Non-catalysed Polymerization of Acrylamide

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It was found that acrylamide which had been left standing in air for several weeks polymerized spontaneously in water at room temperature at a rapid speed of polymerization in spite of the absence of an initiator. Poly(acrylamide peroxide) was found in acrylamide that had stood for a long time and in acrylamide that had been irradiated with daylight, while no peroxide was found in propion amide. These results seem to show that the above spontaneous polymerization was initiated by the peroxide which was formed in the acrylamide monomer. The formation of the peroxide was promoted by light and its decomposition was promoted by the addition of water.

The polymerization of acrylamide was carried out by using the separated poly(acrylamide peroxide). The rate of polymerization increased with increase in the water content, but was slow in solvents containing other polar solvents such as halide solvents and alcohols. No polymer was obtained when a little picric acid was added. When acrylamide was polymerized in water with the peroxide, the rate of polymerization was found to be proportional to the monomer concentration and to the square root of the peroxide concentration. This peroxide also initiated the polymerization of methacrylic acid in water to produce a block copolymer.

IT HAS been known for a long time that various monomers polymerize spontaneously on standing. The origin of these spontaneous polymerizations, apart from photo and thermal polymerization, is considered to be that the peroxides formed by the spontaneous reaction of the monomers with the oxygen in the air initiate the polymerizations[1]. The non-catalysed polymerizations of vinyl monomers have recently been studied but the initiation mechanism is not clear. Imoto and Takemoto[2–6] found that a polymer was formed in the system consisting of methyl methacrylate, cellulose, carbon tetrachloride and water and thought that a complex formed from them functioned as the initiator. However, this monomer and polymer seem to form peroxides easily in air. Barnes *et al.*[1] reported that vinyl compounds such as methyl methacrylate and styrene reacted with oxygen and with air to form polymeric peroxides which initiated polymerization reactions. The present authors found that acrylamide which had been left standing in air for about 20 days after purification, polymerized without an initiator at room temperature in the system consisting of acrylamide, poly(ethylene oxide), carbon tetrachloride and ethanol. It was made clear from a detailed investigation that acrylamide reacted with the oxygen in air on standing to form a polymeric peroxide, which initiated the polymerization reaction.

It was eventually found that the polymerization took place without poly(ethylene oxide) and carbon tetrachloride and that the water in the system promoted the rate of the polymerization of acrylamide by the peroxide. The polymeric peroxide initiated the polymerization of methacrylic acid in aqueous solution to make a block copolymer. These experimental results are presented.

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EXPERIMENTAL

Materials

About 80 g of acrylamide supplied by the Nitto Chemical Industrial Co. Ltd was dissolved on heating in a mixture of 200 ml of benzene and 20 ml of methanol. The hot solution was filtered off and then cooled for recrystallization. The precipitated crystals of acrylamide were filtered off and dried in a dark place in air (m.pt 85°C).

For polymerization, the peroxide in the acrylamide was always measured before use. Freshly prepared acrylamide contained no peroxide.

Ion-exchange water was used as polymerization solvent after boiling it for more than four hours to eliminate the oxygen dissolved in it.

Methacrylic acid was used after distillation under reduced pressure in a stream of nitrogen gas (b.pt 69°C at 15 mm Hg).

Carbon tetrachloride, methanol and ethanol were used after distillation.

Tetrahydrofuran (THF) was purified by first refluxing it with potassium hydroxide for more than 24 hours, then with sodium metal for more than 24 hours, and distilled (b.pt 66°C).

Other solvents of commercially available products (extra pure reagents) were used without further purification.

Preparation and quantitative analysis of peroxide

Poly(acrylamide peroxide) (PAAPO), which was used as an initiator for the polymerizations of acrylamide and methacrylic acid, was prepared as follows. Purified acrylamide was irradiated with daylight for about 50 hours and then put into methanol. The acrylamide monomer was easily dissolved but the polymeric compounds such as polyacrylamide and PAAPO were not. These methanol-insoluble compounds were filtered off, washed with methanol, then dried in air and used as PAAPO. The peroxides in the acrylamide and PAAPO were measured by the ferrous salt–*O*-phenanthroline method[7]. The solution containing an accurately weighed sample was placed in a 25 ml flask, and 0·5 ml of aqueous nitric acid solution (1 : 20) and 0·25 ml of aqueous phosphoric acid solution (0·04 M) were added and the flask shaken. Then 0·5 ml (the volume was increased with increase in amount of peroxide) of aqueous ferrous ammonium sulphate solution (0·002 M) was added, the mixture shaken and left to stand for about 15 minutes for the completion of the reaction $Fe^{2+} \xrightarrow{(O)} Fe^{3+}$. Finally, 2·5 ml of a 0·1 per cent aqueous solution of *O*-phenanthroline containing a little methanol was added and the total volume of the solution mixture was made just 25 ml. After 30 to 60 minutes, the transmission at 510 mμ was measured by a Hitachi spectrophotometer. As the amount of peroxide in the acrylamide and PAAPO changed with each purification and preparation, the quantitative analysis was carried out every time just before use.

Method of polymerization

The polymerization was usually carried out as follows. Solvents, acrylamide (or acrylamide solution) and PAAPO solution from which the gel had been removed beforehand, were placed in a tube so that the total volume of the solution was 10 ml. The system was then degassed twice by the usual method, sealed under vacuum and polymerized by leaving it to stand still at a constant temperature. After a given time, the polymerized system was immediately cooled in dry ice–methanol and put into methanol containing a little hydroquinone. When the system was very viscous or in a gel-state due to the comparatively high conversion and the large molecular weight, the polymer block precipitated in methanol was cut finely with scissors. After the polymer had stood in methanol overnight the polymer was filtered off, washed with methanol, dried under vacuum and weighed.

RESULTS AND DISCUSSION

Polymerization of acrylamide in various solvents

It was accidentally found that the system consisting of 0·05 g of poly(ethylene oxide), 1·5 ml of ethanol, 4·5 ml of carbon tetrachloride and 0·5 g of acrylamide which had been left standing for about 20 days after purification, had formed acrylamide polymer at room temperature (about 10°C) about a week after the preparation of the system. On the other hand, the system consisting of poly(ethylene oxide), ethanol, trichlorethylene (4·5 ml) and acrylamide had not formed a polymer. Polymerization tests were carried out in the presence and absence of poly(ethylene oxide). From the results, it was found that the polymerization was not dependent upon the presence or absence of poly(ethylene oxide).

To investigate the effect of solvents, polymerization experiments were carried out using various solvents. Acrylamide and the solvent were placed in tubes, degassed twice, sealed under vacuum and polymerization allowed to proceed by leaving them to stand still at 35°C.

It was found from the results that in the system of trichlorethylene and methanol, acrylamide was not polymerized even after 20 hours, whereas in the systems of the other halide solvents and methanol such as chloroform–methanol and carbon tetrachloride–methanol, it was polymerized to a small extent (0·5 $\sim$ 2·4 per cent). In the systems such as carbon tetrachloride–THF and carbon tetrachloride–dioxan, the conversion was greater than ten per cent. When water was added to the polymerizing system, the polymerization was considerably promoted. For example, in the system of water–THF–carbon tetrachloride, the conversion reached over 80 per cent after 20 hours. However, except for water, the promoting effect on polymerization for polar solvents such as acetone and ethanol was not found. Polymerization was inhibited by the presence of a little picric acid.

Polymerization experiments were carried out, changing the degree of purification of the acrylamide monomer. It was found from the results that acrylamide which had been left standing for one day after purification was not polymerized, but the one that had stood for several weeks was polymerized 95 per cent in water. The amount of peroxide in these 'new' and 'old' acrylamides was measured. It was confirmed that no peroxide was present in the new acrylamide, while $(3{\cdot}7 \sim 5{\cdot}8) \times 10^{-6}$ mol of peroxide was contained in 1 g of the old one.

It was concluded from the above results that the peroxide formed spontaneously in acrylamide initiated the polymerization described above and that the polymerization was carried out by a radical mechanism due to the peroxide.

Formation and decomposition of PAAPO

As it was found that the peroxide was formed in acrylamide on standing in air, the peroxide was prepared in air. For the promotion of the formation of peroxide, the purified acrylamide was pulverized and irradiated with ultra-violet rays from a mercury lamp (Toshiba SHL-100 UV) at room temperature at a distance of about 15 cm. The results are shown in *Figure 1*.

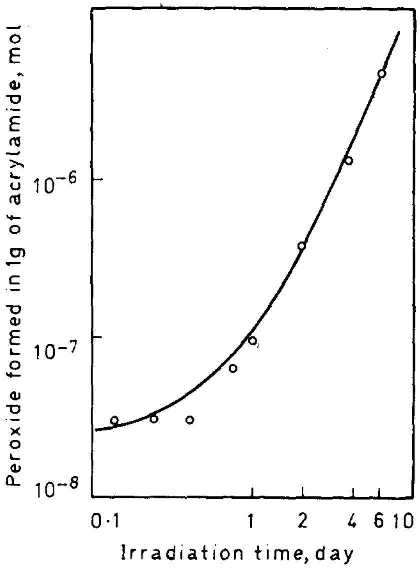

Figure 1—Formation of peroxide with irradiation from an ultra-violet lamp in air at room temperature

It was found that $3{\cdot}9 \times 10^{-6}$ mol of the peroxide was formed in 1 g of acrylamide after six days of ultra-violet irradiation, while $6{\cdot}8 \times 10^{-8}$ mol of the peroxide was formed in the same amount of acrylamide left standing in the dark. The formation of peroxide was promoted with the irradiation of light. Commercially available propion amide was also irradiated under the same conditions as in the above experiment, but no peroxide was formed.

It is known[1,8] that vinyl compounds such as methyl methacrylate and styrene copolymerize with oxygen to form peroxides. Acrylamide also seems to react with the oxygen in air to form the peroxide. Acrylamide, which had been irradiated with ultra-violet rays for six days, was put into methanol and the polymeric part was separated from the monomeric part. In the polymeric part, i.e. the methanol-insoluble part $(3{\cdot}1 \sim 6{\cdot}9) \times 10^{-6}$ mol of peroxide was present per 1 g, while in the monomeric part, i.e. the methanol-soluble part, only $(2{\cdot}5 \sim 4{\cdot}4) \times 10^{-8}$ mol was present. From these results and the fact that propion amide did not form a peroxide even with ultra-violet irradiation, it was considered that the peroxide had a polymeric form. This methanol-insoluble part, PAAPO, had an intrinsic viscosity of 0·291 (measured at 30°C for the aqueous solution by use of an Ubbelohde viscometer). The average molecular weight $\overline{M}$, calculated by use of the equation[9] $[\eta] = 6{\cdot}31 \times 10^{-5}\overline{M}^{0{\cdot}80}$ was $3{\cdot}89 \times 10^4$.

The decomposition of PAAPO in water and solvent mixtures of water and methanol was measured. The results are shown in *Figures 2* and *4*. The rates of decomposition at each temperature were obtained from *Figure 2* and they were plotted against the reciprocal of the decomposition temperature expressed as the absolute temperature, as shown in *Figure 3*. The

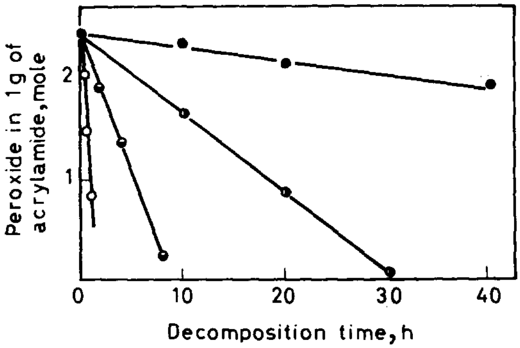

Figure 2—Decomposition of polyacrylamide peroxide at ● 30°C; ◑ 50°C; ◓ 70°C; ○ 90°C. Initial concentration of the peroxide in water was $5{\cdot}65 \times 10^{-5}$ mol/l.

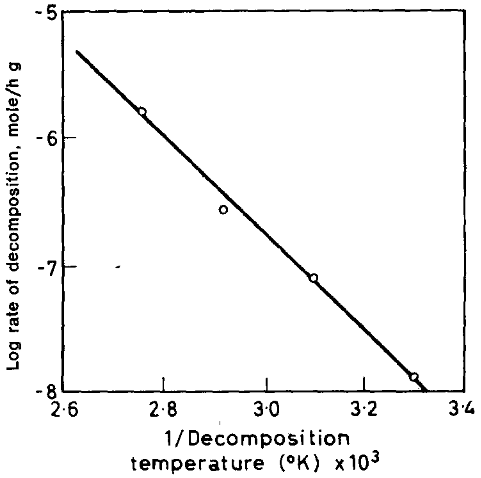

Figure 3—Relationship between decomposition temperature and time

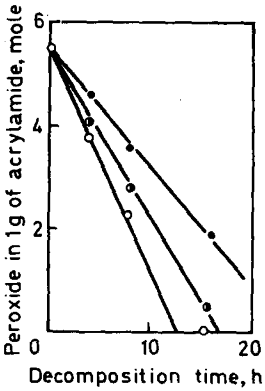

Figure 4—Decomposition of PAAPO in the system of water and methanol. Initial concentration of peroxide was $7{\cdot}92 \times 10^{-5}$ mol/l. at 50°C. Concentration of methanol in water (volume %) ● 40 per cent; ◑ 20 per cent; ○ 0 per cent

activation energy for the decomposition, E_A, obtained from *Figure 3* was $(17{\cdot}4\,^{+4\cdot2}_{-1\cdot8})$ kcal/mol. It was found from *Figure 4* that the decomposition of PAAPO was most rapid in pure water and that it became slower with increase in the proportion of methanol. When the proportion of methanol was increased to near 50 per cent, PAAPO precipitated, so experiments with a higher proportion of methanol could not be carried out.

Polymerization initiated by PAAPO

Polymerization of acrylamide—PAAPO was obtained by irradiating acrylamide monomer with sunshine and separating it by means of methanol. The PAAPO thus obtained was used as the initiator for the polymerization of acrylamide and the effect of the concentration of acrylamide monomer [M], and that of PAAPO [I] on the rate of polymerization, R_p were investigated. The results are shown in *Figures 5* to *8*.

Figure 5 shows the relationship between the polymerization time and the yield of polymer at various acrylamide concentrations. The initial rates of polymerization were obtained and plotted on a log-log scale against the abscissa of the concentration to obtain *Figure 6*. It was found from this figure that R_p was proportional to [M].

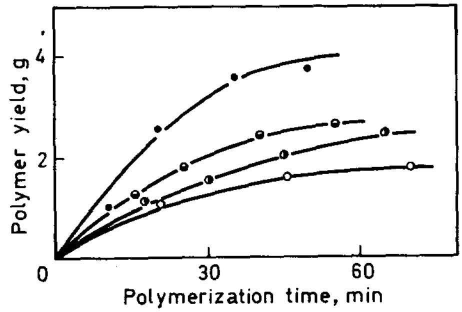

Figure 5 — Relationship between polymerization time and polymer yield at various concentrations of acrylamide of ● 4·92; ◒ 4·21; ◑ 3·52; ○ 2·81 mol/l. Concentration of PAAPO in water was $2{\cdot}03\times10^{-4}$ mol/l. at 50°C

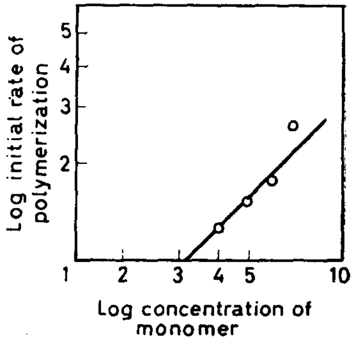

Figure 6—Relationship between concentration of monomer and initial rate of polmerization

The intrinsic viscosities of the aqueous solutions of the polymers formed after polymerization times of 40 to 50 minutes were measured at 30°C by means of an Ubbelohde viscometer. They were found to be 61·0, 55·4 and 49·9, respectively, when [M] was 4·29, 4·21 and 2·81 mol/l. It seems that both intrinsic viscosity and molecular weight increased with increase in the monomer concentration.

Figure 7 shows the relationship between the polymerization time and the yield of polymer at various PAAPO concentrations. The initial rates of polymerization were obtained and plotted on a log-log scale against the concentration as abscissa to obtain *Figure 8*. It was found from this figure that R_p was proportional to $[I]^{\frac{1}{2}}$.

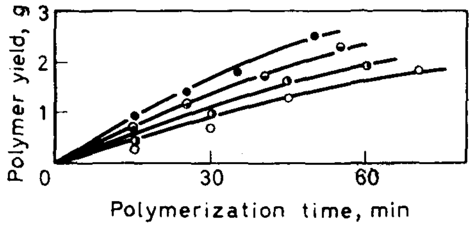

Figure 7—Relationship between polymerization time and polymer yield at concentrations of PAAPO of ● 16×10^{-5}; ◒ 12×10^{-5}; ◑ 8×10^{-5}; ○ 4×10^{-5} mol/l. The concentration of acrylamide in water was 3·52 mol/l. at 50°C. No polymer was obtained without PAAPO

The intrinsic viscosities of the aqueous solutions of the polymers formed after polymerization times of 40 to 50 minutes were measured at 30°C. They were found to be 29·0, 30·0 and 35·7, respectively, when [I] was 12×10^{-5}, 8×10^{-5} and 4×10^{-5} mol/l. It seems that both [η] and molecular weight decreased with increase in the PAAPO concentration. When these results are summarized, it is found that $R_p \propto [M]\,[I]^{\frac{1}{2}}$.

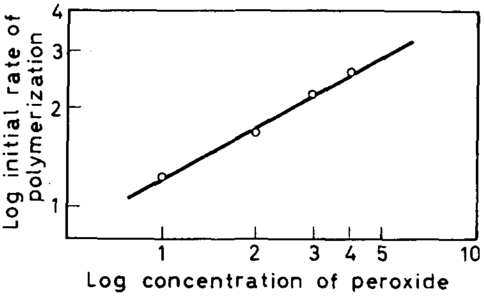

Figure 8—Relationship between concentration of PAAPO and initial rate of polymerization

The results of polymerizations obtained in solvent mixtures of water and methanol of various mixing ratios are shown in *Figure 9*.

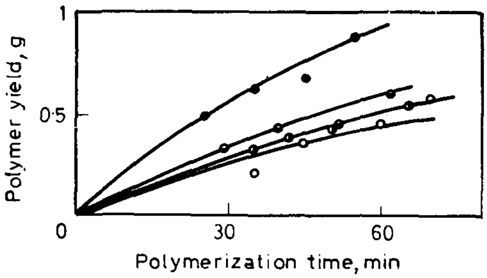

Figure 9—Polymerization of acrylamide in solvent mixtures of water and methanol, the concentrations of methanol in water being ● 0; ◒ 20; ◑ 30; ○ 40 volume per cent. The concentration of acrylamide was 2·81 mol/l. and that of PAAPO was $1{\cdot}28\times10^{-4}$ mol/l. at 50°C

R_p decreased with increase in the proportion of methanol. This seems to be attributable to the decrease in the rate of decomposition of PAAPO due to the increase in the proportion of methanol. The intrinsic viscosities of the aqueous solutions of the polymers formed after a polymerization time of 40 to 50 minutes were measured at 30°C. They were found to be 80·0, 60·4, 65·0 and 48·8, respectively, when the proportion of water was 100, 80, 70 and 60 per cent. A tendency for $[\eta]$ to decrease with increase in the proportion of methanol was found.

The PAAPO which was obtained in this work had a high molecular weight and a high intrinsic viscosity, e.g. $[\eta]=0{\cdot}29$ to 0·96 (measured for the aqueous solution at 30°C). The polyacrylamides obtained using this as an initiator had very high intrinsic viscosities ranging from 29 to 80 for their aqueous solutions at 30°C, as shown above. On account of their extremely high molecular weights, these polyacrylamides took a very long time to dissolve even in water, which was a very good solvent. Some of them took more than ten days to dissolve completely, even with heating on a water bath. As shown by its large k_p, such as $(180 \pm 0{\cdot}15) \times 10^4$ 1/mol sec[10], and its k_t, such as $(1{\cdot}45 \pm 0{\cdot}20) \times 10^7$ 1/mol sec[10] at 25°C in water, acrylamide is very easily polymerized by radicals and its rate of polymerization is large. These properties of the monomer itself, the increase in viscosity of the polymerization system due to the presence of the polymeric initiator, and the rapid increase in viscosity with progress of polymerization (the system became a gel-state when about 0·2 g of polymer had been formed in 10 ml of water) are thought to be the causes for the formation of polymers with very large molecular weights.

Tobolsky and Matlack[11] reported that the cumene hydroperoxide (CHP)–solvent initiation reaction became important in solvents such as benzyl alcohol and pyridine for the radical polymerization initiated by CHP, that the CHP–monomer initiation reaction became dominant in solvents such as benzene and carbon tetrachloride and that $R_p \propto [\mathrm{M}]$ for the former and $R_p \propto [\mathrm{M}]^{1{\cdot}5}$ for the latter.

It is considered that the above relationship of $R_p \propto [\mathrm{M}]\,[\mathrm{I}]^{\frac{1}{2}}$ showed that the initiation by PAAPO was more affected by the reciprocal actions with water–methanol than by those with acrylamide, in the polymerization in the system water–methanol–acrylamide–PAAPO.

Polymerization of acrylamide under oxygen—50 ml of an aqueous solution containing 25·0033 g of pure acrylamide (1 g of this contained $2{\cdot}25 \times 10^{-7}$ mol of peroxide) was prepared and 10 ml portions of the solution were placed in tubes of 15 mm internal diameter. A glass tube of 7 mm external diameter and 6 mm internal diameter was dipped into the bottom of the solution and oxygen was led into the solution through a glass tube tip. Oxygen was bubbled for 1, 3 and 25 hours at a flowrate such that five or six bubbles could always be seen. After the bubbling of oxygen finished, the solutions were left to stand with the top open at room temperature (about 30°C) for 25, 20 and 0 hours, respectively, and then poured into methanol. The solution through which oxygen had been continuously bubbled until it was poured into methanol, formed no polymer, while the solutions through which it had been bubbled for one hour and three hours formed 1·80 g and 5·76 g of polymer, respectively. It is considered that due to the inhibiting effect of oxygen, a polymer was not formed as long as oxygen was continuously bubbled, but that a polymer was formed with the initiation of the peroxide formed in the solution which was left to stand after oxygen had been passed for a short time. Oxygen acts as an inhibitor and at the same time it forms peroxide which initiates the polymerization. It is considered that the propagation reaction predominated over the inhibition reaction when polymer was formed.

Block copolymerization of methacrylic acid by PAAPO—5 ml of an aqueous solution containing 0·174 g of PAAPO (1 g of this PAAPO contained $1{\cdot}9 \times 10^{-5}$ mole of peroxide), 1 ml of purified methacrylic acid and 4 ml of water were placed in a tube, degassed twice, sealed under vacuum and polymerized by leaving it to stand at 50°C. A polymer precipitated as the polymerization proceeded. After the polymerization reaction had been carried out for a fixed time, the polymer mixture was poured into THF. The polymer was filtered off, washed with THF, dried under vacuum and weighed. The results are shown in *Figure 10.*

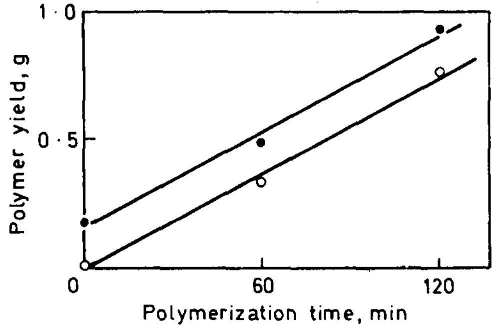

Figure 10—Polymerization of methacrylic acid with PAAPO showing ● yield of all polymers and ○ yield of poly(methacrylic acid). Concentration of methacrylic acid was 1·18 mol/l. and that of the peroxide in water was $3{\cdot}28 \times 10^{-4}$ mol/l. The temperature was 50°C

The yield of polymer increased linearly with time. Poly(methacrylic acid), which was prepared with the initiation of AIBN in another experiment, was soluble in methanol and polyacrylamide is insoluble in methanol. To obtain the block copolymer, the polymer obtained was separated into the methanol-soluble part and the -insoluble part. 0·046 g and 0·073 g of methanol-soluble part were obtained from the polymers of polymerization times of one and two hours, respectively. Elementary analysis gave the nitrogen contents as 7·80 per cent for the methanol-insoluble part in the one hour polymerization, 5·68 per cent for the insoluble part in the two hour polymerization and 3·98 per cent for the methanol-soluble part in the one hour polymerization. The methanol-soluble part still contained nitrogen, that is, it was a block copolymer of polyacrylamide and poly(methacrylic acid), in spite of the fractionation. The molar ratios of acrylamide to methacrylic acid were calculated from the nitrogen contents and the yield of the polymers. They were 1:1·3 from the nitrogen percentage (1:1·5 from polymer yield) for the methanol-insoluble part in the one hour polymerization and 1:2·0 from the nitrogen percentage (1:2·9 from polymer yield) for that in the two hour polymerization, respectively. It was found from the results of the elementary analyses that methacrylic acid-rich block copolymer was extracted by the methanol extraction.

The infra-red spectrum of the polymer (the methanol-insoluble part in the two hour polymerization), which was taken using a film prepared from an aqueous solution on a Perkin–Elmer 337 grating infra-red spectrophotometer, is shown in *Figure 11.* This clearly shows that the absorption bands of polyacrylamide, such as those at about 3 350, 2 920, 1 600 and 1 320 cm^{-1}, can be seen in addition to the bands of poly(methacrylic acid).

It is considered from these results that PAAPO initiated the polymerization of methacrylic acid to form a block copolymer. This block copolymer gradually became water-insoluble with time, while the homopolymers of both polyacrylamide and poly(methacrylic acid) obtained in other experiments were still soluble in water after the same time. The intrinsic viscosity of the block copolymer could not, therefore, be measured.

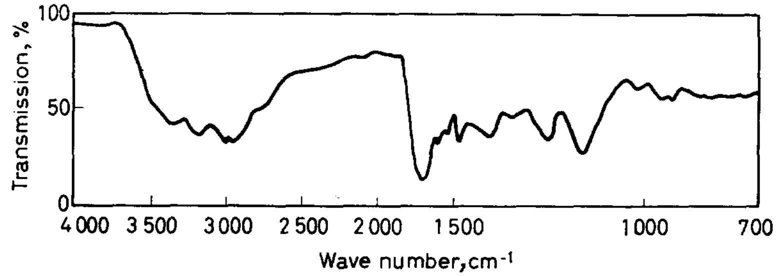

Figure 11—Infra-red spectrum of the methanol-insoluble poly(methacrylic acid) formed with PAAPO after being polymerized in water for two hours at 50°C

The authors are grateful to Dr Kisaka and Dr Okazaki, the Managers of the Wireless Research Laboratory of Matsushita Electric Industrial Co. Ltd, for their assistance and to the Nitto Chemical Industrial Co. Ltd for donating acrylamide.

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(*Received December 1967*)

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