



CHAPTER III

RESULTS AND DISCUSSION

3.1 Poly (vinyl chloride) samples

In this study the PVC samples were taken from different manufacturers. Two samples, PVC-ICI 1 and PVC-ICI 2 were provided by Imperial Chemical Industries; Australia. Three samples, PVC-TP 1, PVC-TP 2 and PVC-TP 3 were from Thai Plastic & Chemical Co. Ltd., Thailand.

The average molecular weight of these samples were identified by dilute solution viscosity method (APPENDIX I). In this method, the flow time of tetrahydrofuran (t_0) and the solutions of PVC samples in tetrahydrofuran (t) were measured by using the same viscometer at 25°C. The relative viscosity (η_r) could be obtained from the ratio of t/t_0 . Finally, the inherent viscosity was calculated from $\ln \eta_r/C$. Consequently, the relative and inherent viscosity of each PVC sample were determined. These results are shown in TABLE 3-1 to 3-5. When the inherent viscosity was plotted against the corresponding concentration of each PVC sample, a straight line was obtained (see FIGURE 3-1 to 3-5). The extrapolation of the straight line of each plot gives the intercept which is the intrinsic viscosity of that PVC solution.

TABLE 3-1 The inherent viscosity of PVC-ICI 1 at various concentrations.

Concentrations C (g.dl ⁻¹)	Flow time t (sec)	Relative viscosity $\eta_r = t/t_0$	Inherent viscosity $\ln \eta_r/C$ (dl.g ⁻¹)
0.2667	119.60	1.2065	0.7039
0.3048	122.60	1.2367	0.6970
0.3556	126.65	1.2771	0.6889
0.4000	130.20	1.3139	0.6825

TABLE 3-2 The inherent viscosity of PVC-ICI 2 at various concentrations.

Concentrations C (g.dl ⁻¹)	Flow time t (sec)	Relative viscosity $\eta_r = t/t_0$	Inherent viscosity $\ln \eta_r/C$ (dl.g ⁻¹)
0.2667	132.50	1.3415	1.1015
0.3048	137.93	1.3914	1.0837
0.3556	144.90	1.4617	1.0675
0.4000	150.75	1.5207	1.0479

TABLE 3-3 The inherent viscosity of PVC-TP 1 at various concentrations.

Concentrations C (g.dl ⁻¹)	Flow time t (sec)	Relative viscosity $\eta_r = t/t_o$	Inherent viscosity $\ln \eta_r/C$ (dl.g ⁻¹)
0.2667	119.50	1.2055	0.7007
0.3048	122.33	1.2340	0.6899
0.3556	126.10	1.2721	0.6767
0.4000	129.20	1.3033	0.6623

TABLE 3-4 The inherent viscosity of PVC-TP 2 at various concentrations.

Concentrations C (g.dl ⁻¹)	Flow time t (sec)	Relative viscosity $\eta_r = t/t_o$	Inherent viscosity $\ln \eta_r/C$ (dl.g ⁻¹)
0.2667	127.55	1.2867	0.9452
0.3048	132.00	1.3316	0.9395
0.3556	137.30	1.3850	0.9160
0.4000	142.50	1.4375	0.9073

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TABLE 3-5 The inherent viscosity of PVC-TP 3 at various concentrations.

Concentrations C (g.dl ⁻¹)	Flow time t (sec)	Relative viscosity $\eta_r = t/t_o$	Inherent viscosity $\ln \eta_r/C$ (dl.g ⁻¹)
0.2667	132.70	1.3386	1.0936
0.3048	138.00	1.3921	1.0854
0.3556	144.35	1.4562	1.0568
0.4000	150.30	1.5162	1.0405

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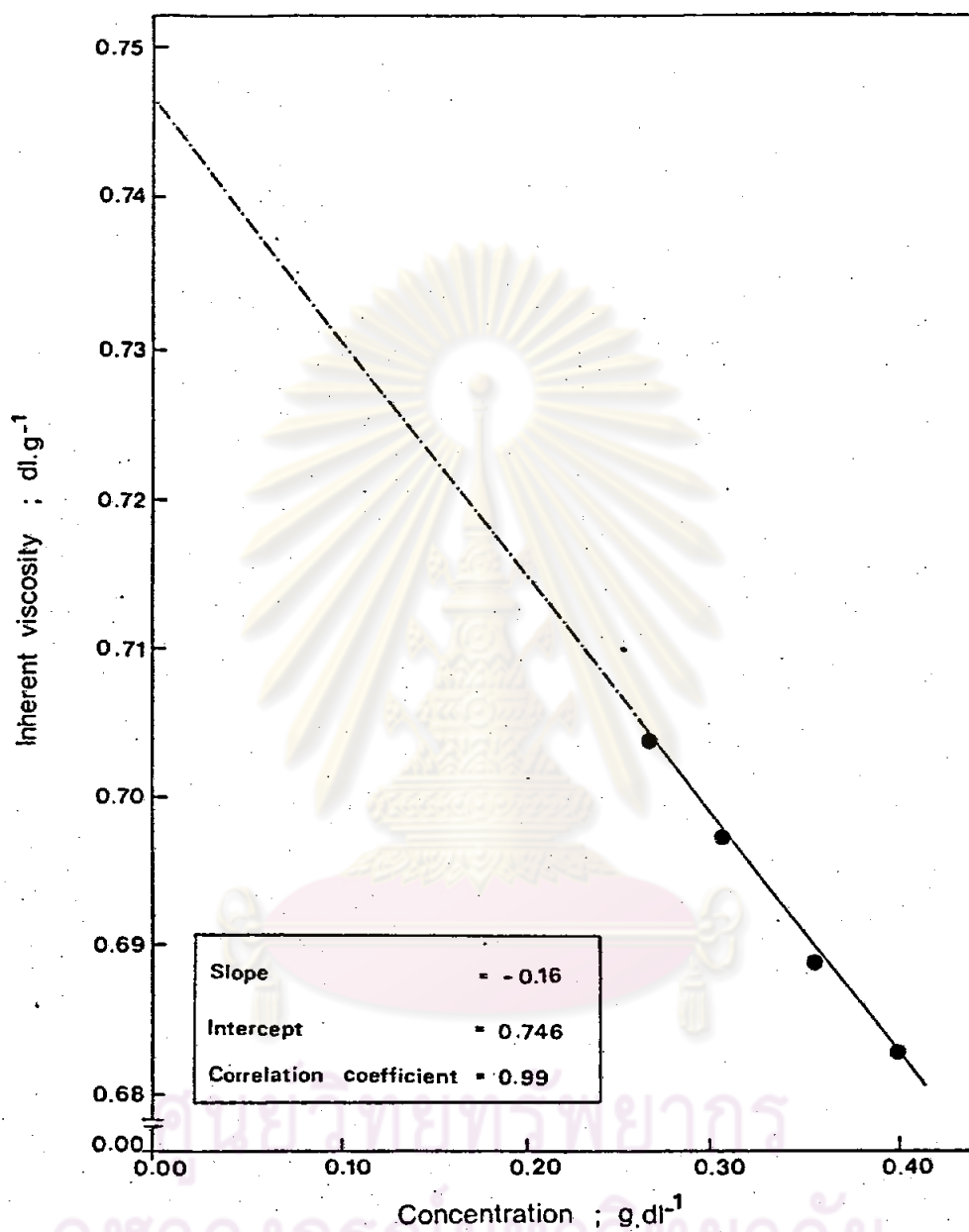


FIGURE 3-1 The plot of concentration of PVC-ICI 1 in tetrahydrofuran with the corresponding inherent viscosity

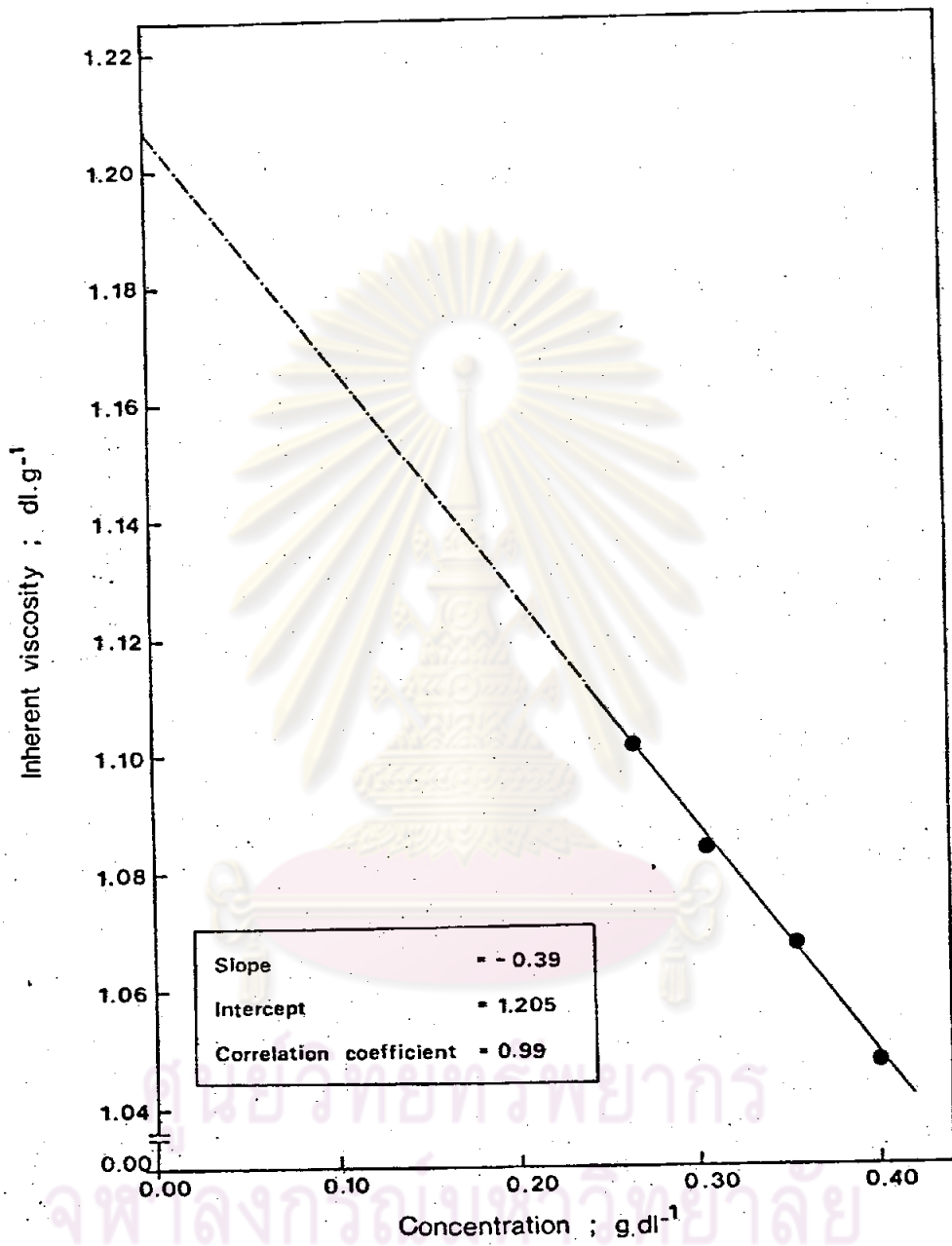


FIGURE 3-2 The plot of concentration of PVC-ICI 2 in tetrahydrofuran with the corresponding inherent viscosity

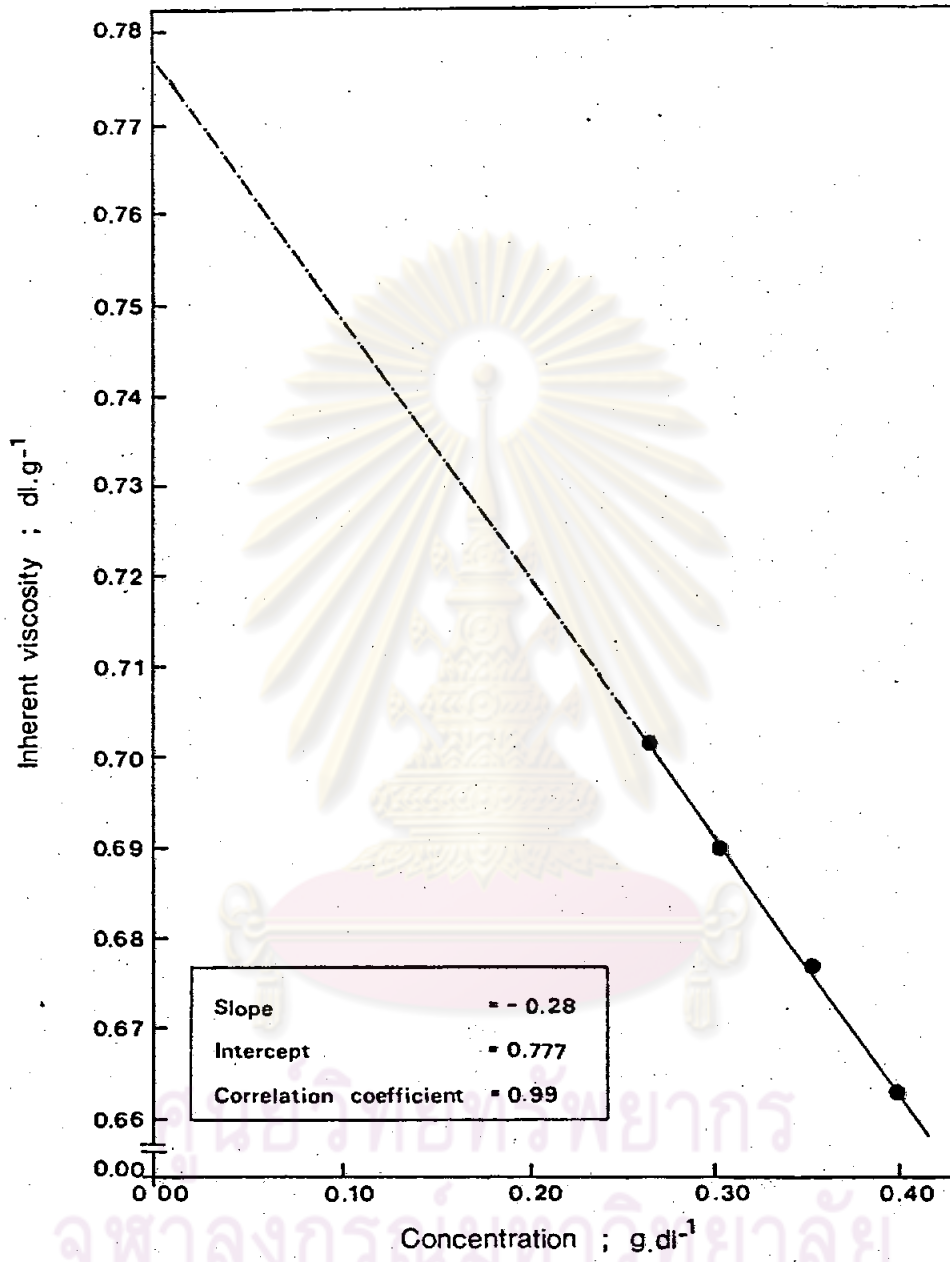


FIGURE 3-3 The plot of concentration of PVC-TP 1 tetrahydrofuran with the corresponding inherent viscosity

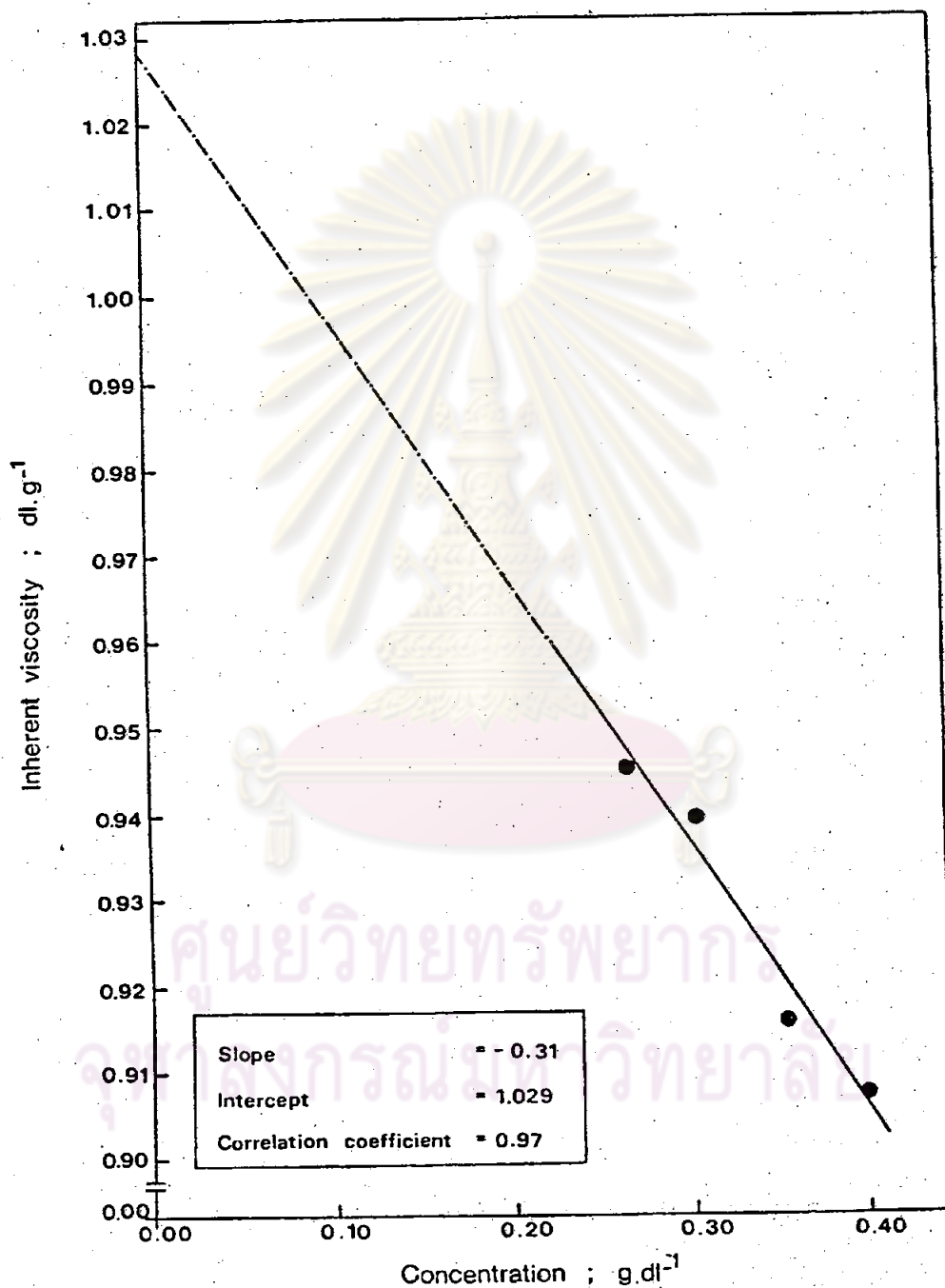


FIGURE 3-4 The plot of concentration of PVC-TP 2 in tetrahydrofuran with the corresponding inherent viscosity

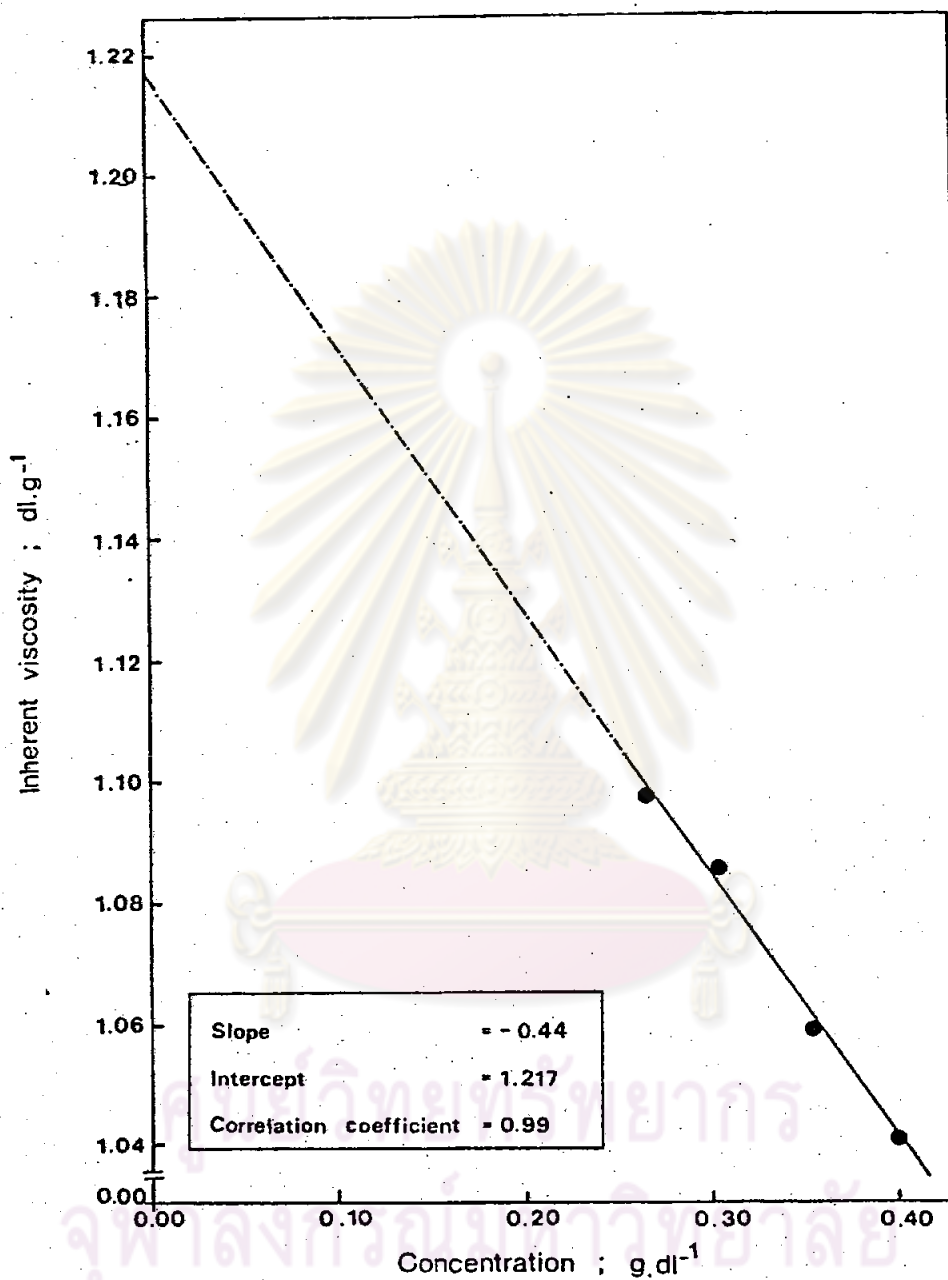


FIGURE 3-5 The plot of concentration of PVC-TP 3 in tetrahydrofuran with the corresponding inherent viscosity.

The viscosity average molecular weight (\bar{M}_v) can then be obtained by calculation using the following equation.

$$[\eta] = K \bar{M}_v^a$$

Where K and a are constants; for PVC in tetrahydrofuran at 25° C $K = 1.5 \times 10^{-4}$, $a = 0.77$. (34)

To characterize the PVC samples, one can also discuss in term of degree of polymerization (DP) which is the number of repeating units in the polymer chain. By this way, one can easily compare the different sizes of the polymer chains. in the case of PVC, the semiempirical formula is $(\text{CH}_2-\underset{\text{Cl}}{\text{CH}})_n$. Therefore, n is the degree of polymerization. Hence, the molecular weight of PVC is equal to n times the molecular weight of the repeating unit which is 50.5. In other words, the degree of polymerization can be calculated by dividing the molecular weight of each PVC sample with 50.5.

Table 3-6 Shows the relationship of viscosity average molecular weight of all five PVC samples and the corresponding degree of polymerization.

PVC sample	Intrinsic viscosity $[\eta]$	Viscosity average molecular weight $\bar{M}_v \times 10^{-4}$	Degree of polymerization [DP]
ICI 1	6.40	6.40	1,024
ICI 2	1.21	11.80	1,888
TP 1	0.78	6.70	1,072
TP 2	0.96	8.80	1,408
TP 3	1.22	12.00	1,920

3.2 Preliminary investigation of the photodegradation study

The photodegradation of 2.0 g.dl^{-1} PVC-ICI 1 in tetrahydrofuran was performed by using the apparatus as shown in FIGURE 2-2. Irradiation was carried out using a medium-pressure mercury lamp (Philips 125 W). The light from the mercury lamp was passed through water in a quartz water-cooled jacket in order to remove the infrared irradiation. Thus, only reaction occurred due to the light, not the heat.

The PVC-ICI 1 solution in the reaction vessel was magnetically stirred to keep the solution homogeneous and to facilitate the evolution of any volatile product formed from the reaction solution. It was found that oxygen interfered the photodegradation of PVC by a chain scission reaction(37). Therefore, it is necessary to remove the oxygen that might be in the PVC solution by bubbling oxygen-free nitrogen through the PVC solution for 15 minutes before irradiation. Furthermore, nitrogen gas is also bubbling through the PVC solution during illumination in order that the volatile product once occurred will be carried away from the solution.

Since it has been known that hydrogen chloride is the only product from the photodegradation of PVC(37), the outlet of the reaction vessel was designed to connect directly to the gas dispersion tube immersed in 80 ml of water in the conductivity measurement cell. The flow rate of nitrogen gas was adjusted, in order to transfer hydrogen chloride with the appropriate rate from the reaction vessel into the conductivity measurement cell while the water was not splashed all over the cell. Usually, the nitrogen flow rate is kept constant at 100 ml/min.

It is reported that 1.84 mole of hydrogen chloride can dissolve in 100 ml of water at 30°C (30). In this research work, the maximum conductivity of the aqueous solution in the conductivity measurement

conductivity of the aqueous solution in the conductivity measurement cell observed is $232.30 \mu S cm^{-1}$. This corresponds to 0.00016 mole of hydrogen chloride in 100 ml of water at $30^{\circ}C$ (according to the conductivity-concentration profile FIGURE 2-9. Consequently, all hydrogen chloride produced during irradiation should be able to dissolve in water rather than escape from the conductivity measurement cell.

After 4 hours of irradiation, few milliliters of aqueous solution in the conductivity cell was taken and acidified. Upon addition of silver nitrate into the acidified solution, fine white precipitates appeared. This test confirms that the chloride is present in the aqueous solution (39). In comparison, no precipitation was observed when silver nitrate solution was added into the acidified deionized water taken from the same source. Thus hydrogen chloride did certainly form during the photodegradation of PVC in tetrahydrofuran.

During irradiation, the conductivity of the aqueous solution in the conductivity measurement cell was recorded every 30 minutes. After 4 hours, the lamp was turned off. The fresh PVC-ICI 1 solution was then irradiated. The results of both reactions, after conversion of the conductivity into the corresponding amount of hydrogen chloride, are shown in TABLE 3-7.

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TABLE 3-7 The relationship between irradiation time and concentration of PVC-ICI 1 in nitrogen.

Irradiation time (min)	Concentration (M x 10 ⁻⁴)	
	I	II
30	-	-
60	0.36	0.31
90	1.82	1.65
120	3.71	3.63
150	6.13	6.05
180	9.25	9.11
210	12.52	12.33
240	16.06	15.91

-the data is undetectable

The plots, between the amount of hydrogen chloride with irradiation time, from both experiments indicate good reproducibility of the reaction as shown in FIGURE 3-6.

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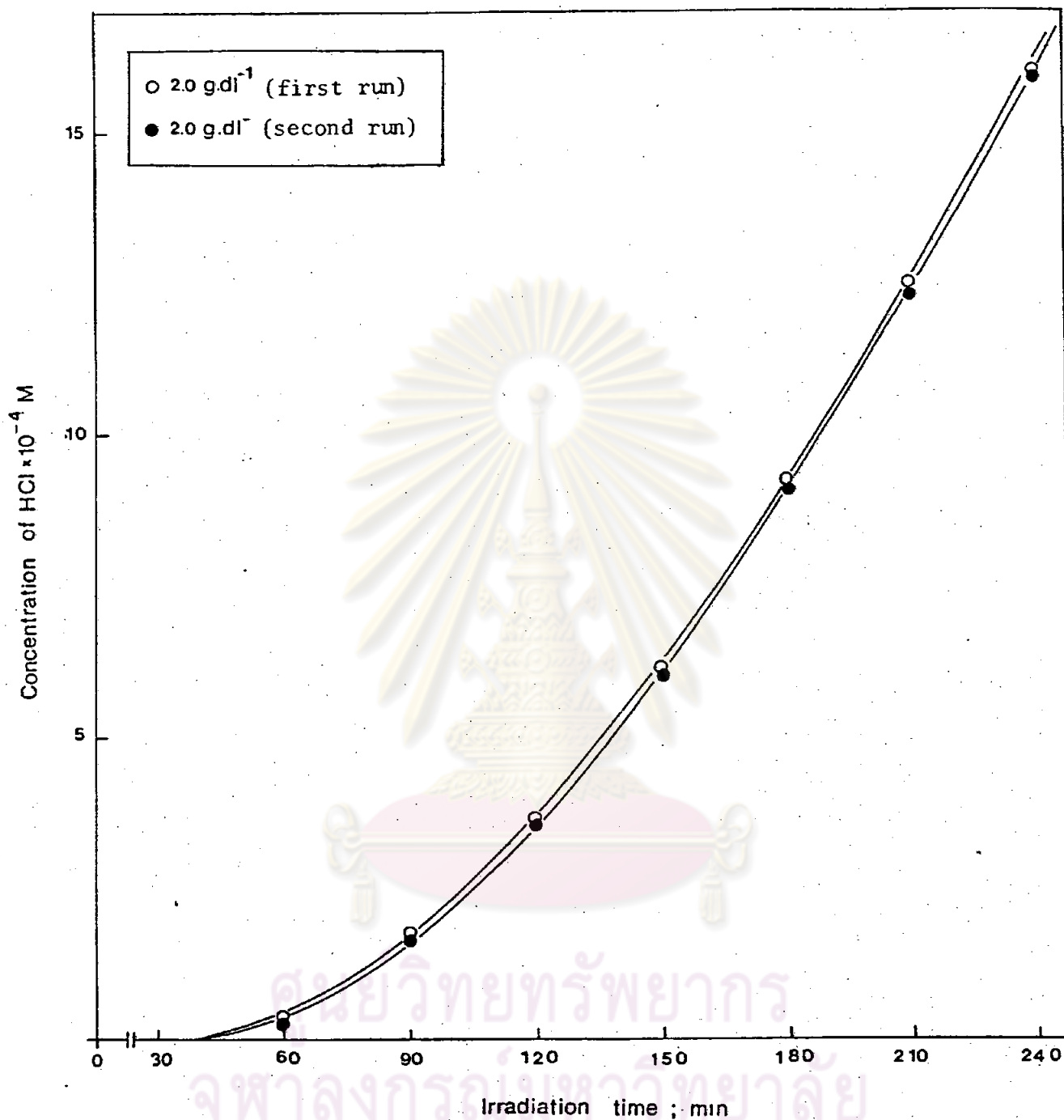


FIGURE 3-6 The plot of concentration of hydrogen chloride produced with time: PVC -ICI 1

The sample of PVC-TP 1 was also irradiated in the same way as PVC-ICI 1. The repetition of the irradiation of PVC-TP 1 gave good result, too. (see TABLE 3-8 and FIGURE 3-7).

TABLE 3-8 The relationship between irradiation time and concentration of PVC-TP 1 in nitrogen.

Irradiation time (min)	Concentration ($M \times 10^{-4}$)	
	I	II
30	-	-
60	0.32	0.18
90	1.55	1.46
120	3.26	3.19
150	5.56	5.35
180	8.19	8.00
210	10.89	10.68
240	13.90	13.71

-the data is undetectable

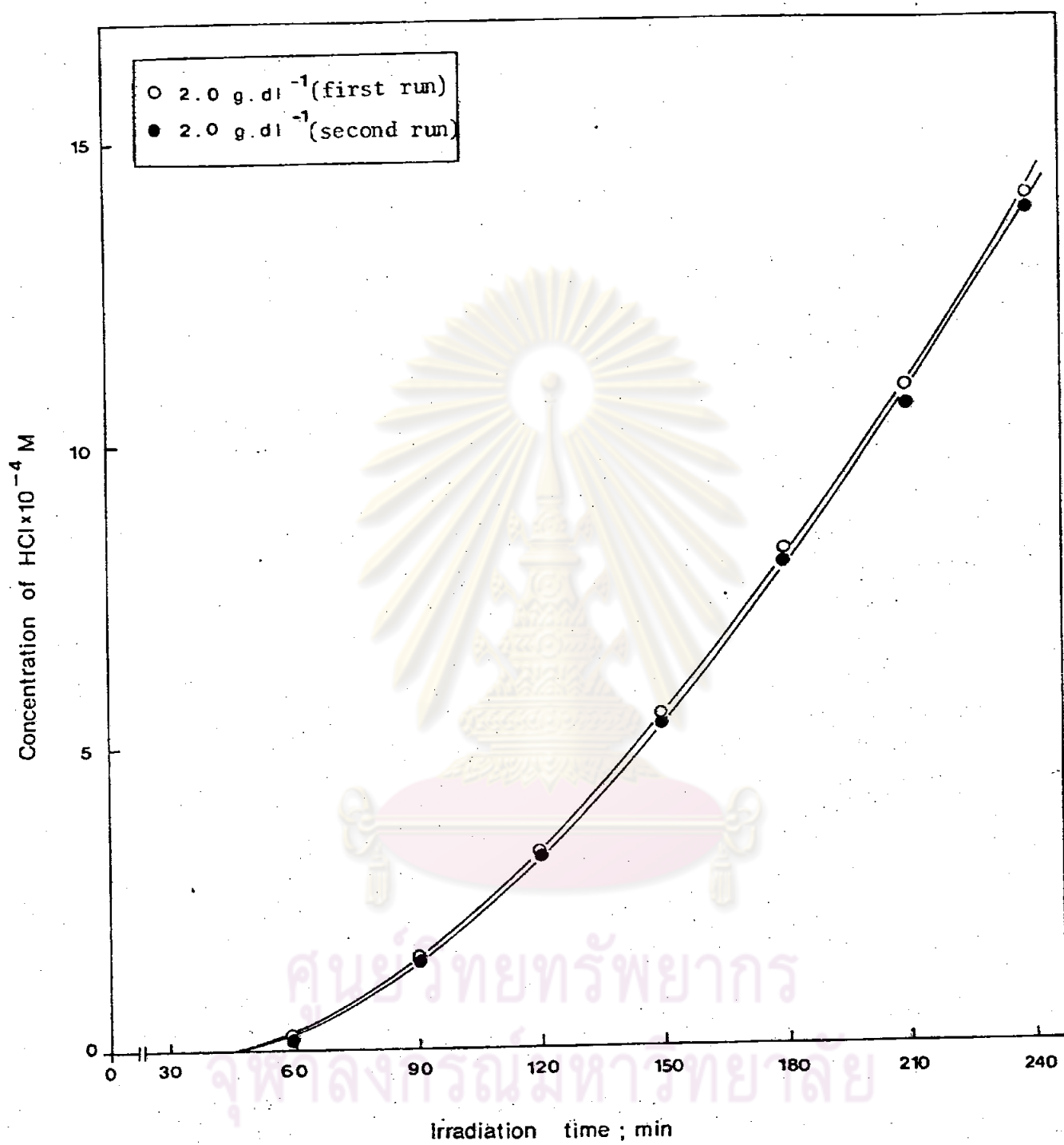


FIGURE 3-7 The plot of concentration of hydrogen chloride produced with irradiation time: PVC-TP 1.

As mentioned before, the infrared light was removed by running water through the quartz water-cooled jacket, not enough heat could then deteriorate PVC. Certainly, temperature in the black box, where the reaction was carried out, was recorded every time, when the lamp was turned off. It was found to be around 35°C. Thus in this case, the degradation of PVC by heat is impossible, because the thermal degradation of PVC would occur only at temperature about 200°C.

In order to ensure that the formation of hydrogen chloride was caused by the photodegradation of PVC, the following control experiments were performed. First, in the absence of light, very small value of conductivity was detected ($0.90 \mu S cm^{-1}$) after 4 hours of reaction, which can be neglected. Second, irradiation of only tetrahydrofuran for 4 hours, the insignificant value of $1.35 \mu S cm^{-1}$ was observed. Even though tetrahydrofuran was reported to be photolyzed to small molecules which were carbon monoxide, hydrogen, methane, ethane, ethylene, propylene, cyclopropane and formaldehyde(31). These products are neutral molecules which are incapable of carrying electrical current(32). Furthermore, such photolysis was made in gas phase and used xenon (147.0 nm) and krypton (123.6 nm) radiation which is totally different from the system operated in this study. According to all the above evidences, the formation of hydrogen chloride conclusively results from the degradation of PVC caused by light, not by heat.



In order to ensure that all hydrochloric acid is scavenged from the reaction solution, another experiment is made. The solution of PVC was irradiated without bubbling nitrogen through the solution, very small value of conductivity was observed after 4 hours. But when the lamp was turned off and nitrogen gas was bubbling through the solution, the conductivity rapidly increased and finally reached constant value (TABLE 3-9 and FIGURE 3-8). After 6 hours of purging, hydrogen chloride (13.28 M of HCl) was detected which is a little more than the one with bubbling nitrogen during irradiation. (12.40 M of HCl). Therefore, the nitrogen flow rate of 100 ml min.^{-1} should be high enough to carry all the hydrochloric acid formed.



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TABLE 3-9 Relationship between concentration of hydrogen chloride produced and time for PVC-ICI 2 after 4 hours of irradiation.

Time (min)	Concentration of HCl x 10 ⁻⁴ M
30	0.95
60	3.12
90	5.46
120	7.24
150	8.67
180	10.94
210	12.01
240	12.92
270	13.21
300	13.27
360	13.28

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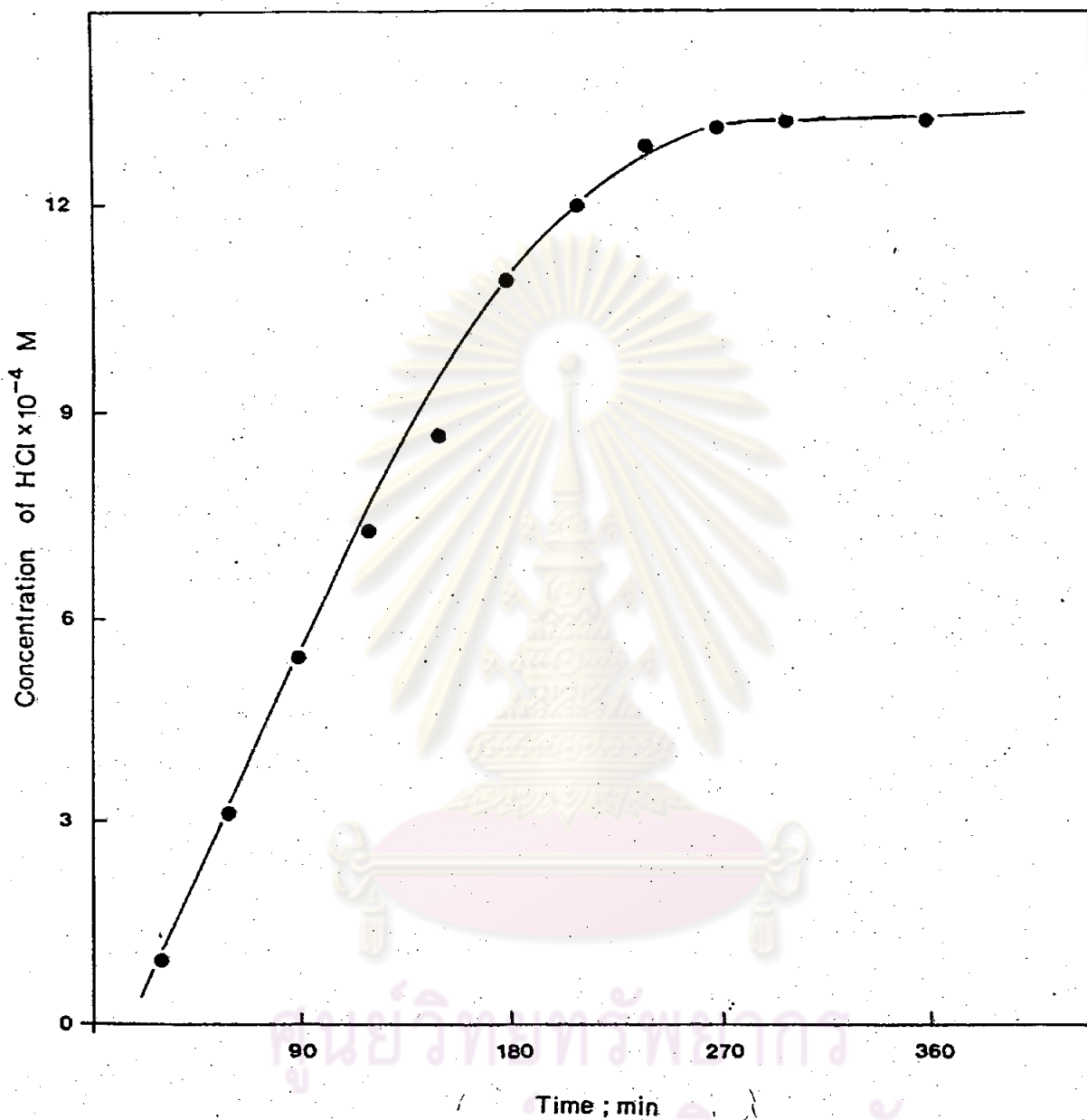


FIGURE 3-8. Concentration of hydrogen chloride produced at various time after 4 hours of irradiation: PVC-ICI 2.

The results therefore indicated that nitrogen gas is necessary for carried hydrogen chloride that produce to monitor at conductivity measurement cell by a conductometer.

3.3 Factors that influence the PVC photodegradation

The investigation of the photodegradation of PVC is performed by measuring the conductivity which is changing due to hydrogen chloride produced with irradiation time. In order to study the effects that influence the photodegradation of PVC, the samples were photolyzed under the same condition except the parameter that is monitoring. Since the purpose of this research is to see the trend of PVC photodegradation in solution, the irradiation is carried out only four hours.

3.3.1 Degrees of polymerization of PVC

In this case PVC samples not only are different in degrees of polymerization but also taken from different manufacture were used. The first two samples were PVC-ICI 1 and PVC-ICI 2 obtained from Imperial Chemical Industries, Australia. The irradiation of these two samples in tetrahydrofuran (2.0 g.dl^{-1}) gave the results shown in TABLE 3-10. It is also illustrated graphically in FIGURE 3-9.

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TABLE 3-10 Relationship between concentration of hydrogen chloride produced and irradiation time for PVC-ICI at various degree of polymerization.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)	
	DP 1024	DP 1888
15	-	-
30	-	-
45	-	-
60	0.36	0.30
75	0.97	0.81
90	1.82	1.41
105	2.68	2.13
120	3.71	2.88
135	4.89	3.76
150	6.13	4.82
165	7.68	5.88
180	9.25	7.06
195	10.81	8.21
210	12.51	9.33
225	14.29	10.72
240	16.06	12.10

-the data is undetectable

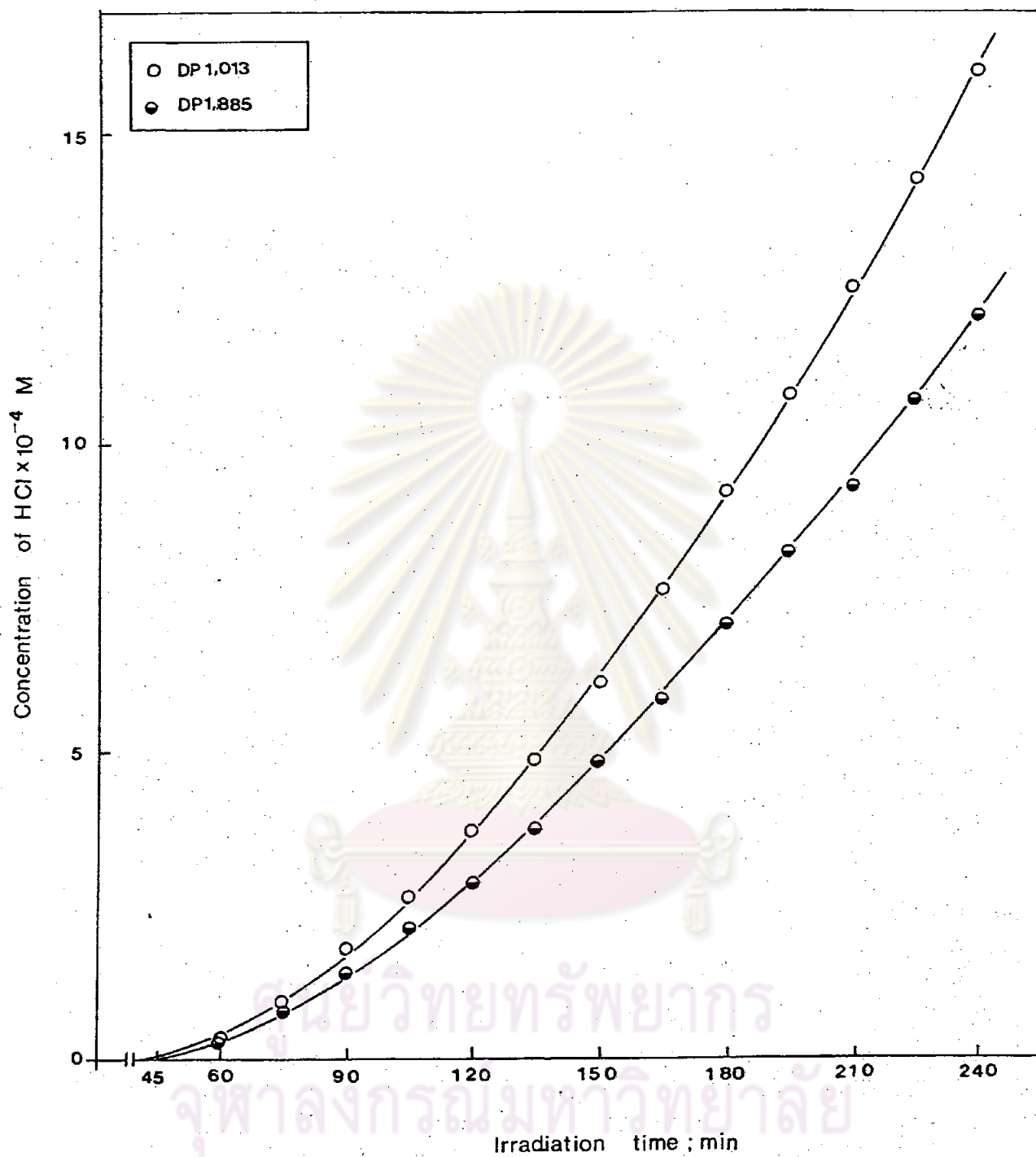
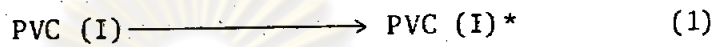


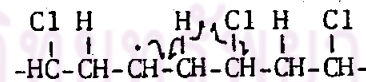
FIGURE 3-9 The effect of degree of polymerization on the PVC photo-degradation: PVC-ICI 1 (DP 1,024) and PVC-ICI 2 (DP 1,885)

From FIGURE 3-9, it should be noticed that hydrogen chloride evolution was not observed until after 45 minutes of irradiation. This could be due to the induction period for which the impurities, assumably some chromophores in the polymer chain, absorb light. Torikai and his coworkers have proposed the following initiation step.(25)

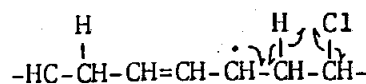


Although other types of alkyl radicals ($-\text{CH}_2-\dot{\text{C}}(\text{Cl})-\text{CH}_2-$ and $-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CHCl}-$) cannot be excluded, the alkyl type radical (Eq. 2) is most likely to be produced in the initiation step of irradiation because the bond dissociation energy of C-Cl is about 20 kcal/mol smaller than that of C-H.

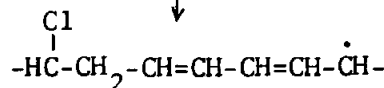
When the free radical is generated, the first molecule of hydrogen chloride will split off and thus the allylic radical will be formed as following:



-HCl



-HCl



The existence of the unsaturation concurrently facilitates the elimination of another hydrogen chloride molecule. Indeed, this is consistent with the increasing rate of hydrogen chloride formation as appeared in Figure 3-9.

The photodegradation of PVC samples from the other manufacturer, Thai Plastic & Chemical Co. Ltd. Thailand gave similar results (TABLE 3-11, FIGURE 3-10).

PVC with DP 1,072 provided more hydrogen chloride than PVC with DP 1,408 which in turn gave more hydrogen chloride than PVC with DP 1,920 (0.00015, 0.00011, 0.00009 mole/100 ml. of water for PVC DP 1,072, 1,408 and 1,920 after irradiation for 4 hours, respectively)

Even though there is no other work concerning the effect of degree of polymerization on the irradiation of PVC, the same results for this effect was reported for the thermal degradation of PVC. Danforth J.D.(33) found that the amount of hydrogen chloride produced was dependent on the chain length of PVC. He heated 80 mg. of each PVC sample which had different DP at 225°C. He found that the rates of hydrogen chloride evolution were 4.0, 2.5 and 2.0% HCl/min. for DP 634, 1,272 and DP 1,381 which are the series of decreasing numbers of polymer chains.

The plausible explanation for this phenomenon involves the probability of the initiation steps to occur. Since the degree of polymerization is the number of the polymer chains, for a given weight, PVC with higher degree of polymerization thus contains lower numbers of the polymer chains. Therefore, PVC with higher degree of polymerization will have less probability to absorb light. That is less hydrogen chloride will be observed.

TABLE 3-11 Relationship between concentration of hydrogen chloride produced and irradiation time for PVC-TP at various degrees of polymerization.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)		
	DP 1,072	DP 1,408	DP 1,920
15	-	-	-
30	-	-	-
45	-	-	-
60	0.33	0.05	0.08
75	0.86	0.43	0.63
90	1.55	0.94	1.01
105	2.35	1.64	1.61
120	3.26	2.38	2.27
135	4.34	3.18	2.94
150	5.56	4.10	3.72
165	6.84	5.04	4.51
180	8.19	6.16	5.32
195	9.47	7.19	6.56
210	10.89	8.40	7.35
225	11.67	9.60	8.41
240	13.91	10.81	9.05

-the data is undetectable

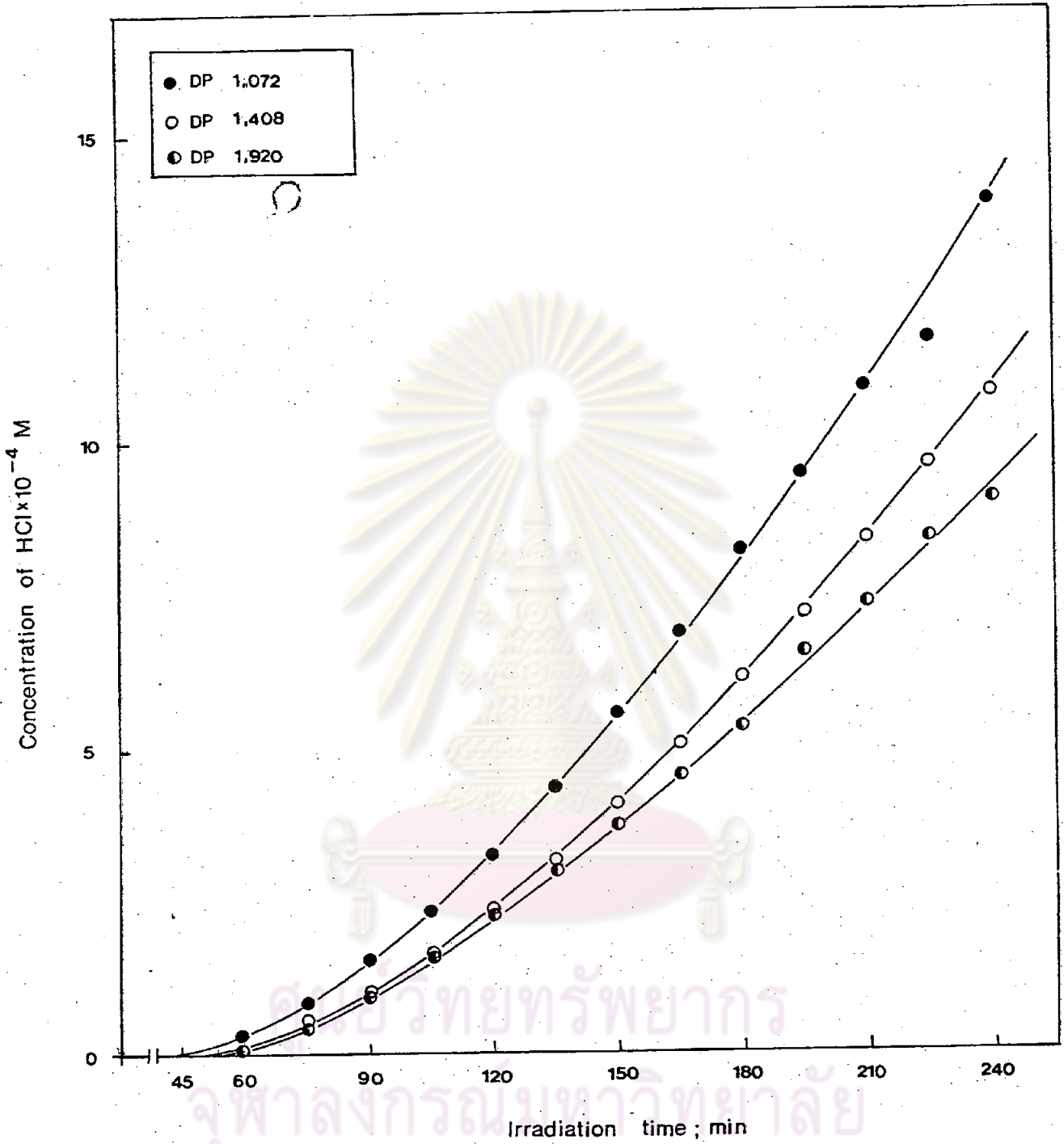


FIGURE 3-10 The effect of degree of polymerization on the PVC photo-degradation: PVC TP 1 (DP 1,072), PVC-TP 2 (DP 1,536) and PVC TP 3 (DP 1,904).

3.3.2 Concentration of PVC

The photodegradation of PVC solution of various concentration were also investigated. In this study two samples of PVC from different manufacturers were used. Firstly, PVC-ICI 1 in tetrahydrofuran with various concentration, 0.5 g.dl^{-1} , 1.0 g.dl^{-1} , 2.0 g.dl^{-1} and 3.0 g.dl^{-1} , were photolyzed for 4 hours. The results are shown in TABLE 3-12 and graphically exhibited in FIGURE 3-11. At the end of reaction, 0.00003, 0.00005, 0.00016 and 0.00028 mole of HCl/100 ml of water were obtained for the PVC-ICI 1 concentration 0.5, 1.0, 2.0 and 3.0 g.dl^{-1} , respectively. Again, the photodegradation of PVC sample from Thai Plastic & Chemical Co., Ltd. Thailand, PVC-TP 1, gave similar results (TABLE 3-13 and FIGURE 3-12).

On the basis of these observation, it is clear that hydrogen chloride produced increases with increasing PVC concentration. This phenomenon can again be explained that there is more polymer chains in the solution of higher PVC concentration. Therefore the solution of higher PVC concentration will have more possibility to absorb light. That is more hydrogen chloride will be produced.

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TABLE 3-12 Relationship between concentration of hydrogen chloride produced and irradiation time for PVC-ICI 1 at various concentrations.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)			
	0.5 g.dl ⁻¹	1.0 g.dl ⁻¹	2.0 g.dl ⁻¹	3.0 g.dl ⁻¹
15	-	-	-	-
30	-	-	-	-
45	-	-	-	0.31
60	-	-	0.36	1.28
75	-	-	0.98	2.57
90	-	-	1.82	4.14
105	-	0.18	2.68	6.02
120	0.07	0.48	3.71	8.35
135	0.28	0.84	4.87	10.69
150	0.52	1.76	6.13	12.82
165	0.79	2.28	7.68	15.02
180	1.10	2.81	9.25	16.87
195	1.43	3.43	10.81	19.43
210	1.82	4.01	12.51	22.58
225	2.17	4.57	14.29	25.46
240	2.56	5.22	16.06	28.30

-the data is undetectable

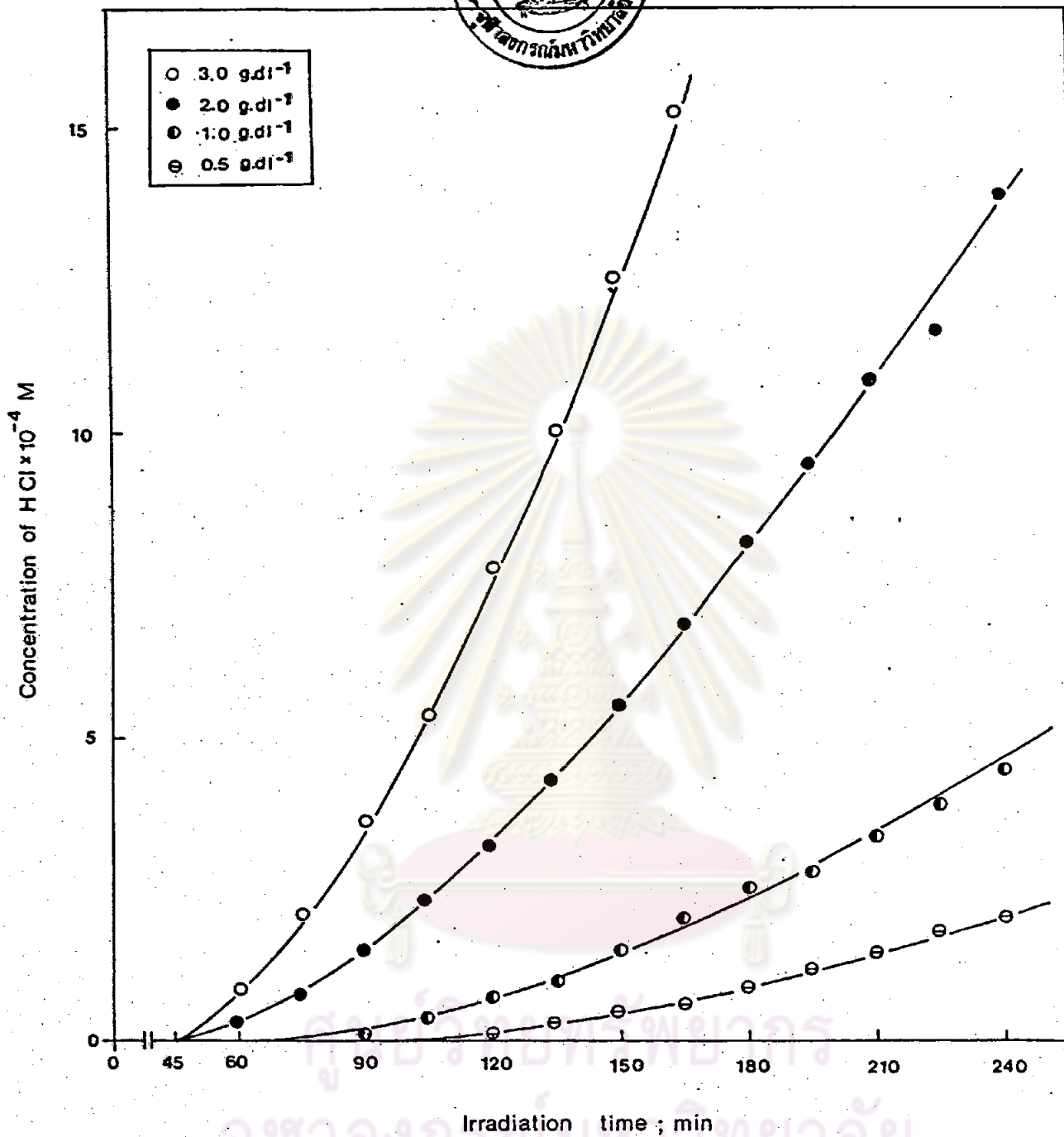


FIGURE 3-11 The effect of concentration on the PVC photodegradation:
PVC-ICI 1.

TABLE 3-13 Relationship between concentration of hydrogen chloride produced and irradiation time for PVC-TP 1 at various concentrations.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)			
	0.5 g.dl ⁻¹	1.0 g.dl ⁻¹	2.0 g.dl ⁻¹	3.0 g.dl ⁻¹
15	-	-	-	-
30	-	-	-	-
45	-	-	-	0.08
60	-	-	0.33	0.89
75	-	-	0.86	2.12
90	-	0.10	1.55	3.63
105	-	0.37	2.35	5.40
120	0.12	0.69	3.26	7.64
135	0.33	1.09	4.34	10.09
150	0.49	1.56	5.56	12.49
165	0.69	2.07	6.84	15.20
180	0.90	2.55	8.19	* -
195	1.19	2.84	9.47	* -
210	1.45	3.41	10.89	* -
225	1.84	3.98	11.67	* -
240	2.13	4.55	13.91	* -

-the data is undetectable

*-the data is not recorded

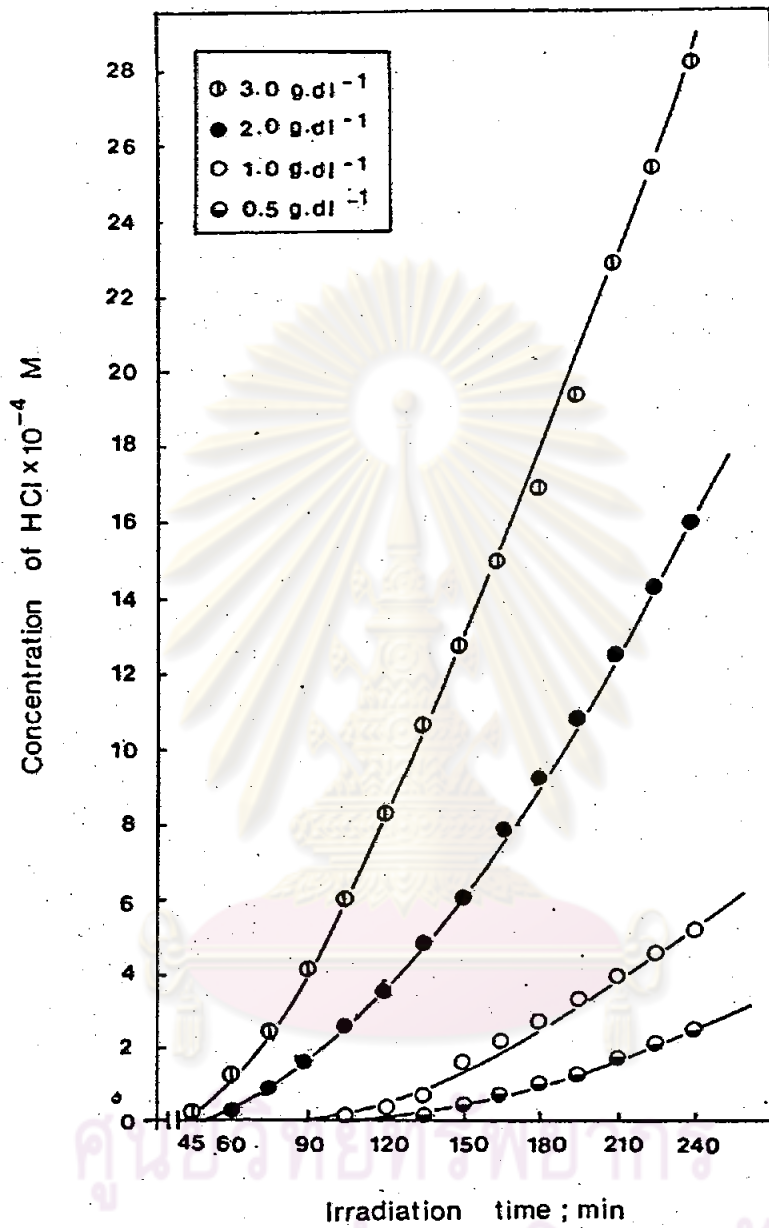


FIGURE 3-12 The effect of concentration on the PVC photodegradation:
PVC-TP 1.

3.3.3 Added additives

3.3.3.1 Plasticizer, Dioctyl phthalate (DOP)

The mechanical properties of PVC can be substantially modified by the use of plasticizers. The function of plasticizer is to lower the heat distortion point on the polymer by penetrating between the polymer chains. The plasticizer molecules therefore increase the distance between them and so enhance their mobility.

It has been reported that, a clear, carboxylic acid ester plasticized PVC containing no ultraviolet light screener, exposed to direct weathering in Florida will last about 10 to 24 months depending on the plasticizer. A similar film of rigid PVC may begin to darken in 2-4 months. Accordingly, the plasticizer would likely suppress the photodegradation of PVC. In order to ensure such assumption, the irradiations of 2.0 g.dl^{-1} PVC solutions in the presence of various concentrations of Dioctyl phthalate were performed. TABLE 3-14 and FIGURE 3-13 exhibit the comparison of the irradiation of PVC solutions with and without DOP. FIGURE 3-14 clearly indicates that in the presence of DOP less concentration of hydrogen chloride was observed. Furthermore, the higher the concentration of DOP, the less of hydrogen chloride was evolved. These experimental results suggest that DOP suppressed the photodegradation of PVC. In addition, the insignificant value of conductivity, $1.20 \mu\text{S cm}^{-1}$ was detected when 2.0 g.dl^{-1} PVC-ICI 2 solution with 1.0% DOP was irradiated for 4 hours. This suggests that about 50phr DOP is sufficient to prevent the PVC photodegradation.

TABLE 3-14 Relationship between concentration of hydrogen chloride produced and irradiation time of PVC-ICI2 solutions with and without DOP.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)		
	without DOP	with DOP 0.5%	with DOP 1.0%
30	-	-	-
60	0.30	-	-
90	1.41	-	-
120	2.88	-	-
150	4.82	-	-
180	7.06	0.11	-
210	9.33	0.39	-
240	12.40	0.69	-

-the data is undetectable

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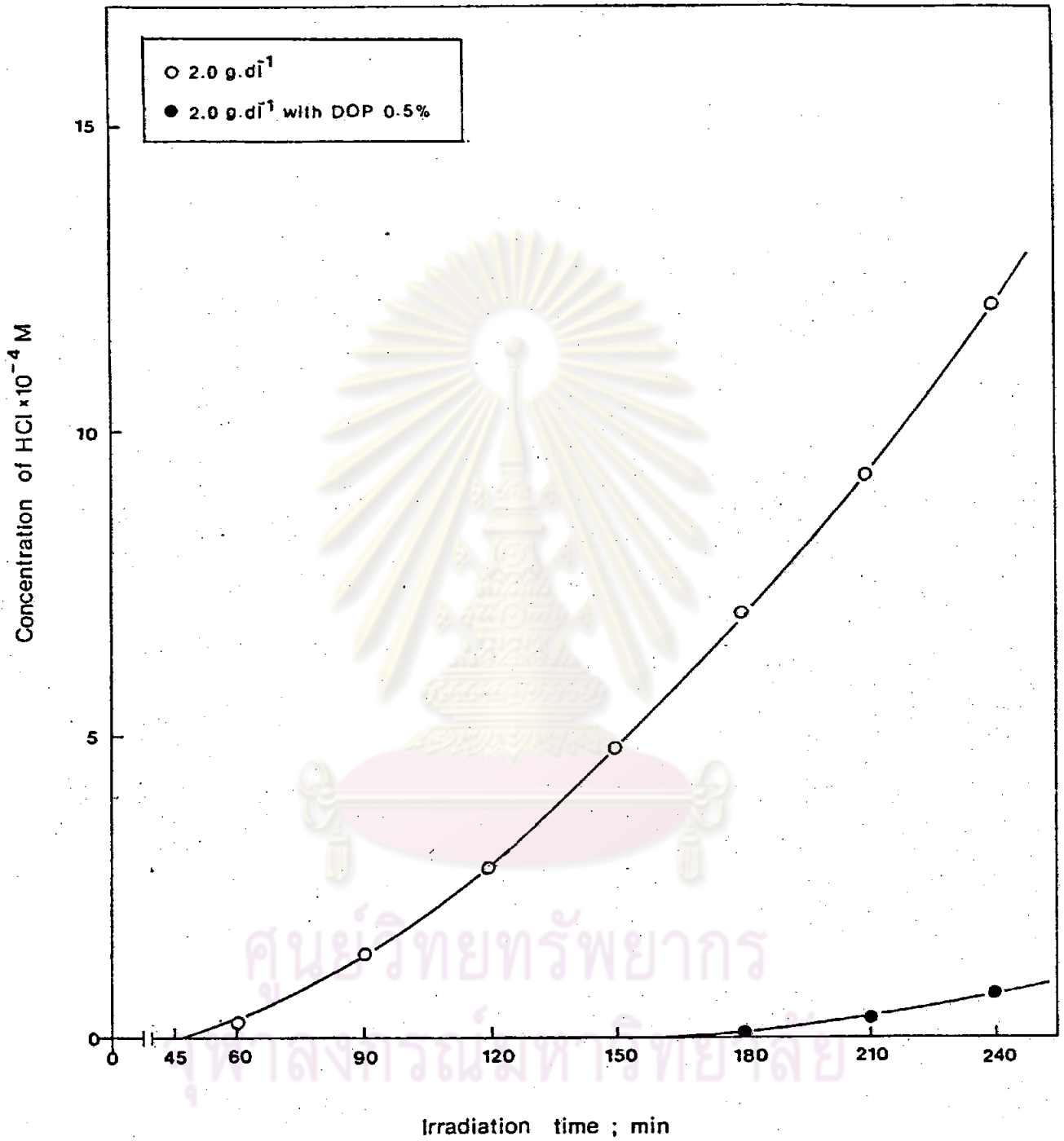


FIGURE 3-13 The effect of DOP on the PVC photodegradation:
PVC-ICI 2.

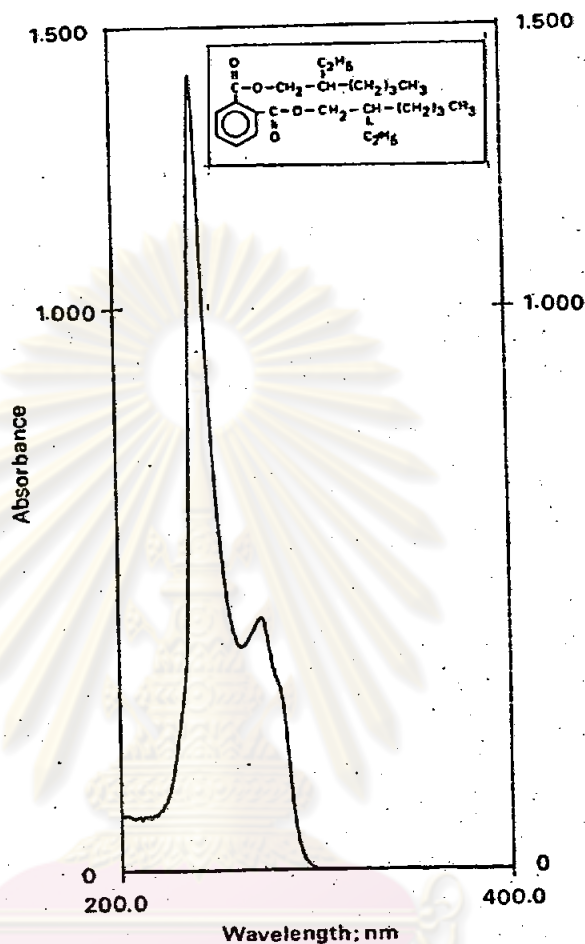


FIGURE 3-14 Absorption spectrum of DOP.

Diethyl phthalate has maximum absorption at 240 nanometers as shown in FIGURE 3-14. Thus, the solvation of the PVC chain by the plasticizer molecule could have stabilizing effect.

3.3.3.2 Stabilizer; 2-(2'-Hydroxy-5'-methylphenyl)benzotriazol (TINUVIN P)

Various kinds of photostabilizers are currently used to stabilize light-sensitive polymers. In this work, 2-(2'-Hydroxy-5'-methylphenyl)benzotriazol has chosen as an Ultraviolet absorber to examine its stabilization effect.

In this study the PVC-ICI 2 solution (2.0 g.dl^{-1})

with various amount of-TINUVIN P (0.1, 0.5 and 1.0%) were photolyzed under the same condition and compared with the one in the absence of TINUVIN P. The results are presented in TABLE 3-15 and FIGURE 3-16 .

FIGURE 3-15 shows that in the presence of TINUVIN P less concentration of hydrogen chloride is produced. Furthermore, when PVC solution containing 25 and 50 phr of TINUVIN P were irradiated, no hydrogen chloride was observed. Therefore 25 phr of TINUVIN P should be enough to prevent PVC photodegradation. FIGURE 3-15 shows the ultraviolet spectrum of TINUVIN P.

The suppression of hydrogen chloride formation in this case can be explained by screening of the light by the TINUVIN P.



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TABLE 3-15 Relationship between concentration of hydrogen chloride produced and irradiation time in the presence and in the absence of TINUVIN P: PVC-ICI 2.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)			
	2.0 g.dl ⁻¹	2.0 g.dl ⁻¹ with TINUVIN P 0.1%	2.0 g.dl ⁻¹ with TINUVIN P 0.5%	2.0 g.dl ⁻¹ with TINUVIN P 1.0%
30	-	-	-	-
60	0.30	-	-	-
90	1.41	-	-	-
120	2.88	-	-	-
150	4.82	-	-	-
180	7.06	-	-	-
210	9.33	0.24	-	-
240	12.10	0.59	-	-

-the data is undetectable

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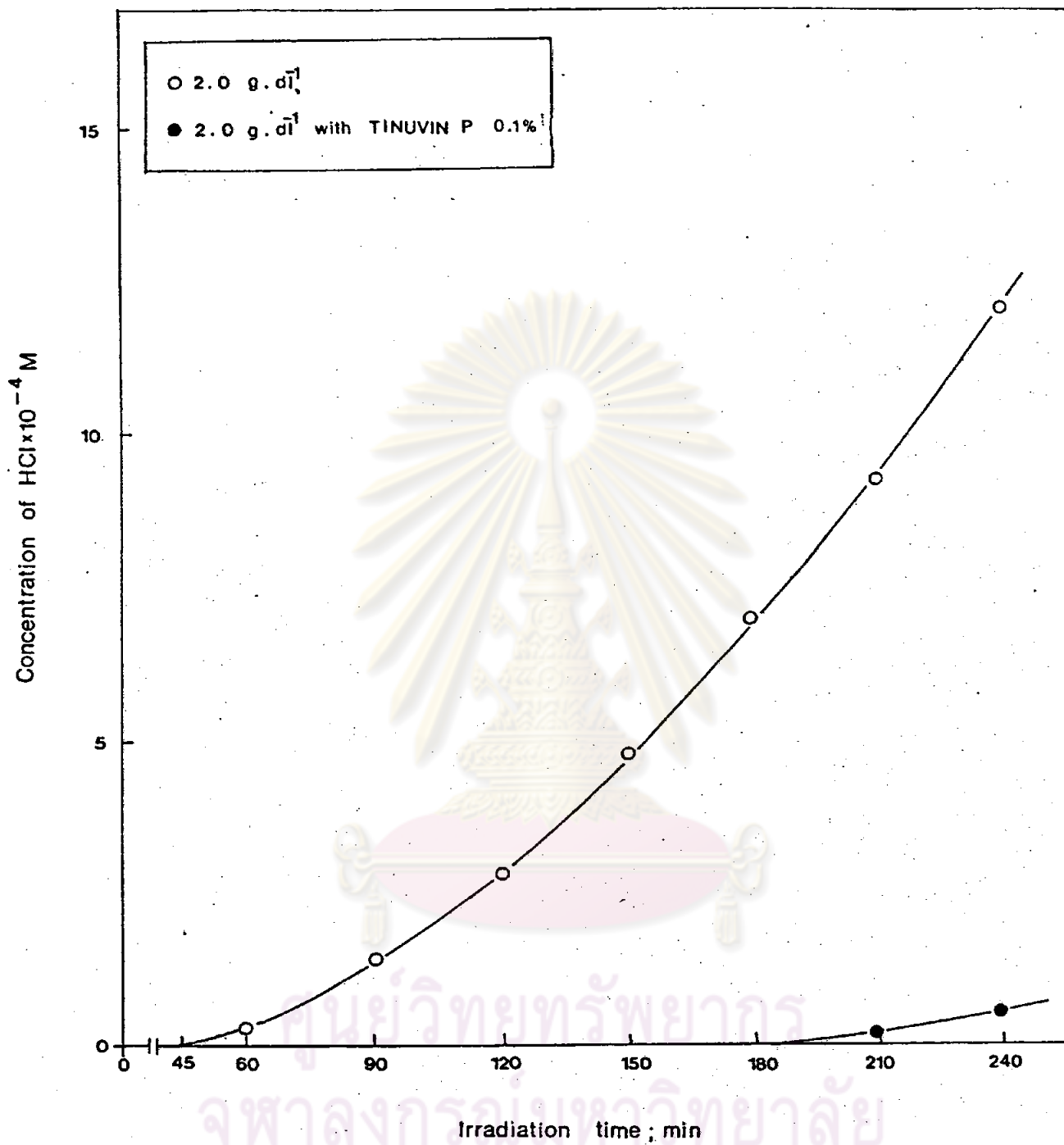


FIGURE 3-15 The effect of TINUVIN P on the PVC photodegradation:
PVC-ICI 2.

3.3.3.3 Pigments; Titanium dioxide, carbon black

Carbon black and titanium dioxide are widely used and important as pigments for plastics. Thus, in this study, titanium dioxide and carbon black pigments are used as the additives to examine its stabilization effects. The illumination of PVC-ICI 2 solutions (2.0 g.dl^{-1}) with and without pigments were performed. TABLE 3-16, 3-17 and FIGURE 3-17, 3-18 show all these results.



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TABLE 3-16 Relationship between concentration of hydrogen chloride produced in the absence and in the presence of carbon black and a titanium dioxide PVC -ICI 2

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)		
	without pigment	with carbon black 0.01%	with TiO ₂ 0.01%
30	-	-	-
60	-	-	-
90	1.41	1.01	0.52
120	2.88	* -	1.48
150	4.82	2.89	2.85
180	7.06	4.25	4.08
210	9.33	5.84	6.78
240	12.10	8.12	9.84

-the data is undetectable

* -the data is not recorded

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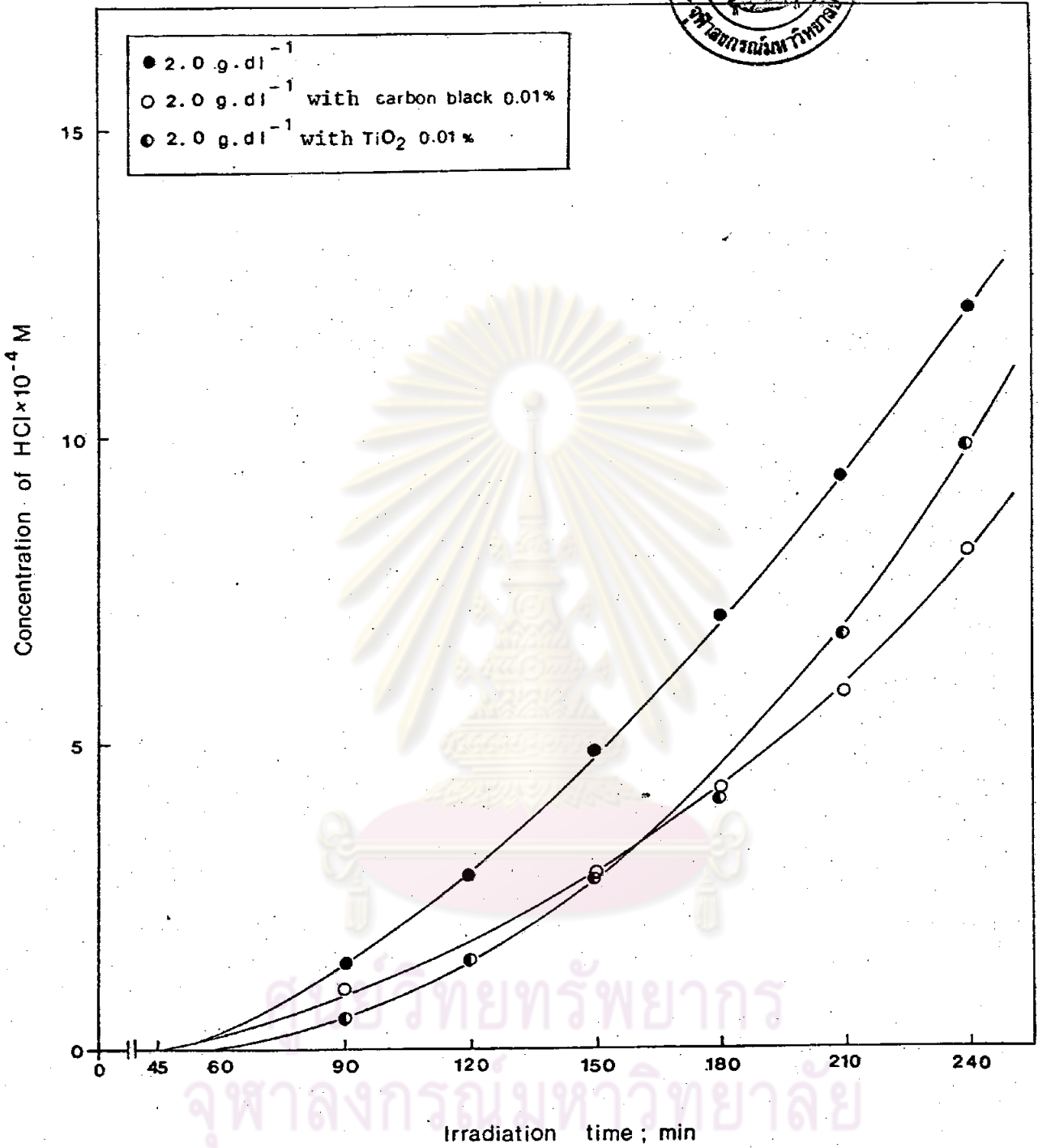


FIGURE 3-17 The comparison of PVC photodegradation in the absence and in the presence of titanium dioxide and carbon black.

TABLE 3-17 Relationship between concentration of hydrogen chloride produced and irradiation time in the presence and in the absence of titanium dioxide: PVC-ICI 2.

Irradiation time (min)	Concentration of HCl ($\times 10^{-4}$ M)		
	without TiO_2	2.0 g.dl ⁻¹ with TiO_2 0.01%	2.0 g.dl ⁻¹ with TiO_2 0.5%
30	-	-	-
60	-	-	-
90	1.41	1.02	0.36
120	2.88	* -	1.12
150	4.82	2.89	2.07
180	7.06	4.25	3.31
210	9.33	5.84	4.87
240	12.10	8.12	6.64

-the data is undetectable

* -the data is not recorded

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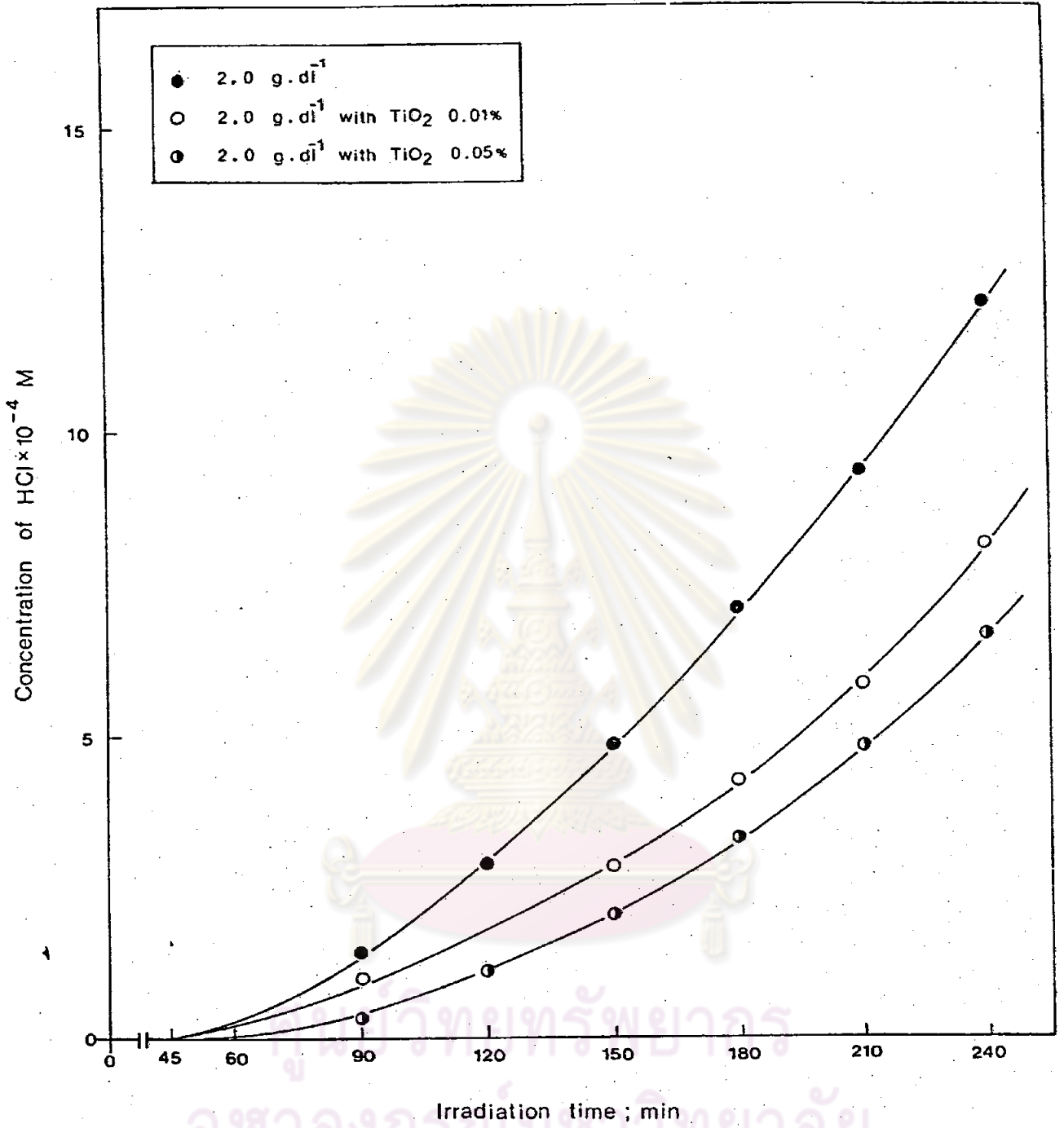


FIGURE 3-18 The effect of titanium dioxide on the PVC photodegradation:
PVC-ICI 2.

FIGURE 3-17 and 3-18 show that the pigments have beneficial effect, the removal of the pigments leads to much hydrogen chloride formation. The results indicate that PVC solution in tetrahydrofuran containing 0.5 phr carbon black are more stable than those containing 0.5 phr titanium dioxide (FIGURE 3-17). The addition concentration of hydrogen chloride produced decrease with increasing the amount of titanium dioxide (FIGURE 3-18). The suppression of hydrogen chloride formation suggests that both pigments have a light-stability effect on PVC. This is due to reflection and scattering of radiation which damaging PVC samples. Thus, PVC containing titanium dioxide exhibits better stability than the one without titanium dioxide. The similar result is shown for PVC with 0.5 phr carbon black that decrease hydrogen chloride produced compared with PVC without pigments.

Moreover, it has been reported that carbon black is recommended for ultraviolet stabilization for outdoor exposure because of their ability to form and react with free radicals and also their ability to absorb ultraviolet radiation and render its harmless. (28)

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3.4.1 The ultraviolet spectroscopic study

Under illumination, PVC both in solid form and in solution, is certainly degraded to give hydrogen chloride. (14,25) Concurrently, an unsaturation or one double bond should appear in the polymer chain for every one molecule of hydrogen chloride evolved .

In order to examine the existence of the unsaturation, the irradiation of PVC-ICI 2 solutions (2.0 g.dl^{-1}) were in nitrogen for 8, 10 and 12 hours. Since Diaz, A. and Doepker reported that tetrahydrofuran was also photolyzed therefore, after each irradiation, the reaction solution was evaporated in order to eliminate all the gaseous product that might be present in the solution. The film of irradiated PVC was then dissolved in fresh tetrahydrofuran. The ultraviolet-visible spectrum of the new solution was then recorded using fresh tetrahydrofuran in the reference cell. Figure 3-19 shows the ultraviolet-visible spectra of irradiated PVC-ICI 2 in nitrogen after irradiation for 8, 10 and 12 hours.

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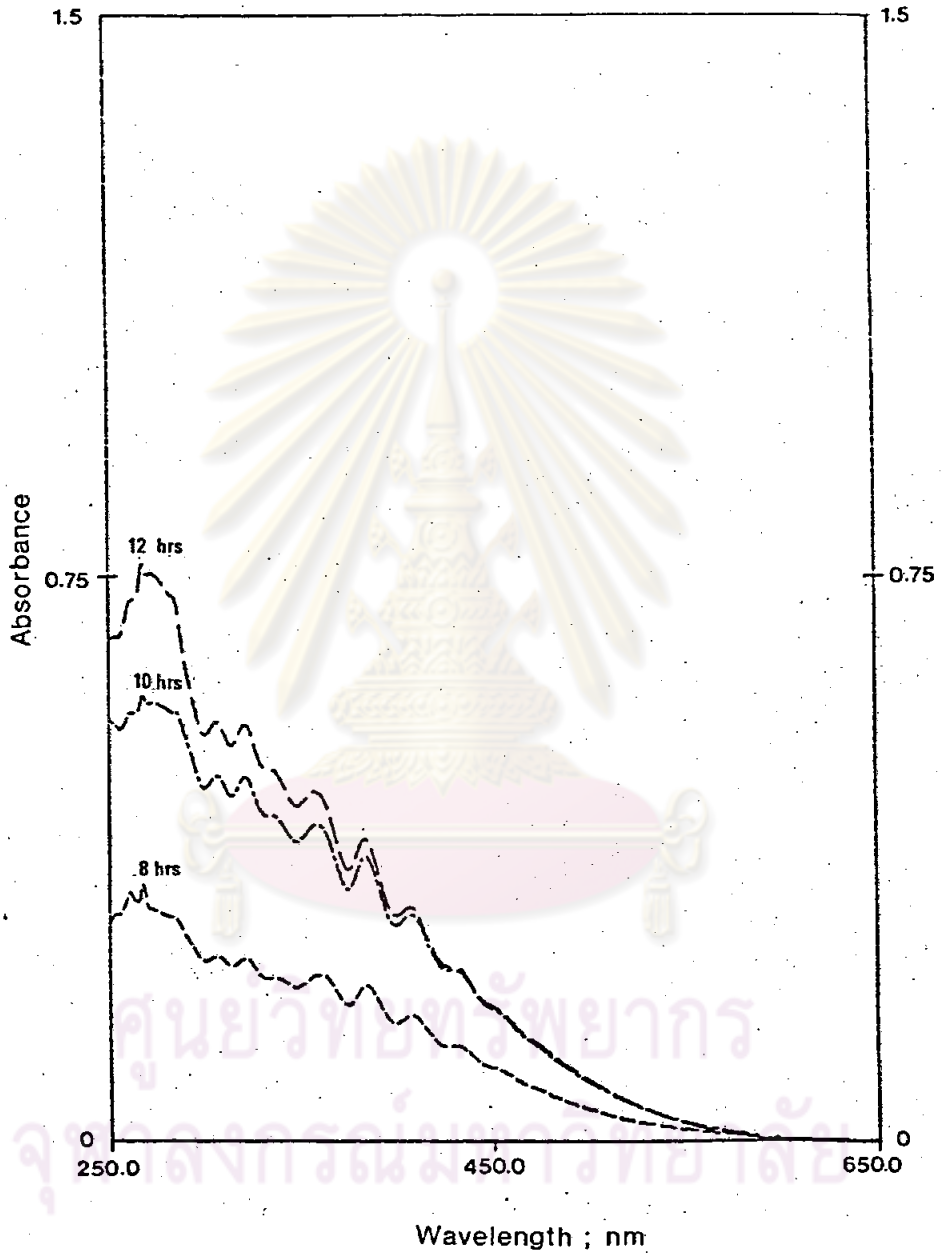


FIGURE 3-19 Absorption spectra of PVC after irradiation in nitrogen; PVC-ICI 2.

The typical feature of each spectrum is the absorption in the range between 250 and 450 nm. These absorption spectra are similar to both thermal and photochemical degradation performed by the other workers (35-38) Most workers agree about the assignments. Particularly for wavelength less than 350 nanometers, which corresponds to polyenes with $n = 6$ (37). For absorbance at 307 nm, the polyene of $n = 4$ is assigned. The species responsible for the absorption maximum at 320 nanometer cannot be identified with certainty but the most probable contributor is some component of an $n = 5$ polyene. The absorbance at 354 is due mainly to an $n = 6$. Absorbance at 380 and 410 nanometers are due to $n = 7$ and 8, respectively.

The absorption maxima at 305-410 nm due to $n = 4-8$ increase with increasing irradiation time but no change in the feature of the spectra was observed. These results indicated that the amount of the same polyenes increase with irradiation time.

However, when the PVC solutions were irradiated in oxygen there probably is some interactions between conjugated systems and oxygen (FIGURE 3-20).



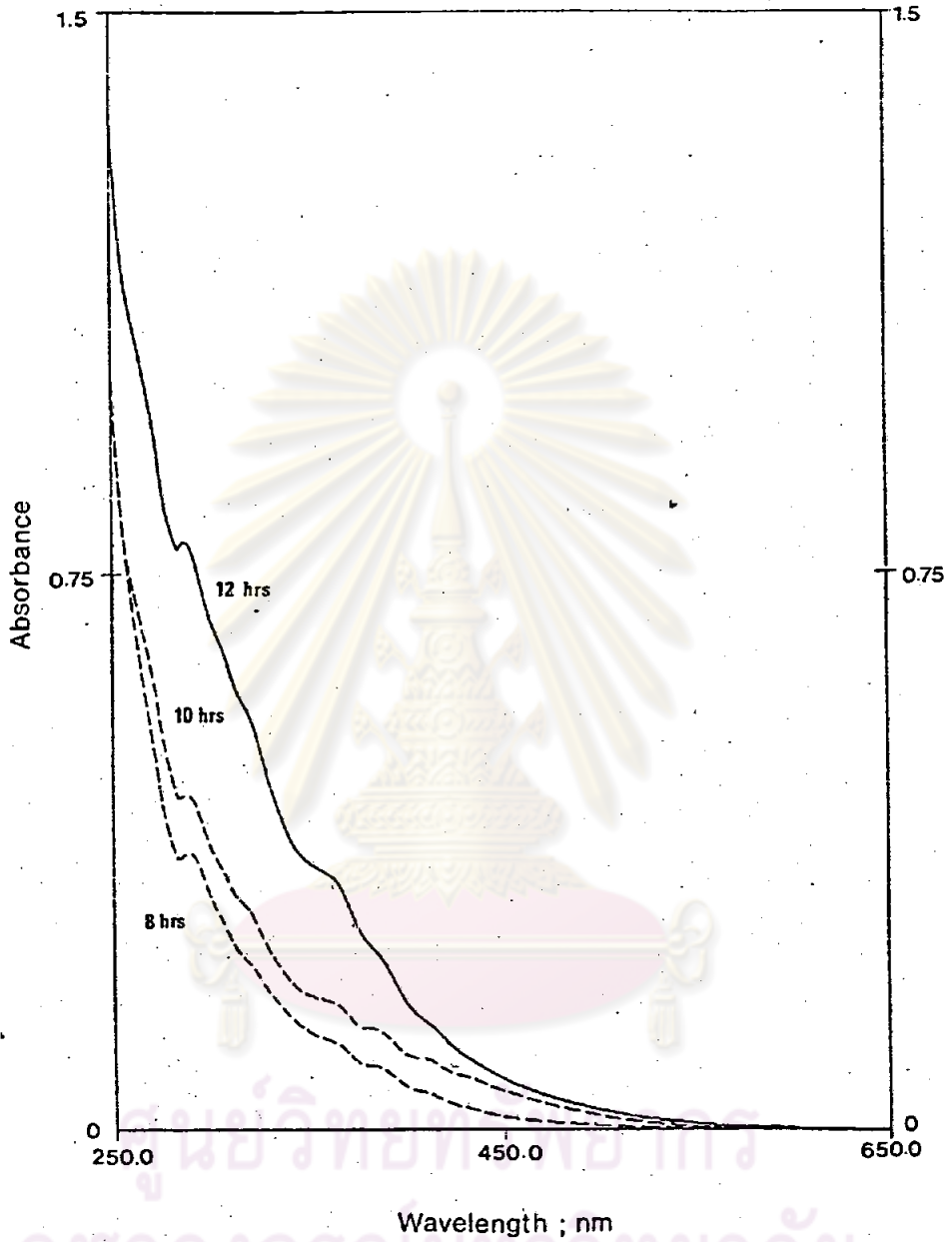


FIGURE 3-20 Absorption spectra of PVC after irradiation in oxygen : PVC-ICI 2.

3.4.2 Infrared spectroscopic study

For the infrared spectroscopic study, the PVC film was used. FIGURE 3-21 is the infrared spectrum of PVC before irradiation. The spectrum shows -C-H stretching at 3.4 μ m, -CH₂ bending at 7.0 μ m and -C-Cl stretching at 14.5 μ m. The absorption at 8.0 μ m is due to -CH bonding in -CH-Cl. Absorption bands in the range 9.1 to 12.0 μ m due to -C-C bonding.

The irradiation of PVC solution in tetrahydrofuran for 12 hours in nitrogen and in oxygen were performed. The infrared spectra of PVC film for both reactions were shown in FIGURE 3-22 is resemble to FIGURE 3-22. Eventhough the unsaturation or double bonds are certainly generated when the irradiation was carried out in nitrogen, these are the internal double bonds which are difficult to vibrate. Therefore, no corresponding vibration could be observed in the infrared spectrum. FIGURE 3-23 clearly exhibits the absorption bands at 1708 and 1742 cm^{-1} . These correspond to the vibration of the carbonyl groups conjugated to double bonds.

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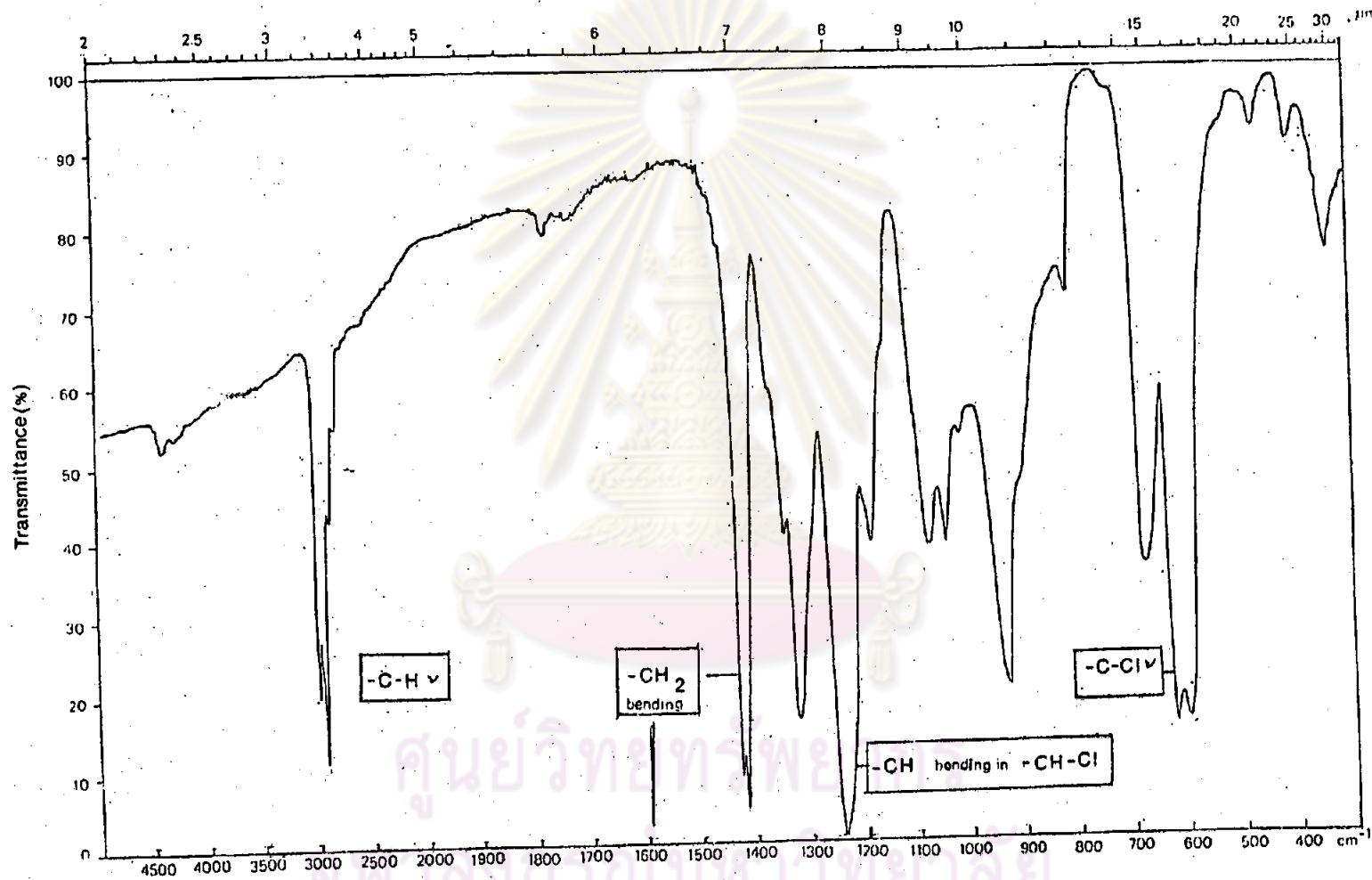


FIGURE 3-21 Infrared spectrum of PVC before irradiation.
(film technique)

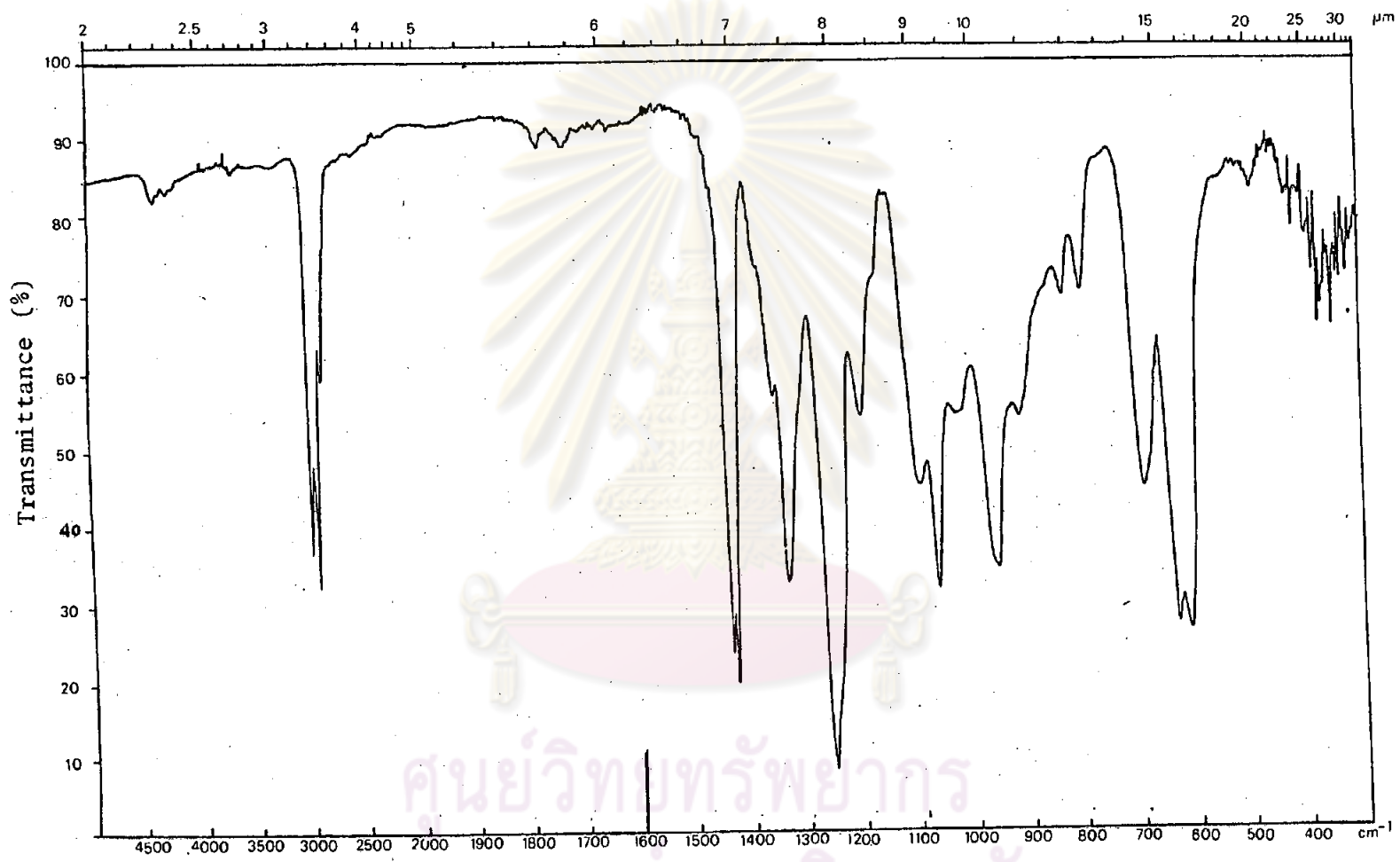


FIGURE 3-22 Infrared spectrum of PVC irradiation for 8 hours in nitrogen.
(film technique)

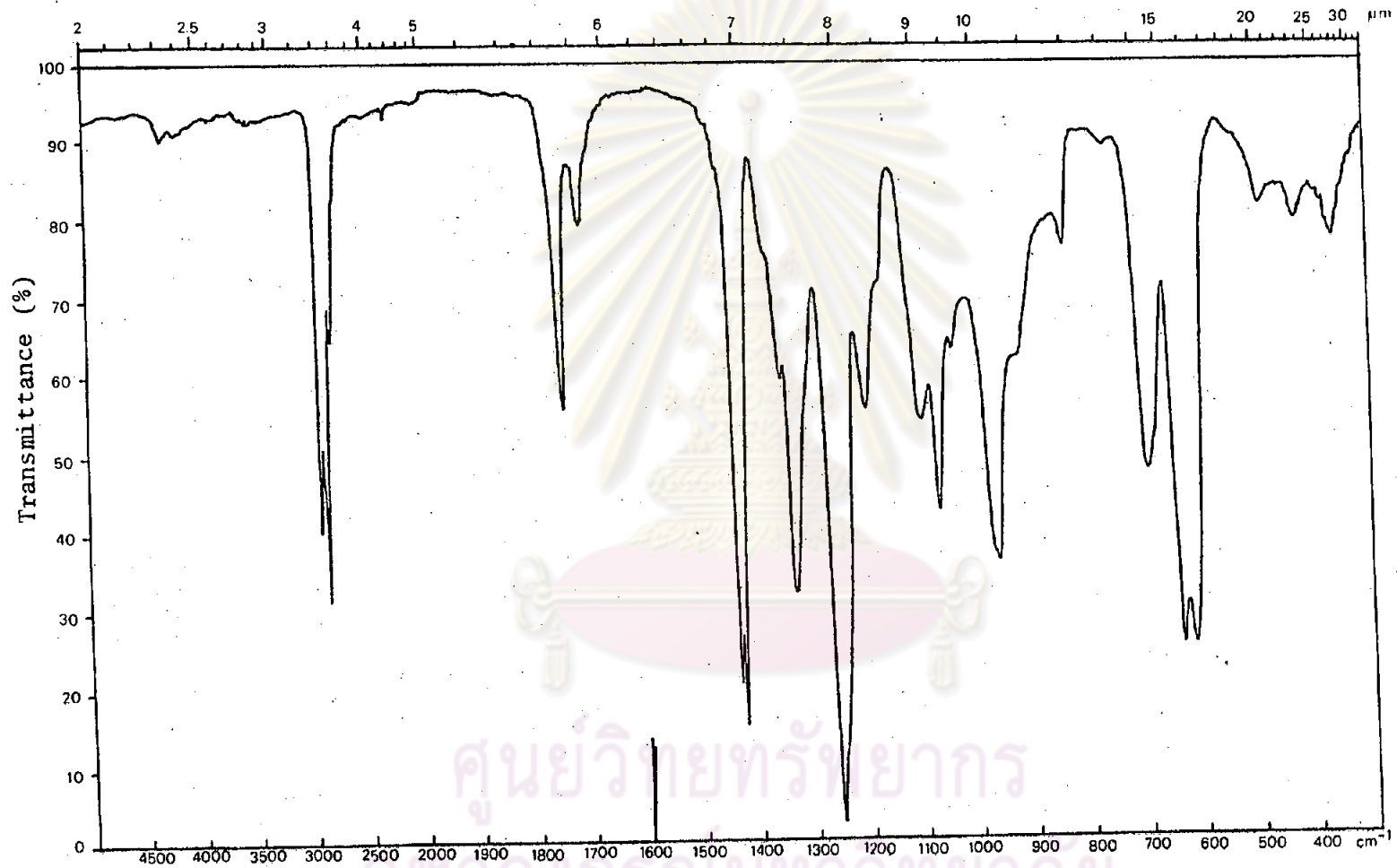


FIGURE 3-23 Infrared spectrum of PVC after irradiation for 8 hours in oxygen.
(film technique)