

# Mechanochemical Copolymerization of Methyl Methacrylate and Styrene Initiated by the Grinding of Quartz

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**ABSTRACT:** The copolymerization of methyl methacrylate and styrene mechanochemically initiated by the grinding of quartz in the monomer mixture was investigated by using a vibrating ball mill. The effect of the grinding of quartz on the copolymerization was investigated by characterizing both the polymer formed and the ground quartz. The copolymerization proceeds apparently from the quartz grindings and was closely related to the total surface area of the ground quartz. The molecular weight distributions of the copolymers formed were unimodal as found in a homopolymer of only methyl methacrylate. It was clear from the composition analysis of the copolymer that the mechanochemical copolymerization of methyl methacrylate and styrene proceeded with a radical polymerization mechanism because of radicals on the quartz surface produced by the grinding. The monomer reactivity ratios obtained by the Fineman–Ross method suggested that the copolymers formed were alternating copolymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2011–2017, 2002; DOI 10.1002/app.10544

**Key words:** mechanochemistry; copolymerization; polystyrene; polymethyl methacrylate; quartz; grinding

## INTRODUCTION

The mechanical properties of the composite materials, which are composed of inorganic powder and organic polymers, depend greatly on the dispersibility of the inorganic powder in the polymer matrix and the interfacial interaction between the powder surface and the polymer molecules. A modification technology for the fine powder surface is very important to improve the dispersibility and interaction.

To effectively utilize mechanical energy in the grinding operations and to modify the surface property of fine inorganic powders, we investi-

gated the mechanochemical polymerization of vinyl monomers such as methyl methacrylate (MMA) and styrene initiated by the grinding of various inorganic solids.<sup>1–4</sup> The results showed that the mechanochemical polymerization was useful as a surface modification for a fine powder.<sup>1</sup> It was found that the fresh surface of many inorganic solids produced by the grinding created polymeric activity for MMA and that there were two types (i.e., radical and ionic polymerizations) of polymerization mechanisms according to the kind of inorganic solids.<sup>2</sup> In addition, the mechanochemical polymerizations of MMA and styrene initiated by the grinding of the quartz were found to proceed with a radical polymerization and a cationic polymerization mechanism, respectively.<sup>3,4</sup> These results encouraged our interest in the mechanism of copolymerization of MMA and

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styrene mechanochemically initiated by the grinding of the quartz.

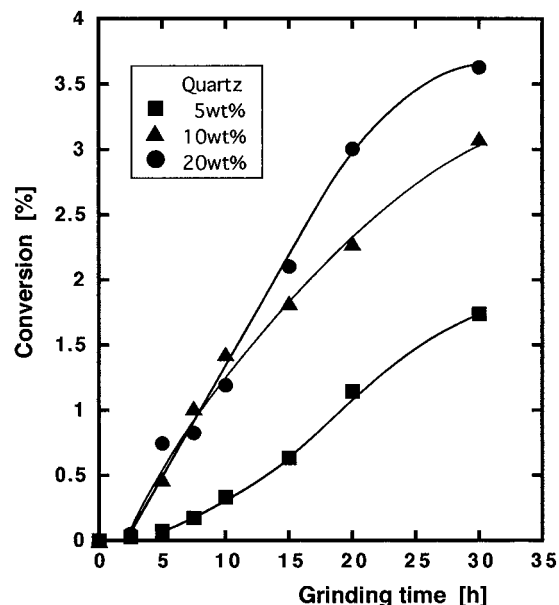
When this method is utilized as a technology of surface modification for fine powders, the more usable the polymer, the more favorable. Therefore, if the surface modification with the copolymer can be performed, the application of this method might be expanded in various fields.

In this work, the mechanochemical copolymerization of MMA and styrene initiated by the grinding of quartz was investigated. The effect of the grinding of the quartz on the copolymerization was investigated by characterizing both the polymers formed and the quartz ground, and the copolymerization mechanism was discussed by analyzing the composition of copolymers formed.

## EXPERIMENTAL

### Experimental Procedure

The experimental apparatus was the same apparatus used in the previous article.<sup>4</sup> The desired amount of the solid sample and the mixture of MMA and styrene monomers were added to a pot, in which grinding balls were charged and nitrogen gas was added, in a glove box under nitrogen atmosphere. The mixture ratio was principally 50% MMA and 50% styrene monomers by volume. All the experiments were conducted in a batch-wise closed system at room temperature under the same grinding conditions performed in the previous article.<sup>4</sup> After grinding for a given time, a large amount of methanol was added to the reaction mixture to make the polymers precipitate. Then the reaction mixture was immediately filtered and dried in a vacuum at 50°C. The conversion of monomer-to-polymer for the mixture obtained after drying was determined by thermal analysis (TAS-200, Rigaku Denki Co., Japan). Soxhlet extraction of the mixture with dichloromethane was also carried out to examine the copolymers formed. The copolymers were characterized by infrared spectroscopy (FT-200, Horiba Seisakusho Co., Japan). The molecular weight of the copolymers were measured by a gel permeation chromatography (TrirotarIII, Nihon Bunko Co., Japan) with tetrahydrofuran as a solvent. The composition of the copolymers was examined by an organic element analyzer (2400IICHNS/O, Perkin-Elmer Co.). Solvents such as methanol, dichloromethane, and tetrahydrofuran were analytical grade reagents and used without further



**Figure 1** Variations of the monomer-to-polymer conversion of monomer mixture with the grinding time at various quartz concentrations.

purification. The specific surface area of the ground quartz was measured by the BET adsorption method (Flowsorb II, Micromeritics Co.) after the polymer in the mixture was decomposed by heating in an electric furnace at 500°C.

### Solid Sample and Monomers

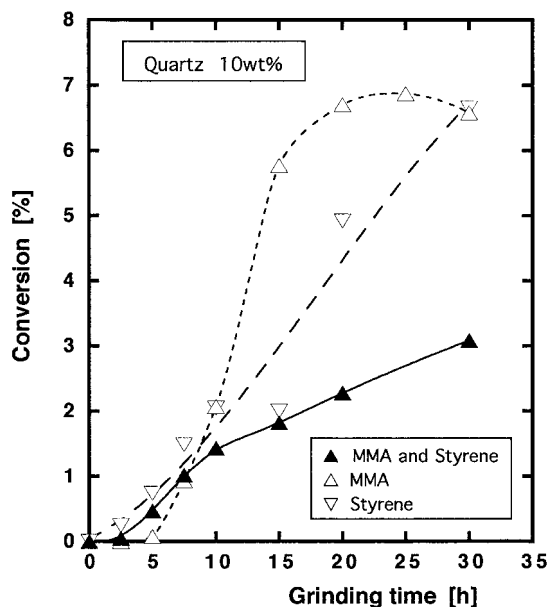
The solid sample used in this study was also the same quartz as was used in the previous article.<sup>4</sup> The quartz from India was in the range of 590–1190  $\mu\text{m}$  in particle size and 2620  $\text{kg}/\text{m}^3$  in density. The quartz concentration in the monomer was within the range of 5–20 wt %.

MMA (Mitsubishi Rayon Co., Japan) and styrene monomers (Kanto Chemical Co., Japan) were freed from inhibitors, dried, and then purified by rectification under a nitrogen atmosphere at a reduced pressure.

## RESULTS AND DISCUSSION

### Copolymerization by Grinding of Quartz

Figure 1 shows the variations of the monomer-to-polymer conversion with the grinding time at various quartz concentrations. Each plot in the figure represents an independent experiment. The conversion of the monomer mixture was found to



**Figure 2** Time-conversion curves in three types of monomers (quartz concentration 10 wt %).

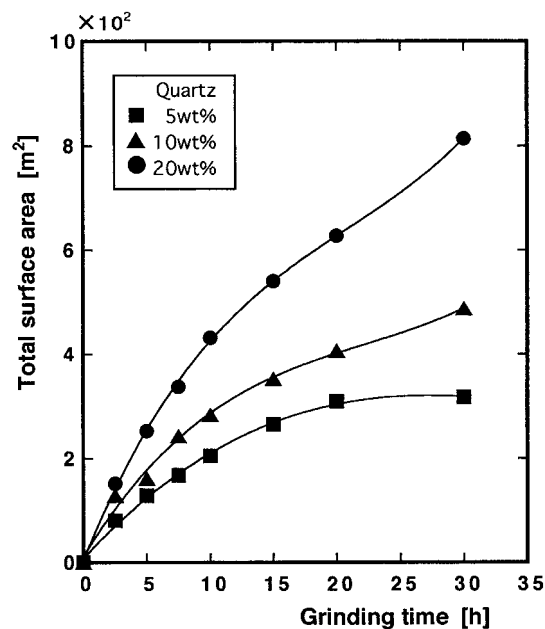
become greater with an increase in the grinding time and in the quartz concentration with a grinding time longer than 15 h. The time-conversion curves indicated that the mixture of MMA and styrene monomers could also be polymerized mechanochemically by the active species, which result from the grinding of quartz. At the initial grinding time, an induction period in which polymerization did not entirely proceed was observed, as found in the case of only the MMA monomer. In addition, the induction periods of 2.5–6 h were found to be approximately equal to those of only the MMA monomer.<sup>3</sup> The polymerization processes in three types of monomers at the quartz concentration of 10 wt % are shown in Figure 2. The polymerization rate of the monomer mixture was smaller than that of the MMA or styrene monomer. This tendency was the same at the other quartz concentrations.

Figure 3 shows the total surface area of quartz, which is calculated by the product of the specific surface area and the quartz filling weight, as a function of the grinding time at various quartz concentrations. The specific surface areas, as mentioned above, do not include those of the polymers formed by polymerization and are the values of only quartz. The total surface area of quartz was found to increase with the quartz concentration at the same grinding time. Therefore, it was proven that the quartz surface produced by grinding obviously participated in the polymer-

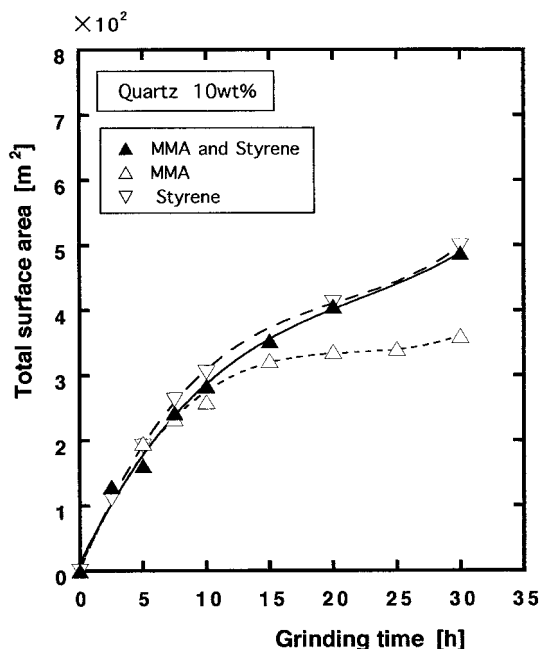
ization. To investigate the effect of monomer types on the grindability of quartz, the total surface area of quartz in three types of monomers as a function of the grinding time is shown in Figure 4. The quartz concentration was 10 wt %. The total surface areas of quartz in the mixture and styrene monomer were almost equal at the same grinding time and were higher than that in the MMA monomer with a grinding time longer than 20 h. The low surface area in the MMA monomer seemed to be attributed to the increase in viscosity of the reaction system due to the greater amount of polymers formed.

### Characterization of Polymer Formed

Figure 5(a) shows the FTIR transmission spectrum of a polymer formed mechanochemically by the grinding of the quartz in the monomer mixture. For comparison, the spectra of (b) polystyrene and (c) polymethyl methacrylate (PMMA), which were synthesized by an emulsion polymerization of each monomer, are also shown in Figure 5. In these emulsion polymerizations, potassium persulfate and sodium dodecyl were used as initiator and surfactant, respectively. The formation of the copolymer was confirmed from the spectrum of (a), which had the adsorption bands marking the polystyrene ( $1603\text{ cm}^{-1}$ ) and PMMA ( $1730\text{ cm}^{-1}$ ).



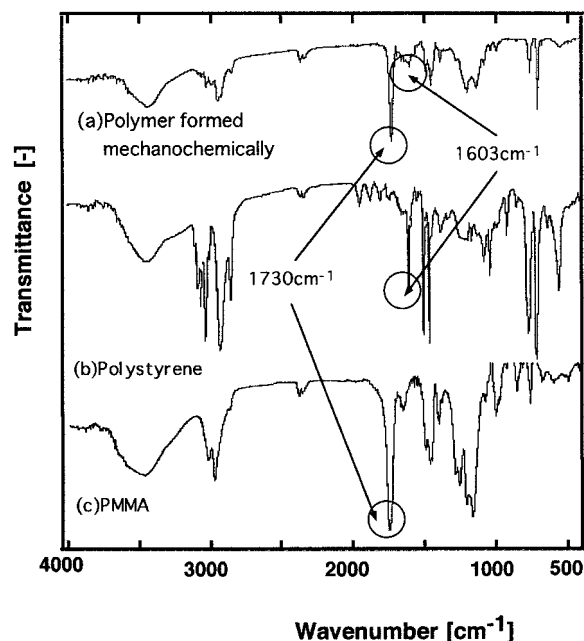
**Figure 3** The total surface area of quartz as a function of grinding time at various quartz concentrations.



**Figure 4** The total surface areas of quartz in three types of monomers as a function of grinding time (quartz concentration 10 wt %).

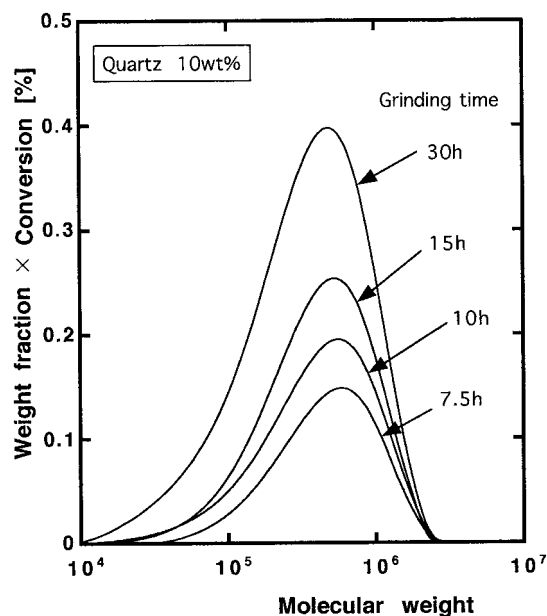
Figure 6 shows the molecular weight distribution curves of the copolymers formed at various grinding times and a quartz concentration of 10 wt %. To clarify the variation of the molecular weight distribution with time, the product of the weight fraction and the conversion of a monomer was chosen in the ordinate of the figure. It was found that all the distribution curves in the figure were unimodal and that the distribution curves became broader with the grinding time. The number-average molecular weight and the heterogeneity of copolymers formed at 10–20 wt % quartz concentrations are summarized in Table I. The number-average molecular weight and the heterogeneity were in the range of  $1.6 \times 10^5$  to  $3.0 \times 10^5$  and 1.8 to 2.4, respectively. The copolymers obtained were found to correspond to the polymer or copolymer formed by an ordinary radical polymerization. The variation of the molecular weight and the heterogeneity with the grinding time suggested that the polymer chains were broken by the mechanical action of grinding.<sup>2,5</sup>

Figure 7 presents the comparison of the molecular weight distribution of a copolymer and two homopolymers formed by mechanochemical polymerization. The concentration of quartz was 20 wt % and the grinding time was 10 h. The distribution curve of the copolymer was similar to one



**Figure 5** FTIR spectra of polymers obtained: (a) polymer formed mechanochemically; (b) polystyrene and (c) PMMA synthesized by an emulsion polymerization of styrene and MMA, respectively.

of the PMMA homopolymers, although the molecular weight was somewhat small. This was supported by the number-average molecular weight



**Figure 6** Shift in molecular weight distribution curves of copolymers formed mechanochemically with grinding time (quartz concentration 10 wt %).

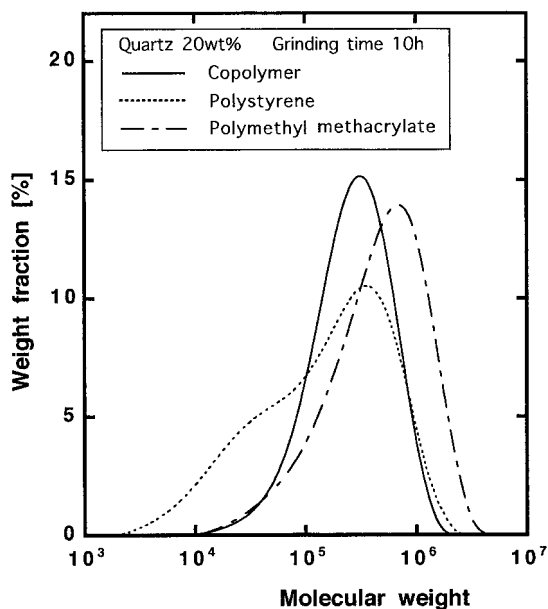
**Table I** The Molecular Weight of Copolymers Formed

Quartz Concentration (wt %)	Grinding Time (h)	Number-Average Molecular Weight	Heterogeneity (—)
10	7.5	$3.0 \times 10^5$	1.8
10	10	$2.3 \times 10^5$	2.2
10	15	$2.5 \times 10^5$	2.0
10	30	$1.7 \times 10^5$	2.4
20	7.5	$2.6 \times 10^5$	1.9
20	10	$2.3 \times 10^5$	1.8
20	15	$2.1 \times 10^5$	2.1
20	30	$1.6 \times 10^5$	2.3
20 <sup>a</sup>	10	$2.9 \times 10^5$	2.7
20 <sup>b</sup>	10	$7.4 \times 10^4$	4.9

<sup>a</sup> Mechanochemical homopolymerization of MMA.<sup>3</sup>

<sup>b</sup> Mechanochemical homopolymerization of styrene.<sup>4</sup>

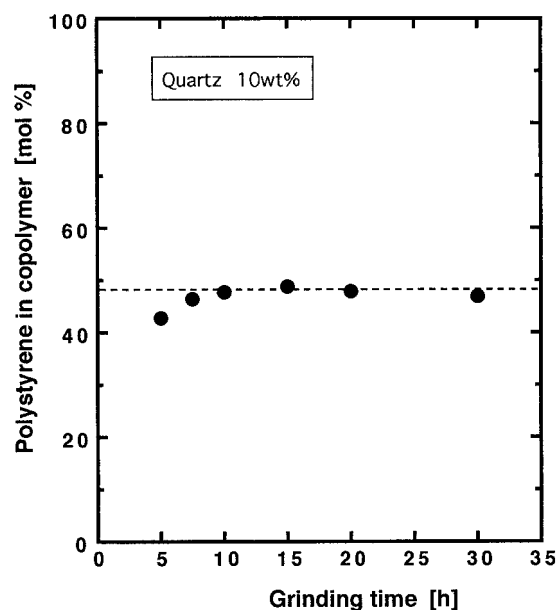
and the heterogeneity of the MMA and styrene homopolymers formed mechanochemically, shown in Table I. The mechanochemical homopolymerization of the MMA proceeded with a radical polymerization mechanism,<sup>3</sup> but in the styrene monomer with a cationic polymerization mechanism.<sup>4</sup> Thus, the results of characterization of the copolymer implied that the mechanism of the mechanochemical copolymerization of MMA and styrene might be a radical polymerization.



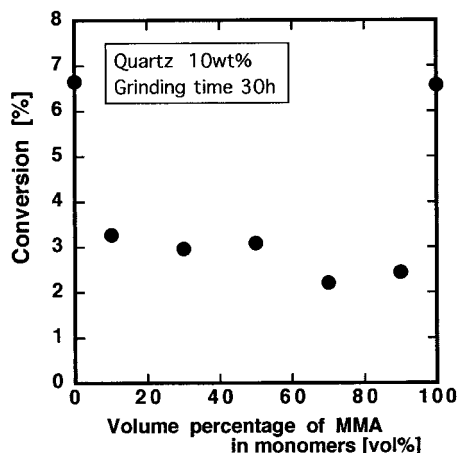
**Figure 7** The comparison between molecular weight distribution curves of polymers formed in three types of monomers (quartz concentration 20 wt %, grinding time 10 h).

### Mechanism of the Mechanochemical Copolymerization

Figure 8 shows the variation of the polystyrene content in the copolymer formed with grinding time at a quartz concentration of 10 wt %. The ordinate in the figure indicates the molar percentage of polystyrene in the copolymer formed, and the horizontal broken line is the molar percentage of styrene monomer charged, 48.2 mol %. The composition of the copolymer formed was found to



**Figure 8** Variation of polystyrene content in copolymer formed with grinding time (quartz concentration 10 wt %).



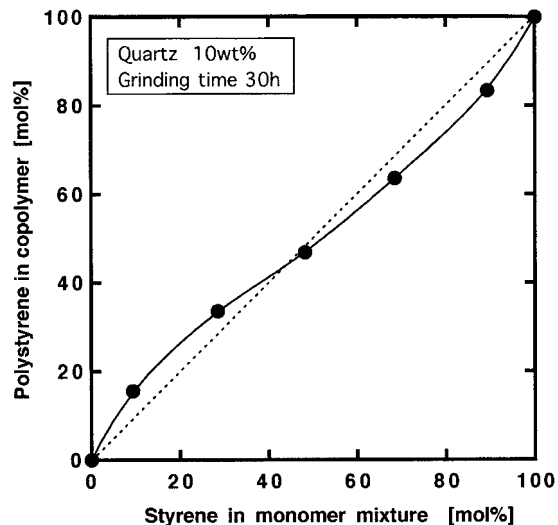
**Figure 9** Relationship between the conversion and monomer composition (quartz concentration 10 wt %, grinding time 30 h).

be approximately equivalent to one of the monomers charged, independent of the grinding time.

In previous experiments, the mixture ratio of MMA and styrene monomers was a constant, 50/50 in volume. Then we carried out the mechanochemical copolymerization experiments with the different mixture ratios of the monomer charged to elucidate the polymerization mechanism of the present system. The conversions of the monomer mixture at a quartz concentration of 10 wt % for 30 h are plotted against the various MMA monomer volume percentages in the monomer mixture in Figure 9. In any mixture ratio of MMA monomer, the conversions of copolymers were smaller than that of MMA or the styrene homopolymer. Although it is generally known that the reaction rate of a normal copolymerization using an initiator is slower than that of homopolymerization,<sup>6</sup> the mechanochemically initiated copolymerization rate was found also to be slower than the homopolymerization rate.

Figure 10 shows a composition curve of the copolymer formed at a quartz concentration of 10 wt % for 30 h. The ordinate and abscissa in the figure are the molar percentage of polystyrene in the copolymer and the molar percentage of styrene in a monomer mixture, respectively. When the composition of the copolymer is perfectly equal to one of the monomers charged, the composition curve is a dotted line in this figure. The composition of the copolymer formed seemed to be roughly determined by the composition of the monomer charged.

From the existence of the induction period and the characterization of the polymer, the reaction

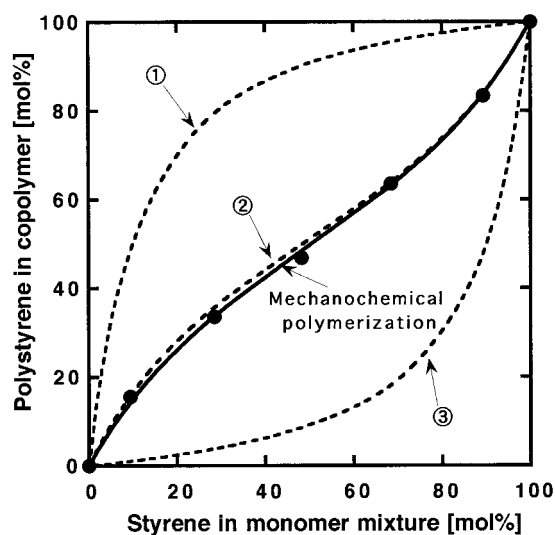


**Figure 10** Composition curve of copolymer formed (quartz concentration 10 wt %, grinding time 30 h).

mechanism of the present system can be considered to be a radical copolymerization. Generally, the following composition equation of copolymerization should hold true to the radical copolymerization<sup>6</sup>:

$$\left(\frac{d[A]}{d[B]}\right) = \left(\frac{[A]}{[B]}\right) \left(\frac{r_1[A] + [B]}{[A] + r_2[B]}\right)$$

where  $[A]$  and  $[B]$  are monomer concentrations of styrene and MMA, respectively, and  $r_1$  and  $r_2$  are



**Figure 11** The comparison of the experimental results with composition curves calculated from reactivity ratios obtained by the Fineman–Ross method.

**Table II** The Reactivity Ratios of Composition Curves

Composition curve	$r_1$	$r_2$	$r_1 \times r_2$
Mechanochemical copolymerization	0.52	0.54	0.28
①	10	0.1	1.0
② <sup>a</sup>	0.57	0.46	0.26
③	0.1	10	1.0

<sup>a</sup> Radical copolymerization of styrene and MMA using AIBN as an initiator.<sup>7</sup>

monomer reactivity ratios. We tried to determine the monomer reactivity ratios by the Fineman–Ross method.<sup>6</sup> As a result, the reactivity ratios obtained were  $r_1 = 0.52$  and  $r_2 = 0.54$  and were described by a composition curve (a solid line) in Figure 11 by using these values. Three dotted curves, ①, ②, and ③, calculated upon the reactivity ratios shown in Table II, were also drawn in the figure. The composition curve patterns of ① and ② are found in an ionic copolymerization of styrene and MMA. In a cationic copolymerization using an initiator such as  $\text{SnCl}_4$ , the styrene content in the copolymers increases. On the other hand, the styrene content decreases in an anionic copolymerization with an initiator such as  $n\text{-C}_4\text{H}_9\text{Li}$ .<sup>6</sup> The composition curve of ② is obtained when the radical copolymerization of styrene and MMA is carried out with azobis-isobutyronitrile as an initiator.<sup>7</sup> The composition curve is found to be almost equal to the curve of the present system. Thus, it is also evident from the analysis of the composition curve that the copolymerization in this reaction system is a radical copolymerization. The generation of radicals in this reaction system, as already reported,<sup>4,8</sup> is due to the quartz grindings, that is, the scissions of the chemical bond,  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ .

The characterization of the copolymer is discussed by the value of  $r_1 \times r_2$ , because the two monomer reactivity ratios are determined by the combination of monomers. When  $r_1 \times r_2 = 1$ , there are two cases. At  $r_1 = r_2 = 1$ , the probabilities of the polymerization between alike monomer molecules and between different monomer molecules are indicated as perfectly equal, and the composition curve is a dotted line shown in

Figure 10. In the cases of composition curves ① and ②, as shown in Table I, the polymerization between alike monomer molecules takes place preferentially. On the other hand, the values of reactivity ratios obtained with the present system are roughly similar to each other and the value of the  $r_1 \times r_2$  is closer to zero. In this case, the polymerization between different monomer molecules proceeds regularly and alternately. Accordingly, the copolymers formed in this reaction system are found to be alternating copolymers.

## CONCLUSION

The mechanochemical copolymerization of MMA and styrene was investigated by the grinding of quartz in a monomer mixture. The results showed that the copolymerization of the two monomers occurred with the resulting activity from the grinding of the quartz and was closely connected to the total surface area of the ground quartz. The molecular weight distributions of the copolymers formed were unimodal as found only in the case of MMA. From the composition analysis of the copolymer formed, it was clear that the mechanochemical polymerization of MMA and styrene proceeded with a radical polymerization mechanism because of radicals on the quartz surface produced by grinding. The monomer reactivity ratios obtained suggested that the copolymers formed were alternating copolymers.

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