

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Radiation-Induced Solid-State Polymerization of n-Butylisocyanate at Low Temperature

I. Sugawara^a; E. Marchal^{ab}; H. Kadoi^a; Y. Tabata^a; K. Oshima^a

^a Faculty of Engineering, University of Tokyo, Tokyo, Japan ^b C. N. R. S., Centre de Recherches sur les Macromolécules, Strasbourg, Cedex, France

To cite this Article Sugawara, I. , Marchal, E. , Kadoi, H. , Tabata, Y. and Oshima, K.(1974) 'Radiation-Induced Solid-State Polymerization of n-Butylisocyanate at Low Temperature', *Journal of Macromolecular Science, Part A*, 8: 5, 995 — 1008

To link to this Article: DOI: 10.1080/00222337408066414

URL: <http://dx.doi.org/10.1080/00222337408066414>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Radiation-Induced Solid-State Polymerization of n-Butylisocyanate at Low Temperature

I. SUGAWARA, E. MARCHAL,* H. KADOI, Y. TABATA,† and
K. OSHIMA

Faculty of Engineering
University of Tokyo
Tokyo, Japan

ABSTRACT

An attempt was made to polymerize n-butylisocyanate at low temperatures (-78 to -196°C) in various (crystalline, glassy, supercooled, and liquid) states. It was found that the polymerization of n-butylisocyanate occurs in the supercooled state, but not in the crystalline and liquid states. It was possible to obtain a polymer when the monomer was irradiated in the glassy state at -196°C. However, it was confirmed that the polymerization does not take place under irradiation at that temperature, but that postpolymerization proceeds during the warming. The effect of additives shows that the postpolymerization of n-butylisocyanate may proceed via an anionic mechanism.

*C.N.R.S., Centre de Recherches sur les Macromolécules,
67083 Strasbourg, Cedex, France.

†To whom correspondence should be addressed.

INTRODUCTION

The polymerization of monoisocyanates by catalysts has been carried out by several authors [1-3]. According to Shashova, isocyanates polymerize at low temperatures (-20 to -100°C) by anionic catalysts such as sodium cyanide or sodium benzophenone. It is well known that isocyanates form cyclic dimers and trimers in the presence of basic reagents. It has been reported by Natta et al. that *n*-butylisocyanate is polymerized by lithium or sodium alkyl catalysts to give a crystalline polymer.

Previously, we reported on the radiation-induced solid-state polymerization of isocyanates [4]. However, detailed investigations on the effect of monomer phases and on the polymerization mechanism were not made.

On the other hand, it has recently been elucidated that the agglomeration state of monomer greatly affects both the mechanism of polymerization and the structure of the polymers formed in radiation-induced solid-state polymerization.

In the present work it has been found that crystalline, glassy, and supercooled states are easily obtained from pure *n*-butylisocyanate, depending on the cooling condition of the liquid monomer. The phase transition was detected by electric conductivity and thermal analysis. This paper is mainly concerned with a study of the effects of phases on the polymerization mechanism and the properties of the polymers obtained.

EXPERIMENTAL

Commercial *n*-butylisocyanate (Tokyo Kasei) was distilled and stored over calcium hydride in a glass vessel at -78°C. Prior to use, dry monomer was introduced by distillation into a 5-cc glass ampule under vacuum, and the ampule was degassed at 10^{-4} Torr and sealed off. All solvents, CCl_4 , $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{C}_2\text{H}_5\text{OH}$, and CCl_3H , were dried and distilled before use.

Samples were irradiated with a 3-kCi ^{60}Co source at dose rates of 1 to 3×10^5 rad/hr in a temperature range of -100 to -196°C. Low temperature control was achieved by the use of liquid nitrogen slushes of organic compounds such as isopentane (-158°C) and *n*-pentane (-131°C). A Dry Ice-methanol mixture was used to maintain -78°C. After irradiation, samples were treated in different ways: 1) the samples were warmed up to -78°C, 2) the samples were warmed up to -158°C, and 3) the samples were ground to

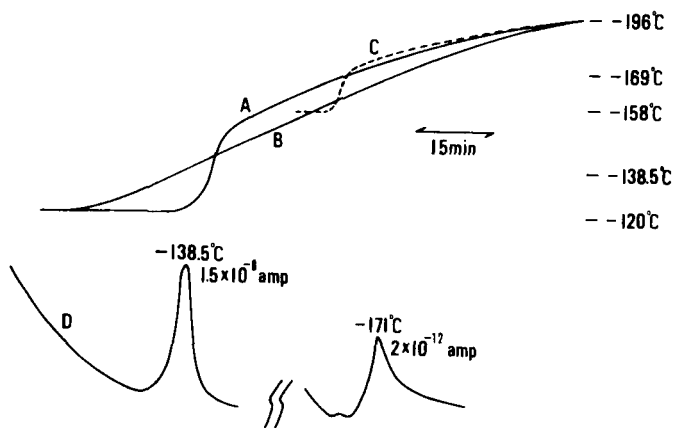


FIG. 1. Thermal analysis and electric conductivity of n-butylisocyanate: (A) glassy sample, (B) crystalline sample, (C) irradiated glassy sample, and (D) electric conductivity of a glassy sample.

pieces in liquid nitrogen and then dissolved quickly in hot acetone to prevent post-irradiation effects. After such treatments, precipitated polymers were filtered and dried under vacuum to a constant weight.

Measurements of electric conductivity and thermal analysis of solid monomer were carried out to detect the glass transition point by the method described in a previous paper [5].

Molecular weight and polydispersity (M_w/M_n) of the polymer were determined from the measurement of dielectric constant of the polymer solution in carbon tetrachloride, using the data of Bur and Roberts [6] as the calibration curve. The apparatus used was described elsewhere [7]. Viscometry was not applicable to these polymers because of the high viscosity of the polymer solution.

RESULTS AND DISCUSSION

In Fig. 1 the results of electric conductivity measurements and thermal analysis of solid monomers are shown as a function of time. The melting point was determined to be -120°C from Curve B. The peaks at -171 and -138.5°C of Curve D were found to correspond to

TABLE 1. Crystalline Samples

Irradiation temp (°C)	Dose (Mrad)	Conversion (wt %)
-196	0.6	0
	2.1	0.4
	4.1	0.3
-158	0.4	0.1
	1.8	0.1
-131	2.3	0.1
	0.8	0.2
<u>Liquid samples</u>		
-78	2.0	0
	5.0	0

the glass transition point and crystallization temperature, respectively. In the Curve C of the γ -irradiated glassy sample, an exothermic phenomenon was observed above the glass-transition point (-171°C).

As shown in Table 1, polymer yield is very small when the monomers are irradiated in the crystalline state, and polymerization does not take place in the liquid state at -78°C.

In Fig. 2 the polymerization of glassy samples at -196°C is shown in plots of percent conversion vs irradiation time when the irradiated samples were treated according to Method 1. At a dose rate of 2.3×10^5 rad/hr, the initial rate of polymerization was 6%/hr without any induction period. A limiting yield (8.5%) was observed.

In order to find the post-irradiation effects, Methods 2 and 3 were examined. The results are shown in Fig. 3 and Table 2, in comparison with those from Method 1. As shown in Fig. 3, the rate of polymerization is higher than 15%/hr in the initial step, with a limiting yield of about 14%. In Table 2 it is seen that when the irradiated samples were rapidly dissolved according to Method 3, the conversion is much lower than when they were slowly warmed up according to Method 1. This seems to show that the polymerization of glass monomers occurs mainly in the warming up process of irradiated samples. This is also supported by the exothermic

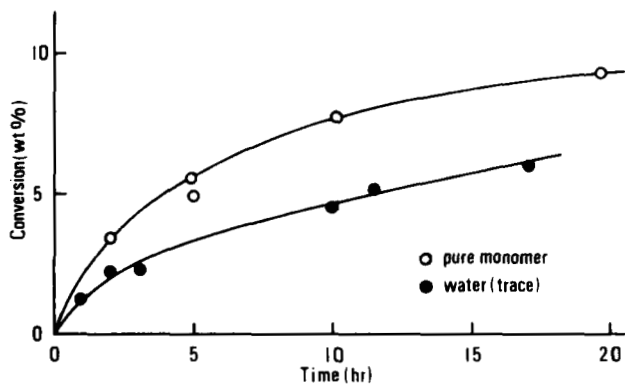


FIG. 2. The polymerization of glassy samples at -196°C and effect of trace amount of water. Dose rate: 2.3×10^5 rad/hr.

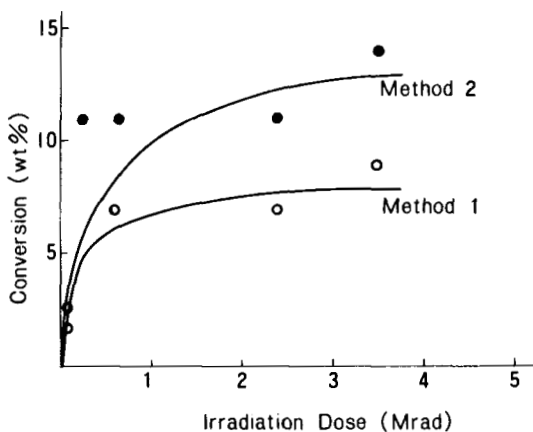


FIG. 3. Effect of after-treatment on the conversion. Method 1 treatment at -78°C . Method 2 treatment at -158°C .

phenomenon observed in the thermal analysis of irradiated glass monomers.

In Fig. 4 the polymerization of supercooled monomers at various temperatures is shown in plots of percent conversion vs irradiation

TABLE 2

Dose (Mrad)	Method 1 (%)	Method 3 (%)
5	6.9	1.2
12	6.6	1.7

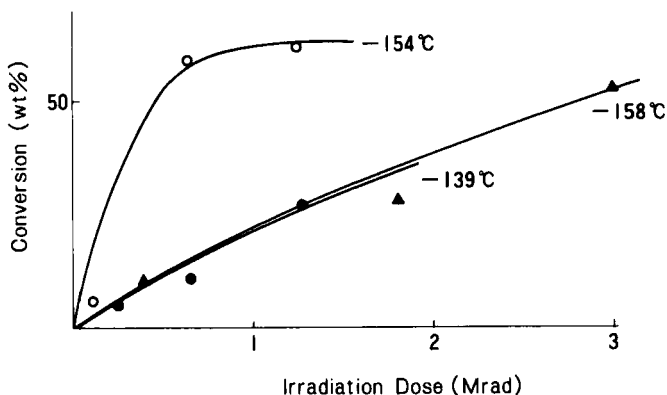


FIG. 4. The polymerization of supercooled monomers at various temperatures. Dose rate: 1.3×10^5 rad/hr.

doses. At a dose rate of 1.3×10^5 rad/hr, the initial rates of polymerization are about 17%/hr at -154°C and 2%/hr at both -139 and -158°C . There is no induction period at any temperature. The limiting yield is about 60% at -154°C . The percent conversions are plotted against temperature at a constant dose of 6.5×10^5 rad in Fig. 5. The maximum rate of polymerization was observed at -154°C . Polymerization in the supercooled state was found to be insensitive to the post-irradiation treatment. Therefore, the in-source polymerization is considered to occur in the supercooled state.

Radical scavengers such as DPPH (1 mole %) or oxygen (trace) were found not to affect the postpolymerization of glass monomers. The effect of water (trace) on the post and in-source polymerization is shown in Figs. 2 and 6, respectively, and in Fig. 7 the effects of triethylamine (1 mole %) and carbon tetrachloride (1 mole %) are indicated. The addition of these ion scavengers reduces the initial

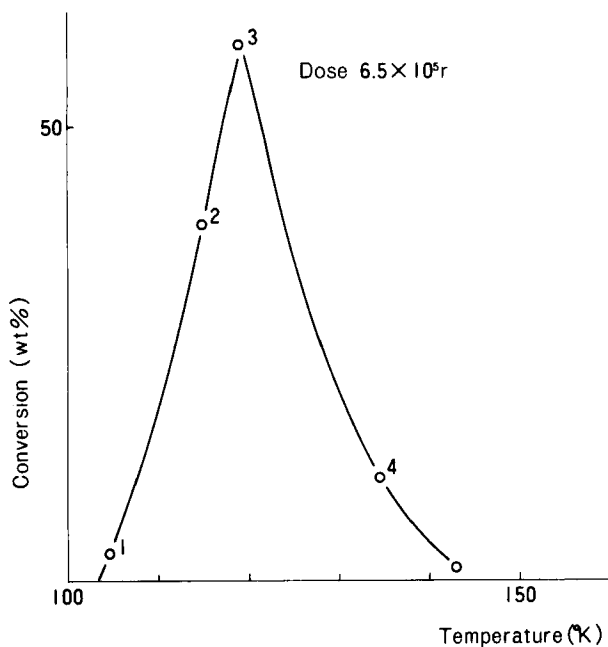


FIG. 5. Effect of temperature. Dose: 6.5×10^5 rad.

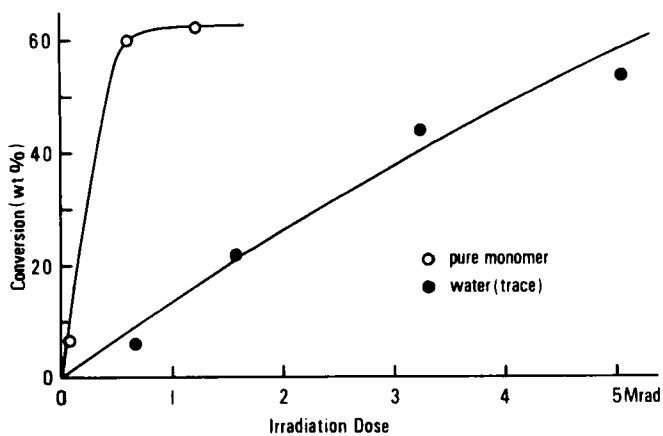


FIG. 6. Effect of trace amount of water for in-source polymerization.

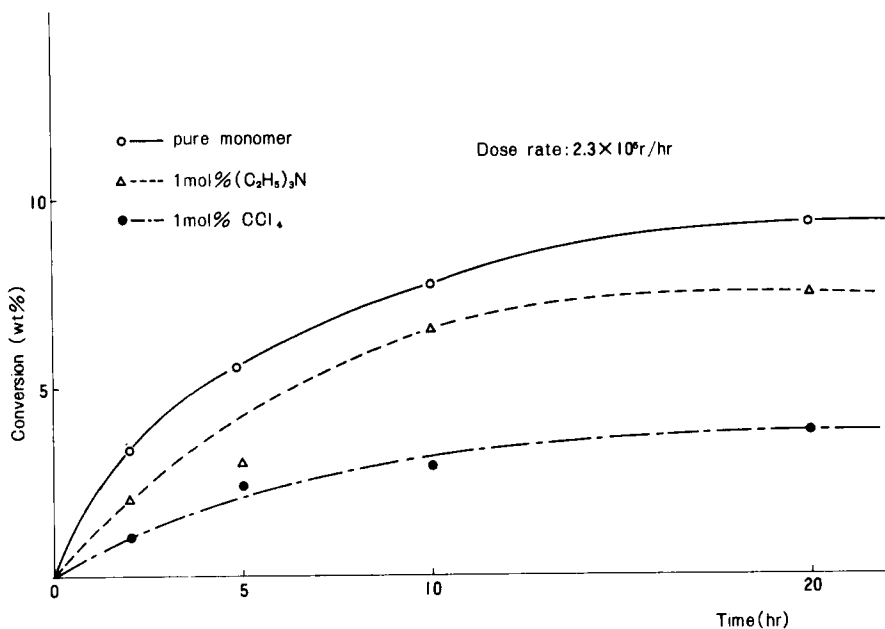
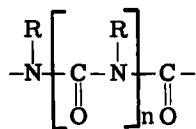


FIG. 7. Effect of additives. Dose rate: 2.3×10^5 rad/hr.

rates of polymerization and limits yields, but no induction period was observed in the presence of these additives.

Conversion in the in-source polymerization also decreases in the presence of a trace amount of water. These results indicate that the polymerization of *n*-butylisocyanate proceeds by an ionic mechanism.

In Fig. 8 the IR spectra of the polymers formed in the postpolymerization are shown. The same spectra were also observed with the polymers obtained by in-source polymerization. These spectra were found to be identical with those of polymers obtained with an anionic catalyst [1, 2] as reported previously [4]. This result indicates that the structure of the polymers obtained by radiation-induced polymerization is the same as that of the polymer obtained by catalytic polymerization, which was reported to have the regular structure:



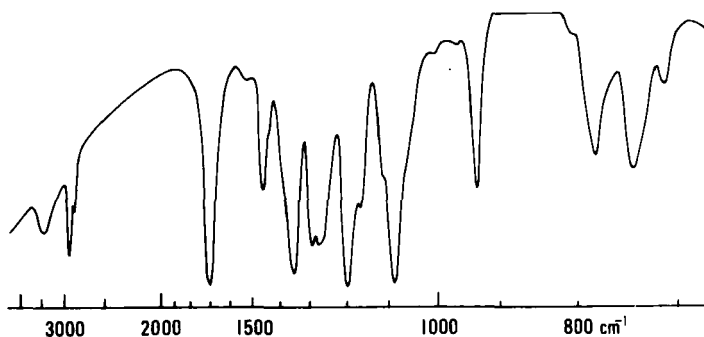


FIG. 8. IR spectrum of the polymer formed in the postpolymerization.

The polymers formed in postpolymerization can be easily dissolved in carbon tetrachloride, toluene, and chloroform, but the polymers obtained at high conversion in the in-source polymerization were only slightly soluble in these solvents. It may be reasonable to conclude that polymers at high conversion have high molecular weights arising from cross-linking or branching reactions.

In Table 3 are shown the molecular weight and the polydispersity of the samples obtained at different temperatures together with G values of initiation (G_1). Polydispersity in the samples at low conversion is close to unity, but it is too high to be determined from the dielectric method in the samples at high conversion. This high polydispersity of the polymers at high conversions is considered to be due to the cross-linking or branching reaction suggested above.

In Fig. 9 the molecular weight and polydispersity of polymers obtained by the postpolymerization are plotted against pre-irradiation time. In the bulk as well as for monomers containing carbon tetrachloride, the molecular weights decrease with increasing irradiation dose. On the other hand, the change of molecular weight by pre-irradiation dose is rather small in the system containing triethylamine. The polydispersity is smaller in the system containing additives than in the pure system.

In Fig. 10 the variation of G_1 for postpolymerization is shown as a function of pre-irradiation time. In both pure monomer and in the system containing triethylamine, G_1 decreases as the pre-irradiation dose is increased, while in the system containing carbon tetrachloride,

TABLE 3

Sample	M_w/M_n	$M_w \times 10^{-5}$	$G_T \times 10^{-3}$	G_i
1	1.18	0.93	0.5	0.47
2	High	-	6.4	
3	-	-	9.6	
4	~ 1.5	5.0	1.9	0.9

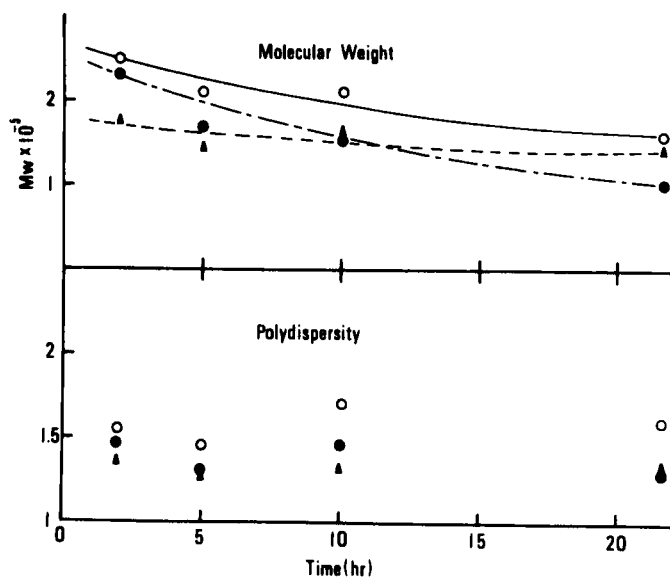


FIG. 9. Molecular weight and polydispersity of polymers obtained by postpolymerization.

G_i is very small and does not change with the pre-irradiation dose.

The decrease in G_i with increasing pre-irradiation dose is probably due to the recombination reactions between different ionic species formed by radiation in the system.

Carbon tetrachloride is known as electron scavenger, and the

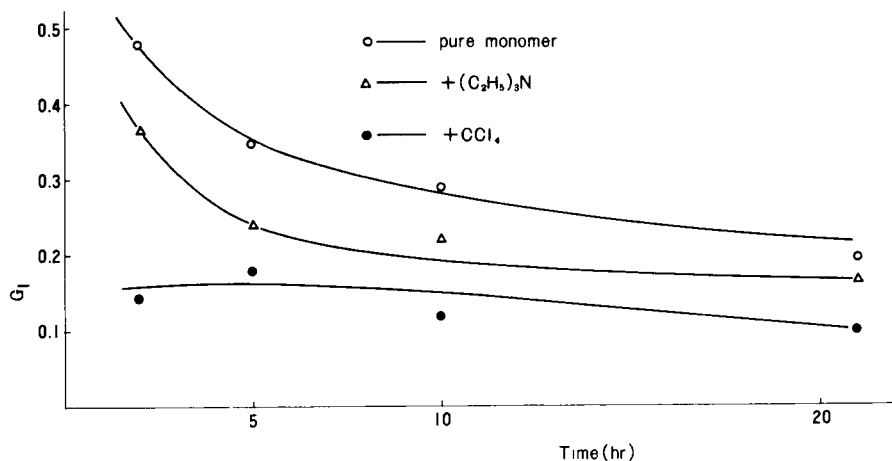


FIG. 10. G_i value of initiation (G_i) for postpolymerization.

decrease in G_i by small amounts of carbon tetrachloride results from the scavenging of anionic species by carbon tetrachloride. Thus it is concluded that postpolymerization proceeds via an anionic mechanism in this system.

Trimethylamine, a well-known cation scavenger, will react with the cationic species formed in the system and yield the corresponding cation species, which probably contribute effectively to the termination reaction.

In Figs. 11 and 12 ESR spectra of irradiated glassy and crystalline monomers are given. The spectrum in the glass monomers is remarkably dependent on the temperature, and gives a quintet with a hyperfine coupling constant of about 20 G above -171°C , which is assigned to the $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}=\text{C}=\text{O}$ radical. On the other hand, the spectrum in the crystalline sample does not change until the melting point where the signal disappears. These spectra change remarkably by photobleaching with an ultrahigh pressure mercury lamp, but polymerization is not affected by photobleaching.

Polymerization was also tried with other isocyanate derivatives, and polymers were obtained by the irradiation of n-propyl and ethyl isocyanates in the glassy state. In the case of ethyl isocyanate, it was found that polymerization takes place rapidly in a narrow temperature region a little lower than the melting point.

From these results and the above discussion, the following mechanism is proposed.

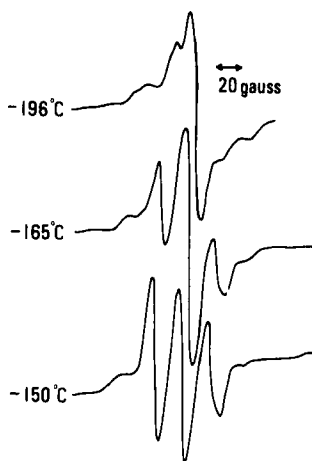
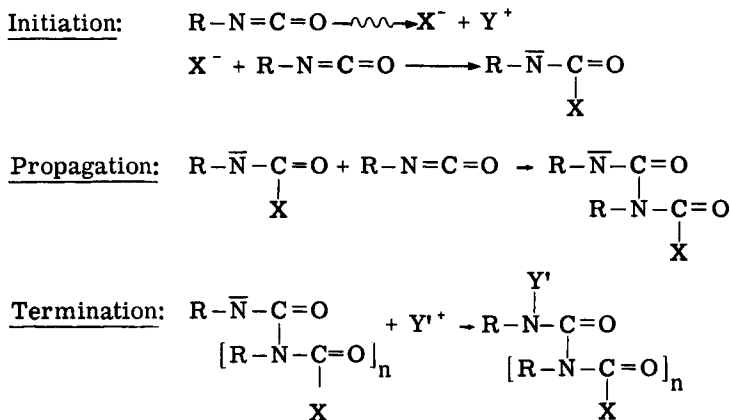


FIG. 11. ESR spectra of irradiated glassy monomer.

To account for the effect of the monomer phase on polymerization, it seems essential to take into consideration two factors: the lifetime of the active species, probably the anionic species, and the mobility of the monomer. The lifetime of the active species may be too short in the liquid state for polymerization to proceed, but it may be long enough in the supercooled liquid state owing to the high

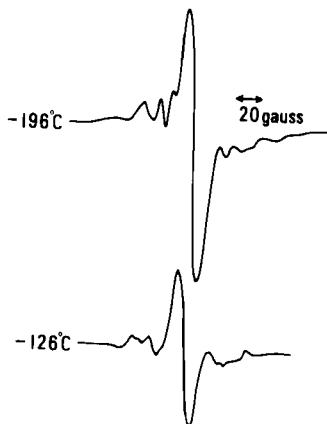


FIG. 12. ESR spectra of irradiated crystalline monomer.

viscosity of the monomers. In the glassy and crystalline states the mobility of the molecules is too small for polymerization. Furthermore, it would be necessary to take into account the effect of the crystalline lattice for crystal monomers.

ACKNOWLEDGMENT

We wish to express our thanks to Dr. Ishigure for useful discussions.

REFERENCES

- [1] V. E. Shashova, W. Sweeny, and R. F. Tietz, J. Amer. Chem. Soc., **82**, 866 (1960).
- [2] G. Natta, J. DiPietro, and M. Cambini, Makromol. Chem., **56**, 200 (1962).
- [3] T. Kashiwagi, M. Hidai, Y. Uchida, and A. Misono, J. Polym. Sci., **B**, **8**, 173 (1970).
- [4] H. Sobue, Y. Tabata, and M. Hiraoka, Ibid., **C**, **4**, 943 (1963).
- [5] H. Kadoi, Y. Tabata, and K. Oshima, J. Phys. Chem., **74**, 3962 (1970).

- [6] A. J. Bur and D. E. Roberts, *J. Chem. Phys.*, 51, 406 (1969).
- [7] E. Marchal, Thesis, University of Strasbourg, France, 1964.

Accepted by editor February 20, 1974

Received for publication March 1, 1974