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RAFT miniemulsion (co)polymerization of methyl methacrylate and n-butyl acrylate

Tesi di laurea sperimentale

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Riassunto

Questo lavoro di tesi si inserisce in un progetto più ampio di sintesi di resine alchidiche da fonti naturali, copolimerizzate con metil acrilato ed n-butil acrilato, che verranno utilizzate per rivestimenti alimentari.

L'obiettivo è quello di controllare la copolimerizzazione di metil acrilato e n-butil acrilato in miniemulsione RAFT. La ricerca è stata suddivisa in tre parti. Prima è stata studiata la omopolimerizzazione di metil metacrilato e n-butil acrilato variando diversi parametri quale la quantità di surfattante, la quantità di iniziatore, il pH e soprattutto il RAFT agent. Quindi sono stati sintetizzati alcuni Macro RAFT agents, come suggerito dalla letteratura esistente. Infine i due monomeri sono stati copolimerizzati utilizzando sia i RAFT agent utilizzati per l'omopolimerizzazione che quelli sintetizzati nella seconda fase.

Per verificare l'ottenuto controllo sulla polimerizzazione, i polimeri sintetizzati sono stati analizzati tramite cromatografia a permeazione di gel, GPC, che fornisce il peso molecolare del polimero e polidispersità.

Abstract

This thesis work is part of a larger synthesis project about alkyd resins from natural sources, copolymerized with methyl acrylate and n-butyl acrylates, which wil be used for coatings purpose.

The aim is to control the copolymerization of methyl acrylate and n-butyl acrylate in RAFT miniemulsion. The research was divided into three parts. First the homopolymerization of methyl methacrylate and n-butyl acrylate was studied by varying different parameters such as the amount of surfactant, the amount of initiator, pH, and especially the RAFT agent. Then two macro RAFT agents were synthesized, as suggested by the existing literature. Finally, the two monomers were copolymerized using both the RAFT used for the homopolymerization and those synthesized in the second stage.

To verify the obtained control over the polymerization, the synthesized polymers were analyzed by gel permeation chromatography, GPC, thus finding their molecular weight and its polydispersity.

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Purpose

The following thesis work has been done in the research Laboratory of the department of Polymer Chemistry at the University of Helsinki. The Laboratory of Polymer Chemistry is one of the many laboratories in the Department of Chemistry, which focuses on environmentally sensitive synthesis.

This research is part of a larger project on the study of the synthesis of alkyd resins from natural sources that will have application in alimentary coatings.

The resin will be copolymerized with methyl methacrylate and n-butyl acrylate to enhance its resistance.

The aim of this research was the study of the control of the copolymerization of methacrylate and n-butyl acrylate through the use of miniemulsion for the control over the mass transfer and the use of RAFT agents for the control over the molecular weight and the polydispersity of the final polymer.

This research is divided in three parts:

- study of homopolymerization of both methyl methacrylate and n-butyl acrylate to find the operating parameters for the copolymerization;
- synthesis of RAFT agents suggested by papers (as per the existing literature on the subject);
- study of the copolymerization of methyl methacrylate and n-butyl acrylate using many RAFT agents (some of which were previously synthesized), starting from the parameters obtained during the study of homopolymerization.

The copolymers obtained during this work will not be used directly for a copolymerization with the resin; the optimal conditions and RAFT agents will be applied in the copolymerization of the resin with the monomers methyl methacrylate and n-butyl acrylate.

1. Introduction

Purpose of this research is to find a suitable Chain Transfer Agent (CTA) for the controlled copolymerization of Methyl Methacrylate (MMA) and n-Butyl Acrylate (BA) in miniemulsion. The most suitable CTA agent will then be used in the preparation of alkyd-acrylics copolymers as coating materials.

Miniemulsion polymerization is chosen because it allows the system to have a more complex and adjustable composition of the copolymer. In particular, it is possible to incorporate hydrophobic components in the system. In this type of emulsion, in theory, the mass transfer is absent and so the droplets behave as mini-reactors that in the beginning already contain all the elements needed in the final polymer. Moreover, the miniemulsion is necessary for further studies with alkyd-acrylic copolymers. [1]

The RAFT polymerization is used because it grants controlled length and low polydispersity of the polymer. Figure 1.1 defines the type of polymerization method used here.

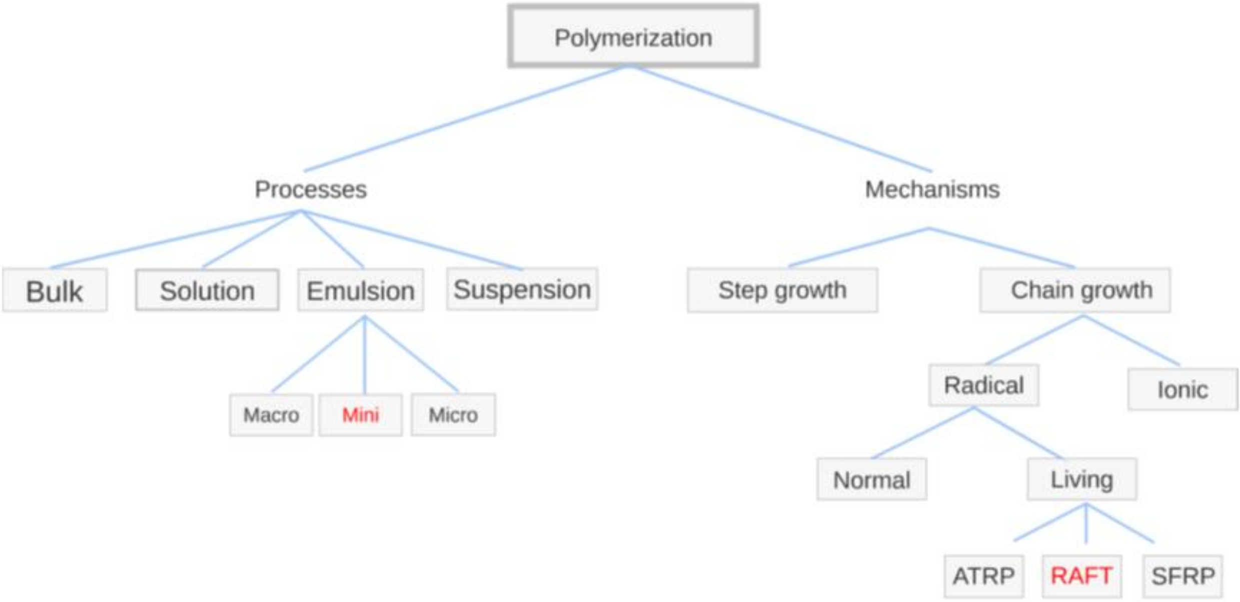


Figure 1.1: schematic of the type of polymerization used. On the right, the classification is based on the reaction mechanism, on the left the classification is based on the reaction process. The methods used in our research are marked in red.

RAFT miniemulsion is not a new technique: since 2000 many articles have been published with significant interest from both academia and industry (figure 1.2).

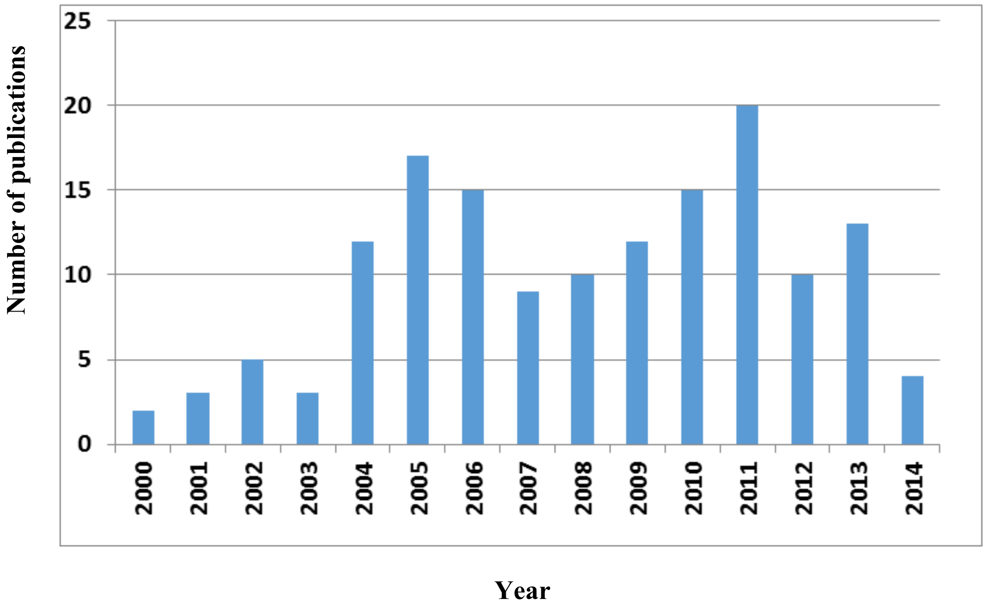


Figure 1.2: number of scientific publications on RAFT miniemulsion (search performed by Scifinder with the following keywords: reversible addition fragmentation chain transfer and miniemulsion and/or RAFT).

This research is structured in three parts. The first part is the homopolymerization of MMA and BA carried out with several CTAs, in order to find the proper operating parameters for the subsequent copolymerization. Second, two CTAs were purposely synthesized and analyzed: poly (acrylic acid) – DDMAT terminated and poly(ethylene glycol) methyl ether 2-(thyododecylthiocarbonoylthio)-2 methylpropionate. Finally, the copolymerization of the two monomers is studied with the above and other different RAFT agents.

1.1 Polymers molecular weight and polydispersity

The molecular weight of a polymer is determined by the chemical structure of the monomer units, the lengths of the chains and the extent to which the chains are interconnected to form branched molecules [2]. The polymer chains that are formed during the reaction are heterogeneous in length and it is necessary the introduction of the average molecular weight.

The chain lengths are distributed according to a probability function, which is governed by the polymerization reaction (figure 1.1.1). There are several possible ways of reporting polymer molecular weight:

- The number average molecular weight (Mn) is the total weight of polymer molecules in a sample (Mi), divided by the total number of polymer molecules in a sample (Ni). It is more sensitive to short chains.

$$M_{n,avg} = \frac{\sum N_i M_i}{\sum N_i}$$

- The weight average molecular weight (Mw) is given by the peak in figure 1.1.1. Is it more sensitive to longer chains and it always greater than Mn.

$$M_{w,avg} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

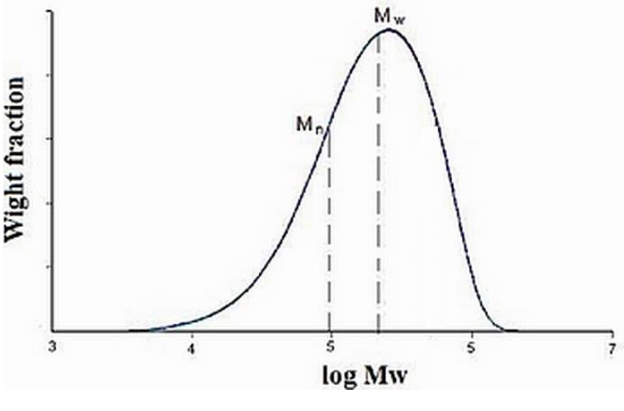


Figure 1.1.1: distribution of molar masses for a polymer sample [2].

The polydispersity index (PDI), is a measure of the distribution of molecular mass in a given polymer sample [2]. It is given by the ratio of Mw and Mn. The greater the ratio, the greater the dispersity is. This value usually varies between 1.1 (it is almost impossible to synthesize a monodisperse polymer) and 2.

The properties of a polymer sample are strongly dependent on the way in which the weights of the individual molecules are distributed about the average. The ratio Mw/Mn gives sufficient information to characterize the distribution when the mathematical form of the distribution curve is known [2].

During this research, the concept of average molecular weight and polydispersity index are quite common. Whenever a molecular weight is given, we're using the number average molecular weight, Mn.

The most common technique to study the molecular weight and polydispersity of a polymer is the Gel Permeation Chromatography (GPC). Gel permeation chromatography is a term used when the separation technique Size Exclusion Chromatography (SEC) is applied to polymers [3].

Unlike gas chromatography (GC) and liquid chromatography (LC), the molecular hydrodynamic volume governs the separation process of SEC, not varied by the type of mobile phase.

A column, which contains gel particles (stationary phase, usually a three-dimensional lattice of a porous copolymer of polystyrene and divinylbenzene), is in equilibrium with a suitable solvent. The pore size of a gel must be carefully controlled in order to be able to apply the gel to a given separation. The eluent (mobile phase) should be a good solvent for the polymer, should permit high detector response from the polymer and should wet the packing surface (e.g. tetrahydrofuran, THF).

The larger molecules are excluded by the smaller pore sizes and pass through the interstitial spaces, while the smaller molecules are able to penetrate deeply into pores increasing their retention time [4] (figure 1.1.2). The first molecules to be eluted are the longer chain polymers while the short ones need more time since they are going through the pores and not only through the interstitial spaces.

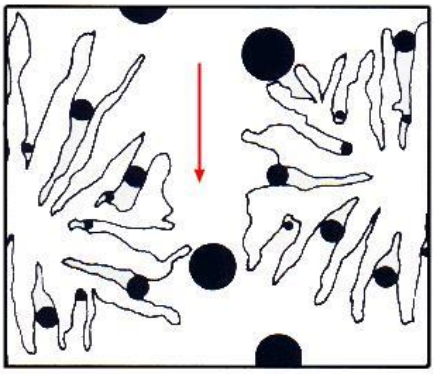


Figure 1.1.2: cross sectional view of porous particle. [6]

In GPC, the concentration by weight of polymer in the eluting solvent may be monitored continuously with a detector. The most common ones are concentration sensitive detectors, which includes UV absorption, differential refractometer (DRI) or refractive index (RI) detectors, infrared (IR) absorption, and density detectors [5].

The resulting chromatogram is therefore a weight distribution of the polymer as a function of retention volume (figure 1.1.3).

The sample solutions are supposed to be prepared in dilute concentration (less than 2 mg/mL). For polymer samples, samples must be dissolved in the solvent same as used for mobile phase except some special cases.

It is recommended to filter the sample solutions before injecting into in order to get rid of clogging and excessively high pressure problems.

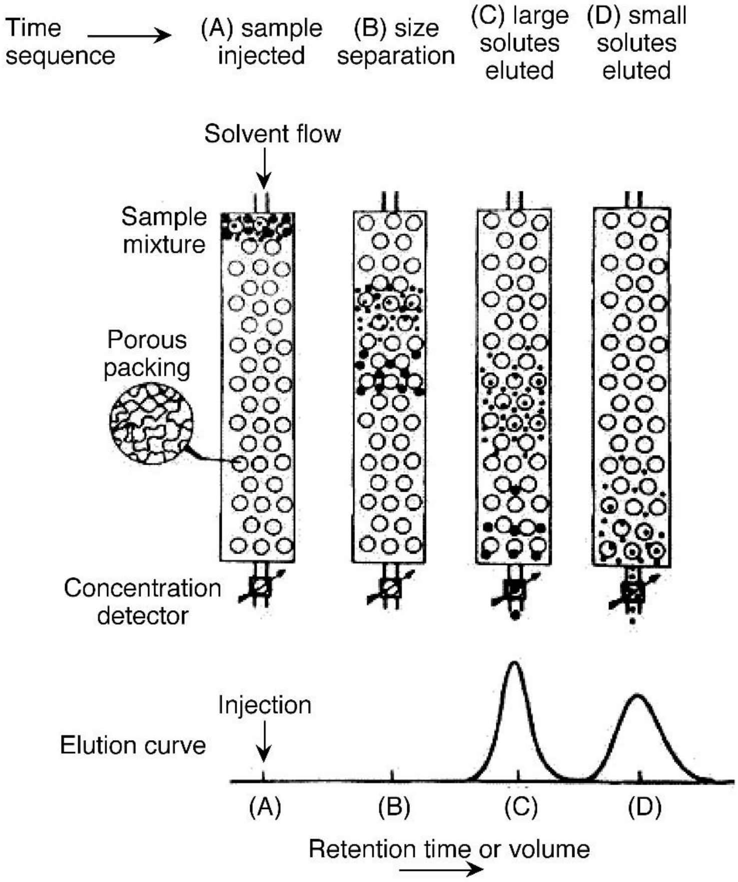


Figure 1.1.3: development and detection of size separation by GPC. [7]

The size exclusion separation mechanism is based on the effective hydrodynamic volume of the molecule, not the molecular weight, and therefore the system must be calibrated using standards of known molecular weight and homogeneous chemical composition [2].

1.2 RAFT polymerization

RAFT (reversible addition-fragmentation chain-transfer) polymerization is a living polymerization, in which a chain transfer agent is used to prevent the radical chain termination and so to obtain longer chains. RAFT living polymerizations control the chain growth through reversible chain transfer. [8]

To start the polymerization process, a traditional initiator is used, but the living character is given by the CTA which typically has a thiocarbonylthio group –C (S) S–. This agent must also have an activating group, Z, and a leaving/re-initiating group, R (figure 1.2.1). The double bond between C and S is highly reactive and influenced by the Z group, while the bond between R and S is weak and easily broken.

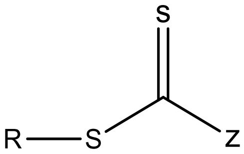


Figure 1.2.1: general structure of CTA.

Shortly, the R group should be a good leaving group, a good re-initiating species toward the monomer and should give stability to the molecule. The Z group, instead, favors the formation of the intermediate and enhances the reactivity of the S=C bond.

Different kinds of CTAs can be used, the right choice depending on the monomer and the conditions of polymerization. The most used classes of CTA are dithiobenzoates, trithiocarbonates, xanthates and dithiocarbamates (figure 1.2.2). Each one of them has different R and Z groups but the core is the same thiocarbonylthio group [9].

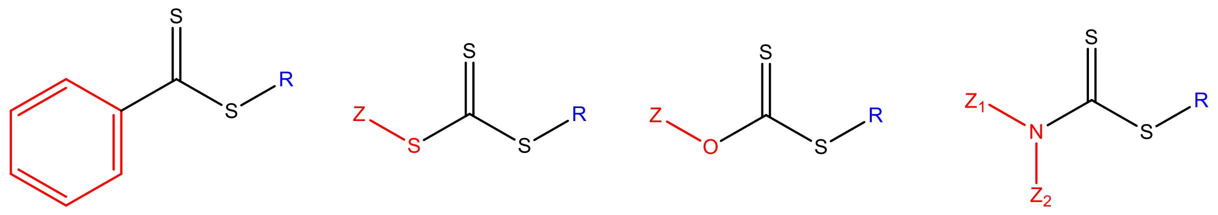


Figure 1.2.2: starting from the left, structure of dithiobenzoates, trithiocarbonates, xanthates and dithiocarbamates. The R group is colored blue, the Z group red. This color scheme will be used from now on.

The mechanism of RAFT polymerization is represented in figure 1.2.3.

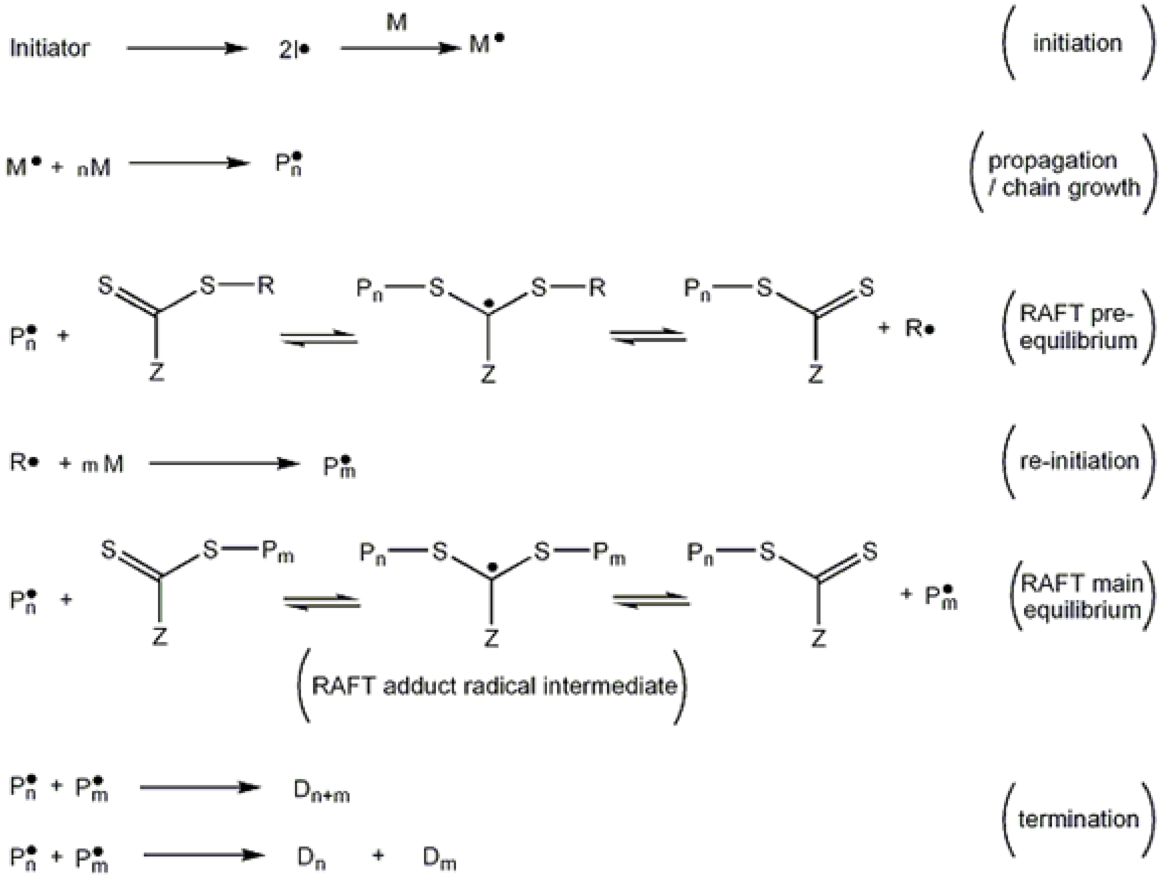


Figure 1.2.3: mechanism of RAFT polymerization. [9]

The number of polymer chains depends on the number of CTA molecules at the beginning of the reaction. The most important step is the formation of a radical intermediate, “RAFT adduct radical intermediate”, which has the same probability to grow one chain or the other. For this reason, the chains will statistically grow in the same way, obtaining a low PDI (sharp distribution, figure 1.2.4).

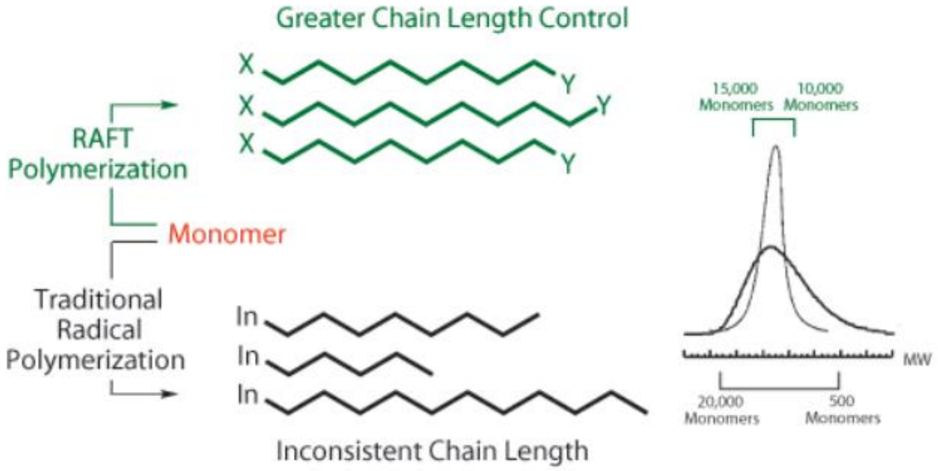


Figure 1.2.4: comparison between living and free radical polymerization.[10]

1.3 Chain Transfer Agents

In our studies, we used several chain transfer agents: their structures and names are summarized in figure 1.3.1.

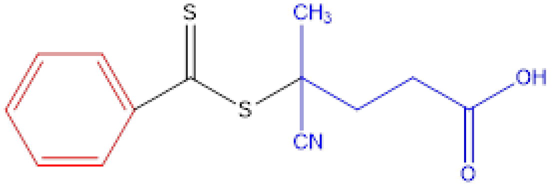
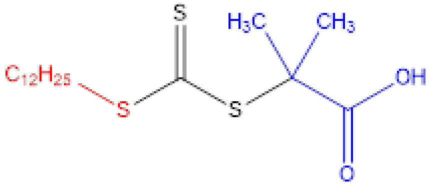
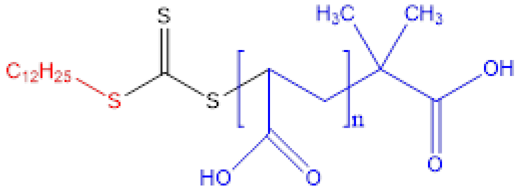
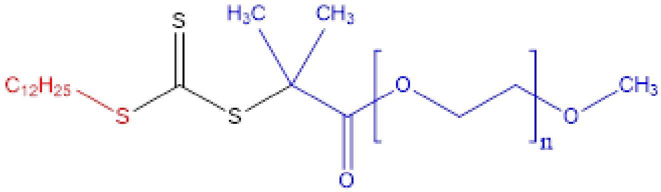
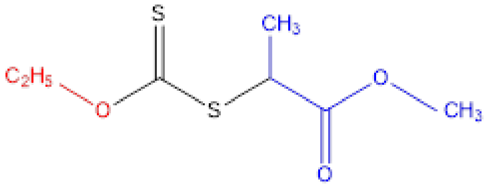
	a, CPADTB
	b, DDMAT
	c, PAA_DDMAT
	d, PEG_DDMAT
	e, MOEXP

Figure 1.3.1: structure and names of CTAs used.

The first CTA studied is CPADTB (4-cyano-4-(phenyl thiocarbonylthio) pentanoic acid) (figure 1.3.1a). Yang et al. [11, 12] polymerized MMA in miniemulsion using a very similar CTA: 2-cyanoprop-2-yl dithiobenzoate. The polymerization exhibited the characteristics of RAFT, i.e. linear growth of molecular weight with conversion and low polydispersity index (PDI < 1.5). While this CTA seems to give low PDI in homopolymerization, the copolymerization of MMA and BA gives “good colloidal stability but poor control of the chain growth process” [13].

DDMAT, 2-(thiododecylthiocarbonylthio)-2-methylpropionic acid (figure 1.3.1 b), has been used for the homopolymerization of butyl acrylate [14]. Many papers point out the necessity of using an amphiphilic RAFT agent based on DDMAT to obtain a low PDI for the emulsion copolymerization of MMA and BA [13,15] or a Macro RAFT agent based on acrylic acid [16,17,18]. It is worth noting, however, that the articles do not specifically mention the miniemulsion process.

Therefore we decided to polymerize acrylic acid using 2-(thiododecylthiocarbonylthio)-2-methylpropionic acid. The obtained product (PAA_DDMAT) is an amphiphilic Macro RAFT agent (figure 1.3.1 c), a poly (acrylic acid) – DDMAT terminated.

PAA_DDMAT presents an hydrophobic ($C_{12}H_{25}S$-) and an hydrophilic group (-(PAA)$C(CH_3)_2COOH$). A leaving hydrophilic R group allows more mobility to the RAFT agent. In the opposite case, in which Z is hydrophilic and R hydrophobic, the CTA would be locked inside the micelles and would have no way of moving from one micelle to another. While the chains would grow with a low PDI in a single micelle, the global PDI could grow [19]. Both cases are shown in figure 1.3.2.

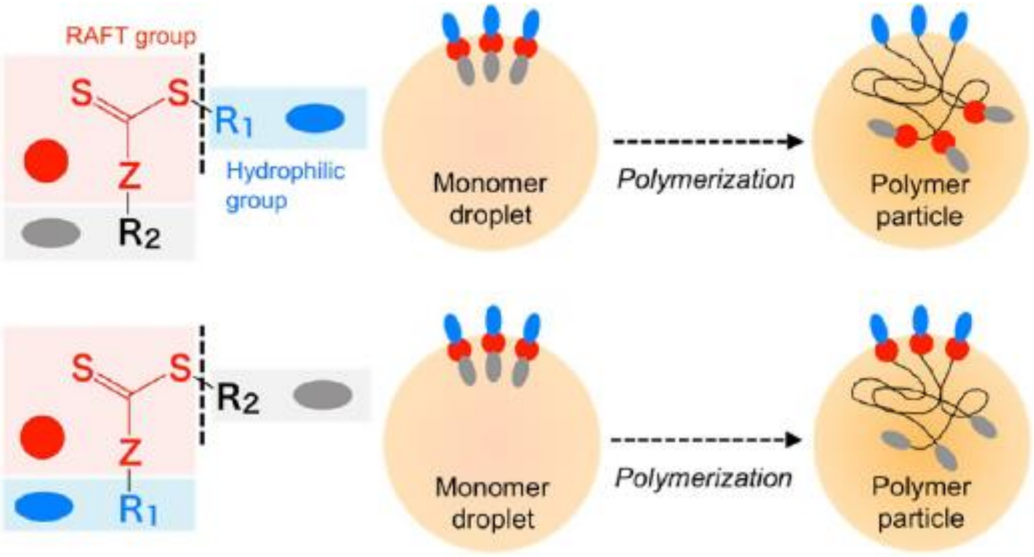


Figure 1.3.2: amphiphilic Macro RAFT agent in the micelle [20].

Another Macro RAFT agent, poly(ethylene glycol) methyl ether 2-(thiododecylthiocarbonylthio)-2-methylpropionate (PEG_DDMAT, figure 1.3.1 d), has been used for RAFT emulsion copolymerization for BA and styrene [21] or for BA and n-butyl methacrylate [13]. A PEG_DDMAT with eight repeating units has been bought from Sigma Aldrich and another one with seven repeating units was synthesized is the laboratory.

The last CTA used is 2-(O-ethylxanthate) methyl propionate (MOEXP) as suggested in paper [22], which is not a Macro RAFT agent, but a CTA belonging to the xanthates class (figure 1.3.1 e).

1.4 Emulsion

In the previous paragraphs, we discussed the RAFT reaction mechanism. Concerning the process adopted, we applied miniemulsion polymerization (figure 1.1).

A brief classification of emulsions will follow:

- Macroemulsions (or simply emulsions): at least one immiscible liquid finely dispersed in another. The diameters of the drops are generally between 1 and 10 µm. The stability is improved by the addition of surfactants.
- Miniemulsions: an emulsion process which involves the use of mixed emulsifier combinations, comprising a mixture on an ionic surfactant, such as sodium lauryl sulfate, and a cosurfactant, such as a long-chain alcohol, e.g. cetyl alcohol, or a long chain alkane, e.g. hexadecane. The product of this process is a stable oil-in-water emulsion with an average droplet diameter in the range 100-400 nm[23].
- Microemulsions: a solution of micelles swollen with monomer. Microemulsions as well usually require the presence of both a surfactant and a cosurfactant [24].

For a better understanding of miniemulsions, some basic concepts regarding emulsions are necessary.

1.4.1 Macroemulsion

Emulsion polymerization is a chemical process that is mostly used to produce waterborne resins with various properties. The product of the polymerization is a latex that is used in a wide range of applications, such as synthetic rubbers, thermoplastics, coatings, adhesives, and so on [24].

Unlike solution polymerization, the physical state of the emulsion system grants an easy control of the process [25]. The viscosity of the dispersion is low, therefore improving the heat transfer. Using this method also results in a faster polymerization rate, and the final product is a polymer with a higher molecular weight.

Emulsion, as stated in IUPAC definitions, is a fluid system in which liquid droplets are dispersed in a continuous phase [26]. The continuous phase is usually water because it is economic, non toxic and efficient heat transfer medium for its high thermal conductivity.

This heterogeneous free radical polymerization process mainly consists of two parts:

- Emulsification of the monomer in the continuous phase with a surfactant (e.g. Sodium dodecyl sulfate, SDS). This results in the formation of big monomer droplets and micelles;
- Addition of the initiator, either water-soluble or oil-soluble, for instance sodium persulfate and 2-2’-azobisisobutyronitrile respectively [27-32].

The surfactant is a molecule that present a hydrophilic and a hydrophobic end. When its concentration exceed a certain value, called critical micelle concentration (CMC), the surfactant forms a cluster: micelles (figure 1.4.1).

The CMC is an important characteristic of a surfactant. For example, the value of CMC for sodium dodecyl sulfate in pure water at 25 °C, at atmospheric pressure, is $8x10^{-3}$ mol/L [33].

Reaching CMC usually entails a change in surface tension: below CMC, the surface tension drops significantly with the addition of surfactant, above CMC, the surface tension is approximately constant.

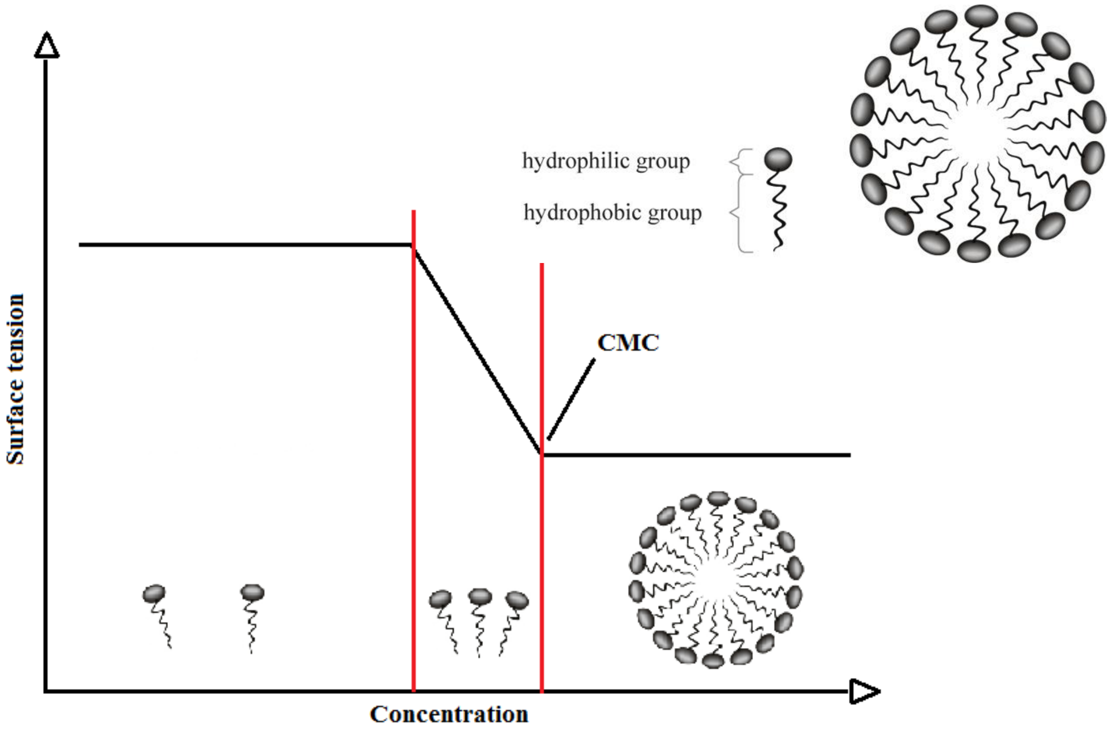


Figure 1.4.1: top, right: typical structure of a micelle [34]. Bottom: effect of the critical micelle concentration on the surface tension.

Each micelle contains approximately 50-150 molecules of surfactant [25]. The number of the micelles directly depends on the amount of surfactant. This also affects the size of the micelles: in particular large amounts of it lead to smaller micelles.

The polymerization can be observed in micelles, droplets and solution. Only the first one will be discussed since polymerization in droplets and solution is not relevant for macro-emulsion: micelles are favored as the reaction site because of their high monomer concentration [25].

The initiator forms the radicals which react with the monomer dissolved in the continuous phase. Therefore these small chains becomes more and more hydrophobic until they reach a critical chain length and then migrate in the micelles. The degree of the polymerization of the radical chains is about 2-5% [35,36].

The micelles, swollen with monomer, become the particle nuclei and they continue growing during the polymerization absorbing monomer migrating from the droplet and from micelles which do not contribute to the reaction. Micelles also acquire surfactant from the shrinking droplets to maintain stability. About one every 100 micelles can be converted into latex particle [24].

All emulsion polymerizations show three different intervals (I, II and III) based on the concentration of polymer particles and the presence of a separate monomer phase (which exists only in intervals I and II). The number of particle nuclei drastically increases in interval I and then is quite constant in the other two. The three intervals can be described as:

I. Particle nucleation;
II. Particle growth;
III. Gel effect.

Particle nucleation

As described above about the polymerization site, in this stage the particle nuclei are formed (figure 1.4.2). The system undergoes a significant change: at the end of interval I all the inactive micelles disappear (micelle exhaustion) and the conversion is around 2-10% (figure 1.4.3).

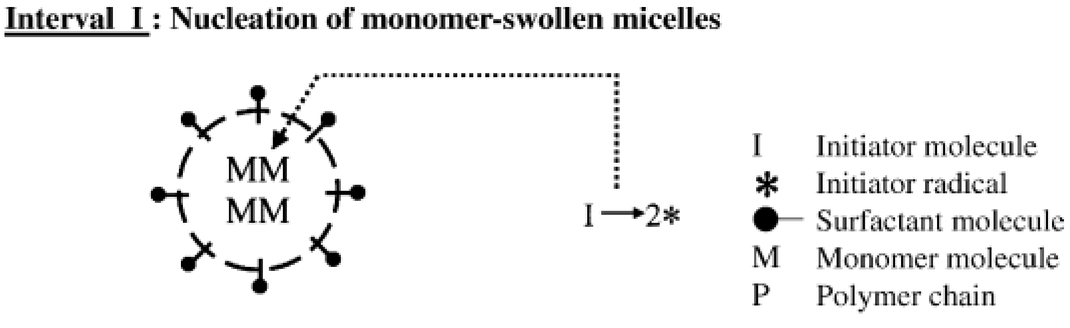


Figure 1.4.2: a schematic representation of the micelle nucleation model, interval I [25].

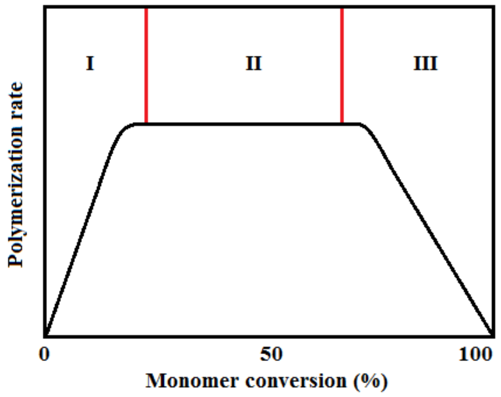


Figure 1.4.3: rate of polymerization as a function of the monomer conversion at intervals I-III.

Particle growth

In this stage, the polymerization proceeds to a conversion of about 60%. The monomer concentration in the micelles is constant due to monomer migration from the solution and monomer migration from droplets to the solution (figure 1.4.4). Micelles are always in a saturation state; the droplets only act as monomer reservoir. The polymerization rate is almost constant or slightly increases with time due to a small gel effect (which will be discussed below). This stage ends when the monomer droplets disappear.

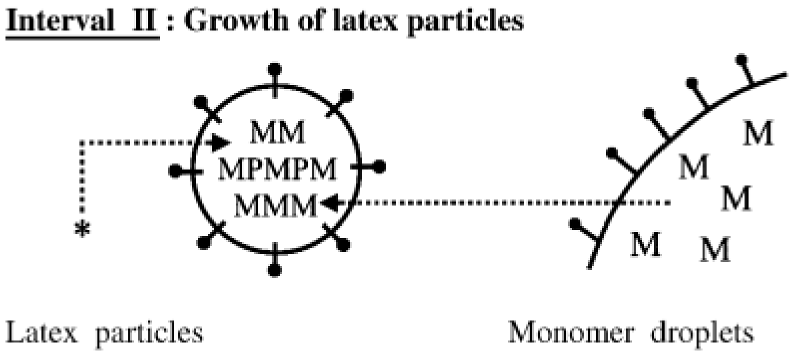


Figure 1.4.4: a schematic representation of the micelle nucleation model, interval II [26].

Gel Effect

When the droplets disappear, the concentration of the monomer inside the micelles decreases; the system becomes monomer starved. Polymerization continue at a steadily decreasing rate until a conversion of 100% is achieved (figure 1.4.5). The system can become very viscous with time, therefore the bimolecular termination is reduced and the polymerization rate may temporary increases between interval II and III. This effect is called gel effect [37,38]. This does not take place if the temperature is above the glass transition temperature of the freshly created polymer system. The final latex particles usually have dimensions between the one of the micelles and the droplets, 50-300 nm.

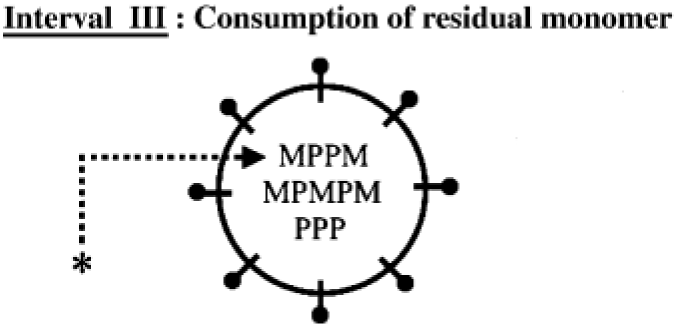


Figure 1.4.5: a schematic representation of the micelle nucleation model, interval III [24].

1.4.2 Miniemulsion

Miniemulsions are a special class of emulsions that are stabilized against coalescence by a surfactant and Ostwald ripening by an osmotic pressure agent, i.e. a costabilizer [39].

In principle, miniemulsions can be used for the synthesis of functionalized polymers either by (co)polymerizing one or several functional monomers, or by the modification of polymers present in the dispersed phase of a miniemulsion [39].

Miniemulsions are formed by applying high shear to a system containing water, monomers, a surfactant and a costabilizer. Miniemulsions rely on the appropriate combination of shear treatment and the two stabilizing agents. [40]

The monomer droplets change rapidly in size throughout sonication (figure 1.4.6). With increasing the time of ultrasonication, the droplet size decreases and therefore the entire monomer/water surface increases. Since a constant amount of surfactant has to be distributed now at larger interphase, the surface tension also increases.

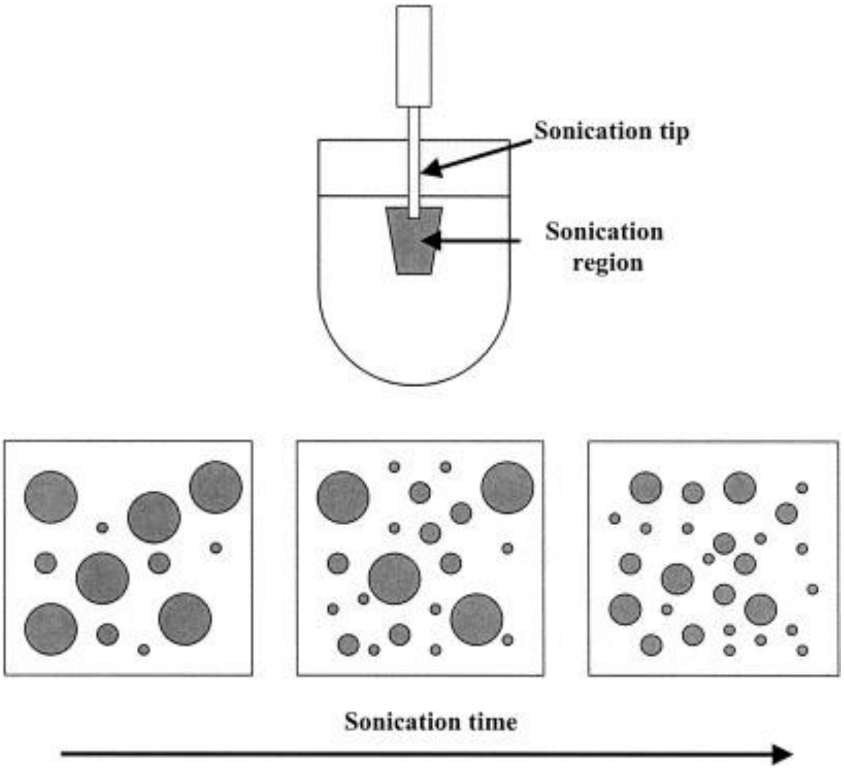


Figure 1.4.6: change in size of the monomer droplets during sonication.

At the beginning of the homogenization, the polydispersity of the droplets is quite high, but by constant fission and fusion processes (figure 1.4.7), the polydispersity decreases and the miniemulsion reaches then a steady state. This also means that miniemulsions come to the minimal particle sizes under the applied conditions, while they make use of the surfactant in the most effective way possible. [41]

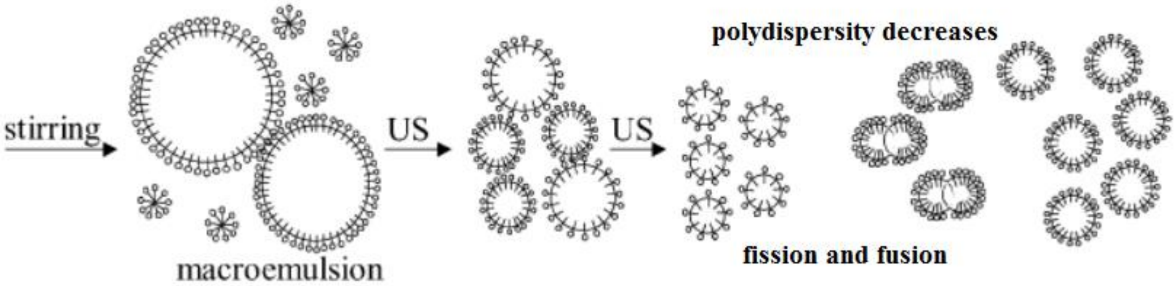


Figure 1.4.7: formation of miniemulsion with ultrasonication, fission and fusion processes for a reduced polydispersity [40].

In the absence of a high-shear device, miniemulsion systems revert to macro emulsion polymerization, indicating that the presence of a costabilizer alone is not sufficient to cause predominant droplet nucleation. In general, it is best to form a coarse pre-emulsion before subjecting the system to a high shear [41].

If the monomer droplet size in a macro emulsion polymerization can be reduced below 0.5 microns, the polymerization site become the monomer droplet. Two phenomena will occur: the droplets will be able to compete successfully for water-borne free radicals with any remaining micelles and the reduction in droplet size will result in a huge increase in interfacial area. This interface requires a monolayer of surfactant to remain stable: the surfactant necessary to support this large interfacial area will come from the breakup of surfactant micelles [41].

Therefore, not only the small droplets compete effectively for micelles, their presence causes the destruction of the micelles, leaving droplet nucleation as the dominant nucleation process.

Being the droplets the sites of polymerization, in an ideal polymerization there should be a 1:1 correspondence between droplets and polymer particles. Any kind of hydrophobic component can be conveniently included in the recipe, since we can be sure that it is going to participate to the polymerization process [41].

In figure 1.4.8, we can see the main differences between a conventional emulsion and a miniemulsion.

In the top image, representing a conventional emulsion polymerization, the polymerization occurs inside the micelles while the monomer droplets only act as monomer reservoir.

In the bottom image, representing a miniemulsion polymerization, the polymerization occurs inside the droplets, which are significantly smaller than in conventional emulsion polymerization. In addition, while in conventional emulsions the micelles only contain the growing polymer chain, the droplets in miniemulsion also contain the costabilizer.

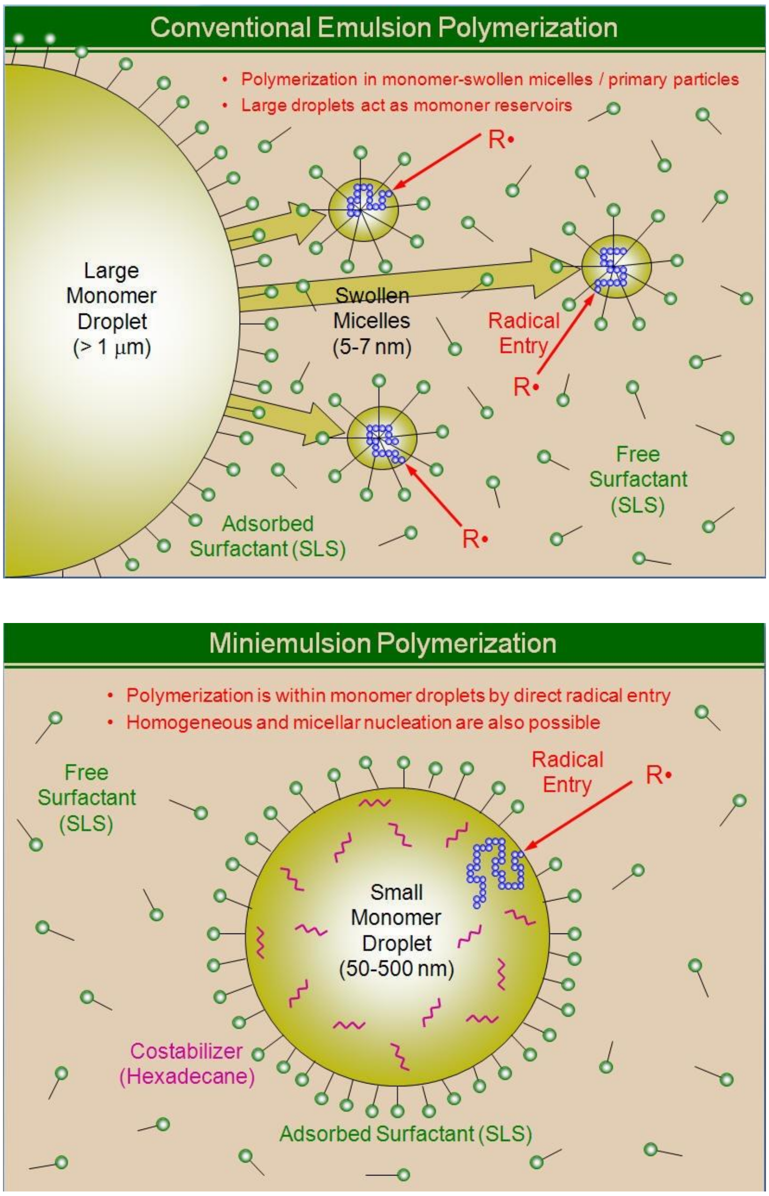


Figure 1.4.8: schematic representation of conventional emulsion and miniemulsion polymerization [42].

A paramount issue in the preparation on miniemulsion is the choice of the costabilizer. These molecules should be highly insoluble in the water phase (they have to remain inside the droplets) and highly soluble in the monomer phase. This because monomer droplets of different size will start to exchange monomer from the smaller ones to the bigger ones without making direct contact (Ostwald ripening, figure 1.4.9). Therefore, if the monomer diffuses out of the droplet, the costabilizer concentration increases in the smaller droplets while the big ones become more diluted. This creates a gradient in the concentration of the surfactant that will lead to an opposite monomer flow. At some point the two processes will be in equilibrium: the costabilizer acts as a barrier to mass transfer not by stopping the Ostwald ripening but by creating an equilibrium.

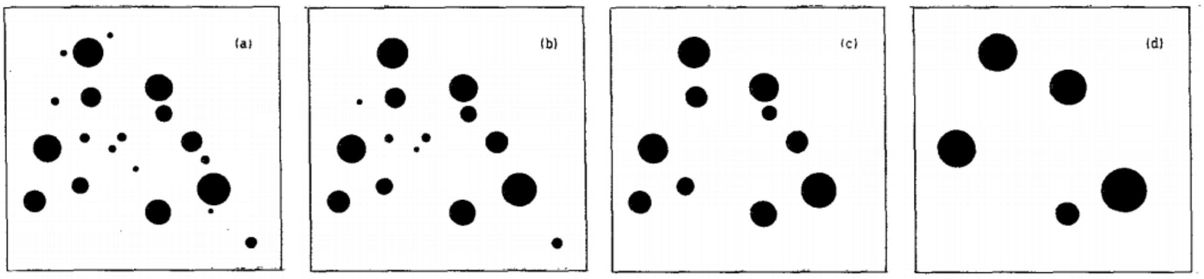


Figure 1.4.9: Ostwald ripening as time evolves from (a) to (d). The total number of droplets decreases while the average droplet radius increases [43].

As stated above, costabilizers can be long-chain alcohol or long chain alkane, e.g. hexadecane, used in the present research. Hexadecane is highly soluble in alcohol, acetone and ether while is almost insoluble in water: the solubility in distilled water is only 0.00009 mg/L [44,45].

2. Results and discussion

As stated above, the research made covers three different topics: the homopolymerization of MMA and BA, the synthesis and analysis of the Macro RAFT agents and the copolymerization of MMA and BA.

2.1 Homopolymerization

The homopolymerization has been prepared mixing monomers M (MMA and BA), costabilizer (hexadecane, HD), CTA, surfactant (sodium dodecyl sulfate, SDS) and initiator (potassium persulfate, KPS) in water as described in the Experimental Section.

Two different CTAs were tested for homopolymerization: CPADTB and DDMAT.

Tables 2.1.1 and 2.1.2 summarize the experimental recipes used respectively for PMMA and PBA syntheses.

Table 2.1.1: experimental recipes used for PMMA studies.

Polymer	**CTA**	**MMA (g)**	**Water (mL)**	**KPS (mol)**	**SDS (wt%)**	**pH adjustment**
PMMA_1B	CPADTB	10	50	[CTA]/3,83	2	No
PMMA_1C	CPADTB	10	50	[CTA]/3,83	2	No
PMMA_1D	CPADTB	10	50	[CTA]/3	5	Yes
PMMA_1F	CPADTB	10	50	[CTA]/3	5	Yes
PMMA_1G	CPADTB	10	50	[CTA]/3	2.5	Yes
PMMA_2A	DDMAT	10	50	[CTA]/3	2.5	Yes

Table 2.1.2: experimental recipes used for PBA studies.

Polymer	CTA	BA (g)	Water (mL)	KPS (mol)	SDS (wt%)	pH adjustment
PBA_1A	CPADTB	10	50	[CTA]/3.83	2	No
PBA_1B	CPADTB	10	50	[CTA]/3,.83	5	Yes
PBA_1C	CPADTB	10	50	[CTA]/3	5	Yes
PBA_1D	CPADTB	10	50	[CTA]/3	5	Yes
PBA_1E	CPADTB	10	50	[CTA]/3	2.5	Yes
PBA_2A	DDMAT	10	50	[CTA]/3	2.5	Yes
PBA_2B	DDMAT	10	50	[CTA]/3	2.5	Yes

The initiator, after the first experiments, was raised from [CTA]/3,83 to [CTA]/3, according to the literature [12] and pH was also raised to a basic level, around 8. This pH value was adjusted to match conditions used in alkyd-acrylate polymerization. The ratio of CTA is always the same, aiming at 200 repeating units of the resulting polymer, as estimated according to the equation:

R.U. = [monomer] / [CTA]

In addition, the percentage of HD is always 4% wt. The SDS is the parameter that mostly changes due to problems during sonication. A value of 2% wt., though suggested in literature [11] is not enough to avoid the formation of big monomer droplets after the sonication, therefore incomplete. After some trials, 2.5 %wt. of SDS was found to be optimal.

The operating parameters chosen for copolymerization are summarized in table 2.1.3.

Table 2.1.3: operating parameters chosen from the first part of the experiment.

CTA (mol)	KPS (mol)	SDS (wt%)	HD (wt%)	T(°C)	pH
[M] / 200	[CTA] / 3	2.5	4	70	8

During and after the polymerization, samples were taken for conversion calculations, NMR and GPC analysis.

The results of the homopolymerization for MMA and BA are summarized respectively in table 2.1.4 and 2.1.5.

Table 2.1.4: time of reaction, conversion, particle size distribution and molecular weight for MMA homopolymers.

Polymer	CTA	Time (h)	Conversion (%)	PDI	Mn (g/mol)	Expected Mn (g/mol)
PMMA_1B	CPADTB	5	64	1.2	11000	13000
PMMA_1C	CPADTB	5.5	83	1.2	14500	17000
PMMA_1D	CPADTB	7	60	1.1	11300	12000
PMMA_1F	CPADTB	20	72	1.2	14000	14000
PMMA_1G	CPADTB	7	70	1.3	27400	14000
PMMA_2A	DDMAT	1	55	1.7	266300	11300

All the polymerizations of MMA with CPADTB show a low PDI and the Mn is similar to the expected one (except for PMMA_1G). This occurs changing the pH adjustment (done only from experiment PMMA_1D), the amount of initiator ([CTA]/3.83 in PMMA_1B and PMMA_1C or [CTA]/3 in all the others) and the SDS (2% in PMMA_1B and PMMA_1C, 5% in PMMA_1D and PMMA_1F or 2.5% in PMMA_1G).

When using DDMAT, instead, the PDI grows from an average of 1.2 (CPADTB) to 1.7 but the Mn is one order of magnitude higher than the theoretical one.

Table 2.1.5: time of reaction, conversion, particle size distribution and molecular weight for BA homopolymers.

Polymer	CTA	Time (h)	Conversion (%)	PDI	Mn (g/mol)	Expected Mn (g/mol)
PBA_1A	CPADTB	6	39	1.3	12000	10000
PBA_1B	CPADTB	6.75	10	-	-	3000
PBA_1C	CPADTB	6	10	-	-	3000
PBA_1D	CPADTB	22	20	-	-	5400
PBA_1E	CPADTB	21	18	-	-	4900
PBA_2A	DDMAT	1.5	96	-	-	25000
PBA_2B	DDMAT	1.75	100	2.8	55000	26000

All BA homopolymers, when the reaction is done with pH adjustment, were insoluble in THF (and many other solvents at different temperatures) and therefore it was impossible to obtain the polydispersity index and the molecular weight from the GPC. Only reactions PBA_1A and PBA_2B gave a result and again, as for the PMMA results, CPADTB gives a low PDI and a good Mn value, while DDMAT does not.

2.2 Syntheses and analyses of Macro Raft agents

2.2.1 Synthesis and characterization of PAA_DDMAT

As stated in paragraph 1.3, many papers insist on the possibility of using Macro RAFT agents in copolymerization reactions: an amphiphilic Macro RAFT agent was synthesized by polymerizing acrylic acid in the presence of DDMAT.

The synthetic method was adopted from E. Velasquez et alt.[15] according to the following reaction (figure 2.2.1):

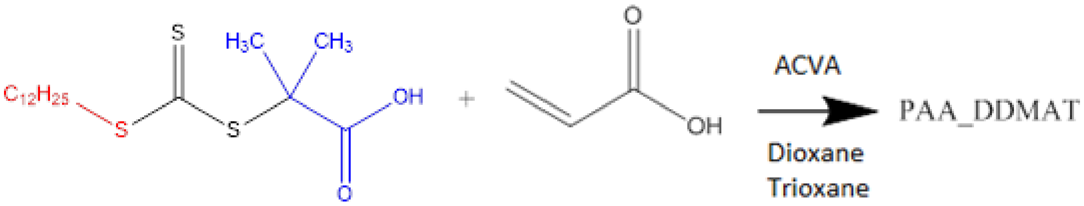


Figure 2.2.1: synthetic route for PAA_DDMAT.

Three syntheses were carried out in dioxane with different feeds. The monomer is acrylic acid, the CTA is DDMAT and the initiator is ACVA, 4,4'-Azobis(4-cyanovaleric acid).

When referring to this Macro RAFT agent, different numbers will be used (e.g. PAA_DDMAT 3), according to the different feeds used for syntheses.

The results of the syntheses are summarized in table 2.1.1. We are aiming at a conversion between 60 and 75% [15].

Table 2.2.1: conversion and molecular weights of the three different products.

	Conversion (%)	Time (h)	Expected Mn (g/mol)
PAA_DDMAT 1	58	5.4	1400
PAA_DDMAT 2	80	4	3200
PAA_DDMAT 3	65	3	2700

The procedure described above gave some problems:

- In the first experiment (PAA_DDMAT 1), there was almost no precipitation in diethyl ether (only 29 mg, while the initial amount of CTA was 500 mg) and the product was separated by drying with rotatory evaporator (Rotavapor). It can therefore be assumed that the product contains both the Macro raft agent and the unreacted RAFT agent. The problem was probably the small conversion. In future works the amount of monomer to CTA was doubled. The PAA_DDMAT 1 was therefore not used in the copolymerization process.

- In the second experiment (PAA_DDMAT 2), after the precipitation, the residual dioxane (that didn't evaporate even after 5 days of drying) was removed by dissolving the product in few drops of methanol and then by freeze drying. The amount of dioxane was effectively reduced while it was not possible to completely eliminate the methanol (attachment 1). The experiment was repeated in a larger batch with less initiator.

- In the third experiment (PAA_DDMAT 3), the initiator's concentration was halved. The precipitation took place without problems. The dioxane was eliminated by keeping the product under vacuum drying for two hours at 120°C. The absence of degradation processes was checked by NMR, as shown in attachment 2 (the DDMAT should degrade at 180°C[46]): the bottom line represents the dried PAA_DDMAT while the top line represents the dried and heated PAA_DDMAT. The only significant difference is the peak of dioxane at 3.55 ppm, as expected.

The PAA_DDMAT 3 was studied by NMR; to understand the broad peak distribution, we first analyzed the NMR of DDMAT in DMSO (table 2.2.2, attachment 3, and figure 2.2.2) and of a PAA standard in DMSO (attachment 4).

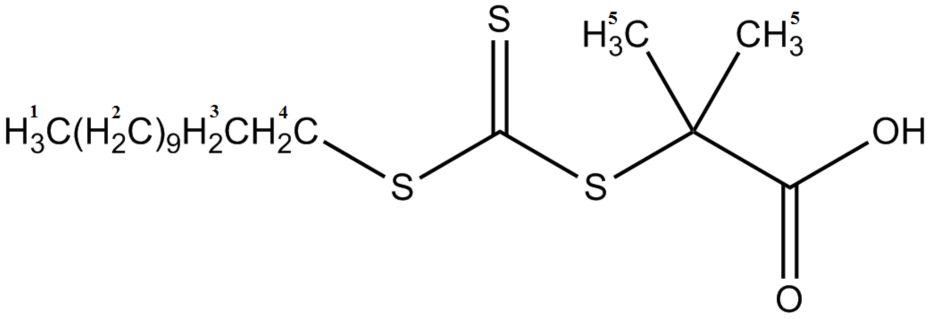


Figure 2.2.2: structure of DDMAT. Protons with different NMR shifts have been assigned a reference number.

Table 2.2.2: NMR results for DDMAT in DMSO.

Proton reference number	Chemical Shift (ppm)	Number of protons
1	0.89	3
2	1.28	18
3	1.65	2
4	3.33	2
5	1.65	6
DMSO	2.54	-

In particular we wanted to see the ratio between the α and β protons (figure 2.2.3) of the PAA part; α protons have a chemical shift of 2 – 2.7 ppm while β protons have a chemical shift of 1.2 – 2.1 ppm. The proportion of β : α should be 2 : 1. This can also be verified from attachment 4.

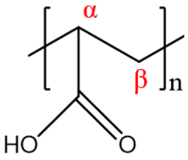


Figure 2.2.3: α and β protons in PAA.

Finally, the PAA_DDMAT 3 spectrum was studied (attachment 5). At 0.89 ppm, there are the three H_1 protons; the six H_5 protons switched to 1.05 ppm, the 20 protons H_2 and H_4 are in the β region. By integrating the peaks, we found the following values for α and β protons:

- α protons: 35
- β protons: 93

As stated above, in the beta zone we also have twenty protons from the DDMAT alone, so the β value becomes 73, which is approximately twice the α value as expected.

Both the PAA_DDMAT and the copolymers successively synthesized using PAA_DDMAT as the CTA, cannot be directly analyzed by Size Exclusion

Chromatography: an end group modification/removal is necessary to avoid the formation of clusters in solution, at least in water and in THF. Clusters in THF were seen in GPC as entities with molecular weight greater than one million (g/mol). The GPC was repeated with a mixture of THF and TBAB (Tetra-n-butylammonium bromide, structure in figure 2.2.4) and the result was a lower Mn, around 200000 g/mol. The expected value was still of 3000 g/mol.

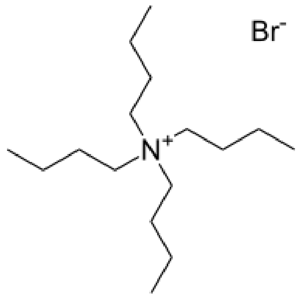


Figure 2.2.4: structure of tetra-n-butylammonium bromide.

There are several methods available to cleave the thiocarbonylthio groups, which is thought to be responsible for the formation of clusters (figure 2.2.5) [46].

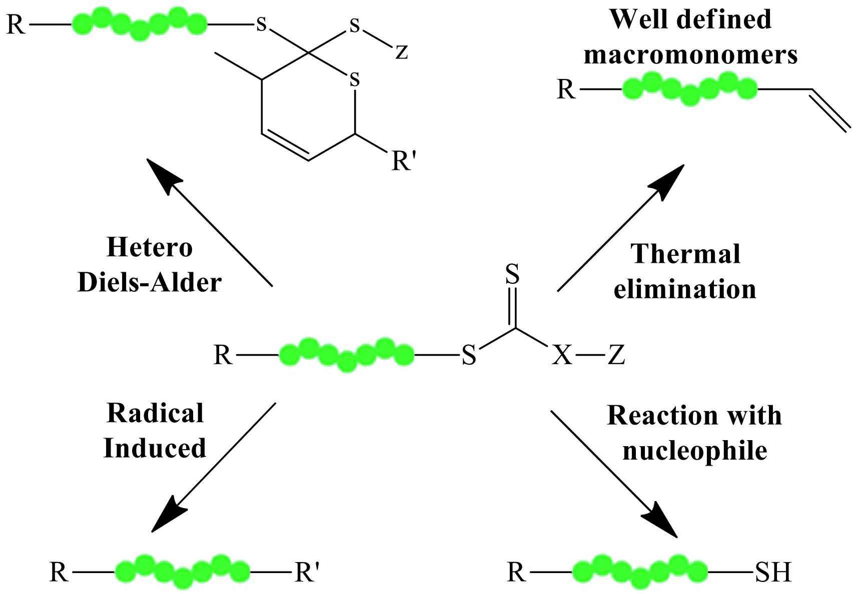


Figure 2.2.5: schematic representing the main methods of RAFT end group conversion [47][50-53].

The thermal elimination, suggested by B. Chong and alt. [48,49] was attempted by TGA with a ramp of 10°/min, from 25°C to 250°C. The thermal elimination should occur at around 180°C. Finally, a methyl esterification [54] was tried several times both on the RAFT agent itself and on the copolymers successively obtained with the same RAFT agent.

The modification mechanism was previously used by L. Couvrer et alt. [55] using trimethylsilyldiazomethane (figure 2.2.6) to methylate the carboxylic acid groups of the RAFT agent.

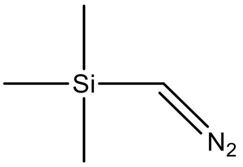


Figure 2.2.6: structure of trimethylsilyldiazomethane.

The general reaction mechanism is described in figure 2.2.7 while in figure 2.2.8 the reaction with our molecule is shown.

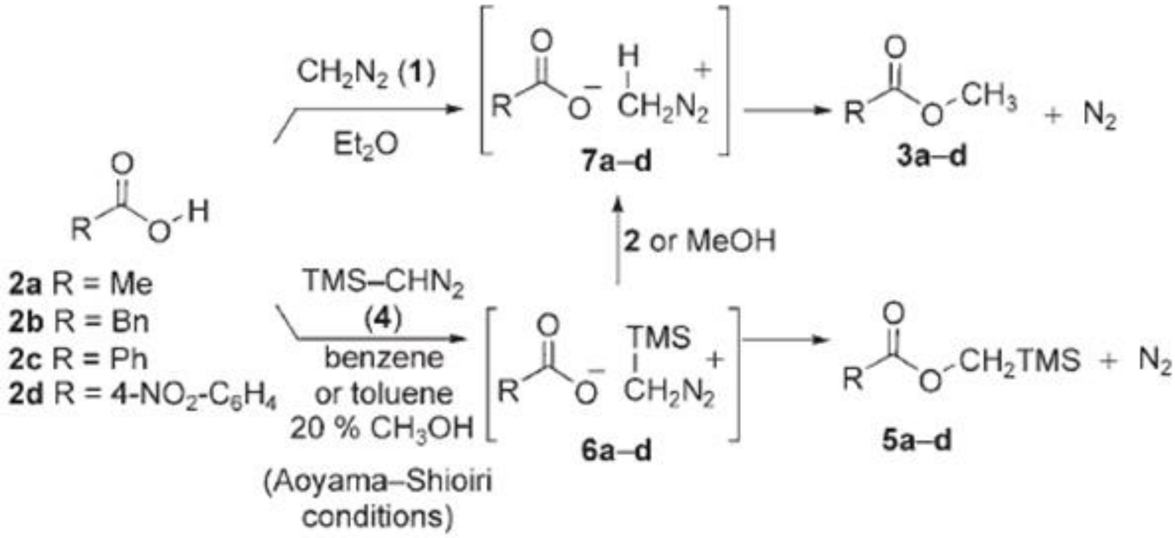


Figure 2.2.7: methyl esterification of carboxylic acids (2) by diazomethane (1) and by trimethylsilyldiazomethane (4).

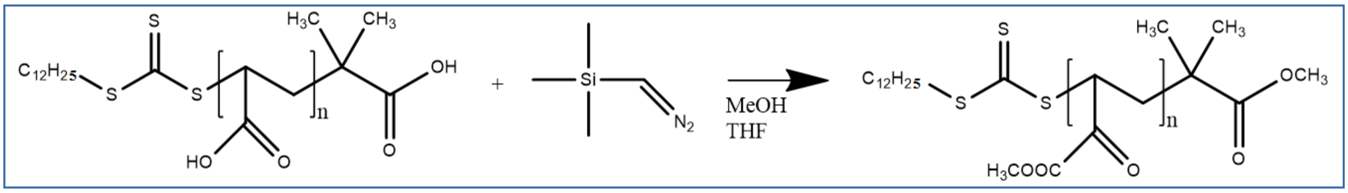


Figure 2.2.8 methylation of PAA_DDMAT.

The methylated PAA_DDMAT was studied by both GPC and NMR. The NMR methylated PAA_DDMAT 3 in DMSO can be seen in attachment 6 (figure 2.2.9): β protons are, again, two times as many as the α protons while γ protons are 65% of the completely methylated quantity. For a complete methylation, the γ protons should be three times as many as the α protons.

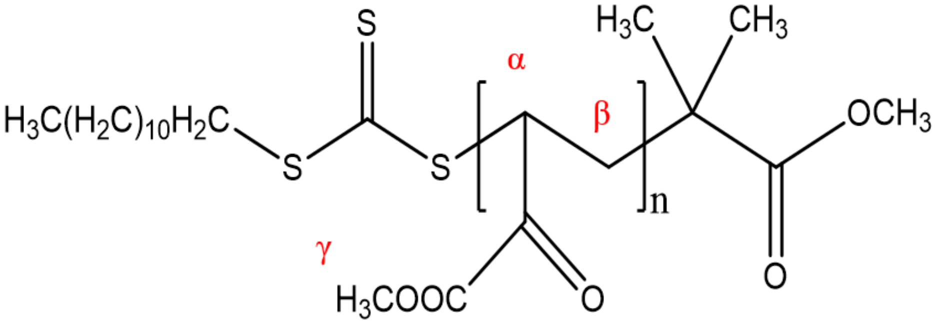


Figure 2.2.9: α, β and γ protons in the methylated PAA_DDMAT.

The GPC results for PAA_DDMAT 1, 2, 3 and the methylated PAA_DDMAT are summarized in table 2.2.3. The Mn are actually averages between coherent results; the expected Mn was calculated for a 50% methylation. We can see an absence of correlation; it is impossible to conclude whether this RAFT agent was successful or not.

Table 2.2.3: PDI, molecular weight and solvent for the three PAA_DDMAT and the methylated version.

CTA	PDI	Mn (g/mol)	Expected Mn (g/mol)	Gpc solvent
PAA_DDMAT 1	1.6	17000	1400	THF
PAA_DDMAT 2	1.3	1000000	3200	THF
PAA_DDMAT 3	1.3	216000	2700	THF + TBAB
Met. PAA_DDMAT 3	1.3	10000	3400	THF + TBAB

2.2.2 Synthesis and analysis of PEG_DDMAT

The Macro RAFT agent PEG_DDMAT was synthesized as described by Jin-ni Deng et alt. [16, 17,] according to the following reaction (figure 2.2.10):

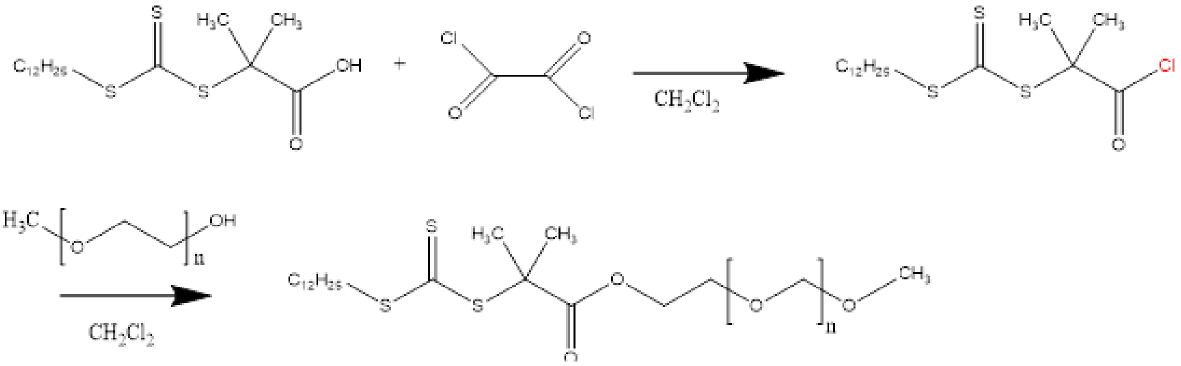


Figure 2.2.10: synthesis of PEG_DDMAT.

DDMAT and oxalyl chloride were dissolved in anhydrous CH_2Cl_2 at room temperature in a nitrogen atmosphere for 3 hours. The product was isolated under reduced pressure and then dissolved again in dichloromethane. Finally, poly (ethylene glycol) methyl ether (mPEG) was added, at room temperature, and the reaction was carried out over the weekend. The PEG_DDMAT was obtained by precipitation with n-hexane and then dried and analyzed by both NMR and GPC.

After the reaction, the PEG_DDMAT was purified in a column with ethyl acetate and n-exane in a proportion of 3:1.

Different fractions were analyzed by NMR and compared to the NMR of the PEG_DDMAT bought from Sigma Aldrich (attachment 7 for reference NMR and 8 for fractions NMR). In the reference spectrum, we assigned the main peaks; in particular, the protons from the alkyl chain have a shift at 3.64 ppm. In attachment 8 we can see that since the first fraction analyzed some alkyl chain is present.

All fractions were washed with chloroform, dried and analyzed with GPC. Since the GPC gave no result the CTA was not applied to further polymerizations.

2.3 Copolymerization

The copolymerization has been prepared as per the homopolymerization but adding both the monomers MMA and BA. The reaction is shown in figure 2.3.1.

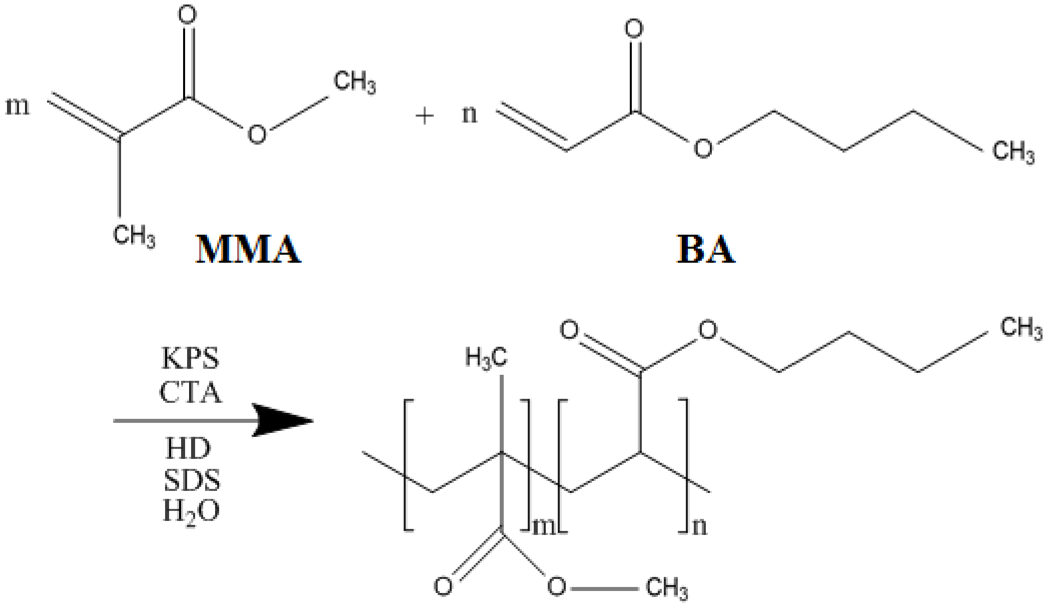


Figure 2.3.1: copolymerization reaction.

The ratio between MMA and BA is always 70:30 wt%, ratio required for the alkyd-acrylic polymerization. Constants in the copolymerization are the repeating units of the resulting polymer (200) and the amount of HD, 4 wt%.

Table 2.3.1 summarizes the experimental recipes used for the copolymerization.

Table 2.3.1: experimental recipes used for copolymerizations.

Copolymer	CTA	Water (mL)	KPS (mol)	SDS (wt%)	pH adjustment
COP_0A	/	50	[CTA]/3.83	2.5	Yes
COP_1A	CPADTB	50	[CTA]/3	2.5	Yes
COP_2A	DDMAT	50	[CTA]/3	2.5	Yes
COP_2B	DDMAT	50	[CTA]/3	2.5	Yes
COP_2C-D	DDMAT	50	[CTA]/10	2.5	Yes
COP_4A	PAA_DDMAT 3	50	[CTA]/3.83	1	Yes
COP_4B	PAA_DDMAT 3	5	[CTA]/3.83	1	No
COP_5A	σPEG_DDMAT	5	[CTA]/3.83	2.5	Yes
COP_5B	σPEG_DDMAT	5	[CTA]/3.83	2.5	Yes
COP_6A	MOEXP	5	[CTA]/3.83	2.5	Yes
COP_6B	MOEXP	5	[CTA]/3.83	2.5	Yes
COP_6C	MOEXP	5	[CTA]/3.83	2.5	No
COP_6D	MOEXP	5	[CTA]/3.83	2.5	No
COP_6E	MOEXP	50	[CTA]/10	2.5	Yes
COP_6F	MOEXP	50	[CTA]/3.83	2.5	Yes

The scale was 50 mL except for polymerizations COP_4B, 5A, 5B, 6A and COP_6D, done at 5 mL scale because of the available amount of CTA. When possible, a scale of 50 mL is preferred. In the copolymerization COP_5A and COP_5B the RAFT agent was the one bought from Sigma Aldrich.

The initiator was initially changed from [CTA]/3.83 to [CTA]/3 [11,12] but then lowered to [CTA]/10; this because, differently from the homopolymerization, the conversions often reached 100% too soon to be able to collect conversion samples.

The SDS was also lowered to 1% for some reactions with PAA_DDMAT (COP_4A and COP_4B): in the copolymerization COP_4A the foam produced by sonication was too much, interfering with the sonication process. The SDS percentage was therefore lowered to 1%. Several papers even suggest to use emulsion polymerization with amphiphilic RAFT agents without a surfactant, obtaining the so-called surfactant-free emulsion polymerization [13,17].

All the experiments done at 5mL scale were not further analyzed since they are not comparable with those at 50 mL scale. The initiator amount has a high importance for DDMAT (exp. 2) but not for MOEXP (exp. 6).

The results of the copolymerization are summarized in table 2.3.2.

Table 2.3.2: time of reaction, conversion, particle size distribution and molecular weight for MMA-BA copolymers.

Copolymer	**CTA**	**Time (h)**	**Conversion (%)**	**PDI**	**Mn (g/mol)**	**Expected Mn (g/mol)**
COP_0A	-	3	100	2.2	655 000	-
COP_1A	CPADTB	3	89	2	22 400	19 600
COP_2A	DDMAT	2	100	2.4	25 000	22 000
COP_2B	DDMAT	1	90	2.9	18 300	19 900
COP_2C	DDMAT	1	40	1.4	9 000	9 000
COP_2D	DDMAT	5	95	1.2	24 000	21 000
COP_4A	PAA_DDMAT3	2	95	-	-	23 900
COP_6E	MOEXP	3	93	2.4	76 300	20 400
COP_6F	MOEXP	8	92	.,5	95 000	20 200

When using no CTA (COP_0A) there is no control, as expected. The molecular weight is much higher than all the others (655000 g/mol) and the PDI is above 2.

The other CTAs gave different results:

- CPADTB, although gave a low PDI for both the homopolymerizations, for copolymerization gives a high PDI (around 2).

- DDMAT, if used with the same conditions as homopolymerization, gives the same bad results. For the reactions COP_2C and COP_2D the initiator was lowered from [CTA]/3.83 to [CTA]/10. The molecular weights correspond perfectly to the expected one and the PDI is low (1.2 for COP_2D).

The two reactions are carried out in the same conditions and it is possible to notice a lower PDI going from a reaction time of 1h to 5h. The second reaction was then studied more carefully, taking conversion samples every 5 minutes until reaching the inhibition time, 40 minutes, and then every hour (figure 2.3.2).

Figure 2.3.3 shows how the PDI and the Mn seem to be inversely proportional. The result is a high conversion and a low PDI. This indicates that DDMAT can grant a good control over the copolymerization.

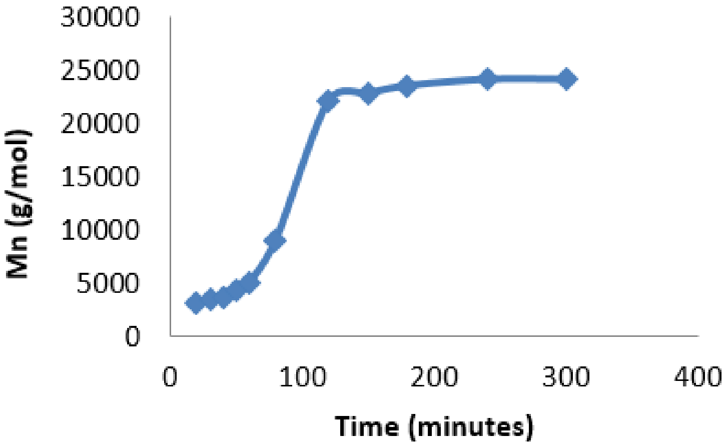


Figure 2.3.2: molecular weight versus time of polymerization. The inhibition time can be seen at around 40 minutes.

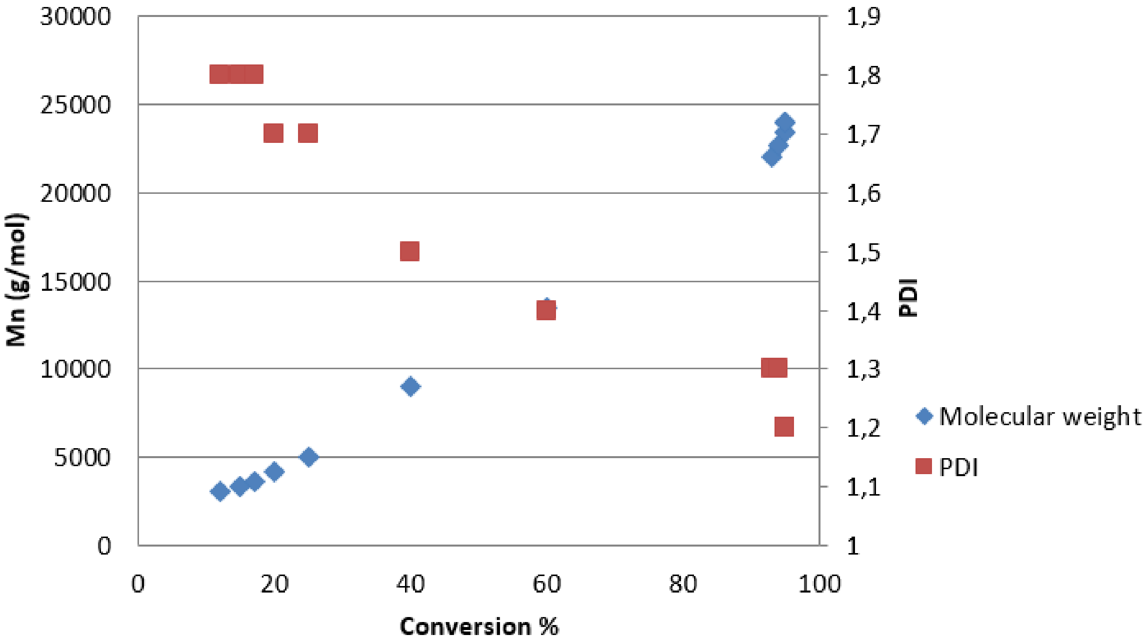


Figure 2.3.3: PDI and molecular weight at different conversions.

- PAA_DDMAT: the copolymers obtained with this CTA could not be analyzed since they were insoluble in every solvent we tried at different temperatures.
- MOEXP: this polymerization has long been studied because the first results, in 5mL scale and low conversion, gave good results in terms of PDI. However increasing scale and reaction times (even with three different concentrations of initiator) has never come to a low PDI corresponding to high conversions.

3. Conclusions

One of the first objectives of this research was to study the homopolymerization of MMA and BA to find the optimal operating parameters to be used in the copolymerization. It is clear from the results that there is no correlation between the two polymerization. In the homopolymerizations the difficulty was in getting a high conversion. In general, the CPADTB RAFT agent provides good PDI and high conversions for PMMA. In the PBA we have few data due to the insolubility of the polymers synthesized when using a basic pH (8). We do not know if high conversions can match low PDI (table 3.1).

Table 3.1: significant results from homopolymerization with CPADTB as RAFT agent.

Polymer	Conversion (%)	PDI
PMMA_1C	83	1.2
PMMA_1D	60	1.1
PBA_1A	40	1.3

In the copolymerization, instead, high conversions occurred in a very short time, even lower than 10 minutes. The problem was getting also low PDI. In the case of MOEXP we have tried many polymerizations with slightly different parameters because the first polymerizations, slow to reach high conversions, gave indeed PDI <1.5. With conversions higher than 80% the PDI becomes greater than 2.

The most successful CTA for the copolymerization of MMA and BA was DDMAT. In the following table we have summarized some significant data regarding the homo- and co- polymerization with DDMAT. The parameter that has allowed us to obtain a good PDI (1.2) with high conversions (95) was concentration of initiator, lowered from [CTA]/3 or [CTA]/3.83 to [CTA]/10, despite what suggested in many papers.

Table 3.2: significant results from homopolymerization and copolymerization with DDMAT as RAFT agent.

Polymer	Conversion (%)	PDI	KPS (mol)

PMMA_2A	55	1.7	[CTA]/3
PBA_2B	100	2.8	[CTA]/3
COP_2B	90	2.9	[CTA]/3
COP_2D	95	1.2	[CTA]/10

The copolymerization of COP_2D showed an inhibition time of about 40 minutes in which the molecular weight remained very low and the PDI was above 1.8, then reached the values shown in the table in about 4 hours. Even the molecular weight obtained by GPC is very similar to the one expected.

The two synthesized Macro RAFT agents have given no results. In particular, the synthesized PEG_DDMAT could not be used in the polymerization, and the one bought from Sigma Aldrich gave high PDI for high conversions.

The synthesized PAA_DDMAT has not provided consistent data from analysis and polymers for which was used as a RAFT agent could not be analyzed (insoluble). Therefore it is not possible to draw any conclusion on its utility.

In conclusion, the DDMAT is the most suitable RAFT agent for a good control over the copolymerization of MMA and BA and will be then used in the production of alkyd resins. In the future, we should also try to run the copolymerization with CPADTB and PEG_DDMAT lowering the level of initiator to [CTA]/10.

4. Experimental section

The ^{1}H NMR measurements were conducted with a 500 MHz Brukner Ultrashield^{TM} 500 plus spectrometer.

Molecular weights and molecular weight distributions were measured using Waters SEC equipment. This equipment consisted of an auto injector, Waters Ultrahydrogel 120, 250 and 2000 columns and Waters 2410 refractive index detector. The eluent was THF with 1% of toluene and the calibration was carried out with PMMA standards (Polymer Laboratories).

4.1 Homopolymerization

The miniemulsion was prepared according to the following procedure. The monomer, MMA or BA, was mixed with HD, the costabilizer, and the CTA. The SDS was dissolved in water and then this solution added to the monomer's one. After 10 minutes of energic stirring to form a coarse emulsion, the solution was sonicated for 5 minutes. Samples were collected after the sonication for DLS analysis. According to the scale of the reaction, the mixture was transferred to a 250 mL three-necked flask with mechanical stirring (50 mL scale) or to a 25 mL two necked flask with magnetic stirring (5 mL scale). The flask was, in both cases, equipped with a condenser and a nitrogen inlet. The mixture was deoxygenated for 30 min with a nitrogen flow while brought to the temperature of 70°C (intermediate between the temperatures suggested in [11] and [12] respectively for MMA and BA).

In the meanwhile, KPS is dissolved in water and deoxygenated for 10 min with a nitrogen flow. The time zero of the polymerization is given when the KPS is added to the reaction mixture.

The synthesized polymers are in figure 4.1.

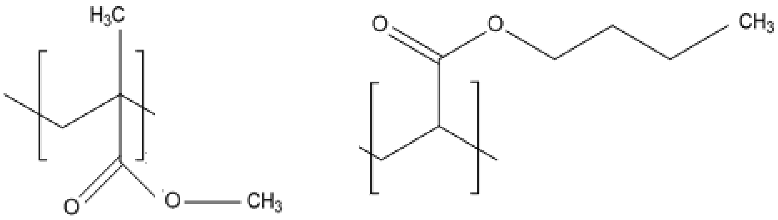


Figure 4.1: structure of PMMA (left) and PBA (right)

4.2 Macro RAFT agents

4.2.1 Synthesis of PAA_DDMAT

The polymerization was prepared according to E. Velasquez et al. procedure. The feeds for the three different runs are in table 4.1.1.

Table 4.1.1: syntheses of PAA_DDMAT.

Run	Monomer (mol%)	CTA (mol%)	Initiator (mol%)	DDMAT (mg)
1	25	1	0.2	500
2	50	1	0.2	175
3	50	1	0.1	800

Trioxane is used as a reference for the conversion analysis (attachment 9).

At the end of the reaction, the product was precipitated in diethyl ether (using a ratio of 5 mL of dioxane for 75 mL of ether). In principle the Macro RAFT agent should separate in the form of a yellow precipitate, while the unreacted RAFT agent and acrylic acid should dissolve in the ether. The solid is then separated by decantation. The filtration on Buchner is difficult as the solid is very fine.

The yellow solid thus obtained can be recovered with a small amount of dioxane which is then evaporated under vacuum at 120°C. The absence of degradation was checked by NMR.

4.2.2 Methylation of PAA_DDMAT

A sample of PAA_DDMAT 3 was dissolved in THF at room temperature with a small addition of MeOH. The solution of trimethylsilyldiazomethane (TMSA) was added obtaining bubbles and a colorless solution. The methylation agent was added until the solution turned yellow again. After 3 hours, acetic acid was added to quench the remaining trimethylsilyldiazomethane and the pH was restored to neutrality with NaOH 1M.

The used amounts of PAA_DDMAT 3, TMSA, THF and MEOH are in table 4.1.2.

Table 4.1.2: methylation of PAA_DDMAT 3.

PAA_DDMAT 3 (mg)	TMSA (mL)	THF (mL)	MEOH (mL)
100	20	2	0.8

4.3 Copolymerization

The miniemulsion was prepared according to the following procedure. The monomers, MMA and BA, were mixed with HD, the costabilizer, and the CTA. The SDS was dissolved in water and then this solution added to the monomer's one. After 10 minutes of energic stirring to form a coarse emulsion, the solution was sonicated for 5 minutes. According to the scale of the reaction, the mixture was transferred to a 250 mL three-necked flask with mechanical stirring (50 mL scale) or to a 25 mL two necked flask with magnetic stirring (5 mL scale). The flask was, in both cases, equipped with a condenser and a nitrogen inlet. The mixture was deoxygenated for 30 min with a nitrogen flow while brought to the temperature of 70°C.

In the meanwhile, KPS is dissolved in water and deoxygenated for 10 min with a nitrogen flow. The time zero of the polymerization is given when the KPS is added to the reaction mixture.

The synthesized polymer is in figure 4.2.

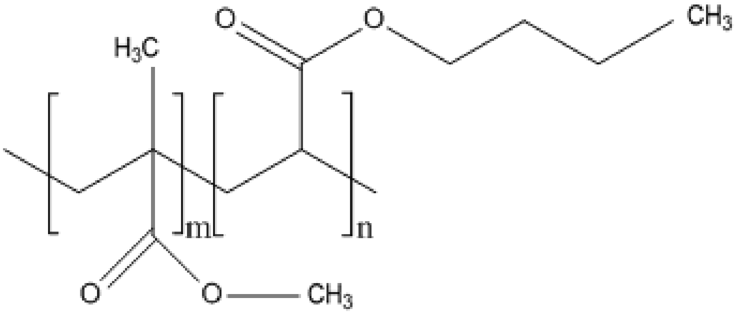
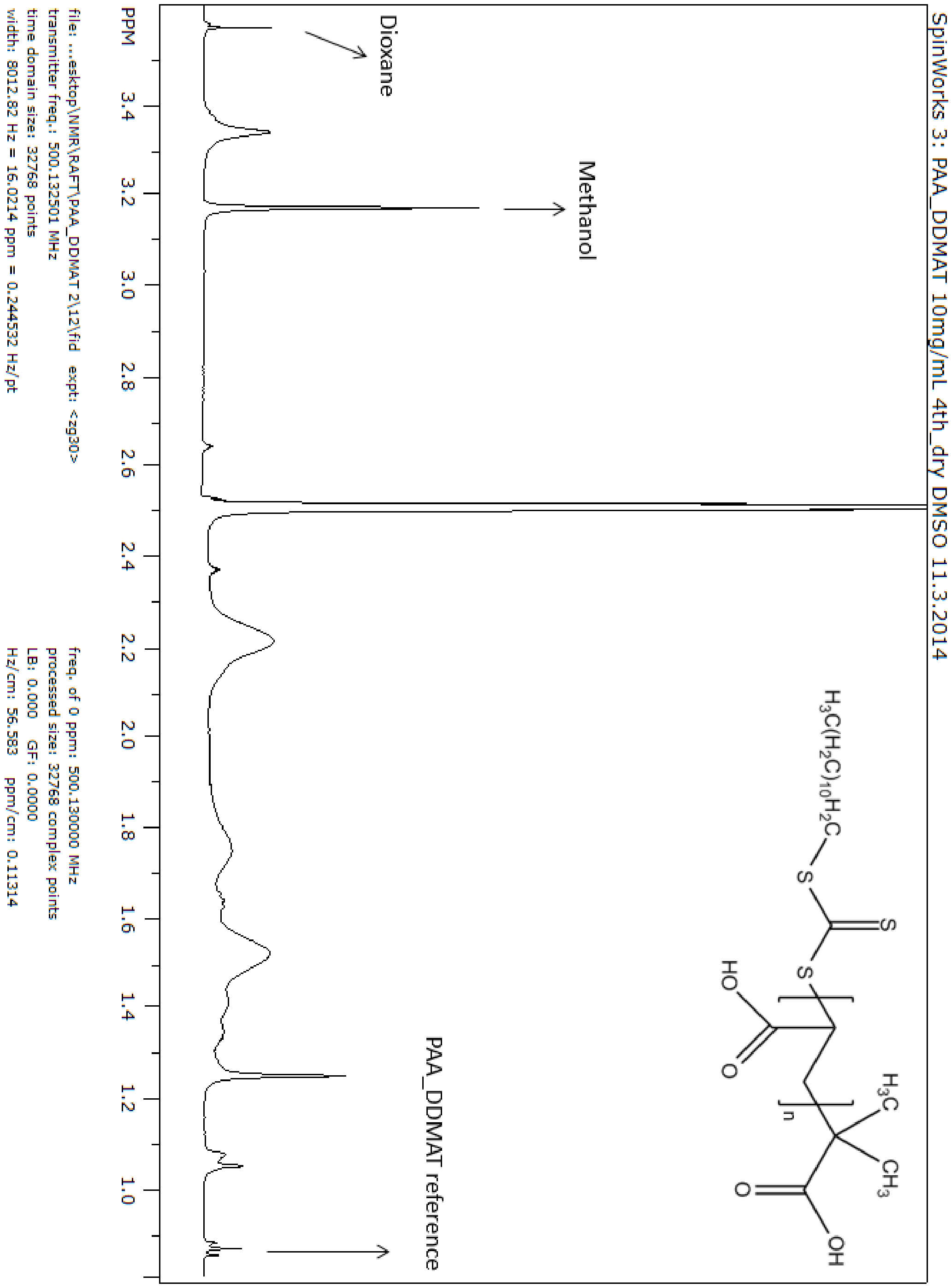


Figure 4.2: structure of the copolymer of mMMA and nBA.

4.4 Attachments

1. PAA_DDMAT 2

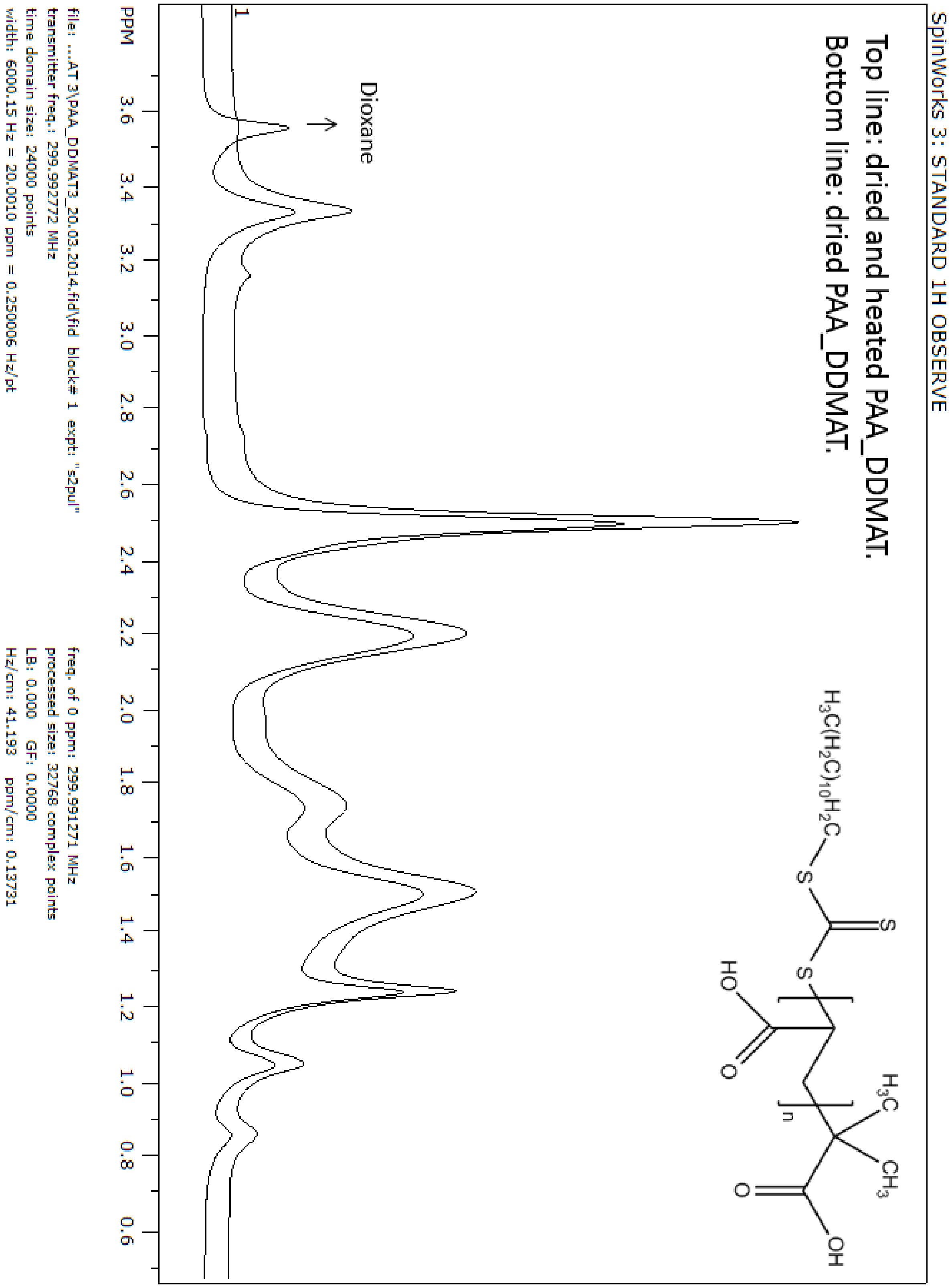


SpinWorks 3: PAA_DDMAT 10mg/mL 4th_dry DMSO 11.3.2014

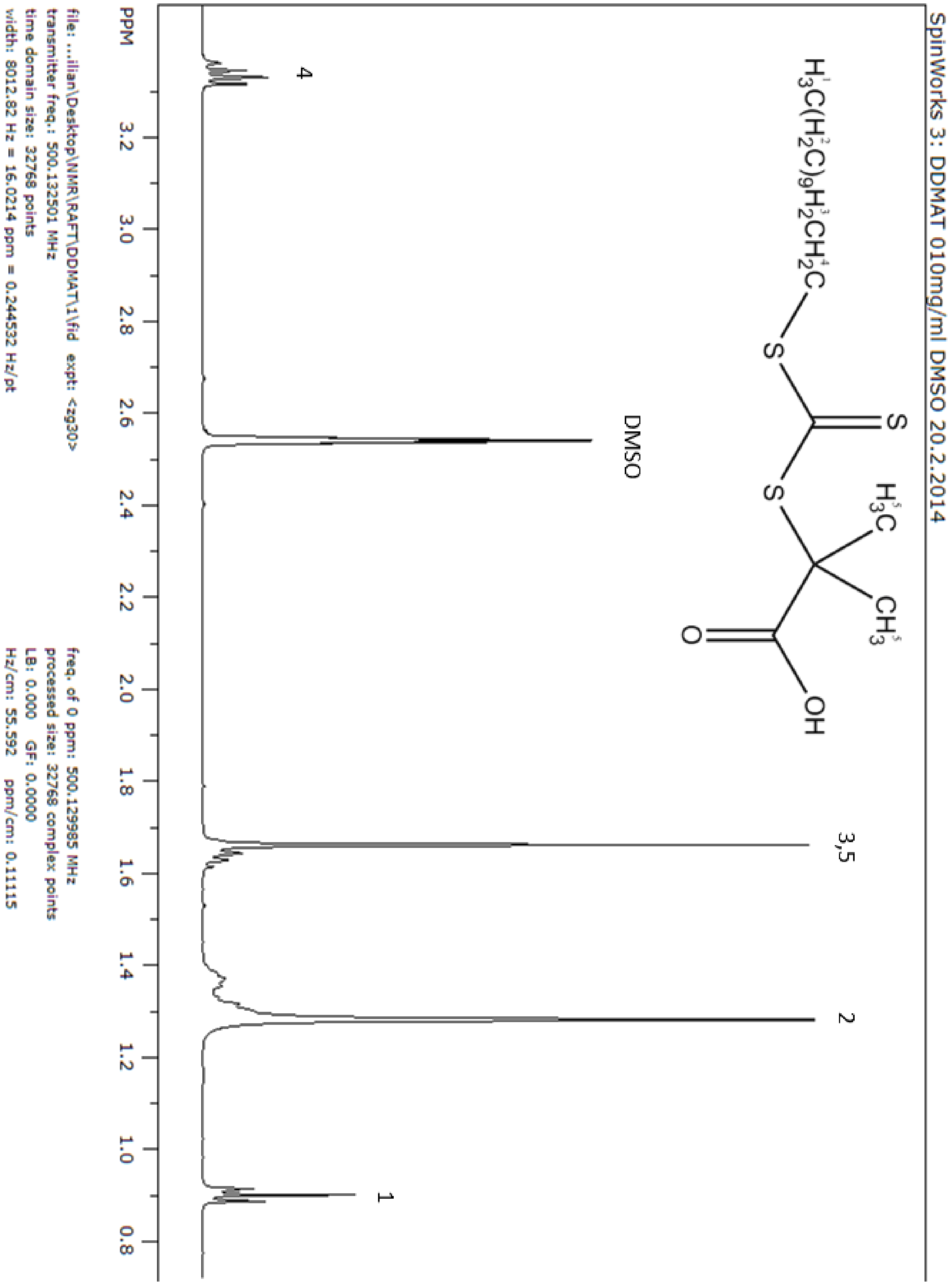
```
file: ...esktop\NMR\RAFT\PAA_DDMAT 2\12\fid   expt: <zg30>
transmitter freq.: 500.132501 MHz
time domain size: 32768 points
width: 8012.82 Hz = 16.0214 ppm = 0.244532 Hz/pt
```

```
freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.000    GF: 0.0000
Hz/cm: 56.583    ppm/cm: 0.11314
```

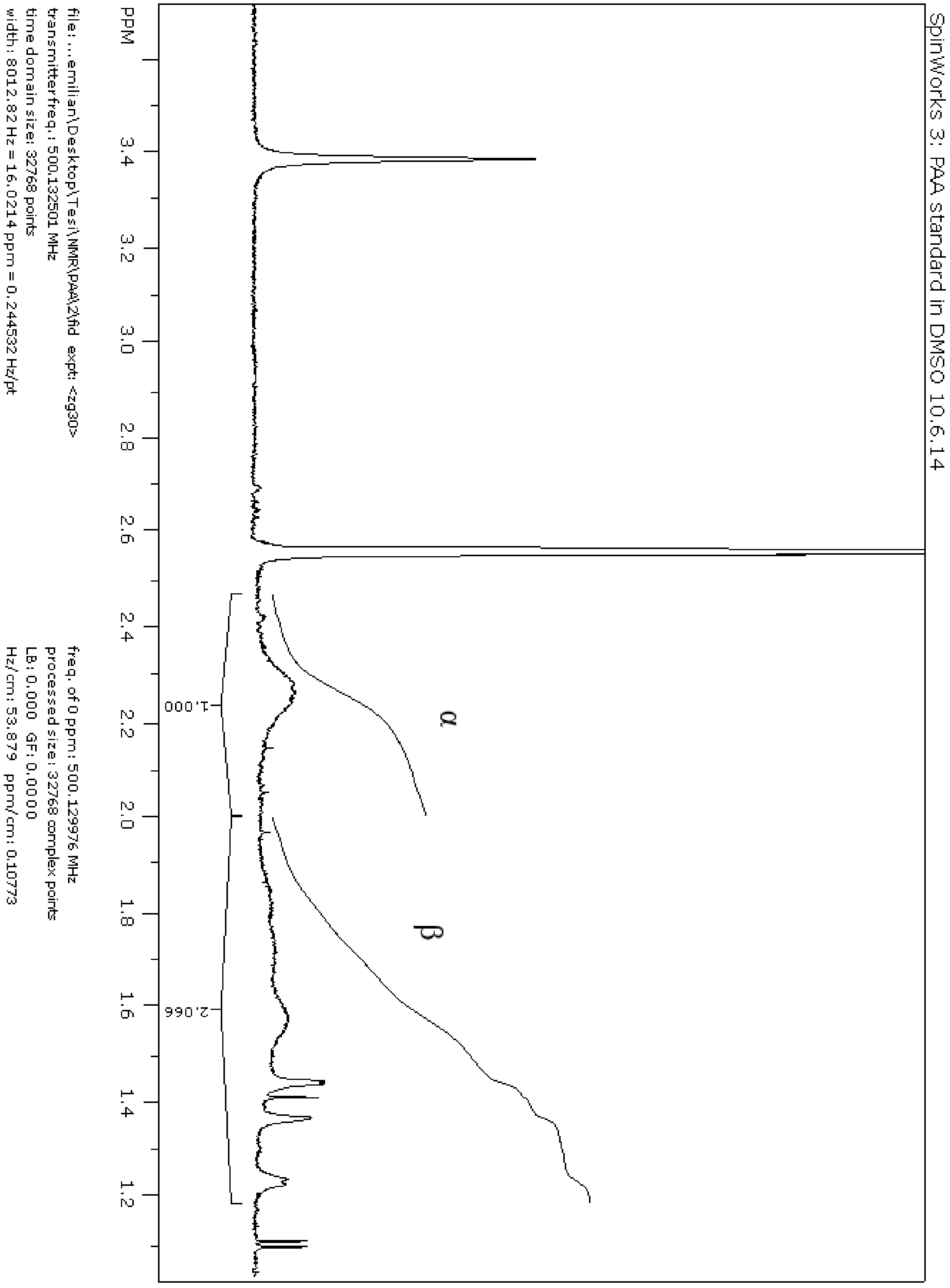
2. Effect of heating on PAA_DDMAT 3



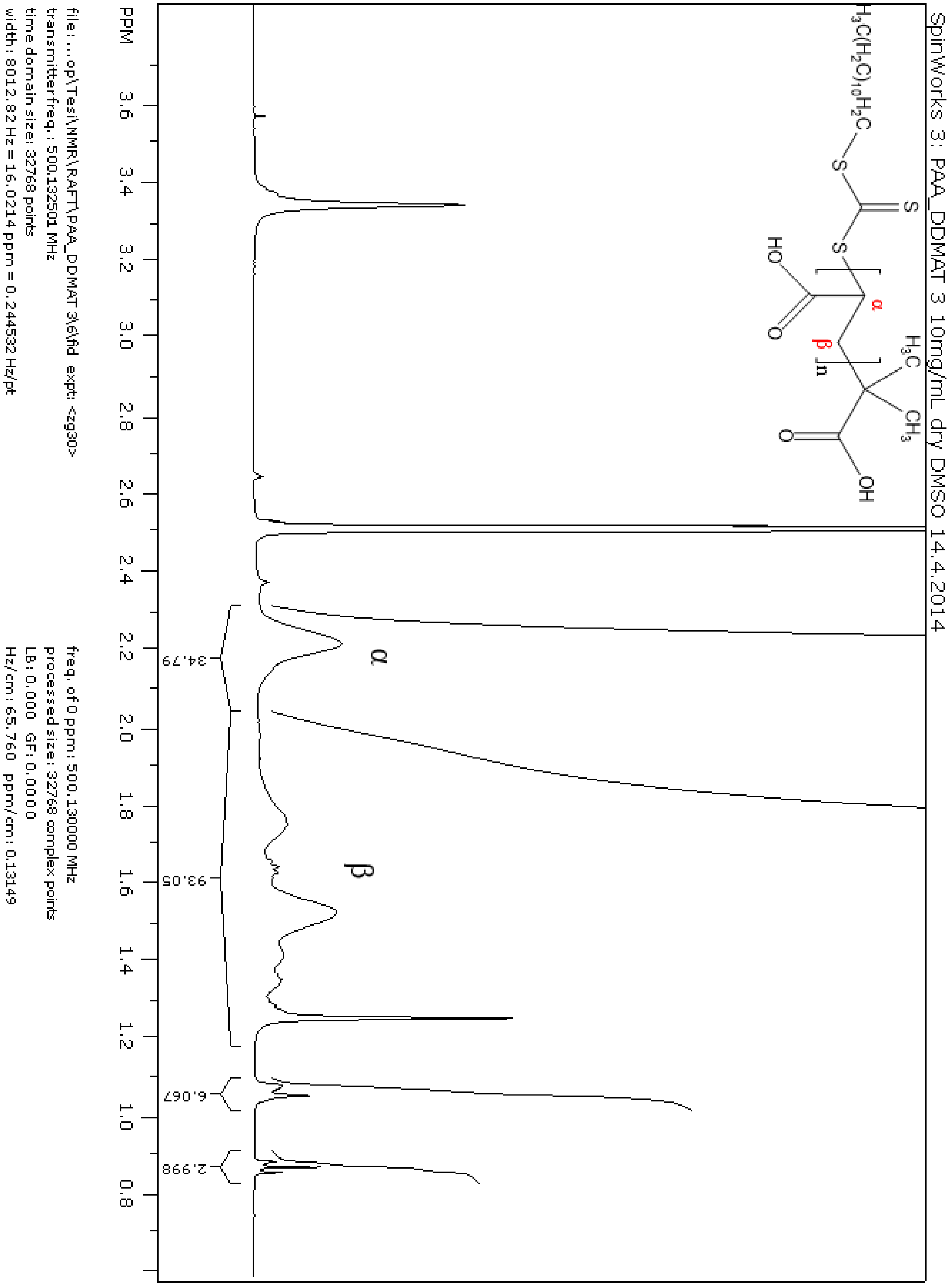
3. DDMAT standard



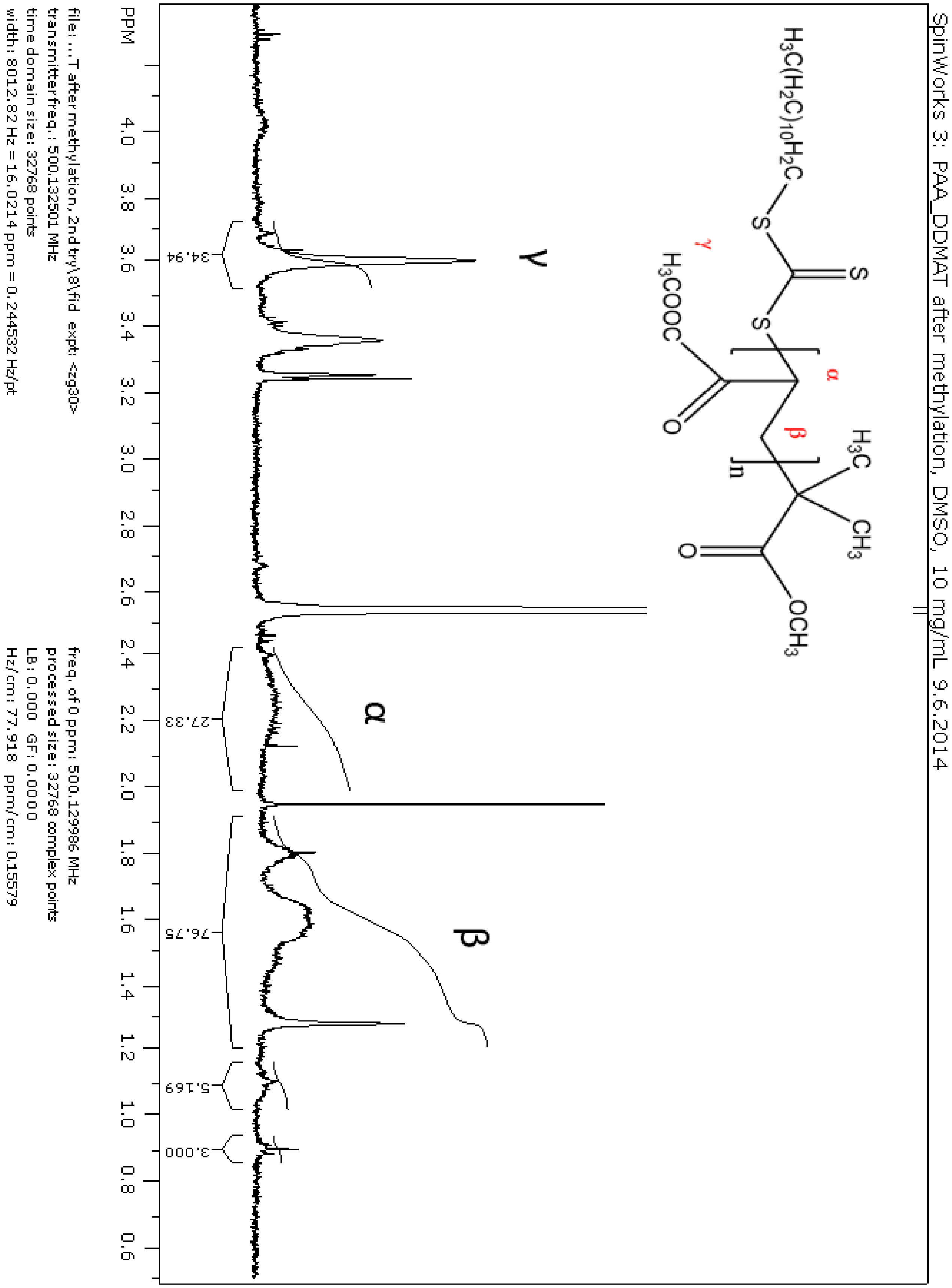
4. PAA standard



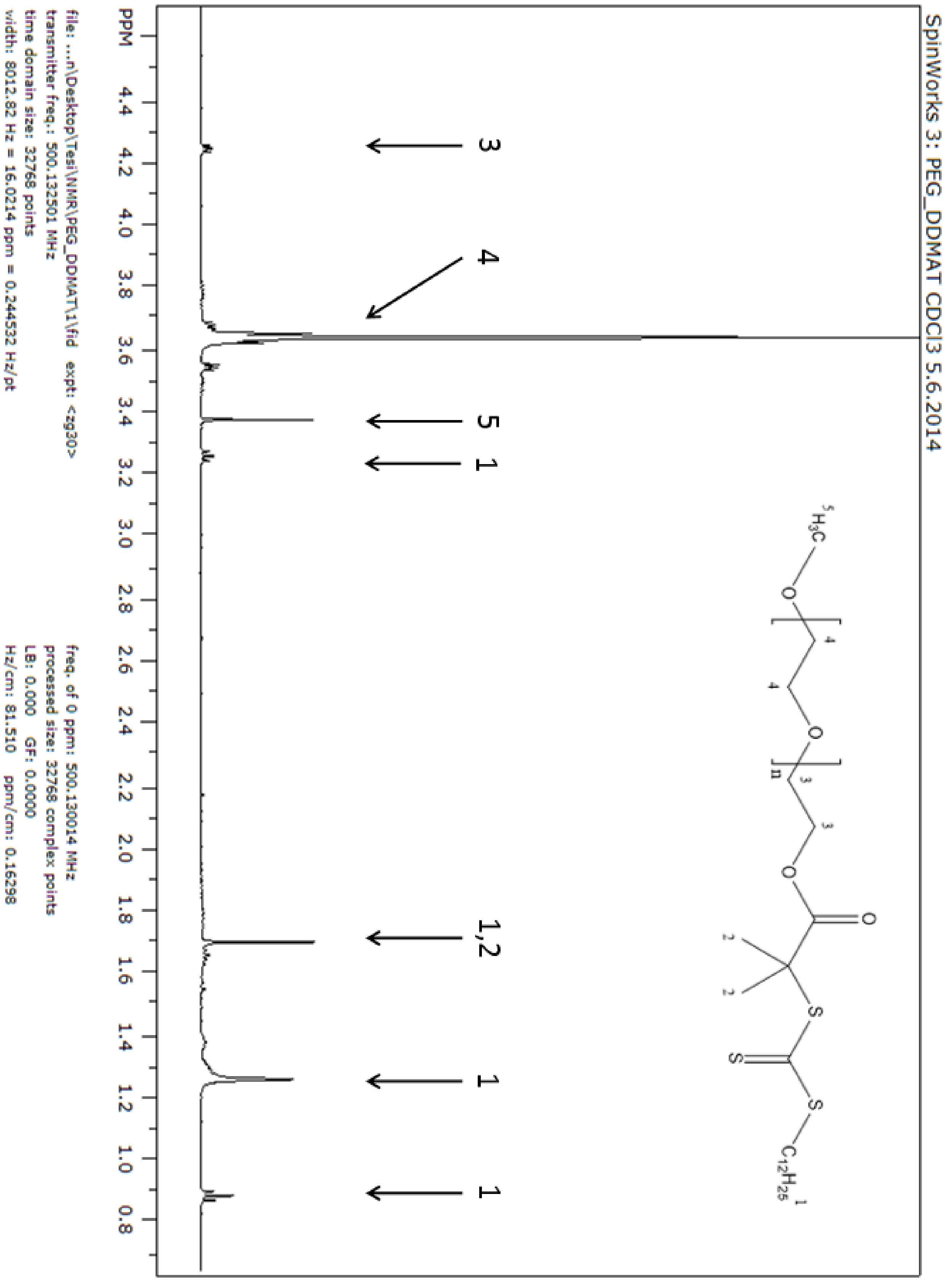
5. PAA_DDMAT 3


SpinWorks 3: PAA_DDMAT 3 10mg/mL dry DMSO 14.4.2014
$H_3C(H_2C)_{10}H_2C$
S
S
S
HO
O
α
β
n
H_3C
CH_3
O
OH
α
β
PPM
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
34.79
93.05
6.067
2.998
file: ...op\Tesi\NMR\RAFT\PAA_DDMAT 3\6\fid expt: <zg30>
transmitter freq.: 500.132501 MHz
time domain size: 32768 points
width: 8012.82 Hz = 16.0214 ppm = 0.244532 Hz/pt
freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 65.760 ppm/cm: 0.13149

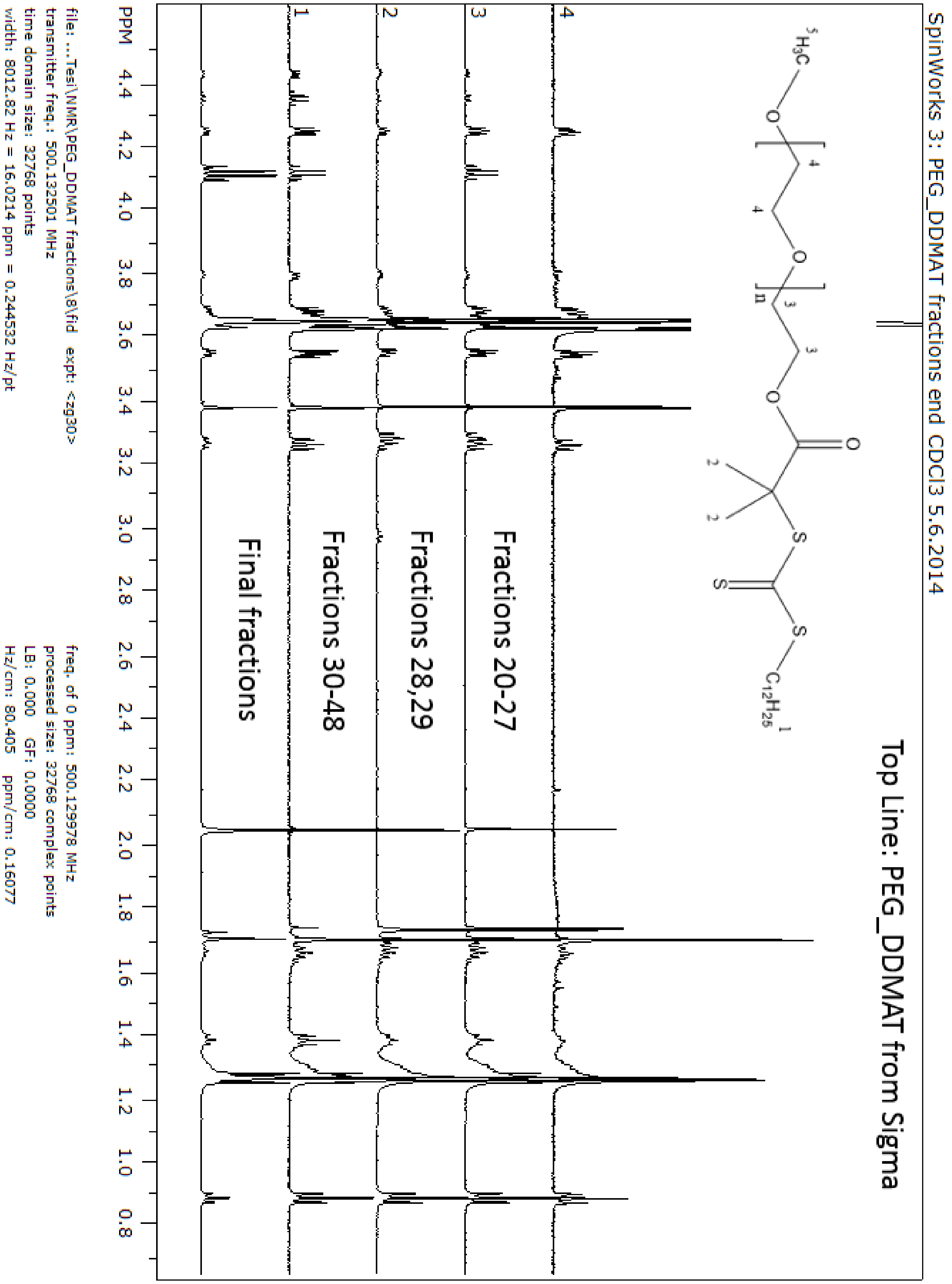
6. Methylated PAA_DDMAT 3



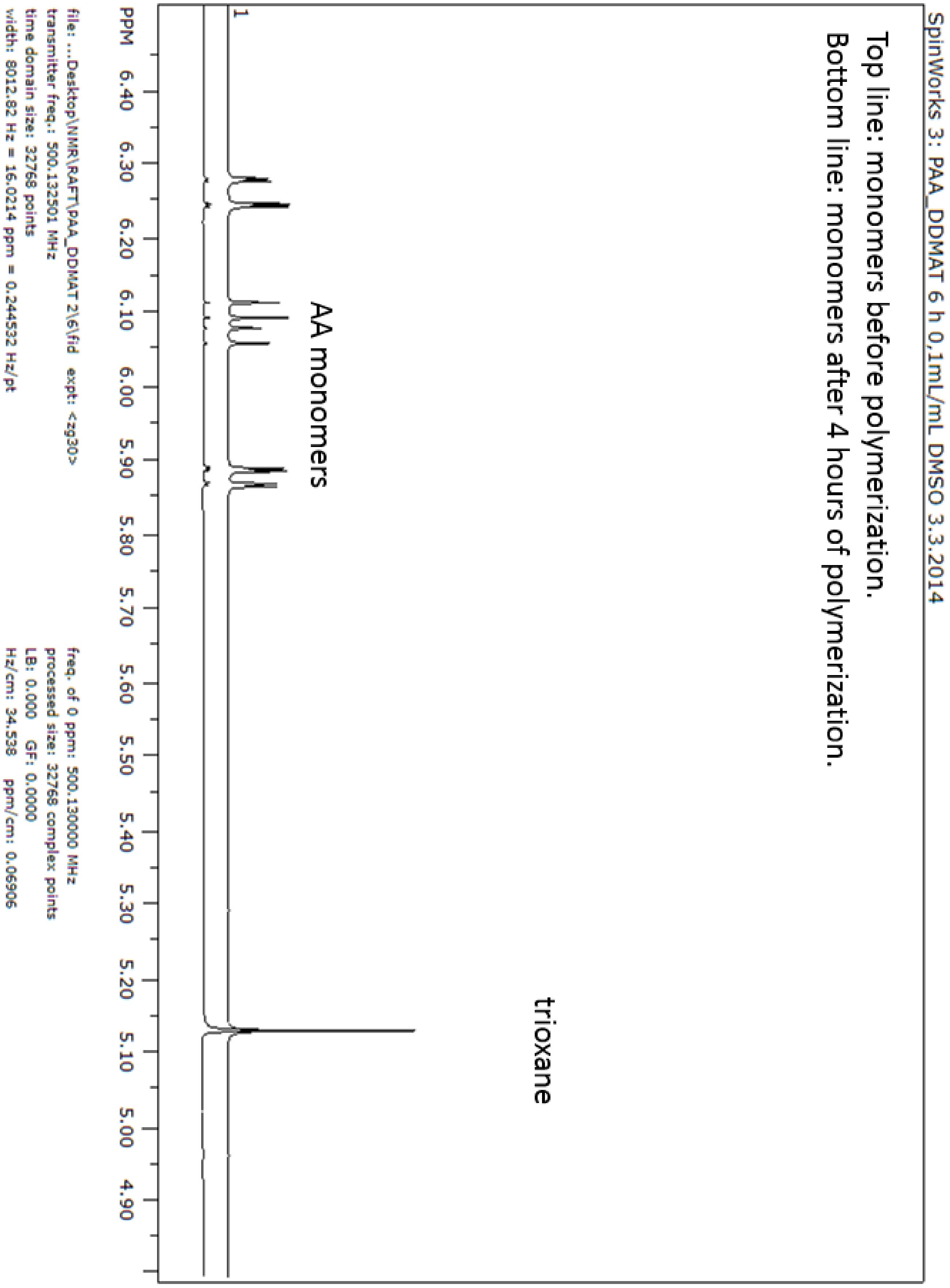
7. PEG_DDMAT standard



8. PEG_DDMAT fractions



9. PAA_DDMAT 3 polymerization



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