RESULTS AND DISCUSSION

2. RESULTS AND DISCUSSION

The aim of the present work was to study the factors affecting the grafting of haloacrylic acids onto cellulose induced by Ce^{4+}. The variables studied were the concentration of initiator, the reaction temperature, the kind as well as the concentration of the inorganic acid used.

Graft Copolymerization of Haloacrylic Acids onto Cellulose:

The grafting reaction described in page (41) was used. Attempted grafting of cellulose by either trans-B-chloroacrylic or trans-B-bromoacrylic acids failed and this might be due to the absence of the vinyl group. Therefore, the grafting reactions studied in this thesis were carried out by using α-bromoacrylic acid.

I. Effect of Cellulose/Monomer Ratio On percent Grafting in water:

The effect of different amounts of ∝-bromoacrylic acid (0.5-2 g) on the percent grafting onto cellulose is shown in Table (1)

Table (1)

Cellulose	: 0.2 gram
Ceric ammonium sulphate concentration	: 10 m Mole
Temperature	: room temperature (28°C)
Time	: 3 hours
Water	: 10 ml.

∝-bromoacrylic acid weight (gm)	% grafting
0.50	50.3
0.75	69.7
1.00	91.3
1.25	86.8
1.50	98.1
1.75	109.2
2.00	124.7

From Table (1) (cf. Fig. 2), it is clear that the percent grafting of ∝-bromoacrylic acid onto cellulose increases steadily with increasing the amount of ∝-bromoacrylic acid. Also, there is a sharp increase in the percent grafting at the initial stage up to 1 gram monomer concentration, then a slow rate in the percent grafting was observed when more than 1 gram ∝-bromoacrylic acid was used. Accordingly, in the following experiments the cellulose/monomer ratio is 0.1/0.5 gm, respectively.

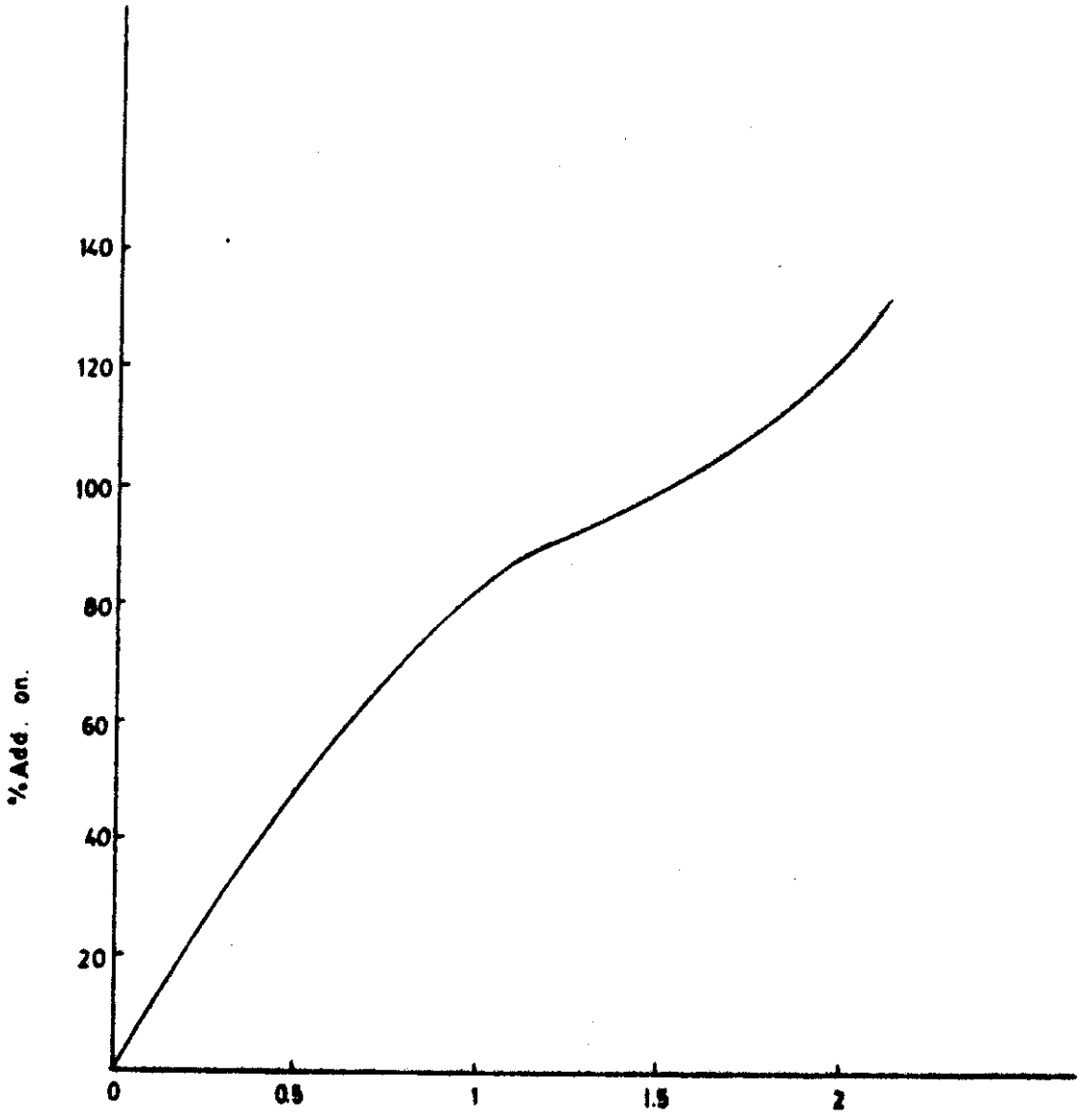


Fig.[2]: Effect of Monomer weight on grafting.

II. Effect of Kind and Concentration of Ceric Ions:

In the present experiments different amounts of either ceric ammonium sulphate or ceric ammonium nitrate were used to study the effect of Ce^{4+} concentration on the percent grafting.

Table (2) shows the effect of Ce^{4+} concentration on the percent grafting.

Table (2)

Cellulose : 0.1 gm
∝-Bromoacrylic acid: 0.5 gm
Temperature : room temperature ($28^{o}C$)
Time : 3 hours
Water : 5 ml

Ce Concentration (m Moles)	$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$	$(NH_4)_2Ce(NO_3)_6$
1	6.0	----
2.5	22.3	----
5	44.5	----
10	78.2	19.5
15	66.0	----
20	60.1	75.3
25	----	----
30	----	70.8

Table (2) (contd.)

Ce Concentration (m Moles)	$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$	$(NH_4)_2Ce(NO_3)_6$
35	----	----
40	----	51.4
45	----	----
50	----	39.3

Table (2) and Fig. (3) show the dependence of the extent of graft copolymerization on the concentration of Ce^{4+} ion expressed as m Mole in water medium (using either ceric ammonium sulphate or ceric ammonium nitrate). The grafting is characterized by initial fast rate reaching a maximum then decreased gradually by increasing the Ce^{4+} concentration.

Similar results were obtained by Varma et al[62], who applied a modification of the mechanism involving reaction reversibility of the grafting of acrylate monomers onto cellulose. They proposed the sequence of reactions eventually leading to the graft copolymerization which may be written as follows:

Initiation:

$$Ce^{4+} + \text{Cell-H} \xrightarrow{k_1} \text{Cell}^{*} + Ce^{+++} + H^{+} \quad (1)$$

$$\text{Cell}^{*} + M \xrightarrow{k_2} \text{Cell-M}^{*} \quad (2)$$

$$Ce^{++++} + M \xrightarrow{k_3} M^{*} + Ce^{+++} + H^{+} \quad (3)$$

Propagation:

$$\text{Cell-Mn}^{*} + M \xrightarrow{k_4} \text{Cell-M}^{*}_{n+1} \quad (4)$$

$$M^{*}_{m} + M \xrightarrow{k_4'} M^{*}_{m+1} \quad (4')$$

Termination:

$$\text{Cell-M}^{*}_{n} + Ce^{++++} \xrightarrow{k_5} \text{Cell-M}_{n} + Ce^{+++} + H^{+} \quad (5)$$

$$M^{*}_{m} + Ce^{++++} \xrightarrow{k_5'} M_{m} + Ce^{+++} + H^{+} \quad (5')$$

$$\text{Cell}^{*} + Ce^{++++} \xrightarrow{k_6} \text{oxidation products} + Ce^{+++} + H^{+} \quad (6)$$

At steady-state conditions involving the reversibility of reaction (1), (2) and (3), the rate of polymerization can be written as follows:

$$R_p = \frac{k_4 k_2 [M]^2}{(k-2) + k_5[Ce^{4+}]} \left[\frac{k_1 [Ce^{4+}] [\text{Cell-H}]}{(k-1)[Ce^{3+}][H^{+}] + k_2[M] + k_6[Ce^{4+}]} \right] \quad (7)$$

III. Effect of Time at Different Temperatures on the Percent Grafting of ∝-Bromoacrylic Acid Onto Cellulose.

1. Grafting In Water At 30°, 40°, 60° and 80°C:

Table (3) illustrates the effect of time on grafting in water at 30°, 40°, 60° and 80°C.

Table (3)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate: 10 m Mole
Water : 5 ml

Time (minutes)	% Grafting 30°	40°	60°	80°
10	----	5.3	----	28.0
20	----	42.1	19.0	35.7
30	27.3	52.6	50.7	31.4
60	85.2	75.0	60.7	47.4
90	----	74.8	69.7	49.3
120	102.2	75.2	65.4	45.8
180	99.2	75.0	73.0	45.2

In our study, grafting reaction in water was carried out at four different temperatures, 30°, 40°, 60° and 80°C,

respectively. Hebeish et al[64] reported that raising the temperature of the graft copolymerization of vinyl monomers on modified cellulose brings about a significant enhancement in the rate of grafting. This is expected, since increasing the temperature would favourably influence the swellability of cellulose, solubility of monomer, diffusion of both initiator and monomer and the initiation and propagation of the graft. The net effect of all these parameters leads to higher grafting. On the contrary, Varma et al[62] found that the percent grafting of cellulose with acrylate monomers in nitric acid medium decreased as the temperature raises from 30° to 50°C. From Table (3) and Fig. (4), it is clear that increasing of the reaction temperature causes a decrease of the percent grafting of α-bromoacrylic acid onto cellulose in water. Thus, after 3 hours the percent grafting onto cellulose decreases in the order $30^{\circ} > 40^{\circ} \gg 60^{\circ} > 80^{\circ}$ (99.2%, 75.0%, 73.0% and 45.2%, respectively).

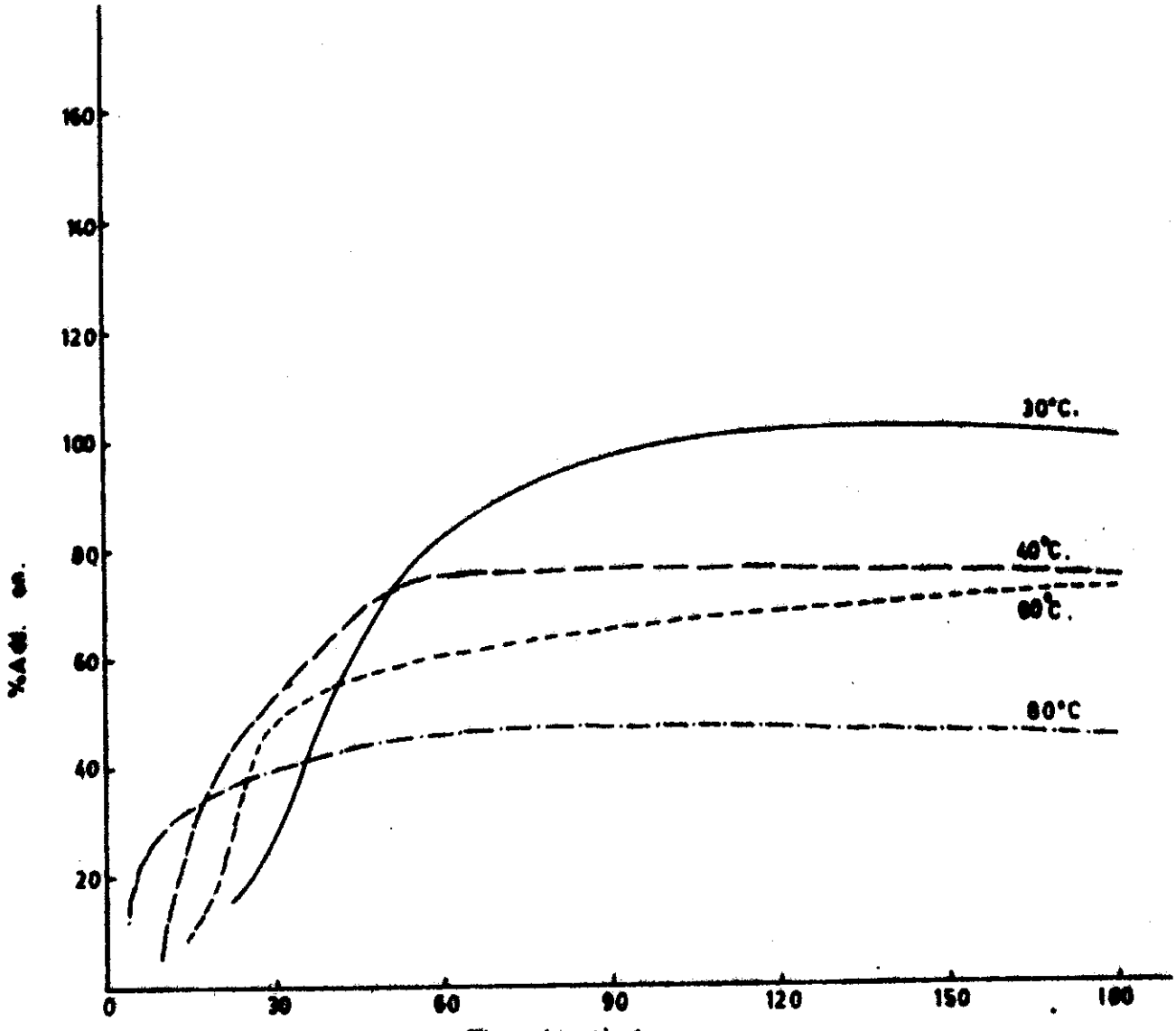


Fig.[4]: Effect of time on grafting in H_2O at 30, 40, 60 and 80°C.

2. Grafting In 0.05 N HNO_3 At 40°, 60° and 80°C:

Table (4) illustrates the effect of time on percent grafting in 0.05 N HNO_3 at 40°, 60° and 80°C.

Table (4)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.05 N HNO_3 : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
5	0.3	----	----
10	20.0	51.0	35.0
20	29.5	72.3	53.9
30	126.0	90.2	59.2
60	131.1	97.2	61.5
90	129.3	75.8	68.8
120	91.1	75.3	49.3
180	103.0	64.0	62.9

From Table (4) and Fig. (5), it is clear that after 3 hours, increasing in temperature causes a decrease in the percent grafting in the order 40° > 60° > 80°C (103.0%, 64.0% and 62.9%, respectively).

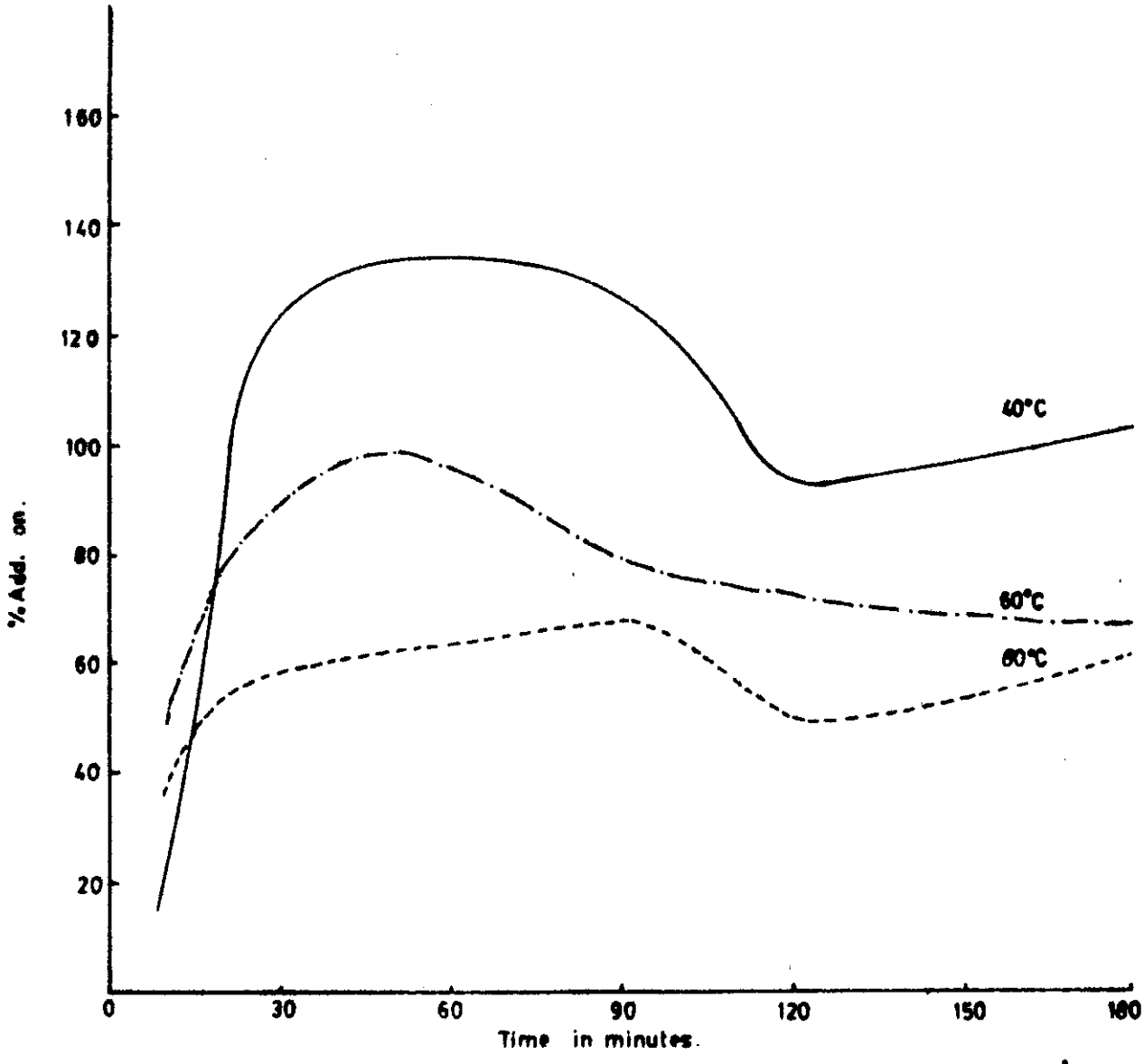


Fig.[5]: Effect of time on grafting in 0.05N HNO_3 at 40,60 and 80°C.

3. Grafting In 0.1 N HNO_3 At 40°, 60° and 80°C:

Table (5) illustrates the effect of time on percent grafting in 0.1 N HNO_3 at 40°, 60° and 80°C.

Table (5)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.1 N HNO_3 : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
5	17.4	----	----
10	34.6	43.0	73.0
20	100.0	61.6	84.9
30	123.7	72.2	100.8
60	109.1	62.5	108.4
90	113.0	49.5	100.1
120	111.0	53.9	106.0
180	115.0	61.0	105.0

Similarily, increasing of temperature causes a decrease of the percent grafting. Thus, in the presence of 0.1 N HNO_3 after 3 hours, the percent grafting decreased in the order 40° > 80° > 60°C and was found to be 115.6%, 105.0% and 61.0%, respectively (cf. Table 5, Fig. 6).

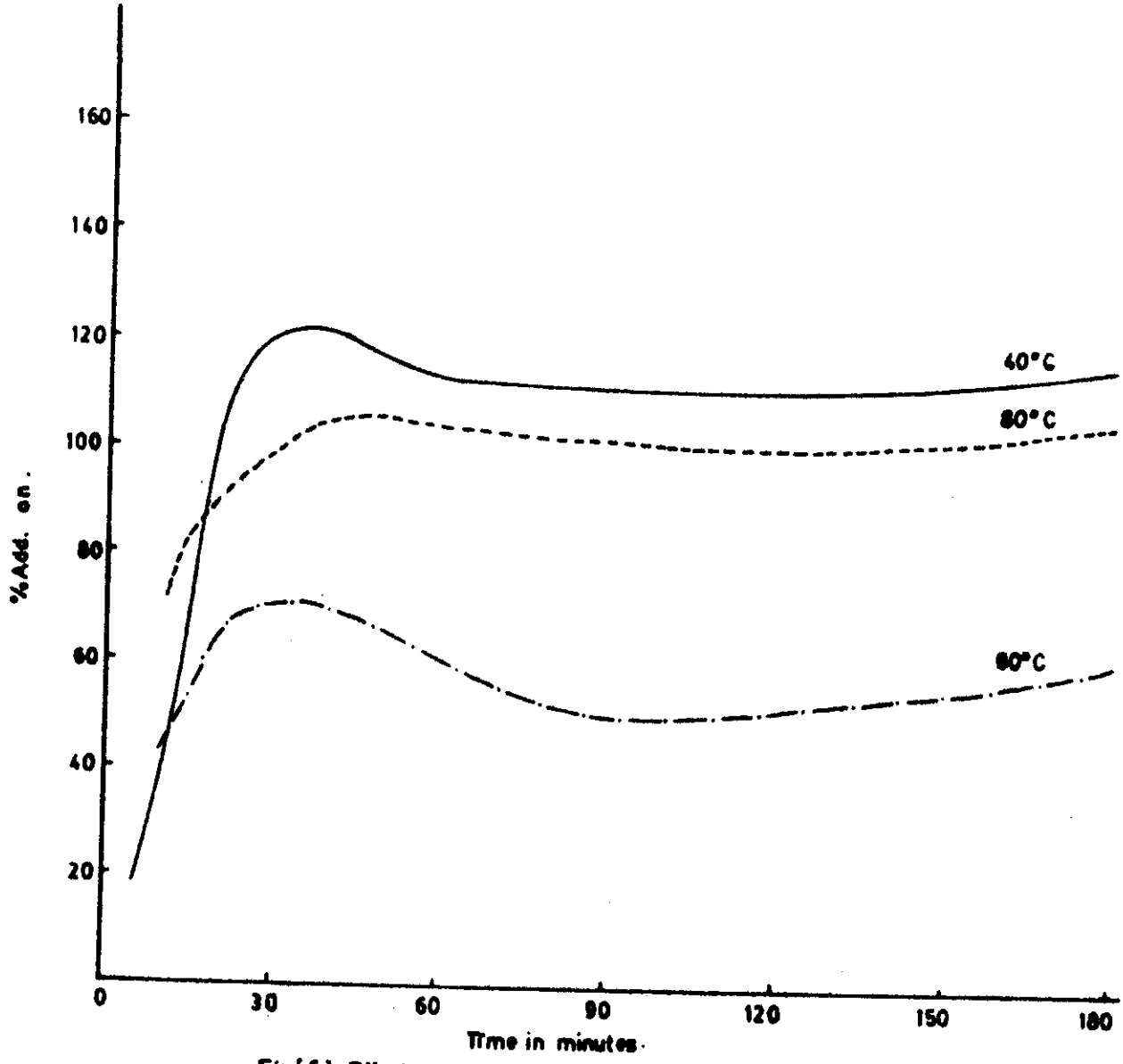


Fig.[6]: Effect of time on grafting in 0.1N NHO_3 at 40,60 and 80°C.

4. Grafting In 0.2 N HNO_3 At 40°, 60° and 80°C:

Table (6) illustrates the effect of time on percent grafting in 0.2 N HNO_3 at 40°, 60° and 80°C.

Table (6)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.2 N Nitric acid : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
5	6.7	----	----
10	23.9	30.1	36.3
20	----	58.3	42.5
30	40.0	92.5	50.4
60	72.6	68.0	62.5
90	86.3	55.8	47.0
120	114.3	53.9	52.6
180	105.4	69.7	57.3

Table (6) and Fig. (7) show that increasing the temperature resulted in a decrease in the percent grafting in presence of 0.2 N HNO_3. After 3 hours, this percent grafting decreased by increasing the temperature in the order of $40° > 60° > 80°C$ (105.4%, 69.7% and 57.3%, respectively).

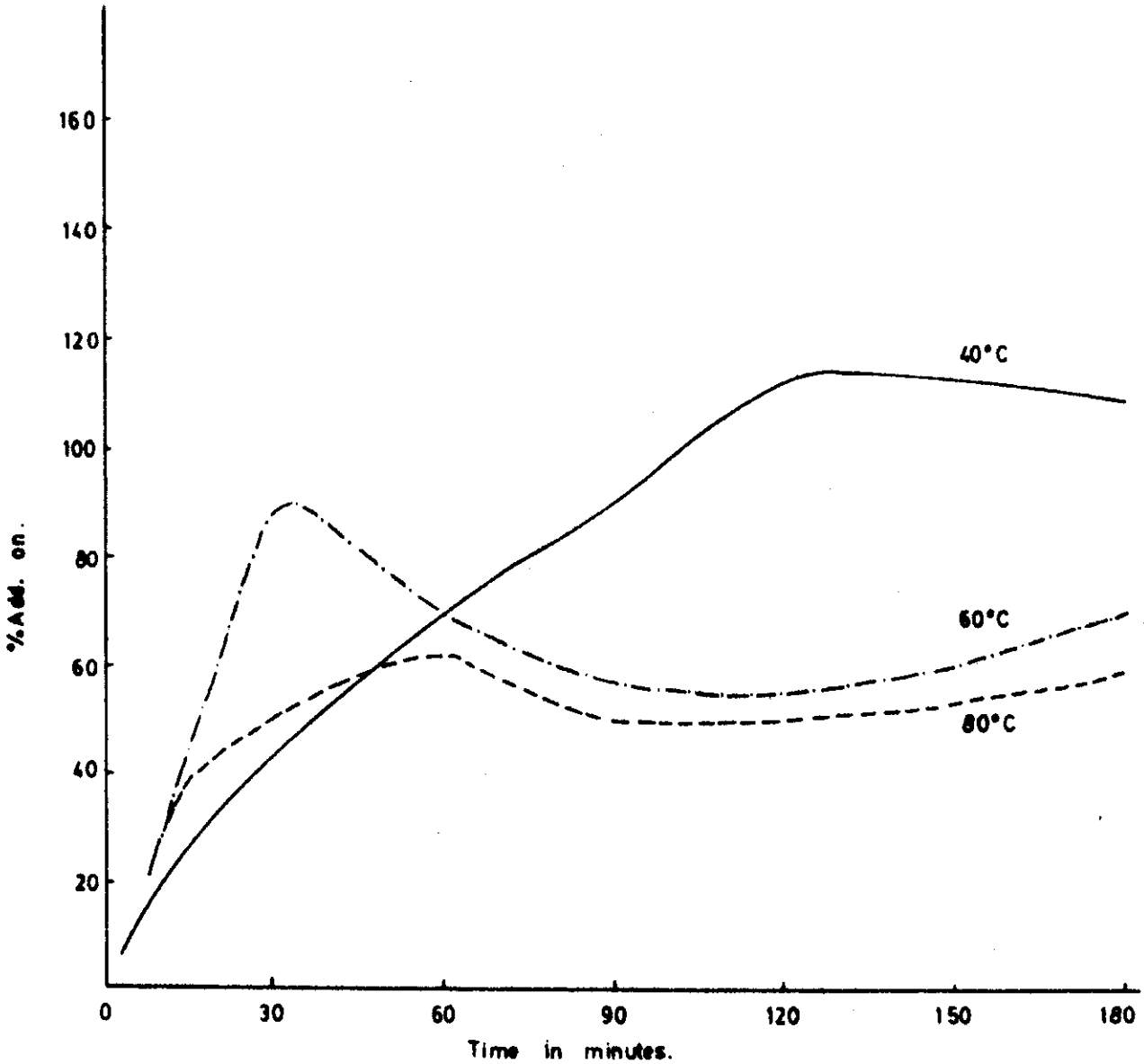


Fig.[7]: Effect of time on grafting in 0.2N HNO_3 at 40, 60 and 80°C.

Thus, from Tables (4), (5) and (6) (cf. Figs. 5, 6 and 7) it was found that the net effect of increasing the temperature in presence of different concentrations of nitric acid causes a decrease in the percent grafting. The same as was found in case when water was used (cf. Table 3 and Fig. 4). These results are in good agreement with the results of Varma et al.[62] Also, it is clear that the percent grafting mostly increases at the initial stage with increasing time in each system and gives a maximum at a certain time then increases steadly with time.

5. Grafting In 0.05 N HCl At 40°, 60° And 80°C:

Table (7) illustrates the effect of time on percent grafting in 0.05 N HCl at 40°, 60° and 80°C.

Table (7)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.05 N HCl : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	8.8	37.6	50.0
20	31.5	55.9	65.9
30	79.7	65.3	72.0
60	105.4	64.3	78.7
90	143.3	66.7	87.8
120	91.6	60.6	95.7
180	75.1	53.2	88.2

Table (7) and Fig. (8) show the effect of time on the percent grafting in presence of 0.05 N HCl at 40°, 60° and 80°C. After 3 hours, it is clear that grafting is affected by temperature and increased in the order 80° > 40° > 60°C (88.2%, 75.1% and 53.2%, respectively).

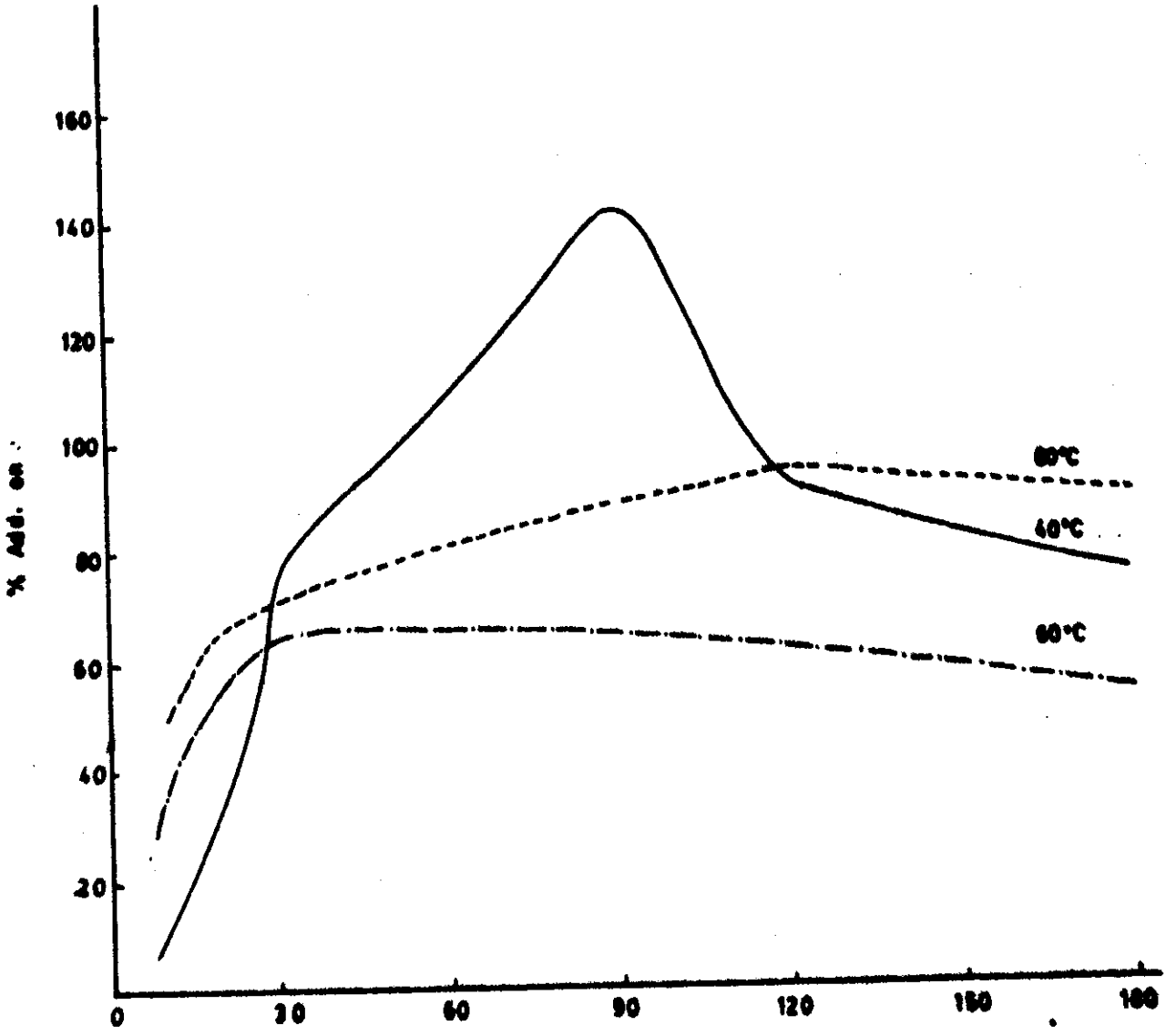


Fig.[8]: Effect of time on grafting in 0.05N HCl at 40, 60 and 80°C.

6. Grafting In 0.1 N HCl At 40°, 60° And 80°C:

Table (8) illustrates the effect of time on percent grafting in 0.1 N HCl at 40°, 60° and 60°C.

Table (8)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.1 N HCl : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	14.5	52.9	44.3
20	64.2	74.9	45.4
30	82.5	79.9	47.2
60	113.9	103.7	59.2
90	104.9	60.1	58.8
120	96.7	57.9	62.5
180	73.3	60.3	68.2

The effect of time on the percent grafting in presence of 0.1 N HCl is shown in Table (8) and Fig. (9) which indicates that grafting is affected by temperature. Thus, after 3 hours the percent grafting increased in the order $40° > 80° > 60°C$ and was found to be 73.3%, 68.2% and 60.3%, respectively.

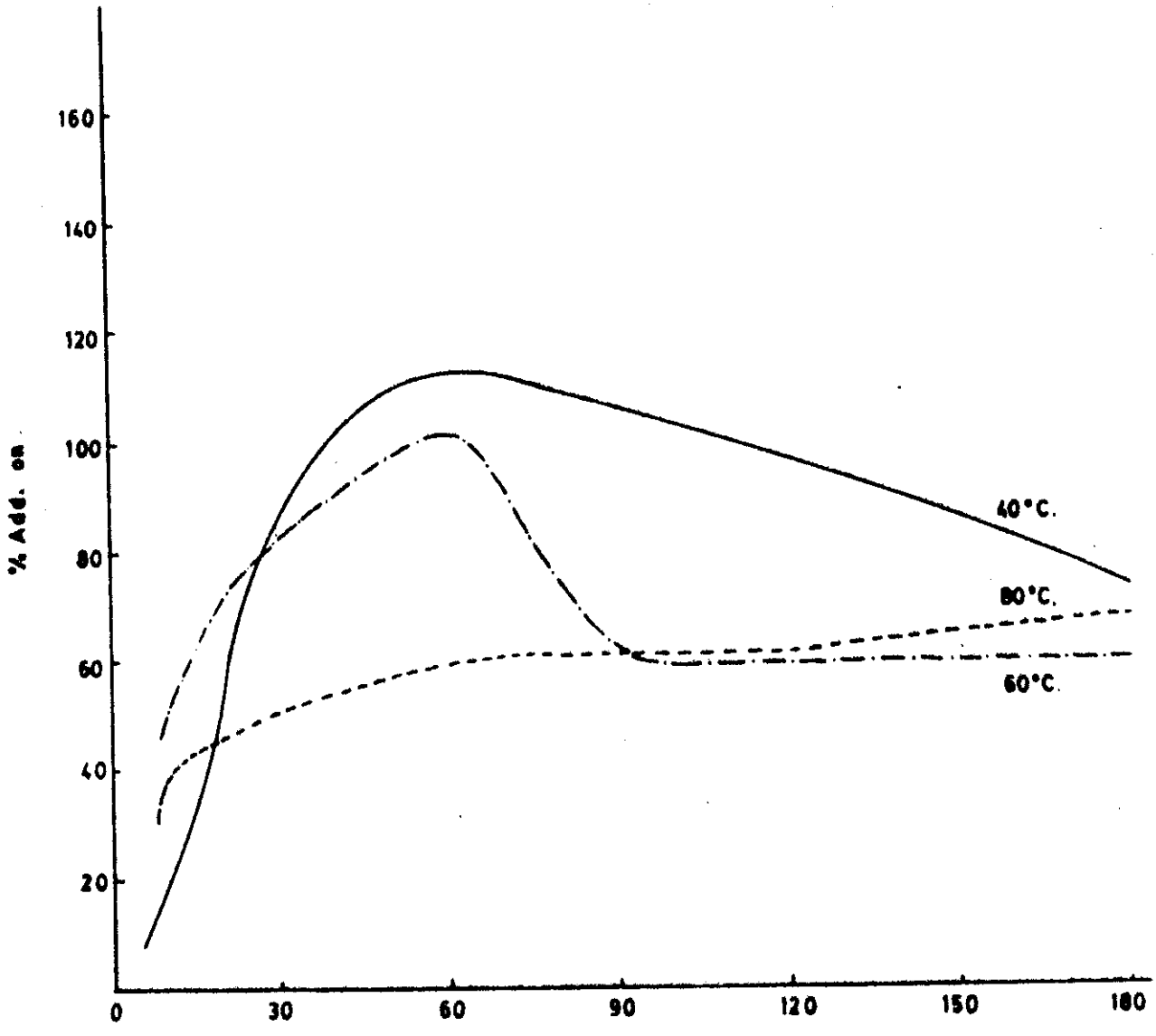


Fig.[9]: Effect of time on grafting in 0.1N HCl at 40, 60 and 80°C.

7. Grafting In 0.2 N HCl At 40°, 60° And 80°C:

Table (9) illustrates the effect of time on the percent grafting in 0.2 N HCl at 40°, 60° and 80°C.

Table (9)

Cellulose	: 0.1 gram
∝-Bromoacrylic acid	: 0.5 gram
Ceric ammonium sulphate concentration	: 10 m Mole
0.2 N HCl	: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	2.7	46.4	26.1
20	42.2	55.4	41.8
30	63.7	55.6	48.7
60	93.7	58.7	59.0
90	66.1	51.1	68.4
120	65.1	48.9	73.0
180	67.8	51.5	90.0

Table (9) and Fig. (10) illustrate the effect of time on the percent grafting using 0.2 N HCl at 40°, 60° and 80°C. It is clear that the effect of temperature after 3 hours increased in the order 80° > 40° > 60° (90.0%, 67.8% and 51.5%, respectively). This order of effect of

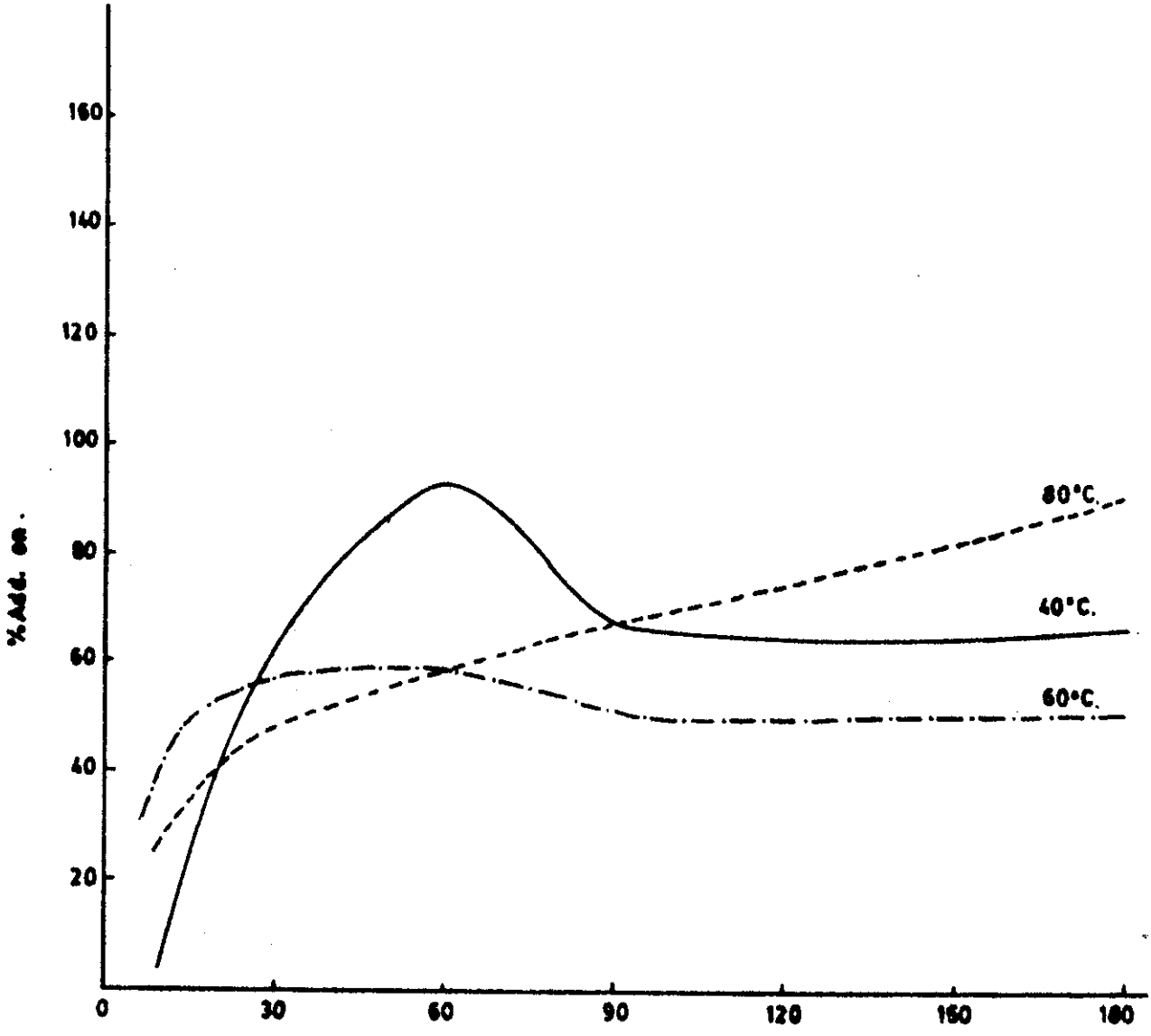


Fig.[10]: Effect of time on grafting in 0.2 N HCL at 40, 60 and 80°C.

temperature on grafting was indicated with the system of 0.05 N HCl.

Therefore, from Tables (7), (8) and (9) and Figs. (8), (9) and (10), it is clear that the net effect of increasing temperature on the percent grafting in presence of different concentrations of hydrochloric acid causes an increase in the percent grafting. These results are in agreement with the results previously reported by Hebeish et al.[64]

8. Grafting In 0.05 N H_2SO_4 At 40°, 60° And 80°C:

Table (10) illustrates the effect of time on percent grafting in 0.05 N H_2SO_4 at 40°, 60° and 80°C.

Table (10)

Cellulose	: 0.1 gram
α-Bromoacrylic acid	: 0.5 gram
Ceric ammonium sulphate concentration	: 10 m Mole
0.05 N H_2SO_4	: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	5.1	25.5	60.2
20	7.8	78.8	80.9
30	59.3	86.5	86.9
60	125.7	83.9	105.1
90	110.3	71.8	118.6
120	64.3	68.2	110.5
180	67.0	68.6	129.0

Table (10) and Fig. 11 show the effect of time on percent grafting at 40°, 60° and 80°C in presence of 0.05 N H_2SO_4. It is clear that the percent grafting after 3 hours is affected by temperature in the order of 80° > 60° ≫ 40°C (129.0%, 68.6% and 67.0%, respectively).

9. Grafting In 0.1 N H_2SO_4 At 40°, 60° And 80°C:

Table (11) illustrates the effect of time on percent grafting in 0.1 N H_2SO_4 at 40°, 60° and 80°C.

Table (11)

Cellulose	: 0.1 gram
∝-Bromoacrylic acid	: 0.5 gram
Ceric ammonium sulphate concentration	: 10 m Mole
0.1 N H_2SO_4	: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	2.9	25.7	68.4
20	31.9	65.0	83.1
30	74.4	87.5	85.2
60	92.9	92.0	96.7
90	98.7	100.4	114.0
120	100.1	90.4	116.0
180	99.7	84.8	141.6

The effect of time on the percent grafting at 40°, 60° and 80°C in the presence of 0.1 N H_2SO_4 is illustrated in Table (11) and Fig. 12. It is clear, that increasing the temperature causes an increase in the percent grafting after 3 hours in the order 80° > 40° > 60°C (141.6%, 99.7% and 84.8%, respectively).

10. Grafting In 0.2 N H_2SO_4 At 40°, 60° And 80°C:

Table (12) illustrates the effect of time on percent grafting in 0.2 N H_2SO_4 at 40°, 60° and 80°C.

Table (12)

Cellulose : 0.1 gram
∝-Bromoacrylic acid : 0.5 gram
Ceric ammonium sulphate concentration: 10 m Mole
0.2 N H_2SO_4 : 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	1.7	46.0	42.2
20	18.1	56.9	59.8
30	59.6	59.2	71.6
60	103.7	70.2	86.6
90	93.7	----	99.7
120	94.8	70.9	90.3
180	84.2	68.0	105.4

Table (12) and Fig. 13 show the effect of time on the percent grafting in the presence of 0.2 N H_2SO_4 at 40°, 60° and 80°C. Thus, after 3 hours, the percent grafting increased with increase in temperature in the order 80° > 40° > 60° (105.4%, 84.2% and 68.0%, respectively). This

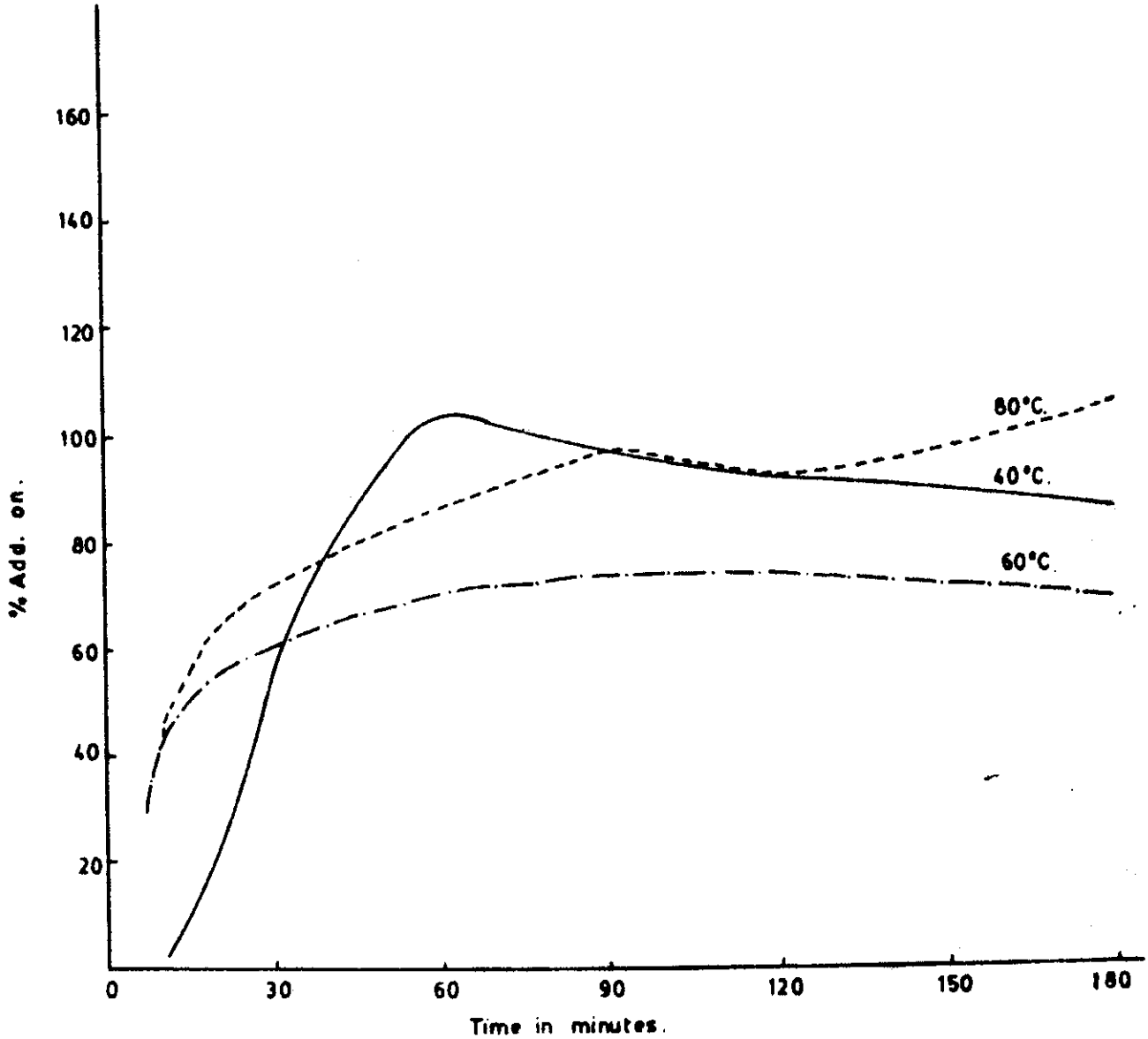


Fig.[13]: Effect of time on grafting in 0.2 N H_2SO_4 at 40, 60 and 80°C.

order of increase is similar to that when the system of 0.1 N H_2SO_4 was used (cf. Table (11) and Fig. 12).

The net result of using different concentrations of sulphuric acid at different temperatures is that increasing the temperature causes an increase in the percent grafting as shown from Tables (10), (11) and (12) and Figs. 11, 12 and 13 which are in agreement with the results reported by Hebeish et al.[64]

11. Grafting In 0.05 N $HClO_4$ At 40°, 60° And 80°C:

Table (13) illustrates the effect of time on the percent grafting in 0.05 N $HClO_4$ at 40°, 60° and 80°C.

Table (13)

Cellulose	: 0.1 gram
∝-Bromoacrylic acid	: 0.5 gram
Ceric ammonium sulphate concentration	: 10 m Mole
0.05 N $HClO_4$	: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	3.9	50.2	60.3
20	62.1	71.6	65.3
30	79.5	73.0	68.5
60	76.9	70.0	73.9
90	95.8	70.3	89.5
120	71.1	66.0	72.7
180	83.2	79.8	86.9

Table (13) and Fig. 14 illustrate the effect of time on the percent grafting in the presence of 0.05 N $HClO_4$ at 40°, 60° and 80°C. Thus, it is clear that increasing the temperature has a little effect on the percent grafting. After 3 hours, the percent grafting increased in the order 80° > 40° ≥ 60°C (86.9%, 83.2% and 79.8%, respectively).

12. Grafting In 0.1 N $HClO_4$ At 40°, 60° And 80°C:

Table (14) illustrates the effect of time on the percent grafting in 0.1 N $HClO_4$ at 40°, 60° and 80°C.

Table (14)

Cellulose	: 0.1 gram
∝-Bromoacrylic acid	: 0.5 gram
Ceric ammonium sulphate concentration	: 10 m Mole
0.1 N $HClO_4$	: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	21.4	49.2	40.0
20	73.0	50.8	55.7
30	77.8	53.1	71.9
60	81.8	57.2	73.1
90	68.4	61.8	91.1
120	54.9	66.3	99.6
180	65.8	74.3	119.4

Table (14) and Fig. 15 show the effect of time on the percent grafting in the presence of 0.1 N $HClO_4$ at 40°, 60° and 80°C and it is clear that increasing the temperature causes an increase in the percent grafting. After 3 hours, the percent grafting increased in the order 80° > 60° > 40°C (119.4%, 74.3% and 65.8%, respectively).

13. Grafting In 0.2 N $HClO_4$ At 40°, 60° And 80°C:

Table (15) illustrates the effect of time on the percent grafting in 0.2 N $HClO_4$ at 40°, 60° and 80°C.

Table (15)

Cellulose : 0.1 gram

α-Bromoacrylic acid : 0.5 gram

Ceric ammonium sulphate concentration: 10 m Mole

0.2 N $HClO_4$: 5 ml

Time (minutes)	% Grafting 40°	60°	80°
10	16.8	54.6	51.2
20	45.8	56.9	64.4
30	59.6	54.6	70.5
60	70.6	64.6	81.3
90	64.0	59.2	85.6
120	70.0	66.0	80.1
180	63.6	72.1	86.1

Table (15) and Fig. 16 show the effect of time on the percent grafting in the presence of 0.2 N $HClO_4$ at 40°, 60° and 80°C. It is clear that increasing the temperature causes an increase in the percent grafting. After 3 hours, the percent grafting increased in the order 80° > 60° > 40°C

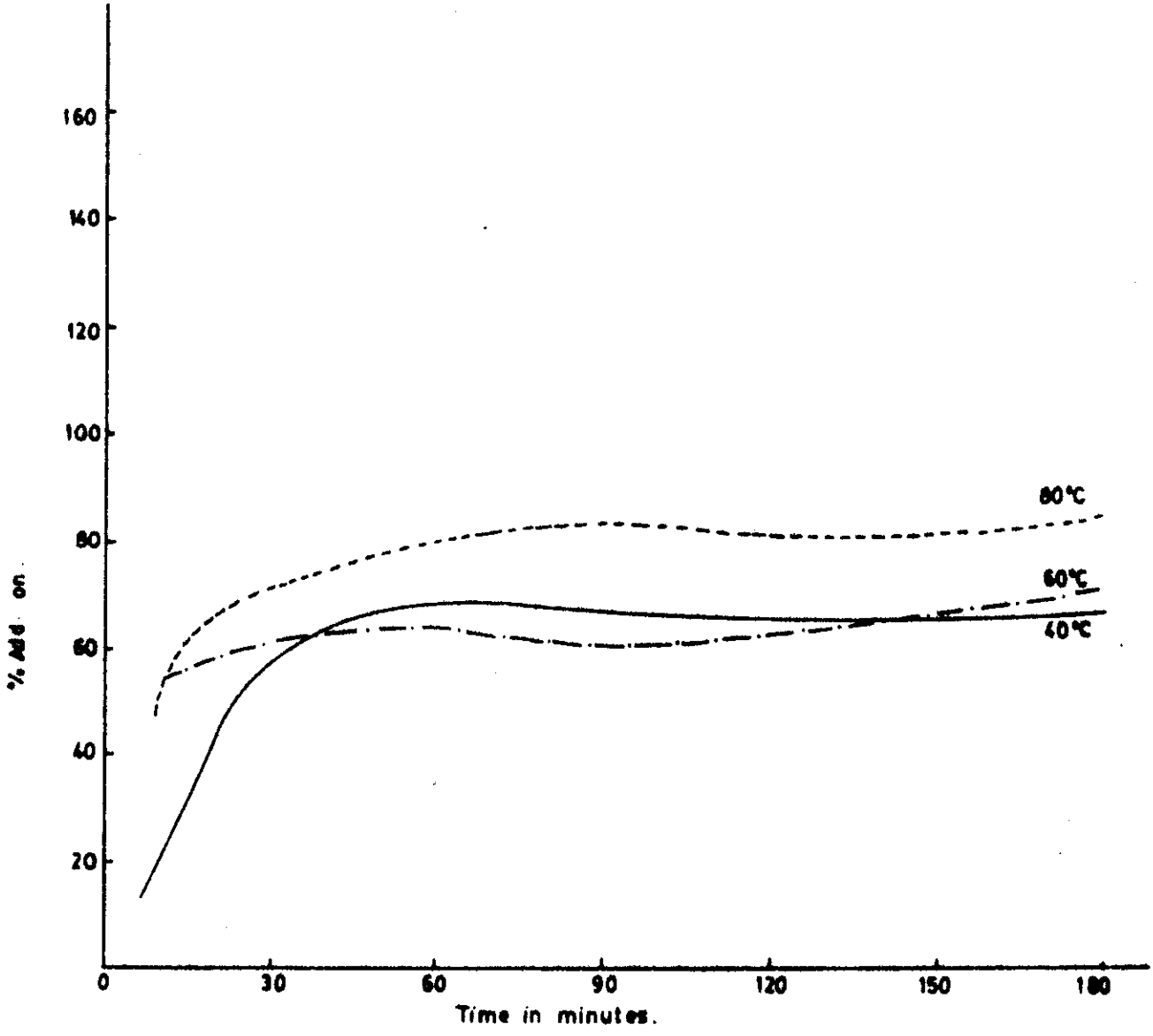


Fig.[16]: Effect of time on grafting in 0.2N $HClO_4$ at 40, 60 and 80°C.

(86.1%, 72.1% and 63.6%, respectively).

The net result of using different concentrations of perchloric acid at different temperatures is that increasing temperature causes an increase in the percent grafting as shown from Tables (13), (14) and (15) and Figs. 14, 15 and 16, which are in agreement with the results reported by Hebeish et al.[64]

Effect of Kind of Acid on Grafting:

The initiation with ceric ion in the graft copolymerization depends very much on the pH value of the system and on the kind of the acid used.[14,51,65,66] In the present investigation, it is obvious that the kind of acid has a great effect on the percent grafting. Thus, at 40°C, using 0.05 N acid concentration the percent grafting after 3 hours followed the order: $HNO_3 > HClO_4 > HCl > H_2SO_4$ (103.0, 83.2, 75.1 and 67.0%, respectively). Using 0.1 N acid concentration the percent grafting was in the order: $HNO_3 > H_2SO_4 > HCl > HClO_4$ (115.0%, 99.7%, 73.5% and 65.8%, respectively); and using 0.2 N acid concentration the percent grafting followed the same order as in case of 0.1 N acid concentration $HNO_3 > H_2SO_4 > HCl > HClO_4$ (105.4%, 84.2%, 67.8% and 63.6%, respectively).

At 60°C, using 0.05 N acid concentration the percent grafting was in the order $HClO_4 > H_2SO_4 > HNO_3 > HCl$ (79.8%, 68.6%, 64.8% and 53.2%, respectively), using 0.1 N acid concentration the percent grafting follows the order $H_2SO_4 > HClO_4 > HNO_3 \gg HCl$ (84.8%, 74.3%, 61.0% and 60.3%,

respectively), and using 0.2 N acid concentration the percent grafting almost follows the order when 0.05 N acid concentration was used $HClO_4 > HNO_3 \gg H_2SO_4 > HCl$ (72.1%, 69.7%, 68.0% and 51.5%, respectively).

At 80°C, using 0.05 N acid concentration the percent grafting was in the order $H_2SO_4 > HCl \gg HClO_4 > HNO_3$ (129.0%, 88.2%, 86.9% and 62.0%, respectively); using 0.1 N acid concentration the percent grafting follows the order $H_2SO_4 > HClO_4 > HNO_3 > HCl$ (141.6%, 119.4%, 105.0% and 68.2%, respectively); and using 0.2 N acid concentration the percent grafting follows the same order as using 0.05 N acid concentration $H_2SO_4 > HCl > HClO_4 > HNO_3$ (105.4%, 90.0%, 86.1% and 57.3%, respectively).

Effect of Acid Concentration on Percent Grafting:

In the present study, using acid concentrations more than 0.1 N cause a lowering in the percent grafting. So, it is clear that, in most cases, increasing of the acid concentration causes a decrease in the percent grafting (cf. Table 16). These results are in agreement with the results of Varma et al[62] who stated that the increase of hydrogen ion concentration leads to a lowering of grafting.

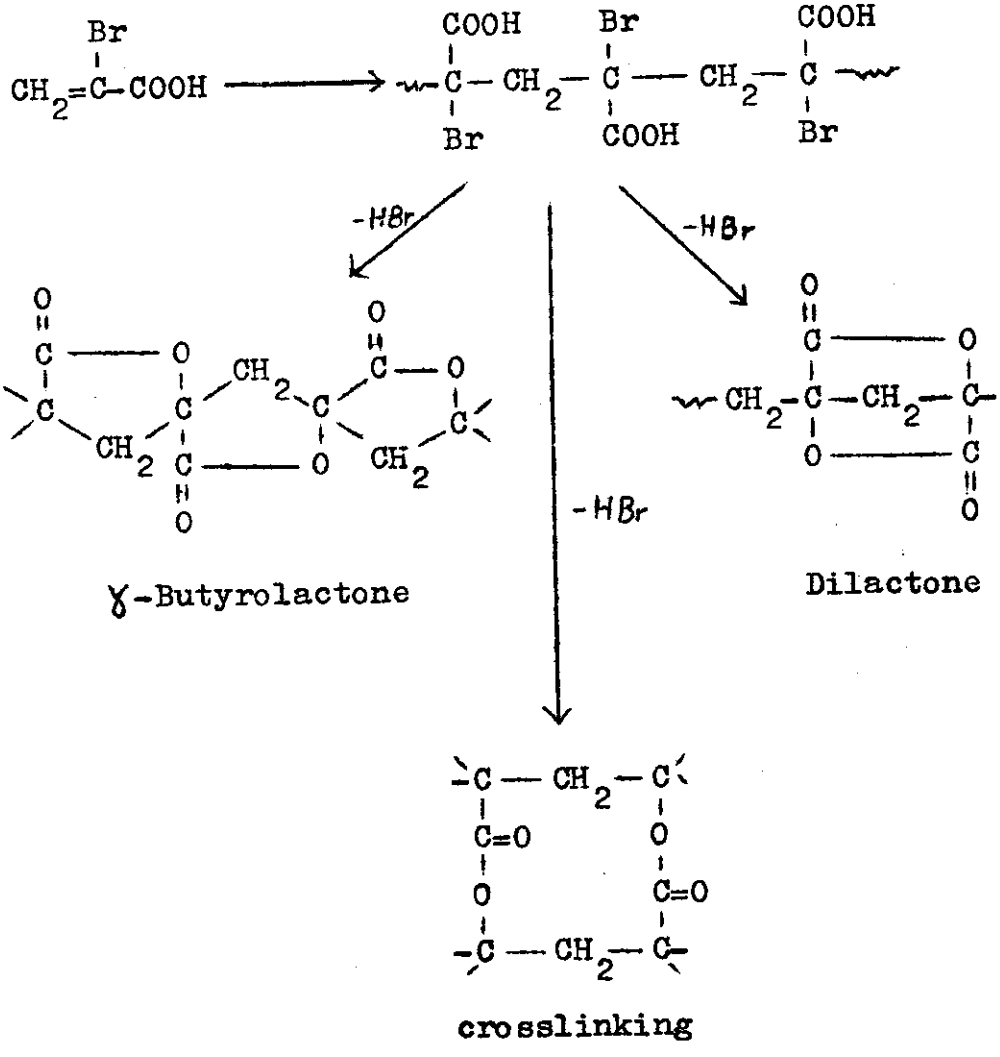
Table (16)

Effect of acid concentration on the percent grafting of α-bromoacrylic acid onto cellulose

Temperature °C	Concentration	% Grafting after 3 h			
		HCl	H_2SO_4	$HClO_4$	HNO_3
40	0.1 N	73.5	99.7	65.8	115.0
	0.2 N	67.8	84.2	63.6	105.0
60	0.1 N	60.3	84.4	74.3	61.0
	0.2 N	51.5	68.6	72.1	69.7
80	0.1 N	68.2	141.6	119.4	105.0
	0.2 N	90.0	105.4	86.1	57.3

Self-lactonization During Grafting Reaction:

It has been reported[52] during γ-ray induced polymerization of α-haloacrylic acids, elimination of hydrogen halide (HCl or HBr) took place, and intramolecular lactone formation was observed and the formation of polymers was assumed to take place according to the following:



It is expected that the intermolecular crosslinking reaction does not occur, and the dilactone structure indicated could not be assumed from the restrictions on the bond angles of C and O atoms. It is considered on the basis of the results of infrared spectra, solubility, and polymer structure that the γ-butyrolactone ring formation reaction is facilitated, at least at the initial stage of the reaction.

It was previously reported[59] that the attempts to determine the percent grafting by bromine analysis failed because lactonization also occured during the grafting reaction of cellulose with α-bromoacrylic acid.

The infrared spectrum of the grafted cellulose (Fig. 17) shows a strong band at 1785 cm^{-1} characteristic for the stretching frequency of C=O of γ-lactones. The band characteristic for the C=O group of carboxylic acids appeared at 1685 cm^{-1} (cf. Fig. 1) but completely disappeared in case of the grafted cellulose. This indicates that self-lactonization has taken place during the grafting reaction with the elimination of HBr to form the γ-butyrolactone structure as previously described.

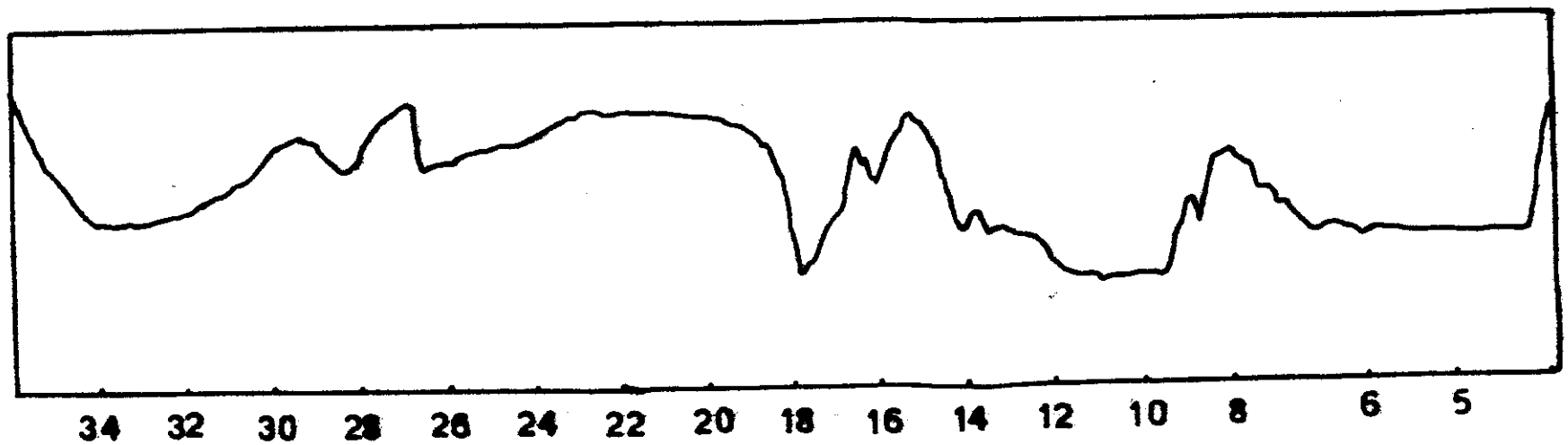


Fig. (17): I.R. Spectrum of the graft copolymer of α-bromoacrylic acid onto cellulose.