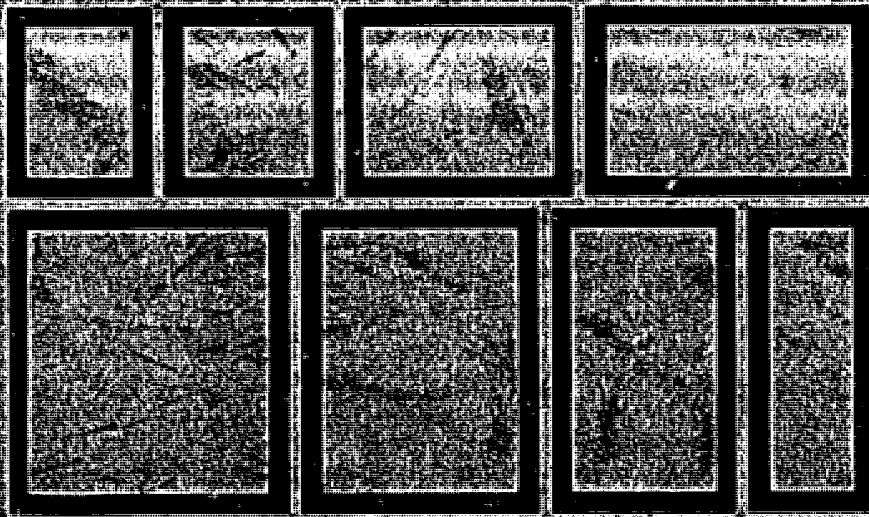


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SYNTHESIS OF ACRYLIC PREPOLYMER



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by

HUSSIN BIN MOHD NOR
DAHLAN HJ. MOHD
MOHD HILMI MAHMUD

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Program: Isotopes and Radiation in Industry,
Nuclear Energy Unit,
Prime Minister's Department,

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Abstract

An acrylic prepolymer was synthesised from glycidyl methacrylate (GMA), butyl methacrylate (BMA), methyl methacrylate (MMA) and acrylic acid (AA). Butyl acetate (BAc), benzoyl peroxide (BzO), 4-methoxyphenol (MPH) and triethylamine (TEA) were used as solvent, initiator, inhibitor and catalyst respectively. Observations of the synthesis leading to the formation of acrylic prepolymer are described.

Introduction

Acrylic prepolymers can be prepared from vinyl or acrylic polymers by copolymerizing monomers containing pendant acid, anhydride, hydroxy or glycidyl groups. These groups are then available for reaction with an unsaturated monomer (e.g. the copolymerisation of glycidyl acrylates or methacrylates with other monomers, produces a copolymer with epoxy groups, which can be reacted with an acid, such as acrylic acid to give acrylic prepolymers). Alternatively hydroxyl groups along the acrylic chain can be reacted with the half adduct of a urethane acrylate¹.

This report describes the procedure of synthesizing radiation curable acrylic prepolymer from a combination of GMA, BMA, MMA and AA monomers. The properties of the monomers and solvent used in this experiment are shown in Table 1.

Table 1: Properties of monomers and solvent

Monomer	F.W	bp°C	flp°F	d(25)g/ml	fp°C	Brand
GMA, 97%	142.15	189.0	169	1.042	-	Aldrich
MMA, 98%	100.12	100.3	50	0.932	-48.2	Wako
BMA, 99%	142.20	160-163	123	0.894	-	Aldrich
BAC, 99%	116.16	126.1	72	0.876	-73.5	Aldrich

Experimental

Materials

Monomers and solvent used are listed in Table 1. Other chemicals were BzO (Merck) , MPh (Aldrich) and TEA (Merck)

which were used as initiator, inhibitor and catalyst, respectively.

Apparatus

The apparatus for the synthesis consisted of a 5-necked reaction flask which was equipped with a reflux condenser, a dropping funnel, a mechanical agitator, a bent thermometer and a nitrogen gas inlet. The apparatus set up used, is shown in Figure 1.

Synthesis of Copolymer

The ingredients for the synthesis are listed in Table 2.

Table 2: Ingredients of the copolymer

Glycidyl methacrylate	- 28.0g
Butyl methacrylate	- 122.8g
Methyl methacrylate	- 50.2g
Benzoyl peroxide (initiator)	- 4.0g (2.0%)
Butyl acetate (solvent)	- 500ml

The process of this synthesis is as follows:-

!-----!
! Charge butyl acetate, start nitrogen purge, agitate, !
! and reflux (T=127°C). !
!-----!

!-----!
! Charge gradually a mixture of GMA, BMA, MMA and !
! BzO within 2 hours. (T=127°C). !
!-----!

 ! Continue reflux for another 3 hours to remove
 ! residual peroxide, then reduce reaction temperature
 ! to 100°C for acrylation process.
 ! -----

Procedure and Observations

500ml butyl acetate was charged into the reaction flask, purged with nitrogen, heated and refluxed (T=127°C). A mixture of 28.0g GMA, 122.8g BMA, 50.2g MMA and 4.0g BzO was charged gradually through a dropping funnel into the boiling butyl acetate within a period of 2 hours. The mixture was further refluxed for another 3 hours. Then the temperature of the mixture was reduced to 100°C for the next acrylation process.

Acrylation of Copolymer

Table 3: Ingredients for the acrylation

Acrylic acid	- 15.8 g
Triethylamine (catalyst)	- 2.0 ml (0.9%)
4- methoxyphenol (inhibitor)	- 60.0 mg (0.02%)

The acrylation process of the copolymer is as follows:-

 ! Charge gradually a mixture of AA, TEA and MPh
 ! within 1 hour at 100°C and maintain the temperature
 ! -----
 !
 ! -----
 ! Further reflux the mixture at 100°C until the acid
 ! value less than 10.0 mg/g sample
 ! -----

! -----!
! Cool the mixture and add 4 methoxyphenol. Remove !
! solvent and residual acid. !
! -----!

Procedure and Observations

15.8g of acrylic acid containing 2.0ml of TEA was charged gradually through a dropping funnel to the mixture within a period of 1 hour. The temperature of the mixture was maintained between 95°C - 100°C until the acid value reduced to less than 10.0mg/g resin. The procedure of acid value measurement is given in the Appendix 1.

In this experiment, a period of 13 hours and 10 minutes was required to achieve the acid value of 9.4 mg/g resin. Then, the experiment was terminated and 60mg 4-methoxyphenol was added. The solvent and residual acid were removed from the acrylic prepolymer by using a vacuum rotary evaporator.

Molecular Weight Determination Measurements

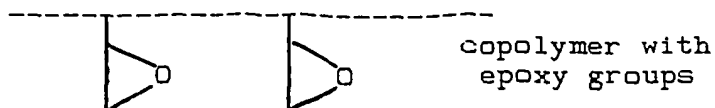
High Performance GPC (Gas Permeation Chromatography) from Tokyo Soda was used to measure the MWD of the synthesized acrylic prepolymer using polystyrene as a standard. The eluent used was tetrahydrofuran (THF) and the concentration of the sample was about 0.5 weight %.

Discussion

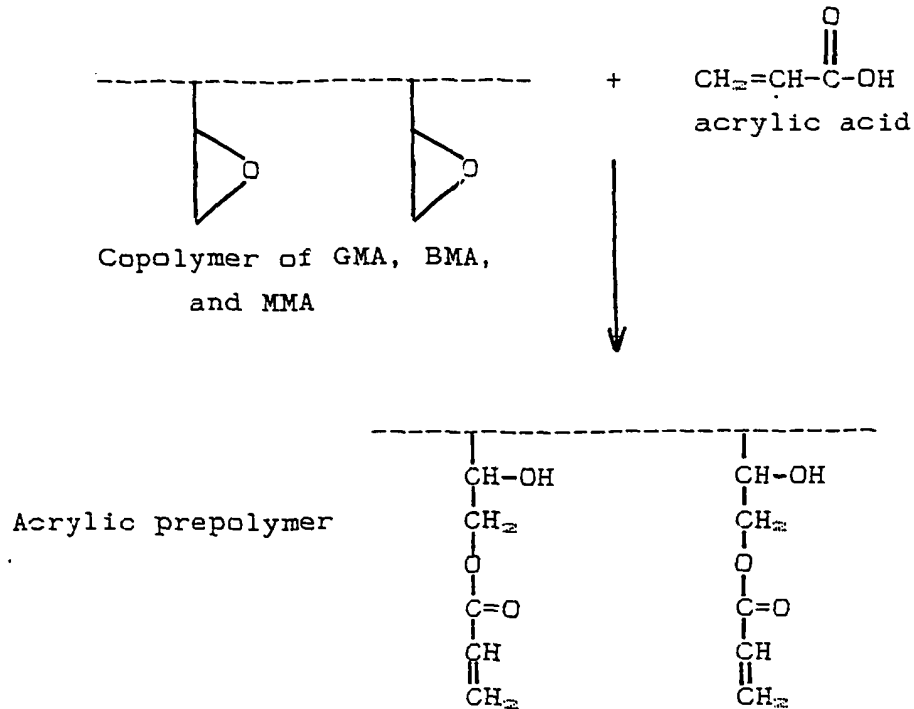
In this work, benzoyl peroxide was used as an initiator. It is known that upon heating between 50°C - 100°C, benzoyl peroxide decompose and forms free radicals as follows²:



These alkyl radicals will initiate the copolymerisation process of the monomers (GMA, BMA, MMA). This reaction is expected to occur randomly. The synthesized copolymer is expected to have pendant groups (i.e. epoxy groups) that can be represented as follows:-



The acrylation was carried out at temperature between 95°C - 100°C. In this reaction, acrylic acid will react with epoxy groups to produce acrylic prepolymers. The reaction was accelerated by TEA.



It is important to mention here, that gelation is the hindrant factor in the acrylation process. Two factors which might be contributory to the gelation are the addition rate of acrylic acid and the temperature. The addition of acrylic acid must be at a very slow rate and during synthesis the temperature should not be exceeded above 120°C. The MWD of the prepared acrylic prepolymer is 14.408 (Figure 2).

References

1. R. Holman, U.V. and E.B. Curing Formulation for Printing Inks, Coatings and Paints, SITA-Technology, 1984, pp41.
2. Paul J. Flory, "Principles of Polymer Chemistry", 11th printing 1981, pp108, Cornell University Press, Ithaca and London.
3. Aldrich, Catalog handbook of Fine Chemicals, 1986-1987. Aldrich Chemical Company, Inc. 940 West Saint Paul Avenue Milwaukee, Wisconsin 53233 USA.

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Acknowledgements

The authors wish to express their thanks to Japanese Government for providing an expert, in the name of Mr. T. Sasaki from JAERI, Takasaki, to assist in the experiment.

Appendix 1

Acid Value Determination

Dissolve 1-2 g of resin with 10 ml acetone and then add a few drops of phenol red : bromothymol blue (1:1 in 90% ethanol) indicator. Titrate with 0.1N KOH which is previously determined its f factor using 0.1N HCl as titrant and phenolphthalein as indicator.

Acid value is the number of milligrams KOH required to neutralize 1 g of resin and calculated by using the following formula:

$$AN = \frac{\text{mg KOH}}{\text{1g of resin}} = \frac{5.61 \times f \times v}{w}$$

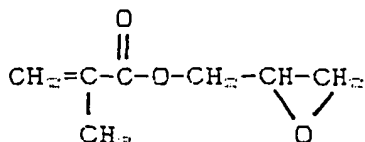
where f is the factor

v is volume of KOH solution

w is weight of resin sample

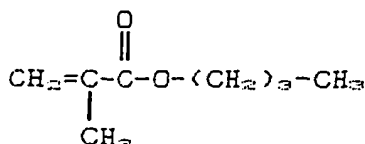
Appendix 2^a

1. Glycidyl methacrylate



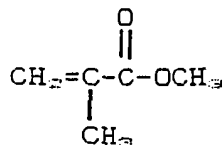
Highly toxic: Cancer suspect agent. Inhibited with 50 ppm hydroquinone (HQ).

2. Butyl methacrylate



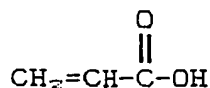
Irritant. Inhibited with 10ppm HQ.

3. Methyl methacrylate



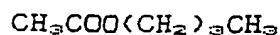
Flammable liquid lachrymator. Inhibited with 10ppm HQ.

4. Acrylic acid



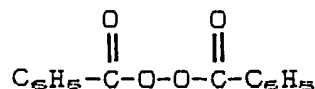
Corrosive, Toxic. Inhibited with 200ppm HQ

5. Butyl acetate



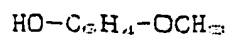
Flammable liquid, Irritant glass-distilled. Filtered through 0.5u filters.

6. Benzoyl peroxide



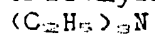
Explosive when heated oxidizer. Widely used initiator, curing agent and crosslinking agent in polymerization processes. Has been found to have skin-tumor-promoting activity.

7. 4-methoxyphenol

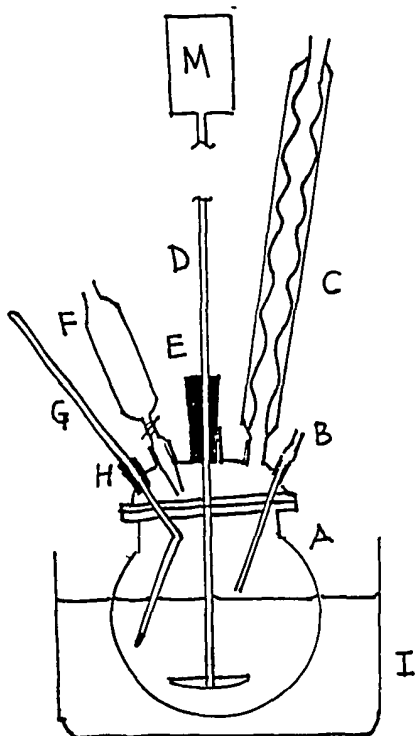


Toxic, Irritant. Polymerization inhibitor, antioxidant & chemical intermediate. Possesses melanocytotoxic activity.

8. Triethylamine

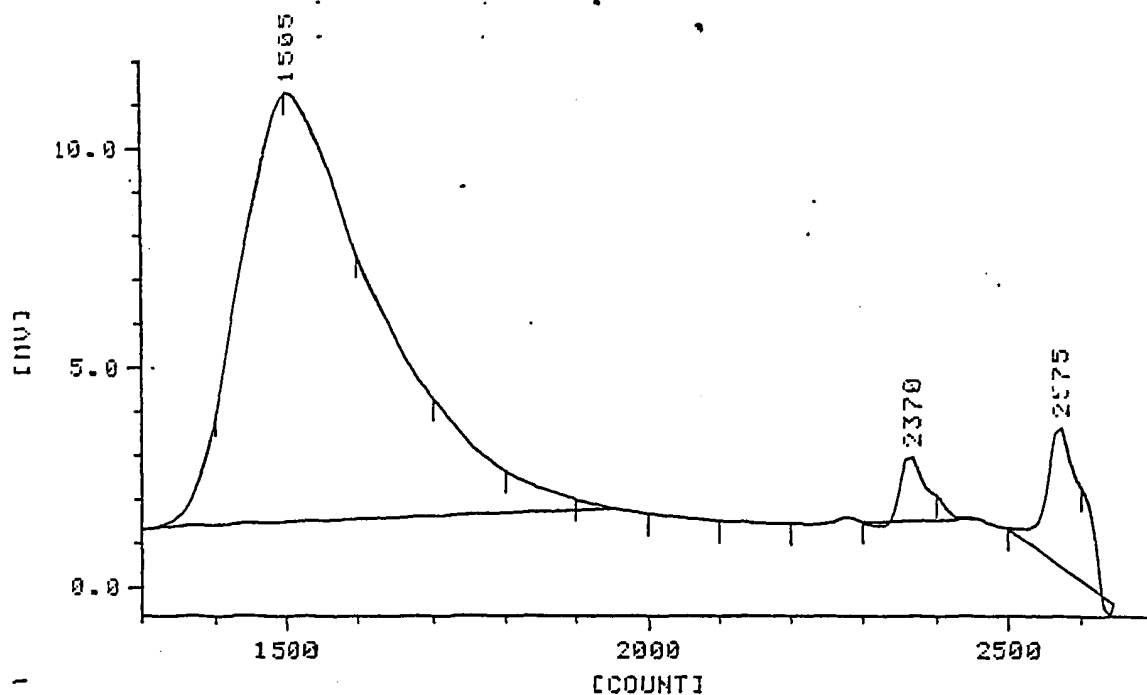


Flammable liquid, Corrosive.



- A. Separable reaction flask
- B. Nitrogen gas inlet
- C. Reflux condenser
- D. Stirring rod
- E. Stirring seal
- F. Dropping funnel
- G. Bent thermometer
- H. Thermometer holder
- I. Oil bath
- M. Mechanical agitator.

FIGURE 1



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SAMPLE NO. 0 NAME: SERIAL NO. 0012

CH.NO 1 METHOD 2

PEAK NO.	1	BASE					
	START	TOP	END	MN	MW	MZ	MU
C	1320	1505	1945	8.52861E+03	1.44084E+04	2.47949E+04	1.44083E+04
U	1.4	11.3	1.8	MW/MN	MZ/MW	AREA	AREA%
M	196518	15051	1318	1.69	1.72	2.17627E+03	89.80

PEAK NO.	2	BASE					
	START	TOP	END	MN	MW	MZ	MU
C	2300	2370	2455	3.33705E+02	3.34718E+02	3.35698E+02	3.34717E+02
U	1.5	3.0	1.5	MW/MN	MZ/MW	AREA	AREA%
M	416	340	270	1.00	1.00	6.37253E+01	2.63

PEAK NO.	3	BASE					
	START	TOP	END	MN	MW	MZ	MU
C	2500	2575	2645	1.94389E+02	1.95117E+02	1.95860E+02	1.95117E+02
U	1.3	3.7	-0.4	MW/MN	MZ/MW	AREA	AREA%
M	240	197	163	1.00	1.00	1.83556E+02	7.57

TOTAL	START	TOP	END	MN	MW	MZ	MU
C	1320	1505	2645	1.74305E+03	1.29618E+04	2.47502E+04	1.29618E+04
U	1.4	11.3	-0.4	MW/MN	MZ/MW	AREA	AREA%
M	196518	15051	163	7.44	1.91	2.42355E+03	100.00

Figure 2: GPC Curve of Synthesized Acrylic Prepolymer.