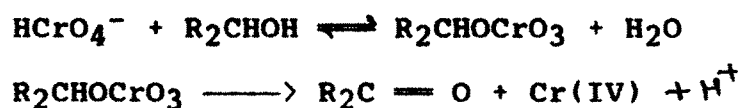

CHAPTER - III

RESULTS AND DISCUSSION

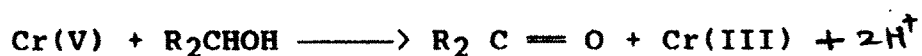
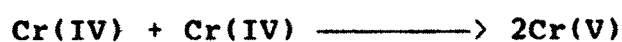
KINETICS OF OXIDATION OF BENZYL ALCOHOL AND
4-METHOXY BENZYL ALCOHOL

Chromium(VI) is a common reagent for the oxidation of organic materials. The mechanistic interest in oxidation by this reagent began with the inception of chemical kinetics as tool for studies of mechanism. The variety of species of chromium(VI) in acid solution, the presumed passage of chromium through transient, unstable species of oxidation number V and IV and the formation of varieties of complexes of chromium(III) all combine to give systems of considerable complexity. The mechanism for one equivalent reducing agents, mainly inorganic ions, King and co-workers¹ proposed a sequence of three-one electron transfer steps to reduce chromium(VI) to chromium(III) with interconversion between chromium(V) and chromium(IV) as the slow step.

For two equivalent reducing agents, the Westheimer² mechanism for oxidation of alcohols has been a focus for discussion and research. Reducing agents with —OH groups form ester with HCrO_4^- . The esters undergo internal oxidation-reduction in the rate determining steps to give chromium(IV).

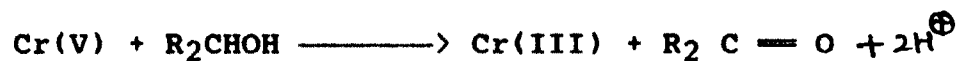
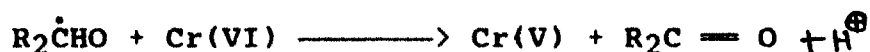
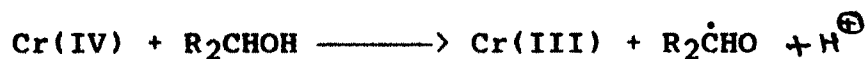


There ^{were} several paths ~~was~~ proposed for subsequent reaction of chromium(IV) thus making possible different mechanisms for the oxidation of alcohols. According to Westheimer and Watanabe^{2,3} subsequent step must involve chromium(VI).



SCHEME - I

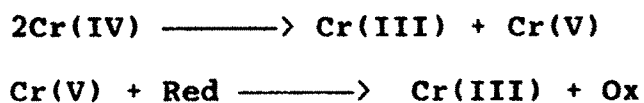
The other mechanism proposed by Westheimer⁴ involves production of ketyl radical.



SCHEME - II

The failure to detect free radicals lead Westheimer to rule out the mechanism involving ketyl radical but Rocek⁴ has observed a one electron oxidation of cyclobutanol by chromium(IV).

Although Westheimer has ruled out reaction between reactive species such as a later chromium(IV), study⁵ of oxidation of hydrazine by chromium(VI) strongly suggested disproportionation as one of the step.

**SCHEME - III**

The possibilities considered above are feasible when the reaction is carried out homogeneously. But if the oxidant is supported on a polymer, which has certain advantages⁶ over homogeneous reactions, the mechanism would be preferably according to scheme II. Therefore in order to investigate the possible path for the polymer supported chromate oxidation the present study was undertaken.

RESULTS

The reaction was studied at constant temperature of 45°C in 1:4 dioxane and the rate of stirring was kept constant for all the runs. The effect of polymeric reagent, alcohol, water and solvent were studied by keeping rest of the concentrations constant. The effect of polymeric reagent was studied between the range of 50 to 80 mg at constant alcohol concentration of 7.5 µl in case of both the alcohols. The results are shown in Table 1 and Table 2 for benzyl alcohol and 4-methoxy benzyl alcohol respectively. The plot of absorbance against time was found to be linear in all cases indicating zero order nature of the reaction. The plots are shown in figures 1 to 4 and Figures 5 to 8 for benzyl and 4-methoxy benzyl alcohols respectively. The

zero order rate constant was obtained from the slope of the plots and are given in Table 3.

The effect of alcohol concentration on the reaction was studied between the concentration range of 5 μ l to 12.5 μ l by taking polymeric reagent of 70 mg initially for all the runs. The data are tabulated in Table 4 and 5 for benzyl and 4-methoxy benzyl alcohols respectively. The linear zero order plots of absorbance against time are shown in Figures 9 to 12 and Figure 13 to 16 for benzyl and 4-methoxy benzyl alcohols respectively. The zero order rate constants obtained from slopes of the linear plots are given in Table 6.

The effect of solvent was also studied by carrying out the reaction in different solvents for benzyl alcohol. The data are shown in Table 7 and the zero order plots are shown in Figures 17 to 20 for 1:4 Dioxane, Chloroform, Carbon tetrachloride and Benzene respectively. The zero order rate constants along with dielectric constants are shown in Table 8. The results of Table 8 indicate that the reaction is facilitated in a solvent of higher dielectric constant.

Table 1: Effect of polymeric reagent concentration on the rate of reaction.

Solvent = 5 ml 1:4 dioxane

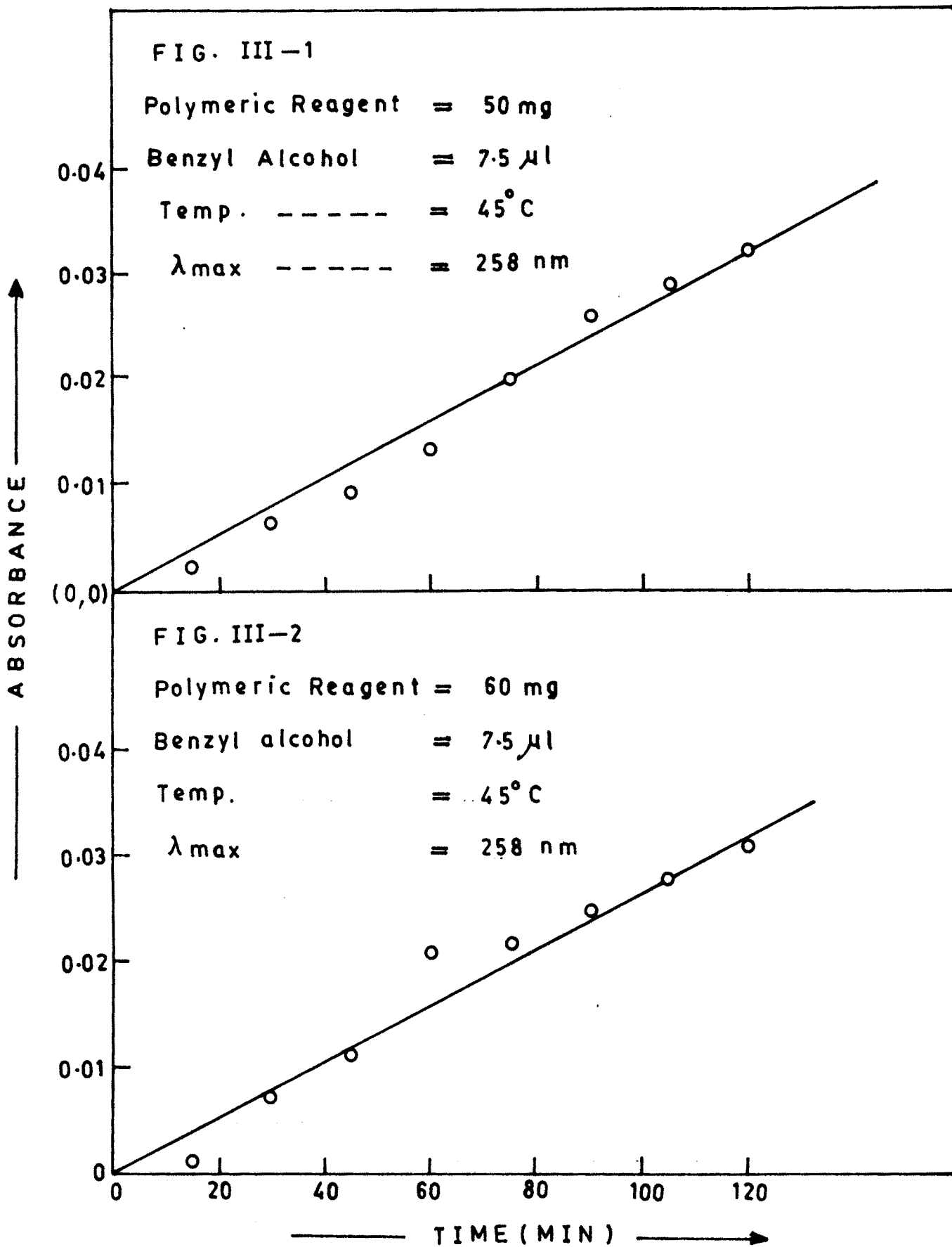
Substrate benzyl alcohol = 7.5 μ l

Temp = 45⁰c

λ_{\max} = 258 nm

Polymeric reagent	50 mg	60 mg	70 mg	80 mg
Time in min	O.D.	O.D.	O.D.	O.D.
15	0.002	0.001	0.001	0.006
30	0.006	0.007	0.010	0.007
45	0.009	0.011	0.008	0.009
60	0.013	0.021	0.012	0.013
75	0.020	0.022	0.015	0.018
90	0.026	0.025	0.022	0.023
105	0.029	0.028	0.026	0.023
120	0.032	0.031	0.028	0.034

Capacity of resin = 3.6 mmol/gm



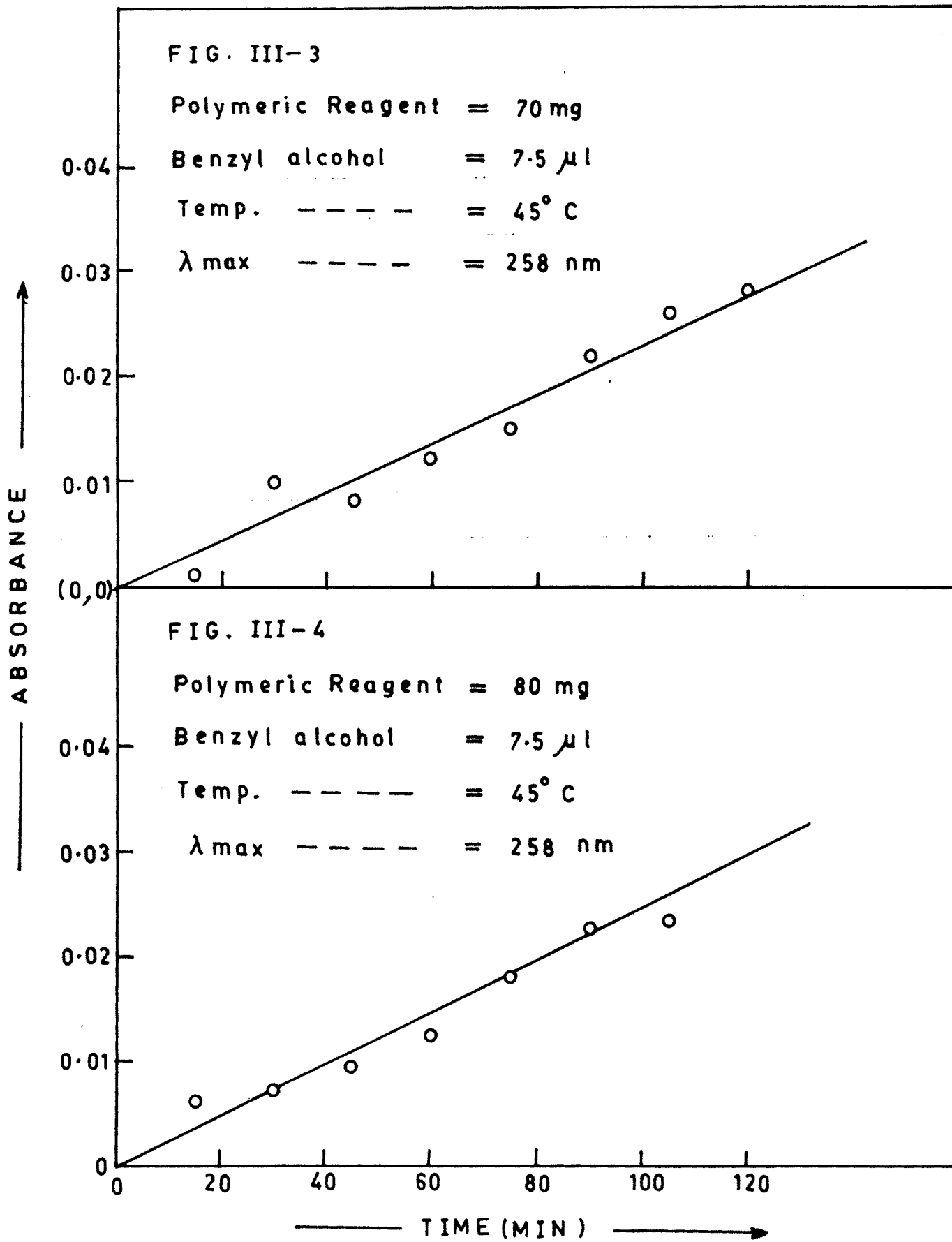


Table 2: Effect of polymeric reagent concentration on the rate of reaction.

Solvent = 5 ml 1:5 dioxane

Substrate (4-methoxy benzyl alcohol) = 7.5 μ l

Temp = 45⁰c

λ_{\max} = 276 nm

Polymeric reagent	50 mg	60 mg	70 mg	80 mg
Time in min	O.D.	O.D.	O.D.	O.D.
15	0.001	0.002	0.001	0.002
30	0.003	0.005	0.003	0.004
45	0.006	0.008	0.008	0.007
60	0.010	0.009	0.010	0.009
75	0.012	0.010	0.013	0.011
90	0.014	0.012	0.016	0.015
105	0.016	0.015	0.017	0.018
120	0.021	0.019	0.023	0.023

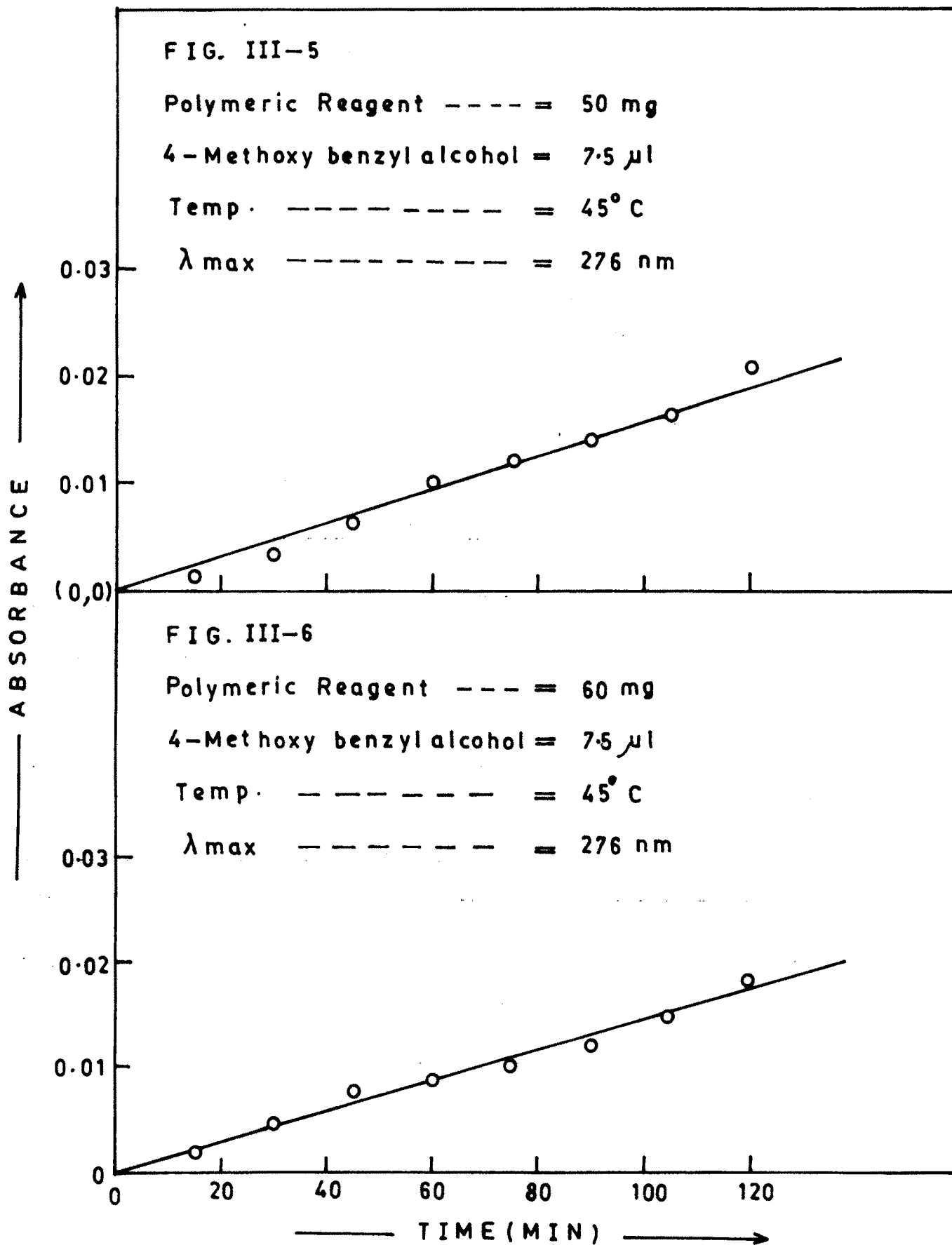


FIG. III-7

Polymeric Reagent ----- = 70 mg

4-Methoxy benzyl alcohol = 7.5 μ l

Temp. ----- = 45° C

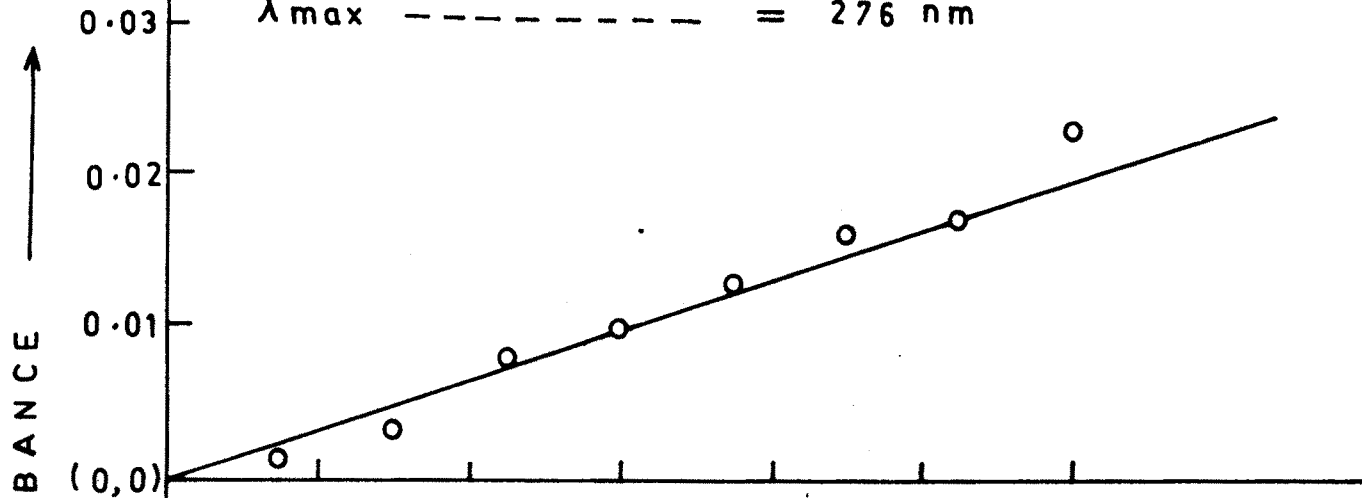
 λ_{max} ----- = 276 nm

FIG. III-8

Polymeric Reagent ----- = 80 mg

4-Methoxy benzyl alcohol = 7.5 μ l

Temp. ----- = 45° C

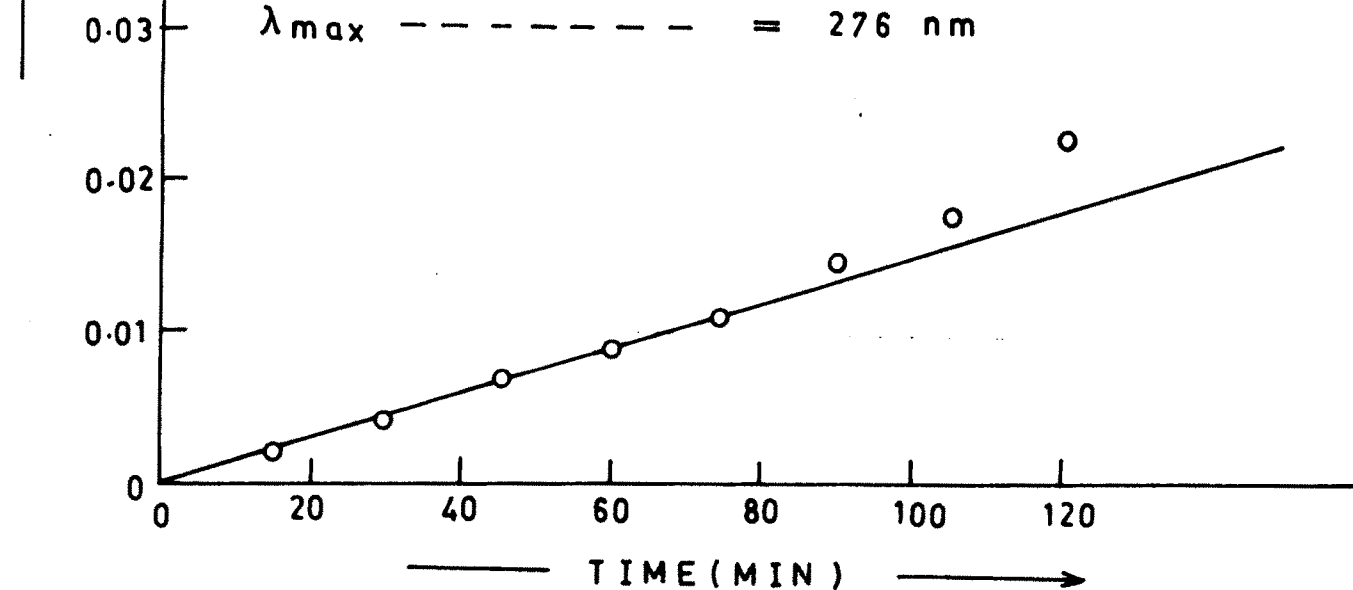
 λ_{max} ----- = 276 nm

Table 3: Rate constant obtained from the slope of the plot for change in concentration of polymeric reagent.

Solvent = 5 ml 1:4 dioxane

Temp = 45⁰c

λ_{\max} = 258 nm for benzyl alcohol

λ_{\max} = 276 nm for 4-methoxy benzyl alcohol

Substrate alcohol taken = 7.5 μ l

Polymeric reagent	$k \times 10^{-4} \text{ min}^{-1}$ for benzyl alcohol	$k \times 10^{-4} \text{ min}^{-1}$ for 4-methoxy benzyl alcohol
50 mg	2.6	1.53
60 mg	2.6	1.51
70 mg	2.3	1.62
80 mg	2.4	1.54

Table 4: Effect of alcohol concentration on the rate of reaction.

Polymeric reagent = 70 mg.

Solvent = 5 ml 1:4 dioxane

Temp = 45⁰c

λ_{\max} = 258 nm

Benzyl reagent	5 μ l	7.5 μ l	10 μ l	12.5 μ l
Time in min	O.D.	O.D.	O.D.	O.D.
15	0.008	0.001	0.007	0.008
30	0.009	0.010	0.009	0.012
45	0.010	0.008	0.010	0.015
60	0.011	0.012	0.012	0.017
75	0.016	0.015	0.019	0.021
90	0.019	0.022	0.025	0.024
105	0.022	0.026	0.027	0.026
120	0.028	0.028	0.032	0.028

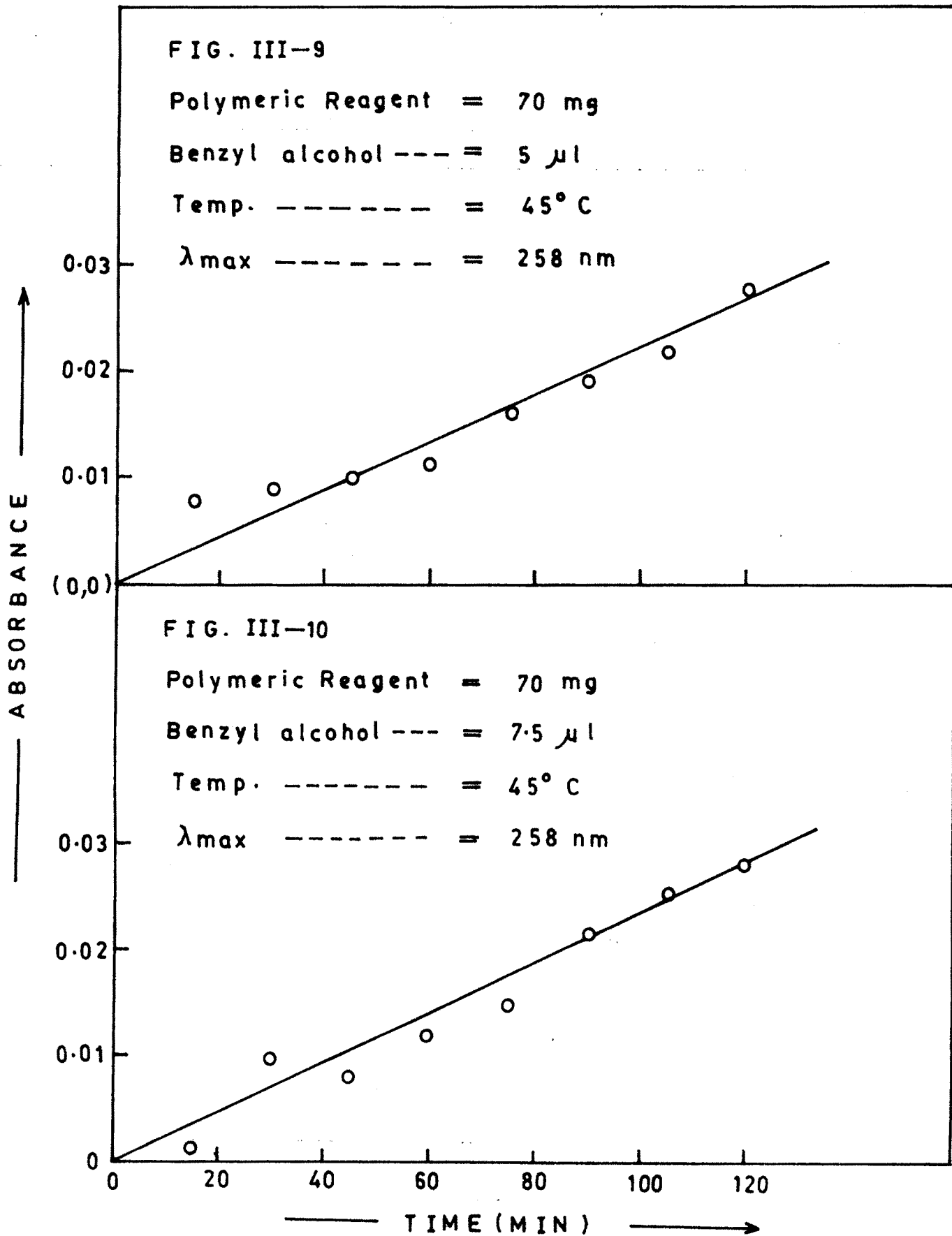
Benzaldehyde mol. wt. 106, density = 1.044

O.D. of diluted solution is 0.313

diluted solution 5 μ l in 50 ml

1:4 dioxane and 1 ml diluted to 50 ml

[Benzaldehyde] = $2 \times 10^{-5}M$



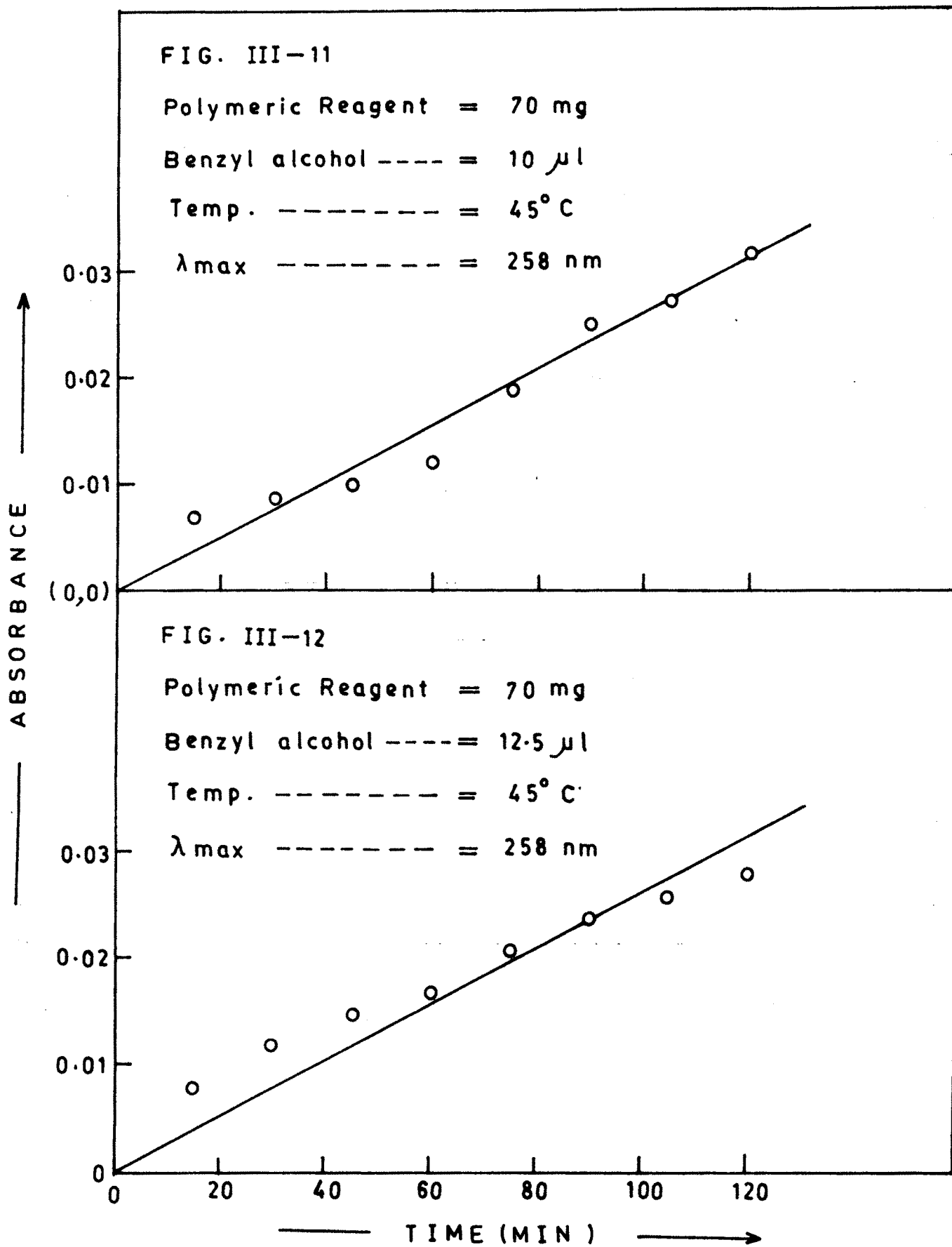


Table 5: Effect of alcohol concentration on the rate of reaction.

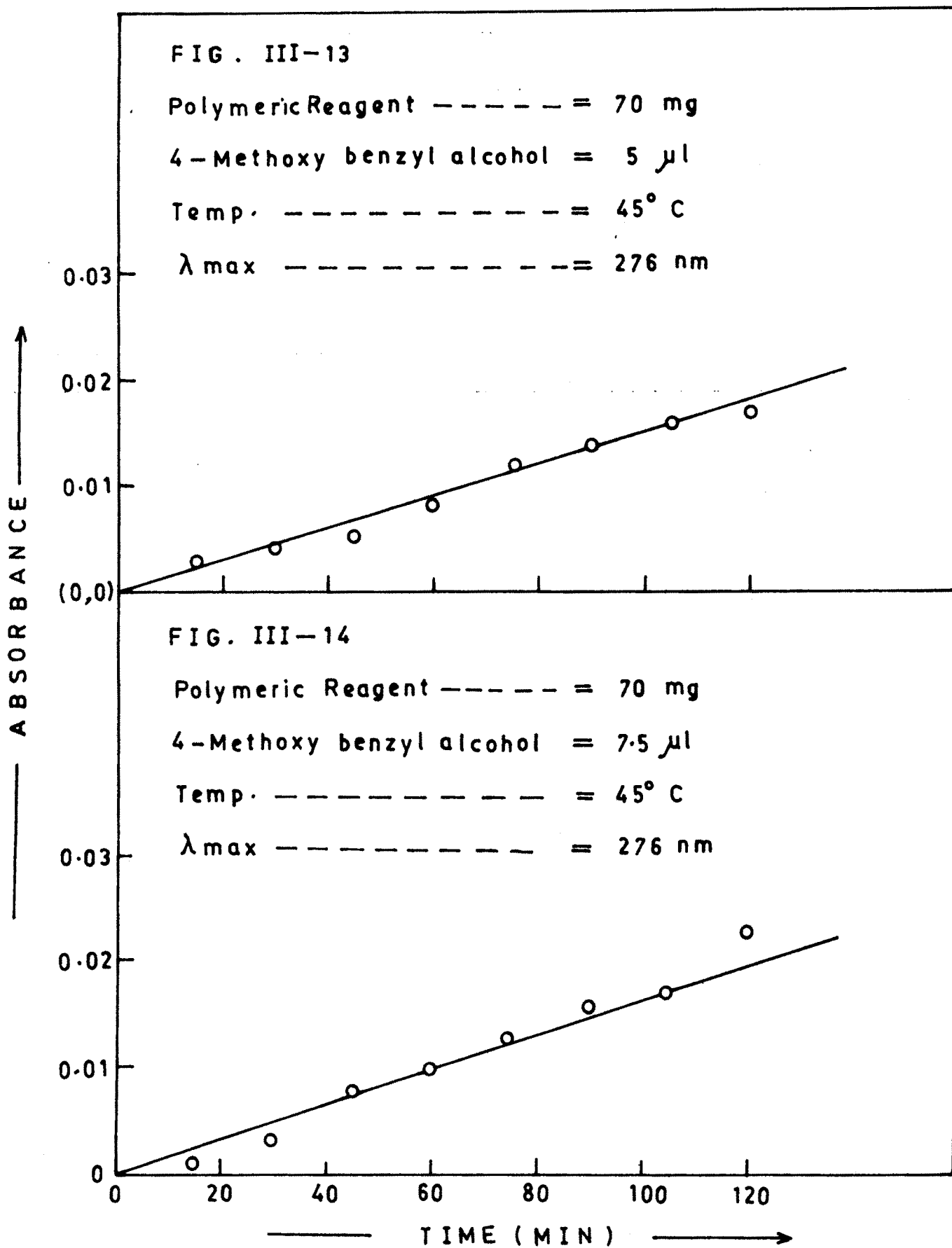
Polymeric reagent = 70 mg

Solvent = 5 ml 1:4 dioxane

Temp = 45°C

λ_{\max} = 276 nm

4-methoxy benzyl alcohol	5 μ l	7.5 μ l	10 μ l	12.5 μ l
Time in min	O.D.	O.D.	O.D.	O.D.
15	0.003	0.001	0.001	0.001
30	0.004	0.003	0.003	0.003
45	0.005	0.008	0.004	0.005
60	0.008	0.010	0.008	0.008
75	0.012	0.013	0.011	0.010
90	0.014	0.016	0.013	0.013
105	0.016	0.017	0.015	0.015
120	0.017	0.023	0.020	0.019



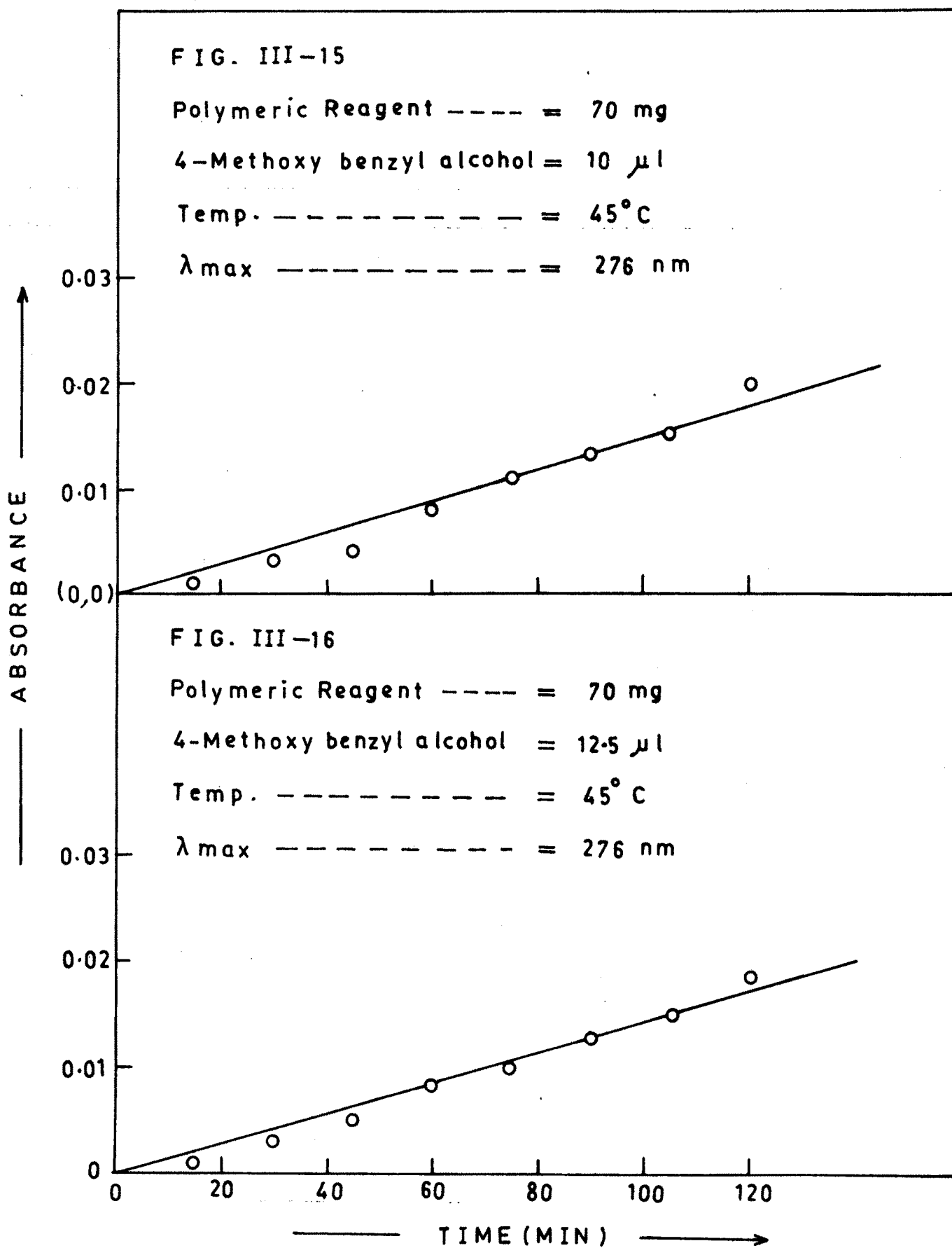


Table 6: Rate constant obtained from the slope of the plot for change in concentration of alcohol.

Solvent = 5 ml 1:4 dioxane

Temp = 45⁰c

λ_{\max} = 258 nm for benzyl alcohol

λ_{\max} = 276 nm for 4-methoxy benzyl alcohol

Polymeric reagent = 70 mg

Amount of substrate (Alcohol)	$k \times 10^{-4} \text{ min}^{-1}$ for benzyl alcohol	$k \times 10^{-4} \text{ min}^{-1}$ for 4-methoxy benzyl alcohol
5.0 μl	2.3	1.54
7.5 μl	2.4	1.60
10.0 μl	2.6	1.50
12.5 μl	2.6	1.50

Table 7: Effect of change in solvent on the rate of reaction

Polymeric reagent = 70 mg

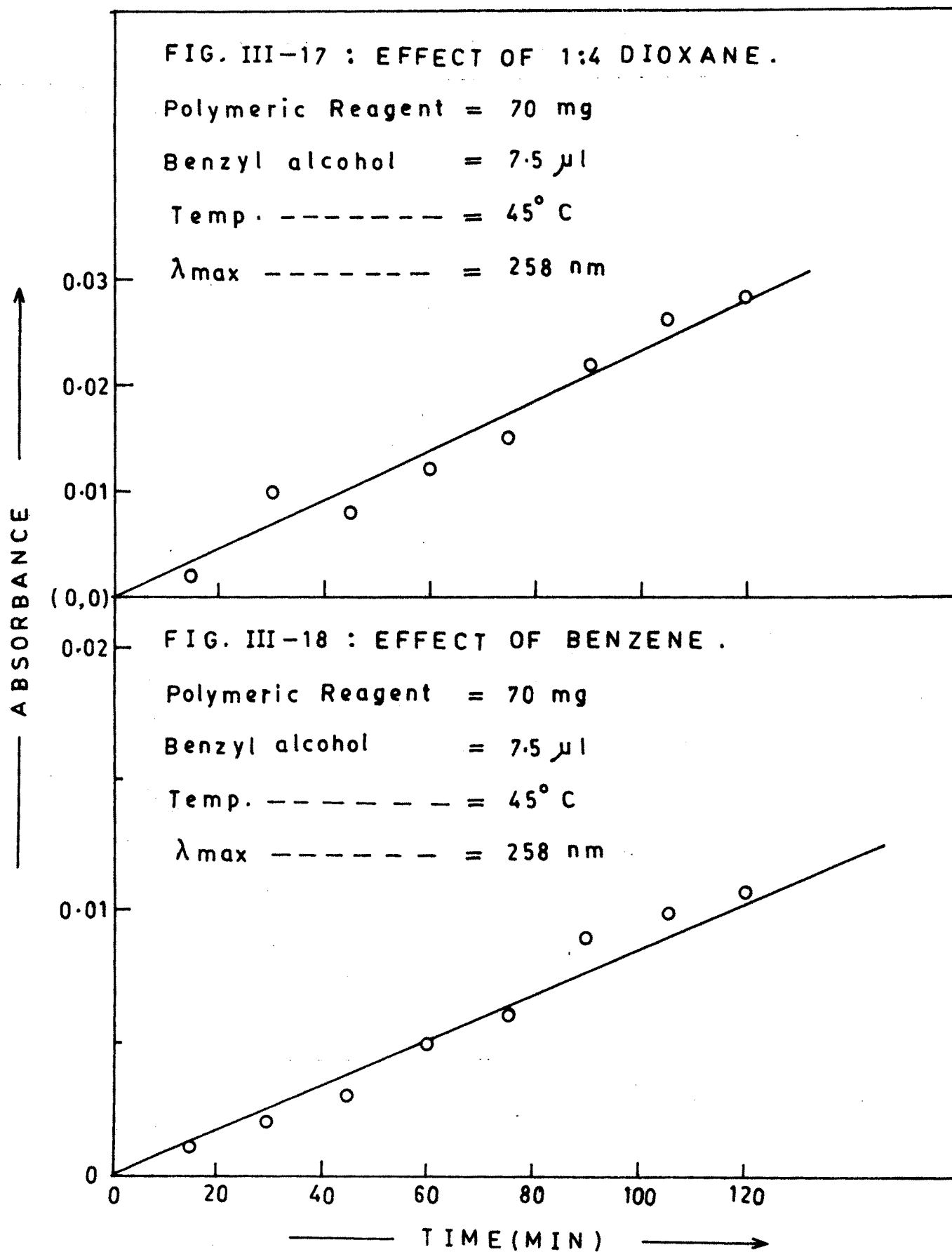
Benzyl alcohol = 7.5 μ l

Solvent = 5 ml

Temp = 45⁰c

λ_{\max} = 258 nm

Solvent	1:4 dioxane	Carbon tetrachloride	Chloroform	Benzene
Time in min	O.D.	O.D.	O.D.	O.D.
15	0.001	0.003	0.002	0.001
30	0.010	0.006	0.007	0.002
45	0.008	0.009	0.018	0.003
60	0.012	0.012	0.025	0.005
75	0.015	0.018	0.030	0.006
90	0.022	0.022	0.040	0.009
105	0.026	0.028	0.045	0.010
120	0.028	0.030	0.055	0.012



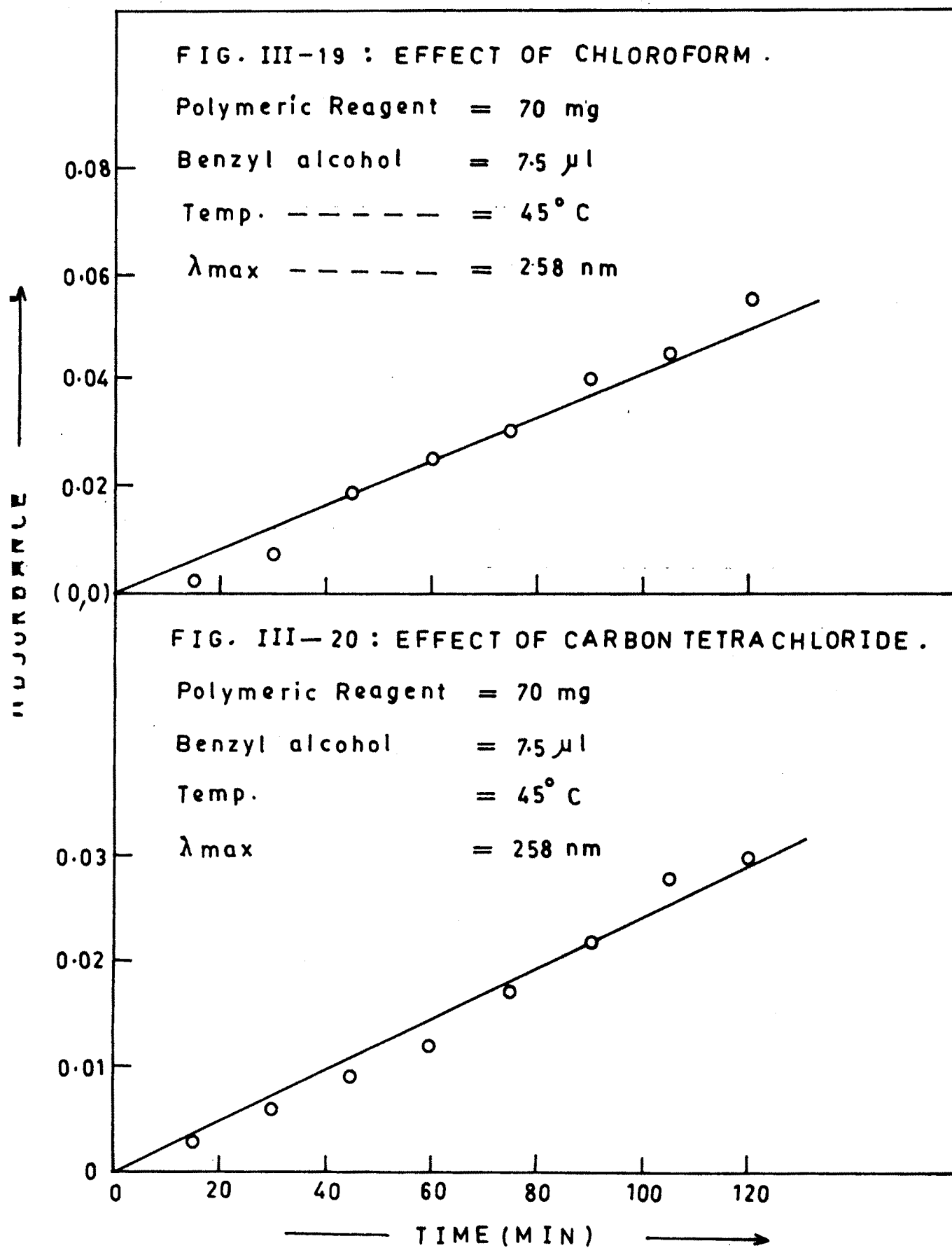


Table 8: Effect of dielectric constant of the solvent on the rate of reaction

Polymeric reagent = 70 mg

Benzyl alcohol = 7.5 μ l

Solvent = 5 ml

Temp = 45⁰c

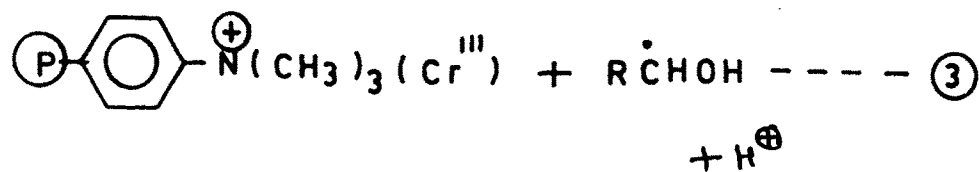
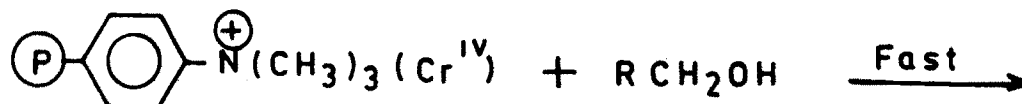
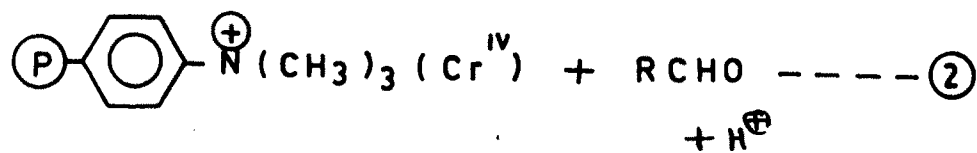
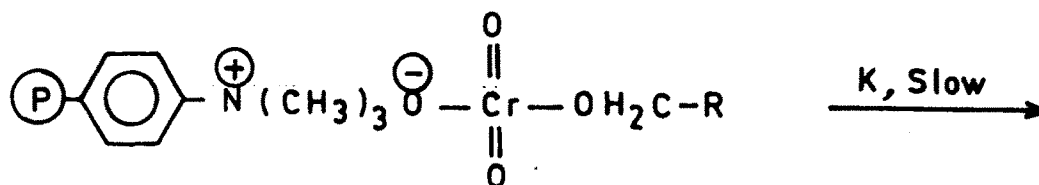
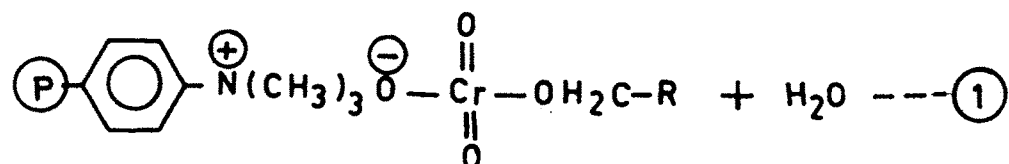
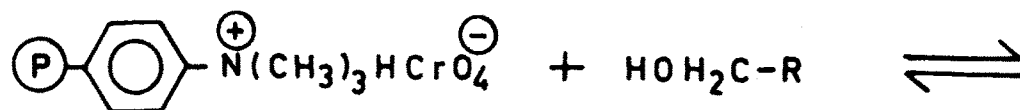
λ_{max} = 258 nm

Solvent	$k \times 10^{-4} \text{ min}^{-1}$	Dielectric constant
1:4 Dioxane	2.3	2.209
Benzene	0.9	2.274
Chloroform	4.1	4.806
Carbon tetrachloride	2.3	2.228

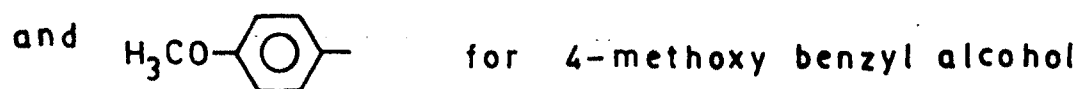
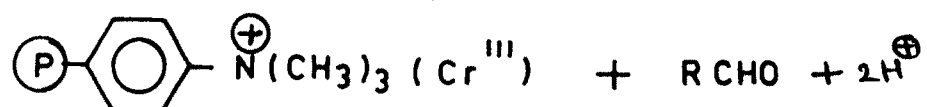
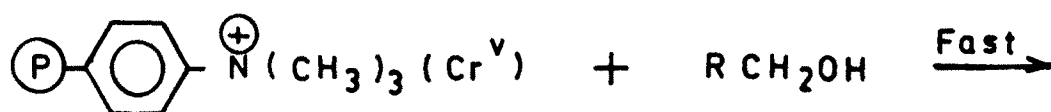
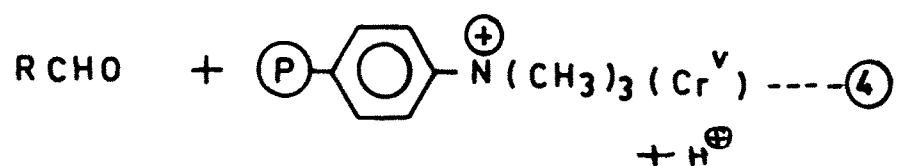
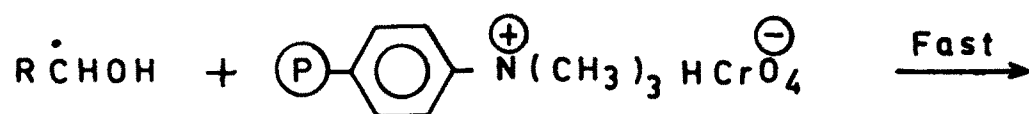
DISCUSSION

The linearity of absorbance against time plots and constancy of the zero order rate constants indicate that the reaction is neither depends on the polymeric reagent nor the alcohol concentration. This anomalous nature of the reaction may be because the oxidant is taken in the form of a solid supported on a polymer. Therefore, the prior equilibria, before the rate determining or the step in which actual reaction takes place giving the product does not seem to contribute to the total rate since they are occurring in a different phase i.e. solid phase. This was observed in our earlier study of benzoin oxidation by polymer supported N-Bromo sulphonamide⁷.

Chromium(VI) oxidation of alcohols as discussed earlier, proceed through formation of an ester. The ester thus formed will undergo internal oxidation-reduction to produce chromium(IV). Since our oxidant was supported on a polymeric material the intermediate chromium(IV) will further oxidise another molecule of alcohol to a free radical. Thus based on the experimental results obtained for the oxidation of benzyl and 4-methoxy benzyl alcohols which were found to be zero order the mechanism may be suggested as per SCHEME IV.

SCHEME - IV

Contd. ---

SCHEME-IV (Contd.)

The mechanism of scheme IV involves an ester formation as preliminary step. The ester formed will be decompose into an aldehyde and intermediate chromium(IV) in the second and slow step. The intermediate chromium(IV) thus formed will further react with another alcohol molecule to produce a free radical. The free radical formation in the reaction was confirmed by the polymerization^{of} the added acrylonitrile to the reaction mixture. Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast step leading to the formation of chromium(V). The intermediate chromium(V) in the last step reacts with alcohol to produce aldehyde. The test for formation of chromium(V) and chromium(IV) by their characteristic induced oxidations of iodide⁸ and manganese(II)² were not successfull probably due to the heterogeneity of the reaction mixture.

According to scheme IV a second order rate law is expected. But since the 1st step of ester formation occurs in the solid phase and assuming that this equilibrium does not contribute to the rate of the reaction we obtain a zero order dependence with rate constant k of the second slow step in which product aldehyde is formed.

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