

CHAPTER II

EXPERIMENTAL



2.1 Materials

- (1) Unplasticized poly (vinyl chloride) powder; two samples from Imperial Chemical Industries, Australia (labelled; ICI 1, ICI 2) and three samples from Thai Plastic & Chemical Co., Ltd. Thailand (labelled; TP 1, TP 2, TP 3)
- (2) Tetrahydrofuran; (Analar, BDH) 99.5% b.p. = 65.0-66.0°C
- (3) Dioctyl phthalate (DOP); (Analar) 98.0% b.p. 384°C
- (4) 2-(2'-Hydroxy-5'-methylphenyl) benzotriazole (TINUVIN P); (commercial)
- (5) Pigments
 - (5.1) Titanium dioxide (Analar)
 - (5.2) Carbon black (commercial)
- (6) Concentrated hydrochloric acid; (Analar) 37.0%
- (7) Sodium hydroxide; (Analar) 98.0%
- (8) Potassium hydrogen phthalate; (Analar) 99.9%
- (9) Deionized water; prepared by double distillation of tap water using "Double Distillation Water Still Model 3 DWS" manufactured by Jame A Jobling Co. Ltd., followed by deionization through the "Elgastat type B 114" unit.
- (10) Oxygen free nitrogen

2.2 Apparatus and Instruments

- (1) Ubbelohde viscometer
- (2) Temperature control unit (25°C)

- (3) Conductometer (Metrohm AG CH-9100 Herisau, Switzerland)
- (4) Electrode; EA 608-C (Metrohm AG CH-9100 Herisau, Switzerland)
- (5) The reaction vessel.
- (6) Quartz water-cooled jacket
- (7) Conductivity measurement cell
- (8) Ultraviolet-240 Shimadzu UV-Visible Spectrophotometer with 10 mm-matched quartz cell
- (9) Shimadzu IR-440 Infrared Spectrophotometer
- (10) Medium -pressure mercury lamp (Philips 125W)

2.3 Average molecular weight determination of PVC sample

An appropriate quantity of tetrahydrofuran (16 ml) was introduced into the viscometer which is sufficient to fill the suspended-level bulb; FIGURE 2-1. Then it was clamped vertically in the water

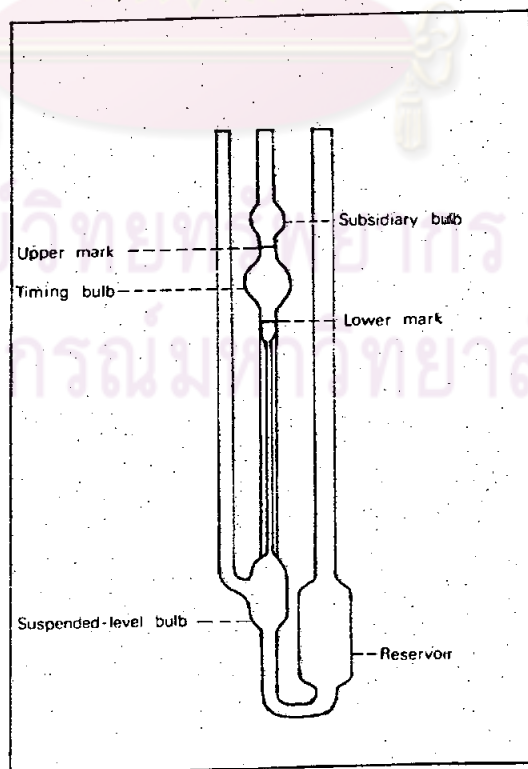


FIGURE 2-1 Ubbelohde viscometer

bath which was kept constant at 25°C until the solution attained thermal equilibrium (about 15 minutes). Consequently tetrahydrofuran was drawn into subsidiary bulb and flowed freely. The time, referred as flow time, was recorded between the point at which the meniscus of tetrahydrofuran passed the upper mark and the lower mark of Ubbelohde viscometer. The measurement of flow time was repeated three times before the solvent was removed from viscometer. The viscometer was then clean and dried by passing a stream of dust-free air through it.

TABLE 2-1 shows the flow time of tetrahydrofuran according to the viscometer used in this research work.

TABLE 2-1 Flow time of tetrahydrofuran.

No. of run	Flow time; t_0 (sec)
1	99.00
2	99.35
3	99.05
Average flow time = 99.13	

Each PVC sample was washed with methanol by using liquid-solid extraction method for 1 day. Then, it was dried at 80°C. The solution of prewashed PVC in tetrahydrofuran (0.4000 g.dl⁻¹) was prepared and introduced into the viscometer. In the same manner as tetrahydrofuran three successive flow time of the first PVC solution was recorded. It was then diluted by adding 2 ml of tetrahydrofuran into the PVC solution in the viscometer. After thoroughly mixing the concentration of PVC solution was changed to 0.3556 g.dl⁻¹. Similarly the PVC solution of 0.3048 g.dl⁻¹ and 0.2667 g.dl⁻¹ were obtained

by adding 3 ml and another 3 ml of tetrahydrofuran into the previous PVC solution, respectively. The flow time of each new PVC solution was measured three times in succession. The whole procedure was repeated for all samples. The flow times and the average flow time of each PVC sample using the same viscometer are exhibited in TABLE 2-2 to 2-7.

TABLE 2-2 Flow time of PVC-ICI 1 solution at various concentrations

Concentration; C (g.dl ⁻¹)	Flow time; t (sec)			
	I	II	III	Average
0.2667	119.60	119.50	119.50	119.60
0.3048	122.60	122.70	122.50	122.60
0.3556	126.70	126.65	126.65	126.65
0.4000	130.25	130.30	130.20	130.25

TABLE 2-3 Flow time of PVC-ICI 2 solution at various concentrations

Concentration; C (g.dl ⁻¹)	Flow time; t (sec)			
	I	II	III	Average
0.2667	133.10	133.33	132.50	132.98
0.3048	138.00	137.80	138.00	137.93
0.3556	145.10	144.60	145.00	144.90
0.4000	151.20	150.40	150.65	150.75

TABLE 2-4 Flow time of PVC-TP 1 solution at various concentrations.

Concentration; C (g.dl ⁻¹)	Flow time; t (sec)			
	I	II	III	Average
0.2667	119.50	119.45	119.50	119.50
0.3048	122.40	122.26	122.33	122.33
0.3556	126.30	126.10	126.20	126.10
0.4000	129.24	129.19	129.17	129.20

TABLE 2-5 Flow time of PVC-TP 2 solution at various concentrations.

Concentration; C (g.dl ⁻¹)	Flow time; t (sec)			
	I	II	III	Average
0.2667	132.75	132.68	132.70	132.70
0.3048	138.00	138.00	138.00	138.00
0.3556	144.40	144.30	144.35	144.35
0.4000	150.20	150.35	150.35	150.30

TABLE 2-6 Flow time of PVC-TP 3 solution at various concentrations.

Concentration; C (g.dl ⁻¹)	Flow time; t (sec)			
	I	II	III	Average
0.2667	132.75	132.68	132.70	132.70
0.3048	138.00	138.00	138.00	138.00
0.3556	144.40	144.30	144.35	144.35
0.4000	150.20	150.35	150.35	150.30

2.4 Typical procedure for the photodegradation study

A 200 ml of the PVC solution (or tetrahydrofuran) was placed in the reaction vessel (FIGURE 2-2) containing a magnetic bar. The light beam from 125-W medium-pressure mercury lamp was passed through the quartz water-cooled jacket, inserted in the reaction vessel, to remove the infrared irradiation. The nitrogen gas (or oxygen gas) was bubbling through the solution via the inlet of the reaction vessel while the outlet was connected to the gas dispersion tube fixed in the conductivity measurement cell.

Usually, a fine stream of nitrogen was passed through the solution of vanadous chloride solution(27) for complete removal of oxygen. It was then bubbling through the PVC solution 15 minutes before irradiation to scavenge oxygen gas that might exist in the solution. During irradiation, nitrogen flow rate (100 ml. min^{-1}) was kept constant by controlling with a gas flow meter.

Thus hydrochloric acid produced from the PVC photodegradation would be carried from the PVC solution in the reaction vessel into the deionized water in the conductivity measurement cell by nitrogen gas. In order to disperse gas thoroughly, the solution was kept stirring during photodegradation. The electrode was fixed in the conductivity measurement cell containing 80 ml of deionized water and connected to the conductometer* where the conductivity could be read out at any time. All the reactions were therefore followed by the conductometric measure-

*The condition of potentiometer

potentiometer "temp."	30.0 °C
potentiometer "cell const."	1.02 cm^{-1}
potentiometer "temp. coeff."	1.0 % K^{-1}

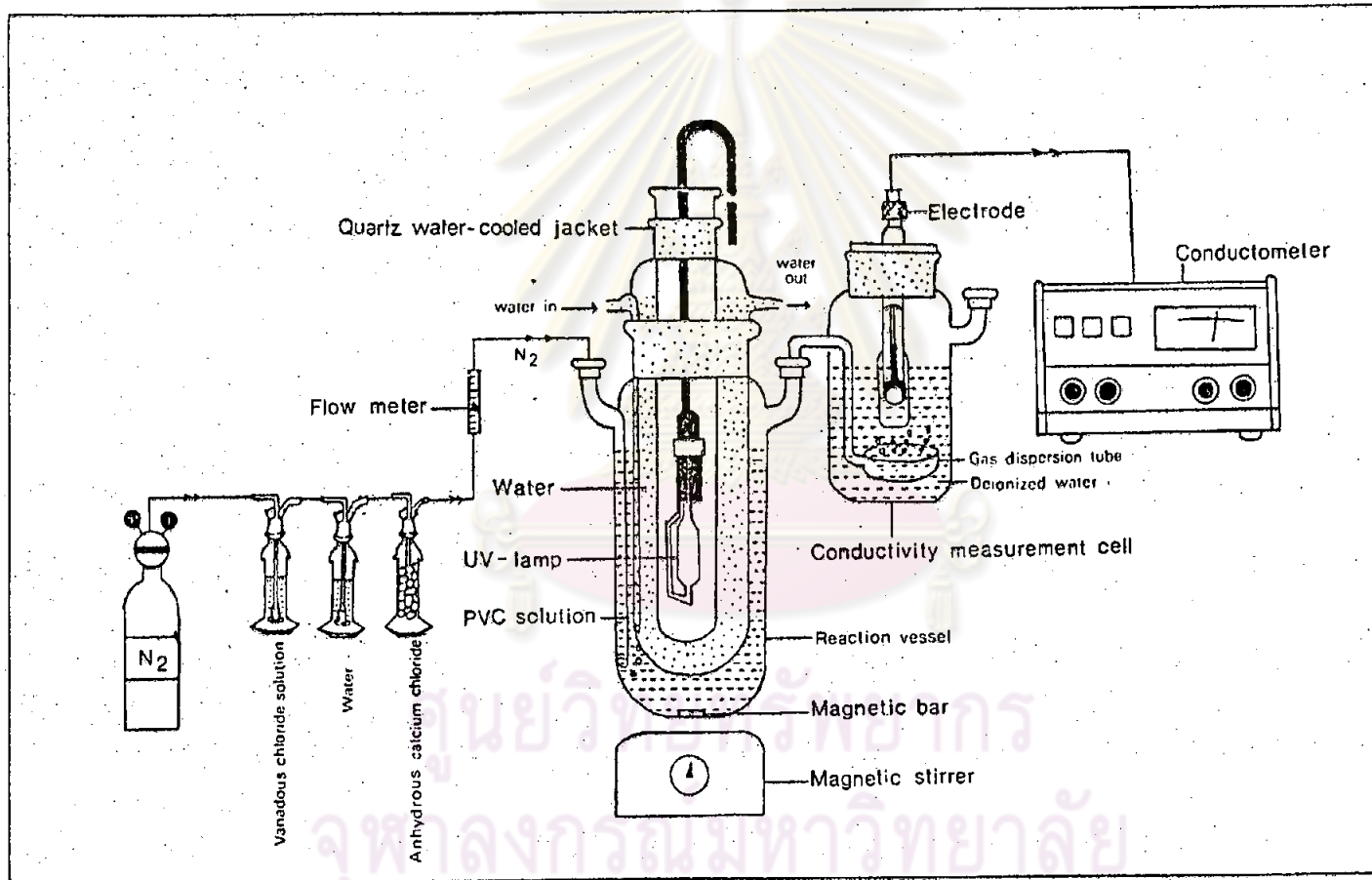


FIGURE 2-2 Apparatus for the photodegradation study

ment of hydrochloric acid produced.

The photoreaction apparatus and the conductivity measurement cell were set up in the fixed position in the black box so that ultraviolet light exposure to the outside could be protected. After a certain length of time, the reaction was stopped. The reaction vessel the quartz water-cooled jacket and the conductivity measurement cell were thoroughly cleaned and dried before the next reaction will be carried out. In some cases, a portion of the reaction solution was transferred into the petri dish and let dry at room temperature. The thin film was finally formed and was spectroscopically determined.

2.5 Preliminary study of photodegradation of PVC

The PVC-ICI 1 solution (2.0 g.dl^{-1}) was prepared by slowly adding 10.0 g of PVC-ICI 1 in tetrahydrofuran which was rapidly stirred during addition. When all the polymer had dissolved the volume was made up to 500 ml by addition of tetrahydrofuran. A 200 ml of this solution was placed in the reaction vessel and the apparatus set up was connected as mentioned in SECTION 2.4. The water was run into the quartz water-cooled jacket and magnetic stirrer was turned on at the certain speed*. The nitrogen gas flow rate was $100 \text{ ml. min}^{-1**}$. After 30 minutes of purging the solution with nitrogen gas, the door of the black box was closed and the lamp was turned on. The conductivity was read and recorded every 30 minutes. The irradiation was repeated with fresh 200 ml of PVC solution. The results of both reactions are shown in TABLE 2-7.

* Which was set the same throughout study of PVC photodegradation.

** measured by soap-film flowmeter

TABLE 2-7 The relationship between irradiation time and conductivity for PVC-ICI 1 in nitrogen.

Irradiation time (min)	Conductivity (μ S cm^{-1})	
	I	II
30	0.85	0.80
60	11.10	10.40
90	31.70	29.32
120	58.30	57.10
150	92.32	91.30
180	136.30	134.30
210	182.30	179.80
240	232.30	230.10

In the same manner, PVC-TP 1 solution ($2.0 \text{ g}\cdot\text{dl}^{-1}$ in tetrahydrofuran) was prepared and irradiated for 4 hours. The results are shown in TABLE 2-8.

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TABLE 2-8 The relationship between irradiation time and conductivity for PVC-TP 1 in nitrogen.

Irradiation time (min)	Conductivity (μ S cm^{-1})	
	I	II
30	0.72	0.67
60	10.62	8.62
90	27.90	26.61
120	52.00	50.96
150	84.40	81.46
180	121.40	118.76
210	159.40	156.40
240	201.90	199.10

2.6 Control experiments for photodegradation study

The PVC-ICI 2 solution ($2.0 \text{ g}\cdot\text{dl}^{-1}$ in tetrahydrofuran) was used for all control experiments. The reaction were performed under the same condition as mentioned in SECTION 2.5 except the parameter that was monitored.

2.6.1 In the absence of light

After purging the solution for 15 minutes, the conductivity was read and recorded every 30 minutes (see TABLE 2-9) without turning on the light.

TABLE 2-9 Conductivity in the absence of light.

Time (min)	Conductivity (μ S cm^{-1})
30	0.02
60	0.10
90	0.22
120	0.30
150	0.43
180	0.73
210	* -
240	0.90

* -the data is not recorded

2.6.2 No poly (vinyl chloride)

Instead of the PVC solution, only tetrahydrofuran (200 ml) was placed in the reaction vessel. Then the lamp was turned on and the conductivity was read and recorded every 30 minutes (see TABLE 2-10).

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TABLE 2-10 Conductivity in the absence of PVC.

Irradiation time (min)	Conductivity (μ S cm^{-1})
30	0.15
60	0.16
90	0.18
120	0.71
150	0.86
180	1.21
210	1.24
240	1.35

2.6.3 Without bubbling nitrogen during irradiation

In this experiment, after purging the PVC solution with nitrogen for 15 minutes, the lamp was turned on and nitrogen was turned off. TABLE 2-11 exhibits the conductivity read every 30 minutes.

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TABLE 2-11 Conductivity in the absence of bubbling nitrogen during irradiation.

Irradiation time (min)	Conductivity (μ S cm^{-1})
30	0.17
60	*-
90	0.72
120	0.84
150	1.04
180	1.22
210	1.42
240	1.47

*-the data is not recorded

After 4 hours, the lamp was turn off and nitrogen gas (100 ml. min^{-1}) was bubbling through the solution. The conductivity was again read and recorded (see TABLE 2-12) until achieving constant conductivity.

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TABLE 2-12 Conductivity after 4 hours of irradiation

Time (min)	Conductivity (μ S cm^{-1})
30	19.40
60	50.00
90	83.00
120	108.20
150	128.10
180	145.50
210	160.10
240	175.20
270	188.00
300	192.10
330	193.00
360	193.10

2.7 The factors influencing the photodegradation of PVC

2.7.1 Degree of polymerization (29)

A 2.0 g.dl^{-1} of each PVC-ICI sample (DP 1,024, DP 1,888) in tetrahydrofuran was prepared and photolyzed under the same condition. During the irradiation, the conductivity was recorded every 15 minutes. The results of these reactions are shown in TABLE 2-13.

TABLE 2-13 Relationship between conductivity and irradiation time
for PVC-ICI

Irradiation time (min)	Conductivity (μ S cm^{-1})	
	DP 1,024	DP 1,888
15	-	0.16
30	0.85	0.76
45	4.56	4.26
60	11.10	10.26
75	19.80	17.46
90	31.70	25.96
105	43.80	36.06
120	58.30	46.66
135	74.70	59.06
150	92.32	73.96
165	114.30	88.90
180	136.30	105.46
195	158.30	121.71
210	182.30	137.46
225	207.30	156.96
240	232.30	176.46



- the data is undetectable

In the same manner, A 2.0 g.dl⁻¹ of each PVC-TP sample (DP1,072, DP 1,408. DP 1, 920) in tetrahydrofuran was prepared and irradiated for 4 hours. The results of all the reactions are shown in TABLE 2-14.

TABLE 2-14 Relationship between conductivity and irradiation time for PVC-TP

Irradiation time (min)	Conductivity (μ S cm^{-1})		
	DP1,072	DP1,408	DP1,920
15	-	-	-
30	0.72	0.74	0.42
45	4.65	3.04	2.72
60	10.62	6.79	7.12
75	18.20	12.09	14.88
90	27.90	19.34	20.30
105	39.20	29.14	28.70
120	52.00	39.54	38.00
135	67.20	50.84	47.50
150	84.40	63.79	58.50
165	102.40	77.14	70.00
180	121.40	92.84	81.00
195	139.40	107.34	98.50
210	159.40	124.35	109.50
225	170.40	141.34	124.50
240	201.90	158.34	133.50

-the data is undetectable

2.7.2 Concentration of PVC

The solutions of PVC-ICI 1 in tetrahydrofuran, 0.5 g. dl^{-1} , 1.0 g. dl^{-1} , 2.0 g. dl^{-1} and 3.0 g. dl^{-1} were prepared by dissolving PVC-ICI 1 1.25 g, 2.50 g, 5.00 g and 7.50 g in 250 ml tetrahydrofuran, respectively. A 200 ml of each PVC-ICI 1 solution was placed in the reaction vessel and the irradiation was carried out for 4 hours. The

results are exhibited in TABLE 2-15.

TABLE 2-15 Relationship between conductivity and irradiation time for the solution of PVC-ICI 1 at various concentrations.

Irradiation time (min)	Conductivity (μ S cm^{-1})			
	0.5 g.dl ⁻¹	1.0 g.dl ⁻¹	2.0 g.dl ⁻¹	3.0 g.dl ⁻¹
15	-	-	-	0.14
30	-	-	0.85	2.64
45	-	0.18	4.56	10.39
60	0.20	0.96	11.10	24.14
75	*-	2.69	19.80	42.24
90	2.35	5.19	31.70	64.34
105	4.50	8.69	43.80	90.84
120	7.00	12.84	58.30	123.64
135	9.95	17.84	74.70	156.64
150	13.35	30.84	92.32	186.64
165	17.25	38.14	114.30	217.64
180	21.55	45.64	136.30	243.64
195	26.15	54.36	158.30	279.64
210	31.65	62.64	182.30	329.64
225	36.65	70.54	207.30	364.64
240	42.15	79.64	232.30	404.64

-the data is undetectable

*-the data is not recorded

In the same manner, 0.5 g.dl⁻¹, 1.0 g.dl⁻¹, 2.0 g.dl⁻¹ and 3.0 g.dl⁻¹ of PVC-TP 1 in tetrahydrofuran were prepared and each solution was subsequently irradiated for 4 hours. The results are shown in TABLE 2-16.

TABLE 2-16 Relationship between conductivity and irradiation time for the solution of PVC-TP 1 at various concentrations.

Irradiation time (min)	Conductivity (μ S cm^{-1})			
	0.5 g.dl ⁻¹	1.0 g.dl ⁻¹	2.0 g.dl ⁻¹	3.0 g.dl ⁻¹
15	-	-	-	-
30	-	-	0.72	1.34
45	0.50	0.75	4.65	7.14
60	0.62	2.45	10.62	18.64
75	2.00	*-	18.20	36.04
90	3.35	7.50	27.90	57.14
105	5.45	11.25	39.20	82.14
120	7.75	15.75	52.00	113.64
135	10.62	21.45	67.20	148.15
150	13.00	28.00	84.40	182.03
165	15.75	35.20	102.40	220.12
180	18.75	42.00	121.40	270.21
195	22.75	46.10	139.40	*-
210	26.50	54.00	159.40	*-
225	32.00	62.10	170.40	*-
240	36.00	70.10	201.90	*-

-the data is undetectable

*-the data is not recorded

2.7.3 In the presence of additives

2.7.3.1 Plasticizer (12), Dioctyl phthalate (DOP)

The mixture of PVC-ICI (2.0 g.dl^{-1}) and DOP was prepared by slowly adding 5.0 g. of PVC-ICI 2 in tetrahydrofuran which was rapidly stirred during addition. When all the polymer had dissolved, 1.25 g of DOP was added to the solution.

and the volume was made up to 250 ml by addition of tetrahydrofuran.

In the same manner, PVC-ICI 2 with 1.0% DOP in tetrahydrofuran was prepared and irradiated for 4 hours. The results are shown in TABLE 2-17.

TABLE 2-17 Relationship between conductivity and irradiation time for the solution of PVC-ICI 2 in the absence and in the presence of DOP.

Irradiation time (min)	Conductivity (μ S cm^{-1})		
	without DOP	with DOP 0.5%	with DOP 1.0%
30	0.76	0.12	0.02
60	10.26	0.14	0.10
90	25.96	0.62	0.22
120	46.66	2.02	0.30
150	73.96	4.47	0.43
180	105.46	7.58	0.73
210	137.46	11.48	0.90
240	176.46	15.78	1.20

2.7.3.2 Stabilizer (10,16) TINUVIN P.

Sample solutions (2.0 g.dl^{-1} PVC-ICI 2 with 0.1% TINUVIN P, 2.0 g.dl^{-1} PVC-ICI 2 with 0.5% TINUVIN P, 2.0 g.dl^{-1} PVC-ICI 2 with 1.0% in tetrahydrofuran) were prepared. Each solution was then irradiated for 4 hours. The results are shown in TABLE 2-18.

TABLE 2-18 Relationship between conductivity and irradiation time for the solution of PVC-ICI 2 in the absence and in the presence of TINUVIN P.

Irradiation time (min)	Conductivity (μ S cm^{-1})			
	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	0.76	-	-	-
60	10.26	-	-	-
90	25.96	0.10	-	-
120	46.66	0.67	-	-
150	73.96	2.60	-	-
180	105.46	5.45	0.05	-
210	136.46	9.45	0.40	0.06
240	176.46	14.40	0.80	0.12

-the data is undetectable

2.7.3.3 Pigments (28); Titanium dioxide, carbon black

Sample solution (2.0 g.dl⁻¹ PVC-ICI 2 with 0.01% titanium dioxide) was prepared as follow. PVC (5.0 g) was slowly added to tetrahydrofuran which was rapidly stirred during addition. When all the polymer had dissolved, 0.025 g of titanium dioxide was added to the solution. Good suspension of the pigment was obtained. A 200 ml of this solution was photoirradiated for 4 hours. The solution was kept in suspension by stirring during irradiation. The result is shown in TABLE 2-19.

Similarly, 2.0 g.dl⁻¹ PVC-ICI 2 with 0.5% titanium dioxide in tetrahydrofuran was prepared and irradiated for 4 hours. The result is shown in TABLE 2.20.

TABLE 2-19 Relationship between conductivity and irradiation time for the solution of PVC-ICI 2 in the absence and in the presence of titanium dioxide.

Irradiation time (min)	Conductivity (μ S cm^{-1})		
	2.0 g.dl^{-1}	2.0 g.dl^{-1} with TiO_2 0.01%	2.0 g.dl^{-1} with TiO_2 0.5%
30	0.76	0.27	0.15
60	10.26	5.47	3.28
90	25.96	20.35	11.10
120	46.66	* -	21.80
150	73.96	46.85	35.20
180	105.46	65.95	52.60
210	137.46	88.35	74.60
240	176.46	120.35	99.60

*-the data is not recorded

In the same manner, 2 g.dl^{-1} PVC-ICI with 0.01% carbon black was prepared and irradiated for 4 hours respectively. The result is shown in TABLE 2-20.



TABLE 2-20 Relationship between conductivity and irradiation time for the solution of PVC-ICI 2 in the absence and in the presence of carbon black or titanium dioxide.

Irradiation time (min)	Conductivity (μ S cm^{-1})		
	2.0 g.dl ⁻¹ .	2.0 g.dl ⁻¹ with carbon black 0.01%	2.0 g.dl ⁻¹ with TiO ₂ 0.01%
30	0.76	0.27	0.25
60	10.26	5.47	4.40
90	25.96	20.35	13.30
120	46.66	* -	26.85
150	73.96	46.85	46.20
180	105.46	65.95	72.00
210	137.46	88.35	101.60
240	176.46	120.35	144.60

* -the data is not recorded

2.8 Standard hydrochloric acid

2.8.1 Preparation of secondary standard 0.001 M sodium hydroxide

The 0.1 M sodium hydroxide was prepared by dissolving 0.1 g of sodium hydroxide in deionized water and the content was diluted to 25 ml with deionized water. A 0.001 M sodium hydroxide solution was obtained by further dilution of the 0.1 M sodium hydroxide with deionized water in the 250 ml volumetric flask.

Potassium hydrogen phthalate was dried at 120°C for 2 hours, and allowed to cool in a desiccator. A 0.005 M potassium hydrogen phthalate was prepared by dissolving 0.2555 g of potassium hydrogen phthalate in deionized water and diluted to 250 ml with deionized water.

Further dilution of 0.005 M potassium hydrogen phthalate with deionized water in a 100 ml volumetric flask gave 0.0001 M potassium hydrogen phthalate.

A 25 ml of 0.0001 M potassium hydrogen phthalate was pipetted into a beaker containing a magnetic bar and the electrode (which connected to the conductometer). It was then titrated with approximately 0.001 M sodium hydroxide by conductometric method (31). A 0.001 M sodium hydroxide was added in a small portion from the burette, and the solution was stirred after each addition. The well-mixed solution was allowed to stand for a minute and the conductivity was recorded. The result of the conductometric titration is shown in TABLE 2-21.

TABLE 2-21 Conductometric titration data for 25 ml of 0.0001 M potassium hydrogen phthalate with approximately 0.001 M sodium hydroxide.

ml of approximately 0.001 M NaOH	Conductivity (μ S cm^{-1})
0.0	17.00
0.1	16.70
1.0	17.20
1.5	18.20
2.0	19.40
3.0	22.30

The plot of the conductivity against the volume of the approximately 0.001 M sodium hydroxide solution was exhibited in FIGURE 2-3.

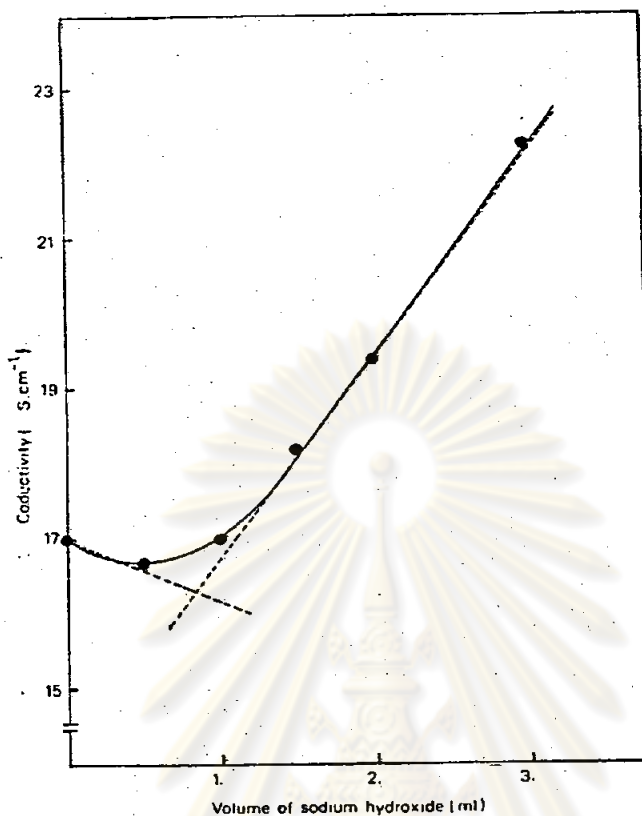


FIGURE 2-3 Conductometric titration of approximately 0.001 M NaOH with 0.0001 M potassium hydrogen phthalate

This was illustrated graphically that the equivalent point of the reaction was 0.85, therefore the concentration of the secondary standard sodium hydroxide was 0.0029 M sodium hydroxide.

2.8.2 Preparation of various concentrations of hydrochloric acid

A 0.1 M hydrochloric acid was prepared by pipetted 0.8 ml concentrated hydrochloric acid into a 250 ml volumetric flask and made up to the mark with deionized water. In addition, series of 0.0001, 0.0005, 0.0010, 0.0015 and 0.00207 M-hydrochloric acid were prepared by further dilution of 0.1 M hydrochloric acid with deionized water. Each solution was titrated with secondary standard 0.0025 M sodium hydroxide. The results are shown in TABLE 2-22 to 2-25.

TABLE 2-22 Conductometric titration data for approximately 0.0001 M hydrochloric acid

ml. of 0.0025 M NaOH	Conductivity (μ S cm^{-1})
0.0	31.00
0.5	24.20
1.0	17.80
1.5	12.70
2.0	11.90
2.5	13.00
3.0	14.50
3.5	16.40
4.0	18.50
4.5	20.20
5.0	22.20

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TABLE 2-23 Conductometric titration data for approximately 0.0005 M hydrochloric acid

ml of 0.0025 M NaOH	Conductivity (μ S cm^{-1})
0.0	99.00
1.0	83.40
2.0	68.00
3.0	55.00
4.0	43.00
5.0	31.80
6.0	29.30
7.0	31.50
8.0	34.00
9.0	37.00
10.0	40.00
11.0	46.00

TABLE 2-24 Conductometric titration data for approximately 0.0010 M hydrochloric acid

ml of 0.0025 M NaOH	Conductivity (μ S cm^{-1})
0.0	163.00
3.1	117.00
6.0	70.20
9.0	441.50
12.0	44.00
15.0	50.50
18.0	57.50
21.1	65.00
23.1	75.50

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TABLE 2-25 Conductometric titration data for approximately 0.0015 M hydrochloric acid

ml of 0.0025 M NaOH	Conductivity (μ S cm^{-1})
0.0	225.00
3.0	178.00
6.0	136.00
9.0	98.00
12.0	67.20
15.0	51.60
18.0	54.20
21.1	60.00
24.1	65.00
27.1	71.20
30.1	77.00

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TABLE 2-26 Conductometric titration data for approximately 0.0020 M hydrochloric acid

ml of 0.0025 M NaOH	Conductivity (μ S cm^{-1})
0.0	293.0
3.1	240.0
6.1	190.0
9.1	148.0
12.1	114.0
15.1	81.8
18.0	58.8
21.0	58.5
24.0	63.5
27.0	67.5
30.0	73.2
36.0	81.4

From data in TABLE 2-20 to 2-24 the conductance is plotted as ordinates against the volume of the 0.0025 M sodium hydroxide. This was illustrated graphically in FIGURE 2-4 to 2-6.

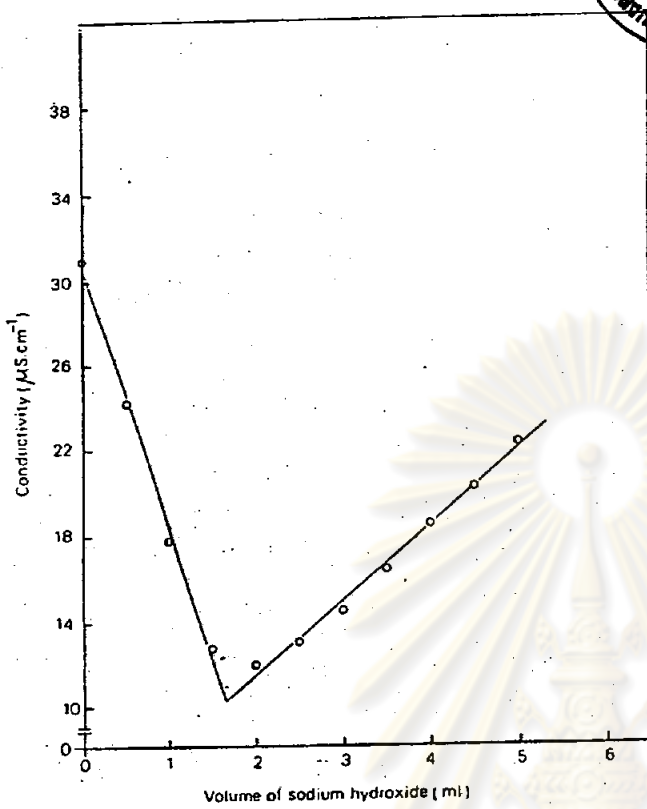


FIGURE 2-4 Conductometric titration of approximately 0.0001 M HCl with 0.0025 M NaOH

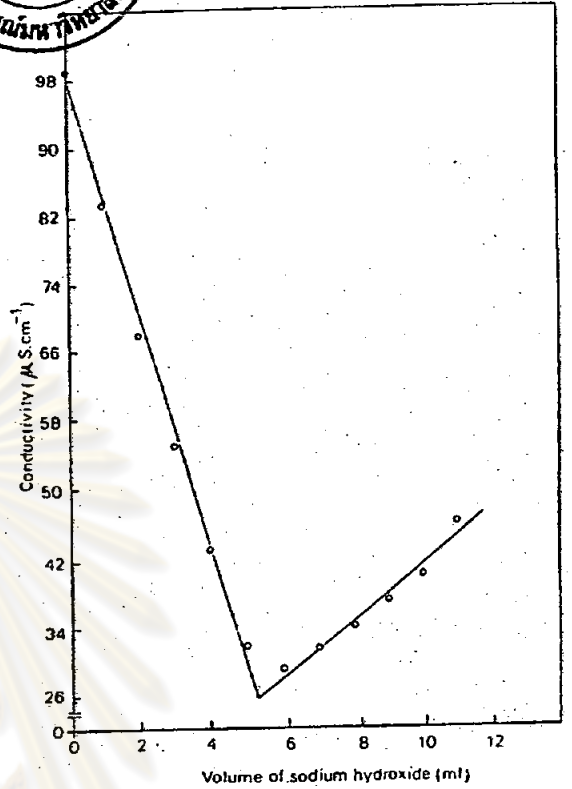


FIGURE 2-5 Conductometric titration of approximately 0.0005 M HCl with 0.0025 M NaOH

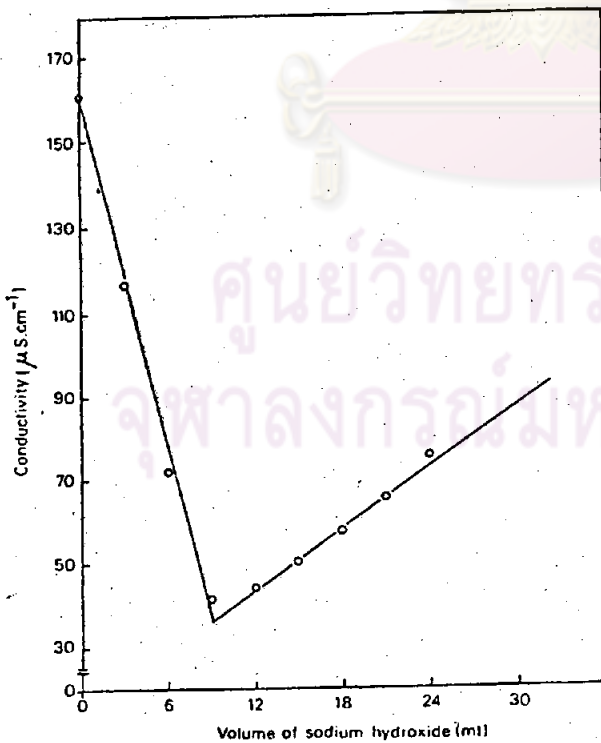


FIGURE 2-6 Conductometric titration of approximately 0.0010 M HCl with 0.0025 M NaOH

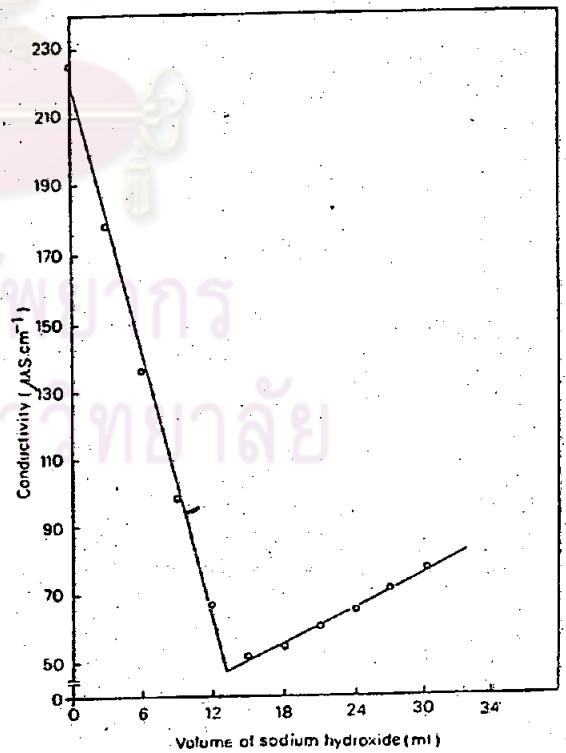


FIGURE 2-7 Conductometric titration of approximately 0.0015 M HCl with 0.0025 M NaOH

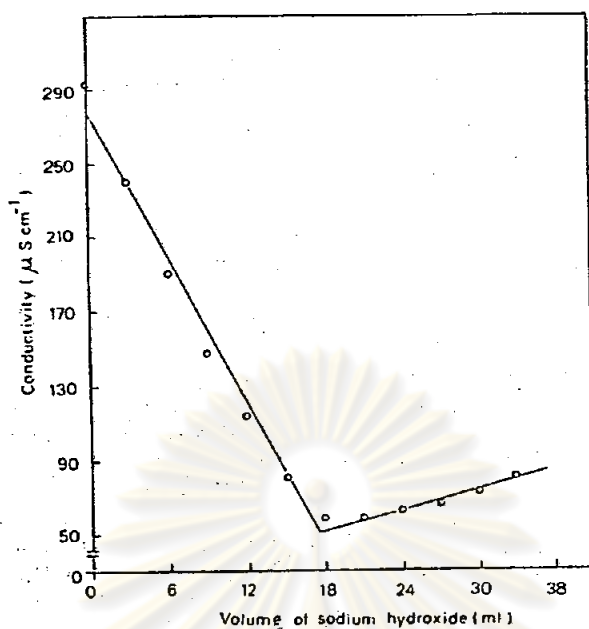


FIGURE 2-8 Conductometric titration of approximately 0.0020M HCl with 0.0025 M NaOH

From FIGURE 2-4 to 2-7 the equivalent point of the reaction were 1.65, 5.30, 9.00, 13.2 and 17.6 respectively. Therefore, the concentration of approximately 0.0001, 0.0005, 0.0010, 0.0015 and 0.0020 were calculated to be 0.00019, 0.00062, 0.00106, 0.00155 and 0.00207 M.

2.8.3 Relationship between concentration of standard hydrochloric acid and the corresponding conductivity

The conductivity measurement of each standard hydrochloric acid solutions were performed (see TABLE 2-27).

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TABLE 2-27 Relationship between concentration of standard hydrochloric acid and the corresponding conductivity

Concentration of standard HCl (M)	Conductivity (μ S cm^{-1})
0.00019	31.00
0.00062	99.00
0.00106	163.00
0.00155	225.00
0.00207	293.00

The conductivity is then plotted against the concentration of standard hydrochloric acid solution. Profile of concentration of hydrogen chloride versus conductivity was obtained (FIGURE 2-9).

From the profile, the concentration of hydrogen chloride that evolution during the photodegradation of PVC was interpreted.

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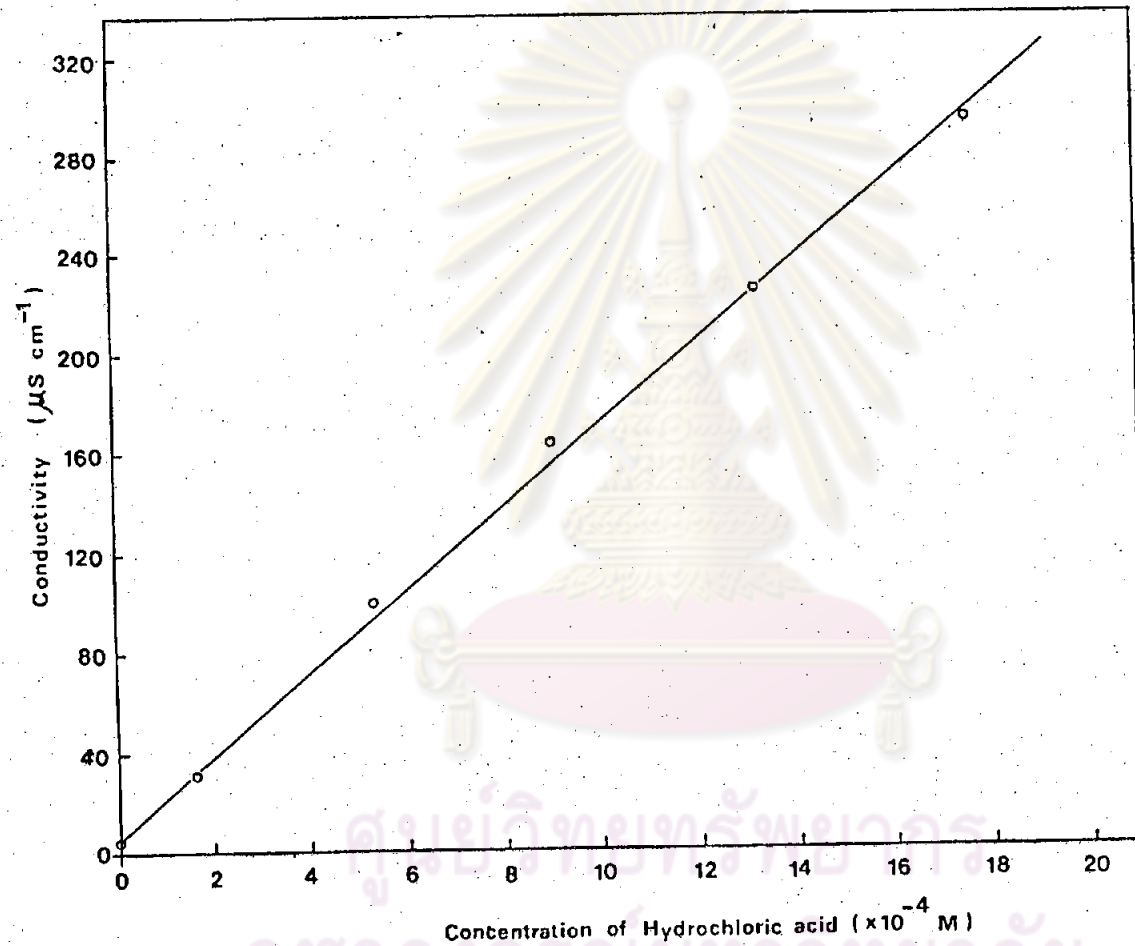


FIGURE 2-9 Concentration-conductivity profile

2.9 Spectroscopic study for determination of PVC photodegradation products

2.9.1 The ultraviolet and visible spectroscopic study

2.9.1.1 Photodegradation of PVC in nitrogen

PVC-ICI 2 in tetrahydrofuran (2.0 g.dl^{-1}) was prepared and irradiated for 8 hours. After 8 hours, the reaction was stopped, the film of PVC was prepared. About 0.1 g (0.1103 g) of this film was dissolved in tetrahydrofuran. When PVC film dissolved, the solution was made up to 10 ml by addition of tetrahydrofuran. Concentration of 1.103 g.dl^{-1} was obtained.

In the same manner, films of PVC-ICI 2 solutions irradiated for 10 and 12 hours were prepared. About 0.1 g of photodegraded PVC-ICI 2 which irradiated for 10 hours (0.1091 g) and 12 hours (0.1021 g) was dissolved in tetrahydrofuran respectively. When each PVC film dissolved the solution was made up to 10 ml by addition of tetrahydrofuran. The solutions concentrated 1.091 g.dl^{-1} and 1.021 g.dl^{-1} were obtained.

Ultraviolet spectra of photodegraded PVC sample in nitrogen at various time were examined using a Ultraviolet-240 Shimadzu UV-Visible Spectrophotometer. The spectra are shown in FIGURE 3-20

2.9.1.2 Photodegradation of PVC in oxygen

Similarly, films of PVC-ICI 2 solutions irradiated for 8, 10 and 12 hours were prepared. About 0.1 g of each film which irradiated for 8 hours (0.1321 g), 10 hours (0.1308 g), and 12 hours (0.1305 g) was dissolved in tetrahydro-

uran and the solution was made up to 10 ml by addition of tetrahydrofuran. The solutions concentration 1.321 g.dl^{-1} , 1.308 g.dl^{-1} and 1.305 g.dl^{-1} were obtained respectively. The ultraviolet spectra are shown in FIGURE 3-21.

2.9.2 The infrared spectroscopic study

2.9.2.1 Photodegradation of PVC in nitrogen

PVC-ICI 2 in tetrahydrofuran (2.0 g.dl^{-1}) was prepared and irradiated in nitrogen for 8 hours. After 8 hours, the reaction was stopped. Approximately 3 ml of this solution was drawn down a glass petri dish to give coat glass surface. After evaporation of tetrahydrofuran at room temperature gave a film of PVC. This film was attached to holder which fitted directly into the sample compartment of a Shimadzu IR-440 spectrophotometer. The spectra is shown in FIGURE 3-23.

2.9.2.2 Photodegradation of PVC in oxygen

Similarly, film of PVC-ICI 2 solution irradiated in oxygen for 8 hours was prepared. The infrared spectra of this film is shown in FIGURE 3-24.

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