School of Chemistry

Department of Inorganic and Materials Chemistry

"Polymerisation of α-Pinene Methacrylate monomer via Cobalt Mediated Catalytic Chain Transfer Polymerisation (CCTP) and Thiol Reactions to yield oligomers"

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I. Abstract

Terpenes are renewable hydrocarbons found in nature. Their structural common characteristic is that they all contain unsaturated double bonds. However, early research has proven that homo polymerisation of these terpenes requires extreme conditions and results in low molecular weight polymers.[1, 2] Modification of these terpenes in two steps via hydroboration/oxidation and esterification respectively to produce a library of terpene (methacrylates) was carried out in the group.[1] In this study, α-Pinene Methacrylate (α-PMA) was the monomer under investigation.

This work focuses on the polymerisation of α-PMA via catalytic chain transfer polymerisation (CCTP) and thiol chain transfer agents with the aim to yield oligomers. The polymerisation of α-PMA via CCTP has been carried out using two different methods. The first uses a pre – prepared catalyst and second sees the formation of the catalyst 'in-situ'. The results of these experiments will be compared to establish which most effectively produces Poly (α-PMA) oligomers. Alongside this, the termination mechanism of free radical polymerisation of α-PMA has also been studied, with a preference towards disproportion being observed. In addition, thiol chain transfer agents were also studied for yield the P(α-PMA) oligomers.

II. Acknowledgements

I would like to thank and acknowledge the following people, not only during the course of this project, but throughout my master's degree. Firstly, I would like to express my gratitude towards my supervisors, Professor Steve Howdle and Professor Derek Irvine, for their unwavering support, valuable guidance and insight throughout this research project. Also, for giving me the opportunity to work on my project.

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Of course, this acknowledgment would not be complete, without thanking my parents and my sister, who supported me throughout my entire journey. My final thanks go to my mother, for always being there for me. Due to her loving support and faith in me, I was able to finish my study.

III. Declaration

I declare that the thesis is the result of my own work which has been mainly undertaken during my period of registration for this degree at The University of Nottingham. I have complied with the word limit for my degree.

Zeynep Onat

28TH September 2018

IV. List of Figures

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VI. List of Schemes

VII. List of Symbols

CCT	Catalytic Chain Transfer
CCTP	Catalytic Chain Transfer Polymerisation
FRP	Free Radical Polymerisation
CTA	Chain Transfer Agent
MWt	Molecular Weight
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
Đ	Dispersity
T_g	Glass Transition Temperature
α-PMA	α-Pinene Methacrylate
MMA	Methyl Methacrylate
PhCoBF	Bis – [(difloroboryl) diphenylglyoximato] Cobalt (II)
$CoBr_2$	Cobalt (II) Bromide
DMG	Dimethyl Glyoxime
DPG	Diphenyl Glyoxime
DDM	Dodecanemercaptan
AIBN	2,2’ – Azobis (2 – methylpropionitrile)
V-70	2,2’ – Azobis (4 – methoxy 2,4 dimethylvaleronitrile)
THF	Tetra Hydro Furan
$CDCl_3$	Chloroform – d
^1H - NMR	Proton Nuclear Magnetic Resonance

GPC	Gel Permeation Chromatography
DMA	Dynamic Mechanical Analysis

1 INTRODUCTION

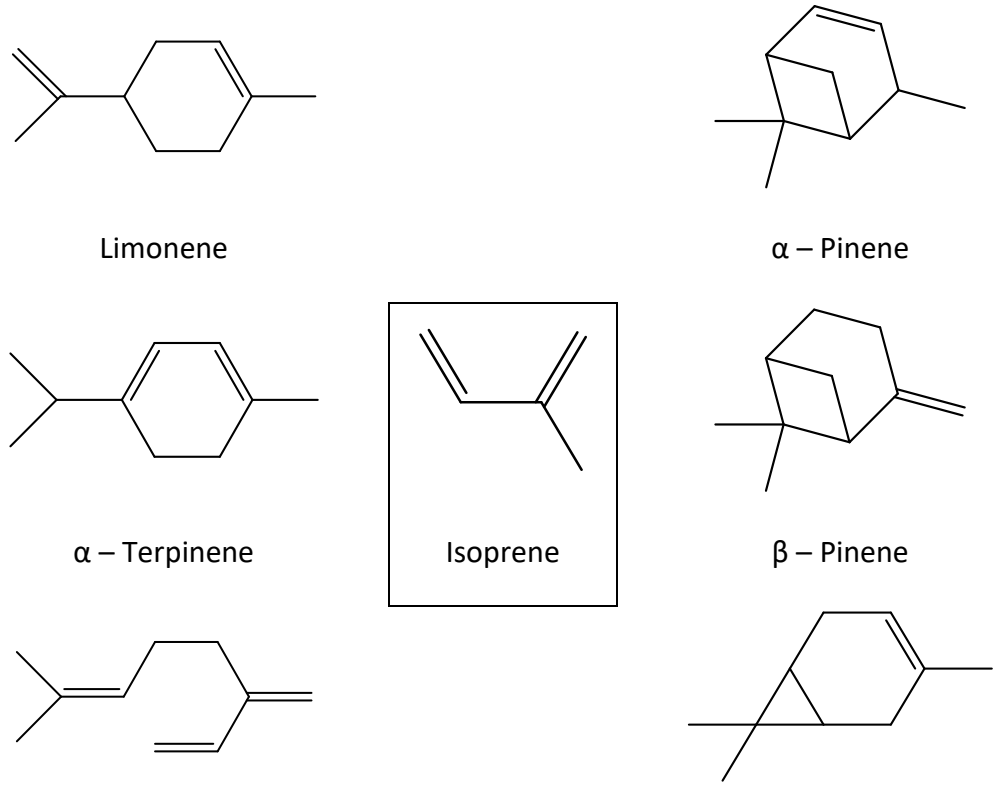
1.1 Terpenes and Terpenoids

As a result of scientific researches, scientists have been inspired by nature in all aspects of life and they have always used nature as an important source, just as in medicine and technology. As a vital part of this ecological system, plants are very abundant in nature. Nature is a system which has self – circulation, and waste is also part of this. Natural resources especially plants, have great potential as a source of production of fine chemical raw materials. In terms of being environmentally friendly, cost-effective, renewable and sustainable species, these qualities make them highly valuable resources. Terpenes also come under part of this plant family. They are the largest member of the natural product category. Due to their structural diversity, there are many different and wide ranges of application in the field of industry e.g. pharmaceuticals, cosmetics (perfumes, fragrances), flavorings and agricultural products etc.[3]

The most abundant terpenes in nature are pinenes. Production of α-Pinene and β-Pinene are about 330 KT per year.[4] In addition to this, another commercially available monoterpene which is limonene produces 60 KT annually in the citrus industry as a side product of citrus juice.[5] The α – Pinene and β – Pinene are the major components of wood turpentine. They are a member of bicyclic terpenes and can be procured from the resin of pine trees (*Pinus*) by steam – distillation.[6]

The molecular structures of terpenoids are contained common properties. They all have carbon backbones, comprising of isoprene units, which is 2-methylbuta-1,3- diene. Isoprene molecule involves five carbon atoms and due to this reason, the number of carbon atoms in any terpenoid is a multiple of five.[7] The name of

"terpene" was originally used for the hydrocarbons found in turpentine, the suffix "ene" indicates the presence of olefinic bonds.[7]



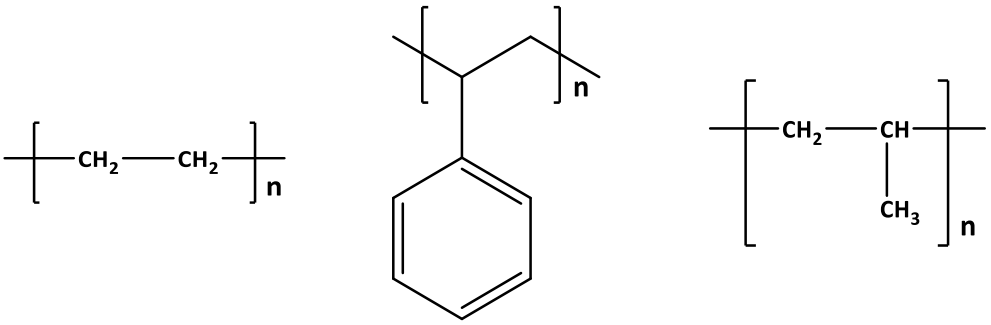
Scheme 1. Some common monoterpenes

In polymer science, terpenes are a potentially renewable and sustainable source of monomer. The emergence of the concept of direct polymerization of terpenes is not a new idea. In previous years, there has been some research works in this field. Alkene moieties in their structure are a possible opportunity for facile polymerization via free radical routes, using readily appropriate conditions. However, research has proven that homo polymerisation or terpenes are difficult.[2] In 2016, Howdle group handled this with a different point of view, and added acrylate and methacrylate functionalities on terpene structures via two

pathways.[1] The procedure was involved in two steps which were hydroboration/oxidation and esterification respectively.[1] Based on this, these functionalized terpene based monomers were found utilizable for standard free radical polymerisations and other controlled polymerisation techniques, to produce new polymers.[1]

1.2 Polymers

The word “polymer”, is derives from the Greek word “poly”, meaning “many” and “meros”, meaning “part”.[8] Hence, polymers are a macromolecular compound and comprise of many small repeating units that are known as monomers. Monomers having two active bonds are known as bifunctional polymer. Monomers with three or more active sites, they are known as polyfunctional polymers.[9] Factors increasing the monomer functionality and polymer chain are degree of polymerization (DP), number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity (Đ).[10] These impact key factors of analysis of polymer chain. The DP is shown with the symbol *n* that represents the repeating units (monomers) in the polymer chain. The molecular weight of polymer (MWt) increases as the number of chain increases. In other words, DP affects and correlates with the MWt of polymer. In Figure 1, poly(ethylene), poly(styrene) and poly(propylene) and their repeating units (*n*) are shown as an example of polymers.



Poly(ethylene) Poly(styrene) Poly(propylene)

Figure 1. Repeating units of some common polymers

There are a number of ways to express the molecular weight of a polymer. The M_n is the number average molecular weight, where the average DP is established and multiplied by the molecular weight of the individual monomer unit. M_w is the weight average molecular weight, this takes into account the molecular weight of the all chains. The larger molecular weight of an individual chain, the more that chain contributes to M_w. M_w is determined by methods that are sensitive to the molecular size rather than just their number, such as light scattering techniques. The dispersity Đ, is used as a measure of the broadness of a molecular weight distribution of a polymer. A monodisperse polymer is one where all the chains are equal length and will give a Đ of 1.0. Đ is defined as;

$$Đ = \frac{Mw}{Mn}$$

The structure of polymer chains affects the polymers properties. These structures can be linear, branched or cross-linked (Figure 2). Linear polymers are the polymers in which monomeric units are linked together to form long straight chains. The polymeric chains are stacked over one another to give well packed structure. As a result of close packing, these polymers have high densities, high tensile strengths and high melting points. Branched polymers are when the monomers are joined to form long chains with side chains or branches of different lengths. These branched chain polymers are regularly packed and therefore, they have low tensile strength, low density, boiling point and melting points than linear polymers. Cross – linked polymers are polymers in which monomer units are bonded together with strong covalent bonds to form a three – dimensional network. These polymers are hard, rigid and brittle because of their network structure. One of the most important properties of cross – linked polymers is that, they are thermosetting, which means, they cannot be melted or dissolved.

Linear Branched Cross – Linked

Figure 2. Polymer structures

Polymers have a wide range of applications in the industry. The most commonly used areas are known plastic and rubber industries.[11] They also take up considerable space in areas such as health, automotive, paint, textile. Many of the polymers used in these fields are petroleum – derived synthetic polymers.

Figure 3. Polymer architectures

The polymers properties are highly dependable on the structure of the polymer chain along with other factors which are mentioned later.[12] Linear polymers are the most common polymer chains produced due to the bonds in the chain being covalent directional. However, polymer chains can also be produce in different structures, such as branched, comb, star and bottle – brush[13-17] (Figure 3).

1.2.1 Homo Polymers

Polymer synthesis may include more than one type of monomer. In this case, there are different chemical structures throughout the polymer chain. As in the of poly(ethylene), homopolymer is used when there is a single chemical structure along the chain, and copolymer definitions are used in the case of two different monomer units. Copolymers synthesized from two different monomers (such as A and B) are also grouped according to their internal arrangement in the chain. In random copolymers, monomers in the chain are line up randomly. In alternating copolymers, the monomer units in the copolymers are arranged as in sequence in the polymer chain. In block copolymers, different monomer units are placed as

blocks in the polymer chain. Another copolymer structure is also known as graft copolymer. In graft copolymers, the other monomer units are located in the copolymer structure as a side chain, not on the main polymer of the chain.

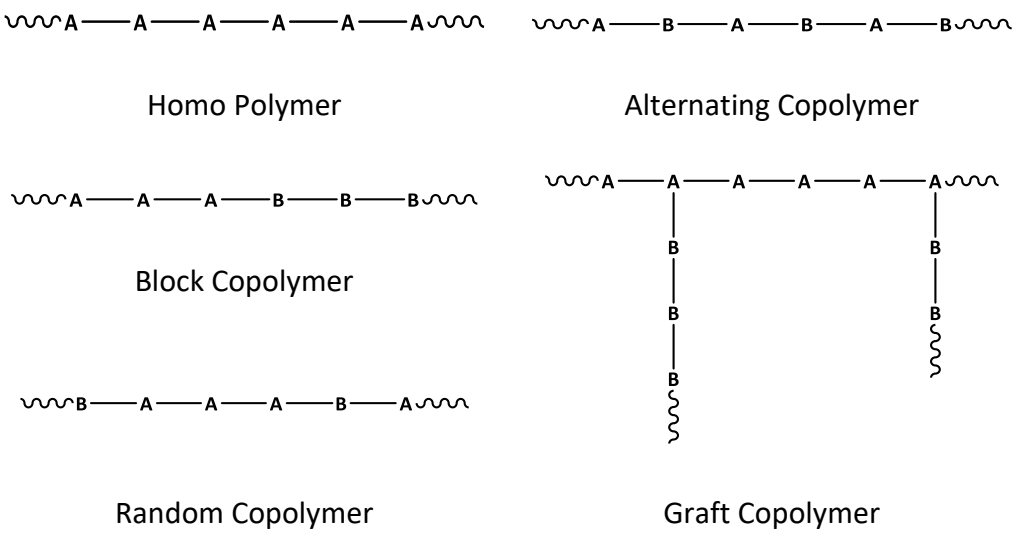


Figure 4. Illustrations of homopolymer and copolymers with different orders

1.3 Polymerisation Types

1.3.1 Free Radical Polymerisation

Free radical polymerisation (FRP) is a type of a chain – growth polymerisation. In FRP polymerization, the active ends of the growing polymer chains are unpaired electrons, i.e. radicals. With the participation of each new monomer to the chain, this radical is transferred to end – group of the chain and the chain continues to grow. For this reason, an initiator which can form free radicals in the polymerisation system to initiate FRP should be used in the presence of the monomers.

The FRP mechanism, like other chain – growth reactions are progressed in three steps which are initiation, propagation, and termination.[18] The initiators decompose, with heat or light to form free radicals (Scheme 2). The formation of radicals can be achieved in various ways. Organic azo compounds and peroxides are widely used initiators and degrade easily to give radicals with the effect of heat.

$$I \rightarrow 2R\cdot$$

Scheme 2. The cleavage of an initiator compound

In the initiation step, the newly formed free radicals can react with the double bonds of the monomers in the medium to form the first monomeric active center.

$$M + R\cdot \rightarrow RM\cdot$$

Scheme 3. The initiation process which involves the formation of monomer active center

The propagation step proceeds with the successive addition of monomers to the first monomer active center.

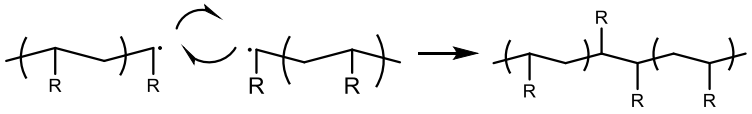
a. $RM\cdot + M \rightarrow RMM\cdot$

b. $RM_{x-1}\cdot + M \rightarrow RM_x\cdot$

*Scheme 4. The propagation process: **(a)** addition of a monomeric species to the primary radical or **(b)** a formed polymeric chain*

The free radicals from the initiator remain at the end of the chain while forming polymer chains by adding monomer molecules. For this reason, the initiator is not a catalyst. Beside the large polymer molecules, the added structures of the initiator to the end of the polymer chain does not significantly contribute to the polymers weight and its properties. For this reason, when the polymer structure is given, the molecular structures come from the initiator are not shown.

In termination step, reaction can proceed in two different ways. These are radical – radical coupling (combination) and disproportionation terminations. Combination termination, two active radical chains combine to produce a dead polymer chain with the high molecular weight.



Scheme 5. The radical – radical combination of a radical polymeric chain where a new C – C bond is formed by the combination of two radical chains

In the case of the disproportionation termination, one polymer extracts a hydride species from the chain of a second polymer resulting in one saturated chain end and one olefinic chain end.

Scheme 6. The disproportionation process of two polymeric radical chains which is followed by the formation of a saturated chain end and a olefinic chain end

1.3.1.1 Chain Transfer Agent

The molecular weight control of polymers is a subject of increasing interest because many of polymers properties, such as physical and mechanical properties, depend on the chain length.[19] In the conventional FRP, it is known that controlling of the polymer chain length is difficult to attain. As a solution, the common way of controlling MWt is the addition of a CTA to the polymerisation medium.[18] Chain transfer is basically a polymerization reaction by which the activity of a growing polymer chain is transferred to another molecule. Chain transfer can also occur to solvent, monomer or polymer.

Common CTAs include thiols, disulfides, halomethanes and other molecules with a readily abstractable hydrogen atom.[18] The general mechanism of chain transfer to CTA, proceeds in the form of hydrogen abstraction associated with the growing radical polymer chain ($P_i \cdot$) and the transfer agent (T). This forms a dead polymer chain and leaves a free radical on the CTA fragment that can be used for the initiation of the monomer.[19]

$$P_i \cdot + T \rightarrow P_i + T \cdot$$
$$T \cdot + M \rightarrow T - P_i \cdot$$

Scheme 7. The chain transfer reaction

The general chain transfer constant, C_s, is defined as the ratio of the chain transfer and the propagation rate coefficients, k_{ct}/k_p, and is a measure of the reactivity of a chain transfer agent. The higher C_s, the lower of the concentration of the CTA required to achieve a particular MWt reduction.[19] The decrease in the MWt that will be attained by the addition of a CTA is quantitatively given by the Mayo equation, which expresses the reciprocal of the degree of polymerisation (DP) as a function of the rate of the chain growth and the chain termination.[20]

$$\frac{1}{DP} = \frac{1}{(DP)_0} + C_s \frac{[CTA]}{[M]}$$

Equation 1. The Mayo equation

In the Equation 1, DP is the degree of polymerisation, $(DP)_0$ is the degree of polymerisation with no CTA, C_s is the chain transfer constant, $[CTA]$ is the concentration of the chain transfer agent, [M] is the monomer concentration.

1.3.2 Catalytic Chain Transfer Polymerisation

Catalytic Chain Transfer Polymerisation (CCTP), is an established very successful and efficient technique employed in free radical polymerization to allow access to low molecular weight vinyl polymers containing an unsaturated double bond end – group.[21, 22, 23, 24] CCTP is mediated by catalytic quantities of a low spin Co(II) complexes which is significantly enhanced the process of chain transfer to monomer during radical polymerization.[25] The most commonly used and commercially available low spin Co(II) catalyst is known as bis[(difluoroboryl) diphenylglyoximato] cobalt (II) (PhCoBF) (Figure 5).

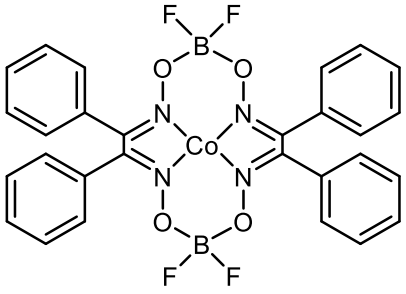
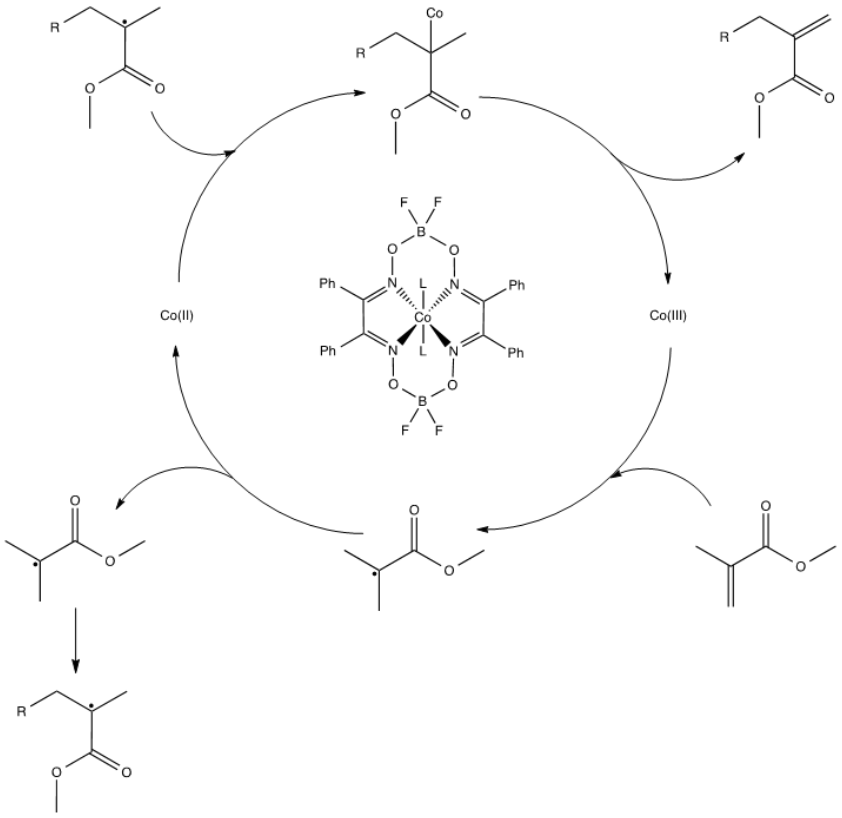


Figure 5. Structure of bis[(difluoroboryl) diphenylglyoximato] cobalt (II) (PhCoBF)

One of the most striking features of CCT is the exceptionally fast rate at which it takes place. The MWt of a polymer can be reduced from tens of thousands to several hundred Dalton (Da), utilizing only ppm concentrations of cobalt catalyst.[25]

The chemistry of low molecular weight oligomers has been relatively unexplored for several reasons. Previous routes to oligomers involved complicated and expensive chemistry, while, thiol chain termination required high levels of toxic or malodorous sub products making use of these CTA unacceptable in different application.[18] This chain end functionality is suitable for further polymerisations and for the synthesis of various polymer architectures. Thus, this technique is a very efficient and versatile polymerisation which have found applications in a wide range of fields.[26] For instance, Haddleton and co – workers have used CCTP, for the polymerisation of divinyl monomers to synthesise a family of branched polymers, which retain vinyl functionality; a range of decorated branched polymers have been prepared via thio – Michael addition.[27]

The disadvantages of CCTP occurs in precipitation step of the produced polymer. The catalyst may need to be removed from the reaction mixture. However, this usually needs a large volume of organic solvent that is not environmentally friendly.



Scheme 8. CCTP catalytic cycle of Methyl Methacrylate (MMA), the cobaloxime catalyst go through to the oxidation state Co^{II} to Co^{III}

The CCTP mechanism is a cycled mechanism and it involves in a two – step process. [28] [25, 26, 29] (Scheme 8). In the first step, Co^{II} complex interacts with the growing polymer chain leading to an intermediate Co^{III} – H complex, called cobalt hydride, and a dead polymer chain terminated with a double bond. In step two, this Co^{III} – H complex reacts with a monomer to form a new monomeric radical and reform the Co^{II} catalyst.[30] However, for mono – substituted monomers the mechanism is slightly different due to the lack of an α-methyl group. It is thought that in this case a hydrogen is abstracted from a secondary position in the polymer backbone, which is less sterically and electronically favourable. This also means that the polymer formed is not terminated with a vinyl group and instead a double bond is

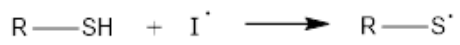
present between the penultimate and last repeating units. Hydrogen abstraction at the α-methyl substituent is more efficient and monomers containing a α-methyl group are therefore very active in CCTP.[25]

1.3.3 Thiol – Ene Chemistry

Tihol – ene reactions have a wide range of applications in chemistry such as, modification of polymeric materials, and fabrication of a wide range of polymeric materials.[31]

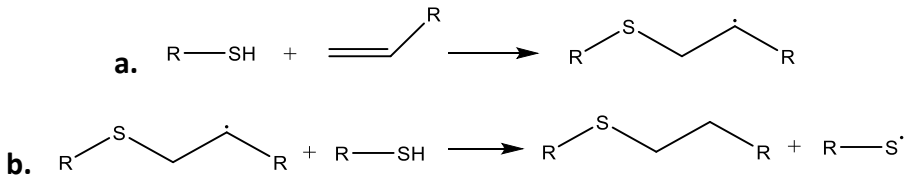
The interest on thiol – ene reactions has been increased in recent years. The reason for that, a versatile and very effective method in providing functionality to the molecules with double bonds.[32] Thiol – ene polymerisations are step – growth radical polymerisation involving a reaction between multifunctional thiol and – ene (vinyl) monomers such as methyl methacrylate and styrene.[18]

The general mechanism of thiol – ene reaction is conducted under standard radical conditions. Under such conditions it proceeds via a typical FRP process with initiation, propagation and termination steps. Initiation involves the treatment of a thiol with a radical initiator in order to generate the thiyl radical via the hydrogen abstraction from the thiol backbone.



Scheme 9. The initiation process contemplates the formation of a thyil radical after hydrogen abstraction from the thiol backbone

Propagation is a two – step process involving first the direct addition of the thiyl radical across the C = C bond. This reaction is followed by the chain transfer of the radical to a thiol functional group, regenerating a thiyl radical, which then restarts the process. Possible termination reaction involves typical radical – radical coupling process.



*Scheme 10. Propagation process which involves the formation of a polymeric radical chain **(a)** and its termination with the regeneration of a thyl radical which can restart the process **(b)***

2 EXPERIMENTAL SECTION

2.1 Materials

α-Pinene Methacrylate (α-PMA, Cornelius Specialist), cyclohexanone (Acros Organics and Scientific Laboratory Supplies), bis-[(difloroboryl) diphenylglyoximato] cobalt (II) (PhCoBF, DuPont), cobalt (II) bromide (Acros Organics), dimethyl glyoxime (DMG, Acros Organics), diphenyl glyoxime (DPG, Alfa Aesar), 2,2'-Azobis(2-methylpropionitrile) 98% (AIBN, Fluoro Chem), 2,2'-Azobis (4-methoxy 2,4 dimethylvaleronitrile) (V-70, Wako), 1-Dodecane thiol (DDM, Alfa Aesar), mercaptosuccinic acid (Sigma Aldrich), 3-Mercaptopropionic acid (Sigma Aldrich), aluminum oxide (Sigma Aldrich), tetrahydrofuran (THF, Fisher Scientific), tetrahydrofuran HPLC – Grade (Fisher Scientific), methanol (Fisher Scientific), hexane (Fisher Scientific), chloroform-d ($CDCl_3$, Sigma Aldrich) were purchased and used without purification. Methyl Methacrylate (MMA, Kaneka Belgium) was passed through basic aluminum oxide to remove the inhibitors before use. All reactions were carried out in sample vials.

2.2 Characterization of Polymers

2.2.1 Nuclear Magnetic Resonance - ^1H – NMR

^1H – NMR spectrum were recorded using a Bruker Avance 400 MHz and Bruker Avance III 400 MHz spectrometers. Chemical shifts were recorded in δ_H (ppm). Samples were dissolved in deuterated chloroform ($CDCl_3$ – d) to which chemical shifts are referenced (residual chloroform at 7.26 ppm).

2.2.2 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was performed using a triple detection Agilent 1260 Infinity HPLC equipped with a differential refractive index, a viscometer, a UV detector and a multi – angle light scattering detector. Two Agilent mixed C columns kept at 40 °C were employed, using THF as the mobile phase with a flow rate of 1 ml/min. GPC samples were prepared in HPLC – Grade THF and filtered through 25 µm filters. The analysis was carried out using Astra as software. The number average molecular weight (M_n) and dispersity (Đ) were calculated using the refractive index increment specific to each polymer. The *dn/dc* used for PMMA 0.089 and for P(α-PMA) was 0.106.

2.2.3 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was used for determination of the polymer's T_g point. Measurements were performed on a Triton Technologies DMA using the powder pocket accessories. For each measurement, the sample (40 mg ± 5 mg) was weighed into a powder pocket. Samples were measured at 1 and 10 Hz. In single cantilever bending geometry between -100 – 250 or -50 – 200 °C depending on the region of interest. The value of T_g was taken as the peak of the tan delta (tan δ) curve.

2.3 Synthesis of The Polymers

2.3.1 General FRP Polymerisation Procedure of Methyl Methacrylate

The following was used as a typical procedure for the synthesis of poly (methyl methacrylate) (PMMA). The initiator V-70 (0.8 g, 2.59 mmol) with different concentrations (Table 1. Various concentrations of V-70 in FRP for MMA monomer) was added to a vial and dissolved in cyclohexanone (4 mL). The monomer MMA (1 g, 9.988 mmol) was added to the same vial which was then sealed, followed by degassing with argon for 30 minutes. Following degassing, the reaction was heated at 45 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into hexane at 0 °C. The resultant polymer was analysed via ^{1}H – NMR and GPC.

Table 1. Various concentrations of V-70 in FRP for MMA monomer

Code	Methyl Methacrylate (g)	Cyclohexanone (mL)	V – 70 (g)	Time (h)
FM1	1	4	0.08	1
FM2	1	4	0.09	1
FM3	1	4	0.1	1

a) *Determined by ^{1}H – NMR.*

b) *Determined by GPC, PMMA dn/dc = 0.089.*

2.3.2 General FRP Polymerisation Procedure of α-Pinene Methacrylate

The following was used as a typical procedure for the synthesis of poly (α-pinene methacrylate) (P(α-PMA)). The initiator V-70 (0.005 g, 0.016 mmol) with different concentrations (Table 2. Various concentrations of V-70 in FRP for α-PMA monomer) was added to a vial and dissolved in cyclohexanone (4 mL). The monomer α-PMA (1 g, 4.504 mmol) was added into the same vial which was then sealed, followed by degassing of the monomer with argon for 30 minutes. Following degassing, the reaction was heated at 45 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into methanol at 0 °C. The resultant polymer was analysed via ^{1}H – NMR and GPC.

Table 2. Various concentrations of V-70 in FRP for α-PMA monomer

Code	α-Pinene Methacrylate (g)	Cyclohexanone (mL)	V-70 (g)	Time (h)
FP1	1	4	0.005	22
FP2	1	4	0.01	22
FP3	1	4	0.02	3
FP4	1	4	0.03	3
FP5	1	4	0.04	1
FP6	1	4	0.05	1
FP7	1	4	0.06	1
FP8	1	4	0.07	1
FP9	1	4	0.08	1
FP10	1	4	0.09	1
FP11	1	4	0.1	1

2.3.3 General CCTP Procedure of α-Pinene Methacrylate

A typical CCTP procedure for the synthesis of P(α-PMA) was used as followed; the initiator AIBN (0.025 g, 0.152 mmol) and PhCoBF (1.5 mg, 0.0024 mmol) at various concentrations (Table 3. Various PhCoBF concentration for α-PMA at 80 °C for 24 h were added to a vial and dissolved in cyclohexanone (2.5 mL). The monomer α-PMA (2.5 g, 11.261 mmol) was added into the same vial which was then sealed, followed by degassing with argon for 30 minutes. Following degassing, the reaction was heated at 80 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into methanol at 0 °C. The resultant polymer was analysed via ^{1}H – NMR, GPC and DMA.

Table 3. Various PhCoBF concentration for α-PMA at 80 °C for 24 h

Code	PhCoBF (ppm)	PhCoBF (mg)	α-PMA (g)	Cyclohexanone (mL)	AIBN (g)
C1	600	1.5	2.5	2.5	0.025
C2	700	1.75	2.5	2.5	0.025
C3	800	2	2.5	2.5	0.025
C4	1000	2.5	2.5	2.5	0.025
C5	1190	3	2.5	2.5	0.025
C6	1300	1.3	1	1	0.015

2.3.4 General Procedures of *'in-situ'* CCTP for Methyl Methacrylate

A typical CCTP *'in – situ'* procedure for the synthesis of PMMA was followed by the initiator AIBN (0.005 g, 0.030 mmol) was added to a vial and dissolved in cyclohexanone (1 mL). Then, the initiator was degassed separately with argon. DMG (0.6 mg, 0.005 mmol) or DPG (0.6 mg, 0.002 mmol) and $CoBr_2$ (0.6 mg, 0.003 mmol) with different concentrations (Table 4) were dissolved in cyclohexanone (3 mL) and added to a vial. The monomer MMA (1 g, 9.987 mmol) was added into the same vial which was then sealed, followed by degassing with argon for 30 minutes. Following degassing, the reaction was heated at 80 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into hexane at 0 °C. The resultant polymer was analysed via ^1H – NMR, GPC.

Table 4. Various DMG, DPG and $CoBr_2$ concentrations of CCTP 'in – situ' reactions for MMA monomer

ppm	$CoBr_2$ (mg)	DMG / DPG (mg)
600	0.6	0.6
800	0.8	0.8
1000	1	1

2.3.5 General Procedures of *'in-situ'* CCTP for α-Pinene Methacrylate

A typical CCTP *'in – situ'* procedure for the synthesis of P(α-PMA) was followed by the initiator AIBN (0.005 g, 0.030 mmol) was added to a vial and dissolved in cyclohexanone (1 mL). Then, the initiator was degassed separately with argon. DMG (0.6 mg, 0.005 mmol) or DPG (0.6 mg, 0.002 mmol) and $CoBr_2$ (0.6 mg, 0.003 mmol) with different concentrations (Table 5) were dissolved in cyclohexanone (3 mL) and added to a vial. The monomer α-PMA (1 g, 4.504 mmol) was added into the same vial which was then sealed, followed by degassing with argon for 30 minutes. Following degassing, the reaction was heated at 80 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into methanol at 0 °C. The resultant polymer was analysed via ^1H – NMR, GPC and DMA.

Table 5. Various DMG, DPG and $CoBr_2$ concentrations of CCTP 'in – situ' reactions for α-PMA monomer

Code	ppm	$CoBr_2$ (mg)	DMG (mg)	DPG (mg)
CP1	**600**	0.6	0.6	-
CP2	**700**	0.7	0.7	-
CP3	**800**	0.8	0.8	-
CP4	**900**	0.9	0.9	-
CP5	**1000**	1	1	-
CP6	**600**	0.6	-	0.6
CP7	**700**	0.7	-	0.7
CP8	**800**	0.8	-	0.8

2.3.6 General Procedures of thiol reactions for α-Pinene Methacrylate

General thiol reaction procedure for the synthesis of P(α-PMA) was followed by the initiator AIBN (0.005 g, 0.030 mmol), 1-Dodecane thiol (DDM) (0.1 g, 0.49 mmol) (Alfa Aesar), Mercaptosuccinic acid (0.1 g, 0.666 mmol) (Sigma Aldrich) or 3-Mercaptopropionic acid (0.1 g, 0.942 mmol) (Sigma Aldrich) with different concentrations (Table 6) were added to a vial and dissolved in cyclohexanone (1,5 mL). The monomer α-PMA (1 g, 4.504 mmol) was added into the same vial which was then sealed, followed by degassing with argon for 30 minutes. Following degassing, the reaction was heated at 65 °C under argon. After 24 hours, the reaction was stopped by exposure to air. The reaction mixture was dissolved in THF followed by precipitation into methanol at 0 °C. The resultant polymer was analysed via ^{1}H – NMR, GPC and DMA.

Table 6. Various DDM, Mercaptosuccinic acid and 3-Mercaptopropionic acid concentrations with the 0.5 % wt. AIBN initiator to 1 g α-PMA at 65 °C for 24 h.

Code	Cyclohexanone (mL)	DDM (g)	Mercaptosuccinic acid (g)	3-Mercaptopropionic acid (g)
T1	1.5	0.1	-	-
T2	1.5	0.3	-	-
T3	1.5	0.5	-	-
T4	1.5	-	0.1	-
T5	3*	-	0.3	-
T6	3*	-	0.5	-
T7	1.5	-	-	0.1
T8	1.5	-	-	0.3
T9	1.5	-	-	0.5

** Mercaptosuccinic acid in cyclohexanone was oversaturated. Because of this reason, solvent concentrations were doubled in the reactions of Codes – T5 and T6.*

3 RESULTS and DISCUSSIONS

This project has been focused on the polymerisation of α-Pinene Methacrylate (α-PMA), a methacrylate derived, natural and terpene-based monomer. There have been some established papers about the polymerisation of this monomer as an example so far.[1, 33, 34] The main idea of this project has been that controlling the molecular weight of the P(α-PMA) and yield lower molecular weight (M_n) polymers (oligomers). Catalytic Chain Transfer Polymerisation (CCTP) is an effective polymerisation type to control the M_n of the polymers. However, in literature, there has not been any study on the polymerisation of α-PMA monomer via CCTP, yet.

Methyl Methacrylate (MMA) is a well – known monomer in the literature and various papers have been published about the polymerisation of MMA.[35-37] For these reasons, MMA was used as a test monomer to make a comparison with α-PMA. For this purpose, the first step of the project was the Free Radical Polymerization (FRP) of MMA.

FRPs have been studied for the investigation of the fundamental kinetics of the monomer MMA. According to the ^1H – NMR results of the final product, the polymerization process of Poly (Methyl Methacrylate) (PMMA) via FRP have been terminated as disproportion termination. This double bond end – group in ^1H – NMR spectrum has proved this termination.

In the ^1H – NMR spectrum, the MMA peaks have been shown by the color turquoise and PMMA peaks has been shown by the maroon color. The MMA's double bond peaks (Hx and Hy) were in δ 6.10 (dq, 1H), 5.55 (p, 1H) while the proton (Hz) related to the bulky group was at δ 3.74 (s, 3H). On the other hand, in the polymer spectrum shifting were observed in terms of chemical shifts. In particular the PMMA double bond end – group (Ha and Hb) peaks were seen in δ

6.20 (dq, 1H), 5.47 (p, 1H), and the bulky group proton (Hc) was in 3.74 (m, 3H). Finally, the polymer peak (Hf) was in δ 3.60 (s, 3H)

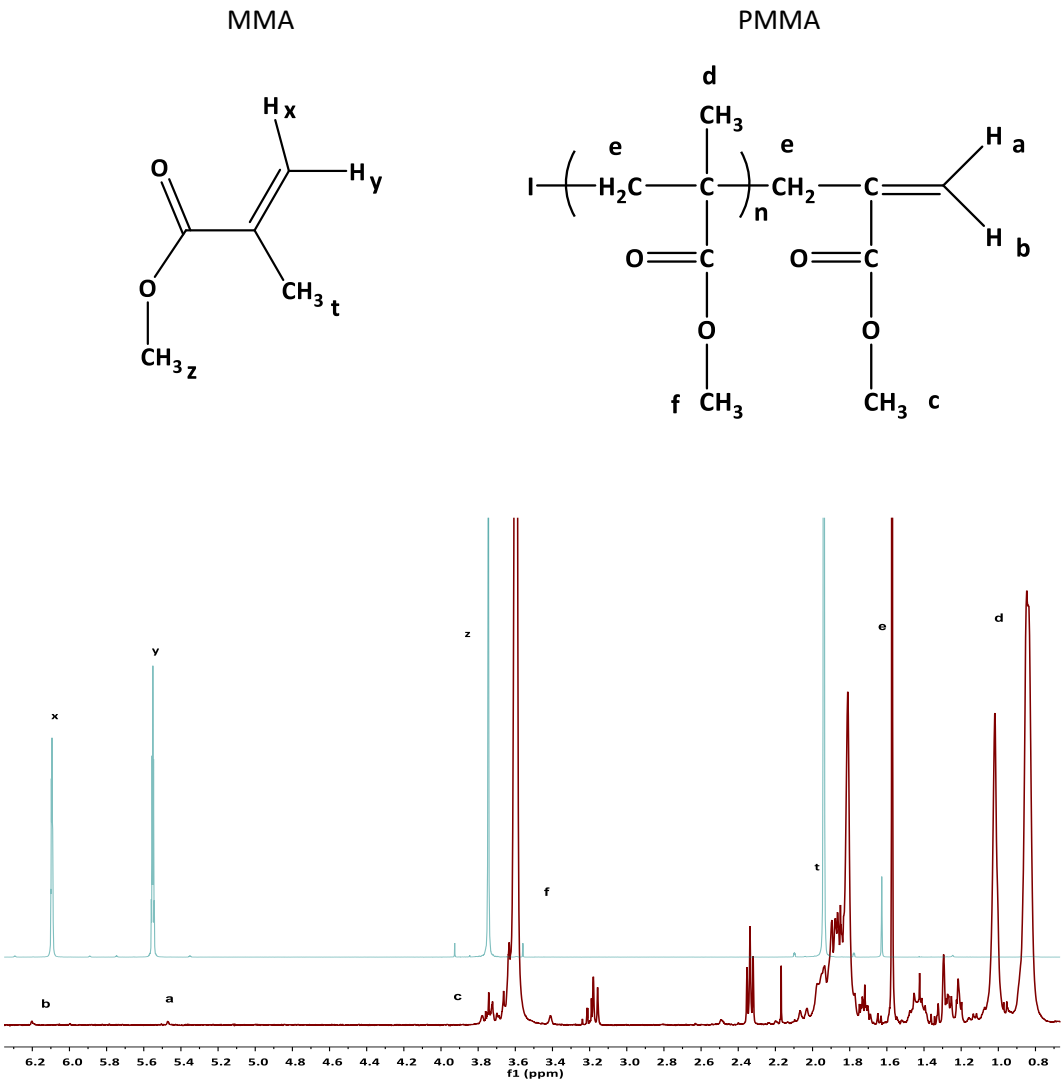
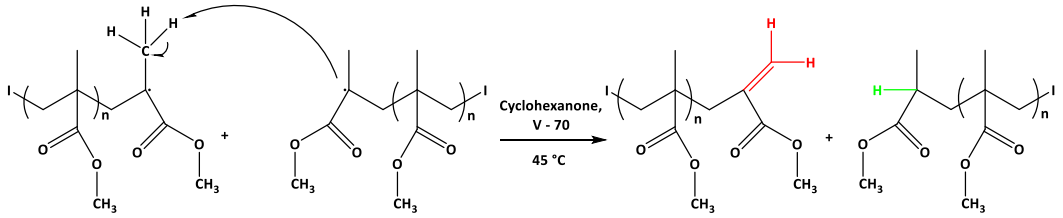


Figure 6. The ^{1}H – NMR analysis of PMMA in $CDCl_3$, synthesised via FRP

^{1}H NMR (400 MHz, ppm, Chloroform-d) δ 0.84 – 1.02 (t, 3H, -$CH_2C(CH_3)$), 1.57 (q, 2H, CH_3CCH_2), 3.60 (s, polymer peak), 3.74 (p, 3H, $COOCH_3$), 5.47 (p, 1H, $HCHCOOCH_3$), 6.20 (dq, 1H, $HCHCOOCH_3$).

On the other hand, the disproportionation percentage of the PMMA has been calculated between 66 – 78%. This calculation method was that the degree of polymerisation (DP) value (calculated from GPC results) multiplied by 3 (because of the 3 protons of the methyl group in the MMA), and polymer peak in the ^{1}H – NMR spectrum integrated and normalized to the final value. Then, the proton peaks integrated. Considering the disproportionation rate as 100%, the double bond end – group and the saturated end chain should be 50%, respectively (Scheme 11). So, the integrated double bond end – group proton peaks divided by 0.5 and the disproportionation rate has been calculated.



Scheme 11. The disproportionation termination of PMMA via FRP at 45 °C

There have been three FRP reaction series studied for MMA monomer. In these reactions the initiator concentration was increased (0.08 – 0.1 g) with the purpose of reducing the M_n of the final polymer product. Synthesis of the lower molecular weight polymers have been allowed to see the double bond end – group in ^{1}H – NMR spectrum more clearly. The results have been given in Table 7.

Table 7. Results of P(MMA) in FRP at 45 °C

Code	V – 70 (g)	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	DP[b]
FM1	0.08	42	8400	12000	1.47	84
FM2	0.09	43	10000	17000	1.66	100
FM3	0.1	43	7800	16000	2.03	78

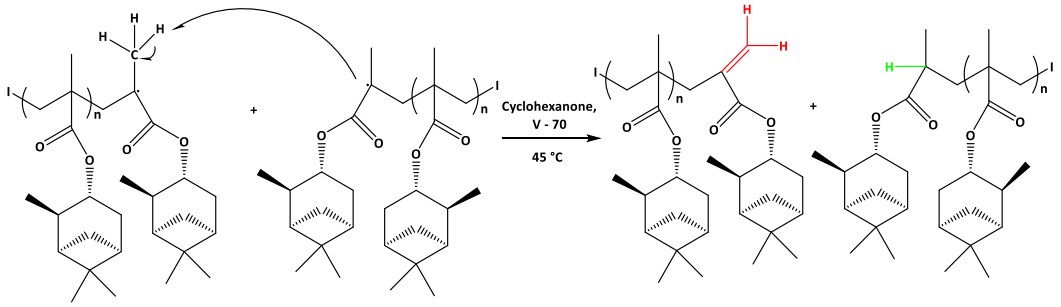
a) *Determined by ^1H – NMR.*

b) *Determined by GPC, PMMA dn/dc = 0.089.*

In these set of reactions, no chain transfer agents were used for the control of the molecular weight. The M_n of the FM2 was the highest, around 10,000 g mol^{-1}. The reason of this higher M_n polymer might be related with the decomposition of the V-70. In fact, the initiator has not been completely decomposed and caused the higher M_n of the PMMA. On the other hand, FM1 and FM3 have shown a reduction of M_n from 8,400 g mol^{-1} to 7,800 g mol^{-1} with the increased of the initiator concentration.

The experiments with MMA have been used as proof of concept for the application of FRP to methacrylate derivate monomers. In light of these results, the following experiments have seen the polymerisations of a new synthetic monomer bearing a methacrylate functionality, the α-PMA. The kinetic study was conducted in order to study the polymerisation properties of such monomer. α-PMA concentrations were kept constant where the V-70 concentrations have been increased, as same as in the previous work with MMA.

α-PMA terminated with disproportionation termination and double bond end – group has been seen in ^{1}H – NMR spectrum (Figure 7). The disproportionation percentage of the P(α-PMA) has been calculated as 60%. This calculation method contemplates the polymer peak in the ^{1}H – NMR spectrum integrated and normalized to the degree of polymerisation (DP) value (calculated from GPC results). Then, the double bond end – group proton peaks was integrated. Considering the disproportionation rate as 100%, the double bond end – group and the saturated end chain should be 50%, respectively (Scheme 12). So, the integrated double bond end – group proton peaks divided by 0.5 and the disproportionation rate has been calculated.



Scheme 12. The disproportionation termination of P(α-PMA) via FRP at 45 °C

In the ^{1}H – NMR spectrum below, α-PMA and P(α-PMA) peaks have been shown using the color turquoise and the maroon color, respectively (Figure 7). The α-PMA's double bond peaks (Hx and Hy) were in δ 6.08 (dq, 1H) and 5.52 (p, 1H) while the proton (Hz) related to the bulky group was at δ 5.08 (ddd, 1H). On the other hand, in the polymer spectrum shifting were observed in terms of chemical shifts. In particular the P(α-PMA) double bond end – group (Ha and Hb) peaks were seen in δ 6.16 (dt, 1H), 5.67 (dt, 1H), the bulky group proton (Hc) was in δ 5.22 (ddd, 1H).

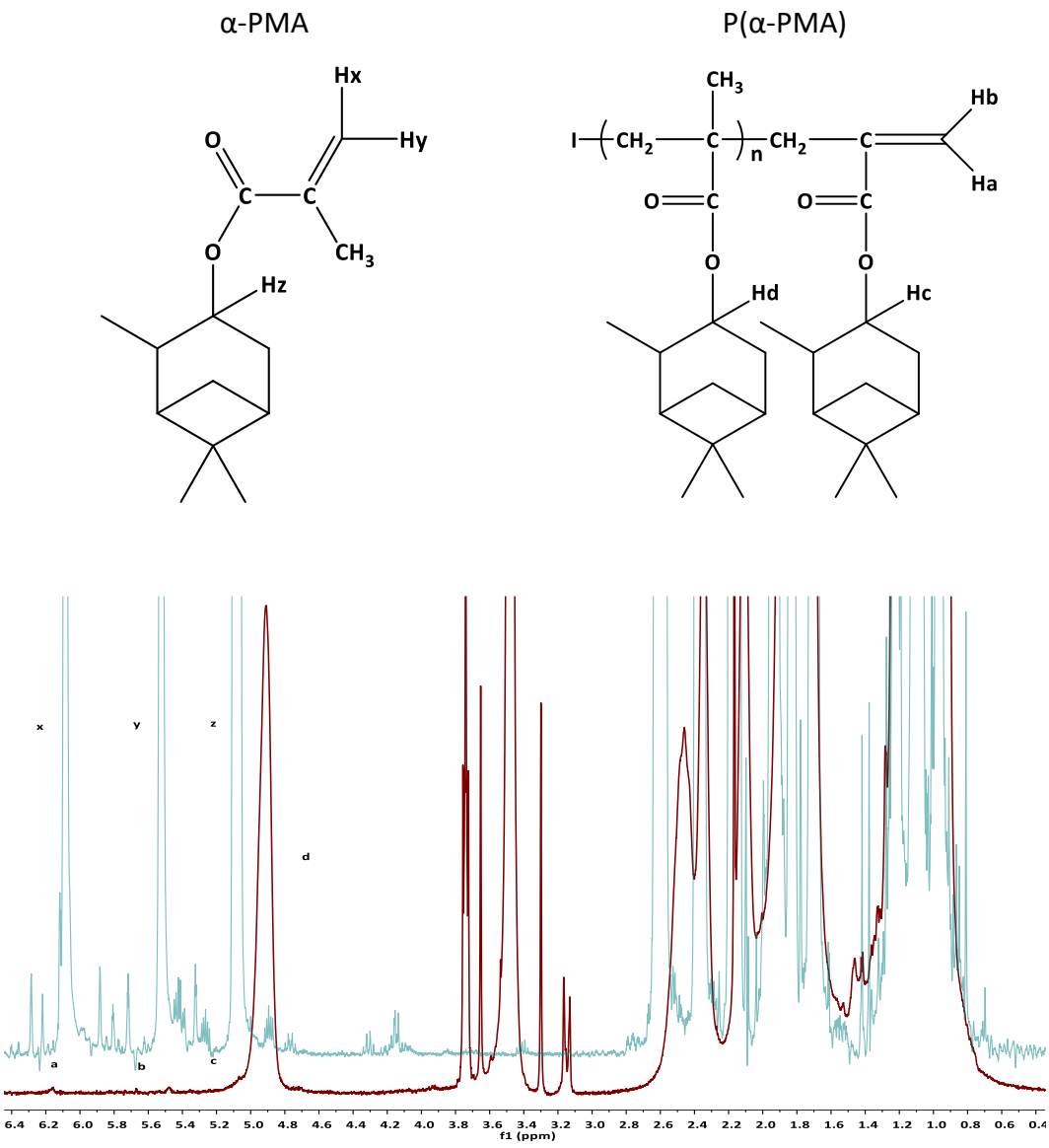


Figure 7. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$, synthesized via FRP

*^{1}H NMR (400 MHz, ppm, Chloroform-d) δ 6.16 (dt, 1H, **H**(CH)C(CH_2)), 5.67 (dt, 1H, H(C**H**)C(CH_2)), 5.22 (ddd, 1H, HC(C**H**)CH_2), 4.91 (s, polymer peak), 2.45 (q, 2H, CH_3C(C**H_2**)), 2.35 (dtd, 1H, (CH_3)**H**CHCH), 2.11 (dd, 2H, CH(C**H_2**)CH), 1.88 (q, 1H, CH(C**H**)CH_2), 1.80 (m, CH(CH_2)C**H**(CH_2)), 1.59 (s, 6H, -C(C**H_3**)), 1.22 (d, 3H, -CH(C**H_3**)), 1.06 (m, 1H, (CH_3)CHC**H**(CH_2)CH), 0.94 (t, 3H, -CH_2C(C**H_3**)).*

The reaction termination step has been influenced by the fast increasing of the concentration of radical species in the reaction system. These phenomena also have been decreased the polymer's conversion leading to lower molecular weight polymers. Table 8 shows the results of P(α-PMA) via FRP.

Table 8. Results of P(α-PMA) in FRP at 45 °C

Code	V-70 (g)	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	DP[b]
FP1	0.005	89	100000	230000	2.29	450
FP2	0.01	92	49000	100000	2.15	220
FP3	0.02	76	32000	66000	2.04	144
FP4	0.03	76	31000	57000	1.87	139
FP5	0.04	51	30000	61000	2.01	135
FP6	0.05	54	21000	43000	2.06	94
FP7	0.06	53	24000	48000	2.01	108
FP8	0.07	53	28000	52000	1.84	126
FP9	0.08	58	17000	30000	1.80	76
FP10	0.09	62	15000	24000	1.63	67
FP11	0.1	62	16000	25000	1.52	72

a) Determined by ^1H – NMR.

b) Determined by GPC, P(α-PMA) dn/dc = 0.106.

According to the table, it has been observed that the molecular weights have shown a downward trend with the increasing of the V-70 concentration. The highest M_n of P(α-PMA) was synthesized around 100,000 g mol^{-1}. As shown by FP11, increased initiator concentration significantly decreased the M_n to 16,000 g mol^{-1}. In some experiments, where the concentration of the initiator was low (0.05 g), the M_n of the polymers were higher than the M_n of the polymers synthesized with high initiator concentration (0.06 g and 0.07 g) (Codes – FP6, FP7, FP8 and Codes – FP10 and FP11). This irregular trend has been shown in the GPC trace below in Figure 8. The reason for this higher M_n is related to the initiator decomposition issue already discussed in the FRP of MMA.

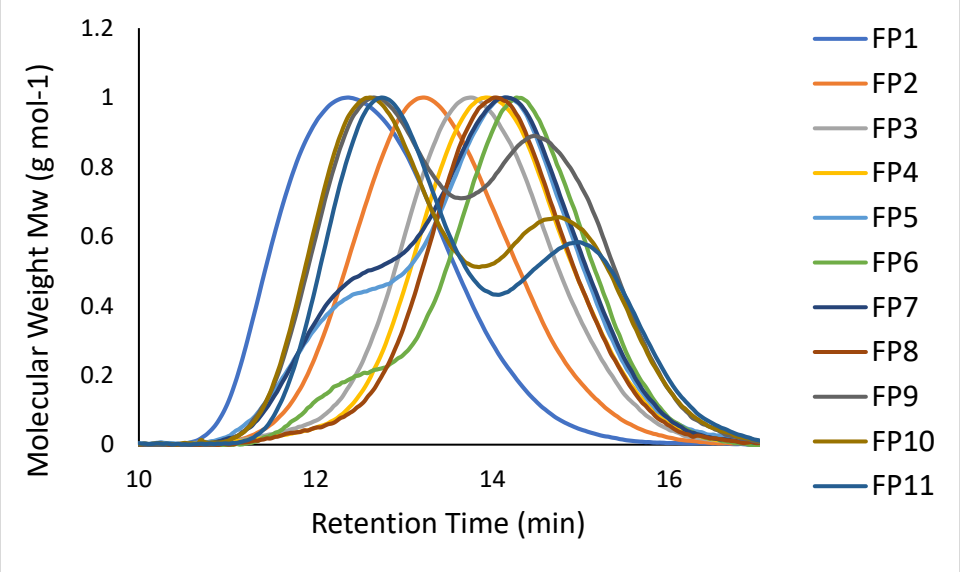
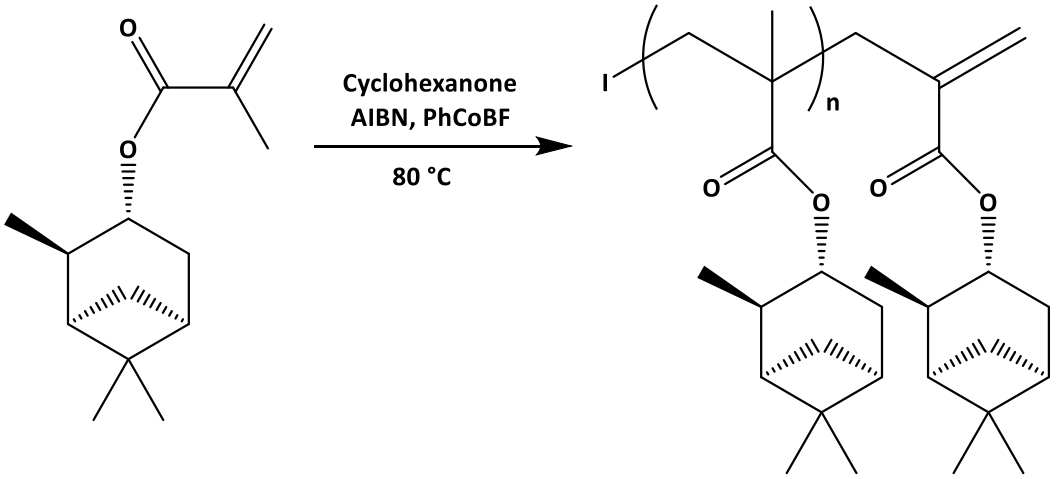


Figure 8. The GPC Trace of FRP for P(α-PMA)

In conclusion, α-PMA is a suitable monomer for the FRP resulting in high molecular weight polymers. The following experiments have been focused on the controlling of the M_n of P(α-PMA). For this aim, Catalytic Chain Transfer Polymerisation (CCTP) was exploited and cobalt based catalyst was used in the reactions. In this project, CCTP was the main polymerisation technique for the synthesis of P(α-PMA) oligomers because of the termination of the mechanism (Scheme 13). As mentioned in previous section (1.3.2), CCTP terminates the mechanism with a double bond end – group and gives macromonomers. This is highly important for further polymerisations and also, adding different functionalities on P(α-PMA).



Scheme 13. The reaction scheme of P(α-PMA) via CCTP

Before starting the series of CCTP reactions, FRP reactions were studied for both; α-PMA and MMA monomers using a different initiator, AIBN. MMA was again used as a test monomer before moving on the α-PMA. These FRPs gave the highest molecular weights of the polymers obtained so far (54,000 g mol^{-1}) which is considered as the threshold baseline. The results have shown in Table 9. FRP results of Poly (α-PMA) and PMMA with AIBN azo initiator at 80 °C for 24 h

Table 9. FRP results of Poly (α-PMA) and PMMA with AIBN azo initiator at 80 °C for 24 h

Code	Monomer	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	DP[b]
F1	α-PMA	96	54000	130000	2.37	243
F2	MMA	91	29000	45000	1.55	290

a) Determined by ^1H – NMR.

b) Determined by GPC, P(α-PMA) dn/dc = 0.106, PMMA dn/dc = 0.089.

CCTP reactions were then studied, in order to compare the effect of the catalyst concentrations on the molecular weights of the polymers to aim at oligomers. ^1H – NMR spectrum for CCTP of α-PMA (Figure 9), the color turquoise represented to monomer α-PMA peaks and the color maroon represented the P(α-PMA). The α-PMA's double bond peaks (Hx and Hy) were in δ 6.11 (dq, 1H) and 5.55 (p, 1H), while the proton (Hz) related to the bulky group was at δ 5.08 (ddd, 1H). On the other hand, in the polymer spectrum shifting were observed in terms of chemical shifts. In particular the P(α-PMA) double bond end – group (Ha and Hb) peaks were seen in δ 6.18 (dt, 1H), 5.50 (dt, 1H), the bulky group proton (Hc) was at δ 5.10 (ddd, 1H). These chemical shifts proved that, α-PMA monomer can be polymerised via CCTP and gives a double bond pending group as a result.

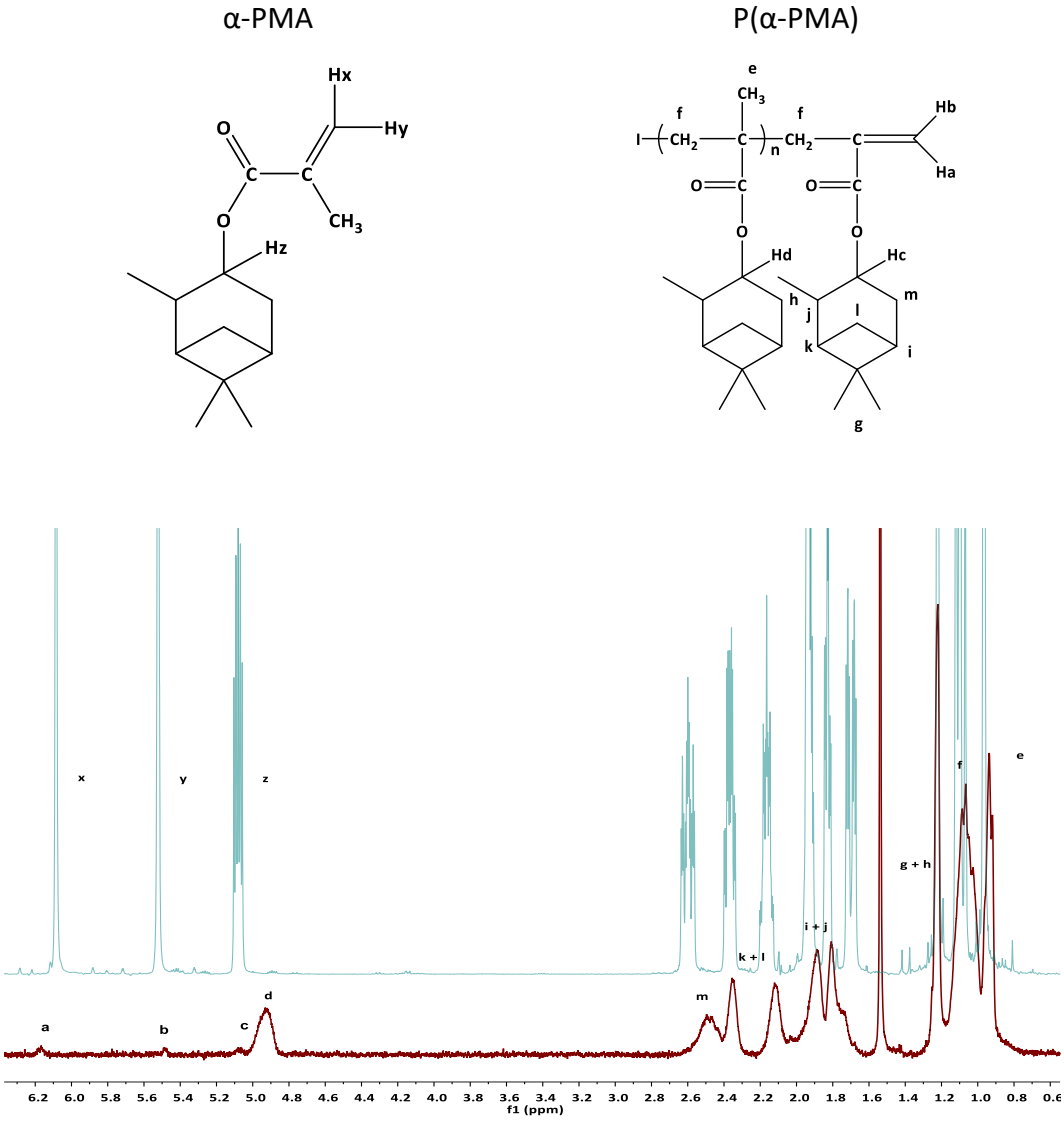


Figure 9. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$, synthesized via CCTP with pre-prepared PhCoBF

*^{1}H NMR (400 MHz, ppm, Chloroform-d) δ 6.18 (dt, 1H, **H**(CH)C(CH_2)), 5.50 (dt, 1H, H(C**H**)C(CH_2)), 5.10 (ddd, 1H, HC(C**H**)CH_2), 4.95 (s, polymer peak), 2.50 (t, 2H, CH(C**H_2**)CH), 2.35 (dtd, 1H, (CH_3)**H**CHCH), 2.11 (dd, 2H, CH(C**H_2**)CH), , 1.91 (q, 1H, CH(C**H**)CH_2), 1.83 (m, CH(CH_2)C**H**(CH_2)), 1.54 (s, 6H, -C(C**H_3**)), 1.22 (d, 3H, -CH(C**H_3**)), 1.09 (m, 1H, (CH_3)CHC**H**(CH_2)CH), 0.96 (t, 3H, -CH_2C(C**H_3**)).*

Table 10. Results of P(α-PMA) with pre – prepared PhCoBF at 80 °C for 24 h

Code	PhCoBF (ppm)	Conv.[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol-1)	M_w[b] (g mol-1)	Đ[b]	T_g[c] (°C)	DP[b]
C1	600	91	5600	5700	12000	2.00	93.1	25
C2	700	90	4400	5100	11000	2.17	96.1	23
C3	800	95	7100	7200	14000	1.95	110.8	32
C4	1000	86	6900	7400	13000	1.79	110.4	33
C5	1190	41	3400	6300	9100	1.48	129.1	28
C6	1300	72	13000	17000	27000	1.57	141.5	76

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*

c) *Determined by DMA.*

It was found that the FRP of α-PMA produced a polymer with a M_n of 54,000 g mol^{-1}. The CCTP reactions of α-PMA were carried out using the same wt. % of initiator, as the FRP reactions, to establish the extent at which the catalyst was reducing the molecular weight of the polymers. As shown by C1, in the presence of the pre – prepared cobalt catalyst (PhCoBF) there was a significant decrease in M_n to 5700 g mol^{-1}. As the amount of catalyst was increased it was expected that the M_n should decrease.[35] This trend however, was not observed for this monomer. The lowest M_n observed for this polymer system was 5100 g mol^{-1} (C2, Table 10) when 700 ppm of PhCoBF was used. As the catalyst concentration increased, the expected decrease in M_n was not observed, with the M_n actually increasing, with the catalyst concentration producing a polymer with the highest M_n. This is further demonstrated by the GPC trace in Figure 10.

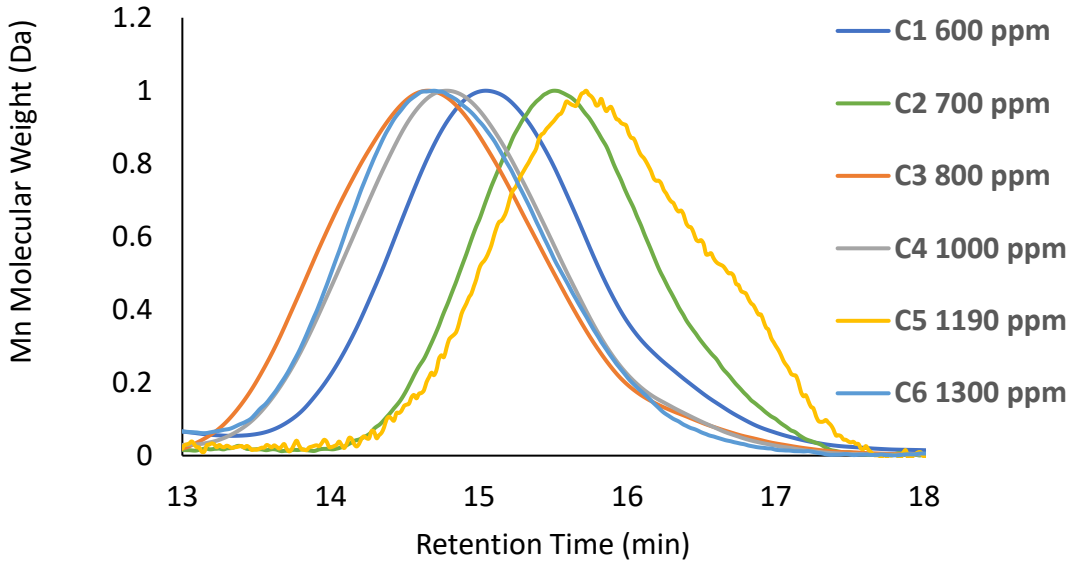


Figure 10. The GPC Trace of CCTP reactions for P(α-PMA) with pre – prepared cobalt catalyst concentrations

The catalyst has reduced the M_n of the polymers, when compared to the FRP (F1, Table 9), but the maximum catalyst concentration limit may have been reached. The PhCoBF was not soluble enough in cyclohexanone as the concentration was increased, even with prior sonication of the catalyst in solvent. Because of this solubility issue, the catalyst was not fully solubilized and therefore could not act as a chain transfer agent effectively. This was the main reason why the M_n of C6 (17000 g mol^{-1}) was significantly higher than other reactions in Table 10. However, when dispersity values have criticised, they have been slightly decreased in order to the catalyst concentrations (ppm) increased. As a result, oligomer could not have synthesized via CCTP with pre – prepared cobalt catalyst (PhCoBF).

As in shown in the GPC traces, C5 have been demonstrated the lowest M_n of P(α-PMA) when 1190 ppm of PhCoBF was used, and the molecular weight order of the P(α-PMA) from higher to lower, is shown as C3 > C6 > C4 > C1 > C2 > C5 respectively. When the crosscheck has made, the M_n calculations with ^1H – NMR has given the same results (C5, Table 10). As a result, GPC traces have matched almost exactly with the molecular weight calculations which were calculated via ^1H – NMR.

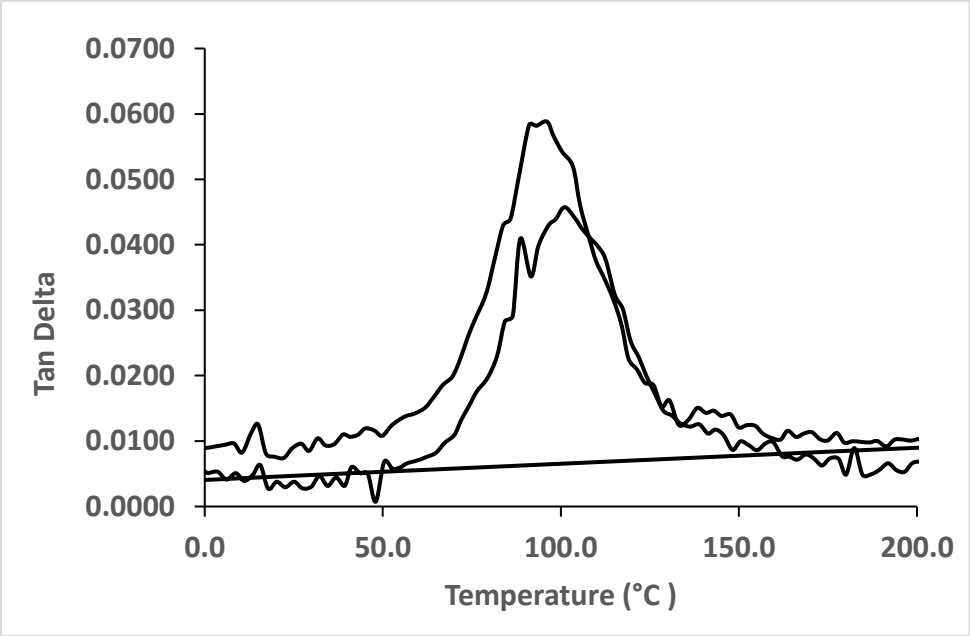
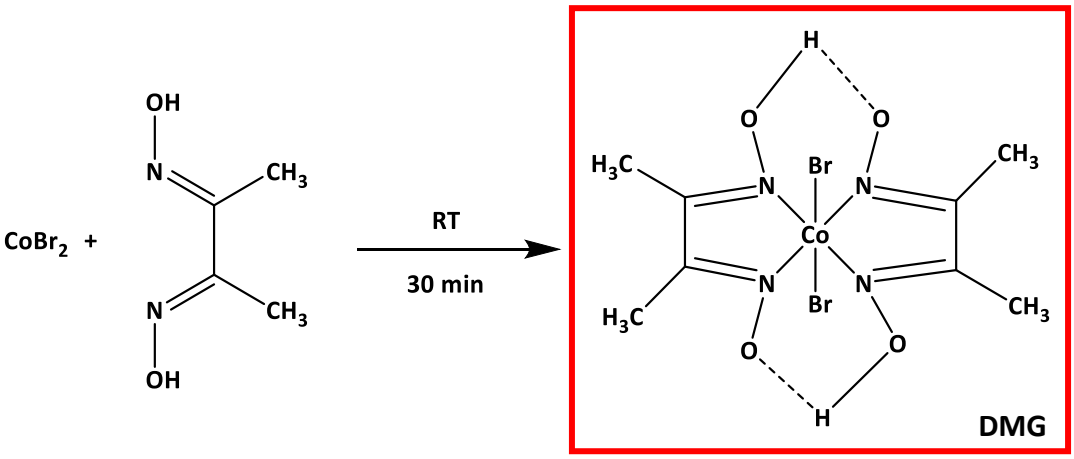


Figure 11. The DMA analysis of Code – C2.

The DMA analysis of C2 showed that, the T_g point measured at 96.1 °C, with the consideration of Tan Delta @ 1.0 Hz. Previously, the T_g point of the P(α-PMA) was established at 142 °C where the M_n calculated to be 22,200 g mol^{-1}.[1] In comparison as expected, it was noted that there was a strong correlation between the DP decreasing in order for the T_g point of C2 to be reduced.

The solubility problem of PhCoBF in cyclohexanone and the higher M_n effect on the P(α-PMA) have been the major reasons to move on to another methodology which was named CCTP *'in – situ'*. Not only this is a methodology economically cost – effective, the '*in – situ'* catalyst results more soluble and effective than the '*pre – prepared'* one. However, the only downside for the *'in – situ'* catalyst manufacturer, was that it increased the reaction steps.[30]

'in – situ' methodology was examined on the formation of the cobalt catalyst with two different equatorial ligands which were dimethyl glyoxime (DMG) and diphenyl glyoxime (DPG), in the presence of cobalt (II) bromide ($CoBr_2$). The reaction scheme of the formation of the cobalt catalyst with DMG has been shown in the scheme below (Scheme 14).[30]



Scheme 14. The reaction scheme of the formation of the cobalt catalyst with DMG as an equatorial ligand in the presence of $CoBr_2$

To see the formation of the cobalt catalyst *'in – situ'* and the effect of the solubility efficiency in cyclohexanone, first of all, MMA was used as tested monomer.

CCTP *'in – situ'* reactions for MMA monomer were successfully done. In ^{1}H – NMR spectrum, the color turquoise represented to monomer MMA peaks and the color maroon represented to the PMMA peaks. The MMA's double bond peaks (Hx and Hy) were in δ 6.09 (dq, 1H), 5.55 (p, 1H) while the proton (Hz) related to the bulky group was at δ 3.74 (s, 3H). On the other hand, in the polymer spectrum shifting were observed in terms of chemical shifts. In particular the PMMA double bond end – group (Ha and Hb) peaks were seen in δ 6.20 (dt, 1H), 5.47 (p, 1H) and, finally, the bulky group proton (Hc) was in 3.74 (m, 3H). These chemical shifts were proved that, CCTP *'in – situ'* reaction mechanism has been terminated with double – bond end group and PMMA macromonomer synthesized. Figure 9. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$

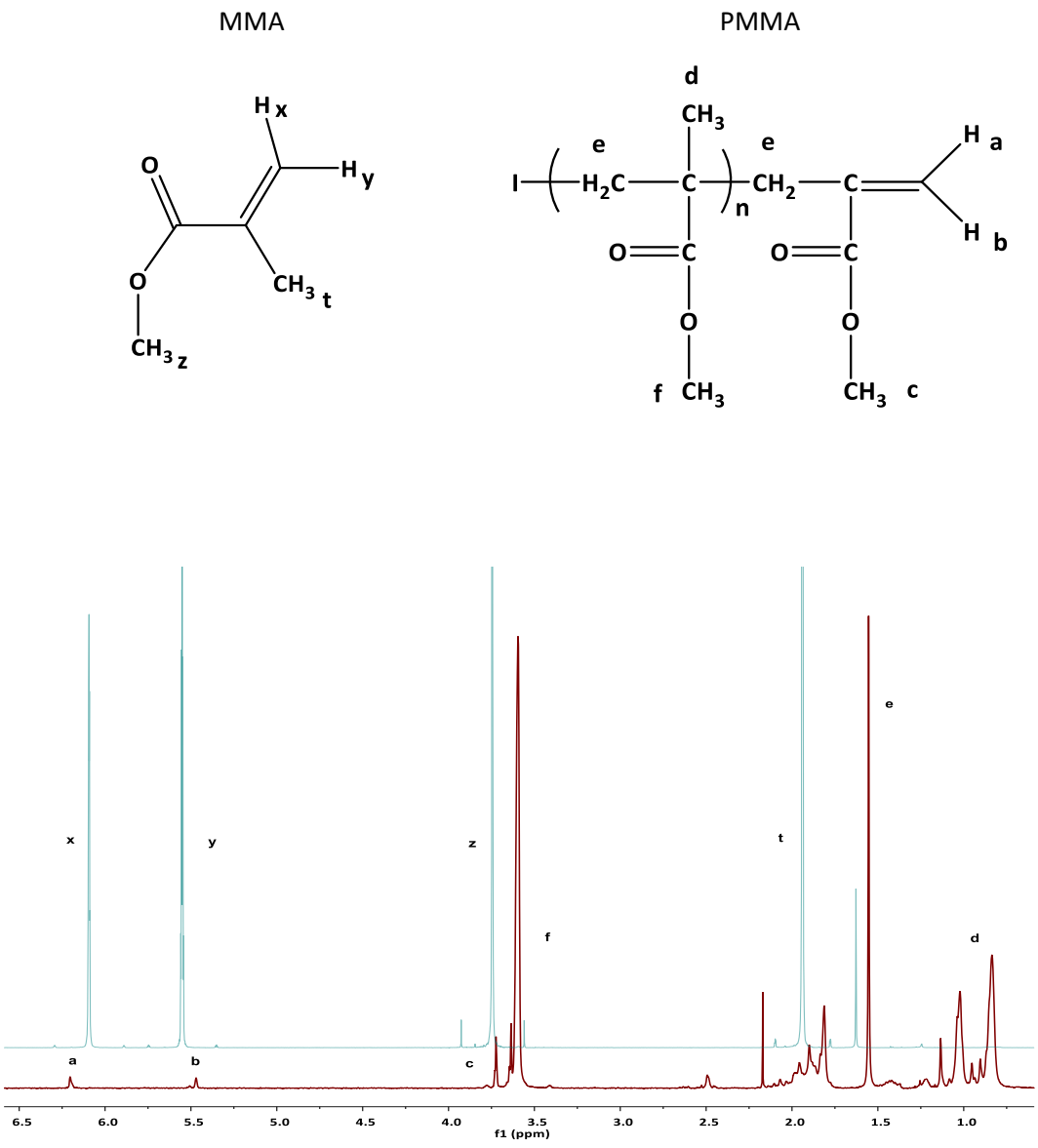


Figure 12. The ^{1}H – NMR analysis of PMMA in $CDCl_3$, synthesized via CCTP 'in – situ'

*^{1}H NMR (400 MHz, Chloroform-d) δ 0.84 – 1.01 (t, 3H, -$CH_2C(CH_3)$), 1.55 (q, 2H, CH_3CCH_2), 3.61 (s, polymer peak), 3.73 (s, 3H, $COOCH_3$) 5.48 (p, 1H, **H**$CHCOOCH_3$), 6.21 (dq, 1H, $HCHCOOCH_3$).*

The results of CCTP *'in – situ'* reactions of MMA monomer with DMG as an equatorial ligand has been shown below in Table 11.

Table 11. CCTP 'in-situ' results of PMMA with DMG equatorial ligand at 80 °C for 24 h

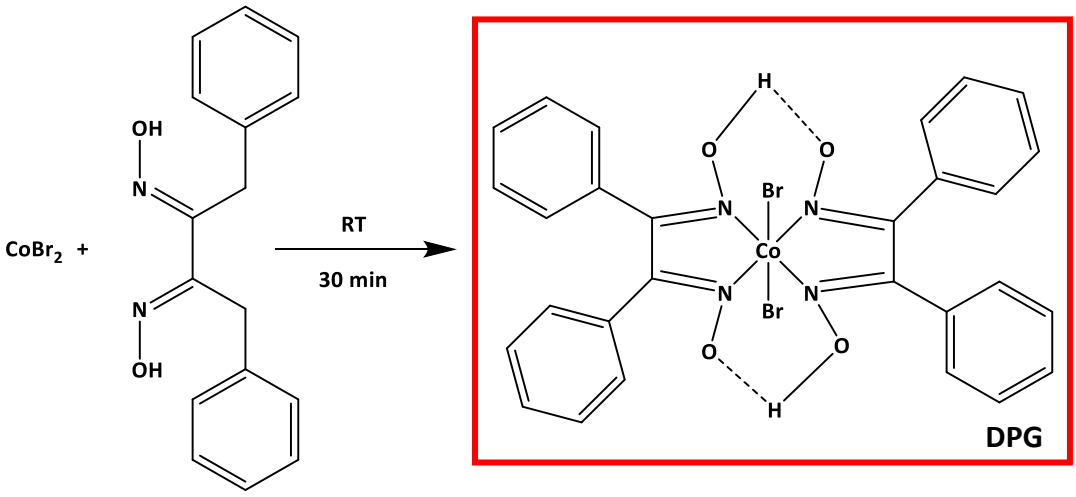
Code	Catalyst ppm	Conversion[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	DP[b]
CM1	600	88	5000	7300	13000	1.81	73
CM2	800	88	2800	2000	4400	2.19	20
CM3	1000	87	1800	1600	2200	1.36	16

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, PMMA dn/dc = 0.089.*

The formation of the cobalt catalyst (MeCoBF) in the reaction system occurred within 30 minutes. During that time, color changes were observed (from light green to light brown). As the concentrations of the cobalt catalyst increased, it is expected that the M_n of the PMMA should decrease.[38] This downstream M_n trend was caught for the MMA monomer. CM3, which corresponds to the reaction obtained by using as catalyst concentration of 1000 ppm, have given the lowest M_n of around 1600 g mol^{-1}. This data can be compared to a previous study, where a similar trend have been obtained for PMMA and which were related to the duration of the reaction time, the solvent – free and bulky conditions . [30]

The next step was carried out DPG as an equatorial ligand of formation of the cobalt catalyst (PhCoBF) *'in – situ'* methodology for MMA. The reaction scheme of the synthesis of PhCoBF 'in – situ' has been given below in Scheme 15. Results have shown in Table 12.



Scheme 15. Reaction of $CoBr_2$ and the formation of the cobalt catalyst with DPG as an equatorial ligand.

Table 12. CCTP 'in-situ' results of PMMA with DPG equatorial ligand at 80 °C for 24 h

Code	Catalyst ppm	Conversion[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	DP[b]
CM4	600	88	9100	13000	19000	1.51	130
CM5	800	86	6000	8000	12000	1.49	80
CM6	1000	88	4000	5300	7000	1.35	53

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, PMMA dn/dc = 0.089.*

MMA has a small pendant group. Because of that, expectations of the catalyst activity with DPG equatorial ligand would be more active than DMG for MMA monomer. In CCTP *'in – situ'* method, previous works also showed the same idea.[30] However, these results have noted that, DMG was more active than DPG, interestingly. Small-scale and less bulky polymerisation might be the reason for this unexpected equatorial ligand comparison, as a result.

The cobalt catalyst with DPG equatorial ligand has been successfully controlled the M_n of the PMMA and, as expected, the regular downstream trend was observed when the concentrations of the cobalt catalyst increased. The lowest M_n of PMMA obtained is around 5300 g mol^{-1} (CM6, Table 12), when the catalyst ppm was around 1000 ppm.

Overall, for the synthesis of lower molecular weight PMMA via CCTP *'in-situ'* with DMG ligand was performed better than DPG. In addition to that, when FRP and CCTP *'in – situ'* methodology compared, the molecular weight of the PMMA was decreased from 29000 g mol^{-1} (F2, Table 9) to 1600 g mol^{-1} (CM3, Table 11). The cobalt catalyst acted as a chain transfer agent and successfully controlled and reduced the molecular weight of the PMMA successfully via CCTP *'in – situ'* methodology.

In the next step, α-PMA was the monomer under investigation for CCTP *'in – situ'* methodology. These reactions also have been carried out using two different equatorial ligands which were DMG and DPG respectively in the presence of $CoBr_2$ to form the cobalt catalyst, as the same in previous work for MMA monomer. The results has been given below in Table 13 and in Table 14.

CCTP *'in – situ'* reactions for α-PMA monomer were successfully done. In ^1H – NMR spectrum, the color dark blue represented to monomer α-PMA peaks. The color maroon represented to the P(α-PMA) peaks with DMG and the color green represented to the P(α-PMA) peaks with DPG (Figure 13). The α-PMA's double bond peaks (Hx and Hy) were in δ 6.09 (dq, 1H), 5.52 (p, 1H), while the proton (Hz) related to the bulky group was at 5.02 (ddd, 1H On the other hand, in the polymer spectrum shifting were observed in terms of chemical shifts. In particular, the P(α-PMA) double bond end – group (Ha and Hb) peaks were seen in δ 6.17 (dt, 1H), 5.48 (p, 1H) and the bulky proton (Hc) was in δ 5.07 (ddd, 1H). As shown in the ^1H – NMR, the chemical shifts of CCTP *'in – situ'* reactions with DMG and DPG as equatorial ligands were in the same peak areas. These chemical shifts proved that, α-PMA monomer can be polymerised via CCTP *'in – situ'* and gives a double bond pending group as a result.Figure 9. The ^1H – NMR analysis of P(α-PMA) in $CDCl_3$

Figure 9. The ^1H – NMR analysis of P(α-PMA) in $CDCl_3$

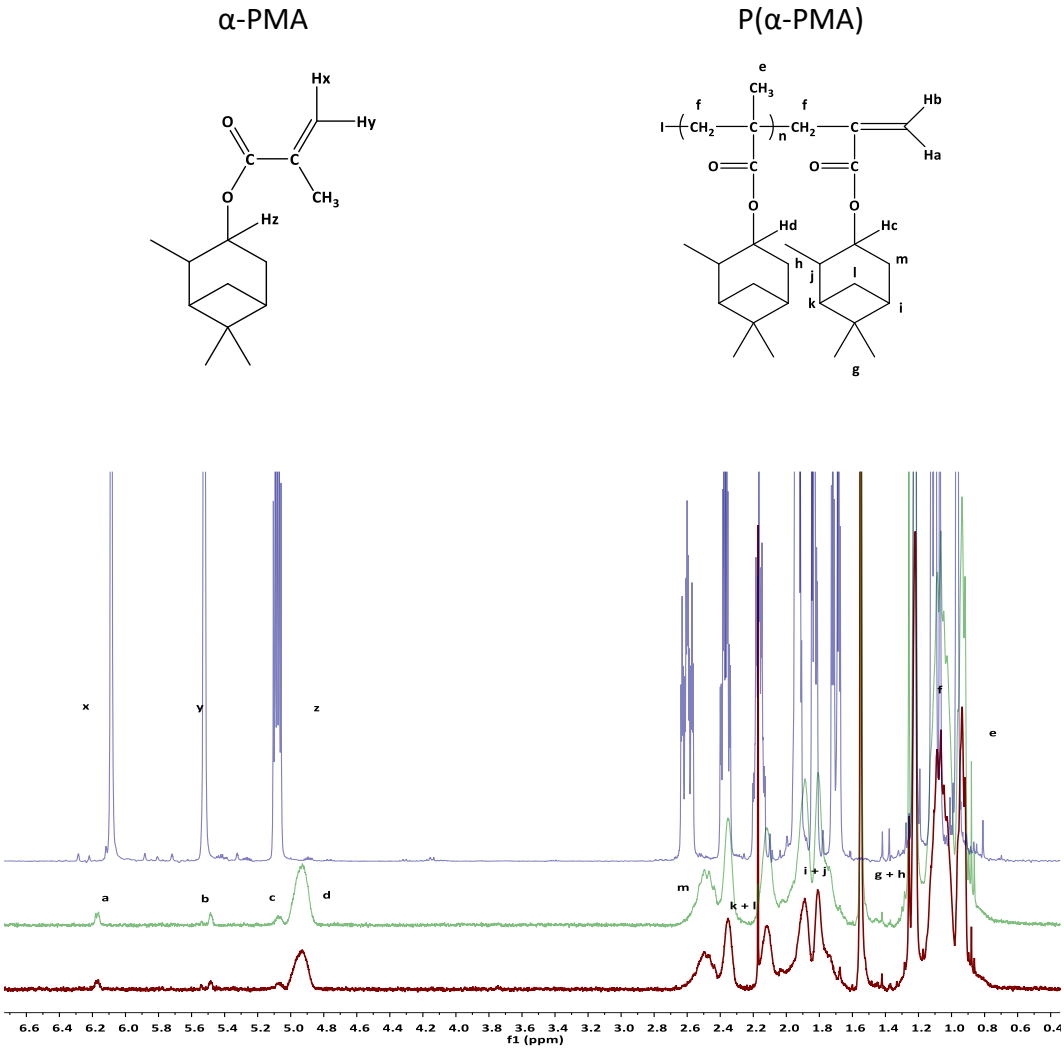


Figure 13. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$, synthesized via CCTP 'in – situ'

*^{1}H NMR (400 MHz, ppm, Chloroform-d) δ 6.16 (dt, 1H, **H**(CH)C(CH_2)), 5.48 (dt, 1H, H(C**H**)C(CH_2)), 5.06 (ddd, 1H, H_3), 4.93 (s, polymer peak), 2.48 (t, 2H, CH(C**H_2**)CH), 2.34 (dtd, 1H, (CH_3)**H**CHCH), 2.11 (dd, 2H, CH(C**H_2**)CH), , 1.89 (q, 1H, CH(C**H**)CH_2), 1.81 (m, CH(CH_2)C**H**(CH_2)), 1.56 (s, 6H, -C(C**H_3**)), 1.22 (d, 3H, -CH(C**H_3**)), 1.06 (m, 1H, (CH_3)CHC**H**(CH_2)CH), 0.93 (t, 3H, -CH_2C(C**H_3**)).*

Table 13. Results of P(α-PMA) 'in – situ' with DMG as equatorial ligand of catalyst at 80 °C for 24 h

Code	Catalyst ppm	Conversion[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	T_g[c] (°C)	DP[b]
CP1	600	89	3200	3200	4300	1.33	88.3	14
CP2	700	86	3300	3700	4300	1.15	70.7	16
CP3	800	75	5600	5600	7400	1.32	61.4	25
CP4	900	79	3400	3700	4500	1.19	51.2	16
CP5	1000	72	3700	3800	4700	1.22	46.8	17

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*

c) *Determined by DMA.*

When the table was examined, it was seen that the molecular weights were in similar ranges with increasing the catalyst concentration. This is because the catalyst concentration in the reaction system has been reached the limit point. As in shown by CP1, the lowest M_n of P(α-PMA) has been synthesised around 3200 g mol^{-1} when the ppm was 600. The M_n results have been shown detailed in the GPC trace below (Figure 14).

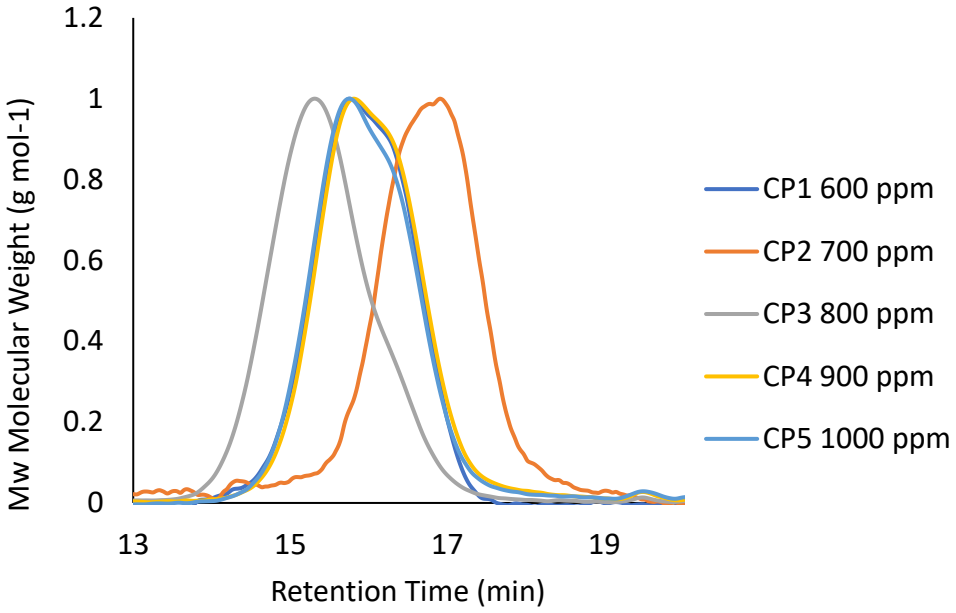


Figure 14. The GPC Trace of CCTP 'in – situ' reactions for P(α-PMA) with DMG as equatorial ligand of the cobalt catalyst

As mentioned above, the molecular weight of the polymers has not been shown a regular downward trend. In GPC traces, the order of the Mn of P(α-PMA) from highest to lower was shown as, CP3 > CP1 = CP4 = CP5 > CP7, respectively.

Table 14. Results of P(α-PMA) 'in – situ' with DPG as equatorial ligand of catalyst at 80 °C for 24 h

Code	Catalyst ppm	Conversion[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	T_g[c] (°C)	DP[b]
CP6	600	59	2500	2700	3900	1.48	80.3	12
CP7	700	43	3100	4200	7200	1.72	71.3	19
CP8	800	57	2900	4100	4600	1.13	99.2	18

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*

c) *Determined by DMA.*

As in shown by CP6, the lowest M_n of P(α-PMA) has been synthesised around 2700 g mol^{-1} when the ppm was 600. The M_n results have been shown detailed in the GPC trace below. In Figure 15, the order of the Mn of P(α-PMA) from highest to lower as, CP7 > CP8 > CP6, respectively.

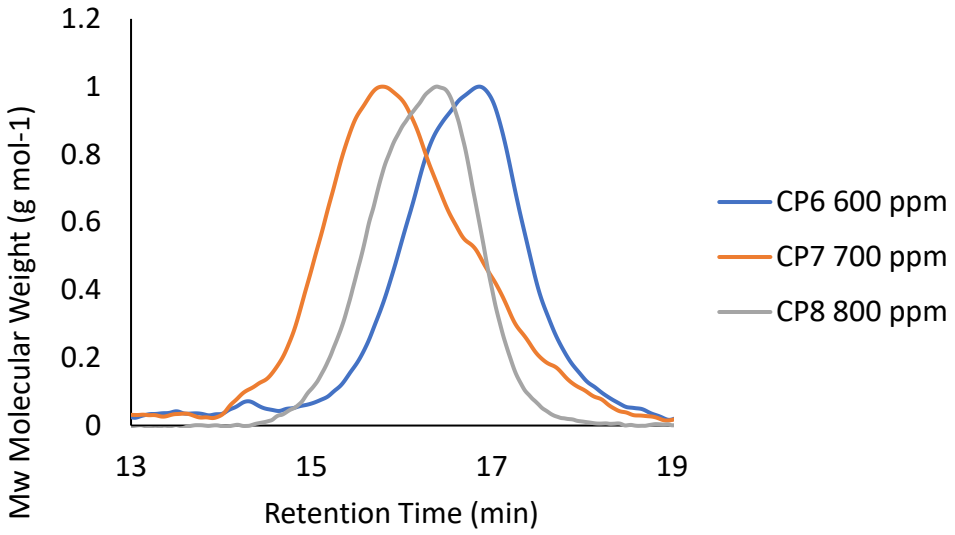
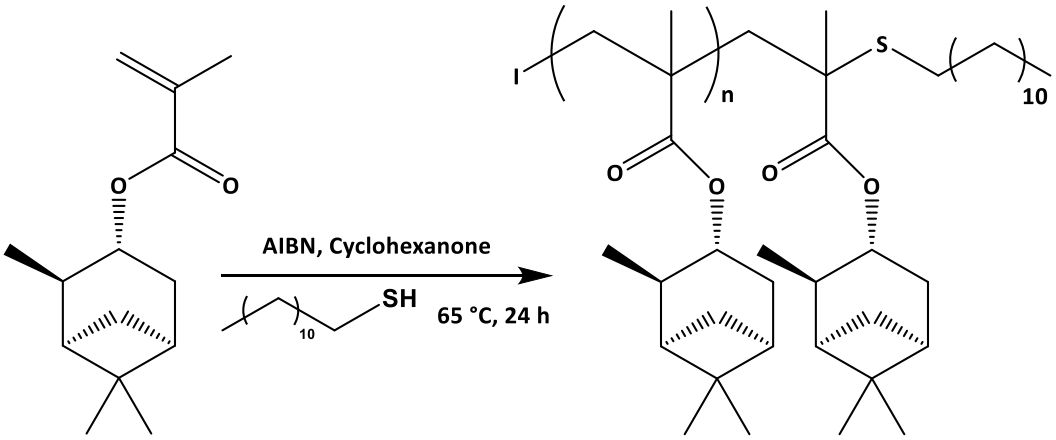


Figure 15. The GPC Trace of CCTP 'in – situ' reactions for P(α-PMA) with DPG as equatorial ligand of the cobalt catalyst

When compared the equatorial ligands, exploited for the *'in – situ'* polymerisation, DPG results bulkier than DMG because of the benzyl groups in its backbone (Scheme 14 and Scheme 15). In addition, α-PMA is characterized by a cyclic pendant group which gives less mobility/reactivity to the whole system. As a consequence, the polymerisation of α-PMA performed by using DPG ligand would be more complicated with respect to DMG and the reason would be related this bulky environment of the two moieties. However, according to the Table 12, DPG ligand has played a more active role than DMG for α-PMA monomer[30] in the control of M_n, in fact, lowest M_n polymer has been synthesized around 2700 g mol^{-1}.

CCTP *'in – situ'* has demonstrated to be a successful strategy for the control of the molecular weight of α-PMA, especially when compared to the FRP. The M_n has seen a reduction from 54000 g mol^{-1} (F1, Table 9), when FRP was applied, to 2700 g mol^{-1} (CP6, Table 13) with the CCTP *'in – situ'*. However, the molecular weight of the P(α-PMA) has not been reduced enough to produce oligomer. Another well – known technique for production of oligomers by exploiting a Chain Transfer Agent (CTA) in the control of molecular weights is the Thiol – Mediated Radical Polymerisation.

The reaction mechanism related to the Thiol – mediated Radical Polymerisation is different from the CCTP (Scheme 16). In fact, using thiols as CTA led to the formation of a thioether functionality as a result of the termination mechanism. This lead to low post-polymerisation strategies when compared to the CCTP. For instance, thiols cannot act as macromonomer for further polymerization as observed in CCTP thanks to the presence of the double bond as the terminal group.[39] In addition, in terms of functionality, thiol reactions with DDM are more infertile than CCTP reactions.



Scheme 16. The reaction scheme of the P(α-PMA) with DDM thiol CTA.

In literature have been reported examples of polymerizations of terpene (meth)acrylates monomers, including α-PMA, with thiol as [1] Sainz et al. have used three different thiols: 1-dodecane thiol (DDM), mercaptosuccinic acid and 3-mercaptopropionic acid. All the reactions with these three different thiol CTAs, have been successfully synthesised of oligomers resulted.

In ^{1}H – NMR spectrum, the color purple represented to monomer α-PMA peaks, the color maroon represented to the P(α-PMA) peaks with DDM, the color green represented to the P(α-PMA) peaks with mercaptosuccinic acid. Additionally, the color turquoise represented to the P(α-PMA) peaks with 3-mercaptopropionic acid. The α-PMA's double bond peaks (Hx and Hy) were in δ 6.09 (dq, 1H), 5.52 (p, 1H), while the proton (Hz) related to the bulky group was at δ 5.08 (ddd, 1H). All the chemical shifts were synthesised by the reactions with thiol chain transfer agents, were seen in the same peak area. As shown in Figure 16, these chemical shifts were proved that thiol reaction mechanism has not been terminated with double bond end – group.

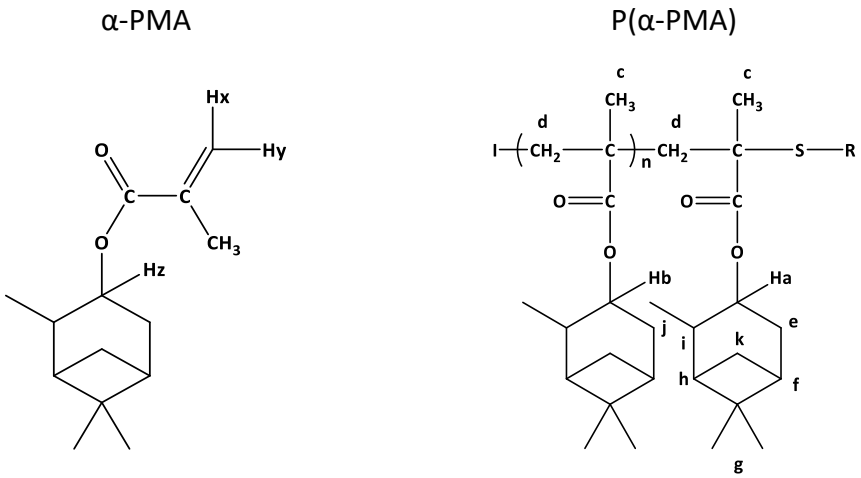


Figure 9. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$

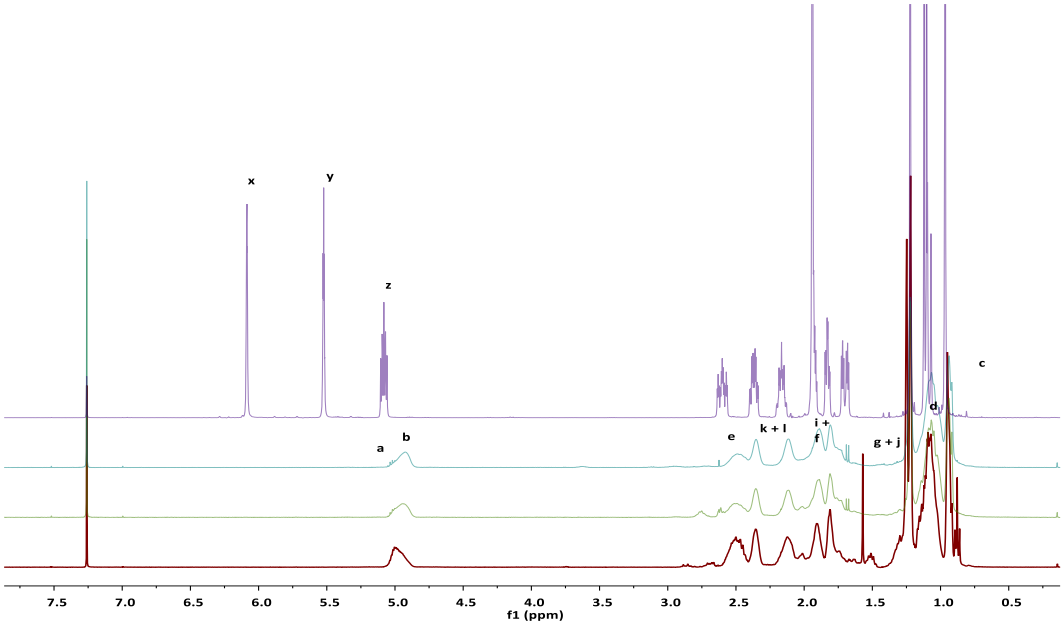


Figure 16. The ^{1}H – NMR analysis of P(α-PMA) in $CDCl_3$, synthesized with thiol chain transfer agents which are DDM, Mercaptosuccinic acid and 3-Mercaptopropionic acid

*^{1}H NMR (400 MHz, ppm, Chloroform-d) δ 4.95 (s, polymer peak), 2.49 (t, 2H, CH(C**H₂**)CH), 2.35 (dtd, 1H, (CH_3)**H**CHCH), 2.11 (dd, 2H, CH(C**H₂**)CH), 1.88 (q, 1H, CH(C**H**)CH_2), 1.80 (m, CH(CH_2)C**H**(CH_2)), 1.24 (d, 3H, -CH(C**H₃**)), 1.08 (m, 1H, (CH_3)CHC**H**(CH_2)CH), 0.96 (t, 3H, -CH_2C(C**H₃**)).*

Previously, DDM was studied for both, α-Pinene Arcylate (α-PA) and α-PMA monomers by Howdle Group.[1] The DDM concentration was taken 1 and 5 wt. % to the monomer concentration, and lower molecular weight Poly (α-Pinene Acrylate) (P(α-PA)) and P(α-PMA) were produced. In this project, the DDM concentration in the previously published paper, was doubled (10 wt. %) to reduce the molecular weight of P(α-PMA). Then, reactions followed by, various higher DDM concentrations and results have given in Table 15.

Table 15. Results of P(α-PMA) with DDM chain transfer agent with the 0.5 wt. % AIBN to 1 g monomer at 65°C for 24 h.

Code	DDM (g)	Conversion[a] (%)	M_n[a] (g mol^{-1})	M_n[b] (g mol^{-1})	Đ[b]	T_g[c] (°C)	DP[b]
T1	0.1	99	3400	4700	1.38	113.5	15
T2	0.3	99	1200	1500	1.28	35.6	5
T3	0.5	99	690	870	1.25	N/A	3

a) *Determined by ^1H – NMR.*
b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*
c) *Determined by DMA.*

According to the Table 15, with the increasing of DDM concentration a decreasing of M_n was observed. In particular, when the amount of DDM adopted was 0.1 g, the M_n was 3400 g mol^{-1} (T1, Table 15). This result is in line with the results reported by Sainz at al.[1] However, aiming to the production of oligomers higher DDM concentrations were tested in order to promote the termination step during the polymerization. By adopting either 0.1 g or 0.5 g of DDM, it was successfully

synthesised a P(α-PMA) in oligomer level (T2 and T3). Because of the lower M_n of the P(α-PMA), the final polymer product has not been precipitated for T3.

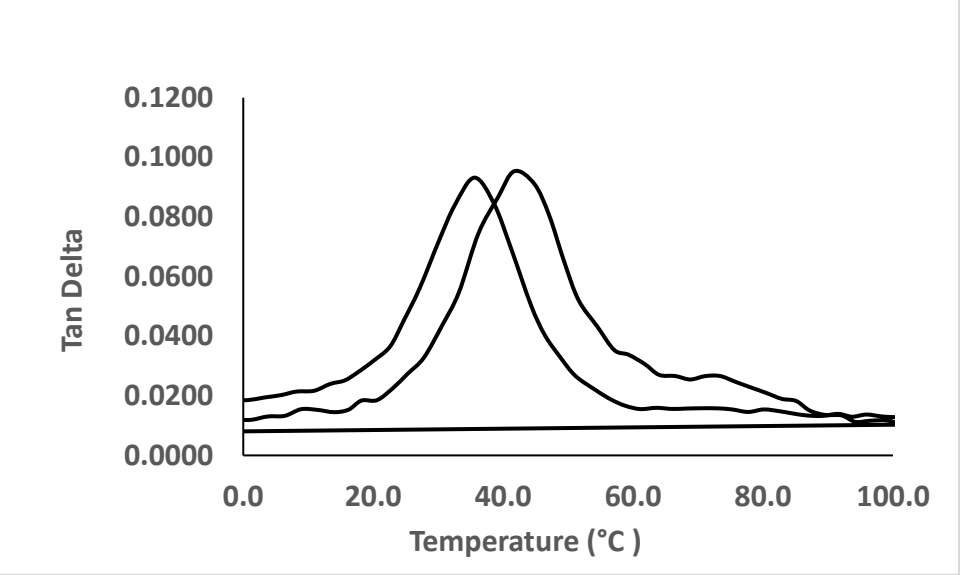
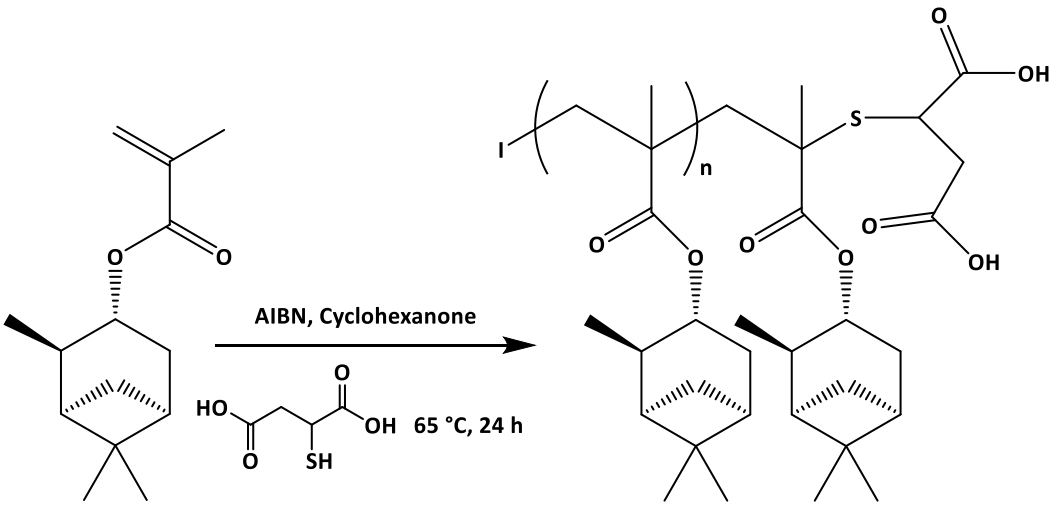


Figure 17. The DMA analysis of Code – T2.

The DMA analysis of T2 was shown that, the T_g point measured at 35.6 °C, with the consideration of Tan Delta @ 1.0 Hz. Previously, the T_g point of the P(α-PMA) was established at 85 °C where the M_n calculated to be 7900 g mol^{-1}.[1] In comparison as expected, it was noted that there was a strong correlation between the DP decreasing in order for the T_g point of C2 to be reduced.

For the synthesis of P(α-PMA) oligomers a new different thiol was used, namely, the mercaptosuccinic acid. Also, the reaction scheme has been shown below (Scheme 17). Mercaptosuccinic acid was chosen because of its functionality, as it is a dicarboxylic acid and the hydroxyl groups can be exploited for further functionalization reactions.



Scheme 17. The reaction scheme of the P(α-PMA) with Mercaptosuccinic acid thiol CTA.

Table 16. Results of P(α-PMA) with mercaptosuccinic acid chain transfer agent with 0.5 wt. % AIBN to 1 g monomer at 65°C for 24 h.

Code	Mercaptosuccinic acid (g)	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	T_g[c] (°C)	DP[b]
T4	0.1	98	3800	5700	1.51	115.9	17
T5	0.3	98	2100	2500	1.21	N/A	9
T6	0.5	98	1300	1700	1.31	N/A	6

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*

c) *Determined by DMA.*

In Table 16, a similar trend to DDM reactions was observed. The lowest concentration of mercaptosuccinic acid (0.1g) produced the highest M_n (3800 g mol^{-1}) (T4). As in shown by T5 and T6, in followed reactions, polymers at the oligomer level were synthesized as expected as the concentration of mercaptosuccinic acid increased. The lowest M_n of the P(α-PMA) synthesized was around 1300 g mol^{-1} when the mercaptosuccinic acid concentration was 0.5 g. Although, because of the entity of the molecular weight, no purification steps followed, and the M_n reported are from the reactions crude.

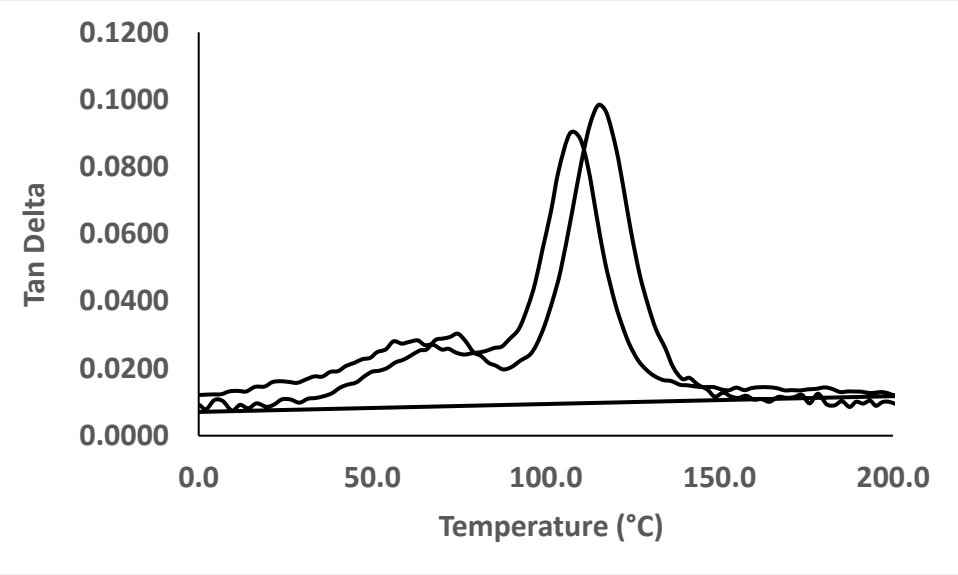
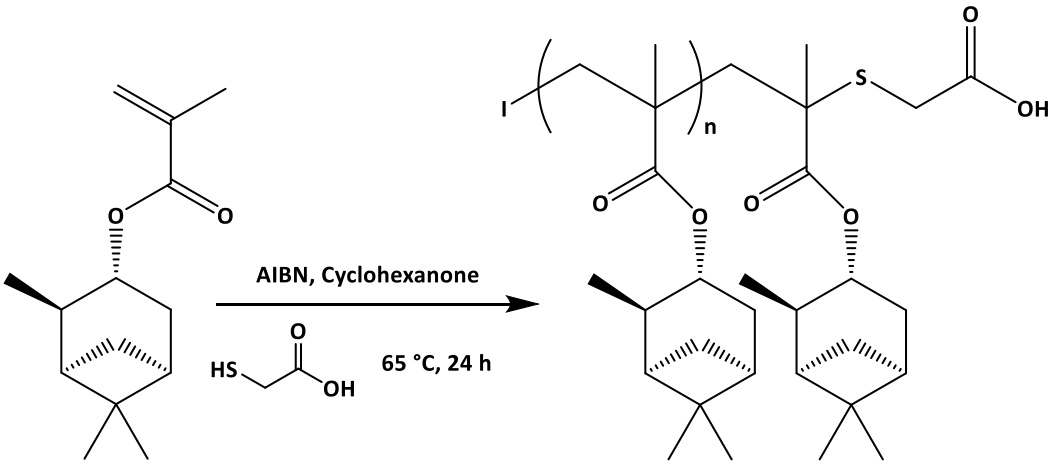


Figure 18. The DMA analysis of Code – T4.

The DMA analysis of T4 was shown that, the T_g point has been measured at 115.9 °C when the M_n was 3800 g mol^{-1} with the consideration of Tan Delta @ 1.0 Hz. Previously, the T_g point of the P(α-PMA) was established at 85 °C where the M_n calculated to be 7900 g mol^{-1}.[1] In comparison, it was noted that the T_g point of the P(α-PMA) increased in order to DP decreased, as unexpectedly.

Finally, the last thiol was employed in the synthesis of α-PMA oligomers (Scheme 18). 3-mercaptopropionic acid was chosen for the presence of the carboxylic acid group which, as in the case of mercaptosuccinic acid, can be exploited in post-functionalisation reactions.



Scheme 18. The reaction scheme of the P(α-PMA) with 3-Mercaptopropionic acid thiol CTA.

Table 17. Results of P(α-PMA) with 3-mercaptopropionic acid chain transfer agent with 0.5 wt. % AIBN to 1 g monomer at 65°C for 24 h.

Code	3-Mercaptopropionic acid (g)	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w[b] (g mol^{-1})	Đ[b]	T_g[c] (°C)	DP[b]
T7	0.1	98	2100	2800	1.33	105.7	9
T8	0.3	97	1200	1500	1.19	N/A	5
T9	0.5	97	1100	1300	1.13	N/A	5

a) *Determined by ^1H – NMR.*

b) *Determined by GPC, P(α-PMA) dn/dc = 0.106.*

c) *Determined by DMA.*

When the 3-mercaptopropionic acid results have been examined, similar results were obtained as in the results of the other two thiols CTAs discussed above. Accordingly, the lowest M_n of the P(α-PMA) has been synthesized around 1100 g mol^{-1} when the 3-mercaptopropionic acid concentration was 0.5 g. T8 and T9 were not purified for the same reason explained above.

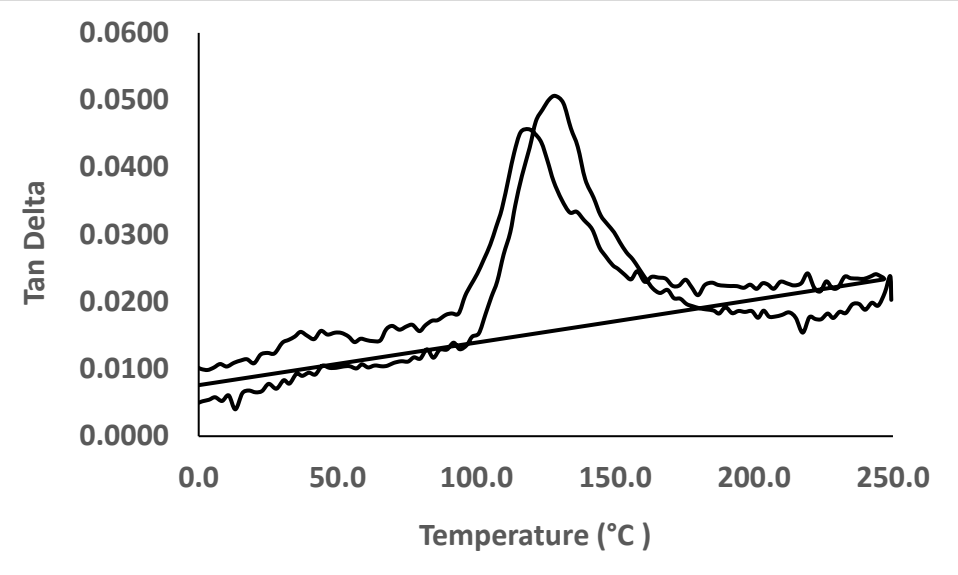


Figure 19. The DMA analysis of Code – T7.

The DMA analysis T7 was shown that, the T_g point has been measured at 105.7 °C when the M_n was 2100 with the consideration of Tan Delta @ 1.0 Hz. Previously, the T_g point of the P(α-PMA) was established at 85 °C where the M_n calculated to be 7900 g mol^{-1}.[1] In comparison, it was noted that the T_g point of the P(α-PMA) increased in order to DP decreased, as unexpectedly. In literature there has not been enough study about α-PMA. However, it is known that, α-PMA has got a highly strained four membered ring in its chemical structure. Also, it is environmentally crowded and bulky monomer. These factors might be the reason of these unexpected results.

4 CONCLUSION

Prior to this project, the polymerisation of P(α-PMA) via CCTP has not been studied in literature. In summary, the research conducted has proved that, α-PMA is a suitable monomer which can be successfully polymerised and the molecular weight of this monomer can be controlled by CCTP and thiol reactions.

Initially, the research was aiming to produce a bottle – brush polymer. This required to yield macromonomers with lower molecular weight polymers (oligomers) which could not be synthesized via CCTP. Although, during the course of this research synthesis of oligomers were attempted, the expected results were not yielded. However, with further research in the future there are possibilities to be explored for α-PMA monomer.

In CCTP reactions with pre – prepared catalyst, the molecular weight of P(α-PMA) successfully reduced in order to increase catalyst concentrations. However, the maximum catalyst concentration (ppm) has been reached to the limit, and there has not been a significant decrease of M_n observed when higher ppm used. On the other hand, CCTP *'in – situ'* methodology was more efficient than the *'pre – prepared'* one. CCTP *'in – situ'* experiments have proved that the catalyst activity with DPG ligand (PhCoBF) is more effective than DMG (MeCoBF) for α-PMA monomer.

It was proved that the aim to yield the oligomer of P(α-PMA), was successfully synthesised via thiol reactions (CTAs). In conclusion, the use of Thiol – mediated Radical Polymerisation was important for the synthesis of α-PMA based –

oligomers. Comparing the activity and the efficacy of the thiols adopted in the synthesis, DDM was the most active thiol agent followed by 3-mercaptopropionic acid and mercaptosuccinic acid. The synthesis was completely successful not only in terms of target molecular weight, but also in conversion. In fact, this latter was above the 90% in the majority of the cases.

5 FUTURE WORK

α-PMA is a methacrylate functionalised terpene – based monomer. Previously a similar terpene – based methacrylate monomer carrying a similar structure i.e. carvone methacrylate was studied and put to the use in industry for the purpose of coating.[1] Therefore with further study and with sight of the research conducted for α-PMA in this thesis, it appears to be promising towards new industrial applications.

A continuation of this study could entail synthesising oligomer of P(α-PMA) via CCTP. Although, the desired molecular weight has not been reduced so far, CCTP is still promising for α-PMA under different reaction conditions, such as it could be performed with various catalyst concentrations and shorter reaction time. P(α-PMA) macromonomer can be used for the synthesis of various polymer architecture, such as bottle – brush polymers as mentioned previously.

In order to form a better understanding of the polymerisation of α-PMA monomer via CCTP in the future, more accurate results should be obtained by performing serial experiments for different monomer that are of a similar chemical structure to α-PMA e.g. Isobornyl Methacrylate (IBMA). For this purpose, IBMA could be used to make a comparison with α-PMA.

6 REFERENCES

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