# Copolymerization of Glycidyl Methacrylate with Methyl Acrylate

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**Abstract** Copolymerization of glycidyl methacrylate(GMA) with methyl acrylate(MA) and the reaction of the copoly mer with primary amines were investigated. The monomer reactivity ratios were determined by Mayo-Lewis intersecting method.

$$r_1 = 0.22 \pm 0.03 (\text{GMA}), \quad r_2 = 0.50 \pm 0.07 (\text{MA}).$$

GMA and MA copolymerized to afford the polymer having good alternate arrangements of the units of the monomers.

## Introduction

Glycidyl methacrylate has a double bond and an epoxy group, it copolymerizes with conventional vinyl monomers and affords an industrial utilization for introducing reactive functional group into the polymers. The copolymerizations[1] of GMA with methyl methacrylate (MMA), styrene[2], acrylonitrile[2], have been reported.

As a part of the investigations of the reactive polymers, the present paper describes the copolymerizability of GMA (vinylidene type) with MA(nonvinylidene type), and the reaction of epoxy group in the polymer molecule with primary amines.

## Experimental

**Materials** GMA was obtained by the condensation of sodium methacrylate with epichlorohydrin[3]; b. p., 85°C/15 mmHg. The commercial methyl acrylate was purified by the usual way; b. p., 40°C/200 mmHg. Chemical pure DMF and amines were used without any further puri-

fication.

**Copolymerization** Fifteen grams of a pair of monomers and 15mg of AIBN were mixed in a sealed tube under nitrogen flow. The polymerization was carried out at 60°C in the thermostated bath until the conversion of the copolymer was attained to approximately 5%. The resulting polymer was purified by reprecipitation with acetone-methanol, dried under a vacuum. The copolymer thus obtained gave IR absorption at 910cm$^{-1}$, which is a characteristic absorption of epoxy group. The purified copolymer submitted to the analysis of epoxy content by HCl-DMF method[4]. The following is a typical analytical example of epoxy group in the copolymer. To 0.1 gram of GMA-MA copolymer were added 35m*l.* of DMF, which was kept for about 3 hrs. at 40°C, then to this solution 25m*l.* of 0.2N HCl-DMF solution were added. The solution was allowed to complete the reaction for 5 hrs. at room temperature, then diluted with water. The solution was titrated with 0.1*N* NaOH-MeOH solution using bromophenol blue as an indicator. A blank determination was also carried out on 0.2N HCl-DMF solution in the

same manner.

**Reaction of copolymer with amine** To 20 ml. of DMF were added 0.5 grams of the copolymer(Run No. 4) and twice amounts of amine as calculated in a sealed tube under nitrogen flow. The solution was shaken and kept at 60°C for 16 hrs. in the thermostated bath. The resulting polymer was purified by the reprecipitation with acetone-methanol, dried under a vacuum, then submitted to the elemental analysis of nitrogen content.

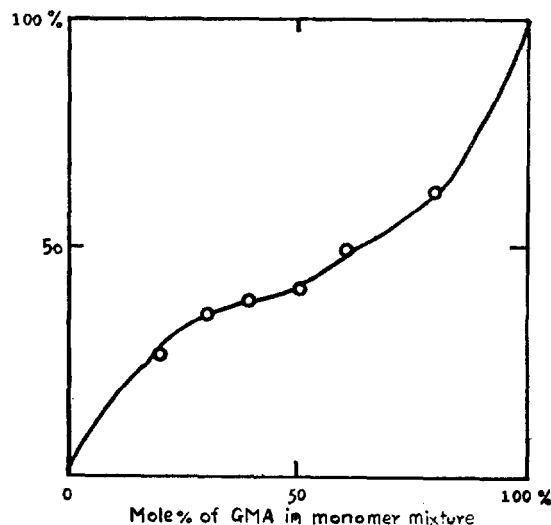The infrared spectra were measured on a Hitachi Model EPI-S-Ⅱ double beam spectrometer.



*Fig.* 1. Copolymer Composition Curve

*Table* 1. Copolymer composition with various monomer ratio

| Run No. | Mole % in monomer $M_1$(GMA) | $M_2$(MA) | Copolymer epoxy% | Mole % in copolymer $m_1$(GMA) | $m_2$(MA) |
|---|---|---|---|---|---|
| 1 | 20 | 80 | 4.10 | 26.03 | 73.97 |
| 2 | 30 | 70 | 5.43 | 36.04 | 63.96 |
| 3 | 40 | 60 | 5.80 | 39.11 | 60.89 |
| 4 | 50 | 50 | 6.09 | 41.18 | 58.82 |
| 5 | 60 | 40 | 7.16 | 51.36 | 48.64 |
| 6 | 80 | 20 | 8.10 | 60.75 | 39.25 |

## Results and Discussion

**Copolymerization of GMA with MA** The copolymerization of GMA with MA was carried out in bulk system at 60°C, using azobisisobutyronirile(AIBN) as radical initiator. The polymer was purified by reprecipitation with acetone-methanol. The compositions of the polymers were determined by analysis of epoxy group in the copolymers obtained. The results of the copolymerization of GMA with MA are summarized in *Table* 1. The copolymer composition curve of GMA with MA is shown in *Fig.* 1.

The monomer reactivity ratios were obtained by the Mayo-Lewis intersecting method[5] from the compositions of the monomer feeds and copolymers obtained. According to the Alfrey-Price equations[6], $Q$ and $e$ values of GMA were calculated using known values of MA($Q_2$: 0.42 $e_2$: 0.60)[7].

$r_1 = 0.22 \pm 0.03$(GMA), $r_2 = 0.50 \pm 0.07$(MA),
$r_1 \cdot r_2 = 0.11$.

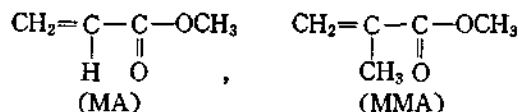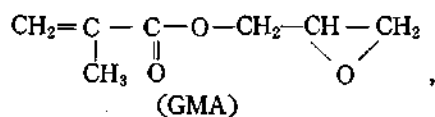$Q_1 = 0.78$(GMA), $e_1 = -0.89$(GMA).

*Table* 2 shows the copolymerization parameters of some vinyl monomers to GMA for comparison.

Compared with other copolymers in *Table* 2, the copolymerization of GMA with MA gave

Table 2. Copolymerization parameters of some vinyl monomers with GMA

| $M_1$ | $M_2$ | $r_1$ | $r_2$ | $r_1 \cdot r_2$ | $Q$(GMA) | $e$(GMA) |
|-------|-------|-------|-------|-----------------|----------|----------|
| GMA | Methyl methacrylate[1] | 0.88 | 0.76 | 0.67 | — | — |
|  | Styrene[2] | 0.53 | 0.44 | 0.23 | 0.87 | 0.40 |
|  | Acrylonitrile[2] | 1.32 | 0.14 | 0.19 | — | — |

better alternateness of the units of the monomers in the copolymer chain. The molecular structures of GMA and MMA are vinylidene type, but MA is a non-vinylidene type.

$$CH_2 = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH - CH_2$$
$$\diagdown O \diagup$$

(GMA)

$$CH_2 = \underset{\underset{H}{|}}{C} - \underset{\underset{O}{\|}}{C} - OCH_3 \qquad CH_2 = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{O}{\|}}{C} - OCH_3$$

(MA)                (MMA)

Lower reactivity of GMA to MA would be mainly due to such steric factor. The great differences of polarities[8] between GMA and MA might contribute to afford good alternate arrangements of the units of GMA and MA in the copolymer chain. However, in the case of the copolymerization of GMA with MMA the arrangements of the units of GMA and MMA is in random as shown in Table 2.

GMA and MA have electron withdrawing ester group linked with vinyl group linked with vinyl group. However, in the case of GMA the electron density of vinyl bond is much increased, due to the electron donation of methyl group. Accordingly, the value of $e_1$(GMA) was calculated by taking negative sign in the Alfrey-Price equation, $e_1 = e_2 \pm (-\ln r_1 \cdot r_2)^{\frac{1}{2}}$.

**The reaction of copolymer with amines** As a preliminary investigation for kinetic determination in the reaction of GMA-MA copolymer with amines, the present work was undertaken to see the reactivity with amines. The reaction

of GMA-MA copolymer with amines was carried out in DMF in the sealed tube at 60°C. The reaction product was purified by reprecipitation with acetone-methanol, dried under a vacuum, then submitted to the analysis of nitrogen content. The results of the reaction of GMA-MA copolymer with amines are summarized in Table 3. The copolymer sample used for the reaction contained 6.09% of epoxy group (Run No. 4).

Table 3 The reaction of GMA-MA copolymer with amines [*a]

| Amine | Nitrogen content, % (Calculated) | Conversion, %[*b] |
|-------|----------------------------------|-------------------|
| $n$-Bthylamine | 1.90(4.60) | 41.3 |
| Ethylenediamine | 5.23(10.4) | 50.2 |
| Monoethanolamine | 3.29(4.80) | 68.5 |

[*a] Reaction time; 16 hrs.

[*b] Conversion $= \dfrac{N\%(\text{Found})}{N\%(\text{Calculated})} \times 100$

As shown in Table 3, the reactivity of GMA-MA copolymer with amine was decreased in the order of monoethanolamine > ethylenediamine > $n$-buthylamine, and also the ring opening of epoxy group by the reaction with amine proceeded smoothly. Such results were similar to the cases of GMA-MMA[1] and GMA-AN[2]. Accordingly the reactivity of GMA copolymer with amines might depend on the basicity of amines.
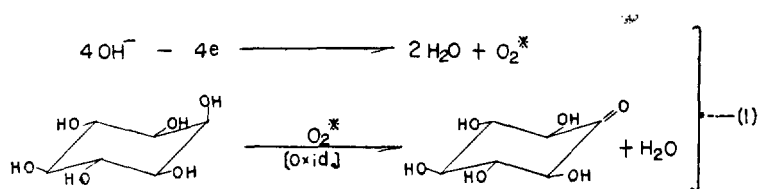
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訂正 ; 본지 p. 130 하단의 산화반응의 과정을 다음과 같이 정정함.

     a) 간접산화

$$4\,OH^- - 4e \longrightarrow 2\,H_2O + O_2^*$$



$$----(1)$$

     b) 직접산화



$$----(2)$$