Mechanochemical Polymerization of Methyl Methacrylate Initiated by the Grinding of Inorganic Compounds

MASAHIRO HASEGAWA,* YASUSHI AKIHO, and YOSHITERU KANDA

Department of Materials Science and Engineering, Yamagata University, Yonezawa, Japan

SYNOPSIS

The polymerization of methyl methacrylate mechanochemically initiated by the grinding of several inorganic compounds was attempted using a vibrating ball mill. The inorganic compounds used were quartz, quartz glass, marble, limestone, feldspar, and talc with the particle size range of 149–210 μm. The results demonstrated that all compounds used in these experiments had the activity for mechanochemical polymerization of methyl methacrylate, and that the degree of the activity at the same grinding time remarkably differed with the kind of compound. The existence of the induction period, which is the time until the polymerization started, was also confirmed in all of the compounds. The molecular weight distributions of the polymer formed were unimodal and somewhat broad in the case of any compound, and the number-average molecular weight was similar to that formed by ordinary radical polymerization. It was suggested that there were two types of the initiation mechanism in the mechanochemical polymerization of methyl methacrylate initiated by the grinding of inorganic compounds. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Composite materials of inorganic compounds and organic polymers, which have a high potential due to the great number of combinations of these materials, have been utilized in various industries and will be used more widely in the future. The mechanical strength of the composite materials depends greatly on the interfacial interaction between the inorganic compound and organic polymer, and will be fairly improved if a chemical bond between them can be formed.

Mechanochemical polymerization seems to be one of the most promising processes for the production of composite materials of inorganic compound and organic polymer, because this process is presumably the easiest way to form a chemical bond between the two.[1] The mechanochemical polymerizations initiated by the grinding of inorganic compounds such as metallic oxides and ionic salts were studied by a few researchers.[2-7] However, in most of their studies the mechanochemical phenomena were only reported qualitatively. The examinations of ground inorganic compounds were not satisfactorily performed, and the relationships between the polymerization and grinding have hardly been investigated. The authors[8] have reported the surface modification of quartz by the use of wet grinding in methyl methacrylate monomer. In this work, we found that it was unnecessary to consider the thermal polymerization of methyl methacrylate (MMA) and that the mechanochemical polymerization was closely related to the grinding process, especially on the surface area of the quartz produced by grinding.

In this work, the activities of several inorganic compounds for the mechanochemical polymerization of MMA are investigated, and the relationships between polymerization and grinding are discussed. Furthermore, it is also one of the purposes of this study to characterize polymers obtained mechanochemically.

EXPERIMENTAL

Samples

The six kinds of inorganic compounds used were quartz, quartz glass, marble, limestone, feldspar, and

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talc. The samples were crushed previously with a jaw crusher to a particle size range of 149–210 μm. Except for marble and limestone, the particles were soaked in dilute hydrochloric acid all day to remove the iron powder contaminated in the precrushing process. Next, the particles were thoroughly washed with distilled water until the washing water was free from chloric ion, and then dried at reduced pressure. The particles of marble and limestone were fully washed with distilled water and then dried. Table I shows the physical properties of the samples. A Hardgrove index[9] is a grindability standard for samples and indicates that a sample with a large index can more easily be ground. The results of the chemical analysis of the samples used are shown in Table II.

Methyl methacrylate monomer, supplied by Mitsubishi Rayon Co., was free from inhibitor, dried, and purified by rectification under a nitrogen atmosphere at reduced pressure. Solvents such as methanol, acetone, and tetrahydrofuran were the analytical-grade reagents and used without further purification.

Experimental Apparatus

A vibrating ball mill (Chuo Kakoki Co., MB-0) was employed in all experiments. A pot with an internal volume of 390 cm^3 was used as the grinding vessel and polymerization reactor. The grinding media charged in the pot were balls with a diameter of 8.5 mm. Both the pot and balls were made of silicon nitride, because we regarded their wear resistance as important.

Experimental Procedure

A desired amount of the sample and monomer were added to the pot, where the grinding balls were

charged and a nitrogen gas was filled, in a glove box under a nitrogen atmosphere. All the experiments were conducted in batchwise closed systems at room temperature under the grinding conditions shown in Table III. After grinding for a given time, a great 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 thermal analysis (Rigaku Denki Co., TAS-200). The molecular weight of polymer extracted with hot acetone from the mixture was measured by gel permeation chromatography (GPC) (Nihon Bunko Co.) with tetrahydrofuran as a solvent. Polystyrene was used as a calibration standard for GPC. The specific surface area of the ground samples was measured by the Brunauer-Emmett-Teller (BET) adsorption method (Micromeritics Co. Flowsorb II) after the polymer in the mixture was decomposed by heating in an electric furnace at 500°C. The mixtures obtained were also observed by means of an electron microscope (Hitachi Seisakusho Co. H-800).

RESULTS AND DISCUSSION

Figure 1 shows the relationships between the conversion of MMA and the grinding time for six kinds of samples. Each plot in the figure is an independent experiment. The time–conversion curves in the figure demonstrated that polymerization in every sample took place as the grinding proceeded and that the polymerization process remarkably differed with the kind of sample. At the grinding time of 30 h, the grinding of talc yielded the highest value for the conversion of MMA. The grinding of limestone and marble followed talc's highest conversion value, and quartz glass yielded the lowest value. The polymer

Table I   Physical Properties of the Samples Used

Sample	Density (kg/m^3)	Specific Surface Area[a] (m^2/kg)	Hardgrove Index (Non-dimension)	Place of Origin
Quartz	2.65 × 10^3	9.0 × 10^1	37	India
Quartz glass	2.15 × 10^3	7.0 × 10^1	48	Products of Kyushu Ceramics Co.
Marble	2.84 × 10^3	2.1 × 10^2	84	Yamaguchi
Limestone	2.70 × 10^3	2.8 × 10^2	77	Okayama
Feldspar	2.55 × 10^3	2.8 × 10^2	54	Fukushima
Talc	2.76 × 10^3	1.1 × 10^3	100	China

[a] Before grinding, particle size 149–210 μm.

Table II Chemical Analysis of the Samples

Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	CaO (%)	MgO	K$_2$O	Na$_2$O	Ig. Loss
Quartz	99.77	0.02	0.04	—	—	—	—	—	0.14
Quartz glass	100	—	—	—	—	—	—	—	—
Marble	—	—	—	—	54.29	0.55	—	—	43.12
Limestone	—	—	—	—	54.80	0.28	—	—	43.29
Feldspar	64.96	20.28	0.03	—	0.12	0.21	10.22	3.77	0.13
Talc	61.69	0.63	—	1.96	—	30.52	0.09	0.24	5.45

content in the mixture of talc and poly-MMA (PMMA) obtained then was a value as high as approximately 40%. It is interesting to note that there were hardly any differences in the conversion curves of quartz and feldspar and of marble and limestone, respectively. Thus, all samples used in these experiments were found to have the activity for mechanochemical polymerization of the MMA monomer, though the degree of the activity at the same grinding time depended on the sample.

The specific surface areas of the six kinds of samples are plotted against the grinding time in Figure 2. The specific surface areas, as mentioned above, do not include those of the polymer formed by polymerization and are the values of only inorganic compounds in the mixture. The specific surface areas of all samples increased with grinding time. At 30 h they became around 50–300 times larger than before grinding. Talc gives the largest specific surface area among the six samples at any grinding time, because an intercalation compound such as talc is extremely brittle and has no chemical bond between the interlayers. Moreover, the good dispersion of talc powder in the monomer is considered to promote remarkably the grinding of talc. In an ordinary grinding operation, the larger the Hardgrove index, the greater the specific surface area produced under the same grinding conditions.

Table III Grinding Conditions

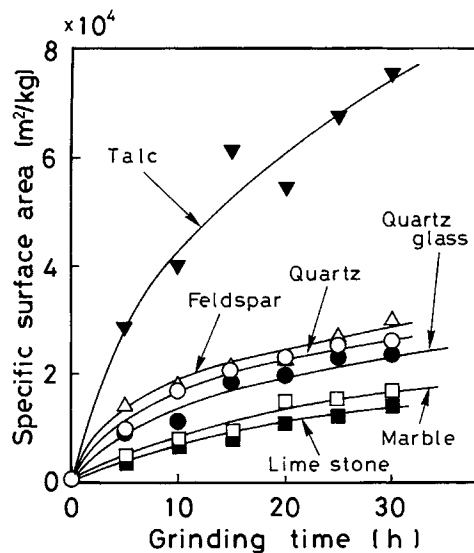|	
Fractional ball filling[a]	0.8
Fractional sample filling[b]	1.0
Sample concentration in monomer	10 wt %
Amplitude of vibration	5.0 mm
Frequency of vibration	24 Hz
Grinding time	0 ~ 30 h

[a] Fractional ball filling = (packing volume of ball)/(internal volume of mill).

[b] Fractional sample filling = (net volume of sample and monomer)/(void volume within balls charged).

However, the specific surface areas of marble and limestone with larger indices are smaller than those of quartz, quartz glass, and feldspar. The grindability of a sample in wet grinding was found to vary with the organic solvent used. This seemed to be attributed to the dispersibility of the sample powder in the organic solvent.

The existence of an induction period in which polymerization did not entirely proceed was also confirmed by the initial grinding time in Figure 1. We roughly estimated the induction period of each sample by extrapolating two plots at the initial stage of polymerization and replotted the conversion vs. grinding time after the induction period. The results are shown in Figure 3. After the polymerization occurred, the rate of polymerization with quartz glass was almost the same as with quartz and feldspar. In the case of talc, the rate of polymerization was also similar to those of limestone and marble with a longer induction period. Agreeing rates of polymer-
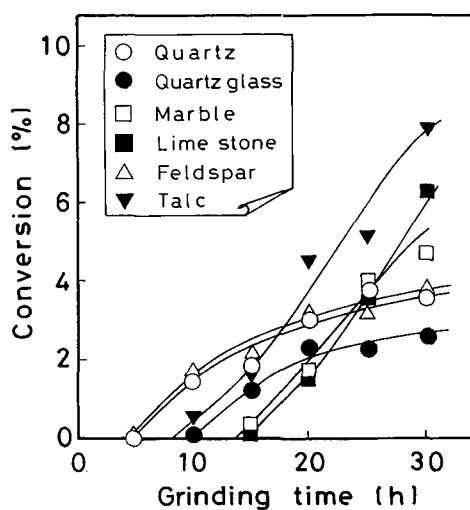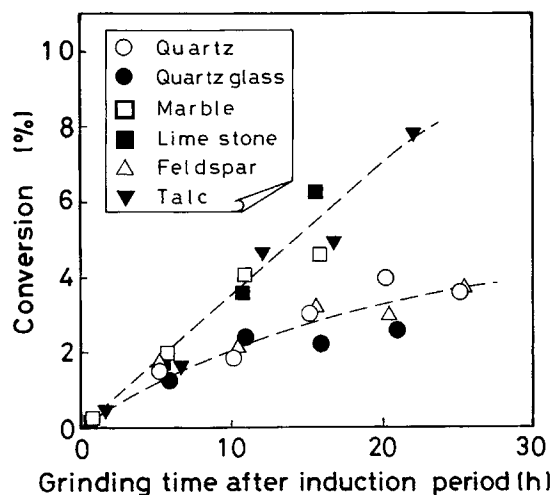

Figure 1 Relationships between monomer-to-polymer conversion of MMA and the grinding time for the six kinds of samples.

Figure 2   Plots of specific surface area vs. the grinding time for the six kinds of samples.

Figure 3   Relationships between the conversion of MMA and the grinding time after the induction period.

ization imply a common mechanism. The two curves in Figure 3 suggest the two different types of the initiation mechanism in mechanochemical polymerization.

Recently, we measured in detail the mechanoradicals on a fresh quartz surface ground by an electron spin resonance (ESR) spectroscopy.[10] As a result, the existence of three kinds of mechanoradicals; E' center ($\equiv$Si·), nonbridging oxygen hole center ($\equiv$Si—O·) and peroxy radicals ($\equiv$Si—O—O·), were shown from the ESR spectra obtained. Therefore, it is obvious that the mechanochemical polymerization with quartz is induced by free radicals rising on fresh surface, as described by Kargin et al.[3] At present we think that the radical species of quartz with the highest activity is an E' center radical for the polymerization of MMA. This holds in the case of quartz glass with the same chemical composition as quartz. Furthermore, from the analogy of the polymerization rate, the polymerization with feldspar will probably also be caused by the same mechanism as quartz. With respect to Al_2O_3, that is one of the principal chemical compositions of feldspar, Kurokawa et al.[6] observed the ESR spectrum to show the generation of free radical from milled alumina. Consequently, both of the radicals formed by the scission of chemical bonds of Si — O and Al — O may have the similar activity for the polymerization of MMA. On the other hand, in the cases of marble, limestone, and talc, the rates of polymerization were found to be greater than that of quartz. Since the chemical bonds of these samples,

Ca — O and Mg — O, were ionic bonds, the polymerization is estimated to proceed by the joining of electrons from the crystal surface ground.[3]

Table IV shows the estimated induction periods and the specific surface area at the start of polymerization for the six samples. This induction period is considered to be due to an inhibiting effect of moisture[3] and oxygen molecules,[8] which are adsorbed on the sample surface and/or contained in the crystal formation. The induction period consequentially varies with the kind and amount of the samples. However, the induction periods in the cases of samples with similar chemical composition are found to be approximately equal, as can be seen in the cases of marble and limestone, and of quartz and feldspar in Table IV. Although the induction period with quartz glass is longer than that with quartz, this difference is caused by air bubbles formed during the production of quartz glass.

Table IV   Induction Periods and the Specific Surface Area at the Start of Polymerization in the Six Samples

| Sample	Induction Period (h)	Specific Surface Area (m^2/kg)
Quartz	4.8	9.6×10^3
Quartz glass	9.1	1.2×10^4
Marble	14.3	6.5×10^3
Limestone	14.5	7.9×10^3
Feldspar	4.6	1.3×10^4
Talc	8.3	3.9×10^4
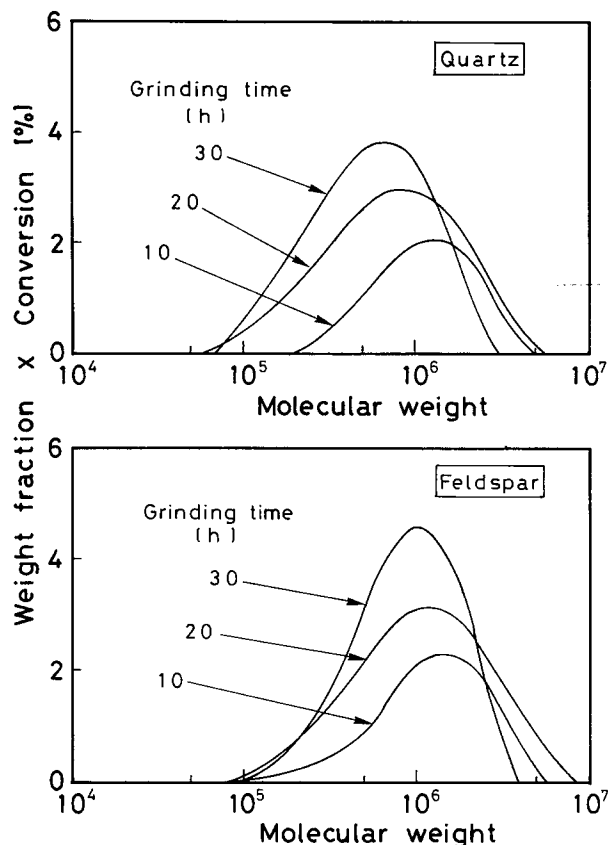
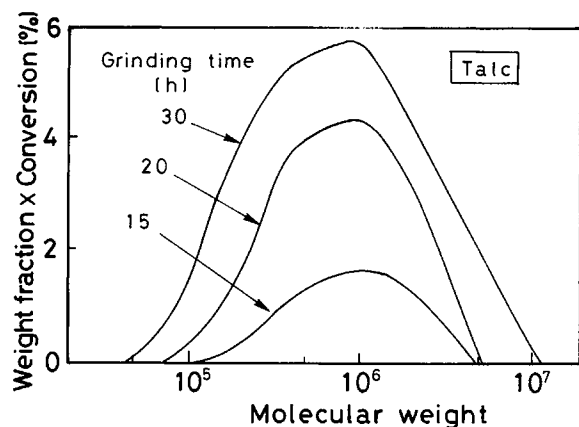**Figure 4** Molecular weight distribution curves of polymer formed by the grinding of quartz and feldspar.

The talc used in this experiment was fairly porous, as is obvious from the largeness of the specific surface area of the talc before grinding in Table I. In addition, talc with the theoretical chemical composition of $3MgO \cdot 4SiO_2H_2O$ contains more moisture than the other samples.[11] Accordingly, it was expected that the induction period with talc would be the longest of the six samples. However, the induction period with talc in Table IV was unexpectedly shorter than those with marble and limestone. This can be explained by taking account of the high grindability of talc, as shown from the fact that the specific surface area of talc at the start of polymerization is about several times larger than those of marble and limestone. Thus, the induction period is essentially determined by the chemical composition and grindability of the compounds.

Figures 4, 5, and 6 show the molecular weight distribution curves of the polymer formed by the grinding of several inorganic compounds. These polymers were extracted by Sohxlet extraction with hot acetone for 10 h from the mixtures obtained. The extracted polymers were 20–40% of the formed

polymer, and the other polymer remained on the surface of the inorganic compounds. To clarify the variation of the molecular weight distribution with time, the product of weight fraction and conversion of MMA was chosen in the ordinate of the figures. It was found that all the distribution curves in these figures were unimodal and that a polymer with a molecular weight as high as 10^6 was obtained. However, the heterogeneity of the molecular weight distribution, that is, the ratio of a weight-average molecular weight to a number-average molecular weight, was 1.5 to 3.2 and these curves were broader to a great extent. The peaks of the distribution curves with quartz and feldspar in Figure 4 had a tendency to shift toward a low molecular weight with grinding time. On the other hand, the peaks in the cases of limestone and marble, as shown in Figure 5, rapidly sharpened and shifted toward a high molecular weight with grinding time. The distribution curves with talc became broader with grinding time. Figure 7 presents the variations of the number-average molecular weight of the polymer with grinding time. These number-average molecular weights were
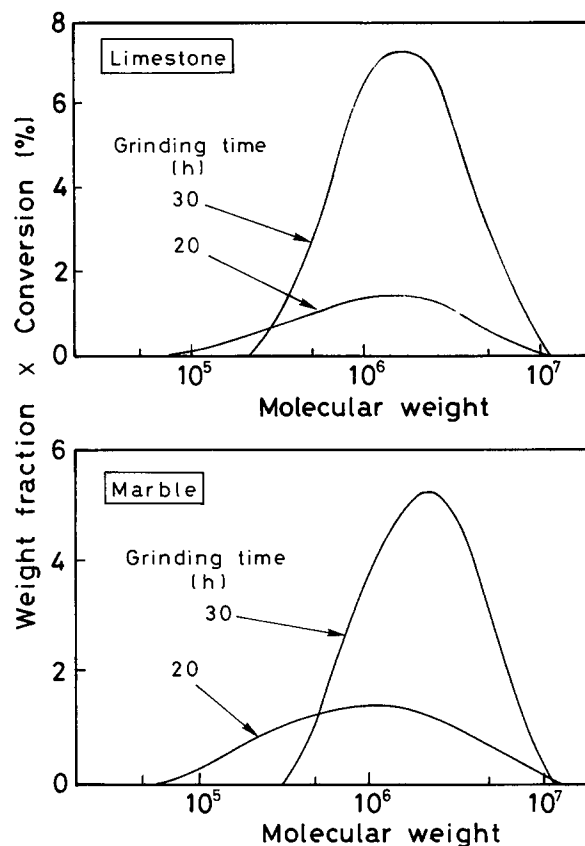
Figure 5 Molecular weight distribution curves of polymer formed by the grinding of limestone and marble.

Figure 6 Molecular weight distribution curves of polymer formed by the grinding of talc.

similar to that formed by ordinary radical polymerization. With quartz, quartz glass, and feldspar, the number-average molecular weight decreased with grinding time, but conversely, the molecular weights with marble and limestone increased. These tendencies also reminded us of the different polymerization mechanisms.

In the present reaction system, the generation of mechanoradicals from the inorganic compounds is maintained as far as the grinding proceeds. After the start of polymerization, the polymer formed also receives the mechanical action of grinding operation. It is well known that the polymer chains are broken and the molecular weight decreases by the mechanical action.[1,12,13] At the same time, the scissions of polymer chains signify the generation of polymer mechanoradicals. Most of the primary mechanoradicals of the polymers generated are able to initiate further polymerization and the activity of the mechanoradicals is much higher than that of similar species of radicals produced by γ-irradiation.[1] The increase in mechanoradical concentration in the reaction system leads to the production of a polymer with low molecular weight. Accordingly, if the grinding operation is further continued after the start of polymerization, the molecular weight of the polymer formed is considered to decrease gradually due to the mechanical scissions of the polymer chain and the increase in the mechanoradicals. The increase in the molecular weights of the polymer formed with marble and limestone seems to be caused by a greater rate of polymerization, but the molecular weights will be also lowered by the subsequent grinding operation. In the case of talc, the rate of grinding as well as polymerization is so great that the molecular weight decreases and its distri-

bution becomes broader. Thus, the present reaction system is very complicated, so that the effective method to elucidate the mechanism of mechanochemical polymerization may be a postpolymerization experiment rather than a simultaneous polymerization, as in this experiment.
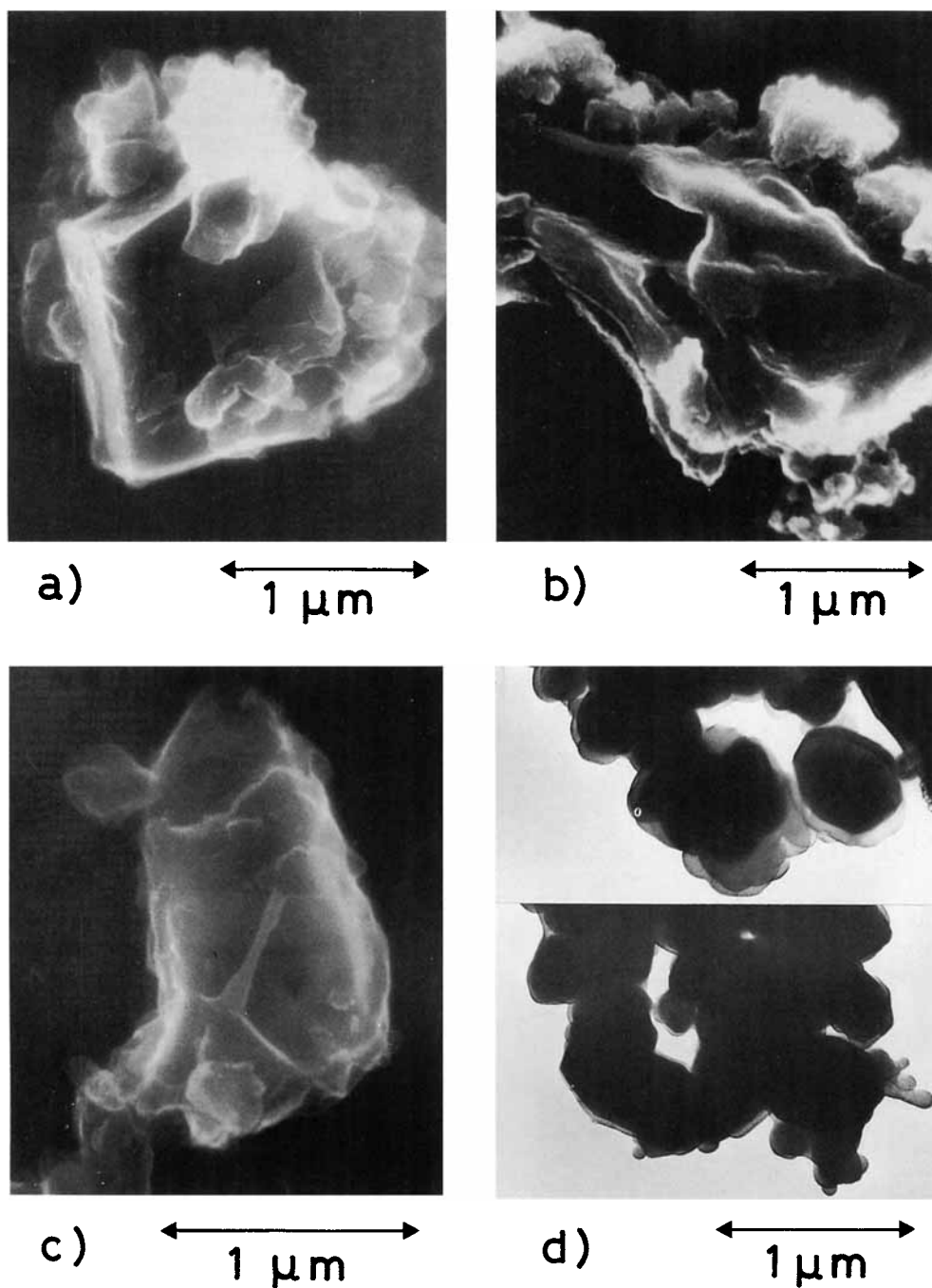
Figure 8 shows electron micrographs of the mixtures of some inorganic compounds and PMMA obtained at the grinding time of 20 h. Micrographs (a), (b), and (c) were observed by scanning electron microscope, and micrograph (d) by transmission electron microscope. The polymer contents of mixtures in micrographs (a), (b), (c), and (d) were 21.5, 22.3, 14.2, and 29.0%, respectively. From these micrographs, it was revealed that a great amount of polymer formed adhered to any powder surface. In micrograph (d) of talc with the highest polymer content, judging from the difference of electron beam transmittance between talc particles and polymer, most of the particle surface was found to be covered with a polymer film of about 0.02–0.06 μm in thickness. In the mechanochemical polymerization process, the particles ground may be encapsulated by the resulting polymer as the polymerization proceeds.

CONCLUSION

The mechanochemical polymerization was performed by grinding several inorganic compounds in an MMA monomer under a nitrogen atmosphere. The results showed that all compounds used in this experiment had the activity for mechanochemical polymerization of MMA, and that the degree of the
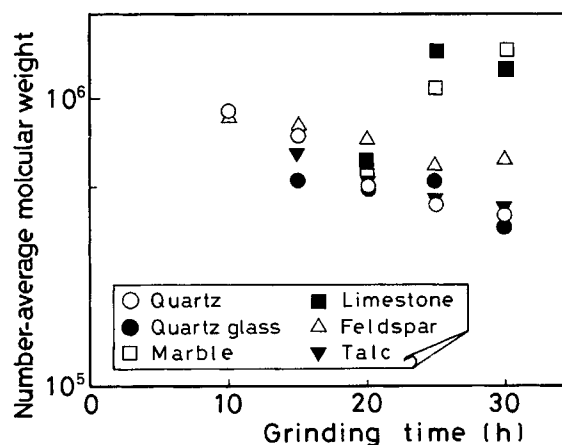
Figure 7 Variation of the number-average molecular weight with grinding time.

Figure 8 Scanning and transmission electron micrographs of mixtures of some inorganic compounds and PMMA: (a) quartz–PMMA, (b) feldspar–PMMA, (c) marble–PMMA, (d) talc–PMMA.

activity at the same grinding time depended on the kind of compound. The induction period was found to be determined by the chemical composition and grindability of the compounds. It was suggested that there were two types of the initiation mechanism in the mechanochemical polymerization of MMA initiated by the grinding of inorganic compounds.

REFERENCES

1. J. Sohma, *Prog. Polym. Sci.,* **14,** 451 (1989).
2. R. E. Benson and J. E. Castle, *J. Phys. Chem.,* **62,** 840 (1958).
3. V. A. Kargin and N. A. Plate, *J. Polym. Sci.,* **52,** 155 (1961); *J. Polym. Sci.: Part C,* **4,** 1027 (1963).

4. H. Takahashi, *Seisan Kenkyu,* **26,** 490 (1974).

5. Y. Momose, K. Yamada, and N. Nagayama, *J. Polym. Sci. Polym. Lett. Ed.,* **12,** 623 (1974).

6. N. Kurokawa, M. Tabata, and J. Sohma, *J. Appl. Polym. Sci.,* **25,** 1209 (1980).

7. C. I. Simionescu and C. V. Oprea, *J. Polym. Sci.: Polym. Chem. Ed.,* **23,** 501 (1985).

8. M. Hasegawa, T. Honma, S. Ishiyama, and Y. Kanda, *Kagaku Kogaku Ronbunshu,* **17,** 1019 (1991).

9. JIS M 8801 (1972).

10. M. Hasegawa, T. Ogata, M. Sato, and Y. Kanda, *J. Soc. Powder Technol. Jpn.,* **30,** 570 (1993).

11. C. Kato, *Soukan Kagoubutsu no Kaihatsu to Ouyo,* CMC, Tokyo 1985, p. 25.

12. K. Goto, *Kogyo Kagaku Zasshi,* **71,** 1319 (1968).

13. A. Ikekawa, *J. Soc. Powder Technol., Jpn.,* **30,** 155 (1993).