Mechanochemical Reactions at High Pressures. III. Reactions of Acrylamide–Methacrylamide and Acrylamide–Propionamide Solid Solutions

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The mechanochemical behavior of acrylamide–methacrylamide (AA–MAA) and acrylamide–propionamide (AA–PA) solid solutions was investigated at room temperature and at static pressures of up to 15 kbar. The AA–MAA solid solution was copolymerized under the experimental conditions. On the other hand, the reaction product of AA–PA solid solution was an amorphous homopolymer of polyacrylamide. That is, the mechanochemical reaction of AA–PA solid solution proceeded only in the acrylamide area by a free radical mechanism. The mechanical behavior of both solid solutions was also discussed.

The previous papers[1,2] were concerned with the design and construction of the apparatus and the reactions of acrylamide and methacrylamide. Both compounds were polymerized by a free radical mechanism under conditions of high pressure combined with simultaneous shear deformation(HP+SSD). The present paper deals with acrylamide–methacrylamide(AA–MAA) and acrylamide–propionamide(AA–PA) solid solutions.

The solid-phase reaction of both solid solutions has not been investigated under high pressures. Only polymerization of acrylamide–propionamide with γ-rays has been reported by several investigators.[3–5]

As a general rule, solid solutions have an unstable crystal structure unlike uni-component materials. Crystal instabilities of both solid solutions are expected to appear in some parameters measured in this type of reaction.

In this paper, the mechanochemical behavior and the pressure effect on acrylamide–methacrylamide solid solution and acrylamide–propionamide solid solution are discussed.

Experimental

The principles of the experimental procedure were similar to the preceding papers.[1,2] Acrylamide, methacrylamide, and propionamide were recrystallized from benzene, respectively.

All the solid solutions were prepared by melting the ingredients in the tubes which were closed to the atmosphere, followed by rapid cooling, so that crystalline films were formed on the walls of the tubes.

The molecular weight of the reaction product from AA–MAA solid solution was estimated by gel-permeation chromatographic analysis, using a Sephadex column made in our laboratory and calibrated by using polyethylene glycol and dextran as the standard substances.

The molecular weight of the reaction product from AA–PA solid solution(polyacrylamide, as will be described below) was determined, by means of the following relation,[6] from the viscosity data obtained from the Ubbelohde viscometer at 30 °C.

$$[\eta]_{30}^{H_2O} = 3.73 \times 10^{-4} M_v^{0.66}$$

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.

Results and Discussion

Reaction of Acrylamide–Methacrylamide Solid Solution. Figure 1 shows the two component phase diagram obtained by a DSC(Differential Scanning Calorimeter) and melting point measurements with the naked eye. This diagram shows that 87 mol% acrylamide–13 mol % methacrylamide mixture melts congruently at 79—80 °C. This congruent transformation is observed for some binary solid solutions. It is thought that this ratio mixture is an optimum experimental sample.

We concluded from the following experimental evidence that AA–MAA solid solution was copolymerized under conditions of HP+SSD. IR spectra of the product were very broad with peak positions at 3200 and 1650 cm^{-1}. The sharp absorption of C=C bonds at 1650 cm^{-1} in IR spectra of the reactant AA–MAA solid solution disappeared during the reaction. The X-ray diffraction patterns of the product showed an

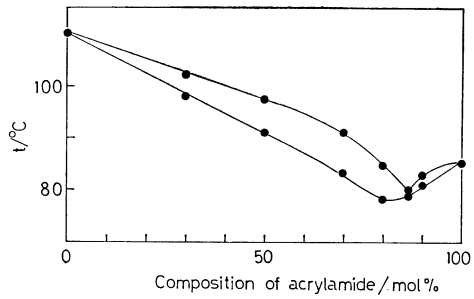

Fig. 1. Binary system phase diagram of acrylamide–methacrylamide.
Upper curve: solidus, lower curve: liquidus.

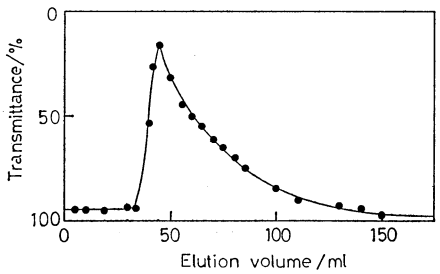

Fig. 2. Molecular weight distribution of the product of AA–MAA solid solution.

amorphous state. The product did not show a definite melting point. In addition, the physical properties of the methanol soluble fraction of the product was the same as the original AA–MAA solid solution. The gel-permeation chromatographic curve showed a single peak as shown in Fig. 2, and its molecular weight was determined as 15000.

Assuming that the ESR data measured immediately after the experiment belong to the growing polymer radical, the molecular weight of the product can be estimated of the order of 10^4 from the following equation if two radicals exist in one polymer chain.

$$(2mNC/n)/m = [R],$$

where m mol of sample, N Avogadro number, C conversion, n the degree of polymerization, and [R] is the radical concentration. The value is similar in magnitude to the chromatographic value.

Table 1. Half widths of X-ray diffraction patterns of various samples

	Acrylamide			
2θ / °	12.0—12.1	19.4	24.1—24.2	28.6—28.7
Half width / °	0.50	0.63	0.62	0.53
	Methacrylamide			
2θ / °	10.8	21.6	23.8	26.4
Half width / °	0.65	0.72	0.75	0.46
	AA–MAA solid solution			
2θ / °	11.8	19.2	23.7	28.2
Half width / °	0.66	0.78	0.75	0.75

Table 1 shows the half widths of the X-ray diffraction patterns of acrylamide,[1] methacrylamide,[2] and AA–MAA solid solution, respectively. The half width of the X-ray diffraction pattern closely relates to the stability of the crystal structure. It seems from Table 1 that the AA–MAA solid solution has a more unstable crystal structure than the others.

The crystal instability or the mechanical weakness of AA–MAA solid solution also appears in Fig. 3, which shows the relation between the conversion and the shearing degree at 5, 10, and 15 kbar (1 kbar= 10^8 Pa) static pressures. The conversion rapidly increased at an earlier shearing stage than those of acrylamide and methacrylamide alone reported in the previous paper.[1,2] The shearing curve at 10 kbar of the congruent solid solution(a) was compared with that of the corresponding (87 mol%AA–13 mol% MAA) mixture(b) as shown in Fig. 4. Although the shearing stress generated in the solid solution was slightly larger than that in the corresponding mixture at an earlier stage of the shearing, the difference gradually increased as the shearing proceeded. The reason for this can be explained by the shear reaction proceeding more actively owing to the instability of the crystal structure of the solid solution. AA–MAA solid solution was not reached 100% conversion even at about 2π rad shearing for the same reason of methacrylamide.[2]

The terminal of this copolymer is an acrylamide radical, because the typical ESR spectrum of the sheared sample is the same as that of acrylamide. No other signals were identified under our experimental conditions. The radical concentrations of the sheared sample at 10 kbar are listed in Table 2 together with the values of the corresponding monomers. Those of AA–MAA solid solution at various shearing degree

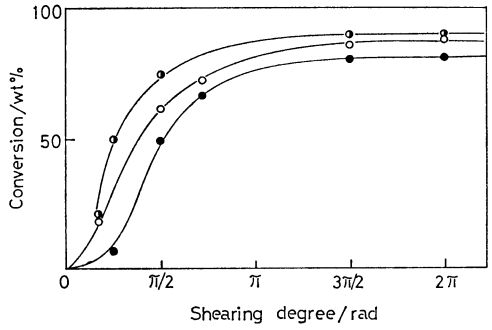

Fig. 3. Relation between conversion and shearing degree at various static pressures for 87AA–13MAA solid solution.
●: 5 kbar, ○: 10 kbar, ◑: 15 kbar.

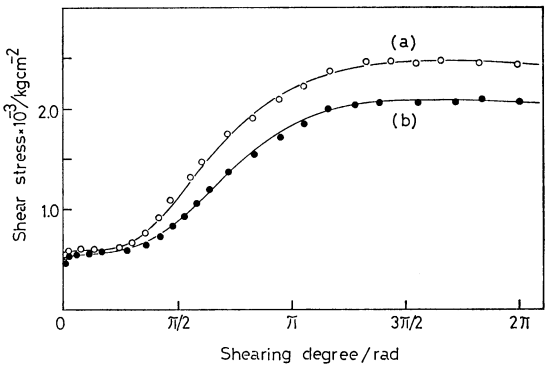

Fig. 4. Shearing curve at 10 kbar for 87AA–13MAA solid solution(a) and 87AA–13MAA mixture(b).

Table 2. Concentrations of free radical generated in sample layer of various samples

P / kbar	Shearing degree / rad	Shearing degree / °	Free radical/spin g^{-1} Acrylamide[1]	Methacrylamide[2]	AA-MAA solid solution
10	2.27	130	1.29×10^{18}	0.98×10^{18}	9.02×10^{18}
10	3.14	180		1.39×10^{18}	10.7×10^{18}
10	4.71	270	4.25×10^{18}	3.39×10^{18}	12.1×10^{18}

are apparently larger than any other. These facts also suggest the relatively low mechanical stability of the original solid solution.

Reaction of Acrylamide–Propionamide Solid Solution. The crystal structure of propionamide was investigated by Fadner and Morawetz,[3] who described it as monoclinic and the dimensions of the unit cell a_0=9.74 Å, b_0=5.74 Å, c_0=9.02 Å, β=113.5°. The unit cell of acrylamide is characterized by a_0=9.69 Å, b_0=5.77 Å, c_0=8.36 Å, β=118°.[7] Therefore acrylamide and propionamide are isomorphous. The mixture of 90 mol% acrylamide–10 mol% propionamide is mainly used as an experimental sample, and 50 mol% acrylamide–50 mol% propionamide and 10 mol% acrylamide–90 mol% propionamide are used for the comparison. Each sample is abbreviated as 90AA–10PA, 50AA–50PA, and 10AA–90PA solid solutions.

A homopolymer was obtained by the reaction of 90AA–10PA solid solution, while the AA–MAA solid solution was copolymerized under the same conditions. The reactive sites of this solid solution are to be polyacrylamide from the following experimental evidence. In the first place, IR spectra of the product were very broad at 1620 cm^{-1}. The sharp absorption of C=C vibration region of 90AA–10PA solid solution has disappeared. Therefore, it is concluded that the C=C bonds of acrylamide were ruptured through this reaction. Secondly, the pattern of the ESR signal of the sheared sample at high pressures was identical with that of polyacrylamide. This fact suggests that the reaction was initiated by the rupture of C=C bonds in acrylamide, in other word, the mechanochemical reaction of this solid solution proceeds only in the acrylamide area by a free radical mechanism, and the propionamide did not participate to the reaction as a reactive monomer.

Figures 5 and 6 show the relations between the conversion and the shearing degree at 5, 10, and 15 kbar static pressures for 90AA–10PA solid solution and for 50AA–50PA solid solution. Figure 6 also shows the range of data because the conversion of this solid solution was fairly low under these experimental conditions. It may be noted that no difference of the conversion with the pressure appear in the latter case. These relations show the S-type curve as well as acrylamide and AA–MAA solid solution. However the values of the conversion of 90AA–10PA and 50AA–50PA solid solutions are respectively smaller and much

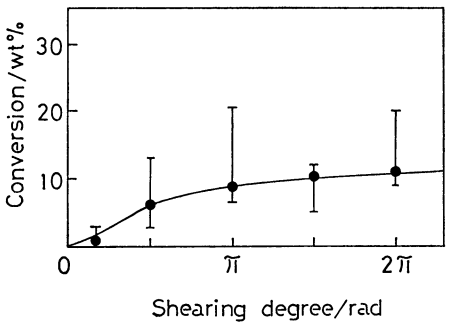

Fig. 6. Relation between conversion and shearing degree for 50AA–50PA solid solution.

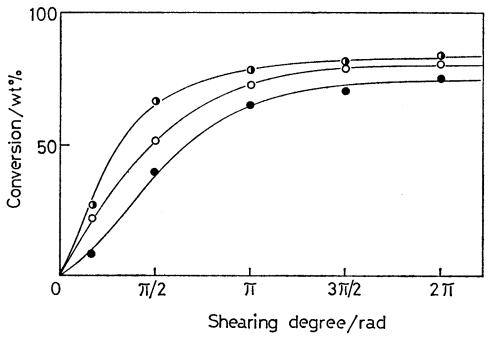

Fig. 5. Relation between conversion and shearing degree at various static pressures for 90AA–10PA solid solution.
●: 5 kbar, ○: 10 kbar, ◐: 15 kbar.

Table 3. Molecular weight of the product polymer of 90AA–10PA

P / kbar	Shearing degree/rad			
	π/2	π	3π/2	2π
5	51900	13200	11800	
10	55600	12800	10600	10200
15	26000	12600	8600	

smaller than those of acrylamide[1] and AA–MAA solid solution. These results suggest that propionamide in solid solutions may act as a surprisingly efficient chain transfer agent, that is, a retarder. This assumption is consistent with the experimental results on γ-ray radiation polymerization of AA–PA solid solution reported by Fadner *et al.*[3] It can be seen that propionamide with the active N–H bond reacts with the propagating radicals, and the degradative chain transfer reaction occurs in the reaction system.

Table 3 shows the viscosity-average molecular weight of produced polymer at 5, 10, and 15 kbar at different shearing degrees. The molecular weight of the polymer obtained by HP+SSD was much lower than those of the polymer obtained by the same technique from acrylamide alone.[1] The shorter polymer chain length presents a clear evidence supporting that propionamide may act as a chain transfer agent (a retarder) in solid solutions as just suggested in Figs. 5 and 6. This table also suggests that this polymer degrades, judging from the molecular weight reduction, with the increase in the shearing degree. Consequently, the same conclusion is derived from the above facts as for acrylamide alone.[1]

The Mechanochemical Behaviors of Both Solid Solutions. The shearing stress reflects both on the conversion (polymer production) and on the stability of the crystal structure. In view of many experimental data, at the early stage of the reaction the shearing stress reflects on the stability of the crystal structure, and at the later stage it does on the conversion. The shearing stresses of both solid solutions were nearly equal at the early shearing degree; later the shearing stress of the AA–MAA solid solution was larger than that of the 90AA–10PA solid solution. It can also be concluded from the above experimental result on

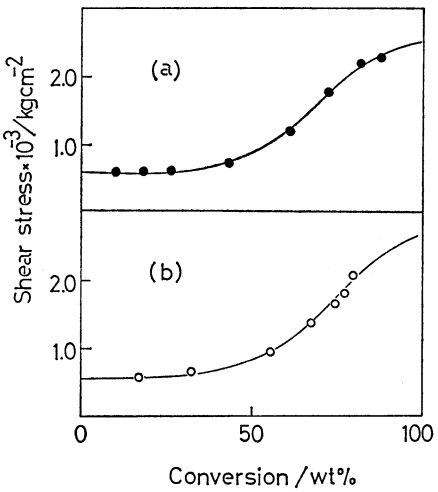

Fig. 7. Relations between shear stress and conversion for AA–MAA(a) and 90AA–10PA(b) solid solutions.

the mechanical behavior that the crystal stability of both solid solutions are similar, and that the conversion of AA–MAA solid solution into copolymer is larger than that of 90AA–10PA solid solution into polymer.

Figure 7 shows the relation between the shearing stress and the conversions of AA–MAA(a) and 90AA–10PA(b) solid solutions.

Some physical properties of two-phase material, k, in which one phase is dispersed randomly in another, can be well-known expressed[8,9] as the corresponding volume fraction, f.

$$k = k_c \frac{1+2f_d\dfrac{1-k_c/k_d}{2k_c/k_d+1}}{1-f_d\dfrac{1-k_c/k_d}{2k_c/k_d+1}} \qquad (1)$$

In this equation the subscripts c and d refer to the continuous phase and to the dispersed phase respectively. This equation is plotted in Fig. 8 for two examples of $k_c/k_d=10$ and $k_d/k_c=10$. As the conversion corresponds to volume fraction of the polymer material in our experiment, measurements should appear between the two curves as a dashed line. The experimental results showed the same relation between the conversion and the shearing stress. It can be concluded, therefore, that the shearing strength of the polymer-monomer composite, τ, may be expressed by the similar equation (2).

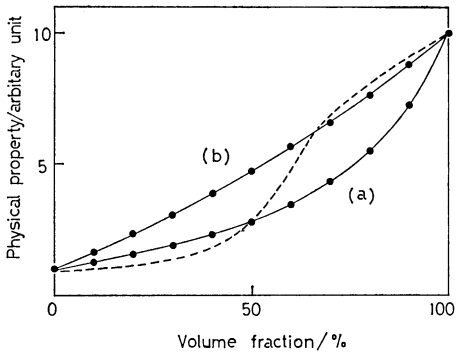

Fig. 8. Plot of Eq. 1.
(a): $k_c/k_d=10$, (b): $k_d/k_c=10$. Dashed line: The curve corresponding to the experimental results. Refer to Fig. 7.

$$\tau = \tau_M \frac{1+2f_d\dfrac{1-\tau_M/\tau_P}{2\tau_M/\tau_P+1}}{1-f_d\dfrac{1-\tau_M/\tau_P}{2\tau_M/\tau_P+1}} \qquad (2)$$

Here the subscripts P and M refer to the polymer and the monomer, respectively, and f_d can be substituted by the conversion into polymer in this case.

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