BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2578—2583 (1969)

Kinetic Features of the Redox-polymerization of Acrolein with the Potassium Persulfate - Silver Nitrate System

Tsutomu KAGIYA, Shigeru MORITA and Kenichi FUKUI

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received November 4, 1968)

The polymerization of acrolein initiated by the potassium persulfate-silver nitrate redox system in water was studied at 0°C from the point of view of kinetics. The potassium persulfate concentration was varied over the range from 15.75 to 157.5 mmol/*l*, and that of the initial monomer, from 0.462 to 2.675 mol/*l*, while the concentration of silver nitrate was 31.5 mmol/*l*. Both the polymerization rate and the molecular weight of the polymer were found to increase with the reaction time in the early stage, while in the stage of higher conversion the polymerization rate was gradually reduced and the molecular weight remained constant. In the early stage of the polymerization, the polymer yield showed a first-order dependence on the potassium persulfate and initial monomer concentrations. The molecular weight of the polymer was proportional to the monomer concentration, independent of the catalyst concentration. From these results, the kinetic features were discussed.

Some detailed studies of the redox-polymerization with potassium persulfate-silver nitrate catalyst system have been reported, especially focused on the polymerization of a monomer such as acrolein[1] and methyl vinyl ketone.[2] Little attention, however, has been paid to the kinetic mechanism of these polymerizations. In order to make clear the mechanism of the redox-type polymerization, the acrolein polymerization with the potassium persulfate - silver nitrate system was studied. The purpose of this report is to describe the characteristic features of this polymerization.

Experimental

Materials. Commercial acrolein was distilled under nitrogen, using a 50-cm column, immediately before use; boiling point, 52.5°C/760 mmHg. Commercial potassium persulfate and silver nitrate (G. R. Grade) were used without purification. The water was purified through ion-exchange resin.

Polymerization Procedure. Definite amounts of potassium persulfate and water were placed into a glass ampoule; then, after cooling to 0°C, acrolein and an aqueous solution of silver nitrate were added to this system under a nitrogen atmosphere. The ampoule was sealed and maintained at 0°C for a definite reaction time. The product was poured into a large quantity of water, separated by filtration or centrifuge, and washed with water. In order to remove the silver salts, the filter cake was dispersed in an aqueous sodium thiosulfate solution of 1 wt%. After several hours, it was filtered, washed several times with water, and finally dried *in vacuo* at room temperature.

Characterization of the Polymer. The infrared spectrum was measured with a Shimadzu Infrared Spectrophotometer (Model IR-27) on KBr pellets. For the viscosity measurements, 100 mg of polyacrolein were mixed with 5 m*l* of a 10% aqueous sulfur dioxide solution in a 10 m*l* volumetric flask. This was allowed to stand overnight at room temperature and then filled to the mark with a 10% aqueous sodium chloride solution. Using this solution, the specific viscosity was measured at 25°C with an Ostwald viscometer. The number-average molecular weight was calculated by using the equation determined with the date reported by Schulz,[3] the η_{sp}/C ranging from 0.02 to 0.10 *l*/g:

$$\bar{M}_n = 16.8 \times 10^5(\eta_{sp}/C) - 2.8 \times 10^4$$

For the quantitative determination of the aldehyde group, the polyacrolein was reacted quantitatively with phenylhydrazine by the usual method.[4,5] The nitrogen content of the product (polyacrolein-phenylhydrazone) was also measured. In order to determine the C–C double-bond content, the polyacrolein was reduced with sodium borohydride, $NaBH_4$, to give a soluble polymer of polyallylalcohol,[6,7] and then the product was hydrogenated with hydrogen in the presence of platinum

---

[1] R. C. Schulz, H. Cherdron and W. Kern, *Makromol. Chem.*, **24**, 141 (1957).

[2] G. S. Whitby, M. D. Gross, J. R. Miller and A. J. Costanza, *J. Polymer Sci.*, **16**, 549 (1955).

[3] R. C. Schulz and H. Cherdron, private communication.

[4] R. C. Schulz, R. Hollander and W. Kern, *Makromol. Chem.*, **40**, 16 (1960).

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

[6] R. C. Schulz, J. Kovacs and W. Kern, *ibid.*, **52**, 236 (1962).

[7] R. C. Schulz and P. Elzer, *ibid.*, **42**, 205 (1961).

dioxide in acetic acid.[8] The amount of hydrogen consumed was also measured.

Results and Discussion

Characterization of the Polymer. The polymer is a white powdery amorphous solid insoluble in organic solvents at room temperature. The infrared spectrum of the polymer showed the peaks characteristic of the vinyl-type polymer $(\text{–CH}_2\text{–}\underset{\text{CH=O}}{\text{CH}}\text{–})_n$[9] and was very similar to that of the polymer formed by radical initiators (Fig. 1.). The elementary analysis of the product by the reaction of polyacrolein with phenylhydrazine showed that the polymer contains 97.5 mol% vinyl-type units (N 18.93, H 6.80, C 73.65%). Since there was no hydrogen absorption in the reaction product with $NaBH_4$, it can be said that the C–C double bond was not present in this system. From these results, it can be concluded that not the aldehyde-type polymer but only the vinyl-type polymer is formed by the redox-pair potassium persulfate-silver nitrate system.

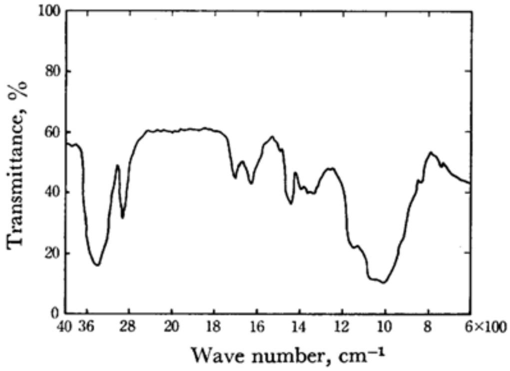

Fig. 1. Infrared spectrum of the polyacrolein formed with the redox system $AgNO_3/K_2S_2O_8$

Characteristic Effects of the Monomer and Potassium Persulfate Concentrations. The effect of the monomer concentration on the polymer yield and the molecular weight of the polymer was investigated; the results are shown in Table 1. Figure 2 indicates that the polymer yield at a constant time increases proportionally with the monomer concentration. The number-average degree of polymerization at a constant time is plotted against the monomer concentration in Fig. 3. It can be seen that the increase in the degree of polymerization with the monomer concentration becomes more pronounced with the reaction time; namely, the polymerizations in the earlier period (until 20 min) are characterized by a proportional increase in the degree of polymerization with the monomer concentration, while in the latter period (after 20 min) the exponent of the monomer concentration becomes more than unity.

Table 1. Effect of monomer concentration and time on polymer yield and molecular weight

Monomer concn. mol/l	Reaction time hr	Polymer yield mol/l	Molecular weight $\bar{M}_n\times 10^{-3}$
2.675	0.17	0.040	13.5
2.675	0.33	0.11	28.5
2.675	0.5	0.21	45.0
2.675	1.0	0.66	69.5
2.675	2.0	1.44	72.0
2.675	3.0	1.84	71.0
2.675	18.0	2.47	67.0
2.12	0.17	0.03	18.4
2.12	0.33	0.11	29.7
2.12	0.5	0.21	36.5
2.12	1.0	0.46	52.7
1.65	0.17	0.011	8.4
1.65	0.33	0.08	14.9
1.65	0.5	0.15	19.4
1.65	0.67	0.21	21.7
1.65	0.83	0.28	23.3
1.65	1.0	0.36	26.5
1.65	1.33	0.51	26.2
1.65	1.67	0.80	20.5
1.65	3.0	1.28	19.1
1.65	4.0	1.28	23.7
1.65	5.0	1.28	18.5
1.205	0.17	0.009	3.6
1.205	0.33	0.042	3.6
1.205	0.5	0.080	4.2
1.205	1.0	0.20	5.5
0.46	0.17	0.006	—
0.46	0.33	0.019	2.6
0.46	0.5	0.037	2.4
0.46	0.67	0.052	2.8
0.46	0.83	0.075	2.6
0.46	1.0	0.10	2.6
0.46	1.33	0.12	2.5
0.46	1.67	0.14	2.7
0.46	2.0	0.17	2.7
0.46	3.0	0.23	2.7
0.46	4.0	0.27	2.5
0.46	5.0	0.30	2.5

Reaction temperature=0°C; $[K_2S_2O_8]_0=[AgNO_3]_0=$ 31.5 mmol/l

The dependence of the polymer yield and the molecular weight of the polymer on the catalyst concentration is shown in Table 2. Figure 4 shows that the polymer yield increases proportionally with the catalyst concentration in the early stage (until 0.5 hr), while in the later stage

---

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

[9] R. C. Schulz, *Kunststoffe*, **47**, 303 (1957).

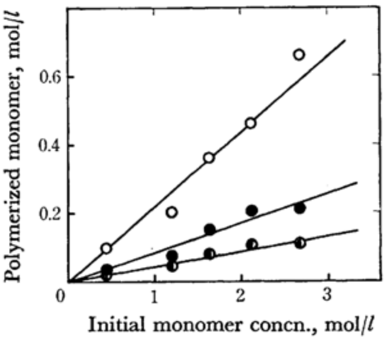

Fig. 2. The amount of polymerized monomer *vs.* initial monomer concentration.
$T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/*l*; reaction time, 0.33 (◐), 0.5 (●), 1.0 hr (○)

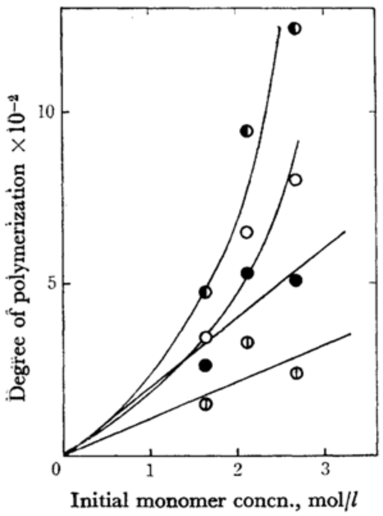

Fig. 3. Degree of polymerization *vs.* initial monomer concentration.
$T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/*l*; reaction time, 0.17 (⦶), 0.33 (●), 0.5 (○), 1.0 hr (◐)

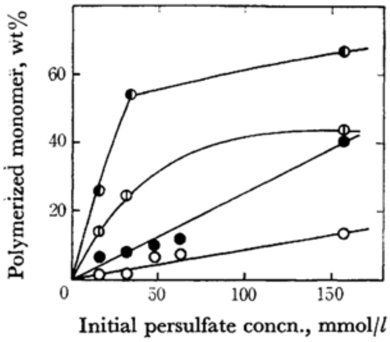

Fig. 4. The amount of polymerized monomer *vs.* initial potassium persulfate concentration.
$T=0°C$; $[AgNO_3]_0=31.5$ mmol/*l*; reaction time, 0.17 (○), 0.5 (●), 1.0 (⦶), 2.0 hr (◐)

TABLE 2. EFFECT OF PERSULFATE CONCENTRATION AND TIME ON POLYMER YIELD AND MOLECULAR WEIGHT

$K_2S_2O_8$ concn. mmol/*l*	Reaction time hr	Polymer yield mol/*l*	Molecular weight $\bar{M}_n\times10^{-3}$
15.75	0.17	0.026	3.7
15.75	0.25	0.033	4.2
15.75	0.5	0.09	8.6
15.75	0.75	0.13	7.0
15.75	1.0	0.19	11.3
15.75	2.0	0.35	12.3
15.75	3.0	0.51	9.0
23.6	0.77	0.13	11.1
23.6	0.92	0.22	10.0
31.5	0.52	0.11	5.6
31.5	0.73	0.18	5.6
47.25	0.30	0.08	2.9
47.25	0.44	0.12	4.0
63.0	0.23	0.06	2.8
63.0	0.43	0.12	4.3
94.5	0.10	0.02	1.3
94.5	0.33	0.13	2.6
157.5	0.11	0.26	0.6
157.5	0.17	0.18	0.9
157.5	0.33	0.44	0.9
157.5	0.5	0.54	1.8
157.5	0.67	0.51	3.0
157.5	0.83	0.68	2.7
157.5	1.0	0.58	3.6
157.5	1.5	0.88	4.5
157.5	2.0	0.90	5.1

Reaction temperature: 0°C; $[AgNO_3]_0=31.5$ mmol/*l*; Initial monomer concentration: 1.34 mol/*l*

the increase becomes less pronounced. It is noted that the degree of polymerization at a constant time is almost independent of the catalyst concentration.

Classification of the Polymerization.[10] The polymer yields at various monomer concentrations are plotted against the reaction time in Fig. 5. In each of several monomer concentrations, S-shape curves are obtained; in the early stage (until 0.5—1.0 hr), there is a marked acceleration in rate, while the polymerization rate is gradually reduced in the later stage.

Figure 6 shows the variation in the molecular weight of the polymer formed with the reaction time. It is a characteristic phenomenon that, in the early stage, the molecular weight of the polymer formed increases proportionally with the reaction time, as does the rate acceleration. In the later stage, however, the molecular weight is shown to remain constant, independently of the reaction time.

---

[10] T. Kagiya, M. Izu and K. Fukui, This Bulletin, **40**, 1045 (1967).

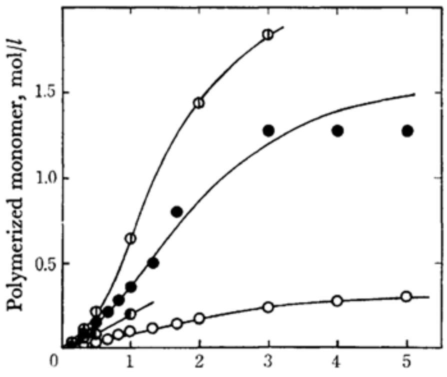

Fig. 5. The amount of polymerized monomer *vs.* reaction time.
$T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/l; initial monomer concentration, 2.675 (⌽) 1.65 (●), 1.205 (◐), 0.46 mol/l (○)

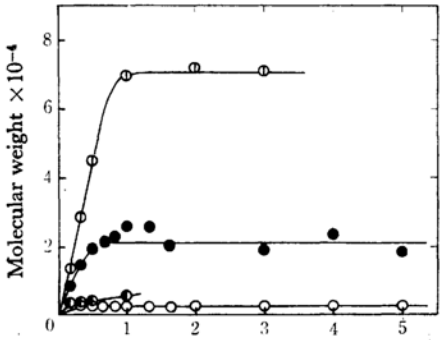

Fig. 6. Molecular weight *vs.* reaction time. Reaction conditions and notes are the same as shown in Fig. 5.

The rate acceleration in the early stage shows the accumulation of propagating species. The initiation reaction may, therefore, be considered to occur continuously in the course of the polymerization; that is, this system is a polymerization with a slow initiation. Since the mole of the propagating species increases with the reaction time, the non-stationary state is realized in this case. Moreover, from the fact that the number-average degree of polymerization increases with the reaction time in the early stage, this stage is a successive polymerization.

On the other hand, the polymerization in the later stage is a chain polymerization, for the degree of polymerization is independent of the reaction time. In order to determine whether the polymerization in the later stage has a rapid or a slow initiation, and whether it has a stationary or a non-stationary state, the following experiments were carried out. At first, it was shown that the addition of excess amounts of sodium chloride inhibits the polymerization reaction completely. Three-fold sodium chloride, NaCl, of silver nitrate, $AgNO_3$, was added at various times in the course of the reaction, while the total reaction time was five hours. We term the reaction before and after the adding of NaCl period I and period II respectively. Table 3 shows that the increase in the polymer yield in period II was not observed in any case. This fact indicates that NaCl reacts with the Ag^+ ion to form a precipitate of AgCl, and that the formation of a new radical is stopped because of the disappearance of the reductant. The lack of any increase in the polymer yield in period II also leads to the consideration that there is a termination of the propagating species which had already been formed before the addition of sodium chloride.

TABLE 3. RESULTS OF TWO-STAGE POLYMERIZATION BY THE ADDITION OF NaCl[a)]

Reaction time hr		Polymerized monomer mol/l		
Period I	Period II	Overall[b)]	Period I[c)]	Period II[d)]
0.167	4.833	0.007	0.006	0.001
0.334	4.666	0.006	0.019	−0.013
0.5	4.5	0.014	0.037	−0.023
0.766	4.234	0.055	0.067	−0.012
1.0	4.0	0.104	0.099	0.005
2.0	3.0	0.152	0.172	−0.020
3.0	2.0	0.194	0.235	−0.041
5.0	0	0.279	0.297	−0.018

a) Reaction conditions: $T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/l; initial monomer concentration: 0.462 mol/l; total reaction time: 5 hr; $NaCl/AgNO_3=3.0$ (molar ratio).
b) Overall polymerized monomer was obtained by subtracting the theoretical amount of AgCl (31.5 mmol/l) from the total yield.
c) The first-stage polymerization (Period I) was carried out as a blank polymerization in the same reaction conditions as that described above.
d) Polymerized monomer in Period II was obtained by subtracting the polymer yield in Period I from the overall polymer yield.

In order to make clear the termination reaction, the polymerization was carried out by a two-stage monomer addition method as follows. The definite monomer was divided into two parts (14.7% and 85.3%). In the first stage the polymerization was carried out with the use of a 14.7% monomer for various reaction times, and then, after the addition of a residual monomer, polymerization (the second stage) was continued for one hour. The experimental results are given in Table 4. The polymer yield in the second stage is plotted in Fig. 7 against the reaction time in the first stage. The polymer yield increased with the time until about three hours, but it decreased thereafter.

TABLE 4. RESULTS OF TWO-STAGE POLYMERIZATION BY THE ADDITION OF MONOMER[a)]

Reaction time in 1st-stage hr	Polymer yield mol/l Overall (P_T)	1st-stage (P_1)	2nd-stage[b)] (P_2) (=P_T-P_1)	$[M_p]_2$[c)]	Degree of polymerization of final polymer $\times 10^{-3}$
0	0.54	0	0.54	0.54	2.1
0.33	0.67	0.02	0.65	0.55	2.9
0.5	0.81	0.04	0.78	0.67	3.2
1.0	1.05	0.10	0.95	0.84	3.4
2.0	1.30	0.17	1.13	1.01	3.0
5.0	1.12	0.30	0.82	0.77	2.7
8.0	0.79	0.34	0.45	0.43	2.5
23.0	0.67	0.48	0.19	0.19	1.1

a) Reaction conditions: $T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/l; monomer concentration added in the first-stage, $[M_1]_0=0.462$: in the second-stage, $[M_2]_0=2.675$ mol/l; reaction time in the 1st-stage: variable, the 2nd-stage: 1 hr.

b) P_2, the total polymer yield in the second-stage, was obtained by subtracting P_1 from P_T.

c) $[M_p]_2$, the polymer yield in the second-stage, was corrected as follows by eliminating the small amount of polymer formed during the second-stage with $[M_1]_0$.

$$[M_p]_2=P_2\times[M_2]_0/([M_1]_0+[M_2]_0-P_1)$$

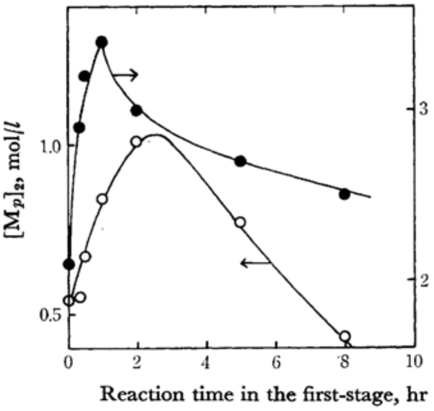

Fig. 7. Polymer yield in the second-stage and the degree of polymerization of the total polymer *vs.* reaction time in the first-stage. Reaction conditions are shown in Table 4.

This indicates that the propagating species accumulate until about three hours have passed, while, after three hours, the number of moles of the propagating species decreases with the reaction time because of the increase in the termination reaction and in the consumption of the catalyst.

It may be concluded from these facts that this redox polymerization is a non-stationary state accompanied by the accumulation of the propagating species in the early stage, and by the consumption of the propagating species in the later stage. The fact that the propagating species increase for three hours leads to the consideration that, in both the early and later stages, this system has a polymerization with a slow initiation.

The polymerization rate and the molecular weight of the polymer, as has been described before, increase continuously with the reaction time in

TABLE 5. EFFECT OF MONOMER CONCENTRATION ON THE NUMBER OF POLYMER CHAIN

Monomer concentration mol/l	Reaction time min	Polymerized monomer mol/l	Degree of polymerization	Number of[a)] moles of polymer chains $\times 10^4$ mol/l
1.65	10	0.011	150	0.73
1.65	20	0.08	270	3.07
1.65	30	0.15	350	4.45
1.65	40	0.21	390	5.39
1.65	50	0.28	420	6.66
1.65	60	0.36	470	7.57
2.12	10	0.03	330	1.00
2.12	20	0.11	530	2.03
2.12	30	0.21	650	3.16
2.12	60	0.46	940	4.90
2.62	10	0.05	480	1.08
2.62	20	0.11	690	1.65
2.62	30	0.23	950	2.48
2.675	10	0.04	240	1.67
2.675	20	0.11	510	2.19
2.675	30	0.21	800	2.64
2.675	60	0.66	1240	5.32

Reaction temperature=0°C, $[K_2S_2O_8]_0=[AgNO_3]_0=$ 31.5 mmol/l

a) Number of moles of polymer chains was calculated from the ratio of the amount of polymerized monomer to the number-average degree of polymerization.

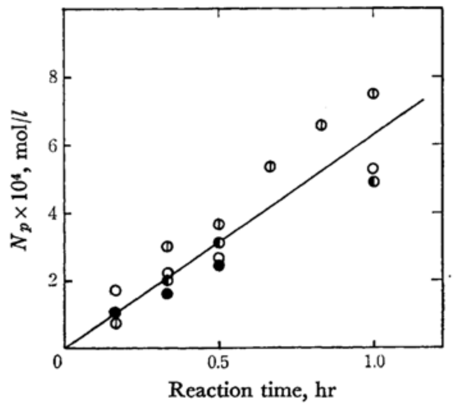

Fig. 8. Number of moles of polymer chains (N_p) *vs.* reaction time at various monomer concentration. $T=0°C$; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/l; $[M]_0=1.65$ (⦶), 2.12 (◐), 2.62 (●), 2.68 mol/l (○)

the early stage. This fact suggests that, in the early stage, neither the chain transfer nor the termination reaction is very remarkable, and that the initiation and the propagation reaction are the main elementary reactions. The effect of the monomer concentration on the number of moles of polymer chains is summarized in Table 5. From the experimental data, the number of moles of polymer chains is plotted against the reaction time in Fig. 8. The fact that an almost linear relation was found between them suggests that these redox systems have polymerizations with slow initiations. Since the number of moles of polymer chains was independent of the monomer concentration, the rate-determining step of the initiation reaction may be considered to be the decomposition reaction of the catalyst.

A more quantitative discussion of this polymerization will be given in a subsequent paper.