

# KINETIC AND MALDI-TOF MS INVESTIGATION OF THE RAFT POLYMERIZATION OF *N*-ISOPROPYLACRYLAMIDE

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## Introduction

Over the last few years, controlled free-radical polymerization using the RAFT (reversible addition-fragmentation chain transfer) technique has gained in importance for the preparation of polymers with controlled molecular weights and narrow MWDs.<sup>1</sup>

We have carried out the RAFT polymerization of *N*-isopropylacrylamide (NIPAAm) with two different chain transfer agents (CTAs), namely benzyl 1-pyrrolicarbothioate and cumyl 1-pyrrolicarbothioate. We have investigated the kinetics of RAFT polymerization of *N*-isopropylacrylamide using near-infrared detection. From in-situ FT-NIR spectroscopy, the monomer conversion can be determined at any time during the polymerization. This method allows the continuous determination of monomer conversion in controlled radical polymerization.<sup>2</sup> The determination of monomer conversion can be more reliable with FT-NIR spectroscopy than with gravimetry. With a gravimetric determination of the conversion by precipitation, oligomeric fractions may not be taken into account as they are often soluble in the solvent/precipitant mixture.

The produced polymers were investigated and structurally characterized by using MALDI-ToF mass spectroscopy for absolute mass determination and endgroup analysis.

## Experimental

**Materials.** *N*-Isopropylacrylamide (Aldrich, 97 %) was recrystallized twice from benzene/hexane 3:2 (v:v) and dried under vacuum prior to use. 1,4-Dioxane (Merck, p.a.) was refluxed over potassium for 3 d and then distilled. Azobisisobutyronitrile (AIBN, Fluka, purum) was recrystallized from methanol and dried under vacuum prior to use.

**Instrumentation.** Fourier-transform near infrared (FT-NIR) spectroscopy was performed using a Nicolet Magna 560 FT-NIR instrument with a PbS detector and a fiber-optic deep-temperature immersion probe (Hellma, quartz glass Suprasil® 300, path length 10 mm). Data processing was performed with Nicolet's OMNIC Series software. Each spectrum was constructed from 32 scans with a resolution of 4 cm<sup>-1</sup>. The total collection time per spectrum was approximately 22 s. Prior to the measurements, a blank spectrum was recorded with the solution of the corresponding chain transfer agent in 1,4-dioxane at 60 °C. After addition of the monomer, the measurement was started and the initiator solution was injected shortly after.

Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph equipped with an RI detector and a UV detector ( $\lambda=254$  nm). PSS SDVgel columns (30 x 8 mm, 5  $\mu$ m particle size) with 10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup> Å pore sizes were used. THF + 0.25 wt.-% of tetrabutylammonium bromide was used as an eluent (flow rate 0.5 mL/min). The injection volume was 100  $\mu$ L and a Spectra Physics P 100 pump was used. As an internal standard, *o*-dichlorobenzene was used. Polystyrene standards were used for calibration.

MALDI-ToF mass spectrometry was performed on a Bruker Reflex III equipped with a 337 nm N<sub>2</sub> laser in the reflector mode. Dithranol (Aldrich, 97 %) was used as matrix. Sodium or potassium trifluoroacetate was added for ion formation. The number-average molecular weights,  $M_n$ , of the polymer samples were determined in the linear mode.

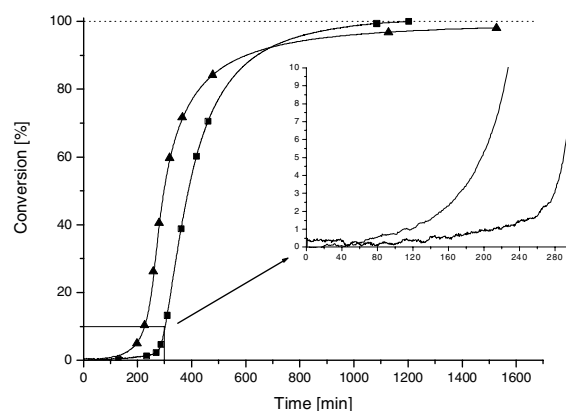
**Synthesis of poly(*N*-isopropylacrylamide).** Benzyl 1-pyrrolicarbothioate (0.413 g, 1.77 mmol) and cumyl 1-pyrrolicarbothioate (0.512 g, 1.96 mmol), respectively, was dissolved in 98 mL 1,4-dioxane and the solutions were degassed by three freeze-thaw evacuation cycles. AIBN (0.115 g, 0.70 mmol) was dissolved in 2 mL 1,4-dioxane and degassed by three freeze-thaw evacuation cycles. The monomer (20.37 g, 0.18 mol) was added via a Schlenk tube under nitrogen to the solution of the chain transfer agent in dioxane. After complete dissolution of the monomer and heating of the mixture to 60 °C (temperature of oil bath), the initiator solution was injected with a syringe. The polymerization was conducted under nitrogen atmosphere and samples were drawn at different time intervals. The samples were immediately immersed into liquid nitrogen and subsequently freeze-

dried. The residues were dried under vacuum, whereby residual monomer was removed by sublimation.

## Results and Discussion

**Polymerization Kinetics.** Samples were drawn at different time intervals in order to determine the kinetics of the polymerizations and the development of the molecular weight distribution. In addition, the course of the polymerization was followed by in-situ FT-NIR spectroscopy. In the FT-NIR measurements, spectra of the reaction mixture were recorded every 30 s. The spectra cover the range from 4500 to 7500 cm<sup>-1</sup>. The variation of the intensity of the bands with time is observed. For the evaluation of the FT-NIR results, those monomer bands were chosen that are not considerably overlapped by other bands, e.g. of the solvent or polymer. For NIPAAm, the vinylic stretching overtone was found at 6157 cm<sup>-1</sup> and used for conversion determination. An absorption at 6727 cm<sup>-1</sup> increasing during the polymerization was attributed to the formation of polyNIPAAm.

The intensities were converted into conversions by evaluating the intensities for zero monomer conversion and for total conversion. Time-conversion plots obtained from FT-NIR spectroscopy show long induction periods for both polymerization processes (Figure 1). After the induction period, the first-order time-conversion plots show a practically linear relationship with only slight deviations towards the end of the polymerization.

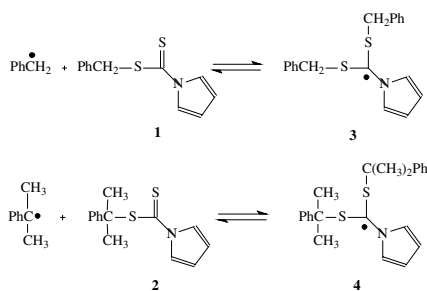


**Figure 1.** Time-conversion plot for the RAFT polymerization of NIPAAm using benzyl CTA (▲) and cumyl CTA (■), respectively.

For the quantitative determination of the induction periods, a tangent was fitted to the steep part of the curves. The values of the induction periods were obtained from the point of intersection of this tangent with the time axis. The induction periods amount to ca. 200 min for the benzyl CTA and to ca. 280 min for the cumyl CTA.

Chain transfer agents containing benzyl or cumyl groups retard the polymerization of acrylates. This might also apply to the RAFT polymerization of NIPAAm. A polymerization series conducted at different chain transfer agent concentrations shows an increase of the induction period with increasing CTA concentration that is accompanied with a decrease of the apparent rate constant for the polymerization. Thus, induction and retardation seem to be correlated with each other. The reasons for the induction periods or retardation observed with some chain transfer agents are not clearly understood. Monteiro et al. suggested termination by addition of a propagating polymer chain to the adduct formed from the polymeric RAFT agent as a reason for retardation.<sup>3</sup> Barner-Kowollik et al. have reported an induction period for the RAFT polymerization of styrene with cumyl dithiobenzoate as chain transfer agent.<sup>4</sup> They tentatively explained this observation by the formation of dicumyl radicals, Ph-C(S-cumyl)<sub>2</sub>. In our case, the induction periods might also be ascribed to the formation of dibenzyl or dicumyl RAFT radicals (**3** and **4**), respectively, via the reaction of excess benzyl CTA (**1**) with benzyl radicals or excess cumyl CTA (**2**) with cumyl radicals (**Scheme 1**). The consequence of this reaction is the reduction of the amount of reinitiation occurring until equilibrium is reached, resulting in an induction period. The observed induction periods agree well with the simulated data of Barner-Kowollik et al.<sup>4</sup> The longer induction period for the polymerization

with the cumyl RAFT agent would imply a higher stability of the dicumyl radicals as compared to the dibenzyl radicals. However, dicumyl radicals should fragment more easily than dibenzyl radicals.

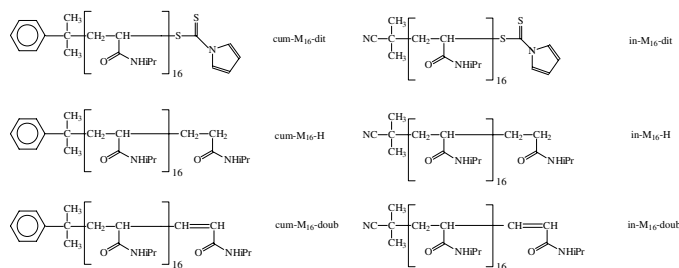
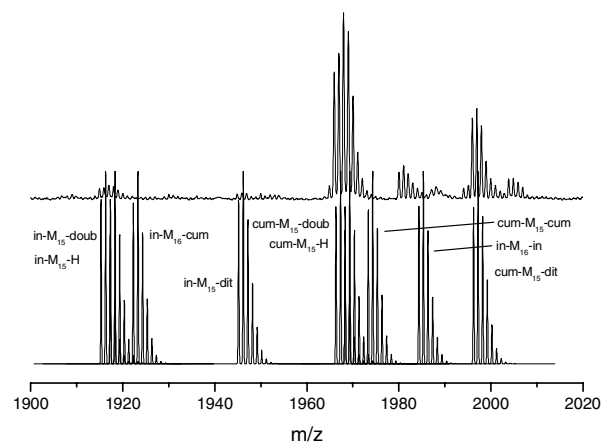


**Scheme 1.** Tentative explanation of the induction period.

**UV and MALDI-ToF MS analysis of the polymers.** The formation of the dithiocarbamate endgroups of the resultant polymers is proven by both UV and MALDI-ToF spectroscopy. The UV spectrum shows a perceptible band with a maximum at  $\lambda = 296$  nm in chloroform, which is ascribed to the pyrrolicarbothioate moiety.

MALDI-ToF mass spectra of the obtained RAFT polymers indicate to which degree the polymerization is living and they give information on the nature of the endgroups. MALDI-ToF mass spectra of poly(NIPAAm) obtained with both benzyl and cumyl CTA were recorded (**Figure 2**). In both spectra, the expected signals (isotopic patterns) of the polymer with transfer agent endgroups are observed (1996.28 Da for cum- $M_{16}$ -dit). In the case of the cumyl chain transfer agent, initiator-derived polymers were observed (1945.26 Da). The peaks at 1950 Da having the highest intensity of all signals might be ascribed to disproportionation/transfer products (cum- $M_{16}$ -doub and cum- $M_{16}$ -H). This is a quite unexpected result as combination of growing radicals is expected rather than disproportionation for poly(NIPAAm). Moreover, kinetics indicate only little termination and transfer. This becomes evident from the linear first-order time-conversion plot, especially at low monomer conversion. Furthermore, the relative intensities of double bond terminated structures to hydrogen terminated ones is not 1:1 but 1:(2.5 $\pm$ 1), which was confirmed by a simulation of the corresponding overlapping isotopic patterns. Therefore, the question arises whether these signals are due to fragmentation of the polymer during the MALDI-ToF measurement. The higher amount of hydrogen terminated chains might result from the respective radicals abstracting protons from the matrix during desorption. In order to prove this assumption, a Post Source Decay (PSD) analysis<sup>5</sup> was performed which showed that macro-CTA- $K^+$  ions readily fragment under loss of the dithiocarbamate endgroup and formation of the corresponding double bond or hydrogen terminated chains but also into other fragments, which corroborates the aforementioned conclusions. This result does not exclude the formation of unsaturated endgroups by the synthetic process but strongly indicates that the corresponding peaks stem from fragmentation during ionization. Since  $\lambda_{\text{max}}$  of the dithioester moiety (296 nm) is also close to the laser frequency (337 nm) for the MALDI process, this observation is not surprising. Thus, it is not unreasonable to assume that the signals attributed to disproportionation/transfer by other authors<sup>6,7</sup> also result from fragmentation.

In addition to the main peaks, signals are observed that cannot be ascribed to the expected chain-end structures. The  $K^+$  ionized MALDI spectrum of the polymer obtained with cumyl CTA reveals two series of signals with good isotopic resolution (1980.10 Da, 2003.97 Da) and another rather noisy signal (1987-1990 Da) that could not be ascribed to any of the possible structures expected from the synthesis. One of the signals (1980.10 Da) would fit to the CTA-derived main product cum- $M_{16}$ -dit as  $Na^+$  adduct. The  $Na^+$  ionized MALDI spectra show the same series of signals as in the  $K^+$  ionized samples shifted by the  $Na^+$  to  $K^+$  mass difference of 16 Da. This seems to identify this signal as a  $K^+$  adduct of a chain with unknown endgroup structure. The signal at about 1987 Da is probably the result of a fragmentation in the flight tube. If the other two signals are also the result of a fragmentation under MALDI conditions, they must have formed in the ion source during ionization rather than during the flight time because of their good resolution.



**Figure 2.** MALDI-ToF mass spectrum of  $K^+$  ionized poly(NIPAAm) obtained with cumyl CTA. Experimental (top) and simulated (bottom) data.

## Conclusions

The RAFT polymerization of NIPAAm with two different chain transfer agents, namely benzyl and cumyl 1-pyrrolicarbothioate, results in polymers with narrow MWDs and  $M_n$  values that agree well with the calculated ones.

In-situ FT-NIR spectroscopy is a powerful technique for the reliable determination of monomer conversions in the RAFT polymerization of NIPAAm. Its advantage is that the conversion can be determined at any time during the polymerization. In our case, it became evident that both polymerization processes show an induction period, where the induction time is higher for the cumyl CTA as compared to benzyl CTA.

The MALDI-ToF characterization of the polymer samples showed that the produced polymers possess the expected transfer agent endgroups together with some initiator-derived polymers. Double bond and hydrogen terminated endgroups probably result from fragmentation under MALDI conditions.

**Acknowledgement.** The authors are grateful to Dr. Ezio Rizzardo and Dr. San Thang, CSIRO Molecular Science, for fruitful discussions and helpful hints.

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