

## Electron-Microscopic Procedure for Acrylic Rubber

TAKEO HAMAZAKI,\* YOSHIHIKO KANCHIKU, RYOJI HANDA, and MIKIO IZUMI,† *Central Research Laboratory, Mitsubishi Rayon Co. Ltd., Ohtake, Hiroshima, Japan*

### Synopsis

The electron-microscopic visualization of acrylic rubber dispersed in a heterogeneous structural resin composition consisting of a rubber-modified two-phase plastic comprising essentially a butyl acrylate rubber phase and an acrylonitrile-styrene copolymer phase, respectively, has been accomplished. This procedure consists of the following: The molded resin specimen is treated with hydrazine hydrate solution to produce the acrylic acid hydrazides. Allow the treated specimen to soak in osmium tetroxide solution. The acrylic rubber may be indirectly fixed and stained. Some micrographs of ultrathin sections of two or three resin compositions, cut by an ultramicrotome, are presented.

### INTRODUCTION

The internal micromorphology of heterogeneous polymeric systems comprising a rubber phase and a resin phase such as ABS resin has so far been studied by means of the phase contrast microscope. However, this procedure has not been able to reveal the internal structure of the polymer in more detail.<sup>1-5</sup> On the other hand, Kato developed the electron-microscopic method for studying polybutadiene latices and other unsaturated polymer particles,<sup>6</sup> in which osmium tetroxide was applied instead of commonly used bromine<sup>7-11</sup> for the purpose of hardening those soft polymer particles. That is to say, osmium tetroxide, when applied in vapor form, produces excellent fixing and staining of polybutadiene latices and other unsaturated polymer particles, resulting in good electron micrographs for the morphologic observation of particles without requiring any additional treatment. Further, applying this fixing and staining method with osmium tetroxide to ABS resin blocks, he<sup>12</sup> succeeded in the visualization of the internal structural details of ABS resin with the electron microscope.

In his fixing and staining method with osmium tetroxide, Kato found that osmium tetroxide reacts with the unsaturated double bonds in the polymeric molecular chains based on polybutadiene and oxidizes them; accordingly, metal osmium, being deposited, gives an excellent image contrast and definition because of the electron staining effect. On the other hand, this method is entirely inef-

\* Present address: Patent Division, Mitsubishi Rayon Co. Ltd., No. 8,2-Chome, Kyobashi, Chuo-ku, Tokyo, Japan.

† Present address: Ryowa Kasei Co. Ltd., No. 10-1, Daikoku-cho, Tsurumi-ku, Yokohama, Japan.

fective on any saturated polymers such as poly(vinyl acetate), acrylate ester polymers, and so on.

On the other hand, Stange et al.<sup>13</sup> reported an electron micrograph of an ultrathin section of Luran S (registered trade name ASA resin) which was an acrylonitrile-styrene copolymer grafted onto acrylic rubber. However, the details of this electron-microscopic technic were not represented. Moreover, they reported that the rubber phase of ASA resin could not be contrasted with osmium tetroxide for electron-microscopic investigations.

The present authors have investigated the electron-microscopic visualization of acrylic rubber dispersed in a heterogeneous structural resin composition consisting of the rubber-modified two-phase plastic comprising essentially poly(butyl acrylate) rubber phase and acrylonitrile and styrene resin phase, respectively. Consequently, it has been found that the indirect electron-microscopic visualization of acrylic rubber might be accomplished by applying hydrazine treatment and osmium tetroxide fixing and staining to the molded resin specimen.

## EXPERIMENTAL

### Materials

The molded specimens obtained by the conventional injection molding and extrusion molding of a heterogeneous structural resin composition consisting of the rubber-modified two-phase plastics obtained by polymerizing the monomer mixture of acrylonitrile and styrene (25/75% by weight) in the presence of 25% by weight of a crosslinked polyacrylate elastomer comprising butyl acrylate/methyl methacrylate/triallyl cyanurate (90/9.5/0.5% by weight) were used. The commercial acrylic rubber-modified plastics Luran S and Vitax were also used. Luran S is ASA resin prepared by BASF (West Germany), and Vitax is ASA resin prepared by Hitachi Kasei (Japan).

### Reagents

Hydrazine hydrate solution, 80% (Tokyo Kasei's Guaranteed Reagent), was used for the hydrazine treatment of the specimens. Osmium tetroxide aqueous solution, 1%, prepared by dissolving osmium tetroxide (E. Merck's Lab Reagent) in distilled water was used as fixing and staining reagent.

### Apparatus

An ultramicrotome Nippon Denshi JUM-5A equipped with a glass knife was used for ultrathin sectioning. An electron microscope Nippon Denshi JM-7A

TABLE I  
Condition of Hydrazine Treatment

Temperature of treatment,	60° C (constant)
Time of treatment,	8 hr
	16 hr
	24 hr
	96 hr

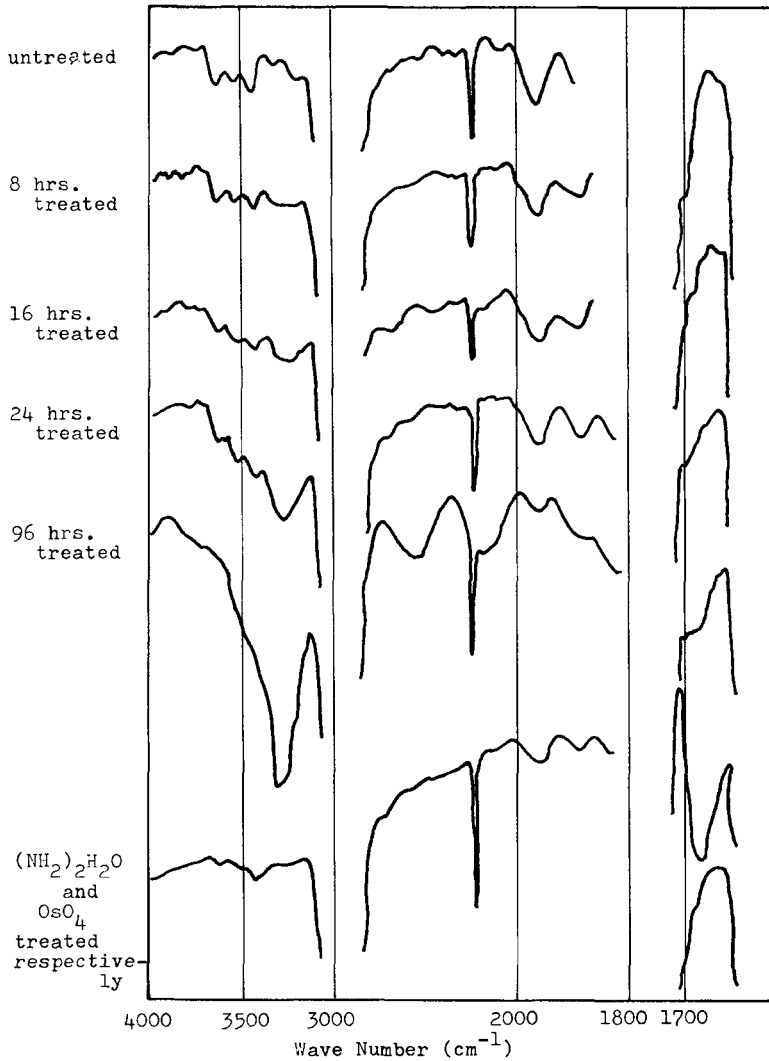


Fig. 1. Infrared spectra of films treated with hydrazine hydrate solution.

was used at an accelerating voltage of 100 kV. An infrared spectrophotometer Hitachi G-2 was used for the measurement of the infrared absorption spectra.

### Sectioning Procedure

Cut the molded resin specimen under study with a razor blade to a size and shape suitable for mounting on the specimen holder of an ultramicrotome in accordance with Kato's method.<sup>12</sup> Subsequently, secure it on the specimen holder. Proceed with a preliminary cut utilizing a glass knife until the cutting face becomes smooth. Remove the resin specimen from the specimen holder and allow it to soak in 80% hydrazine hydrate solution for 24–96 hr at a temperature of 60°C; and after washing it thoroughly, allow it to soak in 1% osmium tetroxide aqueous solution. It is sufficient that the osmium tetroxide treatment

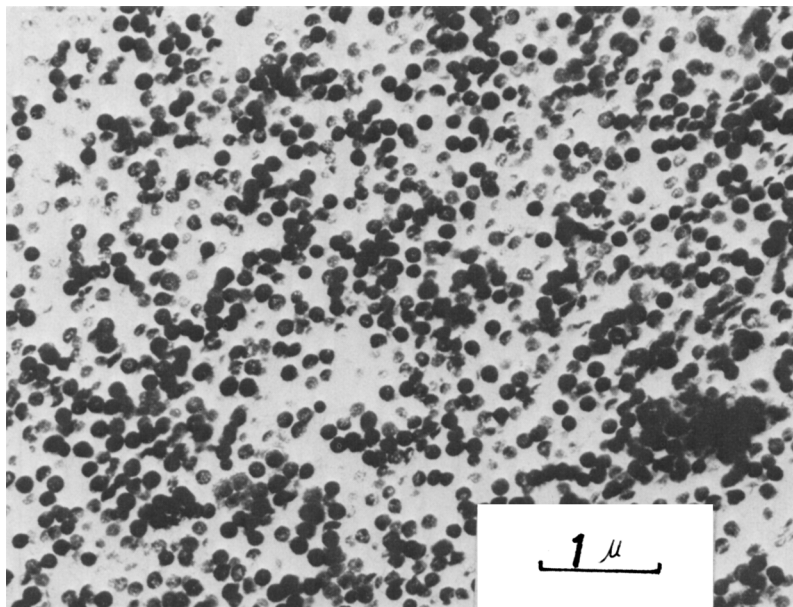


Fig. 2. Ultrathin section of an extrusion-molded specimen having very small rubber particles.

condition is maintained for at least 1 hr at a temperature of 60°C. Control the treatment condition suitably according to each specimen.

Remount the hydrazine hydrate- and osmium tetroxide-treated specimen in accordance with the present procedure in the ultramicrotome holder, but making certain that it is accurately situated in the previous preliminary cutting position. Cut the specimen utilizing a glass knife and obtain ultrathin sections. The ultrathin sections obtained by this manner are ready for electron-microscopic observations.

## RESULTS AND DISCUSSION

### Infrared Absorption Spectrum of Hydrazine Hydrate-Treated Film

The heterogeneous structural resin composition prepared by the present authors was pelletized and subsequently molded by a conventional inflation method (extruder: screw type, 30 mm  $\phi$ ,  $L/D = 20$ , cylinder temp., 180° to 220°C; dice: spiral type, 65 mm  $\phi$ , temp., 220°C, die lip, 1 mm). The film, of a thickness of about 20  $\mu$ , was soaked in 80% hydrazine hydrate solution for surface treatment under condition as shown in Table I.

The alteration in the infrared absorption spectrum of hydrazide group ( $-NHNH_2$ ) accompanying hydrazide substitution was investigated. The results are shown in Figure 1. At the time of measurement of the infrared absorption spectrum, the film was washed thoroughly in running water and dried under reduced pressure in a vacuum desiccator in order to remove the free hydrazine hydrate solution adhering to the surface of this film. As shown in Figure 1, the absorption spectrum neighboring 3200  $\text{cm}^{-1}$  based on secondary amine was not

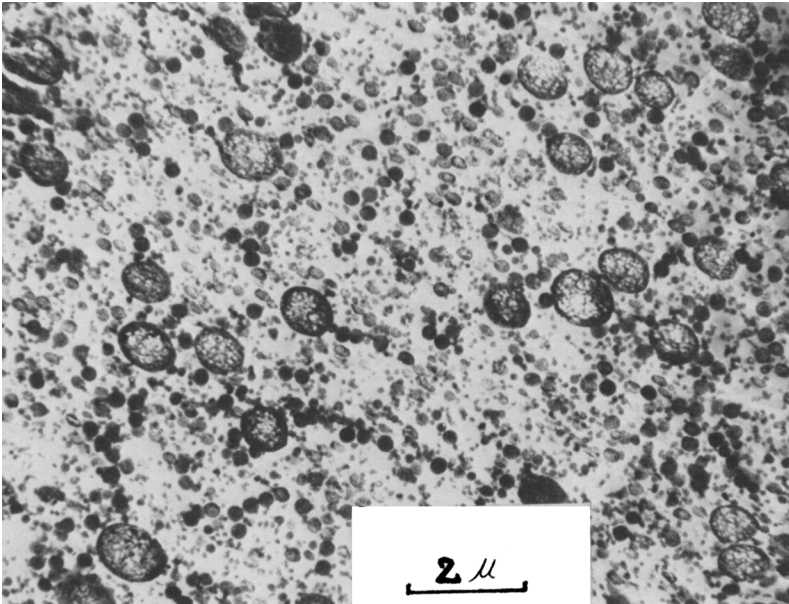
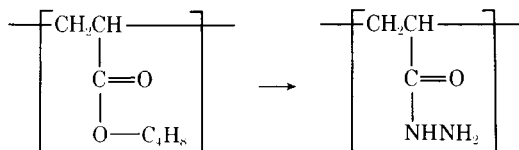


Fig. 3. Ultrathin section of an injection-molded specimen containing large rubber particles and small ones.

observed in the untreated film. When this film was treated with 80% hydrazine hydrate solution, the absorption spectra in the respective neighborhoods of  $1670\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$ , supposedly based on the hydrazide group, were observed slightly after treatment for 24 hr. The spectra obviously were observed after treatment for 96 hr.

Thereafter, these hydrazine-treated films were soaked in 1% osmium tetroxide aqueous solution for 72 hr at  $60^\circ\text{C}$ . These films were observed to be stained black in accordance with the respective duration of the individual hydrazine treatments. In the infrared absorption spectra of these films, the absorption spectra neighboring the respective  $1670\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$  disappeared, and the films gave infrared absorption spectra similar to those of the untreated original film. A typical result is shown in Figure 1.

The present authors theorized from these results that the butyl acrylate polymer in the film basic material might be converted into acrylic acid hydrazides from the surface layer to the inner layer of the film by utilizing the hydrazine treatment as represented by the following formula:



Consequently, the absorption spectra appearing in the respective  $1670\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$  regions appear to be based on hydrazide groups. That is, the present authors suppose that the butyl acrylate polymers in the film were converted to

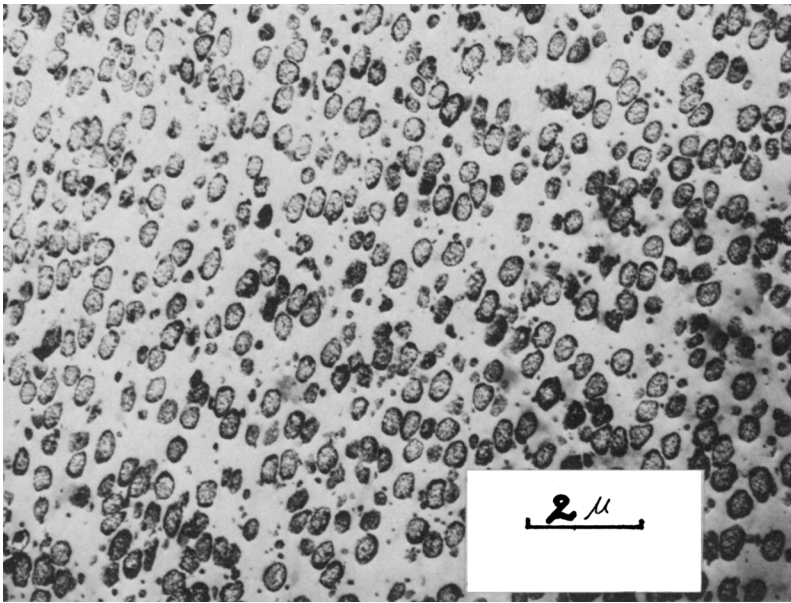


Fig. 4. Ultrathin section through surface layer of an injection-molded specimen.

acrylic acid hydrazides by the soaking treatment with hydrazine hydrate solution. Furthermore, a treatment temperature of 60°C was selected for hydrazine soaking because this temperature did not produce the deformation of the preliminary cutting face of the resin specimen cut by the ultramicrotome prior to hydrazine treatment. Reaction velocity was too slow to be suitable when the temperature was below 60°C. It was confirmed that a treatment temperature of 60°C does not have any undesirable effect on the subsequent osmium tetroxide fixing and staining procedure.

### Electron Micrographs of Materials

Typical electron micrographs are shown in Figures 2, 3, 4, 5, and 6. Figure 2 is an electron micrograph of an ultrathin section of an extrusion-molded specimen having very small particles of rubber. As can be seen from Figure 2, rubber particles having almost uniform particle sizes are selectively fixed and stained to give an excellent contrast and definition against the circumferential resin phase. Figure 3 is an electron micrograph of an ultrathin section of an injection-molded specimen prepared by graft polymerizing a mixture of acrylonitrile and styrene in the presence of a mixture of polyacrylate ester elastomers whose particle sizes were about 0.15  $\mu$  and 0.7  $\mu$ . The internal structure of the large rubber particles revealed a somewhat multiporous structure. Concerning this multiporous structure, some theories are provided. This structure is due to an unstained polymer other than butyl acrylate polymer composing the rubber particles. Moreover, it is due to the occurrence of these separations between the rubber components and the resin components induced by polymerization of a graft monomer infiltrated into the interior of rubber particles as seen ordinarily in the multiporous structure of the interior of rubber particles of ABS resin.

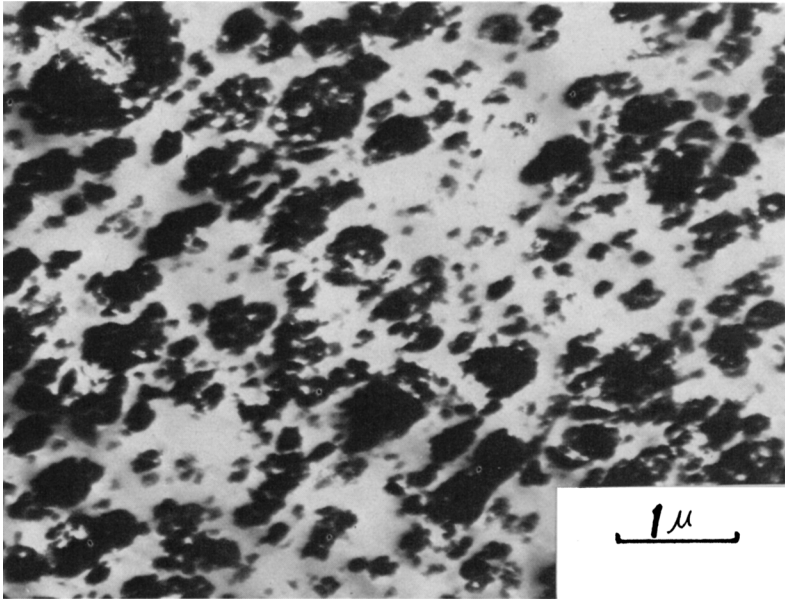


Fig. 5. Ultrathin section of commercial acrylic rubber-modified ASA resin Luran S.

Figure 4 is an electron micrograph of an ultrathin section of an injection-molded specimen, in particular, a surface layer of the specimen adjacent to the mold face. The rubber particles are all elongated in a specific direction. Furthermore, it can be seen that the respective rubber particles are, although not so absolutely distinct, aligned with each other and show a very interesting phase orientation structure similar to that of the rubber particles adjacent to the mold face observed in the injection-mold ABS resin specimen.<sup>14</sup>

Figures 5 and 6 are electron micrographs of ultrathin sections of commercial acrylic rubber-modified resins Luran S and Vitax, respectively. These electron micrographs were obtained in accordance with the aforementioned procedure. The distribution and size of the rubber particles can be observed clearly.

As can be seen from these electron micrographs, the present procedure is very effective for electron-microscopic visualization of acrylic rubber. By using this morphologic analytical procedure, feedback for the design of a polymer structure may be possible.

A molded plastic specimen such as methyl methacrylate polymer, methyl methacrylate-acrylonitrile-styrene copolymer, and ethylene-vinyl acetate copolymer could not be stained with osmium tetroxide solution under the present conditions. This means that the particles of poly(butyl acrylate) elastomer, disperse phase, were stained selectively by the osmium tetroxide and the matrix; acrylonitrile-styrene copolymer was not stained under the present conditions. However, this procedure is applicable to other polyacrylate esters and polymethacrylate esters as well as poly(butyl acrylate) under certain conditions. And it is believed that the application to other saturated polymer, such as acrylonitrile-styrene copolymer, ethylene-vinyl acetate copolymer, and so on, is difficult under the present conditions.

It is well known that hydrazine and its derivatives may react with carboxylic

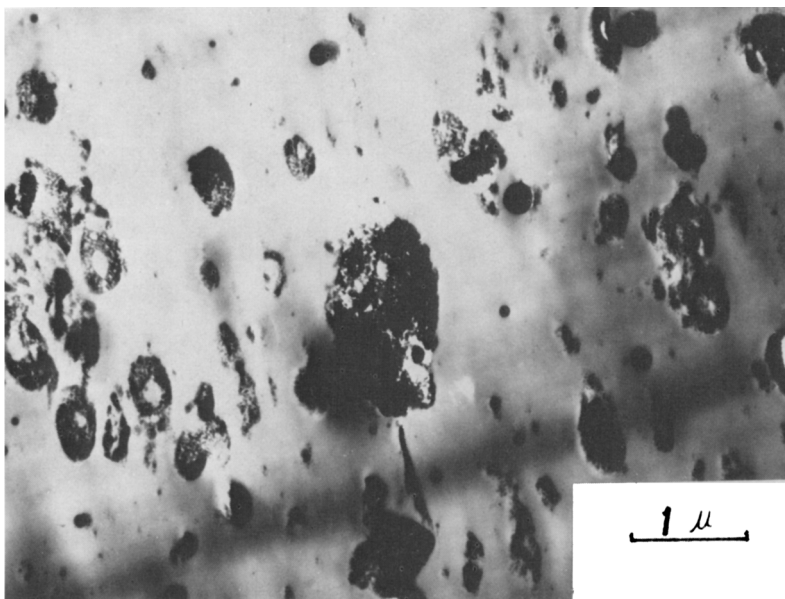


Fig. 6. Ultrathin section of commercial acrylic rubber-modified ASA resin Vitax.

acid ester to produce acid hydrazides<sup>15</sup> which reduce Fehling's solution or ammonium silver nitrate solution. Therefore, butyl acrylate polymer composing the rubber phase may be, first of all, converted to acid hydrazides by hydrazine hydrate solution, and these acid hydrazides may reduce osmium tetroxide and deposit metal osmium in the present procedure. Consequently, the acrylic rubber phase may be fixed and stained with osmium tetroxide. This gives an excellent image contrast and definition for electron-microscopic observations.

The present authors have used only 80% hydrazine hydrate solution for hydrazine treatment in the present procedure, but hydrazine derivatives such as hydrazine sulfate and hydrazobenzene other than hydrazine hydrate may be effective for the present purpose.

The present procedure differs from the osmium tetroxide fixing and staining method in ABS resin in that it requires hydrazine treatment prior to osmium tetroxide fixing and staining. Furthermore, the reaction mechanism of osmium tetroxide rubber components differs slightly from that observed in ABS resin. But the present procedure is very significant in making it possible to visualize the acrylic rubber by the electron microscope after converting, first of all, the saturated polymer such as butyl acrylate rubber into acid hydrazides.

The authors wish to express their sincere thanks to Mr. K. Yoshida for his assistance during this work.

### References

1. E. H. Merz, G. C. Claver, and M. Baer, *J. Polym. Sci.* **22**, 325 (1956).
2. P. A. Traylor, *Anal. Chem.*, **33**, 1629 (1961).
3. G. C. Claver, ASTM Special Technical Publication No. 348, 1964, p. 161.
4. C. H. Basdekis, *ABS Plastics*, Reinhold, New York, 1964.
5. C. B. Bucknall and R. R. Smith, *Polymer*, **6**, 437 (1965).



6. K. Kato, *Polym. Lett.*, **4**, 35 (1966).
7. W. E. Brown, *J. Appl. Phys.*, **18**, 273 (1947).
8. E. A. Williams, J. R. Miller, and E. H. Rowe, *J. Phys. Chem.*, **53**, 357 (1949).
9. S. H. Maron, C. Moore, and A. S. Powell, *J. Appl. Phys.*, **23**, 900 (1959).
10. E. B. Bradford and J. W. Vanderhoff, *J. Colloid Sci.*, **14**, 543 (1959).
11. E. B. Bradford and J. W. Vanderhoff, *J. Polym. Sci. C*, **341**, (1963).
12. K. Kato, *Polym. Eng. Sci.*, **7**, 38 (1967).
13. K. H. Stange, E. Priebe, and K. W. Steiner, *Progr. Plast.*, **32**, August (1970).
14. K. Kato, *Plastics* **19**, 96 (1968) (published in Japan).
15. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 11, 1966, p. 164.

Received August 12, 1975

Revised October 15, 1975