HIGH PRESSURE AND HIGH TEMPERATURE REACTIONS IN THE ORGANIC SOLID STATE

Polymerization of Nitriles

By Kimihiko Hara

Under the extreme conditions at high pressures up to 50 kbar and high temperatures up to about 300°C, dinitriles, such as malononitrile and succinonitrile, are polymerized to give long chain C, N conjugated polymers with the backbone structure: $(-\overset{|}{C}=N-)_x$. It is shown that high pressure is necessary in conjunction with high temperature to achieve the polymerization. The minimum pressure and temperature to cause the reaction for malononitrile and succinonitrile are 20 kbar, 160°C and 25 kbar, 200°C, respectively. The product polymers are heat-resistant and soluble only in dimethylformamide and exhibit semiconducting properties. The mechanism of the reaction can be considered in comparison with the thermal reactions of polyacrylonitrile. The reaction rates were measured.

On the other hand, aromatic dinitriles, such as isophthalonitrile and terephthalonitrile, are polymerized only in the presence of HPO_3 as catalyst at 40 kbar and 450°C.

The thermal reactions of polyacrylonitrile and polymethacrylonitrile, accompanying the polymerization of cyanide groups, were carried out under such extreme conditions. The naphthyridine type product obtained from polyacrylonitrile under high pressure has higher density, which is ascribable to the formation of a crosslinking network structure. The reaction mechanisms of the lower temperature reaction and the higher temperature reaction of polyacrylonitrile under high pressure were studied. In the case of polymethacrylonitrile, the analogous reaction proceeds only slightly even at 300°C under 30 kbar.

By investigating the effect of water on these reations it was found that the polymerization of dinitriles is accelerated and that polyacrylonitrile and polymethacrylonitrile are easily hydrolyzed to give corresponding polyamides.

Introduction

In the past few years there has been considerable interest in the preparation of thermally stable polymer materials with conjugated double bonds containing nitrogen atoms in the chain. It was found in this experiment that under high pressures up to 50 kbar and high temperatures up to about 450°C, a special series of organic compounds is polymerized in the solid state without any catalyst. They are

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dinitriles, such as malononitrile and succinonitrile, whose cyanide groups are polymerized to give a well-developed conjugated system of carbon and nitrogen, *i. e.* polymers with the backbone structure : (−C

R

=N−)$_n$, where R is H or a substituent.   The starting object of this experiment was just to obtain the polynitriles which have semiconducting properties by the application of high pressure to nitriles.

As for aromatic mononitriles, the reaction under high pressure and high temperature has been reported to give the corresponding trimer, *s*-triazine[1].
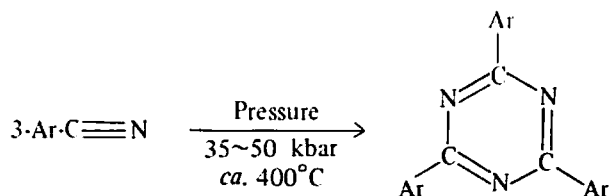
The facilitation of this reaction by the application of pressure has been explained simply as the decrease of the difference in volume between the initial and the transition state.

Under atmospheric pressure, mononitriles, such as benzonitrile, capronitrile and propionitrile, were polymerized in the liquid state by forming stoichiometric complexes with some metal halides to give a long chain polymer[2].

Sosin, Korshak, Vasnev and Baranov[3] reported that a highly heat-resistant polymer was prepared from malononitrile by the treatment with *tert*-butyl peroxide at 200°C in the liquid state under atmospheric pressure.

The thermal reactions of polyacrylonitrile, which can be interpreted as a polymerization of cyanide groups just like those of dinitriles and which produce a naphthyridine-type compound in the solid state, have been widely studied under atmospheric pressure since the original study of Houtz[4]. The various thermally stable products which show semiconductive properties are obtainable in various reaction conditions.

As for the effect of pressure on the electrical resistance of these substances, which had been reported previously[5], the remarkable decrease has been observed, which is attributed to the increasing amount of mobile π-electron overlap and/or the contribution of free radicals.

Recently, the investigation of thermally stable polymer has become active and under atmospheric pressure there are several papers even concerning the mechanism of this reaction[6], but there still remain considerable uncertainties in the reported details.

1) I. S. Bengelsdorf, *J. Am. Chem. Soc.*, **80**, 1442 (1958)
2) V. A. Kabanov, V. P. Zubov, V. P. Kovaleva and V. A. Kargin, *J. Polymer Sci.*, **C4**, 1009 (1963)
3) S. L. Sosin, V. V. Korshak, V. A. Vasnev and Ye. L. Baranov, *Akad. Nauk SSSR, Izv. Oldeleniye Khim. Nauk*, 1644 (1962)
4) R. Houtz, *J. Textile Res.*, **20**, 786 (1950)
5) J. Osugi and K. Hara, *This Journal*, **36**, 20 (1966)
6) J. N. Hay, *J. Polymer Sci.* Part A-1, **6**, 2127 (1968)

By the application of high pressure to organic reactions in the solid state, the expected effects are as follows : i) Melting and decomposition of organic compounds are remarkably suppressed[7]. Organic substance that normally deteriorates near 100°C will withstand 400°C at a pressure of 70 kbar. This makes it possible to introduce the thermal energy necessary to accomplish a desired reaction without decomposing a sensitive material. ii) Compression decreases the distance of reacting sites and makes it shorter enough to cause the reaction. It is said that there is a critical distance to commence the various types of polymerization in the solid state under atmospheric pressure, whose distance is reported to be 4 Å[8]. If this is the case, for the substance whose reacting sites are separated by more than this distance, compression will be the necessary condition to initiate the reaction. iii) Steric hindrance can be removed or lessened. For example, tetramethyl ethylene, which cannot be poly-merized according to conventional procedures because the methyl group hinders the linking of double bonds, forms a polymer at about 35 kbar and 350°C. In the reactions between pyromellitic dianhydride and diamines, a polymer from pyromellitic dianhydride and o-diaminobenzene has been obtained at about 6 kbar, 200°C[9], although several attempts in dimethylfolmamide solution have resulted in failure. Perhaps the steric hindrance present in an o-substituted polypyromellitamic acid is too large to permit the reaction in solution. iv) The reaction rate changes depending on the volume change of the reaction according to the equation, $d \ln k/dP = -\Delta V^*/RT$.   v) Molecular motion is restricted, so that it is impossible for molecules to diffuse over a long distance.

In spite of the above interesting aspects, only a few simple works are reported because of the various technical difficulties.

From these viewpoints, this paper describes a study of the thermal cyanide polymerizations of solid dinitriles, such as malononitrile, succinonitrile, isophthalonitrile and terephthalonitrile, under high pressure and high temperature, in order to investigate the following problems : 1) the structure and the properties of the product, 2) the fact that the reactions proceed really in the solid state under such extreme conditions, 3) the reaction mechanism and 4) the reaction rate.

In polyacrylonitrile a study of pressure effects of the mechanism and the kinetical treatment of a the lower-temperature ring formation reaction was made, in which crosslinking and coloration proceed with no volatiles due to the polymerization of cyanide groups, and the higher-temperature reaction with the evolution of volatiles and the production of thermally stable residue was also studied.

The possibility of the similar reaction in polymethacrylonitrile was investigated in order to examine the mechanism of the polymerization of cyanide groups.

Experimental

Materials

Malononitrile (MN) obtained from Nakarai Chemical Co. was recrystallized from ethanol solution

7)   L. Pan, T. N. Anderson and H. Eyring, *J. Phys. Chem.*, **71**, 2258 (1967)

8)   F. L. Hirshfeld and G. M. J. Schmidt, *J. Polymer Sci.*, Part A, 2, 2181 (1964)

9)   M. Prince and J. Hornyak, *Polymer Letters*, 4, 601 (1966)

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until its pale yellow vanished (mp. 29°C).

Succinonitrile (SN) obtained from Nakarai Chemical Co. was recrystallized twice from acetone solution (mp. 57°C).

Terephthalonitrile and isophthalonitrile which are commercial guaranteed reagents were used without further purification after drying in a vacuum.

Polyacrylonitrle (PAN) (Mn=38,000, $[\eta]$=4.53 at 35°C) obtained by emulsion polymerization (50°C, 2.5 hr) in N, N-dimethylformamide (DMF) was used. Elementary analysis: Observed, C: 68.03%, H: 5.87%, N: 26.15%. Calculated, C: 67.94%, H: 5.60%, N: 26.4%. The sample was fully dried in a desiccator under a reduced pressure.

Polymethacrylonitrile (PMAN) was obtained by polymerization in DMF solution with sulfuric acid as catalyst[10]. Elementary analysis: Observed, C: 70.29%, H: 7.64%, N: 20.83%. Calculated, C: 71.59%, H: 7.54%, N: 20.87%.

Polyacrylamide used as a reference sample was obtained from American Cyanide Co.. Polymethacrylamide sample was obtained by the polymerization in DMF solution with sulfuric acid as catalyst[10].

Apparatus and procedure

Hydrostatic pressures up to 50 kbar were generated in a compact cubic anvil device, whose pressure calibration techniques and other experimental methods are reported earlier in detail[11]. This apparatus was calibrated against some given fixed points, such as Bi(I-II), Ba(I-II), Tl(II-III) and Bi(III-V). The procedure is to determine the applied load versus cell pressure relation at the fixed points.

As a heat source, the cylindrical glassy carbon is served as the results of joul heat by the passage of high ac current through it. By this method, a stable and well-defined temperature was obtained. Temperature was monitored by a chromel-alumel thermocouple, whose lead wires are inserted through the gaps of anvils.

The calibration for the pressure dependence of emf of the thermocouple was not carried out, because the amount of change with pressure is rather small, $i. e.$ about 2°C for 100°C at 70 kbar[12].

Pyrophyllite ($Al_4 [Si_8O_{20}] (OH)_4$) was used as a solid pressure transmitting medium. In order to remove the water which affects the reaction, it was heat-treated at about 550°C for 5 hr just before its use.

Fig. 1 shows a schematic view of pyrophyllite sample cube used for reaction. The edges of the cube are 13 mm long. The sample of about 20 mg was enclosed in a teflon cupsule which is possible to be used up to about 450°C under 40 kbar and it was buried in the center of the pyrophyllite cube. When the desired pressure was reached, the electric current was passed through the furnace by means of opposing anvils and the reaction temperature was reached within 3 min. When the reaction had run for the desired length of time, the current was shut off and the temperature dropped to 30°C

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10) T. Moriyoshi, Unpublished data

11) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

12) H. M. Strong, "Modern Very High Pressure Techniques", p. 93, ed. by R. H. Wentorf, Butterworths, London (1962)
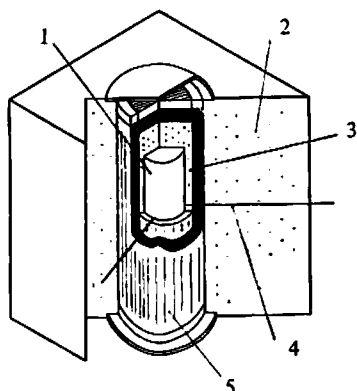
Fig. 1   Schematic view showing the internal construction of the pyrophyllite pressure transmitting cube for the compact cubic anvil apparatus
1: Sample
2: Pyrophyllite
3: Teflon or pyrophyllite sleeve
4: Thermocouple
5: Glassy carbon heater

within 1 min.

A sample cube for resistance measurement is reported elsewhere[13]~[15].

Analysis

The products were analyzed by means of an infrared spectrometer, Japan Spectroscopic Co., Model DS-402G with an NaCl prism, using the KBr pellet technique. The stretching peak of $-C\equiv N$ is sharp enough to be used for determining the amount of cyanide concentration, as will be seen later, while the $(-\underset{|}{C}=N-)_n$ absorption peak is relatively broad. Therefore, the ratio of the area of the $(-\underset{|}{C}=N-)_n$ peak to the height of the $-C\equiv N$ peak was used for determining the amount of the polymer yield. A calibration curve from a different concentration of the product in the reactant was obtained for each substance.

In order to examine the product, the elementary analysis was carried out.

Results

Polymerization of dinitriles

Fig. 2 (a), (b) and Fig. 3 (a), (b) show the infrared spectra of MN and SN samples and their products of polymerization. In both products, the absorption peak of $(-\underset{|}{C}=N-)_n$ appears in the region of 1500~1700 cm^{-1} and in exact correspondence to the appearence, the absorption peak of $-C\equiv N$ disappears.

By examining the 1500~1700 cm^{-1} region in more detail, it is found that in MN the maxima

13)   J. Osugi and K. Hara, *This Journal*. **36**, 81 (1966)
14)   J. Osugi and K. Hara, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **90**. 873 (1969)
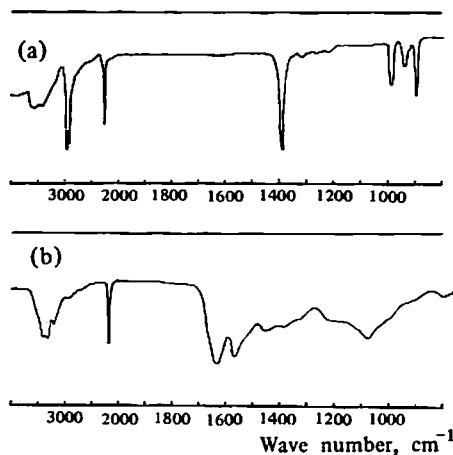15)   K. Hara, *This Journal*, **40**, 93 (1970)

K. Hara

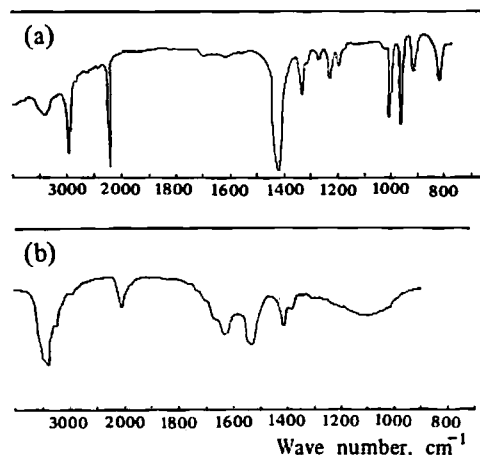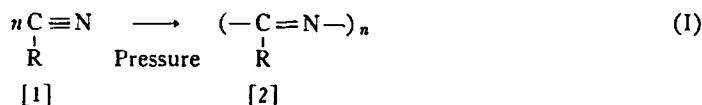Fig. 2 Infrared absorption spectra of (a)
MN sample and (b) poly-MN

Fig. 3 Infrared absorption spectra of (a)
SN sample and (b) poly-SN

exist in 1640 and 1570 cm^{-1} and in SN in 1620~1640 cm^{-1}. From the study of polymerization of nitriles and pyridine in solution, Pravednikov et al.[16] and Kabanov et al.[2] reported that in the s-triazine ring the relatively sharp peak appears at 1580 cm^{-1}, while in the open chain structure, $(-\underset{\underset{R}{|}}{C}=N-)_n$, the rather broad peak appears at 1630~1640 cm^{-1}. Thus, the infrared spectra obtained in this investigation are different from that of the s-triazine ring[2][3]. It seems probable that the product has a form of long chain polymer.

$$n \underset{\underset{[1]}{\underset{R}{|}}}{C} \equiv N \quad \underset{Pressure}{\longrightarrow} \quad \underset{\underset{[2]}{\underset{R}{|}}}{(-C} = N-)_n \qquad \qquad (I)$$

In the case of MN, however, the product from a rather low yield condition has a relatively intense peak at the wave number, 2200 cm^{-1}, close to the initial absorption of cyanide groups, 2278 cm^{-1}. This seems due to the fact that at the first stage only one of the two cyanide groups in MN reacts, while another remains unreacting. This peak also decreases as the yield increases with the increase of pressure and temperature. This suggests that the form of the product becomes a network under higher pressure and temperature. In SN, the reason why such a peak is weak comes considerably from the fact that the two cyanide groups are more separated than those in MN, so that they react independently and possibly intramolecularly without any constraint.

Table 1 contains the results of the elementary analysis of polymers. The theoretical values are those calculated for the open chain structure [2]. Both of the polymers from MN and SN were dark brown powder and highly heat-resistant, and soluble only in DMF. This seems to suggest that

16) A. N. Pravednikov, I. E. Kardash, V. P. Bazov, H. V. Eliceeva, V. A. Sharpatii and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, **151**, 1347 (1963)

the product has a higher molecular weight than that expected from trimer. The limiting viscosity of poly-MN in DMF at 35°C is 0.15 dl/g.

In the case of too high a temperature, the decomposition of the polymer occurred and the evolution of ammonia gas was confirmed.

Table 1   Elementary analysis of the product polymers and calculated values
as open chain structure

	Poly-MN		Poly-SN	
	Observed (%)	Calculated (%)	Observed (%)	Calculated (%)
C	51.0	54.4	58.1	60.0
H	3.5	3.0	4.2	5.0
N	37.3	42.3	25.4	35.0

The electrical resistance and its temperature dependence of the polymer were measured under high pressure. The resistivity of the polymer from MN obtained at 30 kbar, 200°C is about 10^9 $\Omega \cdot$cm at 40 kbar, 20°C. The resistance decreases as the temperature rises. The activation energy for conduction at 30 kbar is 0.3 eV. These aspects are shown in Figs. 4 (a) and (b). This is a semiconducting property that is observed in many other substances. This is due to the mobile free π-electrons in $(-C=N-)_n$ chain structure. On the other hand, the polymer of SN obtained at
$\overset{|}{R}$
30 kbar, 210°C has a resistivity higher than 10^9 $\Omega \cdot$cm at room temperature. This may indicate that the conjugated chain in SN is not so long as that in MN.

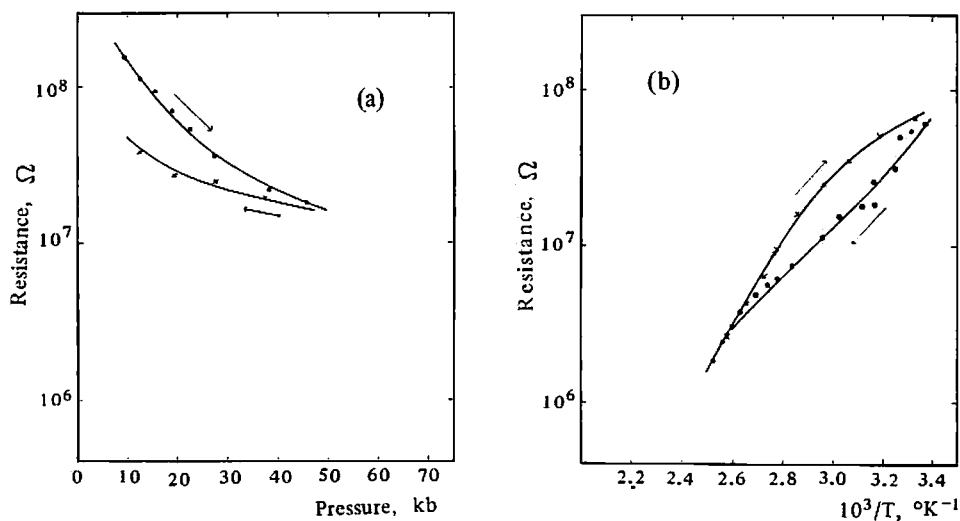Fig. 4   Electrical resistance of MN under high pressure
(a) Pressure dependence of resistance at   (b) Temperature dependence of resistance
room temperature   at 30 kbar

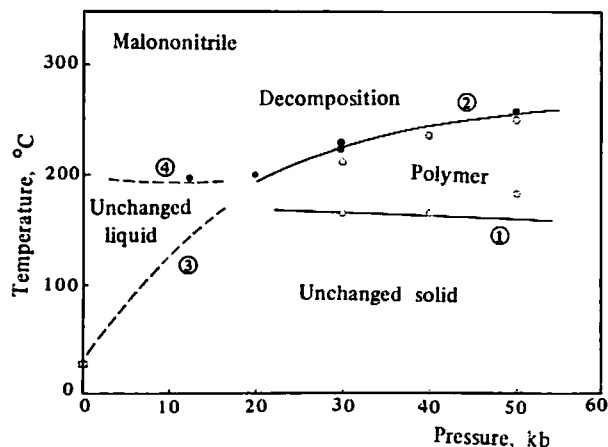Figs. 5 and 6 show the reaction diagrams of MN and SN in which more than one per cent of the

Fig. 5   Reaction diagram for MN

①: Border line above which temperature more than one per cent of the polymer can be obtained

②: Decomposition line of the polymer

③: Melting line of the monomer

④: Decomposition line of the monomer

product can be obtained. The line ① shows the border line above which more than one per cent of the product is obtainable. The line ② is that of the decomposition of polymer. The nearer the temperature is to the melting point and the higher the pressure is, the more readily they react. The minimum pressure and temperature for MN and SN to achieve the reaction are 20 kbar, 160°C and 25 kbar, 200°C, respectively.

In the case of MN, the yield depends on the crystalline size inserted initially, as shown in Table 2. This indicates that the reaction proceeds really in the crystalline state.
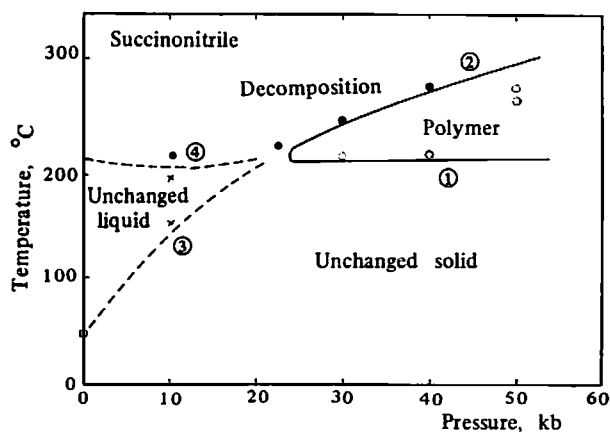

Fig. 6   Reaction diagram for SN

①: Border line above which temperature more than one per cent of the polymer can be obtained

②: Decomposition line of the polymer

③: Melting line of the monomer

④: Decomposition line of the monomer

On the other hand, in SN the dependence on particle size is not observable, because it is quite a glassy or amorphous solid. However, the reaction is thought to proceed in the solid state as shown in the reaction diagram. The reactive region in SN shifts to a higher temperature than in MN.

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Table 2   The effect of particle size of MN monomer

	Yield (30 kbar, 150°C)
Coarse sample (*ca.* 10 mesh)	4.0~6.5%
Fine sample (*ca.* 200 mesh)	10.0~14.5%

In the case of isophthalonitrile and terephthalonitrile, polymerization occurs only in the presence of a catalyst. The catalyst used is HPO_3. The fact that the polymerization is initiated by nucleophilic reagents means that this has the same mechanism as is believed in the polymerization of nitriles in solution by forming complexes with $ZnCl_2$ or $TiCl_4$ under atmospheric pressure and also in the thermal reaction of PAN.

Reaction rates : Figs. 7, 8 and 9 show the relations between the yield and the reaction time in MN under 30, 40 and 50 kbar, respectively. Figs. 10 and 11 show those in SN under 30 and 40 kbar. Experimental error, which mainly comes from the temperature fluctuation during the run and the temperature gradient of the reaction cell, is considerably large, as shown in Fig. 8. In the case of MN, the autocatalytic s-shaped curves were obtained, saturating remarkably in a short time. The induction period is observed apparently at 30 kbar and it becomes shorter as the pressure increases.
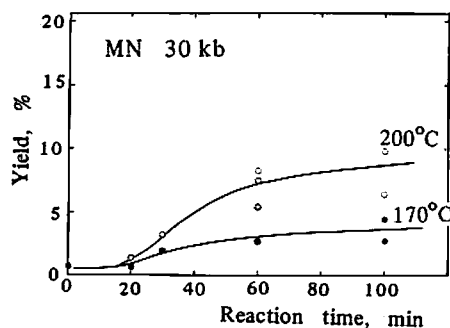

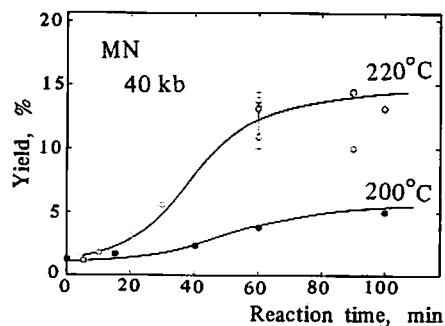Fig. 7   Dependence of the yield of MN polymer on reaction time at 30 kbar

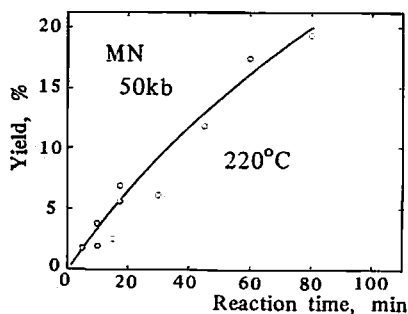Fig. 8   Dependence of the yield of MN polymer on reaction time at 40 kbar

Fig. 9   Dependence of the yield of MN polymer on reaction time at 50 kbar
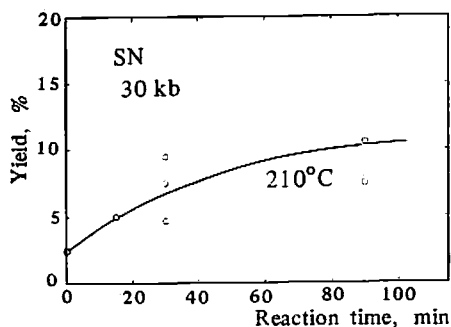
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Fig. 10   Dependence of the yield of SN
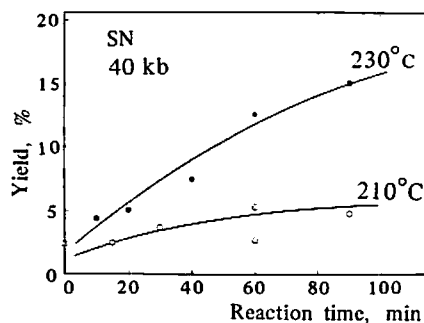   polymer on reaction time at 30
          kbar

Fig. 11   Dependence of the yield of SN
          polymer on reaction time at 40
          kbar

Thermal reactions of polyacrylonitrile

Determination of reaction path under high pressure and high temperature, and property of products : Fig. 12 (a) and (b) show the infrared spectra of the products obtained by the thermal reaction at various temperatures for 1 hr under atmospheric pressure. As the temperature of the reaction rises, $-C \equiv N$ absorption peak (2247 cm^{-1}) decreases, and correspondingly, a relatively broad peak of $(-\underset{R}{C}=N-)_n$ absorption (1550~1700 cm^{-1}) appears.

In addition, the gradual shift of the latter peak accompanying the rising temperature indicates the increase of the conjugated chain length. By Grassie[17] the change of coloration (white → yellow → red brown → dark brown) was also reported to be due to the growing C, N conjugated double bond system.
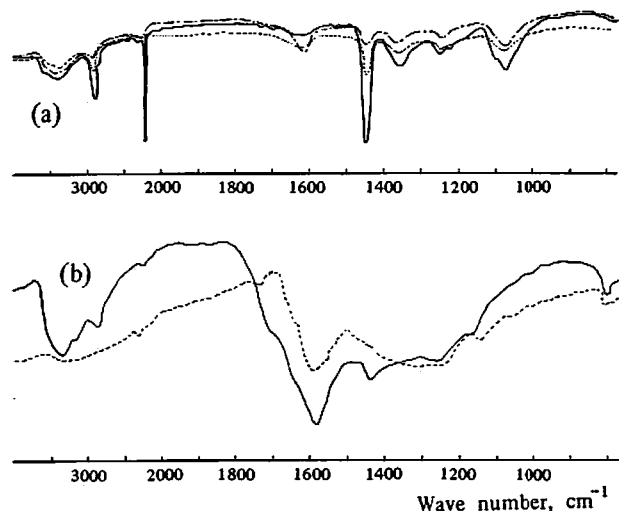

(a)

Fig. 12 Infrared spectra of PAN obtained
        at various pyrolysis temperatures
        under atmospheric pressure

(a) ———— : original sample,
    ················· : heated ot 100°C for 3hr,
    —·——·— : heated at 200°C for 3hr,
(b) ———— : heated at 400°C for 3hr,
    ················· : heated at 500°C for 3hr

Wave number, cm^{-1}

17)   N. Grassie, *J. Polymer Sci.*, **39**, 211 (1964)

Fig. 13 shows the results of elementary analysis of the reaction product for nitrogen and hydrogen. The abscissa shows the reaction temperature and the ordinate shows the ratio of the observed values to the theoretical values for the ring formation reaction [3]→[4], as shown below. Fig. 13 (a) is the result for atmospheric pressure and (b) is for 30 kbar.
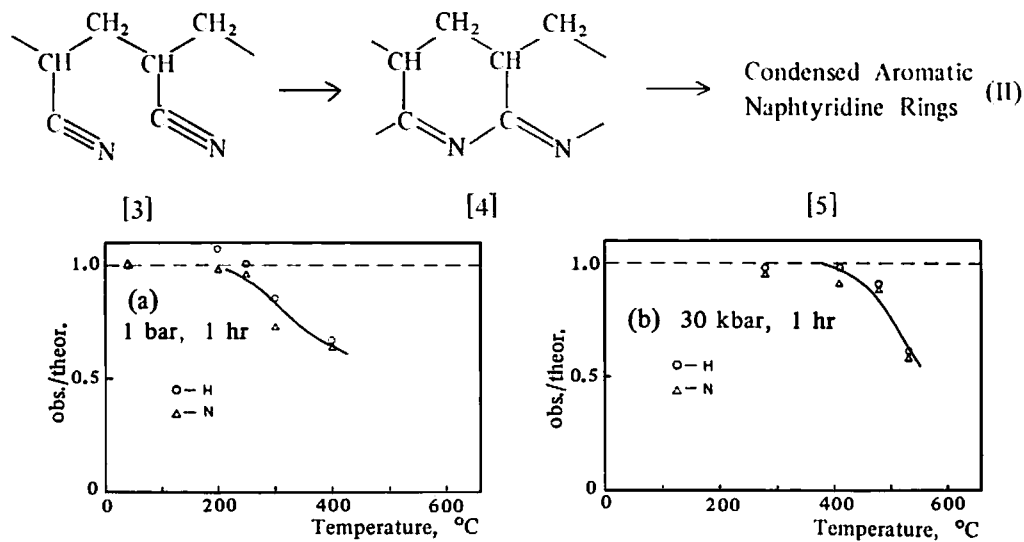

Fig. 13   Elementary analysis of PAN
(a) 1 bar,   (b) 30 kbar   ○ : H,   □ : N

Under atmospheric pressure, at least up to about 250°C the amount of N and H does not change. This indicates that only the ring formation reaction [3]→[4] proceeds up to this temperature. On the other hand, under 30 kbar this reaction proceeds up to 350°C. In the higher temperature another reaction proceeds. Examining the results in more detail, both the elements decrease in the same proportion as are contained initially. This indicates the fact that NH_3 evolves. However, this seems to vary with reaction conditions[18][19].

The change of the electrical resistance was followed under high pressure at temperatures up to 700°C, which is shown in the subsequent paper[15]. The change of the resistance occurs at 400°C under 30 kbar, accompanying the structural change ascribable to [4]→[5], which corresponds exactly to the results of elementary analysis. As the pressure increases, the temperature to commence the reaction [4]→[5] becomes higher.

The density of the samples obtained in various conditions was measured by means of a picnometer. The samples are in powder form, whose foam which is brought about when they are immersed in water can be removed by a centrifuge. The samples are a mixture of the unreacted reactant and the product. As listed in Table 3, the sample from high pressure has a higher density than that from atmospheric pressure.

18)   W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 156 (1956)
19)   S. L. Madorsky and S. Straus, *J. Res. Natl. Bur. Std.*, **61**, 77 (1958)

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Table 3   The densities of PAN obtained under various experimental conditions

Samples	Density, g/cm³
PAN sample	1.15~1.24
1 bar, 200°C	1.20~1.47
30 kbar, 200°C	1.90~2.30

Reaction rates :   Figs. 14, 15 and 16 show the relations between the yield and the reaction time. It was found that these curves were saturated in a short time.

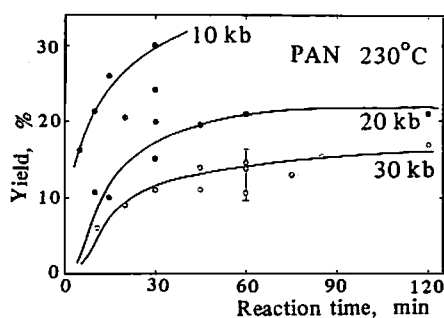
Fig. 14   Dependence of the yield on reaction
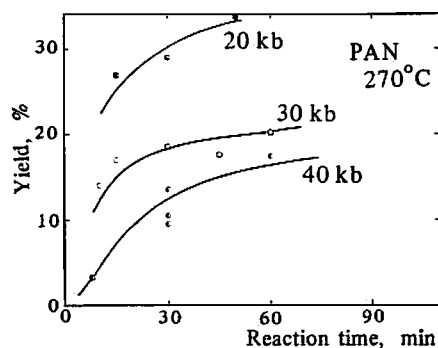   time at 230°C

Fig. 15   Dependence of the yield on reaction
          time at 270°C
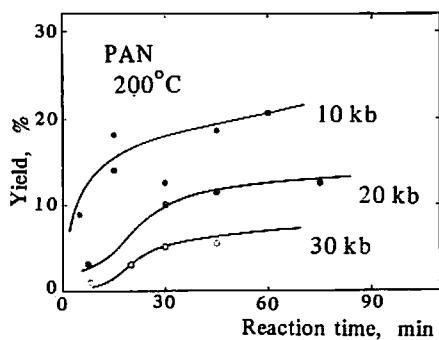
Fig. 16   Dependence of the yield on reaction
          time at 200°C

Effect of water on the polymerization of nitriles

In the polymerization of cyanide groups, the initiation process, which will be shown later, is expected to be accelerated by nucleophilic reagents, such as acid, phenol and water. Thus it is also conceivable that water accelerates the reaction under consideration. Actually, it was found that the polymerization of MN is remarkably accelerated by water, as shown in Table 4.

Table 4   Effect of water on the polymerization of MN

	Reaction condition	Polymer yield ($\%$)
Dry sample	30 kbar, 200°C, 1 hr	5.8~6.5
Wet sample	30 kbar, 200°C, 1 hr	More than 50

On the other hand, in the case of PAN and PMAN, a rather different infrared spectrum was obtained. It was found that by the addition of water PAN is easily hydrolyzed under high pressure to form a gelatinous product, which is obtained in a great yield. This product is soluble in water and pale yellow. Fig. 17 (a) and (b) show the infrared spectra of the product and polyacrylamide sample obtained from American Cyanamide Co. Thus, by comparing the infrared spectra Fig. 17 (a) and (b), the product can be identified as polyacrylamide.
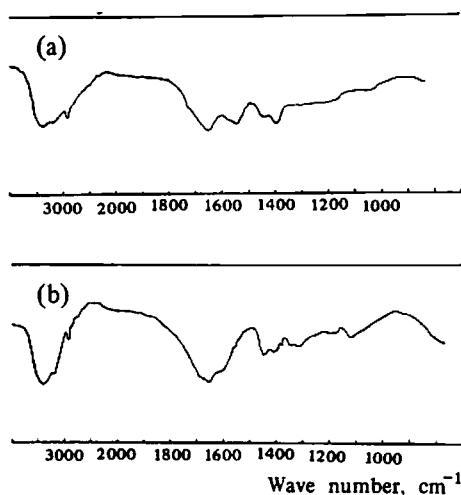

(a)

3000 2000 1800 1600 1400 1200 1000

(b)

3000 2000 1800 1600 1400 1200 1000

Wave number, cm^{-1}

Fig. 17   Infrared spectra of (a) the hydrolyzed
   product of PAN and (b) polyacrylamide
   sample

(a)

3000 2000 1800 1600 1400 1200 1000

(b)

3000 2000 1800 1600 1400 1200 1000

Wave number, cm^{-1}
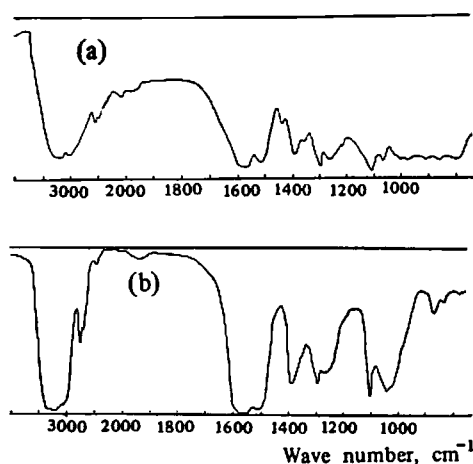
Fig. 18   Infrared spectra of (a) the hydrolyzed
   product of PMAN and (b) polymethacryl-
   amide sample

$$\left(\begin{array}{c} -CH-CH_2- \\ | \\ CN \end{array}\right)_n + nH_2O \xrightarrow[\substack{40\,kbar,\,230°C \\ 1\,hr}]{Pressure} \left(\begin{array}{c} -CH-CH_2- \\ | \\ CO \\ | \\ NH_2 \end{array}\right)_n \qquad (III)$$

PAN   Polyacrylamide

$$\left(\begin{array}{c} CH_3 \\ | \\ -C-CH_2- \\ | \\ CN \end{array}\right)_n + nH_2O \xrightarrow[\substack{30\,kbar,\,250°C \\ 1\,hr}]{Pressure} \left(\begin{array}{c} CH_3 \\ | \\ -C-CH_2- \\ | \\ CO \\ | \\ NH_2 \end{array}\right)_n \qquad (IV)$$

PMAN   Polymethacrylamide
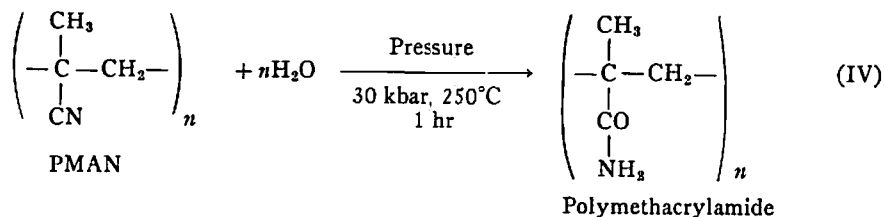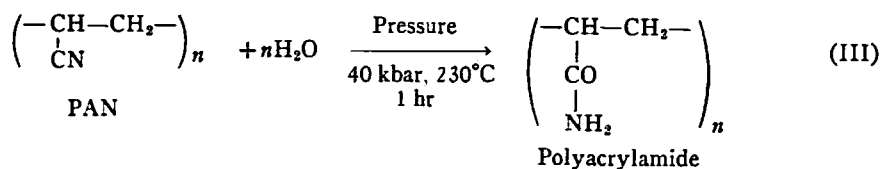
Similarly PMAN is hydrolyzed to form a corresponding amide, polymethacrylamide, whose infrared spectrum is shown in Fig. 18 (a). For comparison Fig. 18 (b) shows the infrared spectrum of pure polymethacrylamide obtained from the polymerization in DMF solution with sulfuric acid as catalyst at atmospheric pressure[10].

Consideration and Discussion

In bulky organic solids, especially, the diffusion of molecules is limited. The self-diffusion coefficients of anthracene at 450°K are of such small values as 7.5×10^{-11} cm²/sec and 4×10^{-11} cm²/sec in two different crystallographic directions[20]. However, the kind of molecular motion needed to cause the reaction of organic molecules in the solid state is different from that in diffusion, so that the measurement of diffusion coefficients may add little to the understanding of reactions occurring in molecular crystals. Moreover, by compression the molecular motion will be inhibited. Therefore, to achieve the reactions in the solid state, the initial geometrical arrangement of reacting sites is considered to be necessary.

Conceivably, the cyanide groups in these compounds are arranged initially in the reactant solid by the strong dipole-dipole interactions of cyanide groups. It is due to this strong intermolecular force between cyanide groups that PAN does not melt before decomposition and exibits various kinds of solid state reactions.

By compressing such substances under more than 20 kbar, the motion as a molecule is suppressed and the reacting sites become nearer enough to interact and to cause the reaction.

In Figs. 5 and 6, the line ③ illustrates the change of melting points of monomer with pressure. The melting point of most organic substances increases more than 100°C in the pressure increase of 10 kbar. In various n-paraffins the increase of 120~140°C per 10 kbar has been observed[21]. This is one of the points of evidence that molecular motion under high pressure is suppressed. The line ④ indicates the change of the decomposition point of monomer. On the other hand, the line ① shows the border line above which more than one per cent of polymer is obtainable.

The line ② shows the change of decomposition point of polymer. The decomposition occurs as a rather fast reaction and this appears as a clear border line with pressure. Under very high pressure the decomposition of some organic solid is reported to proceed explosively. An explosive reaction may occur if the energy produced in the reaction will raise the temperature to a sufficient level and permit the neighboring molecules to react before the local energy has been transferred to a bigger portion of the substance. The compression of solid substances will aid the storage of local energy, which is associated also with the effect of shear stress. Bridgman[22] found that solid sugar decomposes explosively under the compression of 50 kbar. It was thought that the value of $P\varDelta V$ work energy became comparable with the energy of decomposition of the sugar molecule into carbon and water[23]. By

20) C. H. Lee, H. K. Kevorkian, P. J. Rencroft and M. M. Labes, *J. Chem. Phys.*, **42**, 1406 (1965)
21) R. R. Nelson, W. Webb and J. A. Dixon, *ibid.*, **33**, 1756 (1960)
22) P. W. Bridgman, *Phys. Rev.*, **48**, 825 (1935)
23) E. Teller, *J. Chem. Phys.*, **36**, 901 (1962)

compression the initial state is transferred to a higher energy state, whose extent may be high enough to cause a reaction by the local storaged energy. In this case the reaction proceeds fast enough or even spontaneously.

Now, as the decomposition reaction of polymer under consideration is expressed as follows,

$$\text{Polymer (s)} \rightleftharpoons \text{Decomposed polymer (s)} + NH_3\,(g)\,, \tag{V}$$
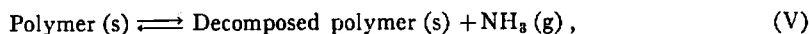
the equilibrium constant K can be considered to be nearly equal to the pressure of ammonia gas P_{NH_3}, that is,

$$K \cong P_{NH_3}\,. \tag{1}$$

Therefore, we can obtain the following equation,

$$\frac{d \ln P_{NH_3}}{d(1/T)} = -\frac{\Delta H}{R} \cdot \tag{2}$$

As $\Delta H < 0$ in this case, P_{NH_3} should increase with increasing temperature.

On the other hand, the change with pressure is expressed by

$$\frac{d \ln P_{NH_3}}{dP} = -\frac{\Delta V}{RT} \cdot \tag{3}$$

As the pressure is raised, P_{NH_3} decreases, since $\Delta V > 0$. That is to say, the decomposition, which is shown in the lines ② in Figs. 5 and 6, should be suppressed, obeying the following equation obtaind from equations (2) and (3).

$$\frac{dT}{dP} = -\frac{T\Delta V}{\Delta H} \cdot \tag{4}$$

This means that compressed materials can be kept stable at much higher temperatures than their normal decomposition temperatures, namely, that this effect of high pressure extends the possibility of the occurrence of solid state reactions, because the thermal energy can be supplied to molecules without being consumed by the dissociation energy.
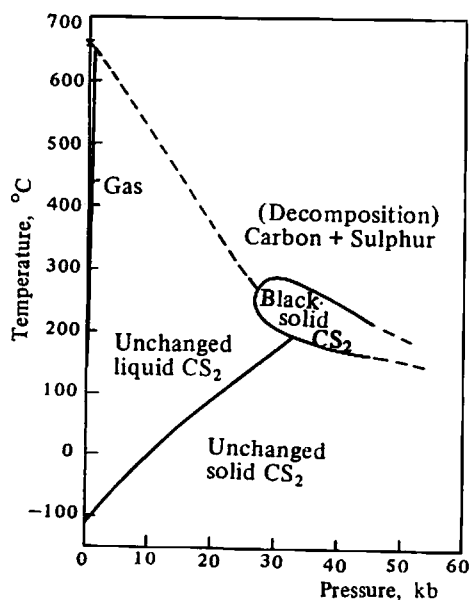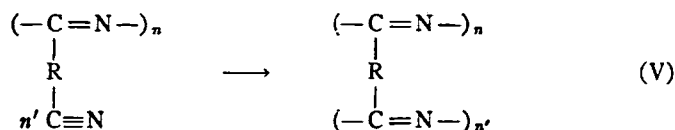
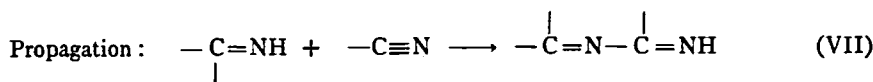

Fig. 19   Reaction diagram of carbon disulfide polymer[24]
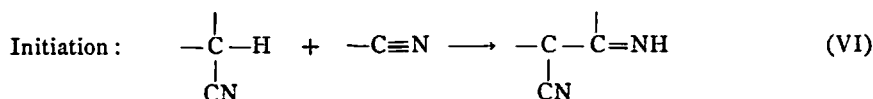
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Although there are few experiments under high pressure like this, the reaction diagram of carbon disulfide[24], as shown in Fig. 19, exceptionally exhibits different decomposition lines. This seems to come from the complex structure of sulfur.

In such a region as where the melting and dissociation are suppressed, $i.\,e.$ the state that molecular motion is retarded, the higher temperature is applicable in the state of solid. In consequence, the applying energy will concentrate to the vibration of bonds and produce quite an active state without consumption in translational motion of molecules.

In the infrared spectrum of poly-MN (see Fig. 2), the peak of $-C\equiv N$ groups remains at a little longer wave length than that of $-C\equiv N$ groups in the initial monomer. This means that in the early stage of the reaction only one of two cyanide groups in dinitrile polymerizes. However, as the reaction proceeds, the peak of the remaining cyanide groups decreases. This means that another cyanide groups polymerize to give a network structure :

$$
\begin{array}{ccc}
(-C=N-)_n & & (-C=N-)_n \\
\ \ |\ \ & & \ \ |\ \ \\
\ \ R\ \ & \longrightarrow & \ \ R\ \ \\
\ \ |\ \ & & \ \ |\ \ \\
n'\ C\equiv N & & (-C=N-)_{n'}
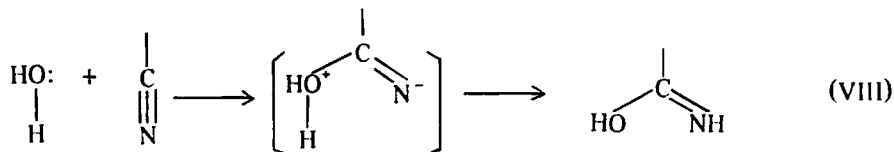\end{array} \qquad \text{(V)}
$$

For the polymerization of cyanide groups, the following Thorpe type mechanism has been proposed from the studies of the lower-temperature reaction of PAN under atmospheric pressure[25][26] :

$$
\text{Initiation:} \qquad
\begin{array}{c}
\ \ | \\
-C-H \\
\ \ | \\
\ \ CN
\end{array}
+ \ -C\equiv N \ \longrightarrow \
\begin{array}{c}
\ \ \ \ \ \ | \\
-C-C=NH \\
\ \ | \\
\ \ CN
\end{array}
\qquad \text{(VI)}
$$

$$
\text{Propagation:} \qquad
\begin{array}{c}
-C=NH \\
\ \ |
\end{array}
+ \ -C\equiv N \ \longrightarrow \
\begin{array}{c}
\ \ \ | \ \ \ \ \ \ | \\
-C=N-C=NH
\end{array}
\qquad \text{(VII)}
$$

In the infrared spectra of Fig. 2 (b) and Fig. 3 (b) there is a shoulder peak at $3180\ \mathrm{cm^{-1}}$, which is ascribable to $=NH$ in poly-MN and poly-SN. As $-C\equiv N$ is a strong electron attractive group, a hydrogen atom at α-carbon atom is easily eliminable. This is another reason why these reactions proceed in the solid state.

If this mechanism is applicable, the initiation is expected to be accelerated by nucleophilic reagents, such as acid, phenol and water. Actually, it is found that the polymerization of MN is remarkably accelerated by water, as is given in Table 4.

In the case of this initiation, the mechanism is expected to consist of the following sequence,

$$
\begin{array}{c}
\text{HO:} \\
\ \ | \\
\ \ H
\end{array}
+ \
\begin{array}{c}
\ \ | \\
\ \ C \\
\ \ ||| \\
\ \ N
\end{array}
\longrightarrow
\left[
\begin{array}{c}
\ \ \ \ \ \ | \\
\ \ \ \ \ \ C \\
HO\cdot \diagdown \diagup \diagdown \\
\ \ \ \ \ \ \ \ \ \ N^- \\
\ \ | \\
\ \ H
\end{array}
\right]
\longrightarrow
\begin{array}{c}
\ \ \ \ \ \ \ | \\
\ \ \ \ \ \ \ C \\
\diagup \ \ \diagdown \\
HO \ \ \ \ \ NH
\end{array}
\qquad \text{(VIII)}
$$

24) E. G. Butcher, M. Alsop, J. A. Weston and H. A. Gebbie, *Nature*, **199**, 756 (1963)
25) N. Grassie and J. N. Hay, *J. Polymer Sci.*, **56**, 189 (1962)

Isophthalonitrile and terephthalonitrile are polymerized only in the presence of a nucleophilic reagent even at 40 kbar, 450°C. In other words, the fact that nucleophilic reagent initiates the reaction explains the applicability of the above mechanism for the polymerization of cyanide groups.

Thus, from the above mechanism, the initiation of MN is envisaged as follows,
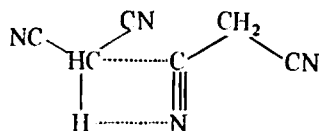
In the case of PAN, the above mechanism is conceivable not only from the observation of the peak of =NH (3180 cm⁻¹) but also from the fact that polymethacrylonitrile, in which a hydrogen atom of α-carbon position in PAN is substituted with a methyl group, is not polymerized without any catalyst under atmospheric pressure[26], nor under high pressure up to 40 kbar.

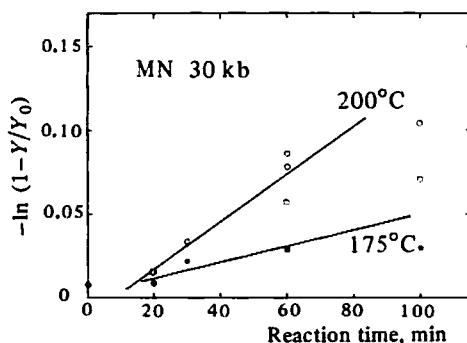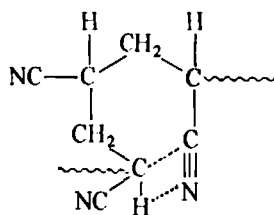Thus the initiation of this ring formation reaction of PAN is envisaged as follows,

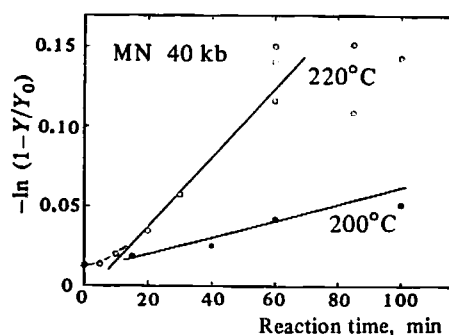Fig. 20 Relation between ln (1—y/y₀) and reaction time for MN at 30 kbar

Fig. 21 Relation between ln (1—y/y₀) and reaction time for MN at 40 kbar

In these reactions first-order kinetics is supposed because the polymerization of $-C\equiv N$ groups in PAN in the solid state follows first-order under normal pressure[27]. The experimental

26) N. Grassie and J. N. Hay, *Makromol. Chem.*, **64**, 82 (1963)

data were replotted according to the relation log y/y_0 vs t, which is shown in Figs. 20 and 21 for MN. The experimental points do not fall on a straight line in the first stage and the higher conversion stage.

At the beginning the solid matrix is so rigid that most of the monomer molecules are not allowed to move in the degree necessary for initiating the reaction. This produces the induction period.

The decrease of the induction period with increasing pressure is apparently related to the increase of shear stress. The application of shear stress under high pressure is reported to cause the scission of covalent bonds, so that the polymerization and degradation of various polymers or radical recombinations occur under such a condition[29]~[33]. Therefore, the increasing shear stress under high pressure will enhance the initiation of this reaction. However, the compact cubic anvil apparatus has an excellent hydrostaticity in pressure among the apparatus used by the method of solid compression. The order of anisotropy for two different directions at 40 kbar is reported to be 2~3 kbar at the greatest and increase linearly with increasing pressure.

That the yield-time relations saturate in a short time seems due to the fact that it is improbable for the reaction to proceed over the particle boundary. The effect of sample size for MN given in Table 2 shows one of the points of evidence.

Although there were only two experimental points for temperature, the rate constants were calculated as a trial under the assumption that the polymerization of cyanide groups follows in first-order kinetics. From the absolute reaction rate theory the rate constant is given by

$$k = \frac{\kappa kT}{h} \exp\left(-\frac{\Delta H^{\ast}}{RT}\right) \exp\left(\frac{\Delta S^{\ast}}{R}\right). \tag{5}$$

Using this equation, activation enthalpy $\Delta H^{\ast}$ and activation entropy $\Delta S^{\ast}$ can be estimated, which are listed in Table 5.

The rather remarkable decrease in the absolute value of $\Delta S^{\ast}$ with the increase of pressure is conceivably caused by the fact that the entropy of the initial state decreases with pressure.

In the case of the thermal polymerization of p-benzamidestyrene in the solid state below the melting point by Morawetz et al.[34] the value of activation energy E is reported to be 43 kcal/mol. On the other hand, Volokhina et al.[35] reported that the value of E for p-aminoperargonic acid is such a large value as 100~200 kcal/mol.

27) N. Grassie and J. C. McNeill, *J. Polymer Sci.*, **27**, 207 (1958)

28) I. Noh, *J. Polymer Sci., Part B, Polymer Letters,* **4**, 721 (1966)

29) A. A. Petrov, M. G. Gonigberg and Dzh. N. Aneli. *Vysokomol. Soed.* Ser A, **10**, 875 (1968)

30) V. M. Kapustyan, A. A. Zharov and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR*, **179**, 627 (1968)

31) A. G. Kazakevich, A. A. Zharov, P. A. Yampoliskii, N. S. Enikolopyan and V. I. Golidanskii, *Dokl. Akad. Nauk SSSR*, **186**, 1348 (1969)

32) H. A. Larsen and H. G. Drickamer, *J. Am. Chem. Soc.*, **61**, 1643 (1957)

33) C. H. Bamford, G. C. Eastmond and J. C. Ward, *Nature*, **192**, 1036 (1961)

34) M. Wakatsuki, T. Ichise, S. Aoki and R. Mori, "Rep. of 12th Symposium on High Pressure", p. 56 (1970)

35) S. Z. Jakabhazy, H. Morawetz and N. Morosoff, *J. Polymer Sci.*, **C4**, 805 (1964)

Table 5   Rate data for the polymerization of MN obtained at 30 and 40 kbar

Pressure (kbar)	Temperature (°C)	k (1/sec)	ΔH^* (kcal/mol)	ΔS^* (cal/deg mol)
30	175	7.8×10^{-6}	19	-42
	200	2.5×10^{-5}		
40	200	8.3×10^{-6}	33	-12
	220	3.6×10^{-5}		

For PAN from the above observations, the following points are evident even under high pressure : i) The disappearance of cyanide groups follows first-order kinetics. ii) A finite amount of cyanide groups remains unreacted.

It is not immediately obvious whether the initiation is an intra- or inter-molecular process. But the former appears more likely, since it is more probable that the attraction in PAN is due to the dipole interaction between pairs of nitrile groups than to the attractions between nitrile groups and tertialy carbon-hydrogen structures. Thus, the bulky structure like [7] is required. The formation of the bulky structure is considered to be retarded by the compression. So, the remarkable retardation by pressure occurs.

Examining the $(-C=N-)_n$ peak region in infrared spectrum in more detail, the gradual shift of the maximum toward the long wave length depending on pressure is observed. Fig. 22 illustrates the changes which occur in $(-C=N-)_n$ portion of the spectra.

It is supposed that the close or tight packing under high pressure allows the reaction to proceed intermolecularly and produce "crosslinking" as follows,
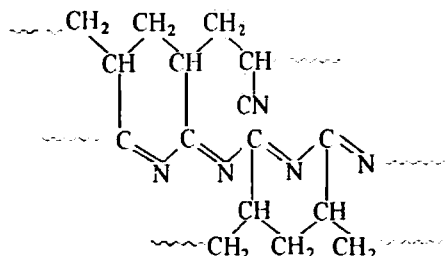
This is verified from the facts that the density of the product obtained under high pressure is somewhat higher and that the product has a smaller pressure dependency on electrical conductivity than that obtained under atmospheric pressure. The latter aspect is illustrated in the next poper[15].

The usual criteria used to distinguish free radical from ionic polymerization are not always applicable to solid state reactions. Nevertheless, in the present study, the conclusion is inevitable that radicals participate in the initiating species. Radicals really existed in the product and their concentration from ESR measurement was 6.14×10^{17}/g for the poly-MN obtained at 30 kbar, 220°C. Additional evidence for this point of view is given by the activation values. It is known that the activation energy values of ionic processes are smaller. The exact nature of the initiating process and the effect of pressure to it are in doubt.
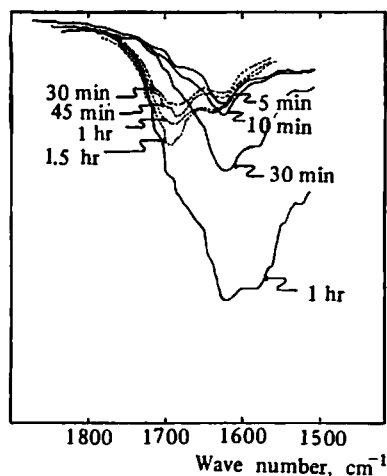
92   K. Hara

Fig. 22 Infrared spectra in the range of
1500~1800 cm⁻¹ for PAN obtained
under 1 bar and 30 kbar at various
reaction temperature

——— : 1 bar
- - - : 30 kbar

While the ionic process is considered to be accelerated under high pressure in the case of liquid state reaction. For example, acetone is condensated at 50 kbar, 320°C[37] without catalyst and Hamann says that this is due to the remarkable acceleration of auto-protolysis under very high pressure. It was found in our preliminary experiment that the other ketones, such as methyl ethyl ketone and diethyl ketone, can be condensated to give similar products to acetone[39].

The reactants selected in this experiment were limited to solid substances, because one of the initial objects was to investigate the reactivity of organic crystals. However, it seems to be also instructive to investigate liquid substances, for the purpose of examining the reactivity of organic substance under such extreme conditions in comparison with that at atmospheric pressure.

Acknowledgment

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36) A. V. Volokhina, G. J. Kudryavtsev, S. M. Skuratov and A. K. Bonetskaya, *J. Polymer Sci.*, 53, 289 (1961)
37) I. S. Bengelsdorf, Unpublished work reported by S. D. Hamann, "Physico-Chemical Effects of Pressure," p. 87, Butterworths Scientific Publications, London (1957)
38) J. Osugi and K. Hara, Unpublished data