

# Mechanochemical Polymerization of Styrene Initiated by the Grinding of Quartz

MASAHIRO HASEGAWA, MITSUMASA KIMATA, SHUN-ITSU KOBAYASHI

Department of Chemistry and Chemical Engineering, Yamagata University, Yonezawa, 992-8510 Japan

Received 19 April 2000; accepted 14 March 2001

**ABSTRACT:** The polymerization of styrene mechanochemically initiated by the wet grinding of quartz was attempted by using a vibrating ball mill with a laboratory scale. The effect of the grinding of quartz on the polymerization of the styrene was investigated by characterizing the polymer formed and the quartz ground. The results showed that styrene could also mechanochemically polymerize by the resulting active species of the grinding of quartz as well as methyl methacrylate. The polymerization was found closely related to the total surface area of the ground quartz. The molecular weight distributions of the polymer formed were not simply unimodal and remarkably broader than those of the methyl methacrylate. It was suggested that the polymerization of the styrene proceeded with a cationic active species from the experimental results and discussions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2849–2855, 2001

**Key words:** mechanochemistry; styrene; polymerization mechanism; quartz; grinding

## INTRODUCTION

It is well known that solids with activated surfaces induce various mechanochemical phenomena.<sup>1</sup> Especially, when the solid surface has a remarkable reactivity immediately following the grinding because of the existence of a radical or ion-type active center and is capable of initiating polymerization of a number of monomers under appropriate conditions.<sup>2–7</sup>

From the viewpoints of both utilizing mechanical energy effectively in grinding operations and modifying the surface of the fine inorganic powders, we have investigated the mechanochemical polymerization of methyl methacrylate (MMA) initiated by the grinding of various inorganic solids.<sup>8–10</sup> As a result, it was found that a large number of inorganic solids such as quartz, quartz glass, limestone, feldspar, talc, and others also

had the active possibility for mechanochemical polymerization of MMA.<sup>8,9</sup> The mechanochemical polymerization of MMA initiated by the grinding of the quartz was found to proceed with a radical polymerization mechanism.<sup>10</sup> We also reported that this process was a useful method capable of the production of fine powder and the surface modification of the powder simultaneously and that the process may be applied to the effective production of inorganic powder fillers to incorporate in polymer matrix.<sup>8</sup>

In this work, the mechanochemical polymerization of styrene, which is a typical vinyl monomer as well as MMA, initiated by the grinding of quartz was attempted, and the effect of the grinding of the quartz on the polymerization of the styrene was investigated by characterizing the polymer formed and the quartz ground. Furthermore, the polymerization mechanism of the mechanochemically initiated styrene was discussed concerning the comparison of the polymerization of MMA.

---

Correspondence to: M. Hasegawa.

*Journal of Applied Polymer Science*, Vol. 82, 2849–2855 (2001)  
© 2001 John Wiley & Sons, Inc.

**Table I Grinding Operation Conditions**

Vibrating ball mill	
Fractional ball filling <sup>a</sup>	0.8
Fractional sample slurry filling <sup>b</sup>	1.0
Amplitude of vibration	5.0 mm
Frequency of vibration	24 Hz
Grinding time	0–30 h
Internal volume of pot	400 cm <sup>3</sup>
Diameter of grinding ball	8.5 mm
Material of pot and ball	Si <sub>3</sub> N <sub>4</sub>
Sample (quartz)	
Density	2620 kg/m <sup>3</sup>
Size range	590–1190 μm
Sample concentration in monomer	5–30 wt %
Monomer (styrene)	
Density <sup>c</sup>	906 kg/m <sup>3</sup>

<sup>a</sup> Fractional ball filling = (packing volume of ball)/(internal volume of mill).

<sup>b</sup> Fractional sample slurry filling = (net volume of sample and monomer)/(void volume within balls charged).

<sup>c</sup> 20°C.

## EXPERIMENTAL

### Experimental Procedure

The experimental apparatus used in this study was the same apparatus used in the previous article.<sup>10</sup> The desired amount of solid sample and monomer was added to a pot, in which grinding balls were charged, and a nitrogen gas was added into a glove box under nitrogen atmosphere. All the experiments were conducted in a batchwise closed system at room temperature under the grinding conditions shown in Table I. After grinding for a given time, a large amount of methanol was added to the reaction mixture to make the polymer precipitate. Then the reaction mixture was immediately filtered and dried in a vacuum at 50°C. The conversion of monomer-to-polymer was determined by a thermal analysis (TAS-200, Rigaku Denki Co., Japan). The polymer formed was characterized by infrared spectroscopy (FT-200, Horiba Seisakusho Co., Japan). The molecular weight of the polymer, which was extracted with dichloromethane from the mixture, was measured by gel permeation chromatography (Trirotar III; Nihon Bunko Co., Japan) with tetrahydrofuran as a solvent. Solvents such as methanol, dichloromethane, and tetrahydrofuran were analytical grade reagents and were used without further purification. The specific surface area of the ground sample was measured by a 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 Monomer

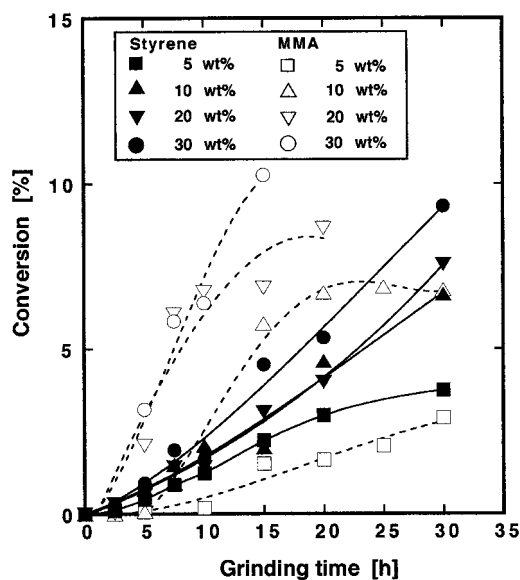
The solid sample was the same quartz as used in the previous paper.<sup>9</sup> The sample was crushed with a jaw crusher and arranged within the size range of 590–1190 μm. After the sample was soaked in diluted hydrochloric acid all day to remove the iron powder contaminated in the pre-crushing process, it was thoroughly washed with distilled water until the washing water was free from chloric ions. Then, it was dried at a reduced pressure. The physical properties of the sample and the sample concentration in the monomer were also shown in Table I.

Styrene monomer (Kanto Chemical Co., Japan) was washed with sodium thiosulfate, sodium hydroxide, and pure water and then dehydrated using calcium hydride for 1 day. Then, the styrene was purified by rectification under nitrogen atmosphere at a reduced pressure and preserved in a freezer.

## RESULTS AND DISCUSSION

### Polymerization of Styrene and Grinding of Quartz

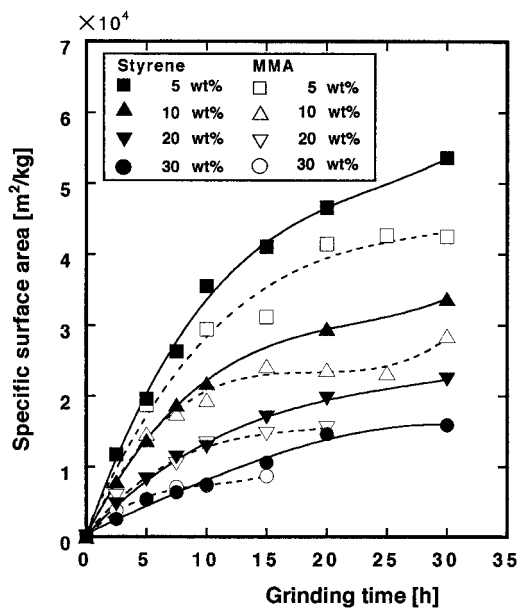
Figure 1 presents the relationship between the monomer-to-polymer conversion of styrene and



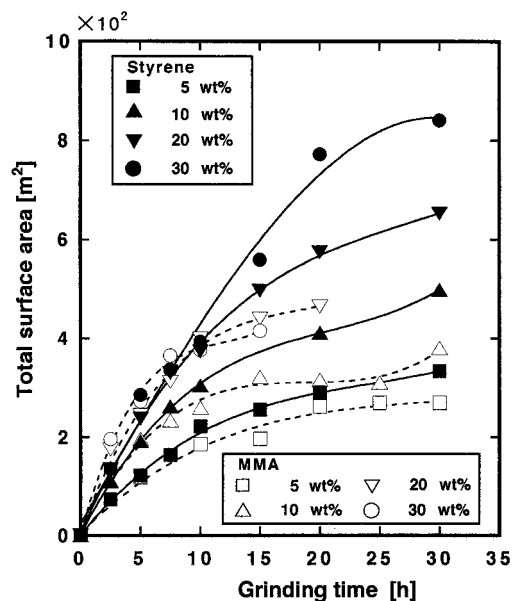
**Figure 1** Relationships between monomer-to-polymer conversion of styrene and grinding time at various quartz concentrations.

the grinding time at various quartz concentrations. The conversions of MMA obtained under the same conditions (broken line)<sup>10</sup> are also shown in Figure 1. Each plot in the figure is an independent experiment. The time–conversion curves of the styrene demonstrated that styrene could also polymerize mechanochemically by the active species which resulted from the grinding of quartz. The conversion of styrene was found to become greater with an increase in grinding time and in quartz concentration. Figure 1 shows that the time and concentration dependencies are different for the polymerization of styrene and MMA. Additionally, in mechanochemical polymerization of MMA, there was an induction period in which polymerization did not entirely proceed at the initial grinding time. This induction period is considered to be due to an inhibiting effect of moisture and oxygen molecules, which will be adsorbed on the sample surface and/or contained in the crystal formation.<sup>8</sup> On the other hand, in the case of styrene, the existence of the induction period was not clearly confirmed. Thus, it is estimated that the mechanism of mechanochemical polymerization of styrene may differ from that of MMA.

The specific surface areas of the ground quartz are plotted against the grinding time in Figure 2. The data for MMA (broken line) are also shown in this figure. There were hardly any differences in the quartz-specific surface areas of both the



**Figure 2** Plots of specific surface area versus grinding time at various quartz concentrations.

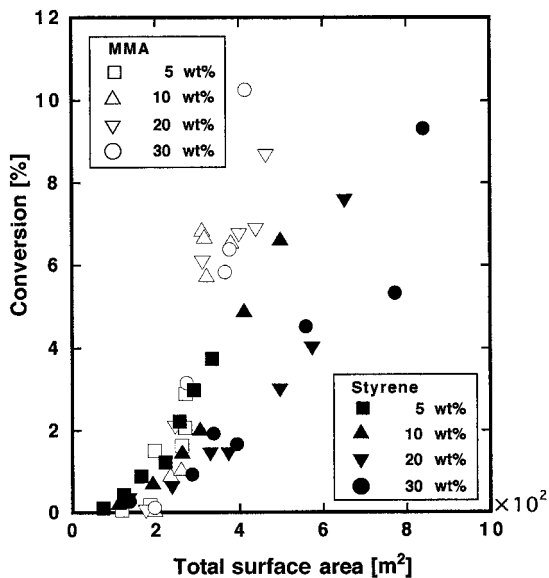


**Figure 3** The total surface area of quartz as a function of grinding time.

monomers at the initial stage of grinding time shorter than about 10 h. When the grinding time became longer than 15 h, however, the difference between styrene and MMA increased gradually with time. This is attributed to the difference in the amount of polymer formed. In the case of styrene monomer, as well as MMA, the specific surface areas at any quartz concentration increased with grinding time. For the same grinding time, the higher the concentration of quartz, the smaller the specific surface area. This result seems to disagree with the result in Figure 1, where the conversion of styrene becomes greater with the increase in quartz concentration.

Figure 3 shows the relationship between the total surface area of quartz, which is calculated by the product of the specific surface area and the filling weight of quartz, and the grinding time. The total surface area of quartz was found to increase with the quartz concentration at the same grinding time, contrary to the results in Figure 2. This demonstrates that the quartz surface produced by grinding participated in the polymerization of styrene as well as MMA.

The relationship between the conversion of styrene and the total surface area of quartz are presented in Figure 4. The total surface area at the start of polymerization indicated approximately the same value, 110 m<sup>2</sup>, at any quartz concentration. Thus, the induction period in the mechanochemical polymerization is essentially deter-



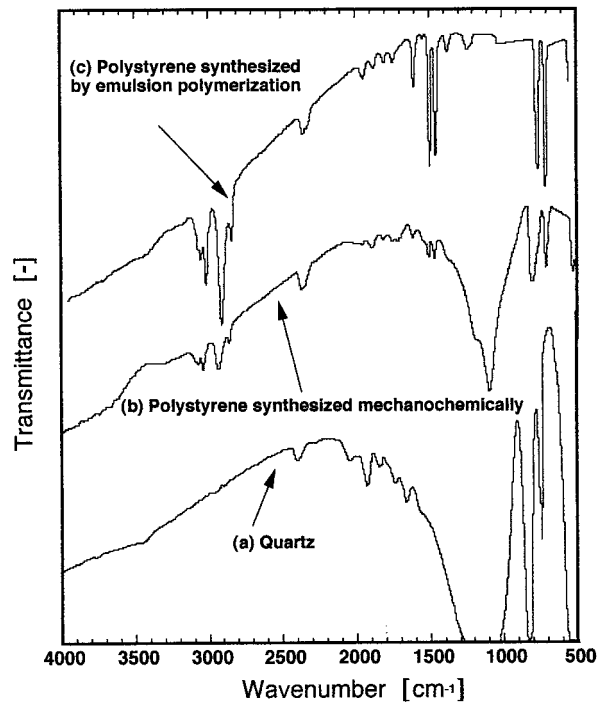
**Figure 4** Relationships between the conversion of styrene and the total surface area of quartz.

mined by the total surface area produced by grinding. Compared to the case of MMA, the total surface area with styrene at the start of polymerization was found to be smaller than that of MMA<sup>10</sup> and appeared to be approximately one-half that of MMA.

### Characterization of Polymer Formed

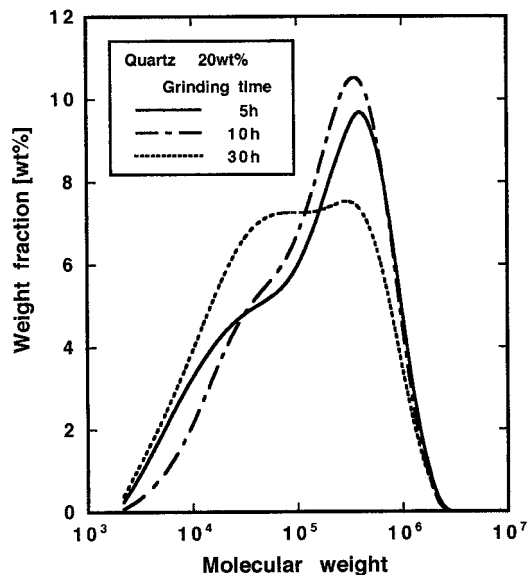
Figure 5 shows the IR transmission spectra of (a) quartz, (b) synthesized mechanochemically composite, and (c) polystyrene. For comparison, the polystyrene was synthesized by an emulsion polymerization of the styrene by using potassium persulfate and sodium dodecyl as an initiator and surfactant, respectively. In the FTIR spectra of the composite and the polystyrene, the adsorption bands at 1603 and 3026, and 2924  $\text{cm}^{-1}$ , which represent benzene ring and methylene group, respectively, were observed. From these results, there is no doubt that the polymer on the composite is made of polystyrene.

Figure 6 shows the molecular weight distribution curves of the polymer formed at three different grinding times and a quartz concentration of 20 wt %. These polymers were extracted by using a Soxhlet extraction method with dichloromethane for 10 h from the composites obtained. It was discovered that two distribution curves at a shorter grinding period had a shoulder at  $4\text{--}7 \times 10^4$  in molecular weight and that the curve at the grinding time of 30 h was bimodal. These

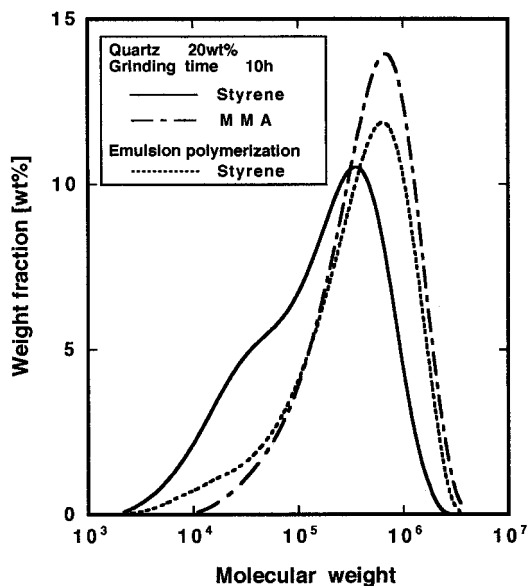


**Figure 5** FTIR spectra of (a) quartz; (b) composite produced mechanochemically; (c) polystyrene synthesized by emulsion polymerization.

tendencies were observed more evidently with a higher concentration of quartz and a longer grinding time. The heterogeneity of the molecular



**Figure 6** Molecular weight distribution curves of polymer formed mechanochemically by the grinding of quartz at various grinding times.



**Figure 7** Comparison between molecular weight distribution curves of polystyrene and polymethyl methacrylate formed mechanochemically.

weight distribution, that is, the ratio of a weight-average molecular weight to a number-average molecular weight, was in the range of 3–7 and the molecular weight fraction of the polymer formed were broad to a great extent.

It is well known that the polymer chains are broken by the mechanical action and that the molecular weight of the polymer decreases.<sup>7,11,12</sup> In the present reaction system, because the grinding operation is further continued after the start of polymerization, the molecular weight of polymer formed is considered to decrease gradually. The formation of polymer with the molecular weight of  $10^4$  order may be attributed to the mechanical scissions of polymer with a larger molecular weight.

Figure 7 shows two molecular weight distribution curves of the polymer formed by mechanochemical polymerization of styrene and MMA monomers under the same conditions. The distribution of a polystyrene sample synthesized by the emulsion polymerization is also presented in this figure. Both the distribution curves are unimodal. The number-average molecular weights of MMA and styrene were  $2.9 \times 10^5$  and  $1.5 \times 10^5$ , respectively. On the other hand, the molecular weight with the mechanochemical polymerization of styrene was  $7.4 \times 10^4$ . Thus, from the results in the molecular weight of the polymer formed, the

**Table II** Reactivities of MMA and Styrene Monomer in Homopolymerization

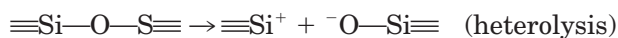
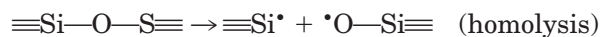
Monomer	Radical Polymerization	Ionic Polymerization	
		Cationic	Anionic
MMA	○	×	○
Styrene	○	○	○

×, no reactivity.

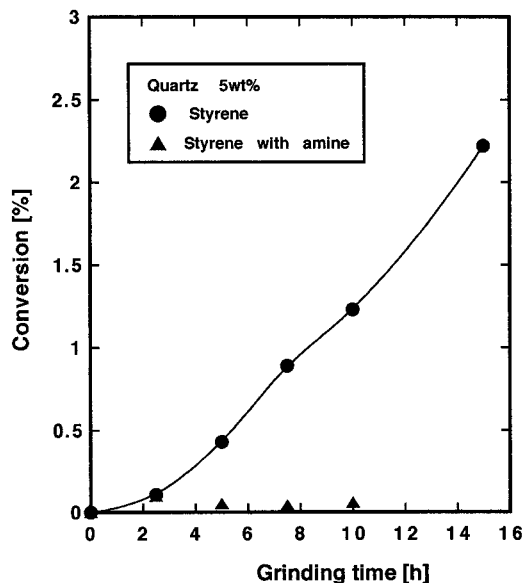
present reaction mechanism also reminds us of a different polymerization mechanism that is not a radical polymerization.

### Mechanism of the Mechanochemical Reaction of Styrene

When quartz with the framework structure of a  $\text{SiO}_4$  tetrahedron is broken by grinding, scissions of chemical bond,  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ , take place within the following two forms<sup>1</sup>



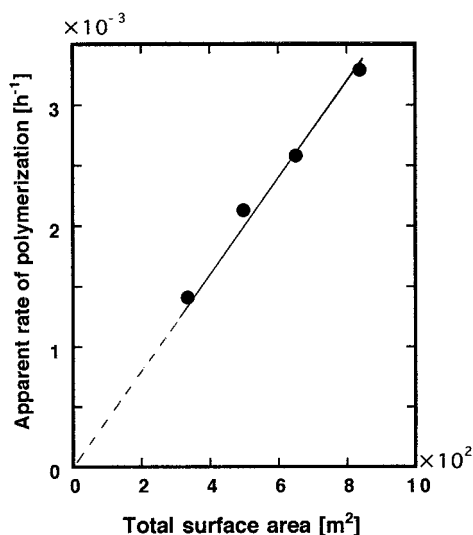
The active centers produced by the grinding of the quartz are both radical and ionic types.



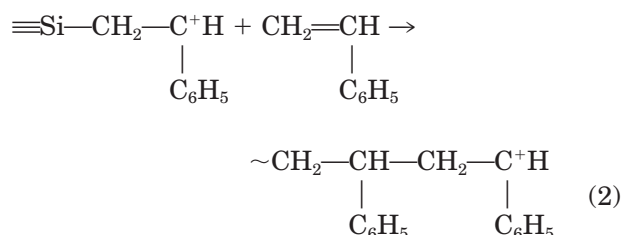
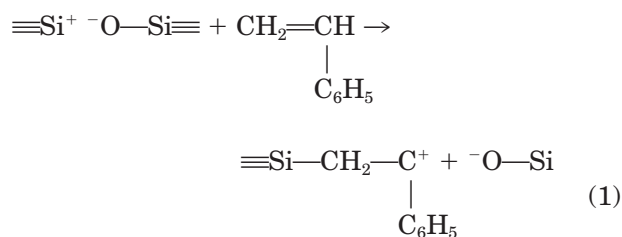
**Figure 8** Effect of the addition of amine on mechanochemical polymerization of styrene.



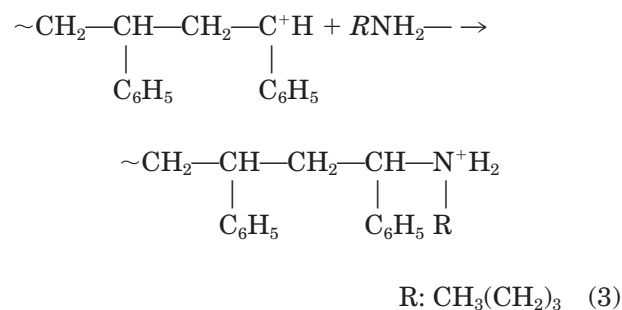
Table II shows reactivities of MMA and styrene monomers in homopolymerization.<sup>13</sup> An MMA monomer could polymerize with either a radical or an anionic mechanism, but the mechanochemical polymerization by the grinding of the quartz principally proceeded with the radical mechanism.<sup>10</sup> In the styrene monomer, polymerization can proceed with any mechanism, as shown in Table II. However, the results of the mechanochemical polymerization of styrene demonstrated that the polymerization mechanism differed markedly from that of the MMA. If the mechanochemical polymerization of styrene does not proceed by the radical mechanism, a cationic polymerization mechanism seems to be the most probable because the  $-\text{C}_6\text{H}_5$  groups of the styrene monomer are an electron-donating group. Because the growing end groups of the polymers in a cationic polymerization have a positive charge, the propagation of the polymer is remarkably controlled by the existence of a basic amine.<sup>13</sup> Here, we undertook the mechanochemical polymerization of styrene with the addition of an *n*-butyl amine. The result shown in Figure 8 revealed that the polymerization of styrene almost never proceeded by the addition of amine. Consequently, the mechanism relating to the mechanochemical polymerization of styrene could be expressed as follows:



**Figure 9** Relationship between the apparent polymerization rate of styrene and the total surface area of quartz.



Furthermore, the growing end groups will become stable ions by the addition of amine, as presented by the following equation:



The polymerization rate,  $R_p$ , in cationic polymerization is generally expressed by the following equation<sup>13</sup>

$$R_p \propto [C^*][M] \quad (4)$$

where  $C^*$  and  $M$  are concentrations of the growing end group and the monomer, respectively. As the monomer concentration remains constant in the present reaction system,  $R_p$  is considered to be proportional to only the concentration of the growing end group,  $C^*$ . The growing end groups in this reaction system are ion-type active species that are produced by the grinding of quartz. Therefore, the concentration of the active species must be proportion to the total surface area of the quartz.

Figure 9 shows the relationship between the apparent polymerization rate of styrene and the total surface area of the quartz at the various concentrations of the quartz. The apparent rates were estimated assuming that the polymerization rate of styrene is constant for 30 h, and the total

surface areas were calculated at 30 h. It was discovered that the apparent polymerization rate was roughly proportional to the total surface area of the quartz. This result also suggests that the mechanochemical polymerization of styrene proceeded with a cationic polymerization mechanism.

## CONCLUSION

The mechanochemical polymerization of styrene was attempted by the wet grinding of quartz in the styrene monomer medium. The results showed that styrene could polymerize mechanochemically by the resulting activity from the grinding of the quartz and that the polymerization was closely connected with the total surface area of the ground quartz. The molecular weight distributions of the polymer formed were simply not unimodal and remarkably broad. It was suggested that the mechanochemical polymerization of styrene initiated by the grinding of quartz proceeds with a cationic-active species from the experimental results and discussions as to the polymerization mechanism.

## REFERENCES

1. Kubo, T. *Mukibutsu no Mechanochemistry*; Tokyo: Sogo Gijutu Shuppan, 1987.
2. Benson, R. E.; Castle, J. E. *J Phys Chem* 1958, 62, 840.
3. Kargin, V. A.; Plate, N. A. *J Polym Sci* 1961, 52, 155; *J Polym Sci, Part C* 1963, 4, 1027.
4. Momose, Y.; Yamada, K.; Nagayama, N. *J Polym Sci, Polym Lett Ed* 1974, 12, 623.
5. Kurokawa, N.; Tabata, M.; Sohma, J. *J Appl Polym Sci* 1980, 25, 1209.
6. Simionescu, C. I.; Oprea, C. V. *J Polym Sci, Polym Chem Ed* 1985, 23, 501.
7. Sohma, J. *Prog Polym Sci* 1989, 14, 451.
8. Hasegawa, M.; Honma, T.; Ishiyama, S.; Kanda, Y. *Kagaku Kogaku Ronbunshu* 1991, 17, 10–19.
9. Hasegawa, M.; Akiho, Y.; Kanda, Y. *J Appl Polym Sci* 1995, 55, 297.
10. Hasegawa, M.; Sato, M.; Sakuyama, S.; Kimata, M. *J Soc Powder Technol Jpn* 1997, 34, 10.
11. Goto, K. *Kogyo Kagaku Zasshi* 1968, 71, 1319.
12. Ikekawa, A. *J Soc Powder Technol Jpn* 1993, 30, 155.
13. Kakiuchi, H. *Shin Kiso Kobunshi Kagaku*; Tokyo: Shokodo, 1990.