



## Polymer Communication

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

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## 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.

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## 1. Introduction

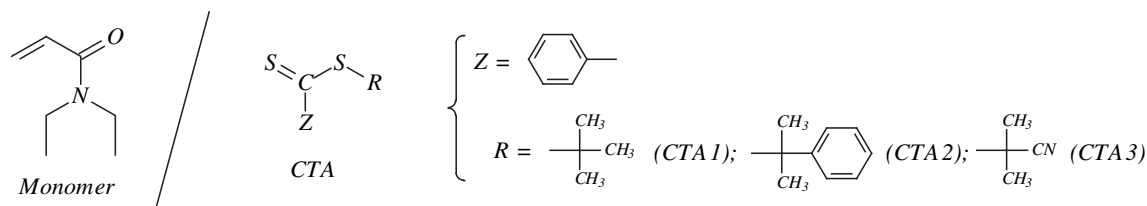
In the last ten years, new materials based on reversible supra-molecular organization have become increasingly important. For instance, some polymers show critical phenomena such as phase transition [1] that can be induced by external stimuli: changes in temperature, pH, solvent, ionic composition, electric 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.

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**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  $\text{CaH}_2$ , 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  $1 \text{ mL min}^{-1}$  at  $30^\circ\text{C}$ . Polystyrene standards (Polymer Laboratories) ranging from  $1400$  to  $1300 \cdot 10^3 \text{ g mol}^{-1}$  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*-

*N*-diethylacrylamide to produce thermo-responsive 4-arm star-shaped porphyrin-centered PDEAm [28].  $^1\text{H}$  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  $^1\text{H}$  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,  $70 \cdot 10^{-3}$  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  $^1\text{H}$  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 <sup>a</sup>	Temp. (°C)	Time (mins)	Conv. (%)	$M_{n,th}^b$ (g mol <sup>-1</sup> )	$M_{n,exp}^c$ (g mol <sup>-1</sup> )	PDI <sup>c</sup>
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

<sup>a</sup> CTA1: *tert*-butyl dithiobenzoate; CTA2: cumyl dithiobenzoate; CTA3: cyanoisopropyl dithiobenzoate.

<sup>b</sup>  $M_{n,th} = ([M]_0/[CTA]_0 \times M_w \text{ of monomer} \times \text{conv})/100$ .

<sup>c</sup> Estimated by PS-calibrated size exclusion chromatography (SEC).

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