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General Lectures and Discussions which follow them and the Author and Subject Indexes will appear in Part 3 of this Symposium.

Effect of Phase Transitions on Polymerization of Monomers below Their Melting Point

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Surveying a number of experimental data on the polymerization of monomers below their melting points one can distinguish two types of reactions: the first type involves "fast" reactions, which are characterized sometimes by explosion rate; the second type involves "slow" reactions in which the rate is rather small or commensurable in comparison with liquid state polymerization. The purpose of this study is to elucidate some of the reasons why fast polymerizations arise and to consider the differences between fast and slow polymerizations in solid state.

I. Fast Polymerization

More than 25 years ago Letort discovered that frozen acetaldehyde polymerized very rapidly near its melting point. It was the first example of fast polymerization in solid state described.¹⁻³ In 1959 we succeeded in carrying out fast polymerization of a number of monomers on the verge of the melting and even at the temperatures considerably below the melting points. This was achieved by using the method of simultaneous high vacuum condensation of monomer and inorganic compound (initiator) vapors on deeply cooled surface (molecular ray method⁴).

Active species were formed in the course of such condensation, owing to the collisions of monomer and initiator molecules either in gaseous phase or directly on the condenser surface, and trapped in the excess of frozen monomer.⁵⁻⁷

This method, in spite of some experimental difficulties, is very useful for studying solid-state polymerization and has some advantages compared with irradiation technique because (1) it is possible to vary the initiators and to choose the most specific ones for a particular monomer; (2) the temperature of the condenser surface can be varied and the solid monomer-initiator mixture can thus be obtained easily in either vitreous or in crystalline state; (3) accumulation of side products in the reaction zone (which is inevitable under irradiation) can be avoided.

The monomers and the inorganic initiators for which we could observe the fast solid-state polymerization are shown in Table I. In all cases the condenser was cooled by liquid nitrogen. At this temperature the monomer-initiator mixtures condense to form homogeneous vitreous films on the

cooled surface. The data show that the initiators act highly specifically. The metals as a rule are effective in case of monomers with electronegative substituents. On the contrary, the metal halides, which have acceptor properties, are effective for monomers with electropositive substituents. The possible mechanisms of initiation are discussed in detail in a previous paper.⁶

TABLE I
Fast Polymerization of Monomers in Frozen Molecular Mixtures^a

Monomer	Catalysts							
	Mg	K, Na	Zn, Cd, Hg	H	NaCl, KCl	BeCl ₂ , ZnCl ₂ , TiCl ₃	MoO ₃	LiCl
α -Methylstyrene	—	—	— ^b			⊕	⊕	⊕
Isoprene	—	—	— ^b			⊕	⊕	
Styrene	—	+	— ^b	+	⊕	⊕	⊕	⊕
Acrylonitrile	⊕	⊕	+	+		—	—	
Methacrylonitrile	⊕	⊕						
Methyl methacrylate	⊕			+	⊕	—	—	
Methyl acrylate	⊕					—	—	
Isopropyl acrylate	⊕							
Acrylamide	⊕							
Methacrylamide	⊕							
Vinyl acetate	+ ^b							
Formaldehyde	⊕	⊕						
Acetaldehyde	⊕	⊕				—		
Acetone	⊕					—		
Butyl ester of vinyl-sulfonic acid	⊕					—		
Dibutyl ester vinylphosphinic acid	⊕							

^a ⊕ = fast polymerization just at the melting point; ⊕ = fast polymerization below the melting point; + = fast polymerization, temperature unknown; — = no polymerization.

^b The metal atoms were excited before interaction with monomer.

In connection with the subject of the present paper the most interesting were the systems in which one could observe the explosion polymerization at the temperatures considerably below the melting points of the monomers. These systems involved acrylonitrile (AN) (m.p. $-83^{\circ}\text{C}.$, explosion polymerization temperature $-160^{\circ}\text{C}.$), methyl methacrylate (MMA) (m.p. $-50^{\circ}\text{C}.$, explosion polymerization temperature $-120^{\circ}\text{C}.$), methacrylamide (m.p. $103^{\circ}\text{C}.$, explosion polymerization temperature $-130^{\circ}\text{C}.$) in combination with magnesium, etc. In all cases conversion was about 100%. For AN-Mg system it has been shown that initiation occurred in the gaseous phase owing to interaction of monomer molecules and Mg atoms resulting in formation of free radicals having a proposed structure of the type $\text{Mg}-\text{CH}_2-\dot{\text{C}}\text{HR}$. The accumulation of radicals in the frozen monomer-initiator mixture was confirmed by an ESR method.⁵ For following

consideration it is important that joint condensation of monomer and initiator vapors results in the formation of the vitreous monomer layer containing trapped active sites. These sites, at a suitable moment start the explosion polymerization. The problem is what is this "suitable" moment?

First of all it has been shown by special experiments that introduction of the same active species into the equilibrium monomer liquid could not

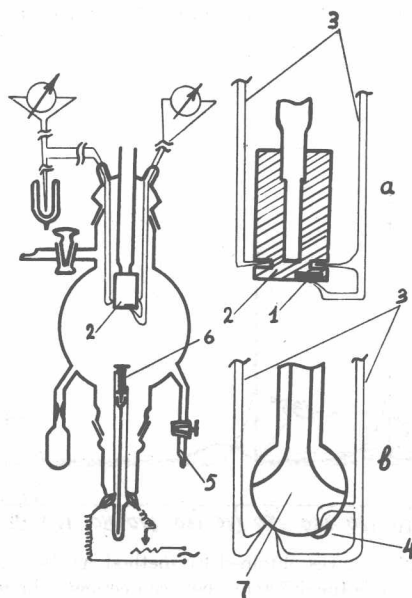


Fig. 1. Apparatus for thermal analysis of frozen molecular mixtures by (a) method A, (b) method B: (1) glass disk; (2) copper cylinder cooled with liquid nitrogen; (3) thermocouples; (4) protector of control solder of differential thermocouple; (5) inlet for monomer; (6) electrical kiln for Mg evaporation, (7) glass condenser.

initiate the fast polymerization.⁶ Hence fast polymerization phenomena are connected with the properties of a nonequilibrium vitreous monomer-initiator mixture.

We assumed that favorable conditions for explosion polymerization are brought about by crystallization of overcooled monomer containing active species.^{8,9} Such crystallization usually occurs considerably below the monomer melting point at that temperature when the time of nucleation (rate-determining step) becomes commensurable with time of experiment. In order to prove this assumption thermographic technique was used. The experiments were carried out in the device shown in Figure 1. Acrylonitrile introduced through inlet tube 5 and magnesium vapor (from electrical kiln 6) were condensed on the surface of the glass disk attached to the bottom of the cooled copper cylinder 2 (Fig. 1a, method A), or on the sur-

face of a glass condenser 7 (Fig. 1b, method B). The use of a combination of very thin thermocouples (0.015 mm.) attached to the surface and sensitive recording potentiometers (EPP-09) permitted continuous recording of the temperature changes in the cooled monomer-initiator mixture. For taking thermographic measurements a thin (0.02–0.03 mm.) AN–Mg layer was obtained on the surface of a condenser cooled by liquid nitrogen. The rate of condensation was controlled so as to maintain a surface temperature not higher than -175°C . The AN–Mg ratio was varied in the range from 1:100 to 1:1000. In Figure 2 typical thermographic curves

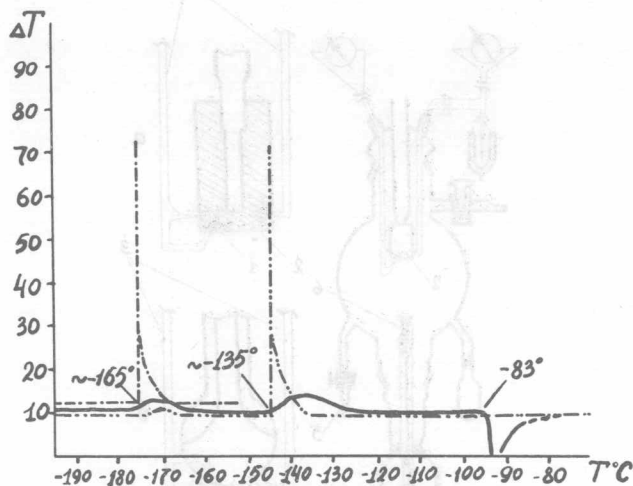


Fig. 2. Thermographic curves obtained by method A: (left to right): (1) and (2) AN + Mg; (3) AN; ΔT is the difference between copper cylinder and glass disk temperatures.

obtained by method A are represented. One can see that explosion exothermic polymerization occurs either at the temperature of -160°C . (curve 1) or at a temperature of -130°C . (curve 2), depending upon condensation conditions and rate of temperature increase. The thermographic curve of vitreous AN recorded in the same manner indicates that at these temperatures two exothermic phase transitions occur (curve 3). The first transition (-160°C .), which is followed by dulling of the layer, corresponds to nonequilibrium crystallization of vitreous monomer film when Tamman's temperature is reached. The nature of the second transition (130°C .) is not quite clear. It is probably related to an additional ordering process in the crystalline mass. Similar thermographic curves were obtained when method B was used (Fig. 3).

As part of the study it was of interest to ascertain whether the polymerization character changed if the monomer in the initial vitreous layer was diluted with large amount of inert diluent.* For this purpose the poly-

* In this part of the study, A. N. Gvozdetzky participated.

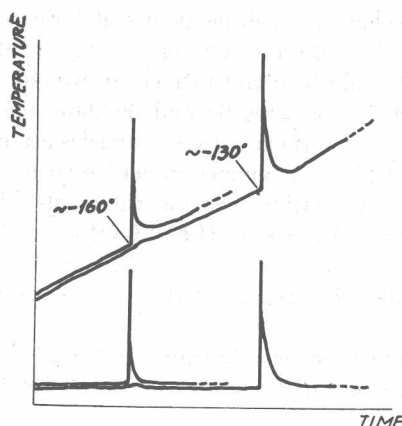


Fig. 3. Thermographic curves obtained by method B: (1) and (2) AN + Mg; (3) AN; (top) integral record; (bottom) differential record.

merization of acrylonitrile-*n*-hexane (AN-H) (m.p. $-95.3^{\circ}\text{C}.$), and acrylonitrile-cyclohexane (AN-CyH) (m.p. $6.5^{\circ}\text{C}.$) frozen molecular mixtures in 1:10 monomer-diluent molar ratio was studied. In special study it was found that at low temperatures the systems AN-H and AN-CyH were exfoliated (Figs. 4 and 5). This means that in course of crystallization of

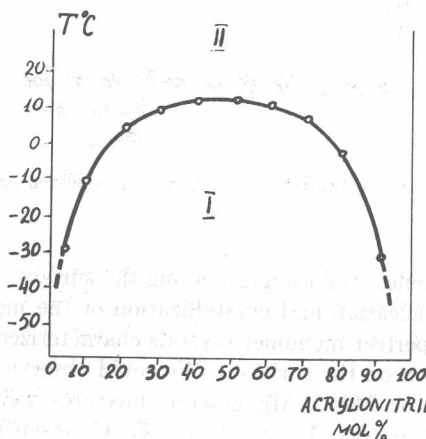


Fig. 4. Phase diagram of acrylonitrile-*n*-hexane: (I) solution area; (II) exfoliation area.

vitreous nonequilibrium mixtures two separate crystalline phases would be formed. In this series of experiments the gaseous AN-diluent mixture of strictly controlled composition and Mg vapors were simultaneously condensed on a surface cooled by liquid nitrogen. As in the case of AN without diluent, fast polymerization occurred when the nonequilibrium vitreous

layer crystallized below the melting points of both organic components. In spite of considerable dilution, AN conversion was about 100%. After melting the diluent could be quantitatively recovered and all polymer remained at the surface. Figures 6a and 6b show the polymer particles formed at the condenser surface. These particles are pseudomorphoses of AN crystals formed at the monomer-diluent mixture crystallization. It follows that fast polymerization occurs at the moment when AN separates into crystalline phase. In cases of H and CyH the picture is quite similar, although the AN melting point ($-83^{\circ}\text{C}.$) lies between the melting points of these two diluents. The results of the experiments are shown in Table II.

If the condenser surface temperature was higher than Tamman's temperature of the monomer under study (but lower than the melting point)

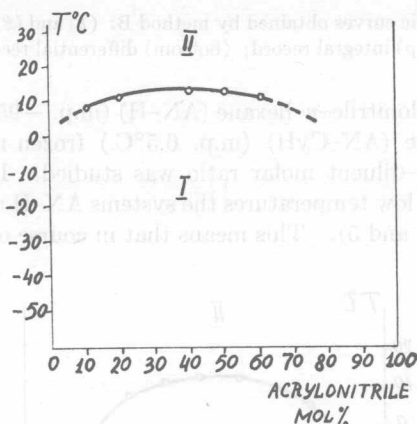


Fig. 5. Phase diagram of acrylonitrile-cyclohexane: (I) solution area; (II) exfoliation area.

the monomer molecules could migrate along the surface. Such migration was followed by nucleation and crystallization of the monomer. In this case aggregates of perfect monomer crystals characterized by typical birefringence were grown on the surface. We could observe such phenomena when the AN-Mg or MMA-Mg gaseous mixtures were condensed on surfaces cooled down to $-110^{\circ}\text{C}.$ and $-75^{\circ}\text{C}.$ respectively. The apparatus used has been described elsewhere.⁴ A photograph of MMA crystalline birefringent aggregate (spherulite) formed at the condenser surface is shown in Figure 7a. This picture was made in polarized light by using the long-focus microscopy technique. Although the crystals contained the initiator species no fast polymerization was observed even at temperatures considerably higher than the vitreous-crystal transition temperatures of the monomers. In perfect MMA crystals at $-75^{\circ}\text{C}.$ or in AN crystals at $-110^{\circ}\text{C}.$ the very slow polymerization proceeded at a

TABLE II
Polymerization of Acrylonitrile-diluent Mixtures (Monomer-Diluent Ratio 1:10)

No.	Diluent	Duration of con- densation, min.	Rate of condensation of mixture, g./min.	Mg evaporated, g.	Polymer formed		Diluent recovered		Molar ratio polymer: diluent recovered
					g.	mole $\times 10^3$	g.	Mole $\times 10^3$	
1	Cyclohexane	45	0.065	0.0055	0.200	3.76	3.203	38.1	1:10.2
2	"	30	0.066	0.0037	0.125	2.24	1.853	22.1	1:10.0
3	"	15	0.092	0.0053	0.082	1.55	1.302	15.5	1:10.0
4	n-Hexane	30	0.011	0.0055	0.168	3.17	3.007	35.0	1:11.1
5	"	30	0.007	0.0030	0.111	2.04	1.989	23.1	1:11.3

rate which was commensurable with irradiation polymerization rates of the crystalline monomers considerably below the melting points. The polymerization could be readily followed by means of the polarized light technique owing to the fact that the birefringence disappeared in the polymerized areas of the crystals. Using this technique we were able to demon-

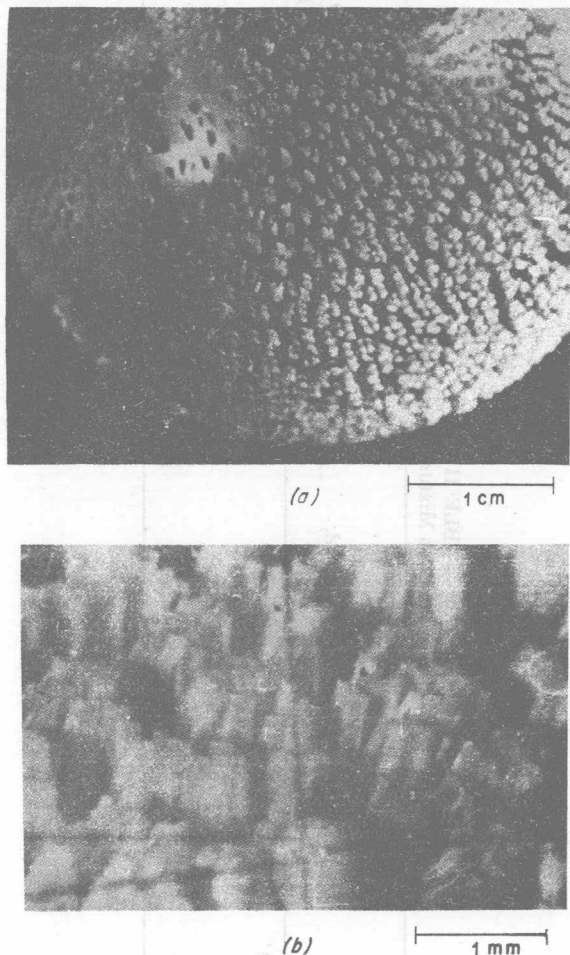


Fig. 6. Polyacrylonitrile particles on the condenser surface after melting of the diluent (a) hexane, (b) cyclohexane.

strate that the slow reaction started at the cracks or at the borders of the monomer crystals and then proceeded heterogeneously on the monomer-polymer interface. This interface could be clearly observed until polymerization was completed. The boundaries dividing polymerized and non-polymerized areas were also clearly detected in polarized light until poly-

merization was completed (Fig. 7b). (This picture is very similar to that for irradiation polymerization of acrylamide described by Adler, Ballantine, and Baysal.¹⁰) A very sharp increase of polymerization rate was observed when the crystals were heated up to 1–2°C. below the MMA melting point. In Figure 7c the same spherulite as in Fig. 7a is shown after completion of the polymerization. (The picture was made without polaroids.)

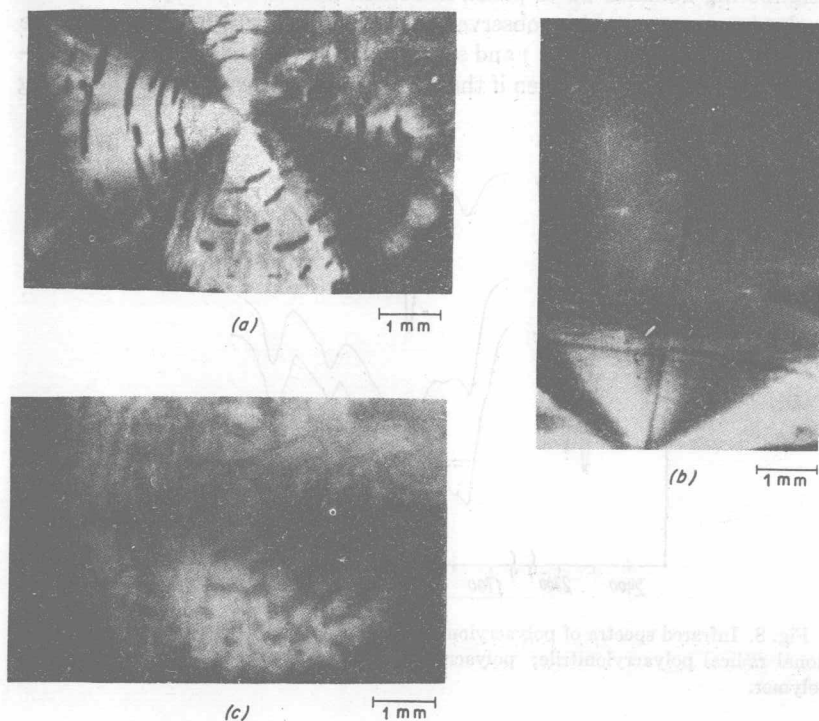


Fig. 7. Crystalline aggregates of MMA at different stages of polymerization: (a) before polymerization; (b) during polymerization; (c) the same area as in a but after polymerization was completed.

The crystalline aggregate was converted to polymer but the initial shape was not changed at all (with exception of some additional cracking owing to contraction). It is very difficult to distinguish the pseudomorphose and original spherulite without using polarized light. This fact shows that in case of good heat exchange the fast polymerization of crystalline monomers on the verge of melting is completed at the moment when the crystal has already reached the critical temperature but has not yet melted and transformed into a liquid drop.

On the basis of experimental data described, it is to be accepted that the fast polymerization in solid state is effected at a time of coordinated ordering or disordering of the monomer molecules. Apparently the ordered

arrangement of the monomer molecules combined with their coordinated mobility is the necessary condition of the instantaneous polymerization rise.^{8,9} It will be noted, however, that it is not necessary to heat the entire volume of the frozen monomer up to transition temperature. In definite case, local heating is enough to effect the explosion polymerization. The local polymerization heat might be sufficient to increase the temperature within neighboring domains up to phase transition and thermal explosion arises. Such phenomena could be observed in the course of condensation of some monomers (AN, MMA, etc.) and some initiators (Mg, Na, etc.) on the surface cooled by liquid nitrogen if the condensation was carried out for a long

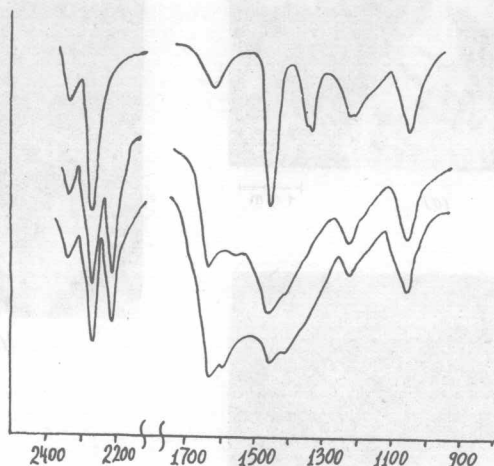


Fig. 8. Infrared spectra of polyacrylonitrile and copolymer (bottom to top): conventional radical polyacrylonitrile; polyacrylonitrile from explosion polymerization; copolymer.

time and resulted in formation of thick molecular mixture layers (owing to an increasing temperature gradient within the progressively thickened vitreous layer)^{4,7,8} Apparently the formaldehyde explosion polymerization observed by Enikolopyan¹¹ and Magat et al.¹² was characterized by the same mechanism.

It is of interest to note that the explosion polymerization peaks on the thermographic curves did not appear at all when the temperature of monomer (AN, MMA)-initiator vitreous layer was increased very slowly. In these cases the temperature increase was followed by crystallization of the monomers, but when the "crystallization" had been completed one could find that all the monomer had converted into the polymer. This means that the nonequilibrium phase transition is the rate-determining stage of the reaction. The explosion polymerization arises as the result of the acceleration of this transition by polymerization heat formation and subsequent disturbance of the steady heat exchange.

The molecular ray method is rather convenient for study of the copolymerization of frozen monomers because it permits homogeneous vitreous mixtures, containing any two or more monomers to be obtained. Such a mixture can be used as universal original system.

The infrared spectra of polyacrylonitrile (PAN) formed as the result of fast polymerization demonstrated that the polymer contained a number of $C\equiv N$ bonds (1640 cm^{-1}), which are practically absent in conventional radical polyacrylonitrile (Fig. 8 *a,b*). Therefore cleavage of $C\equiv N$ bonds proceeded at the same time as polymerization of $C-C$ bonds. In this connection we assumed that AN could be copolymerized with aliphatic nitriles in frozen molecular mixture. The AN-propionitrile (PN)-Mg system was used to confirm this assumption. It was demonstrated in special study that the AN-PN system is characterized with ordinary eutectic mixture of molar composition 43% AN + 57% PN (Fig. 9). There-

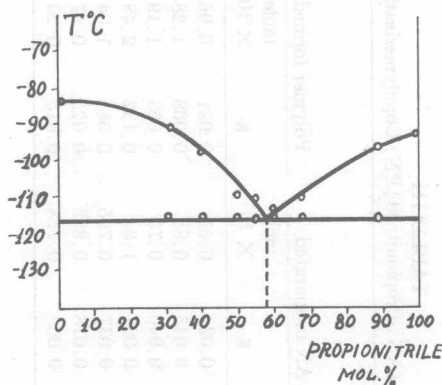


Fig. 9. Phase diagram of acrylonitrile-propionitrile system.

fore in course of crystallization of the AN-PN vitreous mixture the eutectic phase must be formed. It was also demonstrated in special experiments that no polymerization proceeded in the PN-Mg frozen molecular mixture. The data on AN-PN explosion copolymerization when the vitreous AN-PN molecular mixture containing active sites was crystallized (explosion polymerization temperature $-160^{\circ}\text{C}.$) are summarized in Table III. (The monomer ratio was strictly controlled by using gaseous AN-PN mixture of definite composition.)

From these data one could see that PN actually copolymerizes with AN. The infrared spectrum of the copolymer also showed the presence of $C\equiv N$ bonds (Fig. 8c). The copolymer as distinct from polyacrylonitrile obtained in absence of PN is not completely soluble in dimethylformamide. The dark-red, insoluble fraction (about 50 wt.-%) was dissolved only after several hours' hydrolysis with hydrochloric acid in dimethylformamide at elevated temperature (about $70^{\circ}\text{C}.$).