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# Synthesis of Poly(Glycidyl Methacrylate) through Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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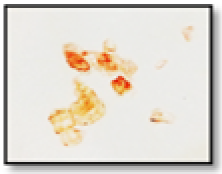
**GRAPHICAL ABSTRACT**



PGMA synthesized from monomer GMA through RAFT polymerization for 14 hours reaction.

**ABSTRACT**

Synthesis of poly(glycidyl methacrylate) (PGMA) from glycidyl methacrylate (GMA) monomer was successfully carried out through reversible addition-fragmentation chain transfer (RAFT) polymerization technique using a RAFT agent 4-Cyano-4-(thiobenzoylthio)pentanoic acid (CPADB) and initiator 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) with mole ratio of 100:1:0.15 for GMA:CPADB:ACPA and temperature of 60 ºC. Synthesis of PGMA was first started with 6 hours of RAFT polymerization. However, since it was unsuccessful, the study was continued to study the optimum time of PGMA polymerization through RAFT polymerization by manipulating the reaction time whereas the mole ratio of GMA:ACPA:CPADB with temperature of reaction, 60 ºC was kept constant. The PGMA polymerization time of reaction was varied and studied for 8, 10, 14, 15, 16, 18 and 22 hours. As the time passed on, the intensity of the pink colour observed from the beginning of reaction decreased but the viscosity of the solution increased. The PGMA polymer was successfully synthesized and precipitated at the 14th and 15th hour. The percentage of conversion for 14 hours and 15 hours was 26% and 29% respectively. The PGMA crude was characterized using $^1$H NMR. NMR confirms PGMA was formed at 14 and 15 hours of polymerization reaction. Several PGMA peaks for below 14 hours polymerization reaction was missing while after 15 hours, there are present indicating PGMA was formed. However, after 15 hours, as the viscosity increases, the polymer formed gel. Gel formation causes no precipitation when the crude was added to methanol since it contains less PGMA. The solid PGMA synthesized at 14 and 15 hours was characterized using FTIR-ATR and confirmed the presence of functional groups of PGMA polymer. In this study, PGMA was successfully synthesized at 14 to 15 hours of time via RAFT polymerization.

*Keywords: poly(glycidyl methacrylates), reversible addition-fragmentation chain transfer (RAFT) polymerization*

## 1. INTRODUCTION

A polymer is a large molecule which is produced from smaller units known as monomers. Rapid increase in demand for manufactured products introduces new materials which are polymers. Products made from polymers are used in a variety of materials around us where clothing are made from synthetic fibers, fiberglass, nylon bearings, plastic bags, polyethylene cups, epoxy glue, polyurethane foam cushion, polymer-based paints and Teflon-coated cookware [1].

Polymer chains consist of repeating units of monomer with several thousand repeating units. The chemical process to synthesize polymer is known as the polymerization process. Most of the macrochains obtained in polymerization reactions are linear polymers, formed by reactions of monomers containing carbon-carbon double bonds (C=C) or which have two active functional groups or bifunctionality covalently bonded to each other [2].

One of the chain-addition polymerizations is controlled or "living" radical polymerization. Among the common living radical polymerization is reversible addition-fragmentation chain transfer (RAFT) polymerization. RAFT polymerization has been in focus in many reported techniques because of its facile reaction condition, robust control for the molecular weight of the polymer even almost quantitative and functionalized by chain transfer agents [3].

Poly(gycidyl methacrylate) (PGMA) synthesized from its monomer glycidyl methacrylate (GMA) is a conventional polymer which attracts researchers in applications of many fields such as polymer chemistry, materials science and biochemistry. Various homopolymers and copolymers based on PGMA can be produced using living radical polymerization, pre-modification of monomers or initiators and post-modification of PGMA [4]. This is mainly because PGMA carries an oxirane group synthesized from its commercially available vinyl monomer GMA.

PGMA was synthesized in this study through the RAFT polymerization technique in bulk polymerization of GMA monomer, initiator 4,4-azobis(4-cyano-valeric acid) (ACPA) and RAFT agent 4-Cyano-4(phenylcarbonothioylthio) pentanoic acid (CPADB), shown in Figure 1, with varying reaction time of RAFT polymerization.

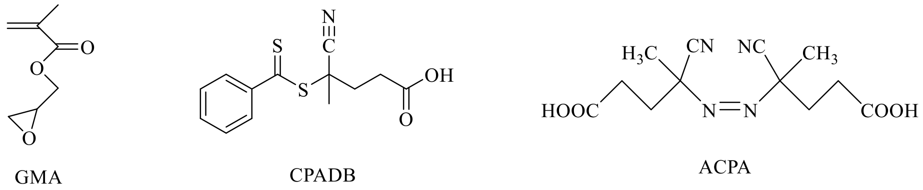


**Figure 1** Molecular structures of the initiators.

## 2. EXPERIMENTAL

The monomer was first purified by passing the solution through a column which was packed with activated alumina to remove the inhibitor for RAFT polymerization of GMA. GMA monomer (1g, 7.03 mmol), ACPA (0.0030g, 0.0105 mmol) and CPADB (0.0196 g, 0.0703 mmol) were mixed by placing in a 100 mL two-necked round bottom flask. The solution was then degassed using nitrogen for 40 minutes. The polymerization was carried out by placing the flask into preheated oil bath at 60 ºC for 6 hours. The reaction mixture was then cooled to room temperature and air were introduced into the flask. The polymer solution from the flask was twice precipitated into excess methanol in a centrifuge tube to remove unreacted GMA monomer and other impurities. The procedure was repeated with 8, 10, 14, 15, 16, 18 and 22 hours in order to find the optimum time to synthesize PGMA. The PGMA obtained for 14 and 15 hours of polymerization were pink solid. The PGMA precipitate was precipitated using a centrifuge tube which was sealed with aluminum foil with few holes to avoid contamination and was left to dry for 24 hours. The polymer crude and purified polymer were analyzed using $^1$H NMR, and FTIR-ATR. The optimum time in synthesizing the polymer was obtained by calculating the conversion percentage of the polymer. The conversion percentage of the polymer from monomer was calculated from the NMR peak as eqn. 1 below:

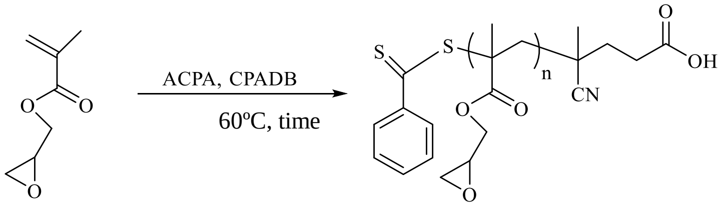
$$\text{Conversion percentage, \%: } \frac{X}{Y-X} \times 100\% \qquad \textbf{(1)}$$

where $X$ represents the polymer peak and $Y$ represents the monomer peak in the NMR

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of PGMA Homopolymer using GMA monomer via RAFT polymerization

In this study, there was no solution used in this polymerization since polymerization was carried out as bulk polymerization. GMA monomer which is in liquid phase act as the solvent to dissolve ACPA and CPADB. The general scheme of the polymerization of monomer GMA via RAFT polymerization to form PGMA is illustrated in Scheme 1.



**Scheme 1** General scheme of the polymerization of monomer GMA via RAFT polymerization to form PGMA.

However, for 6 hours of polymerization to form PGMA, the polymer did not precipitate when dropwise addition of cold methanol was performed. Immiscible droplets formed and spreads when added into cold methanol but when swirled, the methanol turns to pink solution. The polymer was not formed due to short period of time of the polymerization reaction indicating the polymerization of PGMA from GMA might have just started or have not polymerized yet. The study was continued manipulating the time of RAFT polymerization reaction to 8, 10, 14, 15, 16, 18 to 22 hours. The condition for controlled polymerization of GMA with mole ratio of 100:1:0.15 for GMA:CPADB:ACPA respectively and the temperature for polymerization, 60ºC, was kept constant throughout the study.

### 3.2 Time of RAFT Polymerization Varied for Synthesis of PGMA

The pink intensity for 10 hours of polymerization reaction decreased as compared to the other compounds. Besides that, the solution for 10 hours was thicker than 8 hours. The same procedure is used to isolate the polymer. The crude obtained by RAFT polymerization was added dropwise to cold methanol. There was a cloudy layer formed when one drop of crude added in methanol but when swirled the mixture turned cloudy. The formation of cloudy solution after swirling indicates that the polymer have been formed, however, the polymer has low molecular weight causing it not to form a precipitate.

For 14 hours of reaction, the pink colour intensity decreased compared to initial reaction and previous reactions. Beside that, the crude solution was more viscous. When the crude was added to cold methanol in a centrifuge tube, light pink precipitate was formed, and the precipitate sunk to the bottom of the centrifuge tube, indicating PGMA polymer was formed. The crude PGMA for 14 hours RAFT polymerization was characterized using NMR and the dried solid PGMA was characterized using ATR.

As for 15 hours reaction, similar observation to 14 hours reaction was observed where the pink intensity decreases, and the crude was more viscous. In addition to that, a small amount of pink gel product formed in round-bottom flask. When the PGMA crude was added to cold methanol, precipitate formed indicating PGMA homopolymer was formed. The precipitate PGMA formed was in lighter pink in colour compared to 14 hours PGMA formed through RAFT polymerization. NMR was used to characterize the crude while ATR was used to characterize the solid PGMA formed for 15 hours RAFT polymerization reaction.

The PGMA crude obtained for 16- and 18-hours polymerization reaction were in light pink while the PGMA crude for 22 hours reaction turned colourless. Moreover, the viscosity observed increases for these reactions (16, 18 and 22 hours). Similar to 15 hours, there was a gel product formed in the round-bottom flask for 16, 18 and 22 hours. However, it was colourless. When the liquid crude of PGMA added into methanol, there were no precipitation formed but a cloudy solution. Meanwhile, when a small amount of gel crude of 16 hours PGMA retrieved and added to methanol, precipitate was formed. However, the gel formed for 18 and 22 hours was really thick and stucked to the round-bottom flask which made it hard remove it. The gel crude was dissolved with dicholoromethane first and added dropwise to cold methanol, but the mixture did not precipitate.

Bulk polymerization is a polymerization carried out by adding initiator which soluble to pure monomer (liquid state) and heat is supplied during polymerization. As only monomer is in liquid form and it undergoes polymerization, the mixture proceeds to become more viscous. Increase in viscosity of reaction mixture to an extent restricts the mobility of the growing microradicals during the formation of PGMA macromolecules. In the region of the conversion, PGMA with increasing molecular mass were produced rapidly and they are forced to come closer and the interaction between them are noticed. As the viscosity increases, the solution begins to show a transition from a solution to a gel.

### 3.3 Characterization of Homopolymer PGMA

Figure 2, 3 and 4 show the FTIR-ATR spectra of synthesized polymers. From the IR data, there was a distinct absorption band between 1100 $cm^{-1}$ to 1300 $cm^{-1}$ in both GMA and PGMA infrared spectra, which shows the presence of C-O-C vibration. Besides, the strong band adsorption around 980 $cm^{-1}$ shows the symmetrical C-O epoxide ring band in both GMA and PGMA spectra. The absorption band at 1721 $cm^{-1}$ in GMA spectrum while 1722 $cm^{-1}$ and 1718 $cm^{-1}$ in PGMA confirm the presence of C=O of ester. The band appear between 2900 $cm^{-1}$ to 3000 $cm^{-1}$ shows the C-H bond stretching for –CH $sp^3$. However, the –CH $sp^3$ in PGMA was clearly present as compared to the monomer, due to the only –CH $sp^3$ bond present. Moreover, C=C (vinyl) absorption band at 1639 $cm^{-1}$ and –CH $sp^2$ (vinyl) absorption band at 3061 $cm^{-1}$ was present in infrared spectrum of GMA but these absorption band were not present in PGMA infrared spectrum. As this two functional groups in GMA disappeared, this shows that the GMA was polymerized successfully to PGMA through RAFT polymerization.

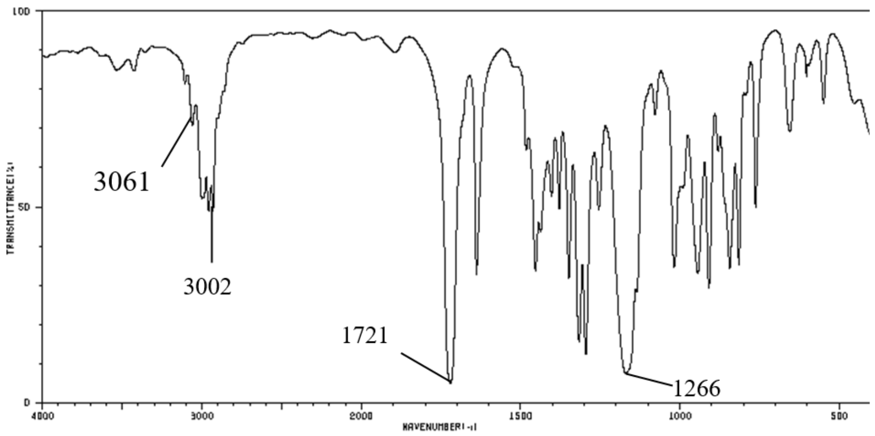


**Figure 2** FTIR spectra of monomer glycidyl methacrylate (GMA) [5].

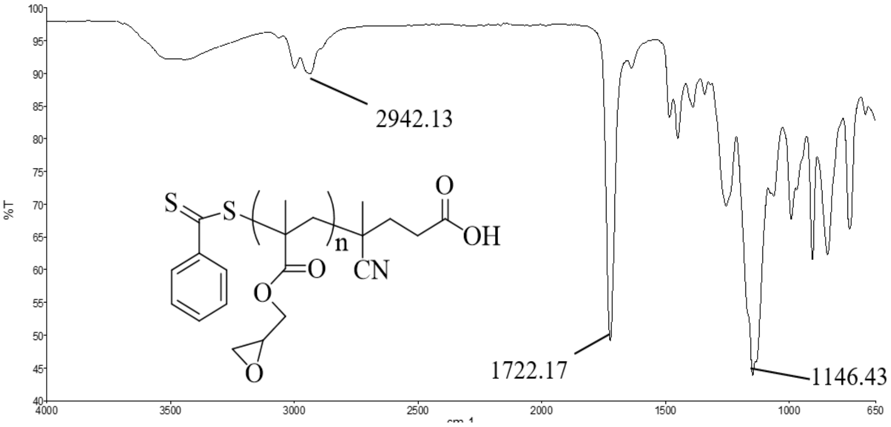


**Figure 3** ATR spectra for 14 hours solid poly(glycidyl methacrylate) (PGMA) macro RAFT.

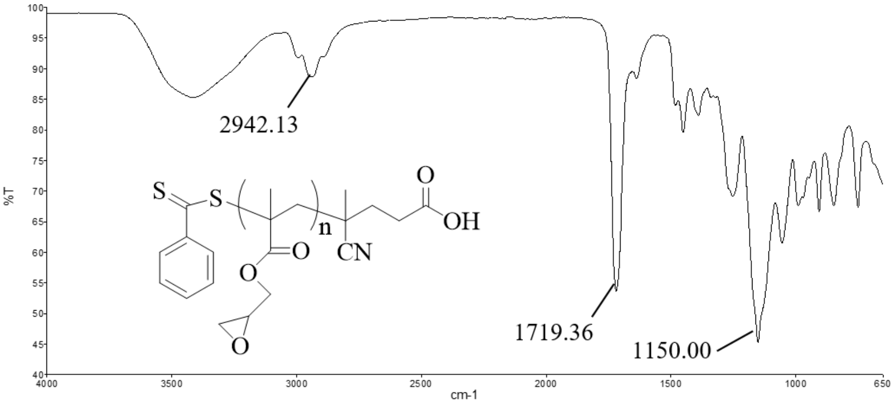


**Figure 4** ATR spectra for 15 hours solid poly(glycidyl methacrylate) (PGMA) macro RAFT.

The $^1$H NMR analysis for 14 hours RAFT polymerization revealed that the polymerization proceeded at vinyl group, retaining the oxirane ring. The two non-equivalent protons (c and c′) of the methylene bonded to the ester oxygen signals were observed at 4.2 – 4.3 ppm and 3.7 – 3.9 ppm. Signal which shows the methane proton (d) of the oxirane ring was detected with a bit difficulty at 3.2 – 3.3 ppm. The two non-equivalent proton signals (e and e′) for the methylene of the ring were seen in the range of 2.8 – 2.9 ppm and 2.6 – 2.7 ppm. Moreover, the signals observe at 1.9 – 2.1 ppm and 0.9 – 1.2 ppm based on the methylene (a) and methyl proton (b) respectively for the main chain. The $^1$H NMR analysis for 15 hours RAFT polymerization also showed that the polymerization proceeded at vinyl group, retaining the oxirane ring as in the 14 hours RAFT polymerization. The monomer conversion for 14 hours PGMA was calculated to be 26% while 29% for 15 hours was observed by $^1$H NMR due to the signal intensity at 3.7 – 3.9 ppm (the polymer PGMA, c′) and 4.00 ppm (the monomer GMA, C′) for one of the two non-equivalent protons of the methylene attached to the ester oxygen. This shows that as time for RAFT polymerization to synthesize PGMA increases, the conversion percentage increases. However, the gel production causes it difficult to study the conversion rate as gel was not able to retrieve. The gel production was due to the increased viscosity and the polymer which brought closer, indicating uncontrolled polymerization.

The characterizations agreed with the PGMA obtained by RAFT polymerization as there is presence of the oxirane rings in the polymer structure and good agreement in the ratio of the respective signal intensity with the PGMA structure. For the NMR spectrum of 6 to 10 hours polymerization reaction, through comparison of the spectrums there are certain peaks which are missing and hard to determine. This indicates PGMA formed but in small amount.

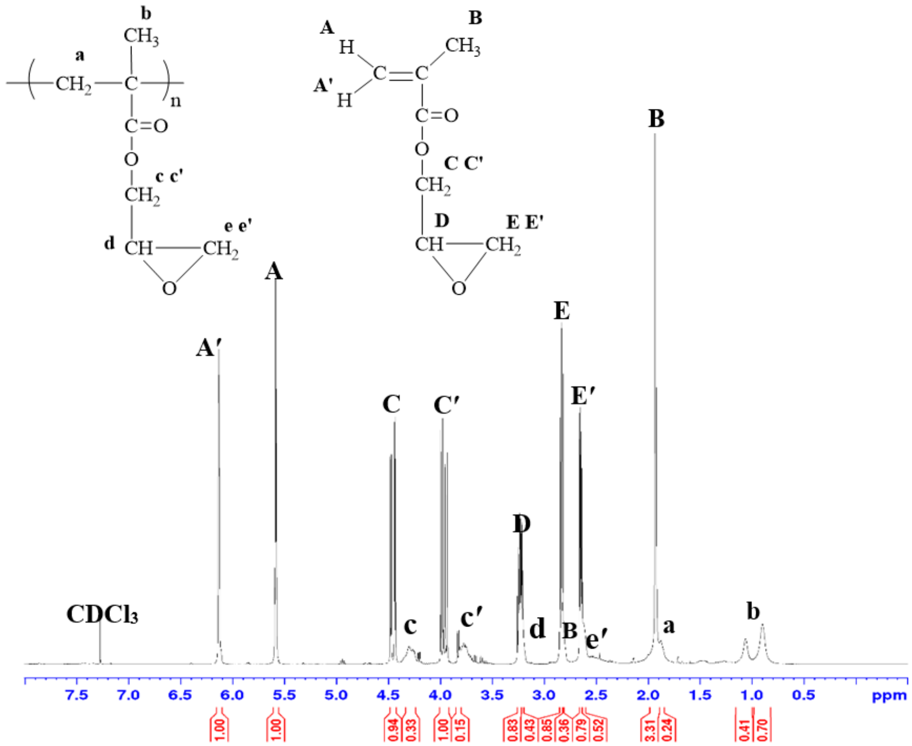


**Figure 5** NMR spectra for 14 hours PGMA crude using $CDCl_3$ as solvent.

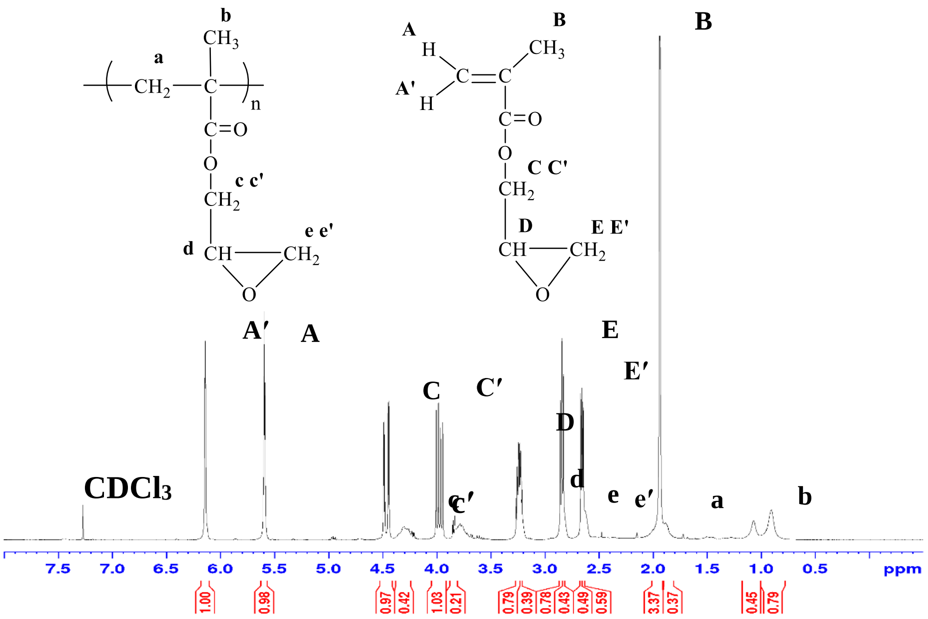


**Figure 6** NMR spectra for 15 hours PGMA crude using $CDCl_3$ as solvent.

## 4. CONCLUSION

Poly(glycidyl methacrylate) (PGMA) was successfully synthesized from glycidyl methacrylate (GMA) using RAFT agent 4-Cyano-4-(thiobenzoylthio)pentanoic acid (CPADB) and initiator 4,4’-azobis(4-cyanopentanoic acid) (ACPA) by reversible-addition fragmentation chain transfer (RAFT) polymerization technique in bulk. In this study, the reaction time of RAFT polymerization of PGMA was varied while the mole ratio GMA:CPADB:ACPA and temperature of polymerization reaction was kept constant. PGMA was successfully synthesized when the mixture was reacted for 14 and 15 hours. The PGMA obtained was confirmed by FTIR-ATR and $^1$H NMR. From the results obtained, it was found that the polymer was not fully polymerized when the reaction time was below 14 hours. At this time the product turned cloudy indicating polymerization reaction to form polymer occurring. Reaction time after 15 hours resulted in a gel product. The gel product, unfortunately, was hard to remove from the round-bottom flask. Hence, PGMA obtained through RAFT polymerization in this research was successfully synthesized from 14 and 15 hours.

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