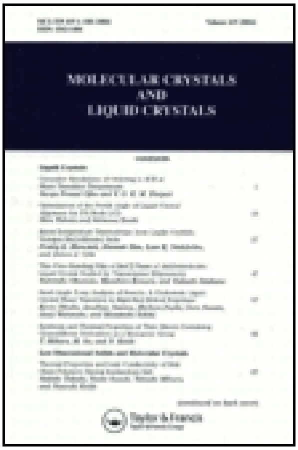

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: Y. Tabata , S. Shu & K. Oshima (1969): Solid State Polymerization Under High Pressure, Molecular Crystals, 9:1, 435-452

To link to this article: http://dx.doi.org/10.1080/15421406908082751

Solid State Polymerization Under High Pressure

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Abstract—The radiation-induced polymerizations in three different types of monomers under high pressure have been investigated.

First, radiation-induced solid state reaction in several radical type polymerization systems has been studied under pressure up to 6,000 atm. It was pointed out from the experiments that only the propagation reaction is affected by applied pressure, and the reaction in the crystal matrix is suppressed, while the reaction in the amorphous matrix is accelerated by pressure.

Second, polymerization of several monomers, such as acrylonitrile, methacrylonitrile, at low temperatures has been studied under high pressure up to 7,000 atm. From these studies, it was shown that the polymerization of acrylonitrile can take place without an appreciable change of the volume at very low temperatures below the transition point at about − 130 °C, and that the polymerization cannot take place in a definite temperature region, under a high pressure, from the melting point at the pressure to a transition point at about − 100 °C at the same pressure, indicating that a change of crystal structure due to the phase transition gives an extremely large influence to the reactivity of monomer crystals.

Finally, polymerization of cyclic monomers such as trioxane, diketene β-propiolactone and propylene oxide, has been investigated. From the investigation, it was observed that the polymerization of diketene and β-propiolactone can be accelerated by applying pressure, while the polymerization of trioxane is retarded by applying pressure.

The pressure effect on solid state reaction is compared among three different types of polymerization.

Introduction

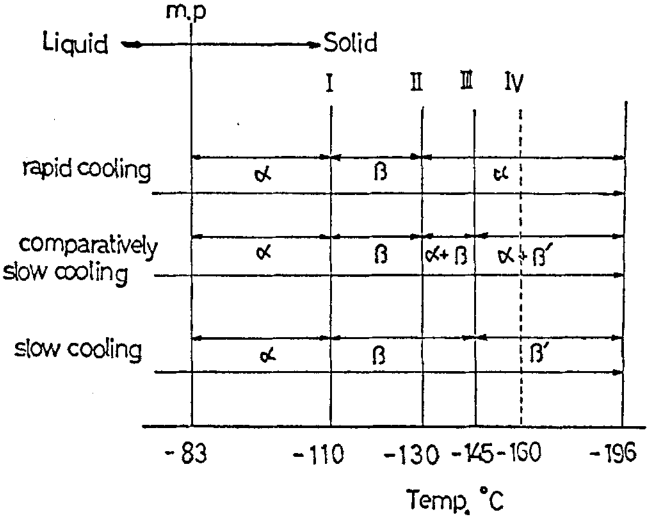
Solid state polymerization induced by radiation has been carried out at high pressure. Three different types of solid state polymerizations have been investigated and the pressure effects were compared with each other. The pressure effect on the solid state polymerization reflects the mechanism of the process and the study is very useful for obtaining information about the nucleation process during the initial stages of polymerization and about the formation of defects, the change of lattice constants and the annealing of the system during polymerization.

Experimental

Several ml of the monomer was introduced into the reaction vessel, The air was not thoroughly purged from the vessel. To prevent the condensation of water in the reaction vessel, it was put in a bag made from polythene film and then frozen at temperatures required for the high pressure experiments. The radiation induced polymerization was initiated by γ-rays from Co^{60} source. Pressures ranging from 1 to 6000 atm and temperatures from − 196 °C to 80 °C were used. The apparatus for the high pressure experiments has already been reported in part.[1] A fuller description will be published elsewhere. Dose rate inside the reaction vessel was determined by the means of Fricke disometry.

I. Polymerization of Acrylonitrile in Solid State

The melting point of acrylonitrile is − 83 °C at atmospheric pressure and − 5°C at 5000 atm, respectively. For the experiments at − 78°C, monomer was precooled at − 109 °C for about 90 minutes and then the pressure was applied at the operating temperature. Then the material was irradiated. For the experiments at − 98 °C the pressure was applied to monomers at − 109 °C for 90 minutes. Then the pressurized monomers were warmed to − 98 °C for 30 minutes and then irradiated. For the experiments at − 109 °C, − 130°C and − 155 °C, pressure was applied at each temperature for about 90 minutes, and then the material was irradiated. By rapid cooling of monomers from room temperature to − 196 °C the α crystal modification, which is stable above about − 110 °C, can be quenched as a metastable crystal form. On the other hand, β-type crystal which is stable below the transition temperature of − 110 °C can be obtained by cooling the monomers from − 130 °C to − 196 °C, after keeping the monomers at − 130 °C for several hours. The phase transitions of the monomers are shown in Fig. 1 schematically.



I crystal – crystal transition $\alpha \rightleftharpoons \beta$
II metastable – stable crystal transition $\alpha \rightarrow \beta$
III crystal – crystal transition $\beta \rightleftharpoons \beta'$
IV glass–crystal transition

Figure 1. Phase transitions of acrylonitrile after annealing several hours at a given temperature.

The polymer was separated from the unreacted monomers with methanol. The isolated polymer was then dried in vacuo. Viscosities were measured in dimethylformamide solution at 25 ± 0.1 °C with an Ubbelohode viscometer, and the molecular weights were calculated by following equation.[2]

$$(\eta)_{25\,^{\circ}\mathrm{C}} = 1.75 \times 10^{-3} M_n{}^{-0.66}$$

The conversion curves at various temperatures are shown in Figs. 2 and 3 for different pressures of 1 and 5000 atm.

It is obvious from these figures, that the polymerization rate is reduced by pressure at all temperatures. This may be due to the annealing of defects in the crystals by applied pressure, and to the deformation of crystal lattice.

It is very interesting that the rate of polymerization is extremely small at – 78 °C and – 18 °C in the solid state under high pressure. At these temperatures the monomer is in liquid state under atmospheric pressure. An increase in the rate of the solid state polymerization

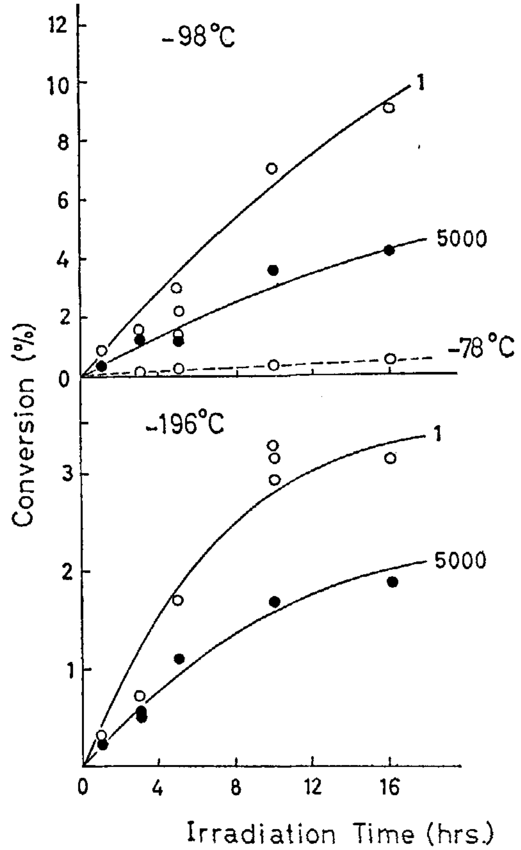


Figure 2. Conversion (%) as a function of irradiation time in solid state polymerization at − 78 °C under 5000 atm, at − 98 °C and − 196 °C under 1 and 5000 atm.

under high pressure in the temperature region above the melting point at atmospheric pressure had been expected. However, the rate was observed to decrease at the higher temperatures. This may be due to the formation of anomalous crystalline structure in this temperature region (γ or γ'-crystals).

Temperature dependence of the polymerization rate at pressures of 1 and 5000 atms are shown in Figs. 4 and 5, respectively. For polymerization at 1 and at 5000 atm, the rate of polymerization shows little temperature dependence below − 130 °C. These results are shown in Fig. 6 as the Arrhenius plots.

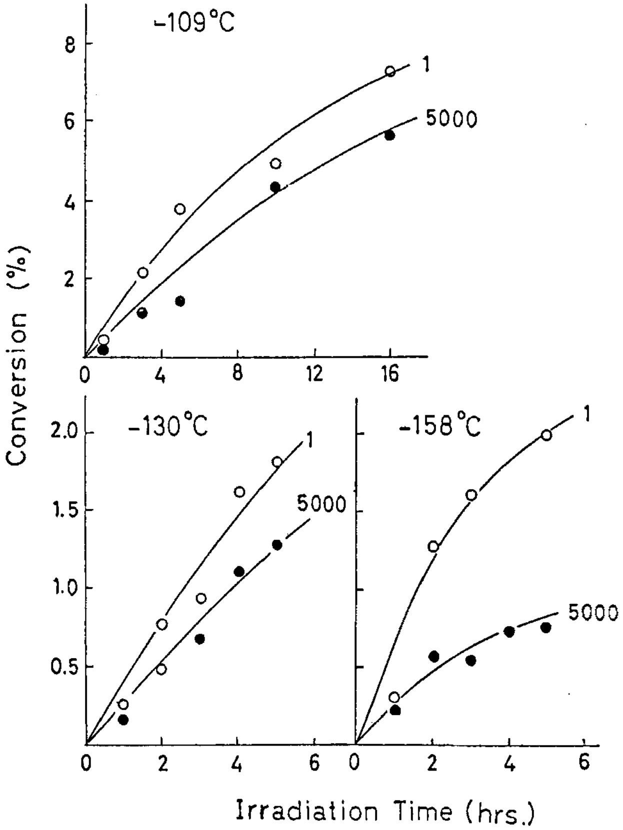


Figure 3. Conversion (%) as a function of irradiation time under 1 and 5000 atm at various temperatures.

The highest reaction rate was observed in the vicinity of − 100 °C for the polymerizations at 1 and 5000 atm. It is quite interesting that the effect of pressure on the solid state polymerization of acrylonitrile is very different above and below the transition temperature of the monomer. Therefore, activation energies should be different in the different temperature regions. These results suggest strongly that the mechanism of acrylonitrile polymerization in the solid state is quite different above and below the transition temperature of the monomer. For the lower temperature region, the values of $(\log R_p)_{1/T \to 0}$ for the polymerizations at 1 and 5000 atm coincide with each other. This suggests that the pressure effect on the solid state

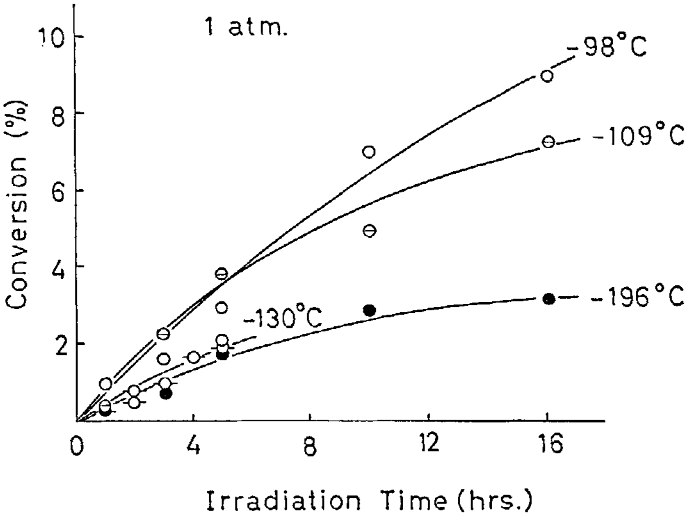


Figure 4. Relations between conversion (%) and irradiation time at various temperatures under atmospheric pressure.

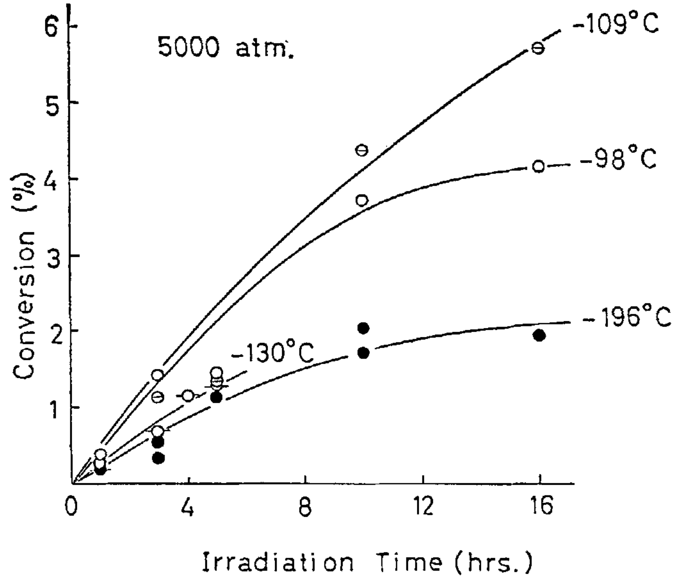


Figure 5. Relations between conversion (%) and irradiation time at various temperatures under a high pressure of 5000 atm.

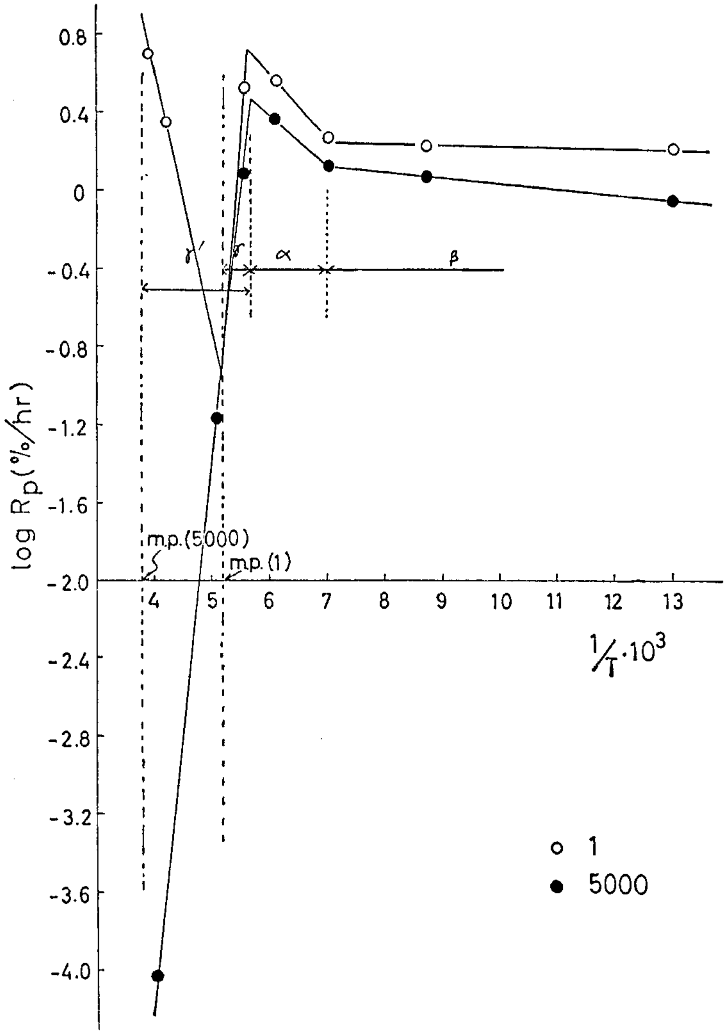


Figure 6. Arrhenius plots of solid state polymerization of acrylonitrile at 1 and 5000 atm.

polymerization of acrylonitrile is not due to a change in the activation entropy by pressure, but to a change in the activation enthalpy, as has been found in the case of methacrylonitrile.[3]

The effect of pressure on the rates of polymerization at − 98 °C and − 196 °C is shown in Fig. 7.

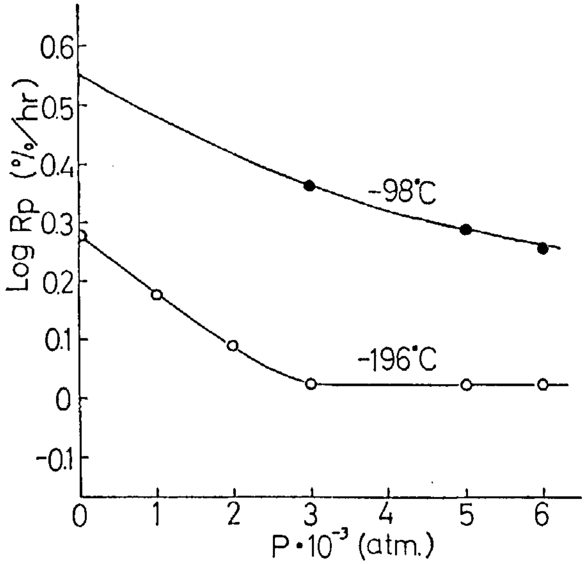


Figure 7. Effect of pressure on the rate of polymerization at − 98 °C and − 196 °C.

At − 98 °C, the rate of polymerization decreases smoothly with increasing pressure until 6000 atm. On the other hand, for polymerization at − 196 °C, the initial rate of polymerization decreases rapidly with increasing pressure until 2000 atm but the rate does not change in the higher pressure range of 3000 to 6000 atm. The activation volume was calculated by Van't Hoff's equation and is shown in Table 1.

$$\left(\frac{\partial \ln R_p}{\partial P}\right)_T = -\frac{\Delta V\ddagger}{RT}$$

Table 1 Activation Volume $\Delta V\ddagger$ in the Solid State Polymerization of Acrylonitrile

Temperature (°C)	Pressure region (atm)	$\Delta V\ddagger$ (ml/mol)
− 98 °C	1–1000	2.67
,,	1000–2000	2.01
,,	2000–3000	1.67
,,	3000–4000	1.33
,,	4000–5000	1.00
,,	5000–6000	0.67
− 196 °C	1–2500	1.37
,,	3000–6000	0

These results strongly suggest that the polymerization at − 196 °C proceeds without any change of volume in the system. This is consistent with the polymerization mechanism which has been proposed by the authors as a collective excitation process and which may be called " electronic polymerization ".

Viscosities of polymers obtained were measured and the results are shown as a function of irradiation time for various temperatures in Fig. 8 and as a function of polymerization temperature for different pressures in Fig. 9, respectively.

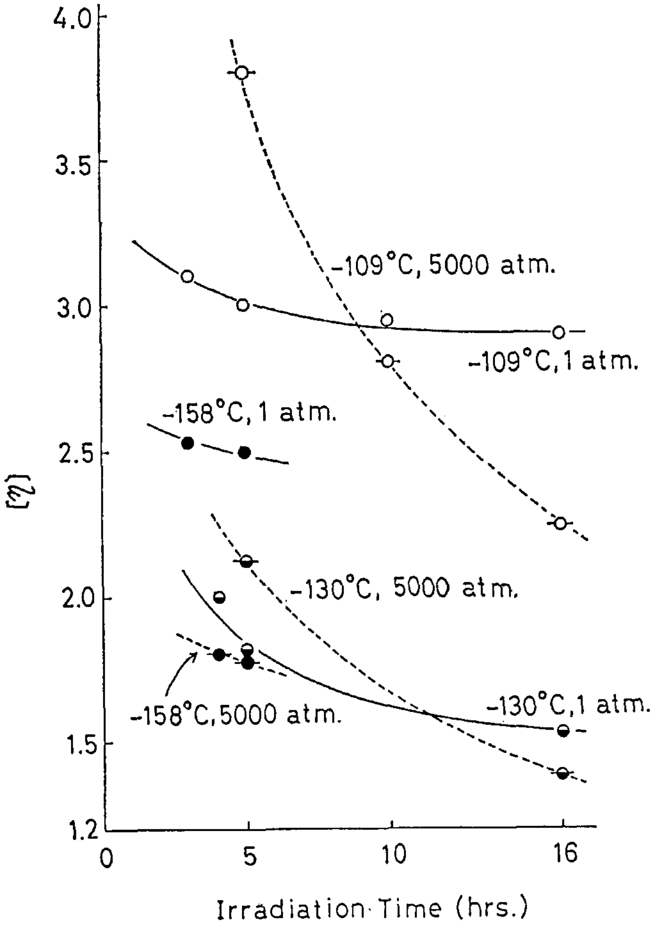


Figure 8. Viscosities as a function of irradiation time at various temperatures at 1 and 5000 atm.

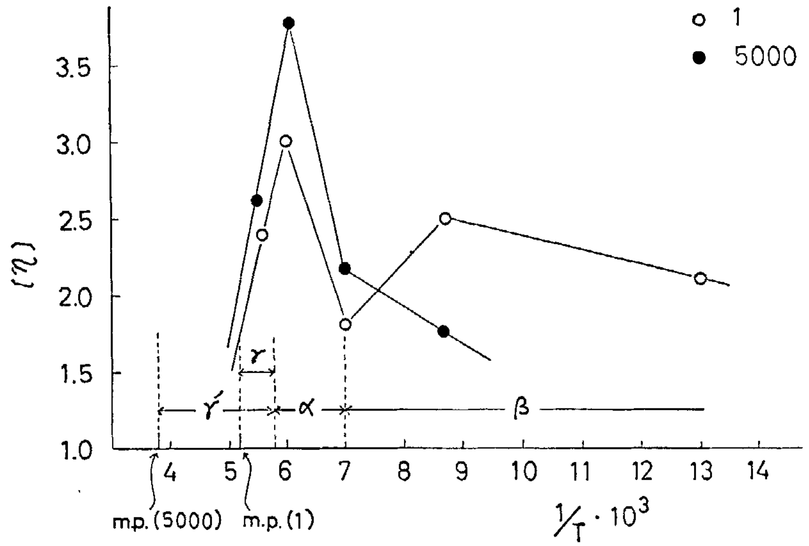


Figure 9. Viscosities as a function of polymerization temperature for different pressures of 1 and 5000 atm.

One can say that the intrinsic viscosity is profoundly affected by both polymerization temperature and applied pressure. In the polymerization in α-phase above the transition temperature, the intrinsic viscosity increases with increasing pressure. In contrast to this, it decreases with increasing pressure in the β-phase, below the transition temperature.

It is also interesting that the intrinsic viscosity decreases sharply with irradiation time at higher pressures, as compared with the behavior at lower pressures.

Dependencies of the intrinsic viscosity on the applied pressure is different in the α- and β-phases. These results are shown in Fig. 10.

The number of average molecular weight is indicated roughly by the intrinsic viscosity and the number of polymer chains is roughly indicated by the ratio of conversion to the intrinsic viscosity, Y/η(Y = wt % conversion). Although the data are rather scattered, the number of polymer chains is smaller in the polymerizations at higher pressures than at ordinary pressure for pure monomers at both − 98 °C and − 196 °C. This suggests that the initiation reaction is more favorable at lower pressures than at higher pressures. if a

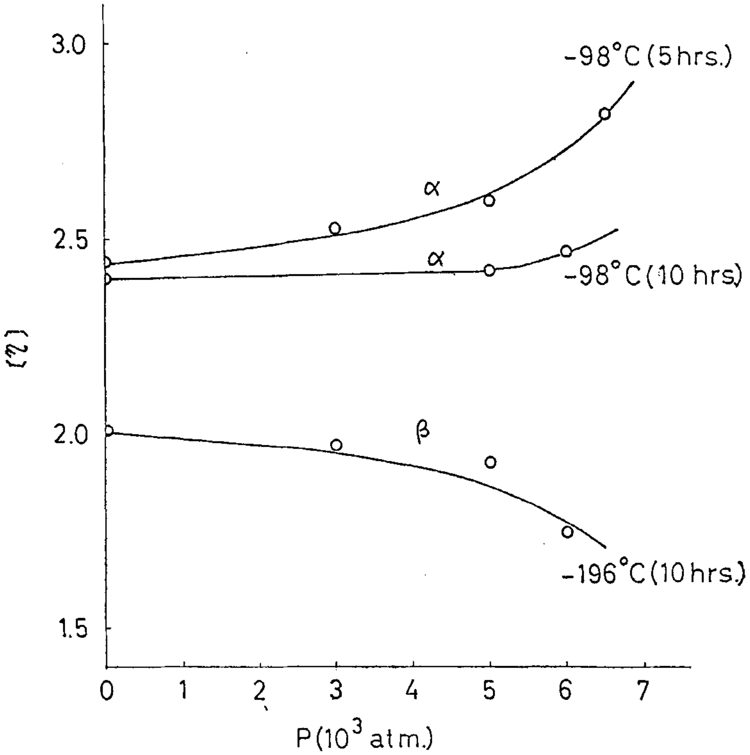


Figure 10. Dependencies of intrinsic viscosity on applied pressure for two different crystal structures (α and β).

chain transfer reaction does not take place. On the other hand, the number of polymer chains is slightly smaller at − 196 °C than at − 98 °C. It seems to indicate that the G-value of initiation reaction is slightly larger at − 98 °C than − 196 °C.

The propagation reaction is most closely connected to the intrinsic viscosity. This in turn is related to the degree of polymerization. The activation energies are different between polymerizations at low and high pressures, and also different above and below the transition temperature at the same pressure. The intrinsic viscosity is clearly larger at higher pressures than at atmospheric pressure above the transition temperature. This indicates that the propagation reaction is more favorable at higher pressures than at atmospheric pressure above the transition temperature. The molecular weight increases with pressure above the transition temperature. On the contrary, the molecular weight decreases with increasing pressure below the transition temperature.

In conclusion, for the polymerization of acrylonitrile, it is pointed out from the pressure effect experiments that another modication of the crystal structure may exist above about − 100 °C and the polymerization may take place with difficulty in this polymorph. On the other hand, it was indicated from the experiments that the polymerization of acrylonitrile takes place in the solid state below the transition temperature without any volume change in the system, suggesting that a collective excitation process might be operative in the polymerization.

II. Polymerization of β-Propiolactone

It was reported in a previous paper[4] that the rate of polymerization is accelerated by pressure at temperatures below − 98 °C, and that the activation energies are estimated to be 0 kcal/mole and 0.2 kcal/mole for polymerizations at 1 and 5000 atm, respectively. It was shown for the entire range of polymerization temperatures that polymer of type II[5] can be obtained.

Arrhenius plots of polymerization rate under pressures of 1 and 5000 atm are shown in Fig. 11.

It is very interesting to note that the Arrhenius plots above the − 100 °C transition temperature of the monomer cross each other. This occurs at − 78 °C. The polymerization below the transition temperature proceeds without activation energy at atmospheric pressure.

Recently, the transition at around − 100 °C was confirmed by X-ray diffraction and by thermal differential analysis in our laboratory.[6] On the other hand, it has been found very recently in our laboratory that the polymerization which produces polymer of type II below the transition proceeds only during temperature elevation after irradiation at − 196 °C, that is, the polymerization which produces polymer type II, does not take place during irradiation but only takes place at the transition on warming up after irradiation. The post-polymerization proceeds rapidly enough and the process may be an ionic.

The fact that the polymerization under high pressure below the

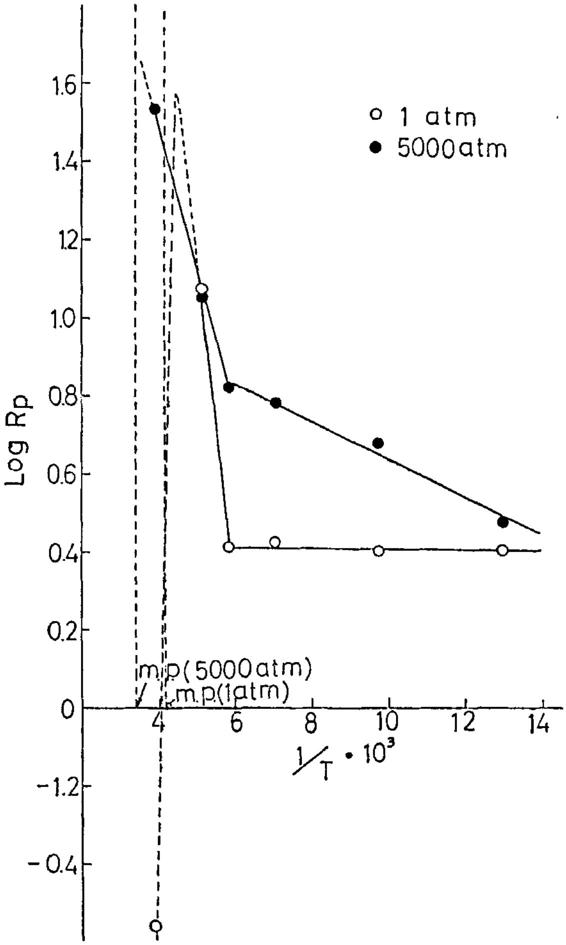


Figure 11. Arrhenius plots of solid state polymerization of β-propiolactone at 1 and 5000 atm.

transition temperature proceeds with a certain value of activation (0.2 kcal/mole) suggests that the polymerization takes place during irradiation under such conditions. It seems from the experimental results that the high pressure induced deformation of the lattice in the monomer crystals enables the monomer to polymerize during irradiation.

Pressure effects on the polymerization at − 196 °C and − 78 °C were examined and are shown in Figs 12 and 13. Activation volumes

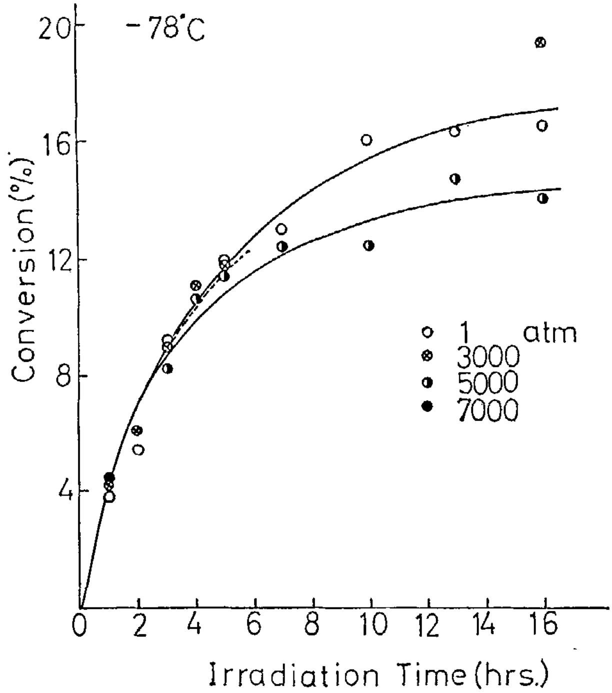


Figure 12. Relations between conversion (%) and irradiation time at −78 °C under various pressures.

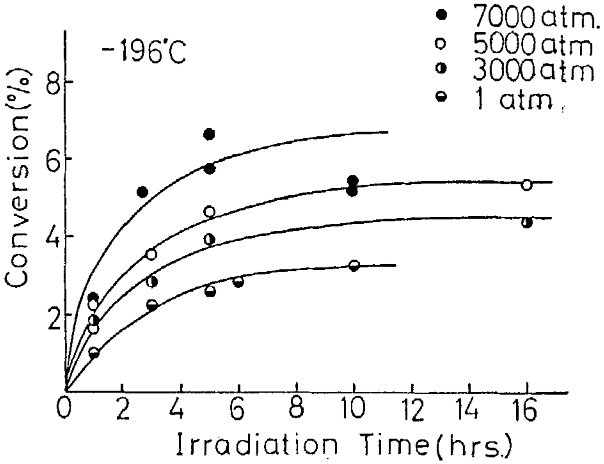


Figure 13. Relations between conversion (%) and irradiation time at −196 °C under various pressures.

in the polymerization at various temperatures were calculated, as indicated in Fig. 14.

Activation volume $\Delta V\ddagger$ decreases with increasing the polymerization temperature below the transition. On the contrary, activation volume $\Delta V\ddagger$ increases sharply with the polymerization temperature above the transition, as shown in the Fig. 14.

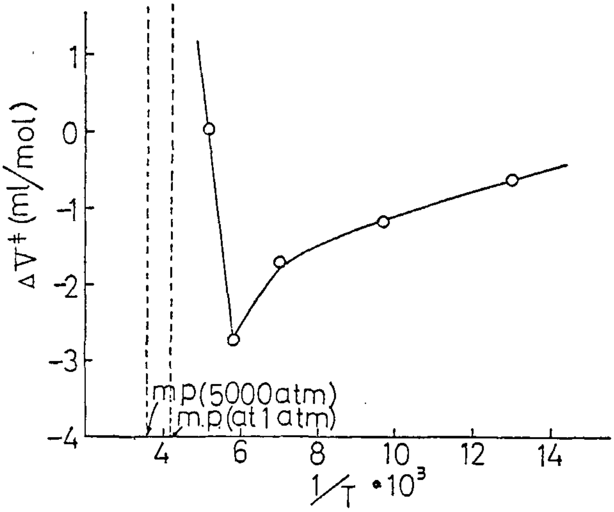


Figure 14. Relation between activation volume $\Delta V\ddagger$ and reciprocal absolute temperature in the polymerization of β-propiolactone.

It seems that, below the transition temperature the ring of the monomer molecule is deformed by applied pressure and the internal stress in the ring structure is built up as functions of temperature and pressure. The deformation arrives at a maximum at the transition temperature. The internal stress may be built up (quenched in) by a strong interaction among monomer molecules below the transition temperature. Therefore, the polymerization takes place with the releasing of built-up strain and then the polymerization becomes possible by applying pressure.

It is a reasonable assumption that a considerably large rearrangement of the conformation of both monomer itself and the crystals takes place by converting monomer crystals to the corresponding polymer crystals.

It was shown in the previous paper[4] that the pressure effect on the solid state polymerization of β-propiolactone is not only due to the change of the enthalpy of activation but also the change of the entropy of activation. This is reasonably explained by taking the change of activation volume as a function of temperature into consideration. Above the transition at − 100 °C, the activation volume, $\Delta V\ddagger$, increases sharply as shown in Fig. 14. Unlike the low temperature phase, in the high temperature phase, the stress given to the ring of the monomer molecule by applied pressure may be easily released by a weak interaction among monomer molecules.

As is obvious from the Fig. 11, the rate of polymerization is much faster at − 18 °C than at − 78 °C in solid state under a pressure of 5000 atm, unlike the case of solid state polymerization of acrylonitrile at high pressures. This means that rapid polymerization becomes possible at the higher temperatures above the melting point at atmospheric pressure by applying pressure which results in elevation of the melting point. This is not true in the polymerization of acrylonitrile.

Polymerization at − 78 °C under various pressures are very interesting. Since the activation volume $\Delta V\ddagger$ is almost zero, the polymerization at this temperature takes place without any change in volume of the system. This suggests that the stress stored by applied pressure can be considered to be compensated by that produced by polymerization.

III. Polymerization of Acrylamide

Pressure effects on the solid state polymerization of acrylamide were already reported by us,[1] and the effect is attributed to the pressure dependence of the activation enthalpy $\Delta H\ddagger$ and the activation entropy $\Delta S\ddagger$ of the propagation step. Unlike the two former cases, the polymerization of acrylamide proceeds very slowly in the initial stages of polymerization. It is accelerated autocatalytically in a later stage. Pressure effects are also very different between the two stages. In other words, the rate of polymerization is suppressed by pressure in the crystalline phase of monomers, while it is accelerated by pressure in the heterogeneous phase where a mixture of monomer crystallites and amorphous polymer is produced. Activation volume $\Delta V\ddagger$ changes depending on the conversion of monomers.

A positive value of $\Delta V\ddagger$ was obtained for the initial stage, while a negative value for the later stage. The $\Delta V\ddagger$ for the polymerization during the initial stage at 28 °C was estimated to be + 2.77 ml/mol as shown in Fig. 15.

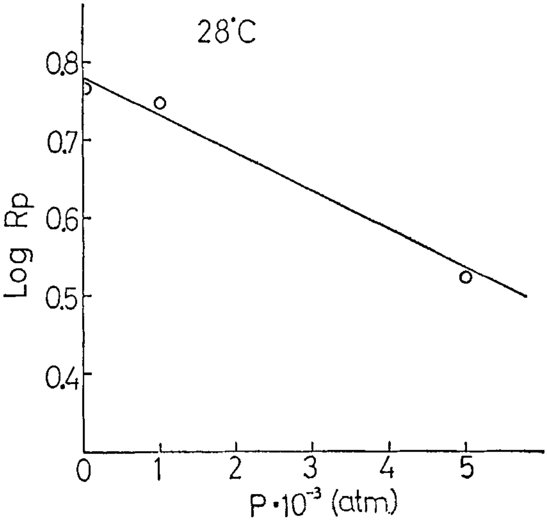


Figure 15. Effect of pressure on the rate of solid state polymerization of acrylamide at 28 °C.

Conclusion

Pressure effects on three different types of solid state polymerizations have been studied and compared with each other. The discussion was mainly focussed to the activation volume, $\Delta V\ddagger$ of polymerization. Activation volume $\Delta V\ddagger$ is a function of temperature, pressure and monomer conversion.

For the polymerization of acrylonitrile, $\Delta V\ddagger$ has always a positive value in both the α and β phases, except for polymerizations above 3000 atm at − 196 °C.

The results are very interesting from the view point of polymerization mechanism. Particularly, zero activation volume above 3000 atm at − 196 °C suggests that the polymerization takes place via " collective excitation process ". For the polymerization of β-propiolactone, $\Delta V\ddagger$ is a complex function of temperature, indicating that the polymerization mechanism is considerably different in the two different phases above and below the transition temperature of − 100°C.

For the polymerization of acrylamide, the most important factor affecting the activation volume is the conversion of monomer, and the activation volume $\Delta V^{\ddagger}$ changes from positive to negative value during the course of polymerization from the initial to the later stage.

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