Mechanochemical Reactions at High Pressures. I. The Design and Construction of the Apparatus and Preliminary Experiments

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An apparatus for investigating mechanochemical reactions at high pressures of up to 50 kbar and preliminary experiments on acrylamide are described. The essentials of the apparatus are a rotating platen inserted in a Bridgman-type opposed-anvil press. The central platen is rotated by the force of an electric motor or by manual strokes under high pressure. The pressure distribution on the anvil surface was evaluated from the changes in the electric resistances of CdSe and CdTe as calibrants. The pressure observed at the center was 4.5 times the nominal load pressure. The phase-transition pressure of naphthalene was identified as about 25 kbar from the measurement of the pressure effect on the shearing strength. The mechanochemical behavior of acrylamide 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 confirmed that the reaction products were amorphous polyacrylamides and that the mechanical shear stress on the conversion of acrylamide to a polymer was exceedingly effective in comparison with static pressure.

The terms "mechanochemistry" and "mechanochemical reaction" have recently been used to designate chemical behavior caused by mechanical energy. Although mechanochemistry is an ambiguous research field at present, the knowledge of mechanochemistry has been widely extended and rapidly advanced in connection with the structure, chemical properties, and reactivity of a solid, *etc.* Thus, the interest in mechanochemistry extends over a wide range of scientific and technical disciplines.

Mechanochemical reactions at high pressures are significant in two important ways.

First, we consider that a strong mechanochemical force on substances, especially on organic materials, can be easily applied at high pressures. Mechanochemical reactions are generally not so appreciable as thermochemical or photochemical reactions. Therefore, a very sensitive detector is required to follow the reaction. The application of pressures makes detection by usual instruments possible.

Second, some shear stress is unavoidable when solid materials are compressed. In other words, solid-phase reactions under high pressures are somewhat or mostly mechanochemical changes.

These experiments were initiated to study the mechanochemical reactions of organic compounds from the above two points of view by means of a self-made high-pressure apparatus which is capable of loading the mechanical force simultaneously.

This unique technique was discovered by Bridgman. However, previous investigations by using this technique have dealt almost exclusively with phase-transitions, except for the group in communist countries. Recently investigations of the organic reaction under high pressures with mechanochemical shear force have been mainly done by Russian scientists, and it seems likely that they each belong to one of two groups. The first is Enikolopyan's group in the Chemical Physics Institute of Academy Sciences USSR. The mechanochemical behavior of many organic compounds has been investigated under high pressure by his group.[1-10] The second, Gonikberg-Zhulin's group in the Zelinskii Organic Chemistry Institute of Academy Sciences USSR, was also studied the organic reactions[11-18] from the same standpoint.

Our series of studies was initiated in order to synthesize new materials by means of solid-phase organic reactions under extreme conditions and in order to investigate the mechanochemical effect, which is unavoidable in solid-phase reactions under high pressures. The present paper will describe the design and the technique of the apparatus for the mechanochemical reactions and will present some preliminary experimental results on the reaction of acrylamide.

Design and Construction of the Apparatus

Despite the great interest in high-pressure studies, very little fundamental work has been reported on the design of high-pressure units (anvils). The development of this apparatus has, therefore, been based mainly on empirical experience gained through use. In the selection of an optimum design for the apparatus, questions regarding the ratio of the diameter of the sample face to that of the body of the anvil, or of the angle of the cone, could not be answered by recourse to the results of systematic studies. It should be emphasized, however, that economical considerations are among the most important factors. The diameter of the anvil surface of 12-mm determined the minimum sample quantity (≈10-mg) required to follow the mechanochemical reaction. (A 5-mm anvil was used in a special case).

The essentials of the apparatus are a flat metal plate (central platen), inserted between Bridgman-type opposed-anvils for pressuring and shearing, and a copper jacket for controlling the temperature. Enlarged views of the anvils, central platen, and sample assemblies are shown in Fig. 1. Two powdered or crystal samples, 1, between the mating surface of three cobalt-cemented

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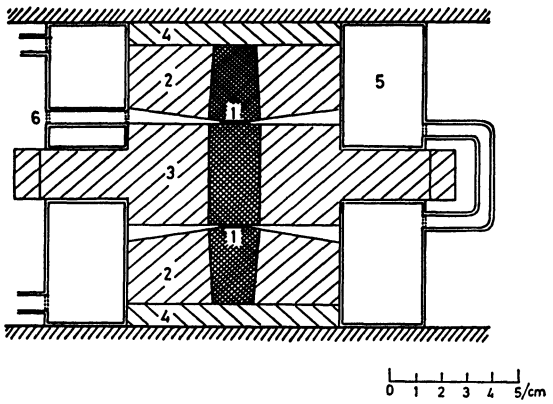

Fig. 1. Schematic diagram of anvil assembly.

tungsten carbides are compressed up to the desired pressure. The tungsten carbide conical cylinders of the opposed-anvils are 20-mm and 17-mm in diameter by 30-mm long and are supported by steel jacket shrunk around them. Both anvils, 2, are ground as truncated cones with 12-mm-diameter flats and a cone half-angle of 85°. The central platen, 3, is pinned into the hub of a 165-mm diameter spur gear. Two flat disks, 4, are attached to the top and bottom of the opposed-anvils. All the parts are surrounded by a pair of copper jackets, 5, through which thermostated water is circulated to keep the temperature constant throughout the experimental period. In order to fit a thermometer for the measurement of the temperature, a narrow hole, 6, is made in the copper jacket. A surface-type thermister thermometer is used to measure the temperature of the anvil surface near the sample region.

The load is applied to these anvils by means of a 50-t hydraulic-ram as the load unit. A pressure of up to 50 kbar (1 kbar$=10^8$ Pa) can be generated between them. During the compression, some of the sample extrudes from between the anvil faces until an equilibrium thickness is attained. Torque was applied to the gear holding the central platen by means of a mechanical drive forcing it to rotate about the common axis at various speeds with respect to the opposed-anvils. A torque can be generated by two different methods. One is the use of a continuous slow rotation in one direction of the central platen against the other by using an electric motor and various gear combinations. In our apparatus, shearing stresses are applied to the sample by rotating the central platen about its vertical axis through a maximum of 2.5° in 60 s. The other method is the use of a manual stroke. Mechanical driving is also given by the movement of the rack connected with the spur gear by means of another 10-t hydraulic-ram, serving as the shear unit instead of an electric motor. In this case, we can calculate the shear stress, τ, by the use of the following equations by assuming a constant value of shear stress across the radius, r:

$$M=\int_0^{r'}\tau r 2\pi r\cdot \mathrm{d}_r \text{ or } \tau = 3M/2\pi(r')^3 = 3PSR/2\pi(r')^3, \quad (1)$$

where M represents the torque; r', the effective radius of the anvils; P, the pressure produced in the 10-t hydraulic-ram to rotate the central platen; S, the surface area of the piston in the hydraulic-ram used as the shear unit, and R, the radius of the spur gear.

Under the conditions of our experiments, heating due to friction is negligible.

Pressure Distribution

Since the pressure at the center of the sample area in the opposed-anvil press is not equal to the applied pressure or to some predictable function of the applied pressure, it is necessary to use various internal standards (fixed points) for determining the actual pressure. We tried to measure the internal (true) pressure on the anvil surface without mechanical shear force by using acrylamide tablet as a model organic sample and cadmium selenide (CdSe) and cadmium telluride (CdTe) as the pressure-standard substances. CdSe and CdTe sharply change in their electrical resistances at 25 and 33 kbar respectively.[19]

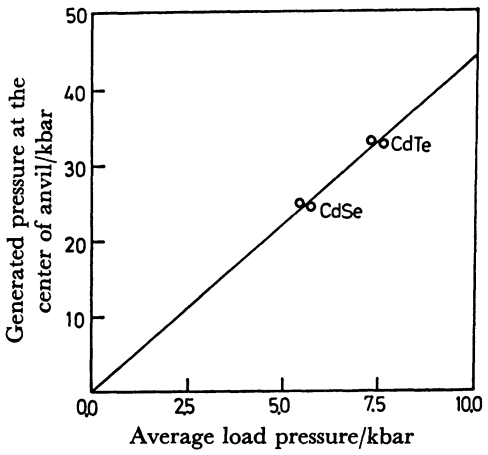

Fig. 2. Generated pressure at the center of anvil by measuring phase transitions of CdSe and CdTe.

Figure 2 shows the pressure at the center of the sample at various load pressures, which are detected by means of the changes in the electrical resistances of CdSe and CdTe. The internal pressure at the center is about 4.5 times larger than the average load pressure, and the two pressures are correlated by a single straight line through the original point. It has been concluded that the "pressure-multiplication effect" is independent of the press force in our pressure range.

Figure 3 shows the pressure distribution on the anvil surface. In this experiment, the semi-conducting materials used were placed in a certain position in the acrylamide tablet.

It can be readily shown that the press force on the anvil surface is expressed by the following formulas:

The force on the sample side, F_{ss}, is:

$$F_{ss}=\int 2\pi r\cdot P(r)\cdot \mathrm{d}r. \quad (2)$$

The force on the hydraulic-ram side, F_{rs} is:

$$F_{rs}=S_2P_{obsd}, \quad (3)$$

where r represents the radius of the anvil surface on the sample side; $S_1(=\pi r^2)$, S_2, the surface areas of the

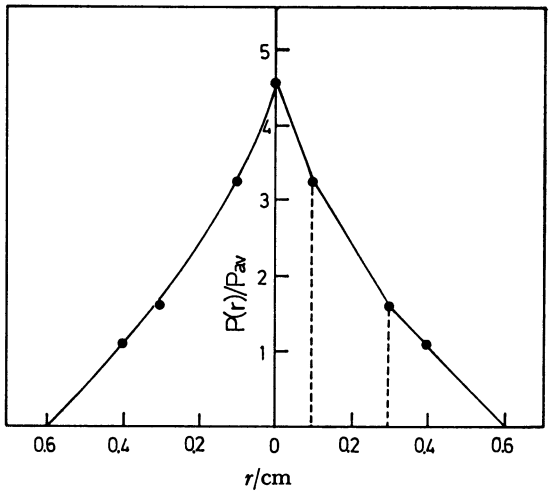

Fig. 3. Pressure distribution on anvil face.

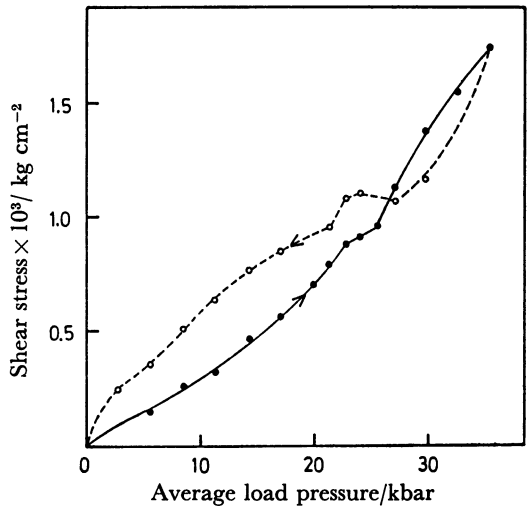

Fig. 4. Shearing curve for naphthalene by using anvil of 5 mm diameter.

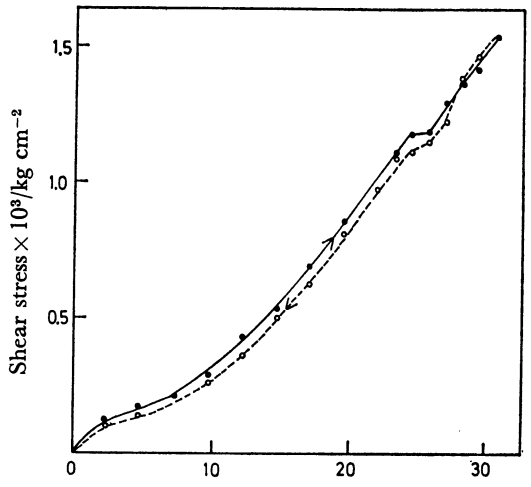

Fig. 5. Shearing curve for naphthalene by using anvil of 12 mm diameter.

anvils on the sample side and the hydraulic-ram side respectively; and P_{obsd}, the pressure as measured by means of a pressure gauge installed at the hydraulic-ram as the load unit. Moreover, one function, $P(r)$, is the pressure distribution on the anvil surface.

Theoretically

$$F_{ss} = F_{rs} = \int 2\pi r \cdot P(r) \cdot dr = S_2 P_{obsd}. \quad (4)$$

Instead of P_{obs}, the average load pressure on the anvil surface, P_{av}, as defined by Eq. 4, we obtain:

$$P_{av} = P_{obsd}(S_2/S_1) \quad (5)$$

$$\int 2\pi r \cdot P(r) \cdot dr / P_{av} S_1 = 1. \quad (6)$$

Since $S_2/S_1 = 62.7$ and $r = 6$-mm in our apparatus, the calculation of Eq. 6 gives $1.294/1.131 = 1.14 \fallingdotseq 1$, where it has been assumed that the pressure distribution, $P(r)$, is a linear function in the three divided regions, as is shown on the right-hand side of Eq. 3. Therefore, the value of P_{av} defined by Eq. 5 has been used as a pressure parameter in the foregoing discussion unless otherwise stated.

The distribution of pressure in the compressed material is evidently complicated when the mechanical shearing stress is loaded (that is, the central platen is rotated). At present, it is impossible to measure directly the distribution of pressure in that case. Although there is, therefore, no definite evidence, it seems reasonable to assume from the following considerations that the pressure distribution becomes uniform as a result of the plastic flow.

In general, the mechanical strengths of the organic substances are dependent on their modifications, which, of course, have different crystal structures; therefore, the curve of the shearing strength should change on passing from one modification to the other.

We have also tried to investigate the effect of the pressure on the shearing strength of naphthalene; some typical shearing curves are shown in Figs. 4 and 5. In this experiment we undertook to squeeze a purified single crystal of naphthalene in the direction of the c-axis and to rotate the central platen by 1 rad/h (1°/min) at room temperature by means of a manual stroke. The shear stress applied to the sample was calculated from Eq. 1 by assuming $r' = r$.

The curves exhibited a characteristic variation at

Table 1. Transition pressure and shear force of naphthalene

	Anvil diameter / mm	Pressure / kbar	Shear force / kg cm^{-2}
Experimental values	12	25[a)]	1.1—1.2×10^3
	12	30	1.5×10^3
	5	23—27[a)]	0.9—1.1×10^3
	5	30	1.35×10^3
Literature values			
Bridgman[20)]	5	25—30[a)]	
	5	50	4.2×10^3
Gonikberg[10)]	4.8	25—27[a)]	2.0—2.3×10^3
Enikolopyan[4)]	4, 5, 10	30	1.3×10^3

a) Transition pressure.

about 25 kbar, which corresponds to the phase-transition of naphthalene. The results of such measurements are summarized in Table 1, together with the literature values.

Under ideal conditions such a transition should be accompanied by a sharp discontinuity in the shearing force itself, but because the pressure is not perfectly uniform over the anvil surface, the transition is spread over the interval of the mean pressure. With simultaneous mechanical deformation, the pressure distribution on the anvil surface would not be so sharp as in Fig. 3. It can be seen that the mechanical shear force induces a flattening of the distribution curve and that the distribution approaches a uniform state by its plastic flow if the rotation of the central platen is appropriate. Considering that our finding agree with the literature value, regardless of the anvil size, it seems reasonable to conclude that the pressure distribution in the organic sample on the anvil surface is almost uniform when mechanical shear force is applied. Therefore, nominal load pressures, as evaluated from Eq. 5, are defined as the operative and the effective pressures.

The above discussions are based on the results for acrylamide and naphthalene. However, it is probable that many organic compounds show the same behavior.

Reaction of Acrylamide

Experimental. Acrylamides were allowed to react at a high pressure (HP) combined with simultaneous shear deformation (SSD). The apparatus described in the preceding chapter will be abbreviated below as HP+SSD. In this experiment, the reactions proceeded at the constant shearing velocity (the rotation speed of the central platen) of 2.51 rad/h (2.4°/min) at room temperature unless otherwise stated. Therefore, 1 h of reaction time corresponds to a rotation angle of the central platen of 300°.

A commercial sample of acrylamide was purified by repeated crystallizations from a benzene solution and was finally vacuum-dried at room temperature for over 24 h. The purity of this acrylamide was proved by its melting point to be 84.5—85.0 °C.

A sample tablet was obtained from the purified acrylamide powder by preforming in a N_2 stream. The preforming pressure was about 5 kbar. The sample tablet was placed into the HP+SSD apparatus, and the experiment was carried out at the desired pressure.

The ESR data were obtained by rapidly inserting the sample into the ESR cavity immediately after the HP+SSD experiment. 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.

A sample sheared at a high pressure was extracted from a large amount of methanol for separating into soluble and insoluble fractions. The insoluble fraction was dried *in vacuo* at room temperature to a constant weight, and the conversion was determined. The identification of the product took place by means of measurements of the melting point, the IR spectrum, the X-ray diffraction pattern, and the intrinsic viscosity.

The molecular weight of the product (polyacrylamide, as will be described below) was determined, by means of the following relations, from the viscosity data obtained from the Ubbelohde viscometer at 25 °C:[21]

$$[\eta]_{25}^{H_2O} = 3.73 \times 10^{-4} M_v^{0.66}$$

$$[\eta]_{25}^{H_2O} = 4.65 \times 10^{-4} M_n^{0.64}.$$

Results and Discussion. Judging from the following experimental evidence, acrylamide was clearly polymerized under conditions of HP+SSD. First of all, the product did not show a definite melting point. Secondly, the IR spectra of the product were the same as those of commercial polyacrylamide, while the IR spectra of the dissolved fraction in methanol were identical with those of the acrylamide monomer. Thirdly, when the X-ray diffraction patterns of the acrylamide monomer were compared with those of the product, the product was shown to be in an amorphous state. Therefore, we concluded that the product of this reaction was amorphous polyacrylamide.

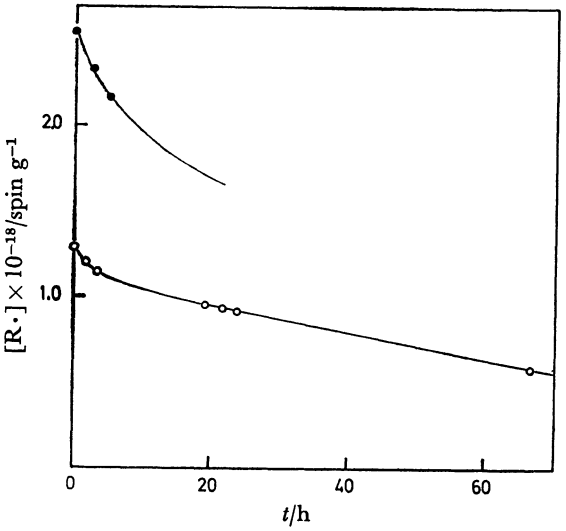

Fig. 6. Time dependence of radical concentrations at room temperature.
● 5 kbar, 4.54 rad; ○ 10 kbar, 2.27 rad.

The curve of the ESR signal yields a resolved three-peak system, about 64 G wide, with the central peak twice the height of the outer ones. No other signals could be identified under our experimental conditions. Such a signal corresponded well to that of the growing polyacrylamide radical reported by Alder and his collaborators.[22] Evidently, therefore, the reaction of acrylamide under the conditions of HP+SSD is a free-radical polymerization or depolymerization; in other words, the mechanochemical reaction of acrylamide proceeds *via* a free-radical mechanism. Figure 6 shows its time-dependence at room temperature. The resulting radicals are fairly stable for a long period. Morawetz and Fadner[23] have reported that the radical concentration obtained by γ-ray irradiation in the solid state was reduced to 67% after 60 h at 25 °C. We concluded, from our similar results shown in Fig. 6,

that the strain in the sheared sample disappears for periods up to several hours after the mechanical stress or static pressure is removed.

It is instructive to compare the experimental data with the time-dependence of the expected radical decay. If bimolecular radical termination is assumed,

$$-\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t = k_2[\mathrm{R}\cdot]^2. \quad (7)$$

This leads to a radical decay of the form:

$$k_2 t = 1/[\mathrm{R}\cdot] - 1/[\mathrm{R}\cdot]_0, \quad (8)$$

and if unimolecular spontaneous termination is assumed,

$$-\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t = k_1[\mathrm{R}\cdot]. \quad (9)$$

This leads to a radical decay of the other form:

$$k_1 t = \ln[\mathrm{R}\cdot]_0/[\mathrm{R}\cdot]. \quad (10)$$

The experimental data obtained are plotted in Figs. 7 and 8 as suggested by Eqs. 8 and 10. The initial parts of the time-dependence curves were satisfactorily expressed by Eq. 8, and the rate constants, k_2, were evaluated from the slopes of the straight line as 2.97×10^{-20} g spin^{-1} h^{-1} for the radicals generated at 10 kbar and as 1.47×10^{-20} g spin^{-1} h^{-1} for those generated at 5 kbar.

However, the hypothesis of chain termination by mutual recombination can be ruled out over the whole experimental range. Equation 10 is apparently verified in the range, as is shown in Fig. 8. Therefore, the hypothesis of a first-order termination of the chains,

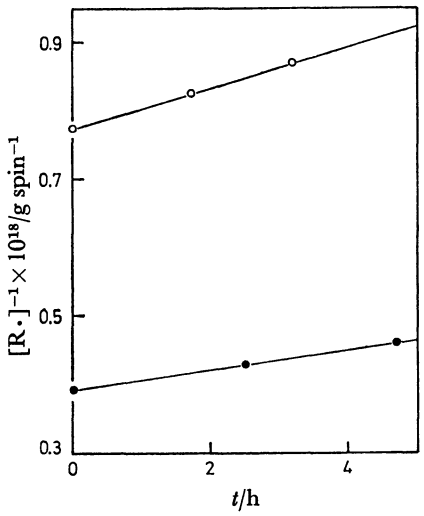

Fig. 7. Reciprocal of free radical concentration as a function of time.
● 5 kbar, 4.54 rad; ○ 10 kbar, 2.27 rad.

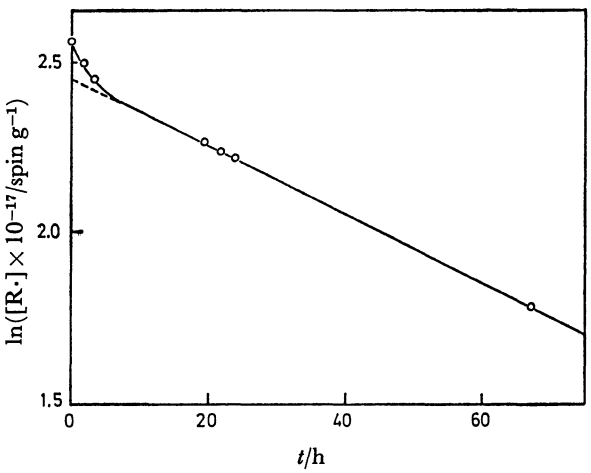

Fig. 8. Logarithm of free radical concentration as a function of time.
(Generated at 10 kbar and 2.27 rad)

deactivated by steric hindrance or by the fact that the free-radical site is "bogged down" in the mass of the polymer formed, is generally applicable.

The conversion of acrylamide to polymer was negligible without the application of mechanical shear force.

Figure 9 shows the relation between the conversion and the shearing degree at 5, 10, and 15 kbar pressures. The relation between the shearing degree and the

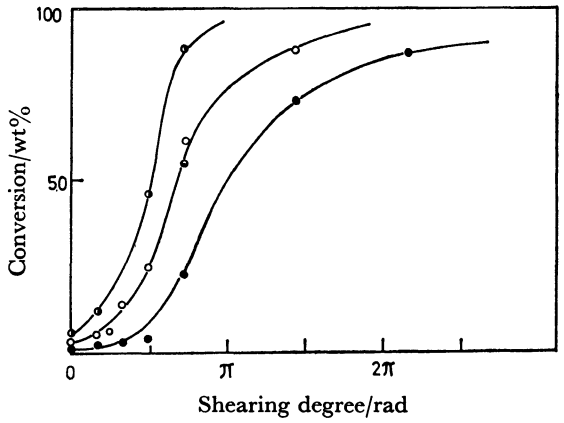

Fig. 9. Relation between conversion and shearing degree at various static pressures.
● 5 kbar; ○ kbar; ◑ 15 kbar; ◒ at different (twice) shearing speed.

Table 2. Molecular weight of the product polymer and the number of polymer molecules and free radicals in a gram of the sheared sample

Pressure / kbar	Shearing / rad	Degree / °	M_v viscosity-average	M_n number-average	Polyacrylamine / molecule g^{-1}	Free radical / spin g^{-1}
5	2.27	130	175000	180000	7.62×10^{17}	2.66×10^{17}
5	4.54	260	59000	59000	7.64×10^{18}	2.56×10^{18}
5	6.81	390	61000	61000		
10	2.27	130	132000	135000	2.77×10^{18}	1.29×10^{18}
10	4.54	260	68000	68000	7.50×10^{18}	4.25×10^{18}
15	2.27	130	67000	62000		

conversion showed a *S*-type curve and was somewhat analogous to a typical solid-phase reaction. Furthermore, the shearing velocities were independent of the conversion in our experimental region.

Table 2 shows the molecular weight of polyacrylamide as obtained by HP+SSD, together with the concentrations of the polymer and of the radical in sample layer, as evaluated from the M_n and ESR data. The molecular weight of the polymer obtained by HP+SSD was considerably lower than those of the polyacrylamides obtained commercially and by radiation-induced solid-phase polymerization.[21] The order of concentration of the polymer was, however, the same as that of the radicals in the sample layer. These facts suggest that the radicals identified by ESR are almost all reacting polymer radicals, as in the preceding discussions. This table also suggests that polyacrylamide degrades at a later stage of the HP+SSD reaction, judging from the facts that the molecular weight becomes much lower with the increase in the shearing degree. It can be roughly concluded from this table that the mechanochemical degradation of polyacrylamide affects this type of reaction in the range of large shear deformations.

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