



## Synthesis of Oligomers of 12-Acryloyloxydodecanoic Acid via Reversible Addition Fragmentation Transfer (RAFT) Polymerisation

Lilian Tichagwa (Corresponding author)

Department of Chemistry, University of Fort Hare

Private Bag X1314, Alice 5700. South Africa

Tel: 27-406-022-266 E-mail: [ltichagwa@ufh.ac.za](mailto:ltichagwa@ufh.ac.za)

Ron D. Sanderson

Department of Chemistry and Polymer Science, University of Stellenbosch

Private Bag X1, Matieland 7602. South Africa

Tel: 27-218-083-172 E-mail: [rds@sun.ac.za](mailto:rds@sun.ac.za)

Harald Pasch

Department of Chemistry and Polymer Science, University of Stellenbosch

Private Bag X1, Matieland 7602. South Africa

Tel: 27-218-083-367 E-mail: [hpasch@sun.ac.za](mailto:hpasch@sun.ac.za)

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### Abstract

A long chain fatty acid carrying an acryloyl functionality, 12-acryloyloxydodecanoic acid (12-ADA), was prepared from 11-hydroxydodecanoic acid and acryloyl chloride and used as monomer in the synthesis of oligomers of 12-ADA via the RAFT controlled polymerisation process. Reversible Addition Fragmentation Transfer (RAFT) reagents were prepared and used to control the polymerisation process and produced an oligomeric product with few monomeric units instead of a high molecular weight polymer of 12-ADA. The transfer reagents were prepared from Grignard intermediates from a reaction of dithioacids with free radical initiators 2,2-azobisisobutyronitrile (AIBN) and 4,4-azobis(4-cyanopropanoic acid) (ACP). It was found that short-chain oligomers in the form of dimers and trimers characterized by Electrospray Mass Spectrometry, ESMS and Gel Permeation chromatography, GPC were the major products obtained when RAFT reagents had been used in the controlled polymerisation. As a control, polymerisation was carried out in the absence of RAFT reagents and high molecular-weight polymers were obtained. This confirmed the effectiveness of the prepared RAFT reagents as polymerisation controllers and provided a way for the synthesis of oligomers. Here, the preparation of oligomers of 12-ADA using AIBN-RAFT reagents is reported. The method is expected to provide one way of preparing oligomers of controlled chain length/molecular mass which also carry a carboxylic acid functional group at one end.

**Keywords:** Chain transfer, Controlled polymerisation, Oligomers, RAFT, Polydispersity index

### 1. Introduction

Controlled radical polymerisations lead to the synthesis of polymers with controlled molecular masses. Reversible addition fragmentation transfer polymerisation, RAFT, is one of the methods for controlling radical polymerisation which offers versatility in providing a route to the synthesis of oligomers (Chieffari et al, 2003, p. 2273). This can be achieved by performing the polymerisation in the presence of chain transfer agents such as dithio compounds which act as RAFT chain transfer agents and provide the polymerisation with "living" characteristics. The amount of transfer agent added determines the extent of control of the polymerisation process and the subsequent molecular mass of the

products. The RAFT technique relies on a sequence of addition-fragmentation chain transfer reactions (Moad et al, 2003, p 520).

RAFT chain transfer agents with the general structure Z-C(S)S-R have been used in controlled polymerisation reactions (Lowe A.B., & McCormick C.L. 2002, p. 4177). The Z group activates the C=S bond towards radical addition while R needs to be a good free radical leaving group capable of reinitiating free radical polymerization (de Brouwer, 2000, p. 9239). The RAFT reagents have Z and R moieties that provide high transfer constants which lead to oligomers with narrow polydispersities. In this study two types of RAFT chain transfer agents based on dithiobenzoates were used, one from the free radical initiator 2,2-azobisisobutyronitrile (AIBN) and the other from 4,4-azobis(4-cyanovaleric acid) (ACP) and used as reagents in polymerisation reactions (Thang et al, 1999, p. 2435) even though AIBN-RAFT polymerisation was the focus of this report. The RAFT reagents were prepared by first preparing Grignard reagents, which were converted to dithioacids and subsequently to bis-thiobenzoyl disulphide compounds as illustrated in Scheme 1. The reagents were then used in the controlled polymerisation of 12-ADA to give corresponding oligomers of 12-ADA. RAFT chain transfer reagents produced from dithioacids were successfully used to produce methacrylate-derivative oligomers with a target degree of polymerization of 10 (Hosseini et al, 2008, p. 2277).

## 2. Synthesis of RAFT reagents

Free radical initiators and dithioacids were used as the main reagents for the synthesis of RAFT reagents.

### 2.1 Materials

Recrystallised AIBN initiator (Sigma); ACP initiator (Sigma); bromobenzene (Acros); carbon disulphide (Sigma); Mg turnings, dry diethyl ether, dry THF

### 2.2 Method

A Grignard reagent was prepared and cooled before carbon disulphide was slowly added followed by water resulting in a precipitate which was filtered off. The resulting red dithioacid product was acidified to pH 1 with fuming HCl and the resulting compound extracted with diethyl ether. The ethereal phase was worked up and dried with anhydrous magnesium sulphate.

To 172 mmol of dithioacid produced above, 353 mmol DMSO and 100 ml dry ethanol solvent were added and the mixture stirred for an hour. The pink product formed was washed with ethanol and dried under vacuum to give crystalline bis(thiocarbonyl) disulphide. To 136 mmol bis(thiocarbonyl) disulphide; (dissolved in 100 ml ethyl acetate) and corresponding initiator, AIBN also dissolved in 100ml ethyl acetate, were added and the resulting mixture stirred and purged with nitrogen and allowed to reflux for about 24 hours. The resulting deep red product was purified by running through a 60-cm silica gel chromatographic column using a 5:1 heptane/ethyl acetate mixture as elution solvent for AIBN-RAFT. The solvent was removed and the resulting RAFT reagent collected as red oil (28% yield). The RAFT reagent was analysed using <sup>1</sup>H-NMR and ESMS.

## 3. Synthesis of 12-ADA

### 3.1 Materials

Analytical grades of 11-hydroxy dodecanoic acid (Sigma), acryloyl chloride (Sigma), triethylamine (Acros), dichloromethane (Merk) were all used as purchased.

### 3.2 Method

The monomer 12-ADA was prepared using a procedure described by Finkelmann H., & Schafheutle M.A. 1986, p. 786) and was prepared according to Scheme 2. The monomer was prepared from 11-hydroxy dodecanoic acid and acryloyl chloride in the presence of triethylamine. Once prepared, the 12-ADA was dried and purified by first dissolving it in a mixture of 4:1 acetone/methanol and filtered before running it down a 60cm long silica gel chromatographic column. Different fractions were collected and verified by TLC. Solvent was removed under vacuum in the dark to avoid spurious polymerisation. The total yield was 76 % and the product was analysed by <sup>1</sup>H-NMR and ESMS.

## 4. Synthesis of RAFT polymers of styrene

Materials: Styrene monomer from Sigma was vacuum distilled; AIBN initiator from Sigma was recrystallised.

### 4.1 Method

The effectiveness of the AIBN-RAFT transfer agent was tested by carrying out bulk polymerisation of styrene in a 3-neck flask using 1.43 mol styrene, 2.80 mmol AIBN initiator and 0.83 mmol AIBN-RAFT reagent. The polymerisation was carried out at 75°C and the variation of molar mass of the oligomers with time studied using Gel Permeation Chromatography (GPC) and the results summarized in Table 1.

## 5. Polymerisation of 12-ADA

The monomer 12-ADA had poor solubility in most of the common solvents and so the polymerisation was carried out in DMSO at 75°C.

In a 3-neck flask, 3,7 mmol of 12-ADA and 0,99 mmol RAFT reagent were dissolved in 10 ml DMSO and 0,33 mmol AIBN initiator dissolved in 1 ml DMSO were added, degassed and polymerised at 70°C for 60 hours. After removing most of the solvent under vacuum, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> before being run down a silica gel chromatographic column (70-230 mesh-*Macherey-Nagel*). Seven fractions were obtained and these were analysed by thin layer chromatography (TLC). The polymeric fraction could not be run down the column. The collective yields obtained were about 60 % oligomeric, 32 % monomeric and about 8 % polymeric fractions. The polymerisation reaction was followed by drawing 3 fractions (F1, F2 and F3) at different stages between the early and last stages of the polymerisation. The fractions were analysed using <sup>1</sup>H-NMR. After the controlled polymerisation, the final oligomer was also analysed by <sup>1</sup>H-NMR in CHCl<sub>3</sub> and ESMS.

## 6. Results and Discussion

### 6.1 Results

ESMS spectrum of AIBN-RAFT:

ESMS (acetonitrile/methanol):

The following were observed: m/z = 120.72 due to - C(CH<sub>3</sub>)<sub>2</sub>CNS; 154.5 due to C(CH<sub>3</sub>)<sub>2</sub>CN; and 221.47=(M<sup>+</sup> of C<sub>6</sub>H<sub>5</sub>CS<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CN

ESMS spectrum of 12-ADA:

ESMS (methanol): m/z = 268.59 (M<sup>+</sup>)

ESMS spectrum of the oligomer:

ESMS (acetonitrile-methanol) m/z = 215.09; 1030.06(M<sup>+</sup>)

The <sup>1</sup>H-NMR spectra of the AIBN RAFT agent, monomeric 12-ADA, products from a RAFT polymerization and oligomeric product are given in Figures 1,2,3 and 4 respectively.

### 6.2 Discussion

From the proton NMR and ESMS results of 12-ADA, it can be confirmed that the monomer had been successfully prepared because the analysis results were as expected for the compound with an estimated purity of > 90%. The RAFT reagent was also successfully prepared as seen by the results of the NMR and ESMS analysis and this also showed an estimated purity of > 90%. The 12-ADA and AIBN-RAFT were then used for the oligomerisation/polymerisation. The test for polymerisation control was illustrated with the use of styrene polymerisation. This showed the difference between RAFT controlled and uncontrolled styrene polymerisations with the controlled polymerisation giving narrow molecular weight distributions and the uncontrolled polymerisations giving polymers with large molecular masses with wide polydispersities.

The NMR and ESMS analyses of the products from the polymerisation confirm the presence of oligomers when transfer reagents are used in the polymerisation. The NMR of Fraction 1 shows a product which is very similar to monomer 12-ADA suggesting that there was ample monomer in the reaction flask. Fraction 2 shows that some reaction had occurred as the NMR spectrum exhibited evidence of monomer depletion as well as the appearance of product carrying an aromatic group which must have been due to the RAFT moiety. The third fraction clearly suggests formation of oligomeric product which was confirmed by the absence of double bonds from monomeric 12-ADA. This was confirmed by giving an NMR spectrum similar to that given by the final oligomer.

On examining the ESMS spectrum of the oligomeric product, it was apparent that mainly trimers and some tetramers had been produced. The base peak at about m/z = 1030, relates to the molar mass of the trimer of 12-ADA (the molar mass of 12-ADA is 270 g/mol) carrying a RAFT moiety which is M<sup>+</sup> = 221.47 was illustrated by the ESMS spectrum of the AIBN-RAFT reagent which is the fragment of C<sub>6</sub>H<sub>5</sub>CS<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CN. Furthermore, the ESMS of the oligomer showed a peak around m/z = 215 suggesting the loss of the fragment CH<sub>2</sub>=CH-C=O, which signifies possible cleavage of the weak ester linkage at C-O accounting for the mass of the fragment which is 55 g/mol and agrees well with the value of 215+ 55 = 270 g/mol for the remaining monomer fragment. The ESMS spectrum also shows that further fragmentation occurred as illustrated by a number of very small and insignificant peaks of lower molecular masses. The spectrum confirmed the presence of oligomers of 12-ADA which had not been prepared before. The experimental run without RAFT reagent did not result in oligomers but instead produced a high molecular mass product which appeared crosslinked as it could not be dissolved in any of the available solvents and was therefore difficult to analyse. The NMR of the oligomer when compared with that of 12-ADA confirmed that 12-ADA did oligomerise to give the trimeric

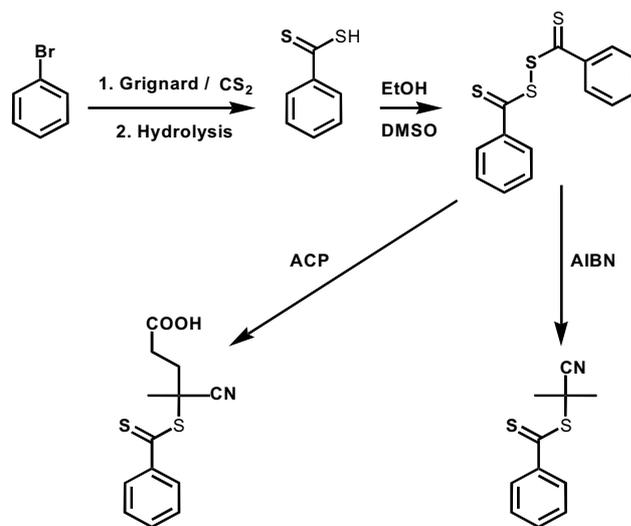
oligomer. This confirmed that the RAFT reagents prepared were effective in controlling molecular mass through a control of the polymerisation process leading to oligomers rather than polymers of 12-ADA.

## 7. Conclusion

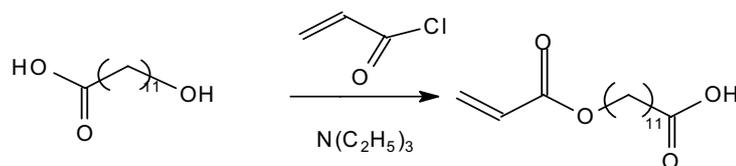
Oligomers of 12-ADA were prepared using RAFT reagents which controlled the polymerisation reaction and stopped the polymerisation from continuing to produce high molar mass products. The control was also demonstrated on the polymerisation of styrene. It would be interesting to extend the methods described to the synthesis of other short-chain compounds which would otherwise give long-chain compounds. In addition to the controlled polymerization, the methods described in this report may be applied in the synthesis of a carboxylic acid-functionalised oligomer.

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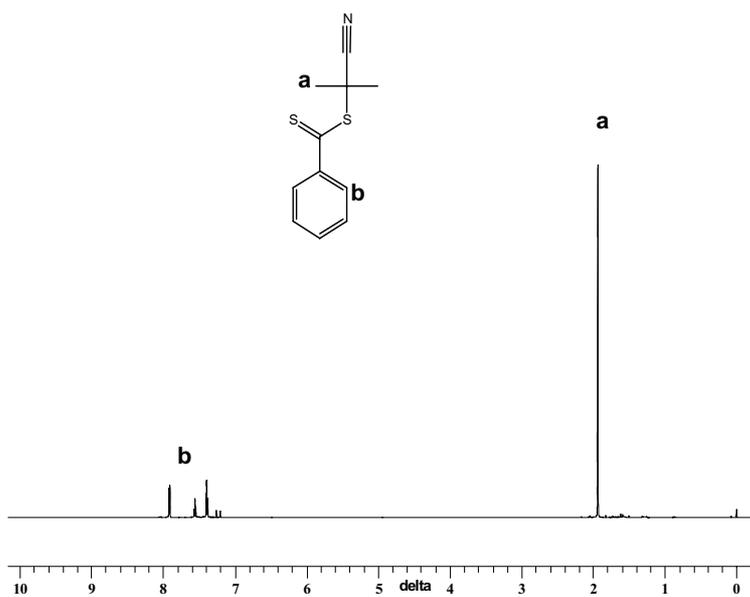
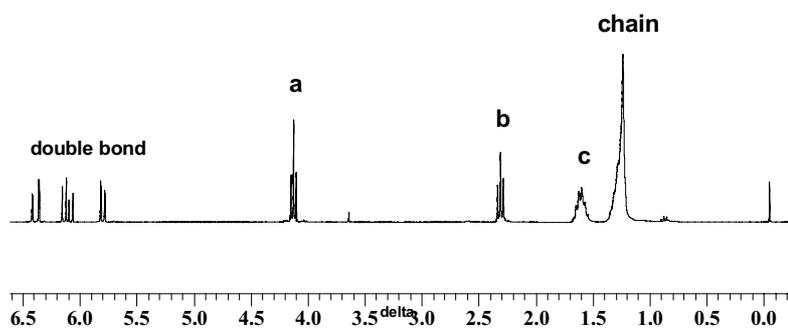
Scheme 1. Reactions showing the synthetic routes to RAFT transfer agents



Scheme 2. Synthetic route to 12-ADA

Table 1. Molar masses of products from polymerisation runs of styrene with &amp; without RAFT reagents

	PS (RAFT)	PS
RAFT reagent added	AIBN	None
Temperature °C	75	75
Polymerisation time in min / $M_n$ / PDI	40 / 1900 / 1.17	40 / 128 000 / 12.1
Polymerisation time in min / $M_n$ / PDI	60 / 2600 / 1.21	60 / 124 000 / 14.1
Polymerisation time in min / $M_n$ / PDI	80 / 3200 / 1.25	80 / 132 000 / 12.6

Figure 1. Proton NMR of AIBN-RAFT reagent in  $CDCl_3$ Figure 2. Proton NMR spectrum of 12-ADA in  $CDCl_3$

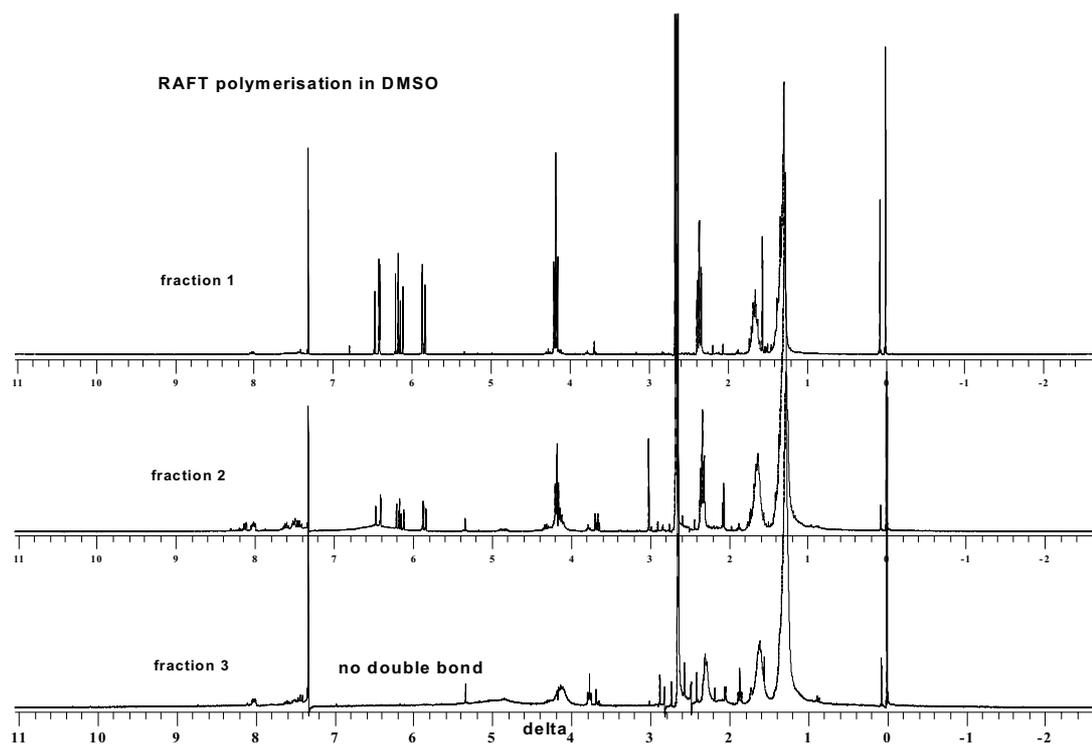


Figure 3. Proton NMR in CDCl<sub>3</sub> of products from a RAFT polymerisation in DMSO as solvent

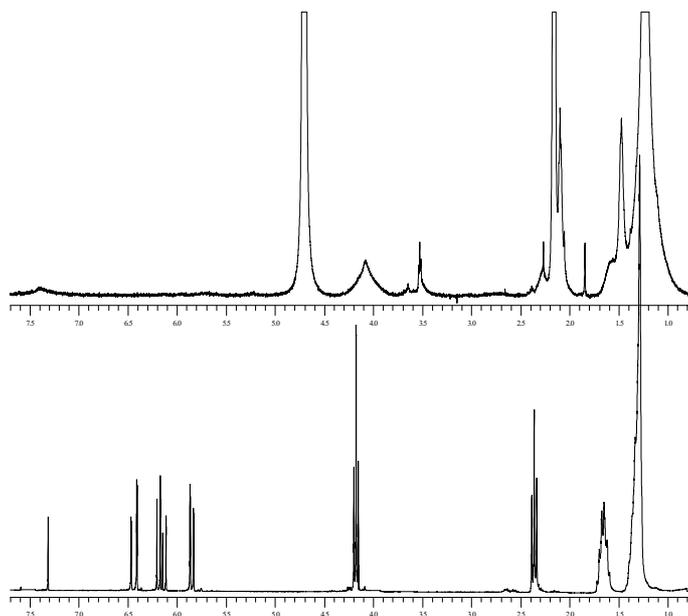


Figure 4. Proton NMR of oligomeric 12-ADA (top) and 12-ADA monomer (bottom)