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Mechanochemical Reactions at High Pressures. II. Reaction of Methacrylamide

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The mechanochemical behavior of methacrylamide was investigated at room temperature and at static pressures of up to 15 kbar. The determinations of the IR spectrum, the ESR signal, the X-ray diffraction pattern, and the molecular weight by GPC apparatus confirmed that the reaction products were amorphous polymethacrylamide. The reaction of methacrylamide under conditions of high pressure combined with simultaneous shear deformation(HP+SSD) is a free radical polymerization. The concentration of radicals of polymethacrylamide and the relation between the conversion and the shearing degree suggest that an acrylamide crystal is less stable than one of methacrylamide. Methacrylamide was not reached 100% conversion even at about 2π rad shearing.

The first paper[1)] of this series described the design and the construction of the apparatus and the reaction of acrylamide. Acrylamide was polymerized under conditions of HP+SSD. We concluded that the polymerization of acrylamide proceeded by the free radical mechanism. The present paper is concerned with methacrylamide. The compound was selected because its similarity to acrylamide suggested that it might undergo an analogous behavior under HP+SSD, and thus allow a comparison of the mechanochemical behavior at high pressure.

Experimental

The experimental procedure is similar to that in the previous paper[1)] except for the molecular weight determination. The molecular weight of the product was determined by gel permeation chromatography(GPC) using a Sephadex column constructed in our laboratory.

In this experiment, the reactions proceeded at the constant shearing velocity of 2.51 rad/h(2.4 °/min) at room temperature.

Methacrylamide was a commercial sample which was purified by repeated crystallization from benzene solution and finally vacuum dried at room temperature for 24 h. The purity of this material was confirmed by its melting point, determined as 109—110 °C.

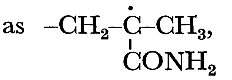
The sample which has been sheared at up to 15 kbar (1 kbar$=10^8$ Pa) static pressure was extracted from a large amount of methanol for separating into soluble and insoluble fractions. The insoluble fraction (as will be described below) was dried *in vacuo* to constant weight at room temperature, and the conversion was determined. The identifications of the product were carried out by means of the measurements of melting point, IR spectrum, X-ray diffraction patterns and molecular weight distribution.

ESR spectra were recorded at 22 °C on a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100 kHz field modulation. The concentrations of free radicals were determined by integrations of the spectra and by subsequent comparison with those of 1,3,5-triphenylverdazyl as references.

Results and Discussion

Methacrylamide was polymerized under conditions of HP+SSD, as occurred for acrylamide. The following experimental evidence showed this. The product did not show any definite melting point. The IR spectra of the product were very broad peculiar to a polymer rather than a methacrylamide monomer. The major difference is in the C=C vibration region at 1660—1580 cm^{-1}, where a strong absorption of C=C bonds has disappeared in the product. When X-ray diffraction patterns of methacrylamide monomer were compared with those of the product, the product was found to be in the amorphous state. Therefore, we concluded that the product in this reaction was amorphous polymethacrylamide.

The ESR signal gives a quintet system, and no other signals were detected under our experimental conditions. This signal suggests that the propagating polymer radicals at the side of such methyl groups as


$-CH_2-\overset{\bullet}{\underset{CONH_2}{C}}-CH_3$,

which resulted from the rupture of C=C bonds, were generated by this type of reaction. Thus, evidently, the reaction of methacrylamide under conditions of HP+SSD is a free radical polymerization similar to that of acrylamide. Table 1 shows the concentrations of free radicals generated in the sample layer, together with those of polyacrylamide at the same conditions. The concentrations of free radicals increase with the shearing degree. Accordingly, the shearing stresses seem to play a major part in the rupture of C=C bonds. There is no difference in the concentration at each pressure for the same

Table 1. Concentrations of free radicals generated in sample layers

P	Shearing degree		Free radical × 10^{-18}/spin g^{-1}	
kbar	rad	°	Methacrylamide	Acrylamide
5	2.27	130		0.27
5	3.14	180	1.49	
5	4.71	270	3.15	2.56
10	0.52	30	0.076	
10	1.22	70	0.22	
10	2.27	130	0.98	1.27
10	3.14	180	1.39	
10	4.71	270	3.39	4.25
15	1.57	90	0.84	
15	3.14	180	2.93	

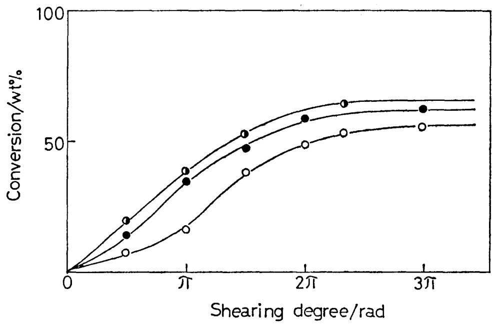


Fig. 1. Relation between conversion and shearing degree at various static pressures.
○: 5 kbar, ●: 10 kbar, ◑: 15 kbar.

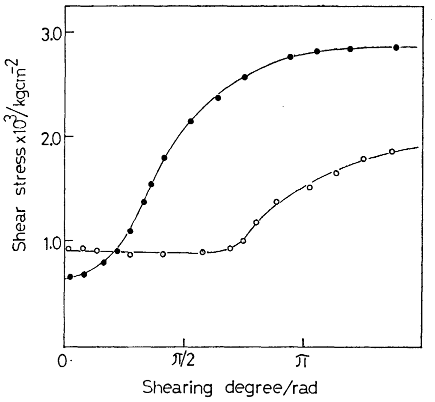


Fig. 2. Shearing curves at 10 kbar.
●: Acrylamide, ○: methacrylamide.

shearing degree (*i.e.* 3.14 rad). The concentration of radicals of polyacrylamide is generally larger than that of polymethacrylamide. It can be seen that the acrylamide crystal is relatively unstable and easily produces radicals due to the mechanical shear force under high pressure. The relation between the conversion and the shearing degree also suggests these conclusions.

Figure 1 shows the dependence of the conversion on the shearing degree at 5, 10, and 15 kbar static pressures, respectively. This relation showed an S-type curve, as do the acrylamide curves. Unlike the relation of acrylamide (refer to Fig. 9 in the previous paper1)), methacrylamide was not reached 100% conversion even at about 2π rad shearing. Figure 2 shows the relation between the shearing stress and the shearing degree. In Fig. 2, the shearing curve for acrylamide is very similar to its conversion curve. It is therefore concluded that the shearing stress is loaded on the full sample layer and reflects directly on the conversion of polyacrylamide. On the other hand, the value of the shearing stress for methacrylamide is nearly constant up to $\theta=\pi/2$ rad. The shearing force does not affect the whole area of the sample, and the only surface destruction which occurs is in the case of methacrylamide. That is presumed from Fig. 3, which shows the time dependence of the polymethacrylamide radical concentrations at room temperature. In this figure, the radical reduction rate was obtained as 13.2%/120 min for polymethacrylamide radicals; this value is larger than that for polyacrylamide radicals, 5.4%/120 min. Polymethacrylamide radicals are thus relatively unstable because most of the radicals are generated in the region of the sample surface.

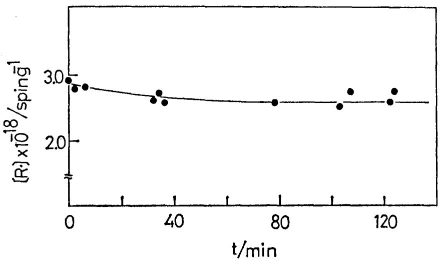


Fig. 3. Time dependence of radical concentrations at room temperature.

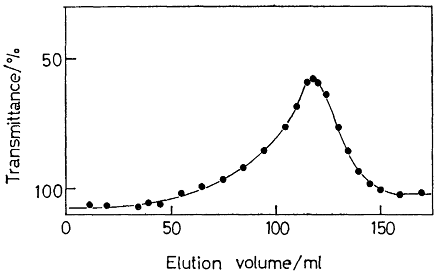


Fig. 4. Molecular weight distribution of the product.

The relations between the intrinsic viscosity and the molecular weight of polymethacrylamide are unknown. Thus a Sephadex column was prepared in our laboratory to determine the molecular weight and its distribution. The experimental result is shown in Fig. 4. We could determine the average molecular weight of the product from this peak, using a calibration curve for this column. Calibration was undertaken by using polyethylene glycol and dextran as calibrants. The molecular weight determined by this method was about 1000. No variation of the average molecular weight was observed with the change of the reaction conditions. The above value, 1000, was also confirmed by another column (G3000PW, manufactured by Toyo Soda Kogyo Co., Ltd.).

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Reference

1) Y. Ogo, N. Nishiguchi, and Y. Okuri, *Bull. Chem. Soc. Jpn.*, **54**, 520 (1981).