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THE MELTING POLYMERIZATION OF ACETALDEHYDE

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The melting polymerization of acetaldehyde is studied. The melting polymerization does not change by the pretreatment of various immersion time in liquid nitrogen and the surface effect with various surface area which is in contact with acetaldehyde, but is affected by the ΔT which is the temperature difference between the melting point of acetaldehyde and the reaction temperature.

The yield and the intrinsic viscosity of the polymer increase as being smaller the ΔT. On the other hand, the intrinsic viscosity diminishes with reaction time.

From the initial rate of the melting polymerization, the value of -4.46 kcal/mole is obtained as the apparent activation energy and this value is in good agreement with the values obtained from the high pressure polymerization of acetaldehyde at low temperature with no catalyst¹⁾.

The presence of the substances mixed homogeneously with acetaldehyde retards the melting polymerization remarkably in the same way as the high pressure polymerization. The effect of small amount of water or acetic acid on the melting polymerization is analogous to the high pressure polymerization rather than the freezing polymerization. Namely, the polymer yield of the melting polymerization is little affected by water, but the presence of acetic acid retards the melting polymerization remarkably.

Introduction

On the polymerization of acetaldehyde, Travers2) and Letort3) had reported with regard to the freezing polymerization in the first place, and it had been confirmed that the solidification of the acetaldehyde was indispensably necessary for the polymerization of acetaldehyde with no catalyst. On the other hand, the polymerization of acetaldehyde also occurred at the melt of acetaldehyde.

With regard to the freezing polymerization of acetaldehyde, the effects of various factors for this polymerization were studied by Hinshelwood4) and Bevington5), etc. However, those studies were made on the freezing polymerization of acetaldehyde, and little attention has been paid to the melting polymerization.

It was found that the high pressure polymerization of acetaldehyde at low temperature with no catalyst took place at the liquid-solid transition by pressure as described in the previous paper1). It

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1) T. Mizukami, *This Journal*, **35**, 51, 60 (1965)
2) M. S. Travers, *Trans. Faraday Soc.*, **32** 246 (1936)
3) M. Letort, *Compt. rend.*, 202, 767 (1936)
4) H. A. Rigby, C. J. Danby and C. N. Hinshelwood, *J. Chem. Soc.*, 234 (1948)
5) J. C. Bevington and R. G. Norrish, *Proc. Roy. Soc.*, **A196**, 363 (1948)

had been found that the effects of the added substances on the high pressure polymerization were different from the freezing polymerization, especially its difference was remarkable on the effects of water and acetic acid. It was found in this experiment that the melting polymerization was more similar to the high pressure polymerization rather than the freezing polymerization. This paper reports the results obtained from the study on the effects of various factors for the melting polymerization of acetaldehyde.

Experimentals

Acetaldehyde and the other substances used are the same as described in the previous paper1).

The schematic layout of the apparatus is shown in Fig. 1. Acetaldehyde (b. p. 20.8~21.0°C) being obtained by the decomposition of paraldehyde is stored in A and distilled into B under reduced pressure. B is the glass burette with the graduation of 0.1 m*l* for measuring the volume of acetaldehyde. In order to measure the volume of acetaldehyde at 0°C, the glass burette is immersed in the jacket C of 0°C. Again 5 m*l* of acetaldehyde at 0°C is distilled under reduced pressure from B into the reaction vessel F. The amount of acetaldehyde is 5 m*l* at 0°C for all experiments in this paper. The distillation under reduced pressure from B to F is performed by maintaining the temperature of B at 0°C and that of F −78°C. After acetaldehyde is distilled into F, the acetaldehyde is frozen by immersing F into liquid nitrogen, and then F is immersed into the cryostat which is kept at the reaction temperature. After the definite time of dipping in the cryostat, F is immersed in water-ice bath to melt the remaining solid acetaldehyde. The solution in F is poured into water. The polymer deposited is recovered, dried under reduced pressure at room temperature and weighed. The intrinsic viscosity of the polymer is measured at 27.5°C in the solution of methyl ethyl ketone by using the Ostwald viscometer.

On the other hand, when the substances are added to acetaldehyde, after the substances are put in F, F is maintained below the freezing point of the substance. Removing the air in F, acetaldehyde is distilled under reduced pressure from B to F and the following treatments are carried out as described above.

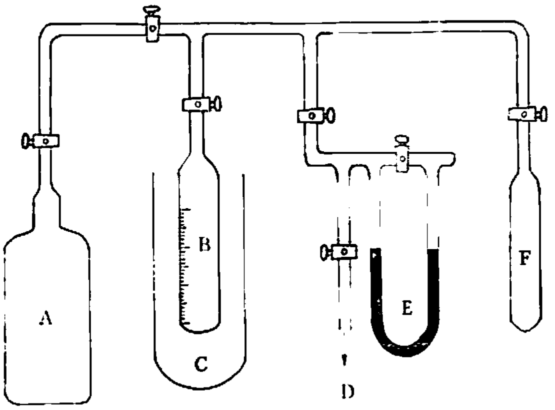

Fig. 1 Apparatus
A: storage of acetaldehyde
B: glass burette
C: jacket
D: system of vacuum pump
E: manometer
F: reaction vessel

The reaction vessel F is made of glass of 16 mm in inner diameter and 18 mm in outer diameter. Except for the study on the effect of the surface this reaction vessel F is always used in the present experiments. The cryostat consists of a Dewar vessel containing petroleum ether which is stirred. The temperature of the cryostat is controlled within ±0.1°C by dropping liquid nitrogen into the copper tube which is placed in petroleum ether. Temperature is measured by calibrated iron-constantan thermocouple.

Results and Considerations

Nature of polymer

The infrared spectrum of the polymer is shown in Fig. 2. The solubility of the polymer in the solvents is the same as described in the previous paper[1]. Then, the polymer obtained by the melting polymerization is the atactic polyether type polymer.

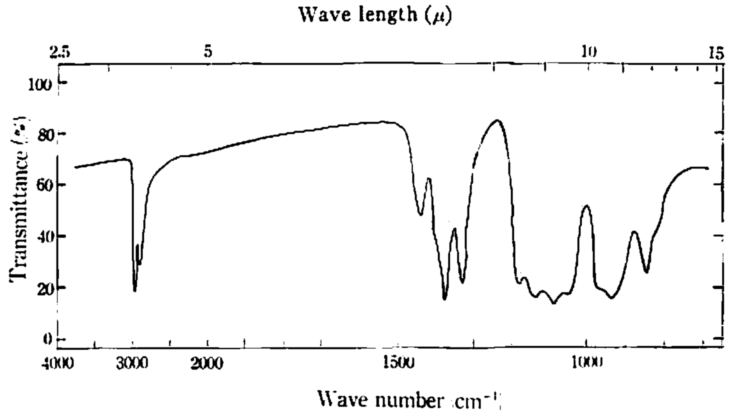

Fig. 2 Infrared spectrum of polymer

Reproducibility of experiment

Table 1 Reproducibility of experiment

		a	b	
		Y	Y	$[\eta]$
1		4	122	4.52
2		6	126	4.43
3		5	125	4.50
4		4	127	4.40
$\bar{x}$	mean value	5	125	4.46
s^2	variance	0.688	3.500	0.0024
s	standerd deviation	0.828	1.866	0.049
$s/\bar{x}$	coefficient of variation	0.166	0.375	0.0079
σ_e^2	unbiased variance	0.917	4.667	0.0033

Y; the polymer yield (mg) $[\eta]$; the intrinsic viscosity (dl/g)

In order to ascertain the reproducibility of experiment the following experiments are carried out. Experimental condition of case (a); the immersion time in liquid nitrogen is 10 minutes and the solid acetaldehyde is melted in the ice-water bath, and that of case (b); the immersion time in liquid nitrogen is 10 minutes and the melting polymerization is performed at −120.0°C for 20 minutes. The reproducibility of experiment is very good as shown in Table 1.

Effect of immersion time in liquid nitrogen

The effect of the immersion time in liquid nitrogen for the melting polymerization is studied. The experimental conditions of cases (a) and (b) are the same as described above.

Table 2 Effect of immersion time in liquid nitrogen

Time (min)		5	10	20	60	120	1440
a	Y	4	5	6	4	4	5
b	Y	122	125	125	127	125	121
	$[\eta]$	4.38	4.46	4.40	4.57	4.52	4.48

Kargin et al⁶⁾. found that the radiation induced polymerization of acetaldehyde showed the effect of pretreatment which had the difference of the immersion time in liquid nitrogen before radiation. However, the difference of the immersion time has no effect on the melting polymerization. The polymer yield and the intrinsic viscosity are not changed by the difference of the immersion time as shown in Table 2. On the other hand, it is evident from case (a) that the polymerization does not take place at the solid state.

Effect of reaction vessel

The effects of the diameter of the reaction vessel and the surface area being in contact with acetaldehyde are studied. The thickness of the glass of the reaction vessel is 1 mm, and the inner diameters are 16 mm for case (a), 20 mm for (b) and 24 mm for (c). The surface area being in contact with acetaldehyde is smaller as following order, (e)>(d)>(a)>(b)>(c). The experimental condition is as follows: the immersion time in liquid nitrogen; 10 minutes, reaction temperature; −120.0°C, reaction time; 20 minutes. The results obtained are shown in Table 3.

Table 3 Effect of reaction vessel

Reaction vessel	a	b	c	d	e
Y	125	123	128	127	122
$[\eta]$	4.46	4.62	4.38	4.54	4.51

Norrish⁵⁾ found that the surface nature of the receiver for acetaldehyde vapor did not affect the freezing polymerization. In this study, it is found that the melting polymerization is not affected by the difference of the surface being in contact with monomer and by the gradient of temperature on the

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6) V. A. Kargin, V. S. Pshezhctskii and N. A. Bakh, *Bicokomolek. Coedinenya*, 3, 925 (1961)

solid monomer changed by the difference of the vessel diameter. Accordingly, it is considered that the melting polymerization is not initiated by the mutual action of the vessel surface and acetaldehyde, but the catalytic action of the nucleus of crystal of acetaldehyde at the liquid-solid interface.

Effect of reaction temperature

At various reaction temperatures and 10 minutes immersion time in liquid nitrogen, the changes of the yield and the intrinsic viscosity of the polymer are studied as shown in Table 4.

Table 4 Effect of reaction temperature

Temperature (°C)		Reaction time (min)					
		5	10	20	30	60	90
−125.0	Y	6	6	4	5	6	4
−123.0	Y	125	179	200	210	230	235
	$[\eta]$	6.61	5.80	5.27	4.86	4.27	3.82
−121.5	Y	114	135	140	150	155	152
	$[\eta]$	6.30	5.47	4.90	4.42	3.96	3.57
−120.0	Y	110	120	125	133	135	135
	$[\eta]$	5.93	4.95	4.46	3.92	3.45	3.36
−118.0	Y	100	109	117	124	126	
	$[\eta]$	5.49	4.75	3.67	3.30	3.28	
−116.0	Y	79	82	85	84	86	
	$[\eta]$	5.10	4.23	3.42	3.24	3.23	
−114.0	Y	65	68	70	68	69	
	$[\eta]$	4.78	3.94	3.15	3.09	3.09	

The melting point of acetaldehyde is −123.5°C, so at −125.0°C acetaldehyde remains in the solid and does not polymerize. The relation of the yield and reaction time at various reaction temperatures is shown in Fig. 3. As shown in Fig. 3 and Table 4, the yield is remarkably enhanced and the intrinsic viscosity is also high at the initial period of the reaction time, but the increasing ratio of the yield to reaction time is smaller and the intrinsic viscosity is lower with reaction time. As the melting polymerization is not affected with the vessel surface as described above, the other reason for this phenomenon must be considered.

In the melting polymerization, it is supposed that any acetaldehyde being at the solid-liquid interface has not always the ability of polymerization but acetaldehyde being the conjugate alignment of the carbonyl group performs the polymerization by the catalytic action of the nucleus of crystal of acetaldehyde at the solid-liquid interface.

As the conjugate of the carbonyl group and the melting speed of acetaldehyde may be determined by the ΔT which is the difference of the temperatures between the melting point of acetaldehyde and reaction temperature, it is considered that as far as the interface of the solid-liquid is in existence, the melting polymerization occurs at a constant ratio in the experimental condition. However,

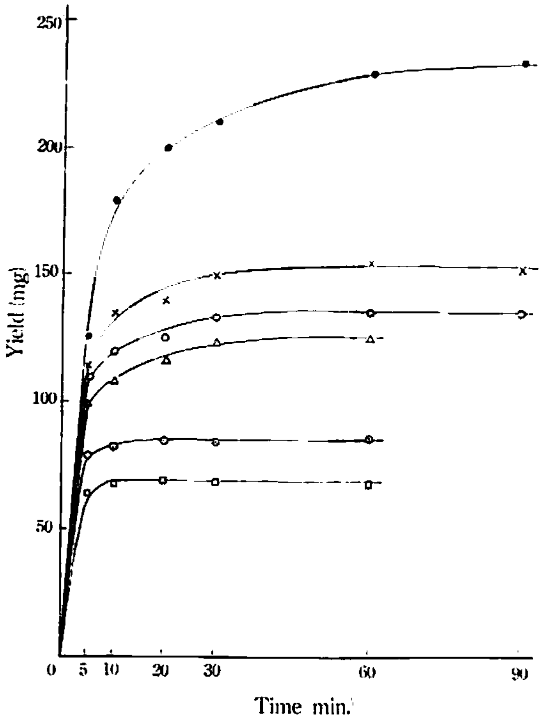

Fig. 3 Yield-time curves at various reaction temperatures
−123.0°C (●) −121.5°C (×)
−120.0°C (○) −118.0°C (△)
−116.0°C (⊙) −114.0°C (□)

the liquid acetaldehyde having melted with no polymerization alters the liquid-solid interface to the unfavourable state for the melting polymerization of acetaldehyde. And then the yield is remarkably enhanced and the intrinsic viscosity is high at the initial period of reaction time.

The initial rate of the melting polymerization is obtained from Fig. 3 as shown in Table 5.

Table 5 The initial rate

Temperature (°C)	−114.0	−116.0	−118.0	−120.0	−121.5	−123.0
$k_i \times 10^5$	4.78	5.93	7.53	8.86	10.19	11.53

Plotting the initial rate against the ΔT and the intrinsic viscosity, the linear relations are obtained as shown in Figs. 4 and 5. This indicates that the relations of those factors are in the following equations (1) and (2), and the melting polymerization is settled with the ΔT. From equations (1) and (2), equation (3) is obtained. Plotting the initial rate against the intrinsic viscosity, the linear relation is given as shown in Fig. 6. Fig. 6 shows that the second term of equation (3) is negligible, then equation (4) is obtained.

$$k_i = \alpha \Delta T + \alpha' \tag{1}$$

$$[\eta] = \beta \Delta T + \beta' \tag{2}$$

$$k_i = \gamma [\eta] + \gamma' \tag{3}$$

$$k_i / [\eta] \fallingdotseq \text{constant} \tag{4}$$

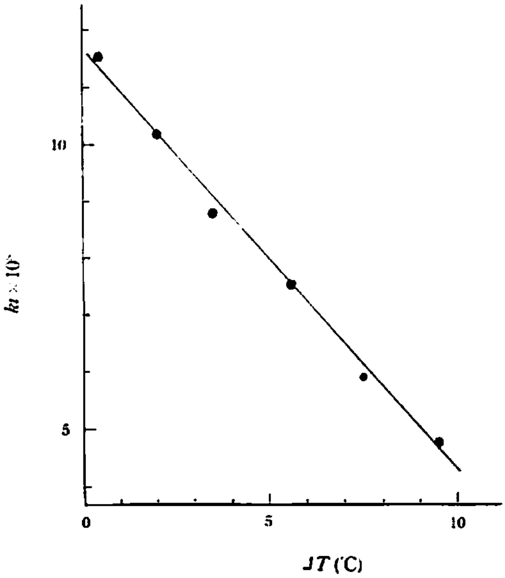

Fig. 4 Relation between the ΔT and the initial rate

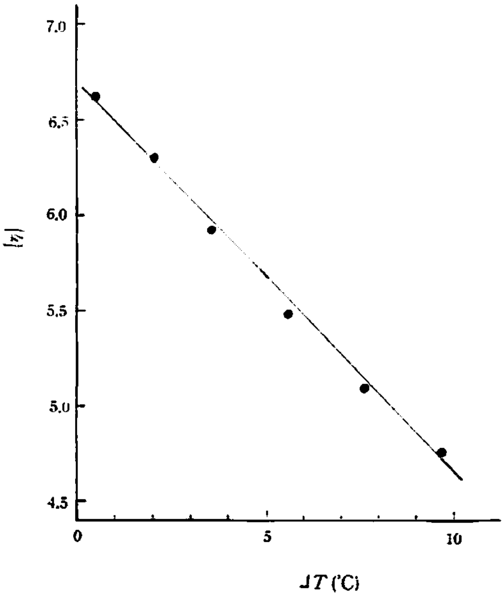

Fig. 5 Relation between the ΔT and the intrinsic viscosity

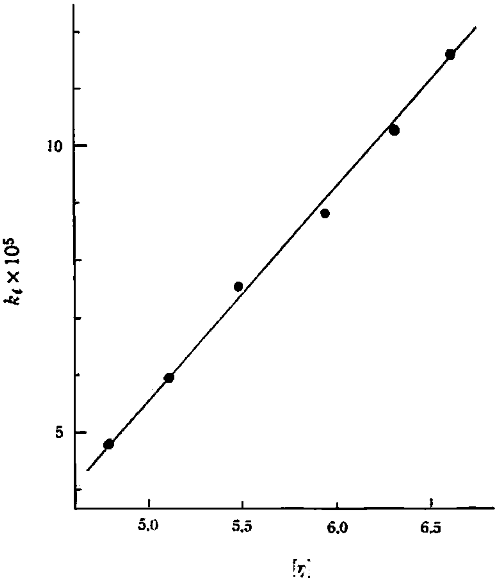

Fig. 6 Relation between the intrinsic viscosity and the initial rate

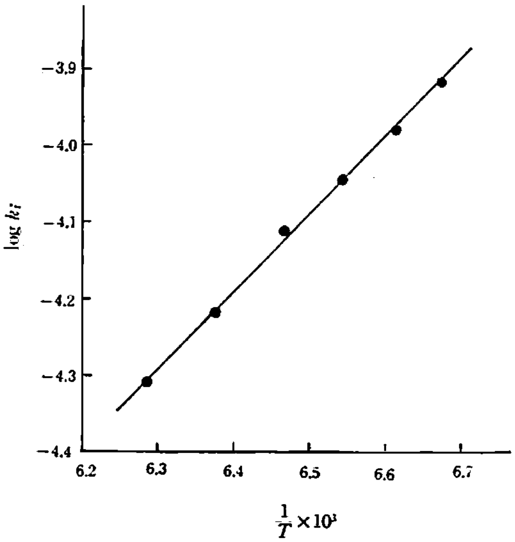

Fig. 7 Effect of temperature on the initial rate

This proves that the numbers of the polymer are essentially the same on each polymerization. and the initiation of the melting polymerization occurs at a constant ratio as described above.

The apparent activation energy is obtained from the slope of plot of the logarithm of the initial rate against the reciprocal of absolute temperature as shown in Fig. 7. The obtained value is −4.46

kcal/mole. This value is in good agreement with the values $-3.17 \sim -4.51$ kcal/mole obtained by the high pressure polymerization of acetaldehyde as described in the previous paper[1]. Applying the relation $E \fallingdotseq \Delta H^{\ddagger}$, from the apparent activation energy and the frequency factor the value of -104.7 cal/deg. mole is calculated as the activation entropy at -123.0°C. This value is also in good agreement with the values of the high pressure polymerization[1].

Accordingly, it is concluded that those values show the activated state of the melting polymerization has the limiting alignment of acetaldehyde, and then the melting polymerization is affected by the liquid acetaldehyde.

Effect of solvent

Using the solution of acetaldehyde which has the volume ratio of 1 : 1, the effects of the solvents are studied under the same experimental condition as described in the effect of reaction vessel. The solvents studied are the essentially same as described in the previous paper[1], for example, alcohols, ketones, halogenated hydrocarbons, hydrocarbons etc.

In the solvents of hydrocarbons, the melting polymerization takes place as in the high pressure polymerization[1]. Varying the amount of solvents, the effects of the hydrocarbons are studied as shown in Table 6.

Table 6 Effect of solvent

Solvent		Amount of solvent (ml)				
		1	3	5	7	10
iso-pentane	Y	36	30	22	18	15
	$[\eta]$	1.90	2.00	1.86	1.92	1.85
petroleum ether	Y	40	31	27	25	22
	$[\eta]$	2.00	2.12	1.94	2.07	1.90
n-pentane	Y	59	54	53	55	40
	$[\eta]$	2.36	2.27	2.48	2.35	2.33
n-hexane	Y	72	70	70	68	69
	$[\eta]$	2.76	2.54	2.65	2.55	2.54
n-heptane	Y	92	90	82	83	71
	$[\eta]$	2.76	2.65	2.58	2.63	2.60
cyclohexane	Y	97	93	77	73	72
	$[\eta]$	4.10	4.32	4.33	4.21	4.25

It is considered that in the high pressure polymerization those hydrocarbons are separated from acetaldehyde before the initiation of the polymerization reaction, and then there is no difference for the influences of those solvents. However, in the melting polymerization, those hydrocarbons are not separated from acetaldehyde into two phases for being frozen rapidly in liquid nitrogen. Then, the state at the solid-liquid transition is affected by those hydrocarbons, and the different effect among those solvents for the yield and the intrinsic viscosity occurs in the melting polymerization.

Considering that the melting polymerization is settled with the ΔT, the reason for this difference among the hydrocarbons exists in the melting points of these solvents. The melting points of hydrocarbons are −159.9°C for iso-pentane, −129.7°C for *n*-pentane, −95.3°C for *n*-hexane, −90.6°C for *n*-heptane, 6.5°C for cyclohexane and petroleum ether is frozen at −146.5°C. Accordingly, it is considered that iso-pentane, petroleum ether and *n*-pentane are perfectly melted at reaction temperature and affect the interface of the solid-liquid of acetaldehyde. On the contrary, *n*-hexane, *n*-heptane and cyclohexane are remained in the solid state at reaction temperature, then the influence for the polymerization is not so large as the former.

On the other hand, the yield is decreased and the intrinsic viscosity is not changed with the increase of the amount of solvent. The facts are explained by considering that the initiation of the polymerization is affected by the change of the interface of the solid-liquid of acetaldehyde, and is diluted with the increase of the amount of solvent and then the yield is decreased, but the proceeding of the polymerization is not affected by the increase of the amount of solvent as those hydrocarbons are not mixed with acetaldehyde at that temperature and then the intrinsic viscosity is not changed.

Effect of impurity

The influences of water, acetic acid and paraldehyde as impurities in acetaldehyde are studied under the same experimental condition as described in the effect of reaction vessel.

Table 7 Effect of impurity

Impurity		Amount of impurity (vol %)				
		0.1	0.5	1.0	2.0	6.0
water	Y	127	129	120	118	94
	$[\eta]$	2.37	2.36	2.53	2.25	2.47
acetic acid	Y	62	53	34	20	11
	$[\eta]$	2.16	1.54	0.82	0.57	0.41
paraldehyde	Y	65	31	6		
	$[\eta]$	2.23	1.27	0.42		

The influences of impurities for the melting polymerization are analogous to the high pressure polymerization rather than the freezing polymerization as shown in Table 7. In the presence of small amount of water in acetaldehyde, the yield is almost the same as that of pure acetaldehyde, but the intrinsic viscosity is decreased, and those values are not changed with a little increase of the amount of water. On the other hand, the presence of acetic acid in acetaldehyde decreases the yield and the intrinsic viscosity, and the both values are remarkably decreased with the increase of the amount of acetic acid. The retarding effect of paraldehyde for the melting polymerization is also remarkable. These phenomena are analogous to the high pressure polymerization.

On the contrary, in the freezing polymerization the retarding effect of water is very remarkable. For example, the polymer can not be obtained by adding 1.57 mole per cent of water to acetaldehyde, and the yield is increased by adding acetic acid to acetaldehyde.[5]

Accordingly, it may be concluded that the melting polymerization is strongly affected by the presence of the substance which disturbs the limiting alignment of acetaldehyde, as well as the high pressure polymerization.

It is concluded that the melting polymerization is not affected by the pretreatment of immersion time in liquid nitrogen and the surface being in contact with acetaldehyde, and occurs by the catalytic action of the nucleus of crystal of acetaldehyde at the solid-liquid interface, and is strongly affected by the factors altering the interface of the solid-liquid of acetaldehyde, and then proceeds with the similar mechanism of the high pressure polymerization. The values of the apparent activation energy of -4.46 kcal/mole and the activation entropy of -104.7 cal/deg. mole are in good agreement with those values obtained from the high pressure polymerization. Those values support the above explanation that the melting polymerization is similar to the high pressure polymerization.

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