence on the induction period which remained the same in all experiments carried out in a same solvent whereas Müller et al. showed that the induction periods increased with increasing CTA concentration in the case of the polymerization of N-isopropylacrylamide using benzyl or cumyl 1-pyrrolecarbodithioates as chain transfer agents, in dioxane at 60 °C [32].

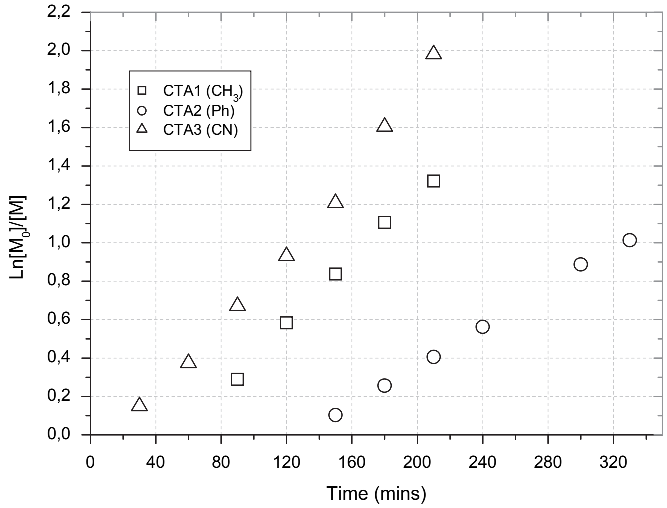


Fig. 2. Pseudo-first order kinetic plots for the RAFT polymerization of N,N-diethylacrylamide in toluene at 80 °C using CTA1, 2, and 3 and AIBN as initiator. [Monomer]/[CTA]/[AIBN] = 56/6/1. [Monomer] = 1.37 M.

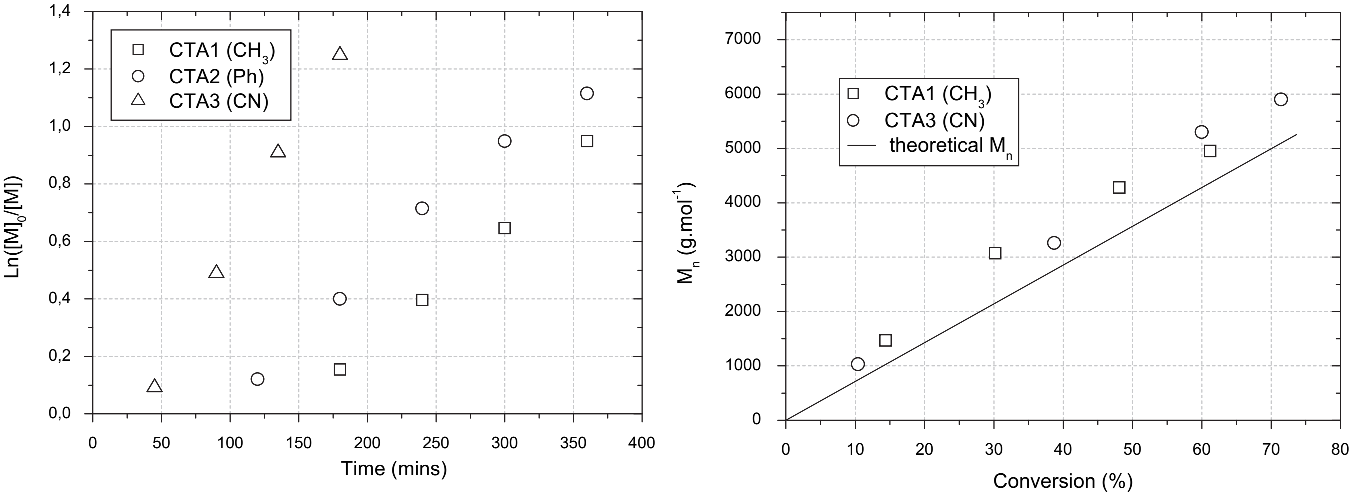


Fig. 3. (Left) Pseudo-first order kinetic plots for the RAFT polymerization of N,N-diethylacrylamide in bulk at 80 °C using CTA1, 2, and 3 and AIBN as initiator; (Right) Number-average molecular weight (determined by ^{1}H NMR) vs conversion plot for the polymerization of N,N-diethylacrylamide in bulk at 80 °C using CTA1 and CTA3, and AIBN as initiator. [Monomer]/[CTA]/[AIBN] = 56/6/1. [Monomer] = 7.34 M.

3.2. *Effect of R substituent*

In the RAFT mechanism (Scheme 2), propagating radicals are first generated as in a conventional radical polymerization. Then, a propagating radical is added to the dithiobenzoate derivative to form an adduct and finally, the latter fragments to form on the one hand a polymer terminated by a dithiobenzoate and on the other hand a radical $R^{\bullet}$ which reacts to form a new propagating radical. As a consequence, the effectiveness of the RAFT agent depends on the properties of the *Z* group and the free radical living R group. Both of them must be carefully chosen to achieve an efficient RAFT polymerization.

As the *Z* group is the same for all CTAs, we assumed that the efficiency of the chain transfer agents depended on the R substituent (Scheme 3). From the RAFT mechanism, reversible chain transfer can be considered as the key-step concerning the influence of the R group and two important points must be taken in consideration: (i) the fragmentation of the intermediate radical **1** and (ii) the ability of the R free radical leaving group to reinitiate the polymerization.

It is well known, from the literature, that cyanoisopropyl and cumyl groups provide a better fragmentation rate compared to the tert-butyl substituent [6]. It is also obvious, from electron-withdrawing effects, that tert-butyl radical better reinitiate the polymerization than cumyl or cyanoisopropyl radicals. For instance, absolute rate constants for radical addition to methyl acrylate at 60 °C proved to be 110 000, 800, and 367 M^{-1} s^{-1} for $^{\bullet}C(CH_3)_3$, $^{\bullet}C(CH_3)_2Ph$, and $^{\bullet}C(CH_3)_2CN$, respectively [29]. In the case of cyanoisopropyl dithiobenzoate (CTA3), the fragmentation of the intermediate radical **1** was favored due to the strong electron-withdrawing effect of the cyano group. As a consequence, the obtaining of $R^{\bullet}$ was extremely privileged and even if this radical was stabilized by electronic effects, the addition to the N,N-diethylacrylamide was not a limitation and the rate of polymerization was the highest in comparison with other CTAs. Moreover short period of inhibition was observed with cyanoisopropyl dithiobenzoate chain transfer agent probably due to a fragmentation easy to achieve as resulting radical $R^{\bullet}$ was stabilized.

On the reverse, CTA1 and 2 showed relatively long period of inhibition. The latter was explained in the literature by two

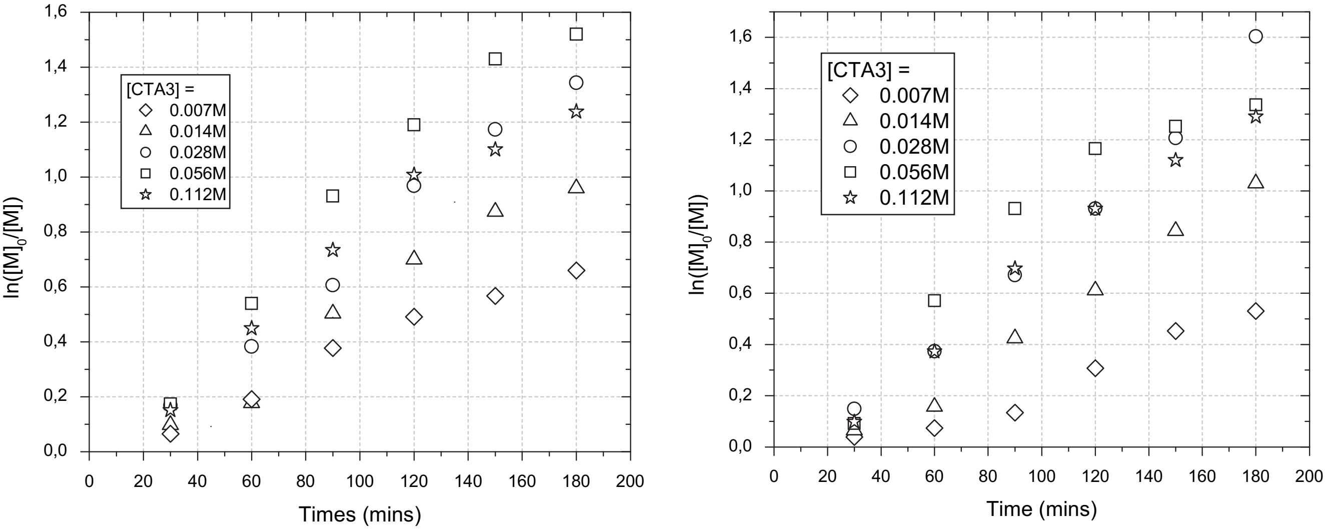
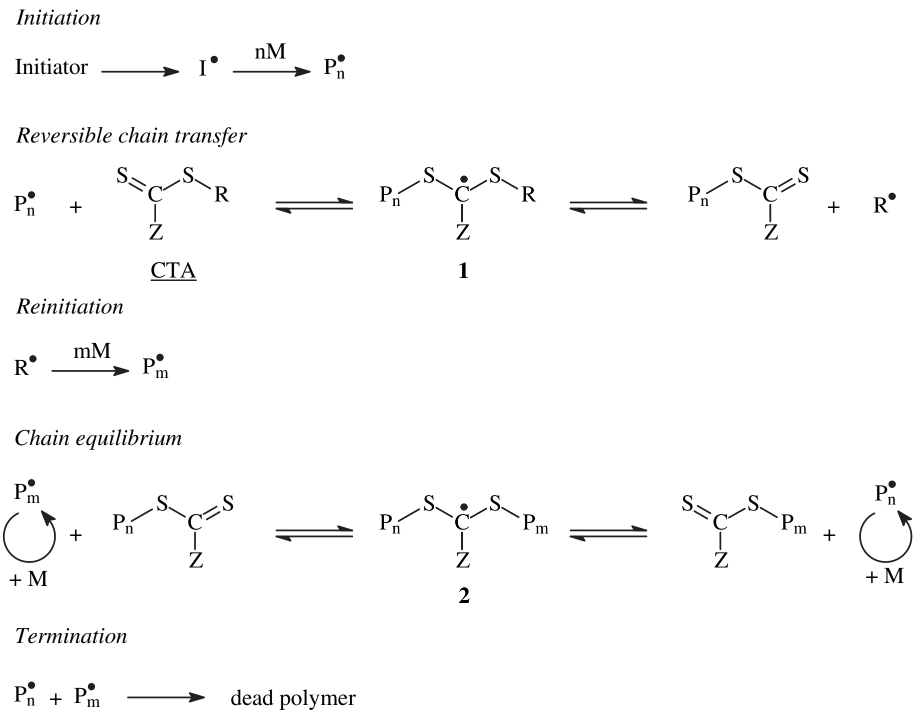
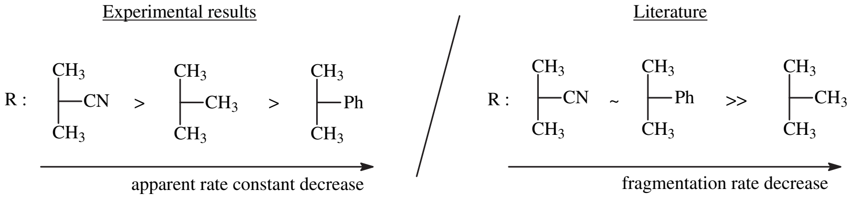


Fig. 4. Pseudo-first order kinetic plots for the RAFT polymerization of N,N-diethylacrylamide in dioxane (left) and in toluene (right) at 80 °C using CTA3 and AIBN as initiator for various chain transfer agent concentrations (0.007 M, 0.014 M, 0.028 M, 0.056 M, 0.112 M).



Scheme 2. General mechanism of RAFT polymerization explaining the different polymerization rates observed with the chain transfer agents used.

different approaches as already mentioned in the introduction of this manuscript. In the first one, it was reported that inhibition was governed by the fragmentation rate of the pre-equilibrium RAFT radical **1**, the slow fragmentation of the intermediate radical [33] leading to inhibition, and by the ability of the leaving group to reinitiate the polymerization. Concerning cumyl dithiobenzoate (CTA2), it has been demonstrated by γ-radiation experiments that the RAFT radical formed in the pre-equilibrium (species **1**) might be very stable and survive for significant time [34]. As a result, cumyl was considered to be a worse leaving group than cyanoisopropyl, for instance on RAFT polymerization of methyl acrylate [35]. A second approach was given to explain inhibition. Indeed, Monteiro et al. [25] proposed that irreversible cross-termination occurred between the propagating radical and the intermediate radical. It was shown by a combination of simulations and experimental data that this mechanism for induction was through termination of the intermediate radical **2**, notably when cumyl dithiobenzoate was used as RAFT transfer agent [36]. This phenomenon led to three-arm dead chains [37–39]. Nevertheless, Barner-Kowollik et al. argued that, even if irreversible termination reactions were possible, they were more likely the result of slow fragmentation of the intermediate macro-RAFT radical **2** and not the primary cause of rate retardation in some RAFT systems [40]. Perrier et al. [26,27] also proposed a unifying model which explained experimental results obtained in this work. Indeed, concerning our experimental results on the polymerization of N,N-diethylacrylamide, both approaches (slow fragmentation of the intermediate radical and irreversible termination reactions) can be discussed as conversion time and molecular weight measurements are not able to provide a definite answer indicating which kinetic model is operational, as both models fit the macroscopic data well. For instance, the evolution of the molecular weight versus conversion in dioxane at 80 °C showed that M_n were slightly higher when cumyl dithiobenzoate was used as chain transfer agent, in comparison with other CTAs (when all molecular weights were determined by SEC for all CTAs). This could be explained by the presence of a few percent of irreversible termination reactions which led to higher values for the molecular weights as a little quantity of macro-RAFT agent was lost by this side reaction. On the other hand, comparison of experimental results obtained when cumyl dithiobenzoate (CTA2) and tert-butyl dithiobenzoate (CTA1) were used as CTAs were in accordance with a likely slow fragmentation of radicals **1** containing the cumyl group. From its chemical structure, it is normal to observe a relatively high induction period for CTA1 because fragmentation of intermediate radical **1** is not favored in that case as resulting $R^{\bullet}$ group (${}^{\bullet}C(CH_3)_3$) is not stabilized by electronic effect. On the reverse, cumyl radical (${}^{\bullet}C(CH_3)_2Ph$) should be easily obtained as it is strongly stabilized by electron-withdrawing



Scheme 3. (Left) Apparent rate constant decrease for the polymerization of N,N-diethylacrylamide; (Right) Guideline for selection of RAFT agents described in the literature (Handbook of RAFT polymerization, C. Barner-Kowollik, Ed., WILEY-VCH Verlag GmbH&Co., pp. 193).

Table 2
Induction period, and apparent rate constants (k_{app}) as a function of the solvent (dioxane, toluene or in bulk) for the three different chain transfer agents (CTAs). [Monomer]/[CTA]/[AIBN] = 56/6/1. [Monomer] = 1.37 M.

Solvent	CTA	Induction period (mins)	10^5 k_{app} (s^{-1})
Dioxane	CTA1	100	9.0
	CTA2	125	4.7
	CTA3	5	13.0
Toluene	CTA1	55	14.4
	CTA2	130	8.5
	CTA3	10	16.8
Bulk	CTA1	150	7.3
	CTA2	100	7.0
	CTA3	30	14.4

effect of the phenyl group. Nevertheless, experimental results in organic medium showed that induction period was less important for CTA1 (60–75 min) than for CTA2 (100–120 min). This implied that RAFT radicals **1** that contain the cumyl group fragmented slowly. We can also take in consideration the initialization process. Indeed, the latter could help elucidating our experimental results. In such approach, in situ ^{1}H NMR experiments were achieved to investigate the very early stages of the RAFT-mediated polymerization, and to tempt explaining the induction period [23,41–43]. Klumperman et al. showed that, at the very beginning of the polymerization, the RAFT chain transfer agent was selectively converted into a RAFT agent containing one monomer unit. The period in which the RAFT agent was converted to this first monomer adduct was called “initialization”, and the addition of monomer units only increased after the majority of the RAFT agent was first consumed. As a consequence, the rate determining step during the initialization period appeared to be the addition of the leaving group radical to monomer. In our case, this addition is more favored for CTA1 than for CTA2 and can explain why the induction period is higher with cumyl dithiobenzoate compared to tert-butyl dithiobenzoate. Nevertheless, the initialization process cannot alone clarify the difference of induction period between the cumyl and cyanoisopropyl dithiobenzoates as both cumyl ($^{\bullet}C(CH_3)_2Ph$) and cyanoisopropyl ($^{\bullet}C(CH_3)_2CN$) radicals are stabilized by a similar electron-withdrawing effect. We concluded that our experimental results could only be explained combining Klumperman work with other results reported in the literature by Barner-Kowollik et al., Monteiro et al. and Perrier et al..

3.3. *Effect of solvent*

We also noticed that solvent had an influence on the induction period and on the apparent rate constants values (Table 2). This was notably proved by the polymerization carried out in bulk with CTA1 in which induction lasted 150 min. Tert-butyl dithiobenzoate was probably more difficult to solubilize in N,N-diethylacrylamide than other chain transfer agents. As a result, the different equilibrium were slowed down and $^{\bullet}C(CH_3)_3$ radicals were produced less rapidly. Moreover, the solvent could also have an influence on the life-time of the intermediate radicals and/or on cross-termination reactions. Finally, the apparent rate constants, k_{app}, were determined as the slopes of the first-order time/conversion plots. The increasing induction periods were in general accompanied by a decrease of the apparent rate constants, as already reported in the literature [32], except for the polymerization in bulk. At constant RAFT agent concentrations, all polymerizations achieved in the same solvent led to quite close rates when the induction period was over. This was expected since as soon as the initial RAFT agent was consumed, the fragmenting group was the propagating polymer chain. As a consequence, the kinetics was quite similar, and independent of the initial RAFT agent. On the reverse, k_{app} was more dependent on the solvent used for the RAFT polymerization of N,N-diethylacrylamide. Best result (highest k_{app} value) was obtained with cyanoisopropyl dithiobenzoate in toluene.

4. Conclusion

RAFT polymerization of N,N-diethylacrylamide was achieved using three different chain transfer agents (cyanoisopropyl, cumyl, and tert-butyl dithiobenzoates) in three reactional media (dioxane, toluene, or in bulk). Polymerizations were controlled with all experimental conditions as poly(N,N-diethylacrylamides) were synthesized with controlled molecular weights and low polydispersities. The best results were obtained with CTA3 in toluene, at 80 °C. Concerning the influence of the solvent, as expected, a better solubilization of the different intermediate species led to less inhibition and higher reactivity. Toluene which has a chemical structure close to those of chain transfer agents permitted to achieve the best experimental results. Moreover, cyanoisopropyl dithiobenzoate (CTA3) led to the highest efficiency. On the reverse, in the case of cumyl (CTA2) and tert-butyl (CTA1) dithiobenzoates, a relatively long period of inhibition was observed, the latter being higher for CTA2. Two opposing explanations were given in the literature to explain this phenomenon. The CAMD research group [33] assumed that the intermediate radicals were stable enough to cause no termination with $P^{\bullet}$ whereas Monteiro et al. [25] reported that the intermediate radical underwent cross-termination. Klumperman et al. also reported the existence of the initialization process [23]. Our results could be in accordance with these explanations as all models reported in the literature fitted the macroscopic data well.

Next experiments will be focused on a more extensive study of induction period. We will notably try to determine if cross-termination occurred during the polymerization of N,N-diethylacrylamide. These experiments will be achieved notably using MALDI-TOF mass spectroscopy [44] or PREDICI modeling [23,24]. Once this point elucidated, we will also study the polymerization of other type of monomers (acrylate, methacrylate, styrene, …) to evaluate experimental conditions, such as solvent, and chain transfer agent chemical structure on kinetics.

References

[1] Gil ES, Hudson SA. Progress in Polymer Science 2004;29:1173–222.
[2] Kikuchi A, Okano T. Journal of Controlled Release 2005;101:69–84.
[3] Purushotham S, Chang PEJ, Rumpel H, Kee IHC, Ng RTH, Chow PKH, et al. Nanotechnology 2009;20:305101.
[4] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TP, et al. Macromolecules 1998;31:5559–62.
[5] Perrier S, Takolpuckdee P. Journal of Polymer Science, Part A: Polymer Chemistry 2005;43:5347–93.
[6] Barner-Kowollik C. In: Handbook of RAFT polymerization. Weinheim: WILEY-VCH Verlag GmbH & Co; 2008.
[7] Idziak I, Avoce D, Lessard D, Gravel D, Zhu XX. Macromolecules 1999;32:1260–3.
[8] Kawaguchi H. In: Arshady R, editor. Microspheres, microcapsules and liposomes, Vol. 1. London: Citus Books; 1999. p. 237–51.
[9] Chan JW, Yu B, Hoyle CE, Lowe AB. Chemical Communications; 2008:4959–61.
[10] Chan JW, Yu B, Hoyle CE, Lowe AB. Polymer 2009;50:3158–68.
[11] Li HB, Yu B, Matsushima H, Hoyle CE, Lowe AB. Macromolecules 2009;42:6537–42.
[12] Coote ML, Davis TP, Klumperman B, Monteiro MJ. Journal of Macromolecular Science Reviews in Macromolecular Chemistry and Physics 1998; C38:567–93.
[13] Coote ML, Davis TP. European Polymer Journal 2000;36:2423–7.
[14] Jovanovic R, Dube MA. Journal of Applied Polymer Science 2004;94:871–6.
[15] Monge S, Darcos V, Haddleton DM. Journal of Polymer Science, Part A: Polymer Chemistry 2004;42:6299–308.
[16] Paris R, De La Fuente JL. Journal of Polymer Science, Part A: Polymer Chemistry 2005;43:6247–61.

[17] Benaglia M, Rizzardo E, Alberti A, Guerra M. Macromolecules 2005;38: 3129–40.
[18] Wood MR, Duncalf DJ, Findlay P, Rannard SP, Perrier S. Australian Journal of Chemistry 2007;60:772–8.
[19] Barner-Kowollik C, Buback M, Charleux B, Coote ML, Drache M, Fukuda T, et al. Journal of Polymer Science, Part A: Polymer Chemistry 2006;44:5809–31.
[20] Monteiro MJ. Journal of Polymer Science, Part A: Polymer Chemistry 2005;43:3189–204.
[21] Gunzler F, Junkers T, Barner-Kowollik C. Journal of Polymer Science, Part A: Polymer Chemistry 2009;47:1864–76.
[22] Coote ML, Izgorodina EI, Krenske EH, Busch M, Barner-Kowollik C. Macromolecular Rapid Communications 2006;27:1015–22.
[23] McLeary JB, Tonge MP, Klumperman B. Macromolecular Rapid Communications 2006;27:1233–40.
[24] Feldermann A, Coote ML, Stenzel MH, Davis TP, Barner-Kowollik C. Journal of the American Chemical Society 2004;126:15915–23.
[25] Monteiro MJ, H. DB. Macromolecules 2001;34:349–52.
[26] Konkolewicz D, Hawkett BS, Gray-Weale A, Perrier S. Macromolecules 2008;41:6400–12.
[27] Konkolewicz D, Hawkett BS, Gray-Weale A, Perrier S. Journal of Polymer Science, Part A: Polymer Chemistry 2009;47:3455–66.
[28] Yusa SI, Endo T, Ito M. Journal of Polymer Science, Part A: Polymer Chemistry 2009;47:6827–38.
[29] Chong YK, Krstina J, Le TPT, Moad CL, Postma A, Rizzardo E, et al. Macromolecules 2003;36:2256–72.
[30] Severac R, Lacroix-Desmazes P, Boutevin B. Polymer International 2002;51: 1117–22.
[31] Chiefari J, Mayadunne RTA, Moad CL, Moad G, Rizzardo E, Postma A, et al. Macromolecules 2003;36:2273–83.
[32] Schilli C, Lanzendorfer MG, Muller AHE. Macromolecules 2002;35: 6819–27.
[33] Barner-Kowollik C, Quinn JF, Morsley DR, Davis TP. Journal of Polymer Science, Part A: Polymer Chemistry 2001;39:1353–65.
[34] Barner-Kowollik C, Vana P, Quinn JF, Davis TP. Journal of Polymer Science, Part A: Polymer Chemistry 2002;40:1058–63.
[35] Perrier S, Barner-Kowollik C, Quinn JF, Vana P, Davis TP. Macromolecules 2002;35:8300–6.
[36] Venkatesh R, Staal BBP, Klumperman B, Monteiro MJ. Macromolecules 2004;37:7906–17.
[37] Kwak Y, Goto A, Tsujii Y, Murata Y, Komatsu K, Fukuda T. Macromolecules 2002;35:3026–9.
[38] Kwak Y, Goto A, Fukuda T. Macromolecules 2004;37:1219–25.
[39] Kwak Y, Goto A, Komatsu K, Sugiura Y, Fukuda T. Macromolecules 2004;37:4434–40.
[40] Barner-Kowollik C, Coote ML, Davis TP, Radom L, Vana P. Journal of Polymer Science, Part A: Polymer Chemistry 2003;41:2828–32.
[41] McLeary JB, Calitz FM, McKenzie JM, Tonge MP, Sanderson RD, Klumperman B. Macromolecules 2004;37:2383–94.
[42] McLeary JB, Calitz FM, McKenzie JM, Tonge MP, Sanderson RD, Klumperman B. Macromolecules 2005;38:3151–61.
[43] McLeary JB, McKenzie JM, Tonge MP, Sanderson RD, Klumperman B. Chemical Communications; 2004:1950–1.
[44] Bathfield M, D'Agosto F, Spitz R, Ladavière C, Charreyre MT, Delair T. Macromolecular Rapid Communications 2007;28:856–62.