Mechanochemical Polymerization of Acetylene

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Synopsis

Gamma alumina, γ-Al$_2$O$_3$, was fractured in an atmosphere of acetylene monomer at room temperature to test whether they would be polymerized by mechanochemistry method on the surface of the alumina. The experimental results were obtained by several different methods, including CP–MAS ^{13}C-NMR, ESR, pressure drop measurements of the monomer, optical absorption spectroscopy, and solvancy. The results proved the mechanochemical polymerization of acetylene monomer on surfaces of the fractured alumina. Several other combinations of either silica and acetylene monomer or polymers and acetylene monomer were tested for mechanochemical polymerization. This process proceeded with less efficiency in the silica system but no mechanochemical polymerization of acetylene was found in the combinations of the polymers and acetylene monomer.

INTRODUCTION

Mechanochemical polymerization was reported at first by Kargin and Plate.[1] An exhaustive review on mechanochemical polymers reactions is found in the book by Casale and Porter.[2] Mechanochemical polymerizations of several monomers induced by fracture of polymers were investigated by Sakaguchi and Sohma.[3] Mechanochemical polymerization of ethylene and propylene induced by fracture of metallic oxides, such as Al$_2$O$_3$, SiO$_2$, TiO$_2$, and B$_2$O$_3$ were first found by one of the authors (M.T.).[4] Polymerization of acetylene has been studied by Hatano et al.,[5] in 1960, and subsequently a technique, by which acetylene was polymerized into a film of polyacetylene, was found by Shirakawa and his co-workers.[6,7] By using films of polyacetylene, electric and other physicochemical properties of acetylene have been extensively studied in this decade.[8] Ziegler-type catalysts were used for polymerization of acetylene, and few other techniques for the polymerization have been reported. It was found that fracture surfaces were covered with newly generated polymers by the mechanochemical polymerization, and surface properties of the fractured materials in this case were determined not by the bulk nature but by the polymers covering the surfaces.[4] It thus seems of interest to find out whether or not acetylene is polymerized by the mechanochemistry method, leading to polyacetylene film generation directly on the surface of either polymers or metallic oxides. In this paper mechanochemical polymerization of acetylene initiated by fracture of alumina is reported.

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EXPERIMENTAL

Samples. The gamma alumina (Al_2O_3) (Merck Co.) was activated at 700°C for 2 h after 6 hrs at 200–700°C. Commercial acetylene was obtained from Hokusan Co., and used after drying. Acetylene enriched with ^{13}C from Stohler Isotope Chemical Co. was dried and diluted down to 4 wt % before use.

Apparatus. A ball mill combined with the special ampoule was used for mechanochemical reactions, both of which have been described previously.[1,4] Ball milling was carried out at either 77 K or room temperature. The ampoule containing the pretreated alumina was evacuated at room temperature, and the purified acetylene monomer gas was introduced into the degassed ampoule. The amount of the monomer gas was estimated by measurement of the pressure before and after an introduction of the monomer gas.

A PE-1 X band ESR spectrometer (JEOL) was used with 100 kHz modulation. ^{13}C-NMR spectra from solid samples were observed by a combination of the crosspolarization (CP) and the magic angle spinning (MAS) methods, using a Bruker CXP-300 FT NMR spectrometer jointed with a probe for the CP–MAS measurements. The frequency used for ^{13}C-NMR was 75 MHz.

Optical absorption spectra were observed by the reflection method using a Beckman DK-2A Ratio Recording Spectrum Photometer.

RESULTS AND IDENTIFICATION OF SPECIES

Color Changes and Optical Spectra

The color of the pretreated γ-alumina powder changed from white to weak purple after contact with the acetylene gas at room temperature. After milling γ-alumina in an acetylene atmosphere either at 77 K or at room temperature, the sample changed in color from weak purple to dark violet. Similar color changes were observed when α-alumina, viz., corundum, was used instead of γ-alumina. The optical absorption spectra in a region from visible to UV for alumina, α and γ, which were fractured in the acetylene atmosphere, and that of the nonfractured γ-alumina are shown in Figure 1. The spectrum of γ-alumina after milling shows a very wide spread absorption band from 800 nm to 350 nm. However, such a broad band was not detected for the samples of γ-alumina prepared without any milling. It was reported that the absorption peaks of polyacetylene appear at 594 nm for the cis form and 700 nm for the trans form.[9] The spectra observed from the milled alumina includes these two characteristic peaks of polyacetylenes, although they are much broader than observed in the reported spectra.[9]

ESR

No ESR spectrum was observed from the nonfractured γ-alumina in the case of noncontact. The ESR spectra observed from γ-alumina after milling at 77 K in both the presence and absence of acetylene gas are shown in Figure 2. Both spectra appear as broad singlets but differ in terms of the g factors, line widths, and line shapes. The spectrum indicated by the broken
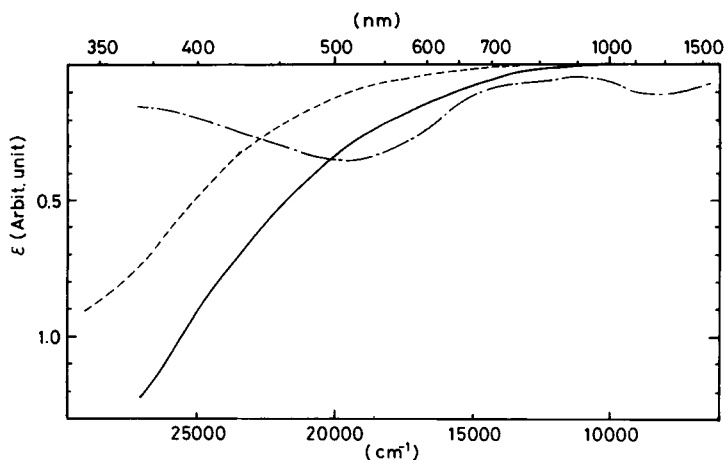
Fig. 1.   Absorption spectra obtained by the reflection method: (—) spectrum observed after fracture of γ-Al$_2$O$_3$ in an acetylene atmosphere; (- - -) spectrum of the α-Al$_2$O$_3$ (corundum) fractured under the same experimental conditions; (— · —) spectrum of a mixture of γ-Al$_2$O$_3$ and acetylene before the fracture.

line originates from the mechanoradicals in the milled alumina[4]; however, the other spectrum should be attributed to alternative origins because of the differences in their ESR parameters. The difference in the origins of these spectra is also demonstrated by the decay behavior of the spectra, as shown in Figure 3. The spectrum from the fractured alumina without contact with acetylene decayed in a low temperature range, but that from alumina milled in an acetylene atmosphere was found to be more stable and begin to decay above 250 K. The ESR spectrum observed for γ-alumina milled in an atmosphere of acetylene at room temperature is shown as a in Fig. 4. The line-shape appears more symmetrical than that in Figure 2, due to the absence of distortion of the line shape caused by the superposition of the spectrum originating from Al$_2$O$_3$. The experimental value of the g factor determined from this spectrum is 2.0034, which is nearly equal to the value of 2.0030[10] of the ESR spectrum observed from polyacetylenes produced by using catalysts of the Ziegler type. The spectrum observed from the usual trans polyacetylene is known to be from polyenyl radicals, which
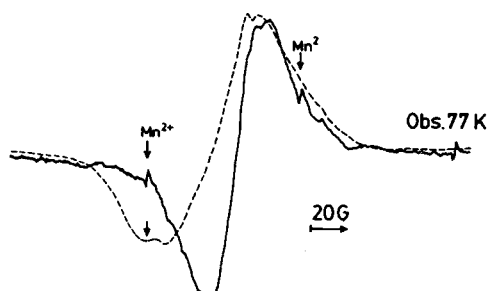

Fig. 2.   (- - -) ESR spectrum observed from the alumina milled for 5 h at 77 K in vacuum; (—) ESR spectrum observed from alumina milled for 5 h at 77 K in the presence of acetylene. The small peaks with arrow are the peaks from Mn^{2+} used as a reference.
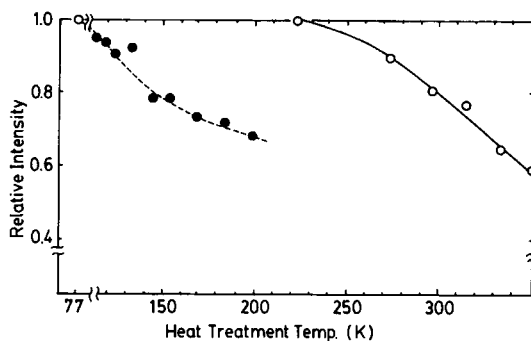
Fig. 3. Changes of ESR intensities after annealing at different temperatures. The ESR observed at 77 K after 5 min at each annealing temperature: (●) data from the Al_2O_3 milled in the absence of acetylene; (○) data from Al_2O_3 milled in the presence of acetylene.

are simultaneously produced in the polymerization of acetylene and are stabilized in polyacetylene.[5,6] The spectrum b in Figure 4 shows a line shape observed after contact with oxygen. A weak shoulder appeared in the position marked with an arrow, and the line shape became asymmetric after contact with air. The shoulder is attributed to the $g_{\|}$, the g parallel component, of the g factor, of peroxy radicals,[11] which are produced by the reaction with oxygen. The asymmetric line shape was changed into a symmetric one by heat treatment at higher temperatures [Figs. 4(c), and (d)], and changes in both intensity and the line width were accelerated in the presence of oxygen.

Experimental results obtained from the ESR studies of γ-alumina milled in an acetylene atmosphere may be summarized as follows:

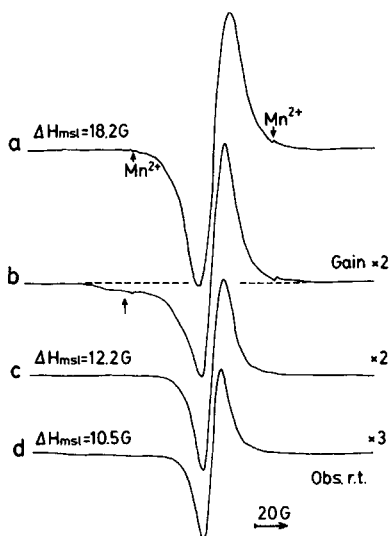(1) The ESR spectrum was different from that of the mechanoradical of γ-alumina.

Fig. 4. ESR spectra observed from Al_2O_3 milled in the presence of acetylene at 293 K: (a) before contact with O_2; (b) after the contact with O_2 at 293 K for 13 h; (c) after the contact with O_2 at 408 K for 1 h; (d) after the contact with O_2 at 408 K for 6h.

(2) The observed *g* value and the line shape are close to the values obtained from spectra of polyenyl radicals in the usual trans polyacetylenes.

(3) A high reactivity with oxygen, which is one of the features of polyenyl radicals, was observed.

On the basis of these experimental results we assign the spectrum observed from γ-alumina fractured in the presence of acetylene molecules to polyenyl radicals[12] produced by mechanical polymerization of acetylene rather than to the broken bonds on the milled alumina.

Gas Consumption

The ball milling was carried out in sealed ampoules,[1,4] in which the alumina of known weight, acetylene monomers of known amounts and the milling balls were enclosed. Decreases in the acetylene gas pressure were detected with an increase of milling time at room temperature, and the observed pressure drop was much more than that caused by adsorption of gas on the porous alumina. Moreover, the pressure drop never leveled off to a value which would be expected in the case of adsorption. These results demonstrate that the decrease in the monomer gas pressure was caused not by adsorption but by the conversion of acetylene monomer gas into solid compounds. The amounts of acetylene gas converted was estimated from the observed pressure drop and the known volume of the ampoule. Figure 5 compares the volume of acetylene gas converted as a function of the milling time, with the number of radicals evaluated from the observed ESR intensities.

CP–MAS[13]C-NMR

^{13}C-NMR spectra were measured using the CP–MAS method after milling in an acetylene atmosphere at room temperature. The contact time used in the measurement was 1 ms, and the spinning frequency of the MAS was adjusted in the vicinity of 2 kHz. Chemical shifts are expressed (ppm) with respect to tetramethylsilane (TMS) as standard. Although the rotor contained a sample of 0.510 g, only one band with a poor S/N ratio was merely observed in the range of 130–140 ppm, which includes the chemical shift
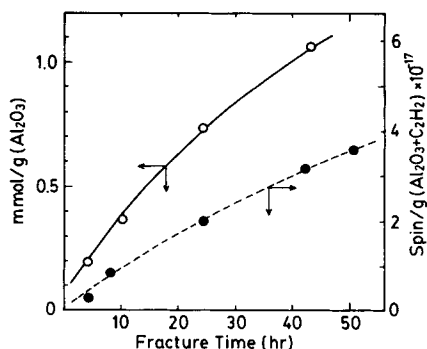

Fig. 5.   Acetylene gas consumption (○) and the radical concentration (●) plotted against the milling time at room temperature.
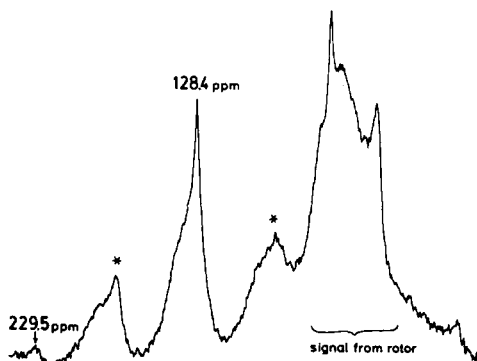
Fig. 6.   CP–MAS ^{13}C-NMR spectrum observed from γ-Al$_2$O$_3$ milled in the presence of acet-
ylene monomers at 77 K the peaks with asterisks are the spinning side band. The strong band
appearing in the high field side is the spectrum from the rotor consisting of deuterated
poly(methyl methacrylate).

of 136 ppm for *trans*-polyacetylene. The weak intensity of the observed ^{13}C-
NMR, in spite of the sufficient amount of the total sample, indicates that
the organic compounds detected by ^{13}C-NMR were a small fraction of the
total sample, in which the organic compounds had been produced as thin
layers on the milled alumina. After the milling of alumina in an atmosphere
of ^{13}C enriched acetylene the CP–MAS ^{13}C-NMR was measured from a sam-
ple of the same weight (ca. 0.510 g). An example of the observed spectra is
shown in Figure 6. The strongest band from 15–50 ppm is associated with
the rotor which was made of partially deuterated poly(methyl methacry-
late). The band appearing around 128 ppm is assigned to polyacetylene,[13,14]
and the bands with asterisks are the spinning side bands. There is another
band in the range of 229 ppm which is difficult to assign to a definite
chemical group because of its unresolved structure. The broad band of 128
ppm appears asymmetric, and the low field shoulder indicates the presence
of other peak smeared by the overlapping. The band shape was simulated
by the superposition of the two peaks shown as b in Figure 7. The parameters
obtained from the best simulation were as follows: the chemical shifts 128
ppm and 135 ppm, the line width 1.2 ppm and 8.8 ppm, and the relative
intensities 1.0:2.1, respectively. The line shapes were taken as Lorentzian
for the sharp component and gaussian for the broad component. The ob-
served line shape is satisfactorily represented by the simulation as shown
in Figure 7(a). This decomposition of the observed band into the two peaks
shows that the band originates from polyacetylene in both forms of cis (128
ppm) and trans (135 ppm), and their relative fractions are 1.0:2.1.

IR Observations

An attempt was made to observe the IR spectra from the alumina after
milling in an atmosphere of acetylene at room temperature using FT-IR
spectrometer, but the band corresponding to polyacetylene was completely
masked by the absorption band of the alumina. No information has been
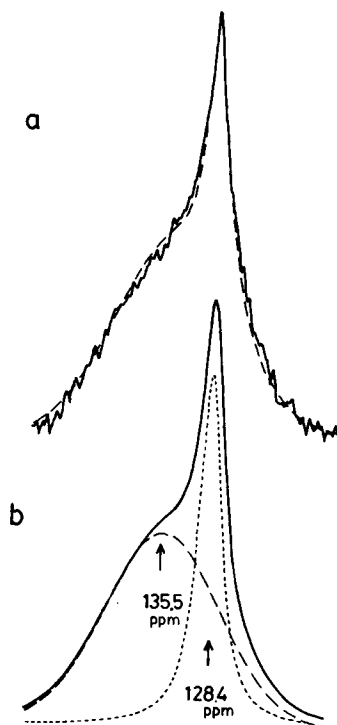obtained from IR measurements at the present stage.

Fig. 7.   (a) Comparison between the observed band and the best fit simulated curve. (b) The simulated spectrum and its components.

Other Systems

It has been found that other metallic oxides,[4] such as SiO_2, Al_2O_3–SiO_2, B_2O_3, and TiO_2, and polymers like polytetrafluoroethylene initiate mechanochemical polymerization with varying degrees of effectiveness. Some other combinations than the alumina–acetylene system were tried to test whether mechanochemical polymerization of acetylene may be initiated.

Silica–Acetylene System

Silica powder was milled in an atmosphere of acetylene at room temperature using the same apparatus described above. A large pressure drop down to 70% of the initial value was found after milling for 24 h, and the color of the sample was slightly changed from white to purplish white. The ESR spectra measured from silica milled in the presence of acetylene is shown in Figure 8. The sharp but weak singlet is a part of the spectrum from the mechanoradicals of the milled silica. The broad, strong component with a g factor of 2.0034 originates from compounds produced from the acetylene gas. This assignment of the two components is supported by the observation that the sharp singlet was observed from the silica milled in vacuum, and the singlet was gradually converted into the broad component after contact with acetylene monomer. The g factor, the line width, and the line shape are close to the corresponding radicals of the ESR spectra
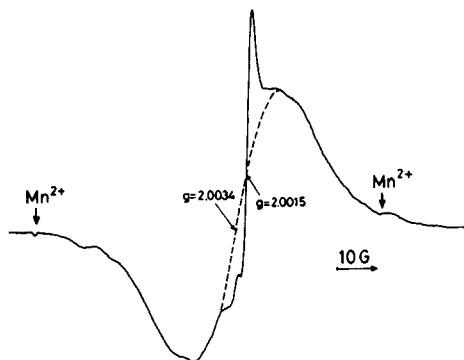
Fig. 8. ESR spectrum observed from silica milled in presence of acetylene at room temperature: (- - -) a decomposition into a broad component and a narrow one.

observed for the alumina–acetylene system after milling. No change in the IR spectra of the compound was detected after milling, but this was mainly due to the fact that the characteristic band was masked by the strong absorption of silica. These results, the marked pressure drop, the color change, and the ESR spectra, indicate that some organic compounds containing polyenyl radicals were mechanochemically produced on the surfaces of the milled silica.

Polymer–Acetylene System

Three polymers, polytetrafluoroethylene (PTFE), poly(methyl methacrylate) (PMMA), and polyethylene (PE), were chosen to test whether the mechanochemical polymerization of acetylene was observed in the case of the polymer–acetylene systems. Only small pressure drops were measured after milling, and no changes in the color were observed in all these cases. No positive evidence for the mechanochemical polymerization of acetylene was obtained in these cases. So far as our trials were concerned, favorable evidence for the mechanochemical polymerization of acetylene was obtained only in the case of silica, but no positive evidence was gained for other cases.

DISCUSSION

Mechanochemical reactions occur on fresh surfaces which have been produced by fracture of metallic oxides,[4] alumina in this study. The amount of product generated by the mechanochemical reaction is very limited and is deposited as thin layers on the surface of the fractured alumina. It is difficult to separate the reaction product from the matrix with solvents. It was also impossible to dissolve the products made from acetylene monomers, since no solvent is known for polyacetylene. Clear identification of the products deposited on the alumina surfaces was very difficult using conventional analytical methods because of the difficulties of solvent extraction and the effects of the matrix, such as superposition in the spectra.

The most positive experimental method to identify polyacetylene produced by mechanochemical reaction appears to be CP–MAS ^{13}C-NMR. Al-

though the observed values from different investigations of polyacetylene chemical shifts are scattered within a range of 3 ppm,[14-17] the chemical shift, 128.4 ppm, observed in our experiments agrees with the value determined by Gibson et al.[15] for *cis*-polyacetylene. The chemical shift of the other peak determined by simulation to be 135 ppm, as shown in Figure 7, deviates a little from the reported value[15] for *trans*-polyacetylene. The chemical shift determined for the broad component is less accurate than the other sharp peak. The deviation of 1.7 ppm from the reported value should be considered to be within the error limit of the simulation. Thus the observed ^{13}C-NMR spectrum provides positive experimental evidence for the formation of polyacetylene by the mechanochemical method.

It is well known that polyacetylene produced by the conventional method always contains polyenyl radicals.[5-7,18] In other words, polyacetylenes are always accompanied by polyenyl radicals, which are detected easily by ESR. Thus, the observed ESR spectrum of polyenyl radicals in a sample made from acetylene monomers indicates the presence of polyacetylene. In this experiment the polyenyl radicals were clearly proved to exist in the products on the surfaces of the milled alumina. This result alone is convincing evidence for the formation of polyacetylene. However, the experimental results obtained by the other methods, such as NMR, ESR, the pressure drop, the optical absorption spectrum, and the solubility, all indicate that the mechanochemical polymerization of acetylene occurrs on the surfaces of the milled alumina.

Sharp peaks at both 594 nm and 700 nm, which correspond to *cis*- and *trans*-polyacetylene, were not resolved in the observed spectra in Figure 1. The observed spectra in this range may be reasonably explained by assuming a wide distribution of molecular weights of polyacetylene. It is well known that a long conjugated molecule like polyene absorbs light in the visible region, but the absorption peak shifts to longer wavelength with the degree of conjugation.[19] The absorption spectrum of conjugated systems having a wide distribution of the degree of conjugation will show a continuously broadened band in the range from ca. 220 nm to longer wave lengths. Thus, it is reasonable to attribute the observed broadness of the band to a wide distribution of molecular weights of polyacetylene produced by mechanochemical methods.

The wide molecular weight distribution of polyacetylene, which was assumed above, is supported by the observed decrease in the line width of the ESR spectra after heat treatment, as shown in Figure 9. The ESR line width of polyenyl radicals decreases with the length of conjugation, and the line width is expressed as following[12]:

$$\Delta H_{msl} \propto n^{-0.5}$$

where ΔH_{msl} is a line width expressed by a separation of maximum slope and n is the degree of conjugation. The observed decrease in the line width after the heat treatment demonstrates that some polyenyl radicals survived even after a long heat treatment at high temperatures. This indicates that the distribution with molecular weights of the mechanochemically produced polyacetylene is reduced by the heat treatment. A similar conclusion con-
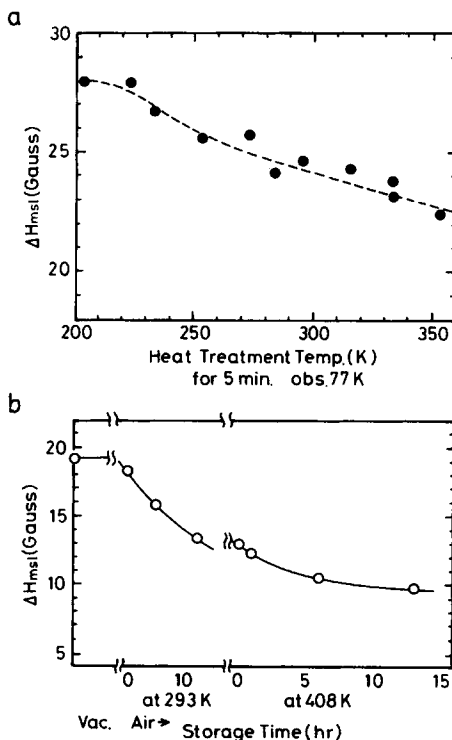
Fig. 9. Changes in the line width of ESR spectra by the heat treatment. Observations were carried out at 77 K after each heat treatment: (a) in vacuum; (b) in the presence of air.

cerning the distribution of molecular weight may be drawn from the broadened NMR peaks corresponding to cis- and trans-polyacetylenes. The spectra of polyacetylene produced by normal methods are reported to be much narrower than those in Figure 7, except for those of AsF$_5$-doped polyacetylenes.[20] It is most reasonable to attribute this broadness in the NMR spectra to a wide distribution of molecular weights. However, the polyacetylenes in these experiments were produced in thin layers on the surfaces of the milled alumina. Thus, the electron orbitals of carbon in the polyacetylene could be perturbed by electrons in energy bands of the solid alumina, on which the polyacetylenes were deposited. In such a case the chemical shifts of polyacetylenes would be distributed widely due to a varying degrees of perturbation. This possible origin for the broadened NMR spectrum is not completely ruled out.

Since γ-alumina is well known to have a catalytic action, it is possible that the observed polymerization was caused not mechanochemically but by catalytic action. In order to check which was the genuine mechanism in initiation polymerization, a different kind of alumina, α-alumina, which has ca. 1/100 of the surface area and little catalytic activity, was used under the same experimental conditions of milling. Similar results in terms of the radical formation, the consumption of gaseous acetylene and the absorption spectrum as shown in Figure 1, were obtained for the fine α-alumina. The result shows that polyacetylene was produced by the milling

of α-alumina. Polymerization of acetylene caused only by the contact of acetylene monomer with a γ-alumina surface was reported by Heaviside et al.,[21] but the amount of polyacetylene produced in their experiment without milling was ca. 1/100 as small as our production by milling. Thus we concluded that the mechanochemical polymerization of acetylene occurs on the surface of alumina powder as a result of milling. However, the mechanism of the mechanochemical polymerization of the milled alumina is still open to question. An investigation to clarify the reaction mechanism is in progress.[22]

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