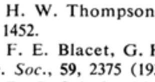
Polymerization of Acrolein Initiated by Gamma-rays

By Yoshio TOI, Toshikatsu FUJII and Yoshikazu HACHIHAMA

(Received August 10, 1963)

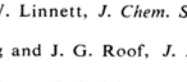
It is known that acrolein is polymerized easily upon standing alone at room temperature, yielding an insoluble product. Moureu and Dufraisse[1] reported that the polymerization is greatly accelerated by heat and light. Scherlin[2] demonstrated the polymerization by Diels-Alder reaction under the action of heat. Thompson and Linnett,[3] and Blacet, Fielding and Roof[4] investigated the photochemical polymerization of acrolein in the vapor phase by irradiation with an ultraviolet light. Schulz, Kern and their co-workers[5-14] published a series of papers on the polymerization of acrolein in the presence of radical and ionic initiators. Under the action of gamma-rays at room temperature, acrolein is polymerized easily, yielding an insoluble polymer in common organic solvents.[15,16]

Generally the acrolein-polymer obtained by radical polymerization is assumed to consist of the following structural units, while the insolubility of the polymer is assumed to arise by means of the formation of intermolecular cross-linking as shown by D.



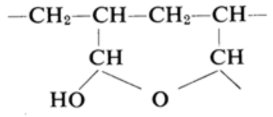
$-CH_2-\underset{CHO}{\underset{|}{CH}}-$

(A)

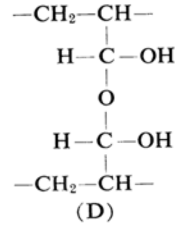


$-CH_2-\underset{H-C(OH)_2}{\underset{|}{CH}}-$

(B)



(C)



$$\begin{array}{c} -CH_2-CH- \\ | \\ H-C-OH \\ | \\ O \\ | \\ H-C-OH \\ | \\ -CH_2-CH- \end{array}$$

(D)

In the present paper, the bulk polymerization at various temperature under irradiation by gamma-rays will be studied, and the influence of the polymerization temperature on the properties of the polymers obtained has been investigated.

Experimental

Material.—Commercial acrolein was distilled, dried over anhydrous cupric sulfate, and distilled again immediately before polymerization; the distillate at b. p. 52.5~53.5°C was used as acrolein monomer.

Polymerization Procedure.—The monomer was sealed under reduced pressure of nitrogen atmosphere in a glass tube after degassification and was kept at the desired temperature and for the desired length of time in the gamma-ray field with a constant dose rate. After irradiation, the resulting reaction mixture was transferred into a large excess of methanol; the polymer obtained as a precipitate was isolated, washed with methanol, and dried under reduced pressure at room temperature.

Analysis of the Polymer.—The measurement of the aldehyde content of the polymer was done as follows: 0.1 g. of the polymer and 0.4 g. of hydroxylamine hydrochloride were dissolved in 20 ml. of pyridine with a small amount of anhydrous sodium carbonate, and the mixture was warmed at 70°C for 3.0 hr. The polyoxime obtained in the reaction mixture was isolated by the precipitation method from water, dried under reduced pressure at room temperature, and subjected to an elementary analysis by nitrogen. The aldehyde content of the polymer was calculated from the nitrogen content of polyoxime.

The determination of the degree of unsaturation of the polymer (I-S-3) was made as follows; 1.0 g. of the polymer was dissolved in 20 ml. of pyridine, and to this solution 10 ml. of an aqueous solution in which 0.5 g. of sodium boron hydride has been dissolved was stirred in. The mixture was kept at room temperature for 20 hr. and was then dialyzed by water. From the dialyzed aqueous solution, the water was removed by distillation

---

* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[1] C. Moureu and C. Dufraisse, *Compt. rend.*, **169**, 621 (1919).

[2] S. M. Scherlin, T. A. Sserebrennikowa and F. E. Rabinowitsch, *Chem. Zentr.*, I, 1971 (1939).

[3] H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, **1935**, 1452.

[4] F. E. Blacet, G. H. Fielding and J. G. Roof, *J. Am. Chem. Soc.*, **59**, 2375 (1937).

[5] R. C. Schulz, *Makromol. Chem.*, **17**, 62 (1955).

[6] R. C. Schulz and W. Kern, ibid., **18/19**, 4 (1956).

[7] R. C. Schulz, H. Fauth and W. Kern, ibid., **20**, 161 (1956).

[8] R. C. Schulz, H. Cherdron and W. Kern, ibid., **24**, 141 (1957).

[9] R. C. Schulz, H. Fauth and W. Kern, ibid., **21**, 227 (1956).

[10] R. C. Schulz, *Kunststoffe*, **48**, 257 (1958).

[11] R. C. Schulz, E. Muller and W. Kern, *Makromol. Chem.*, **30**, 39 (1959).

[12] R. C. Schulz, S. Suzuki, H. Cherdron and W. Kern, ibid., **53**, 145 (1962).

[13] R. C. Schulz, J. Kovacs and W. Kern, ibid., **54**, 146 (1962).

[14] R. C. Schulz and W. Passmann, ibid., **60**, 139 (1963).

[15] A. Henglein, W. Schnabel and R. C. Schulz, ibid., **31**, 181 (1959).

[16] Y. Toi and Y. Hachihama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo kagaku Zassi*), **62**, 1924 (1959).

TABLE I. SEPARATION OF SOLUBLE PART FROM I*

Exp. No.	Monomer g.	Dose rads. × 10^{-5}	Polymer g.	Conversion %	I-S g.	I-S %**
1	16.850	2.75	0.238	1.26	0.238(I-S-1)	100.0
2	16.850	5.86	0.542	3.22	0.514(I-S-2)	95.0
3	16.850	8.88	0.905	5.36	0.657(I-S-3)	72.6
4	16.850	14.9	2.992	17.70	1.308(I-S-4)	43.7
5	16.850	25.0	6.138	36.40	1.089(I-S-5)	17.7

* Solvent: pyridine, Temperature: room temperature

** Percentage based on total polymer obtained.

under reduced pressure to isolate the product, and the resultant polyalcohol was dried under reduced pressure at room temperature. 0.5 g. of the polyalcohol obtained was dissolved in 90 ml. of acetic acid, and the experimenters tried to hydrogenate it in the presence of 0.2 g. of platinum black under atmospheric pressure and at room temperature. However, no hydrogenation of the polymer was observed.

Dosimetry. — A ceric solution was used for the dosimetry.

Results

Polymerization.—The conversion curves obtained in the gamma-ray-initiated polymerization of acrolein in bulk at various temperatures are shown in Fig. 1. It appears that the conversion increase proportionally to the irradiated dose in the early stages, but that after this stage the overall rate of polymerization increases acceleratively. This acceleration of the rate might be due to the fact that, in the higher range of conversion, above a ca. 10% precipitation of product in the reaction system appears. This behavior is more remarkable in polymerization at higher temperatures. Figure 2 shows the Arrhenius plot of the overall rate of polymerization derived from the slope of the portion of the straight line of the conversion curve in the early stages. The overall activation energy, calculated from the slope of the straight line of Fig. 2, was 3.1 kcal./mol.

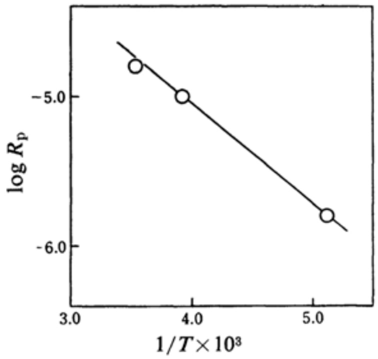


Fig. 2. Arrhenius plot of the rate of bulk polymerization of acrolein.

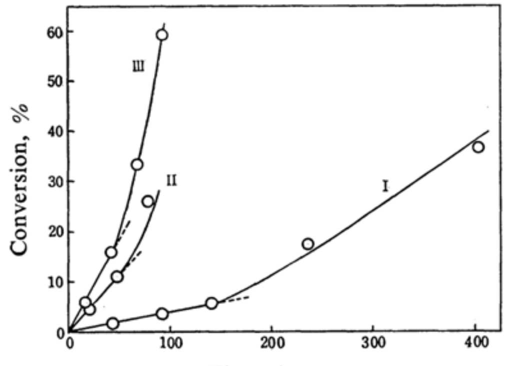


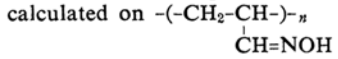
Fig. 1. Conversion curves of bulk polymerization of acrolein.

Curve I : −78°C, 1.76 rads./sec.
Curve II : −20°C, 1.76 rads./sec.
Curve III : 10°C, 1.88 rads./sec.

Properties of Polymer.—For convenience, the polymers obtained at −78°C, −20°C and 10°C are designated I, II and III respectively. I consists of the soluble part (I-S) and the insoluble part (I-InS) in pyridine at room temperature. The result of the separation of I-S from I by extraction with pyridine is shown in Table I. I-S is a white powder which is soluble in pyridine, dimethylformamide, and

TABLE II. ALDEHYDE CONTENT AND SOLUTION VISCOSITY OF I-S

Polymer	Nitrogen content* %	Aldehyde content %	[η]**	k'***
I-S-1	16.11	81.6	0.34	1.1
I-S-2	16.50	83.7	0.34	1.1
I-S-3	16.52	84.0	0.36	1.1
I-S-4	16.58	79.0	1.20	1.1
I-S-5	15.27	77.5	0.32	1.1

* Theoretical value of nitrogen content is 19.72% calculated on

$-(-CH_2-\underset{\substack{| \\ CH=NOH}}{CH}-)-_n$

** In pyridine at 30°C, c: 0.5 g./dl.

*** Huggins' constant

dimethylsulfoxide at room temperature and is decomposed at about 320°C. The results of both the analysis of the aldehyde content and the measurement of the solution viscosity of I-S are shown in Table II. I-InS, which is insoluble at room temperature, becomes soluble at elevated temperatures, 120～150°C, in pyridine, dimethylformamide and dimethylsulfoxide. However, the polymer recovered from the solution by the reprecipitation method becomes insoluble again in the same solvents. The same behavior was reported in the polymer obtained by redox polymerization.[17] The variation in aldehyde content and solution viscosity induced by heat treatment in pyridine on I-InS was also investigated; the results are presented in Table III. The fact that the solution viscosity decreases with the increase in the duration of heat treatment supports the degradation of intermolecular cross-linking (D). The aldehyde content also decreases slightly as the duration of the heat treatment increases.

TABLE III. ALDEHYDE CONTENT AND SOLUTION VISCOSITY OF I-InS AFTER HEAT TREATMENT*

Time min.	Nitrogen content %	Aldehyde content %	Inherent viscosity 0.5 g./dl.
60	17.00	86.4	0.49
100	16.46	83.5	0.44
140	14.67	74.5	0.42
180	15.11	76.6	0.35

* Sample: I-InS obtained in Exp. No. 3 of Table I.
Treatment: 0.25 g. of sample in 50 ml. of pyridine was heated at 150°C in sealed glass tube under nitrogen atmosphere.

TABLE IV. FRACTIONATION OF II AND III BY SOLUBILITY IN PYRIDINE

Polymer	Conversion %	Soluble part[a] %	Soluble part at elevated temp.[b] %	Insoluble part[c] %
II	11.1	0.7 (85.2)[d]	99.3 (58.8)[d]	—
	25.8	—	77.5	22.5
III	15.8	—	21.6 (47.6)[d]	78.4
	33.4	—	14.5	85.5

a) Soluble in pyridine at room temperature
b) To be soluble in pyridine by treatment at 170°C for 1.0 hr.
c) Quite insoluble resinous compound
d) Aldehyde content (%)

In the case of II, a small amount of a soluble part is observed at a lower conversion, but most of II is soluble in pyridine only at elevated temperatures, 150～170°C, and with an increase in conversion the part of resinous compound which is entirely insoluble is increased. In the case of III, most of it is a resinous compound. The result of the separation of the parts of the polymer on II and III by extraction with pyridine are shown in Table IV.

Discussion

When acrolein is polymerized in bulk at various temperatures, at −78°C, −20°C and 10°C, by irradiation by gamma-rays, the resulting polymer precipitates in the reaction medium at a higher conversion because the polymer is not soluble in its own monomer, and the acceleration of the overall rate of polymerization is observed. However, in the early stage of polymerization, up to approximately 10% conversion, the reaction proceeds without any remarkable precipitation of the polymer and linear conversion curves are observed. The value of the overall activation energy, 3.1 kcal./mol., calculated from Fig. 2 is a reasonable value, one which supports the that theory, in the temperature range from 10°C to −78°C (the melting point of acrolein is −86.95°C), the polymerization of acrolein proceeds by a free radical mechanism. In the case of the radical polymerization of acrolein in dimethylformamide with azobisisobutylonitrile, the overall activation energy is 25.4 kcal./mol.[18] The *G*-values of the conversion in the early stage at each temperature are presented in Table V. The influence of the reaction temperature is important on the properties of the polymer obtained, especialy on the solubility of the polymer in organic solvents. That is, in the polymerization at −78°C most of the polymer obtained is soluble in pyridine, etc., but with an increase in the reaction temperature the soluble part of the polymer decreases extremely. The formation of intermolecular cross-linking, assumed to be the next reaction

TABLE V. *G*-VALUE OF CONVERSION IN BULK POLYMERIZATION OF ACROLEIN

Temp., °C	Dose rate rads./sec.	*G* (conversion)
−78	1.76	9.85×10^{2}
−20	1.76	5.99×10^{3}
10	1.88	9.55×10^{3}

---

[17] R. Hank, *Makromol. Chem.*, **52**, 108 (1962).

[18] Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

of aldehyde after the polymerization reaction, is disturbed by taking a lower reaction temperature; the mechanism mentioned above is supported by the fact that the aldehyde content of the polymer obtained decreases with an increase in the reaction temperature (Tables II and IV). On the other hand, the monomer or polymer concentration in the polymerization system might be important on such a gel-formation, but not as important as the effect of temperature. Actually the percentage of the soluble part of I decreases greatly above an approximate 15% conversion (Table I). On the other hand, in the solution polymerization of acrolein by gamma irradiation(15,16) or radical catalysts,(8) the resulting polymers are not soluble in organic solvents at room temperature. For example, the polymerization of acrolein at 40～70°C by azobisisobutylonitrile in dimethylformamide, which can dissolve the polymer I-S, gives an insoluble polymer (the aldehyde content is 70～90%). That is, it is suggested that the influence of the polymerization temperature is predominant over other effects on the solubility of the polymer obtained. In the polymerization of acrolein initiated by gamma-rays, the reaction proceeds by a free radical mechanism through a carbon-carbon double bond. This theory is supported by the high aldehyde content and the very small content of the carbon-carbon double bond in the polymer, contrary to the existence of a double bond in the polymer obtained by ionic initiators. For instance, unlike I, which contains 75～85% of aldehyde and no unsaturation group, the polymer obtained by the bulk polymerization in the presence of boron trifluoride etherate at −78°C contains 16% of aldehyde and 62% of carbon-carbon double bond in the side chain.(18) The same behavior of acrolein on anionic polymerization, the predominant role of the carbonyl group on the polymerization reaction, was reported by Schulz and his coworkers.(14)

Summary

The bulk polymerization of acrolein initiated by gamma-rays at various temperatures has been studied. Most of the polymers obtained at −20° and 10°C are insoluble in organic solvents. On the other hand, most of the polymers obtained at −78°C are soluble in pyridine, dimethylformamide, and dimethylsulfoxide at room temperature. The aldehyde content of the soluble polymer is 75～85% of the theoretical amount, and its intrinsic viscosity is 0.32～1.20.

The influence of the polymerization temperature on the solubility of the polymer in organic solvents has been discussed, as has the polymerization mechanism.

The authors wish to express their thanks to the Nippon Kayaku Co., which supplied acrolein to this study.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku Osaka