

Synthesis and Characterization of Glycidyl Esters of Acrylic and Methacrylic acids for NIPU Coatings

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Abstract: Glycidyl acrylate (GA) and Glycidylmethacrylate (GMA) are the reaction products of the epichlorohydrin (ECH) with acrylic acid (AA) and methacrylic acid (MAA) respectively. These monomers were synthesized via two different routes i.e. direct reaction of AA and MAA with ECH and second by reaction of AA and MAA with Sodium hydroxide to form sodium salt of the acid followed by reacting with ECH. The polymerization inhibitor used was tert-butyl hydroquinone (TBHQ) and catalysts used were triethylamine (TEA) and quaternary ammonium salt. Experimental results show that first route is suitable for synthesizing GA and second route is suitable for synthesis of GMA. The catalysts also have drastic effect on the conversion to the respective glycidyl esters. The study of the effect of catalyst and polymerization inhibitor has been carried out via both routes.

Keywords: Diethylamine, Epichlorohydrin, Glycidyl acrylate, Glycidyl methacrylate, Triethylamine, Tert-butyl hydroquinone

I. INTRODUCTION

Glycidyl acrylate and glycidyl methacrylate are very important monomers and they find application in industrial polymers, surface coatings etc. One of their uses is in synthesis of non isocyanate polyurethanes. These monomers have a characteristic double bond and epoxy ring in the same molecule. Double bond is utilized in the radical polymerization of these monomers and epoxy functionality is used for reaction with carbon dioxide to create cyclic carbonate groups. In this paper these monomers have been synthesized by two different routes. These are one of the very starting raw materials for the synthesis of Non Isocyanate Polyurethanes (NIPU). Polyurethanes based coatings are very popular due to their excellent chemical and mechanical properties, but due to some drawbacks like toxicity of isocyanates, moisture-sensitivity and environmental regulations, a need of development of an environment friendly polyurethane was felt in across the coating world. Non isocyanate routes for synthesis of PU are very important step which is mostly based on cyclic carbonate + aliphatic/cycloaliphatic amine chemistry^[1]. The main challenge is to retain the positive characteristics of conventional PU in the new chemistry. PU coatings are mainly used as top coats over primed surfaces or an intermediate coats because of various properties like (a) High gloss colour finish (b) Tough and abrasion resistance, excellent in area of high wear (c) Hardness and flexibility is very good (d) Good chemical resistance (e) Excellent weather ability; resistance to high levels of UV and extremes of weather^[2]. In addition the PU coatings are also recently being used directly on the cleaned metal surface without any primer. This is one of the most popular high performance coatings especially in pipeline coatings, sea-shore applications and, marine coatings.

Polymeric epoxides can be converted into corresponding five-membered cyclic carbonates effectively by reacting with carbon dioxide and this process is called carbonation of epoxy rings. It is one of the most inexpensive methods to incorporate CO₂ into organic compounds. The general reaction of epoxy ring and CO₂ is shown in figure (Fig.1)^[3].

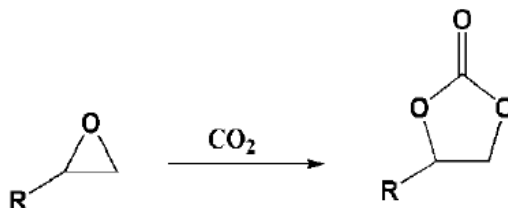


Figure 1: Conversion of Epoxy to cyclocarbonate group

The reaction between cyclic carbonates and amines gives one of the most satisfying alternatives to the conventional synthesis of Polyurethanes. The target is to synthesize the glycidyl acrylate monomer which can be used for polymerisation in CO₂ atmosphere produces a polymer having both cyclic carbonate groups and epoxide groups (Fig.2). The transformation of the resulting polymer into polyurethane can be carried out by hydrolysis of epoxy groups by reacting with aqueous HCl at room temperature in presence of solvents like DMSO, DMF and further by reacting with amines.^[4]

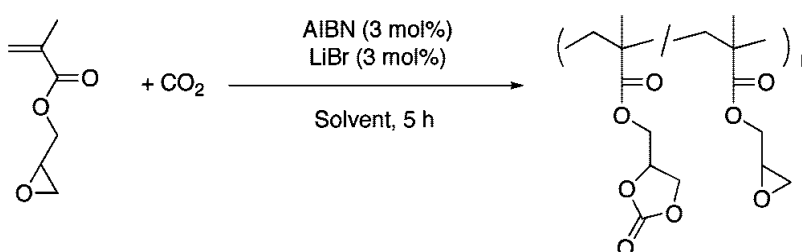


Figure 2: Fixing CO₂ during polymerization of Glycidyl methacrylate

II. GLYCIDYL ACRYLATE

Glycidyl acrylate is an interesting monomer. It has two very special functional groups, One is unsaturation i.e. double bond and other is epoxide group.

Route 1: Reaction of AA with ECH in presence of a catalyst and polymerization inhibitor (Fig.3).

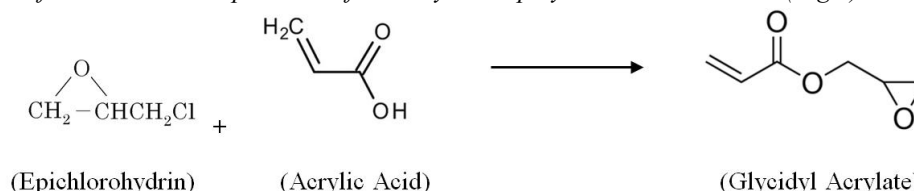


Figure 3: Reaction between Epichlorohydrin and Acrylic Acid

Similar to above reaction, glycidylmethacrylate is synthesized by the reaction of methacrylic acid and epichlorohydrin.

Route 2: Reaction of AA and MAA with NaOH to form sodium salt of these acids followed by reaction with ECH.

III. EXPERIMENTAL PROCEDURE

The following materials were purchased from Thomas Baker, Mumbai. Their names are given below and used as received.

Acrylic Acid (AA), Methacrylic acid (MAA), Epichlorohydrin (ECH), tert-butyl hydroquinone (TBHQ), 4-methoxyphenol (MEHQ), triethylamine (TEA), diethylamine (DEA), and Sodium hydroxide. Acid value was calculated as per ASTM.

Procedure Route 1: 1 mole (72 g) of acrylic acid was reacted with 92.5 g of ECH, TEA was taken 0.5 g and polymerization inhibitor 0.15 g. All the four materials were dispersed in a 3-necked flask with reflux condenser, nitrogen inlet and placed on heated to 80 °C for 1 hour then 105 °C for 2 hours on a heater with magnetic stirrer. The reaction mixture was then mixed and stirred with an almost equal amount of 3% dilute aqueous solution of NaOH, kept

standing, water layer was removed followed by 2-3 times washing with distilled water. Excess ECH was removed by vacuum distillation (Fig.4).



Figure 4: (a) Synthesis of Glycidyl acrylate and (b) Washing filtration

Procedure Route 2: Preparation of sodium salt of acrylic acid- In a 3 necked flask added water 80g, NaOH 102g and stirred at 60 °C. From the dropping funnel 100mL of acrylic acid was added drop by drop. After dispersing for about 1 hour it was spray dried, cooled to room temperature and spread into a stainless steel plate and oven dried at 65 °C.

GMA Synthesis: In a three necked flask, 80 g of sodium methacrylate, 500g of ECH, 0.4g of polymerization inhibitor, 1.5g of catalyst consisting of a tetramethyl ammonium bromide was added, stirred and reacted at 110 °C. When cooled NaCl crystallizes out and removed by filtration. Excess ECH is removed by vacuum distillation of the filtrate.

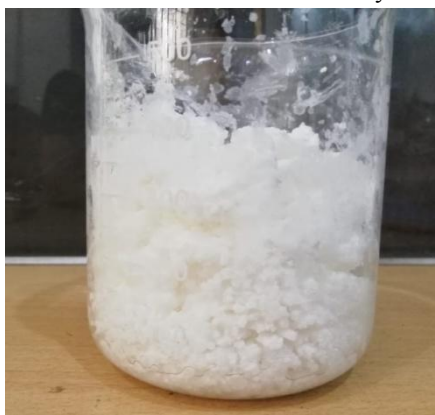


Figure 5: Dessicant of Sodium Methacrylate

The first route involves an inconvenient step of removal of chlorine by treating the liquid mixture with alkali hydroxide. The simplicity of performance and the higher yields (80-90 %) of product can predetermine the application of this method. Following data demonstrates the experimental procedure for synthesis of GA and GMA.

Table 1: Molar ratio of the components for synthesis of GA and GMA

	GA1	GA2	GMA1	GMA2
Acrylic Acid/ Methacrylic Acid	72g	72g	86g	86g
Epichlorohydrin	92.5g	92.5g	92.5g	92.5g
Triethylamine	0.5	0.5	0.5	0.5
TBHQ	0.15	0.15	0.15	0.15

IV. RESULT AND DISCUSSION

The reaction of AA/MAA with ECH was tracked by acid value. The graphs of the acid value vs time for both reactions in similar conditions are shown below in figure 6 and 7.

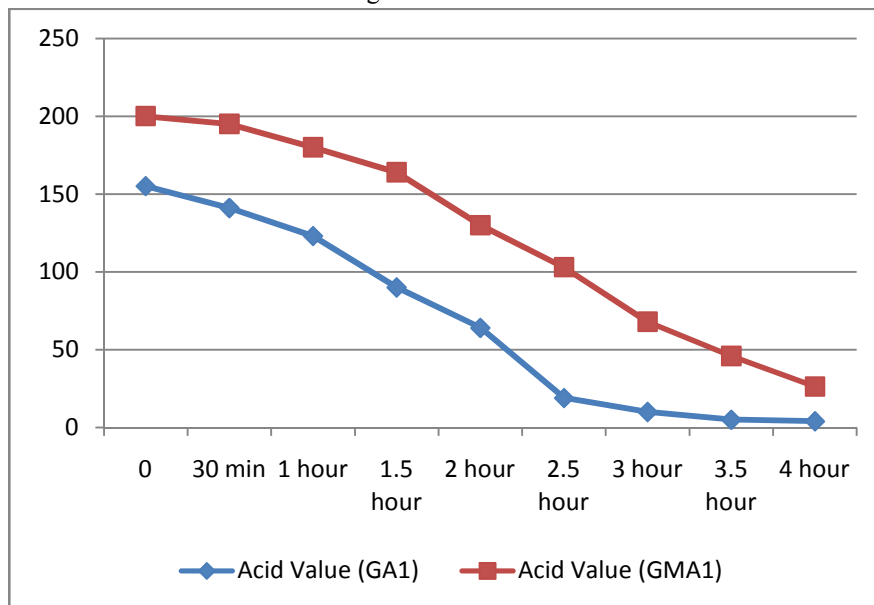


Figure 6: Acid Value change in route 1

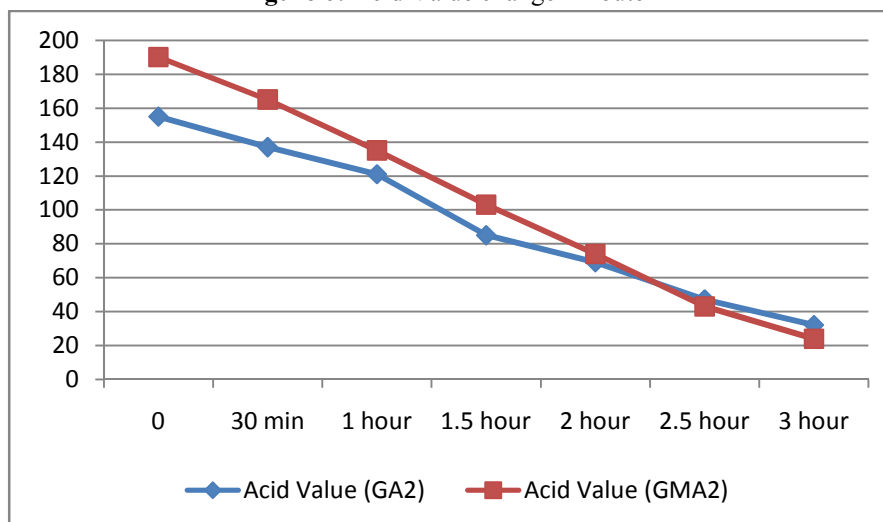


Figure 7: Acid value change in route 2

Fourier Transform Infrared (FT-IR): The analysis of GA and GMA by FT-IR spectroscopy was performed using ABB laboratory spectrometer instrument (MB3000) equipped with DTGS detector and Potassium bromide as beam splitter. The analysis was averaged over 16 scans with 4cm resolution for all of the spectrum. The FT-IR spectrum of GA1 and GMA1 are shown in Figure 8 and Figure 9 respectively. The spectrum reveals: GA1: 810(C-H bending), 910(Oxirane), 1056(Primary alcohol), 1180(C-O stretching of ester), 1635(C=C), 1720(α,β -unsaturated ester); GMA1: 748(C-H bending), 987(C=C stretching), (Primary alcohol), 1180(C-O stretching of ester), 1404(O-H bending carboxylic acid).

The absence of oxirane group in GMA1 shows the inefficiency of the method. Phase transfer catalyst is required for its synthesis as represented in route 2. Route 1 is suitable for synthesis of glycidyl acrylate.

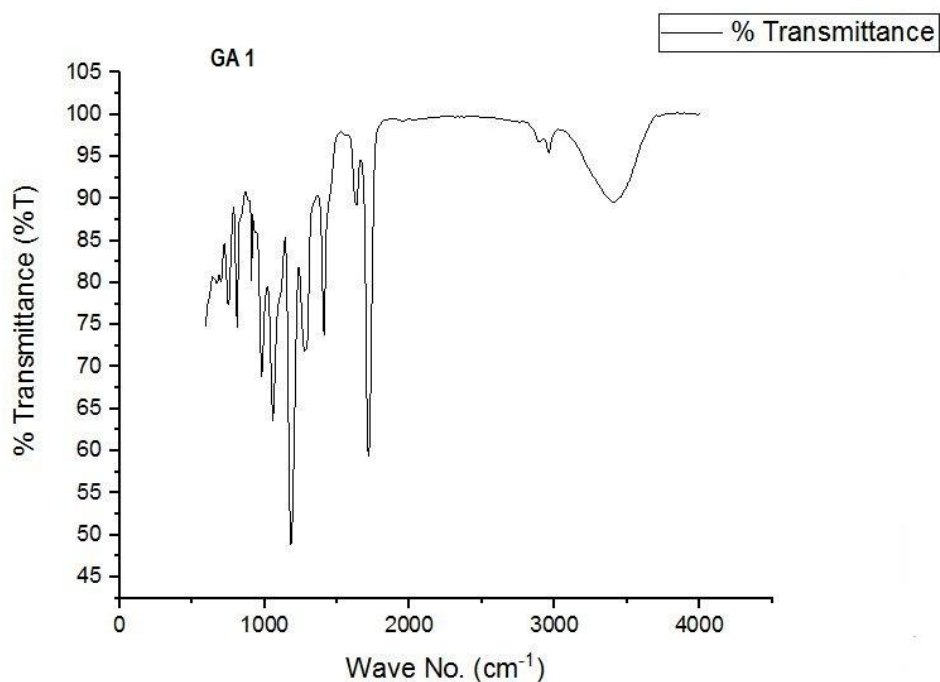


Figure 8: FTIR Report of GA1

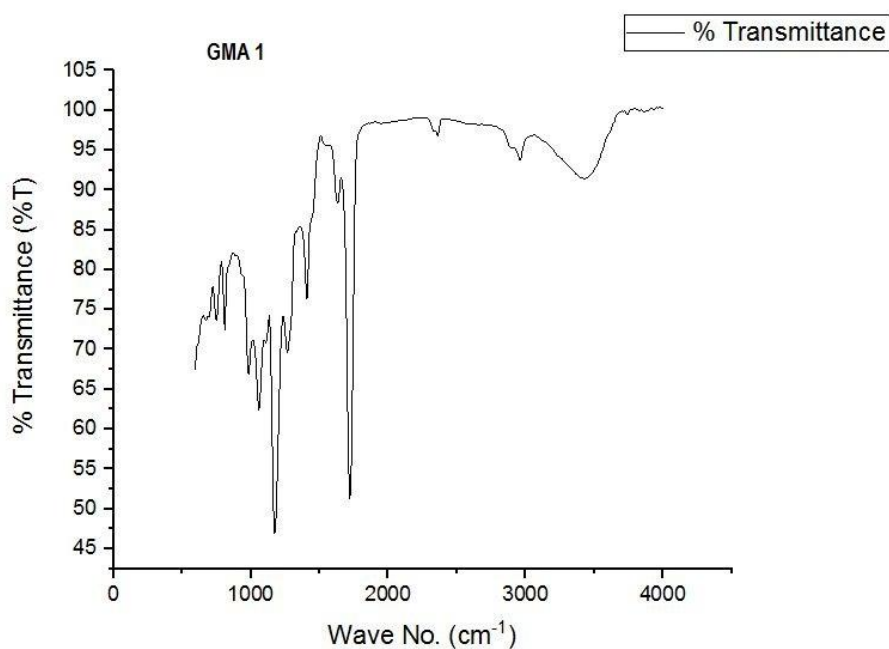


Figure 9: FTIR of GMA1

Table 2: Other physical properties of GA and GMA

Property	Glycidyl Acrylate (GA1)	Glycidyl Methacrylate (GMA1)
Colour	Light Yellow	Light to dark Yellow
Refractive Index	1.47	1.34
Solubility in water	Inslouble	Inslouble
Solubility in Acetone	Soluble	Soluble
Density	1.112	1.107

The Mechanism via the 1st route is as follows: TEA or DEA act as nucleophile and attack on the ECH to produce quaternary ammonium salt and carbocation of ECH. This carbocation then attacks on acrylic acid molecule to result in the formation of glycidyl ester of AA and MAA. triethylamine attacks on epichlorohydrin which generates ammonium chloride. The acrylic acid and the carbocation undergoes esterification to generate glycidyl acrylate. The reaction between acrylic acid and oxiranes in presence of DMF solvent follows first order kinetics. Route 2 used two separate steps for synthesis of GMA, it can also be synthesized in one step. A potential phase transfer catalysts like tetramethylammonium chloride would consist of a single step esterification by mixing methacrylic acid, NaOH, PTC, ECH. Hydrolysis of the epoxide in one step reaction can be attributed to proper choice of base^[5].

Kinetic study of addition of carboxylic acids to epoxides in presence of chromium (III) ethanoate have concluded that the rate of reaction cannot be explained by strengths of acids alone. The type of solvent and epoxide also have role^[6,7]. The use of phase transfer catalysts generally excel over the conventional methods and offers a comparatively simple, efficient, and high quality products as compared to that of the traditional methods. These methods also help to reduce the air pollution by minimizing the use of solvents^[8]. Glycidyl methacrylate can be copolymerized with numerous acrylate monomers which has a wide application in different industries. The copolymers of n-butyl acrylate and glycidyl methacrylate, when added to epoxy resin the thermal and mechanical properties have found to be improved.^[9]

The purpose of the above reaction is to incorporate both unsaturation and epoxy group in a single monomer. This monomer is capable of undergoing radical polymerization and also the reactions of epoxide groups. Three Different Routes for cyclic carbonates:

- Polymerization of Glycidyl acrylate in presence of Carbon dioxide
- Polymerization of glycidyl acrylate followed by carbonation
- Carbonation of glycidyl acrylate followed by radical polymerization

V. APPLICATIONS OF NIPU

Polyurethanes have a very wide application area because of its extraordinary properties. Non isocyanate polyurethanes also find various applications in coatings, polymer, and ink industry. NIPU systems could be employed for thermosetting coatings, UV stable coatings, monolithic floorings etc. NIPU coatings may gradually turn to yellow on exposure to light which is unsuitable for transparent applications. UV stable coatings can be prepared by using acrylic monomers having cyclic carbonate which provides excellent UV resistance and superior mechanical properties. Low to Zero VOC coatings can also be synthesized which eliminates hazardous exposure with isocyanate materials.^[10]

VI. CONCLUSION

The cyclic carbonate amine chemistry is very useful for synthesis of polyurethanes via a non isocyanate route. The carbonation of epoxy group to cyclocarbonate group is the first and very important step for synthesis of NIPU. Glycidyl acrylate can be suitably synthesized by reaction of acrylic acid and epichlorohydrin. The reaction of sodium salt of methacrylic acid and epichlorohydrin produces glycidyl methacrylate in presence of tertiary ammonium salts as catalyst. These glycidyl esters can be polymerized in CO₂ atmosphere for the preparation of cyclic carbonate oligomers.

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