CHAPTER III

EXPERIMENTS AND RESULTS

3.1 Chemicals and Apparatus

3.1.1 Chemicals

1. Acetic acid (Analyticals, Carlo Erba)

2. Acetone (Baker Analyzed [R] Reagent)

3. Aluminum chloride (Fluka Chemika)

4. $\in$-Caprolactone (Fluka Chemika)

5. Ceric ammonium nitrate (Pronalys[*] AR, M & B)

6. Diethyl ether (Baker Analyzed [R] Reagent)

7. Ethyl bromide (Laboratory Reagent, May & Baker)

8. Hydrochloric acid (Analytical Reagent, Mallinckrodt)

9. Iodine crystal (Local purchased, P & N Associates Ltd.)

10. Magnesium turning (Fluka Chemika)

11. Methanol (Proanalysi, Merck)

12. Methylacrylate (Siam Resin Chemical Ltd.)

13. Nitrogen (OFN, Locally purchased, Rattachoke Co., Ltd.)

14. Petroleum ether (Baker Analyzed Reagent)

15. Polystyrene standard

16. Polyvinyl acetate (Laboratory Reagent, BDH Chemical)

17. Polyvinyl chloride (Thai Plastic and Chemicals Co.,Ltd.)

18. Potassium bromide (Analytical Grade, Carlo Erba)

19. Starch (Locally purchased, Cassava starch and glutinous
    rice flour from Harng Pang Thai, Ltd., Corn
    starch from CPC/AJI (Thailand), Ltd.)
20. Sodium metal (Fluka Chemika)
21. Tetrahydrofuran (Baker Analyzed Reagent)
22. Toluene (Baker Analyzed Reagent)

3.1.2 Apparatus

1. Differential Scanning Calorimetry, DuPont 910

2. Double Stage High Vacuum Pump, Javac JD 60

3. Electrical Balance, Oertling NA 264

4. Gel Permeation Chromatography, Waters 600 E system controller, Differential Refractometer Waters 470

5. Heating Mantle, Isopad

6. Hot Plate & Stirrer, Heidolph MR 2002, Labinco L 32

7. Infrared Spectrophotometer, Perkin-Elmer 781 and Perkin-Elmer 1760x.

8. Mechanical Stirrer, Janke & Kunkel RE 16

9. Rotary Evaporator, Heidolph VV 2000

10. Oven, Termaks TB 5260

11. Vacuum Oven, Forma Scientific, Inc. model 6515

3.2 Procedure

3.2.1 Synthesis of poly(ε-caprolactone)

3.2.1.1 Synthesis of ethyl magnesium bromide

The Grignard reagent was prepared adaptably by the method suggested by Adams (59). A 8.00-g of magnesium turnings and a small crystal of iodine were placed in a 250-ml two necked round bottomed flask provided with a Claisen adapter bearing an addition funnel and a vertical condenser. A 150 ml of dry ether dehydrated over Na wire (see Appendix A) was introduce directly into the flask. A 27.00 ml of ethyl bromide was placed in the addition funnel and it was allowed to flow drop by drop into the flask. The reaction mixture was stirred vigorously until the reaction has started, as evidenced by disappearance of the iodine color, appearance of turbidity, and spontanenous boiling. The flask was cooled by cubed ice and adjust addition rate of halide to keep the ether reflux gently. The reaction was complete when the magnesium has dissolved. After completion of the reaction, the product was stirred for 30 mins under nitrogen atmosphere introduced into the flask via its side neck and then proceed the next step without delay. The set of reaction system is shown in figure 3.1.

The obtained solution of this Grignard reagent was dark color and reacted rapidly with air and moisture.
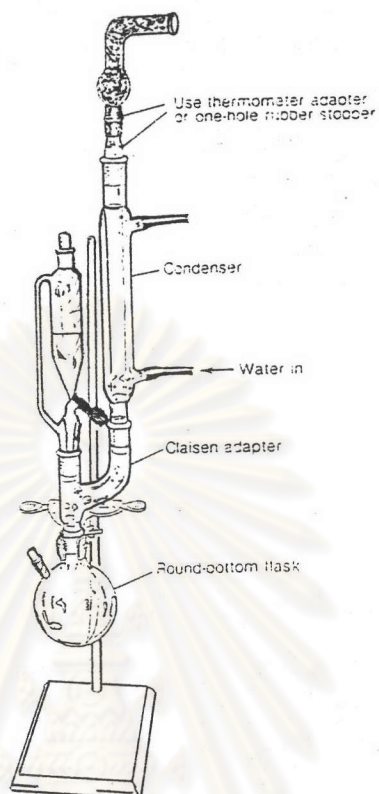
Figure 3.1 Apparatus for preparing the Grignard reagent

3.2.1.2 Synthesis of triethyl aluminum

A 8.80-g of anhydrous aluminum chloride
was dissolved in 100 ml of dry ether under nitrogen atmostphere
in a dry bag (Fig. 3.2). The solution was added to the same
funnel used in previuos step and let it flow drop by drop into
the flask containing ethyl magnesium bromide at the rate that made
spontaneous reflux gently. After 2 hrs'reflux, the excess ether
was distilled off, then the triethylaluminum etherate was
distilled from the magnesium halide on a vacuum system.

Inlets for
gas piping and
electrical leads

Large opening
for loading
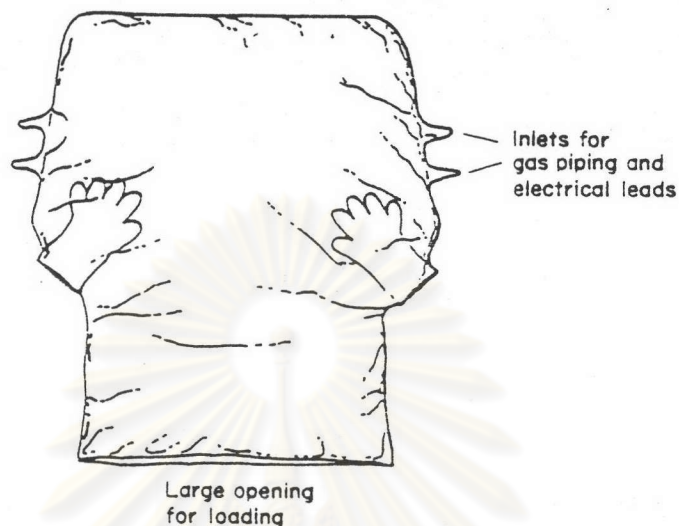
Figure 3.2 A 'dry bag'

        The colorless triethylaluminum was obtained
from distillation at 68-70 $^\circ$ C, under reduced pressure of 1.5
torr.   The obtained initiator was stored in sealed bottle under
nitrogen atmosphere.

3.2.1.3 Polymerization of $\in$-caprolactone

            In the dry bag purged with a stream of dry
oxygen-free nitrogen (OFN), a 500 ml three-necked round
bottomed flask was filled with a magnetic bar, dry toluene
(Appendix A), refined $\in$-caprolactone and ($\in$-CL) triethylaluminum
in various quantities as shown in Table 3.1. The flask was imme-
diately fitted with a condenser protected with a drying tube, a

thermometer, and a gas inlet through which the flask was swept with nitrogen. The set of reaction was taken out of the bag and fitted with stands while nitrogen gas was still flowing through

Table 3.1 Conditions for synthesis of poly($\in$-caprolactone)

No.	Amount of $\in$-CL[*] (ml) [(g)]	Amount of AlEt$_3$ (ml) [(g)]	Volume of toluene (ml)	Concentration ratio of monomer and inititor
1	45.00 [48.42]	0.50 [0.42]	200.00	115.33
2	25.50 [27.44]	0.20 [0.17]	120.00	161.76
3	93.50 [100.61]	1.70 [1.42]	0.00	70.76
4	46.50 [50.03]	0.70 [0.58]	200.00	86.41

-CL = -Caprolactone

the solution. Then the solution was heated to 80 ° C and stirred continuously under a nitrogen atmosphere for 1 hr. The polymer was precipitated by pouring a fine stream of the viscous toluene

solution into a petroleum ether-Dry Ice mixture at -80 ° C while
stirring vigorously. The polymer was dried for 16 hrs. in a
vacuum oven at 40 ° C and 1 torr.

The physical properties of the synthesized
polymers investigated by the procedures in Section 3.2.3 are
shown in Table 3.2.

Table 3.2   Results of $\in$-caprolactone polymerizations

No.	Percentage yield	Molecular weight	Appearance
1	85.49	7857	white fine powder
2	98.76	12654	white fine powder
3	45.41	64227	white flake
4	97.08	76764	white flake

3.2.2 Synthesis of methylacrylate grafted starch

The factors were assumed to affect the graft copoly-
merization of polymethylacrylate onto cassava starch. In this
study the effects of them on suspension copolymerization were
studied in the following steps.

3.2.2.1 Effect of variation of reaction volume

A 3.5000-g of cassava starch and a 60.00 ml
of double distilled water were filled in a 500 ml wide-necked
reactor with multiple socket lids connected with a mechanical
stirrer, a condenser, a thermometer, a gas inlet and a rubber
septum attached to a syringe. The suspended starch in water
was heated to 45 + 1 C and stirred at the rate of 500 rpm for
1 hr under nitrogen atmosphere generated by a slow stream of
nitrogen flowing through the suspension. A 0.4500-g of ceric
ammonium nitrate, as an initiator, was weighed and dissolved in
1.00 ml of 1.00 M nitric acid. After 1 hr of stirring a 9.00
ml of freshly distilled methylacrylate monomer was added. The
mixture was sitirred for 15 mins and then into it the initiator
was added drop by drop of 0.2 ml initiator solution in every
30 min-intervals. After the last drop of initiator was added,
the reaction was still stirred for 30 minutes and then pour a
200 ml of water to the product mixture. The grafted product was
filtrated and washed with 150 ml of 0.50 M of nitric acid for 3
times. The remained acid in product was removed by washing

and decanting with distilled water until the neutral filtrate was obtained. The adsorped water was taken out of the product by a rotary evaperator and the product was completely dried by a vacuum oven at 70 C for 6 hrs. The total dry product was weighed.

The ungrafted polymethylacrylate was separated from the grafted product by soxhlet extraction. A certain amount of crude polymer was extracted with toluene for 1 hr. Each sample was extracted for 3 times for which a fresh toluene was used. The obtained grafted product was dried in a vacuum oven at 60-70 °C overnight. The dry grafted product was weighed.

The weight of grafted polymethylacrylate was obtained by measurement of the product from starch extracting of grafted product. A 0.5-g grafted product and 100-ml of gracial acetic acid was added to a 250-ml round flask connected with a condensor. The mixture was stirred in the flask and heated it up to 80-90°C for 30 mins or until homogenized mixture was obtained. A 3.0-ml of concentrated HCL was introduced to the mixture. The mixture was stirred until the clear solution was obtained. The solution was poured into the cold water then filter the precipitated grafted polymer. Wash the grafted polymer several times. The product was dried by air, then in an vaccuum oven at 40 °C for 2 hrs. The obtained grafted polymer was weighed.

The grafting parameters as defined below were calculated.

Apparent grafting yield G is the ratio of grafted polymer to original starch.

True grafting yield G_T is the ratio of grafted polymer to true-grafted polymer to true-grafted starch.

Grafting efficiency GE is the ratio of grafted polymer to total synthetic polymer.

Total conversion of monomer to polymer C_t is the monomer fraction that polymerizes.

Graft conversion C_x is the monomer fraction that affords grafted polymer.

Homopolymer conversion C_h is the monomer fraction that affords homopolymer.

Starch conversion C_c is the starch fraction actually grafted.

For other experiments with various reaction volumes were varied by changing water volume to be 80.00, 100.00, 120.00, 140.00 and 160.00 ml respectively. The procedures for each experiments are the same as that for the experiments with

reaction volume of 60 ml. All experiments were run at 45 ˚C. The grafting parameters from the experiments were plotted against the reaction volume. The appropriate volume was choosen to be the constant factor for running other experiments. The grafted polymers and their grafting parameters are shown in Tables 3.3 and 3.4 respectively.

Table 3.3 Effect of reaction volume

No.	Reaction volume (ml)	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G1	70.00	9.9962	7.3938	2.6024	4.0847	3.3091
G2	70.00	8.8860	6.6136	2.2724	3.4548	3.1588
G3	90.00	10.3518	7.7953	2.5565	4.2969	3.4984
G4	90.00	10.6468	7.4830	3.1638	4.1413	3.3417
G5	110.00	11.1422	7.2408	3.9014	4.1292	3.1116
G6	110.00	11.0223	7.8128	3.2095	4.5021	3.3107
G7	130.00	11.1606	8.0232	3.1374	4.5816	3.4416
G8	130.00	11.4550	7.8144	3.6406	4.4784	3.3360
G9	150.00	10.9198	7.9482	2.9716	4.5236	3.4246
G10	150.00	11.0955	8.1072	2.9983	4.6896	3.4176
G11	170.00	11.1148	7.0396	4.0751	3.9449	3.0947
G12	170.00	11.1861	5.7145	5.4752	2.5023	3.2086

It was found that when the reaction volumes were increased up to the value around 140 the increases of grafting yield could be found but the too large volume beyond that value caused the opposite effect. The grafting efficiency did not depend on the reaction volume of the range between 70 and 150 ml but above upper limit of the range the grafting efficiencies were declined like the corresponding grafted products. The fluctuation of starch conversions were also found and by its effect, the ratios of the grafted polymers to the related total products were caused to be constant. The reaction volume which gave maximum grafting yield was estimated to be 140 ml. This value was fixed as a constant factor for the following experiments.

Table 3.4 Grafting parameters of polymers in Table 3.3

No.	G	G_T	GE	C_t	C_x	C_h	C_s
G1	116.71	123.43	40.86	77.74	47.48	30.25	94.55
G2	98.71	109.37	38.92	70.07	40.16	26.42	81.68
G3	122.77	122.82	41.51	79.67	49.95	29.72	99.95
G4	118.32	123.93	38.90	84.92	48.14	36.78	95.48
G5	117.98	132.70	37.06	93.36	48.00	45.35	88.90
G6	128.63	135.99	40.84	89.65	52.34	37.31	94.59
G7	130.90	133.12	41.05	89.73	53.26	34.96	98.33
G8	127.95	134.24	39.10	94.38	52.06	40.56	95.31
G9	129.24	132.09	41.43	87.13	52.59	33.11	97.85
G10	133.99	137.22	42.27	89.26	54.52	33.29	97.65
G11	112.71	127.47	35.49	93.23	45.86	45.40	88.42
G12	71.49	77.99	22.37	92.74	29.09	61.00	91.67

3.2.2.2 Effect of time-interval for the addition of initiator

The reaction volume was 140-ml but the amount cassava starch, monomer, ceric ion and nitric acid for dissolving ceric compound, were fixed and used the same amount as in Section 3.2.2.1. The varied factor was the time-interval for adding the initiator into the reaction mixture in such a following series; each 0.20 ml portions of 1.00 ml of ceric ion solution was added drop by drop in each time-interval of 5, 10, 15,20, 25, and 30mins. The experiments were run at 45° C. The narrowest time-interval which gives highest yield is preferred. The results of grafted polymers obtained with varying time-intervals are shown in Table 3.5. The grafting parameters are shown in Table 3.6.

The initiator introduction with low speed (wide time-interval) gave the higher grafting yield. The grafting yield, grafting efficiency, and graft conversion were constant in the range of 15 and 30 mins. When the narrow time-intervals were used, the three former parameters were encountered the increase of homopolymer conversion. All the starch conversions were over 93 %. The time-interval of 15-min was chosen as a narrowest time-interval for addition of the initiator. This interval was used as a constant factor for the next experiments.

Table 3.5 Effect of time-intervals for

the addition of initiator

No.	Time intervals (min)	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G13	30	11.0724	8.2608	2.8116	4.9322	3.3286
G14	30	11.2310	8.0811	3.1499	4.6989	3.3822
G15	25	11.3642	8.2563	3.1079	4.8716	3.3847
G16	25	11.0911	8.1361	2.9550	4.7350	3.4011
G17	20	11.1266	8.1822	2.9444	4.8546	3.3276
G18	20	11.2833	8.2496	3.0337	4.8552	3.3944
G19	15	11.1400	8.2312	2.9088	4.8500	3.3812
G20	15	11.0248	8.2067	2.8181	4.7967	3.4100
G21	10	11.3076	7.8641	3.4435	4.5745	3.2896
G22	10	11.2729	7.6177	3.6552	4.2917	3.3260
G23	5	11.1385	7.5631	3.5754	4.1893	3.3738
G24	5	11.3144	7.3248	3.9896	3.9468	3.3780

Table 3.6   Grafting parameters of polymers in Table 3.5

No.	G	G_T	GE	C_b	C_x	C_h	C_s
G13	140.92	148.18	44.54	90.02	57.34	32.68	95.10
G14	134.25	138.93	41.84	91.24	54.62	36.62	96.63
G15	139.19	143.93	42.87	92.76	56.63	36.13	96.71
G16	135.29	139.22	42.69	89.40	55.04	34.35	97.17
G17	138.70	145.89	43.63	90.67	56.43	34.23	95.07
G18	138.72	143.04	43.03	91.71	56.44	35.27	96.98
G19	138.57	143.44	43.54	90.20	56.38	33.81	96.61
G20	137.05	140.67	43.51	88.52	55.76	32.76	97.43
G21	130.70	139.06	40.46	93.21	53.18	40.03	93.99
G22	122.62	129.03	38.07	92.38	49.89	42.49	95.03
G23	119.69	124.17	37.61	90.26	48.70	41.56	96.39
G24	112.77	116.84	34.88	92.26	45.88	46.38	96.51

3.2.2.3   Effect of variation of initiator

For the experiments in this section, the amount of starch was the same as in the previous section. The reaction volume was 140 ml and the time interval was 15 mins. A 1-ml of 1 M nitric acid was used. The varied factor was the amount of ceric ion. The ceric ion was varied as shown in Table 3.7. The procedure for graft copolymerization and determination of

grafting parameters were the same as the previous section. The calculated parameters are shown in Table 3.8.

Table 3.7 Effect of variation of initiator

No.	Amount of initiator (g)	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G25	0.1500	6.6121	4.6948	1.9173	1.6298	3.0650
G26	0.1500	6.4476	4.6358	1.8118	1.6346	3.0012
G27	0.2500	10.8176	6.7637	4.0539	3.5436	3.2201
G28	0.2500	10.4904	6.9011	3.5893	3.7529	3.1482
G29	0.3000	10.9384	8.0800	2.8584	4.7088	3.3712
G30	0.3000	10.9405	7.8243	3.1162	4.4217	3.4026
G31	0.3500	11.4880	8.3050	3.1830	4.9906	3.3144
G32	0.3500	11.1610	8.4122	2.7488	5.0862	3.3260
G33	0.4000	11.2565	8.2144	3.0421	4.7893	3.4251
G34	0.4000	11.2032	8.3567	2.8465	4.9252	3.4313
G35	0.4500	11.1400	8.2312	2.9088	4.8500	3.3812
G36	0.4500	11.0248	8.2067	2.8189	4.7967	3.4100
G37	0.5500	11.2822	7.2436	4.0386	3.8181	3.4255
G38	0.5500	11.0476	7.0441	4.0035	3.6323	3.4118
G39	0.6500	11.3199	6.9155	4.4044	3.7284	3.1871
G40	0.6500	11.0424	6.8397	4.2027	3.4673	3.3724

Table 3.8 Grafting parameters of polymers in Table 3.7

No.	G	G_T	GE	C_a	C_x	C_h	C_s
G25	46.57	53.17	24.65	41.23	18.95	22.29	87.57
G26	46.70	54.46	25.35	40.06	19.00	21.06	85.75
G27	101.25	110.05	32.76	88.32	41.19	47.13	92.00
G28	107.23	119.21	35.77	85.35	43.63	41.73	89.95
G29	134.54	139.68	43.05	87.97	54.74	33.23	96.32
G30	126.33	129.95	40.42	87.63	51.40	36.23	97.22
G31	142.55	150.57	43.44	95.02	58.02	37.00	94.70
G32	145.32	152.92	45.57	91.08	59.13	31.95	95.03
G33	136.84	139.83	42.55	91.04	55.68	35.36	97.86
G34	140.72	143.53	44.13	90.35	57.26	33.09	98.04
G35	138.57	143.44	43.54	90.20	56.38	33.81	96.61
G36	137.05	140.67	43.51	88.53	55.76	32.77	97.43
G37	109.09	111.46	33.84	91.33	44.39	46.95	97.87
G38	103.78	106.46	32.88	88.77	42.22	46.54	97.48
G39	106.53	116.98	32.94	94.54	43.34	51.20	91.06
G40	99.07	102.81	31.40	89.16	40.31	48.86	96.37

The behavior of the effect caused by the variation of initiator amount was similar to that of the effect of the reaction volume. The grafting parameters such as grafting yield, grafting efficiency, and graft conversion tended to be in

the same manner. The change in those just mentioned parameters was clearly seen. All the starch conversions were more than 85%. The homopolymer conversions reached the minimum value at 0.3500 mole intercept. The maximum value of grafting yield was obtained when 0.3500 -g of ceric ammonium nitrate was used. This amount of initiator was used for the next sections.

3.2.2.4 Effect of variation of monomer

The optimum conditions from the previous sections as follows; reaction volume of 140-ml, time-interval of 15 -mins and 0.3500 g of ceric ammonium nitrate were fixed. The amount of monomer was varied as shown in Table 3.9. The temperature was kept at 45° C for all experiments. Like the previous sections the smallest volume giving the highest product yield was selected to be a constant factor for other following experiments. Shown in Table 3.10 are the grafting parameters of the obtained synthetic copolymers.

From Tables 3.9 and 3.10, it was found that the grafting yield as a funtion of monomer concentration had its maximum value at methylacrylate concentration of 0.7939 molar. The grafting parameters were smoothly changed in the concentration range of 0.7145 and 0.7780 but the changes of them were quite sharp when the more concentrated monomers were used. The optimum value of monomer concentration (0.7939 M) was fixed as a constant factor for the next experiments.

Table 3.9 Effect of variation of monomer

No.	Concn. of monomer (M)	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G41	0.7145	11.4880	8.3050	3.1830	4.9906	3.3144
G42	0.7145	11.1610	8.4122	2.7488	5.0862	3.3260
G43	0.7542	11.3487	8.3856	2.9631	5.0624	3.3232
G44	0.7542	11.3663	8.4063	2.9600	5.1064	3.2999
G45	0.7780	11.5857	8.4316	3.1541	5.1378	3.2938
G46	0.7780	11.6044	8.4397	3.1647	5.2750	3.4591
G47	0.7939	11.9392	8.6335	3.3057	5.5974	3.0361
G48	0.7939	11.9811	8.6305	3.3506	5.4792	3.1513
G49	0.8097	11.7240	8.3217	3.4023	4.8503	3.4714
G50	0.8097	11.6557	8.3556	3.3001	5.2160	3.1396
G51	0.8335	11.2148	7.6665	3.5483	4.6175	3.0490
G52	0.8335	11.1087	7.7048	3.4039	4.3009	3.2116
G53	0.8732	9.1654	7.1477	2.0177	3.8329	3.3148
G54	0.8732	8.7542	6.2376	2.5166	3.7210	3.2943

Table 3.10 Grafting parameters of polymers in Table 3.9

No.	G	G_T	GE	C_4	C_{x}	C_h	C_{s}
G41	142.59	150.57	43.44	95.02	58.01	37.00	94.70
G42	145.32	152.92	45.57	91.08	59.13	31.95	95.03
G43	144.64	152.34	44.61	88.39	55.75	32.63	94.95
G44	145.90	155.03	44.93	88.84	56.24	32.60	94.28
G45	146.79	155.98	44.35	88.52	54.85	33.67	94.11
G46	150.71	152.50	45.45	90.10	56.32	33.79	98.83
G47	159.93	184.36	46.88	93.15	58.56	34.59	86.75
G48	156.55	173.87	45.73	92.38	57.33	35.06	90.04
G49	138.58	139.72	41.37	84.65	49.75	34.90	99.18
G50	149.03	166.14	44.75	87.35	53.50	33.85	89.70
G51	131.92	151.44	41.17	81.37	46.01	35.36	87.11
G52	122.88	133.92	38.72	76.77	42.86	33.92	91.76
G53	109.51	155.63	41.82	55.65	36.46	19.19	94.71
G54	106.31	122.95	42.50	59.33	35.39	23.94	94.12

3.2.2.5 Effect of amount of nitric acid

The conditions for this section were 140-ml
reaction volume, 15-min time-interval, 0.3500 g initiator, 0.7939
M of monomer. The proton(H^+), from both nitric acid used as a
solvent for the ceric ion solution and nitric acid which was
added directly to the reaction mixture, was expected to affect
the reactions in either ways, increase or decrease the grafted
products. The varied total amounts of proton (moles) from both
sources used in each experiments in this section are shown in
Table 3.11. The reactions were run by the similar procedure used
in the previous sections. The calculated grafting parameters are
shown in Table 3.12.

When small amount or low concentration of
nitric acid was present in the reaction mixture it was found that
some grafting parameters, excluding starch conversion and total
conversion of monomer to polymer, were inreased rapidly and they
reached the apex when the total amount of 0.5×10^{-3} mole-nitric
acid was used. The changes of starch conversions and total
conversions of monomer to polymer occurred in an insignificant
magnitude. At too much amount of nitric acid the grafting yield
and grafting efficiency were dramatically decreased.

Table 3.11 Effect of amount of nitric acid

No.	Amount of HNO$_3$ (mole) x 1000	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G55	0.0000	12.0917	6.9493	5.1424	3.7087	3.2406
G56	0.0000	11.9742	7.0016	4.9726	3.6290	3.3726
G57	0.2500	12.1550	8.4124	3.7426	5.1477	3.2647
G58	0.2500	12.0867	8.3507	3.7360	5.1264	3.2243
G59	0.5000	12.1127	9.8775	2.2352	6.6930	3.1845
G60	0.5000	12.0349	9.5042	2.5307	6.2990	3.2052
G61	0.7500	11.9828	8.8034	3.1794	5.6910	3.1124
G62	0.7500	11.9808	9.0459	2.9349	5.9084	3.1375
G63	1.0000	12.0932	8.7199	3.3733	5.5713	3.1486
G64	1.0000	12.0012	8.5467	3.4545	5.5045	3.0422
G65	3.0000	11.9466	6.2845	5.6621	3.1359	3.1486
G66	3.0000	11.8394	6.2826	5.5558	3.0349	3.2477
G67	6.0000	11.0584	5.3879	5.6705	2.2722	3.1157
G68	6.0000	10.9847	4.7902	6.1945	1.5716	3.2186
G69	11.0000	10.9732	4.8466	6.1266	1.5249	3.3217
G70	11.0000	9.8751	4.7837	5.0914	1.5132	3.2705

Table 3.12 Grafting parameters of polymers in Table 3.11

No.	G	G_T	GE	C_t	C_{sl}	C_h	C_s
G55	105.96	114.44	30.67	92.60	38.80	53.80	92.59
G56	103.69	107.60	30.31	89.99	37.97	52.03	96.36
G57	147.08	157.68	42.35	93.01	53.86	39.16	93.28
G58	146.47	158.99	42.41	92.72	53.63	39.09	92.12
G59	191.23	210.17	55.26	93.41	70.03	23.39	90.99
G60	179.97	196.52	52.34	92.38	65.90	26.48	91.58
G61	162.60	182.85	47.49	92.81	59.54	33.26	88.93
G62	168.81	188.32	49.32	92.52	61.82	30.71	89.64
G63	159.18	176.95	46.07	93.58	58.29	35.29	89.96
G64	157.27	180.94	45.87	93.73	57.59	36.14	86.92
G65	89.60	99.60	26.25	93.93	32.81	59.24	89.96
G66	86.71	93.45	25.63	89.88	31.75	58.13	92.79
G67	64.92	72.93	20.55	83.10	23.77	59.33	89.02
G68	44.90	48.83	14.31	81.25	16.44	64.81	91.96
G69	43.57	45.91	13.90	80.05	15.95	64.10	94.91
G70	43.23	46.27	25.32	69.10	15.83	53.27	93.44

3.2.2.6 Effect of variation of temperature

Like other factors, the reactions were run under various controlled temperature as shown in Table 3.13 in order to examined how they were affected by the temperature. The obtained products and their parameters are shown in Table 3.14.

Table 3.13 Effect of variation of temperature

No.	Temp. (°C)	Total product (g)	Grafted product (g)	Homo polymer (g)	Grafted PMA (g)	Grafted starch (g)
G71	32 + 1	12.1650	4.8882	7.2768	1.8888	2.9994
G72	32 + 1	12.0677	4.8932	7.1745	1.8806	3.0126
G73	40 + 1	11.5340	7.0272	4.5068	3.9068	3.0664
G74	40 + 1	11.9422	6.7315	5.2107	3.6187	3.1128
G75	45 + 1	12.1127	9.8775	2.2352	6.6930	3.1845
G76	45 + 1	12.0349	9.5042	2.5307	6.2990	3.2052
G77	50 + 1	10.8717	7.8015	3.0702	4.7342	3.0673
G78	50 + 1	10.7945	7.7725	3.0220	4.7578	3.0147
G79	55 + 1	11.3191	4.9237	6.3954	1.6820	3.2417
G80	55 + 1	10.9648	5.1446	5.8202	1.9237	3.2209
G81	60 + 1	10.4973	6.6092	3.8881	3.5983	3.0109
G82	60 + 1	9.8751	6.2025	3.6726	3.2467	2.9558

Table 3.14 Grafting parameters of polymers in Table 3.13

No.	G	G_T	GE	C_t	C_x	C_h	C_s
G71	53.97	62.97	15.53	95.89	19.76	76.13	85.70
G72	53.73	62.42	15.58	94.74	19.68	75.06	86.07
G73	113.17	129.17	34.34	88.59	41.44	47.15	87.61
G74	103.37	116.25	30.30	92.38	37.86	54.52	88.94
G75	191.23	210.17	55.26	93.41	70.03	23.39	90.99
G76	179.97	196.52	52.34	92.38	65.90	26.48	91.58
G77	135.26	154.34	43.55	81.65	49.53	32.12	87.64
G78	135.94	157.82	44.08	81.40	49.78	31.62	86.13
G79	48.06	51.89	14.86	84.51	17.60	66.91	92.62
G80	54.96	59.73	17.54	81.02	20.13	60.89	92.03
G81	102.09	119.51	34.28	78.33	37.65	40.68	86.03
G82	92.76	109.84	32.88	72.39	33.97	38.42	84.45

Though the quantities of all reactants in each batch in this experimental section were the same, it was observed that the grafting parameters were the function of temperature.   At the temperature less than 45 °C, the grafting yield and efficiency were directly proportional to temperature but inversely at the temperature more than 45 °C. There existed a strange relationship of the parameter and temperature at 60 °C and more as expected.

3.2.2.7 Comparative study of graft copolymerization of methylacrylate onto different starches

The conditions for synthesizing of methylacrylate graft onto different starches such as cassava(CAS), corn (COS), and glutinous rice starches (GRS), were the optimum conditions obtained from the previous sections. The grafting parameters of the obtained products are shown in Table 3.15.

Table 3.15 Grafting parameters of polymethylacrylate graft onto different starches.

No.	G	G_T	GE	C_t	C_x	C_h	C_s
CAS1	191.23	210.17	55.26	93.41	70.03	23.39	90.99
CAS2	179.97	196.52	52.34	92.38	65.90	26.48	91.58
COS1	62.77	73.92	18.75	91.50	22.98	68.52	84.91
COS2	57.42	67.27	17.04	92.08	21.03	71.05	85.36
GRS1	115.70	128.88	36.99	81.66	42.37	39.29	89.77
GRS2	107.99	118.07	34.66	80.59	39.54	41.04	91.46

3.3 Characterization of the synthesized polymers

IR and FT-IR spectra of the synthesized polymers were obtained by measurement of the samples in the form of homogenized pellet of polymers and fine powder of KBr.   Poly($\in$-caprolactone) and some of its polymer blends which were casted into films, could be run for their spectra directly. The IR spectrum of poly ($\in$-caprolactone) and its functional assignment obtained from dispersive infrared spectrometer (Perkin Elmer model 781) is shown in Figure 3.3 the compared IR spectra of starch, grafted product, and grafted polymethylacrylate from fourier transform infrared spectrometer (Perkin Elmer 1760x) are shown in Figure 3.4. Shown in Appendix C are the spectra of some polymer blends.

^{1}H and ^{13}C NMR spectra of poly ($\in$-caprolactone) was run by Bruker ACF 200 MHz.   The chemical shift was determined by "external lock" with respect to that of the solvent used to dissolve the polymer.   The ^{1}H and ^{13}C spectra of poly($\in$-caprolactone) are shown in Figures 3.5-3.6 respectively.

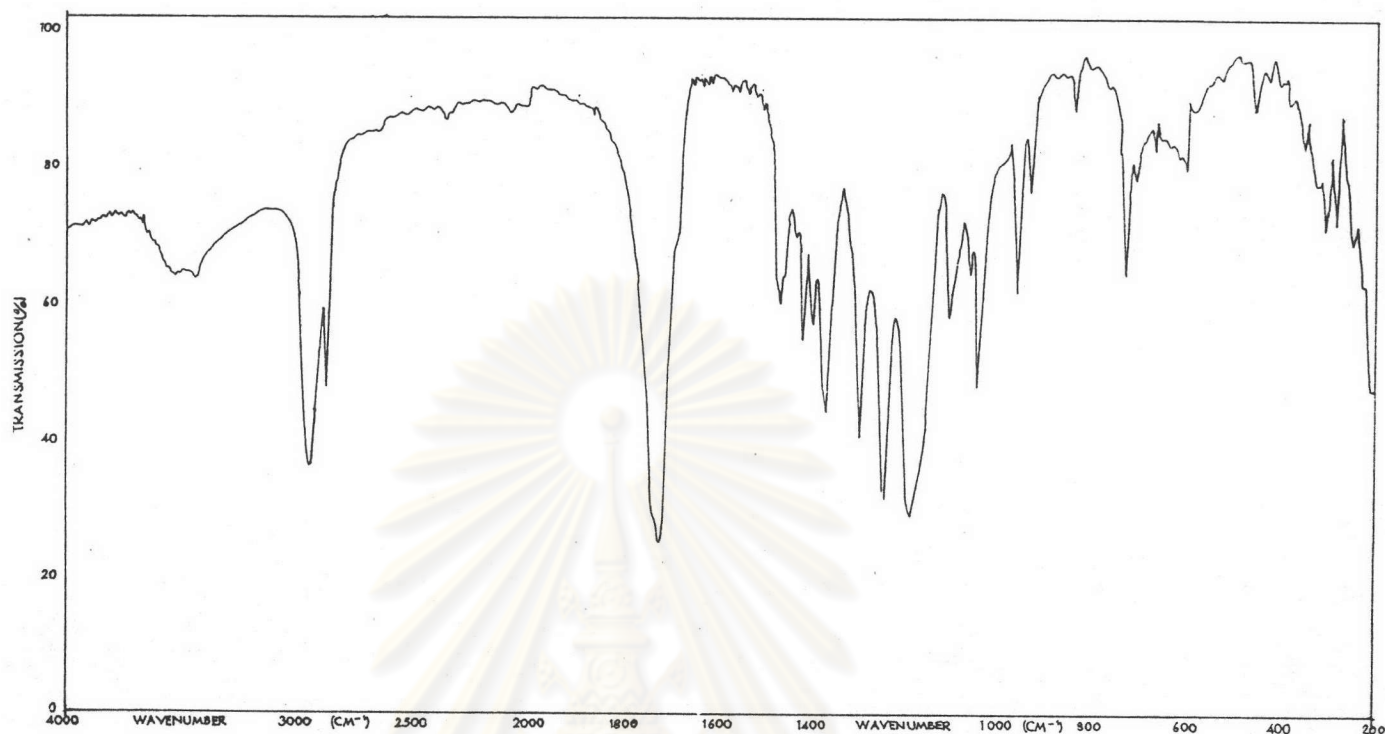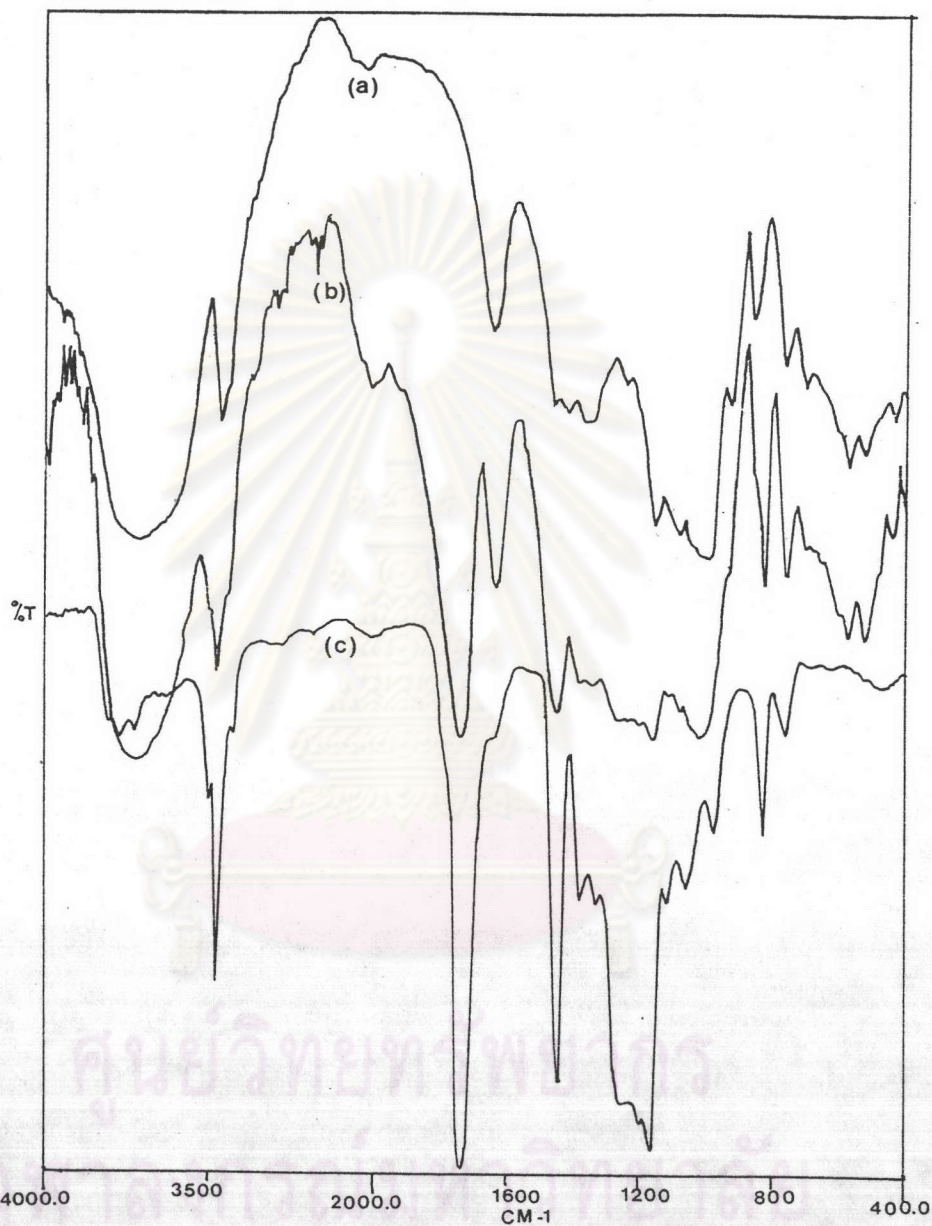Figure 3.3   IR spectrum of poly(∈-caprolactone); KBr pellet

Poly(∈-caprolactone)

wavenumber (cm^{-1})	assignment
2850-2950	C-H stretching aliphatic
1720	$\overset{\displaystyle O}{\underset{\displaystyle \shortparallel}{-C-}}$
1200	C-O

Figure 3.4 IR spectra of starch in KBr pellet : (a),
methylacrylate grafted onto starch in KBr
pellet : (b), and grafted polymethylacrylate
film : (c)*.

Starch (A)

wavenumber (cm^{-1})	assignment
3400	-OH stretching
2900	C-H stretching
1200	O-H bending
1000	C-O stretching

Grafted polymethylacrylate

wavenumber (cm^{-1})	assignment
2900	C-H stertching aliphatic
1750	C=O
1450	CH_3-
1150	C-O stretching

* IR spectrum of polymethylacrylate graft starch composes of both the peaks of starch and polymethylacrylate.
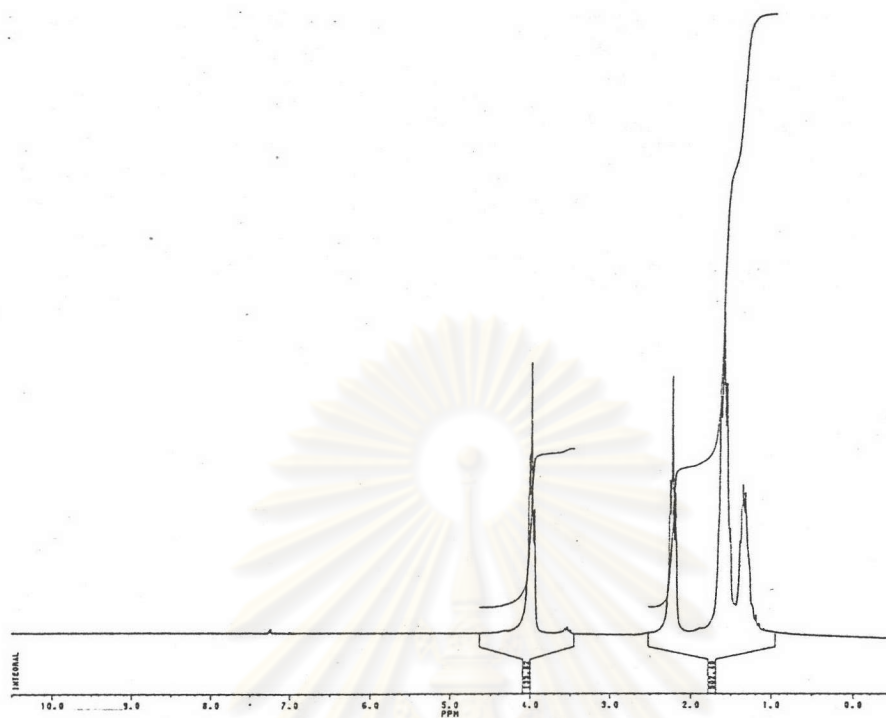
Figure 3.5 ^{1}H-NMR spectrum of poly (∈-caprolactone)
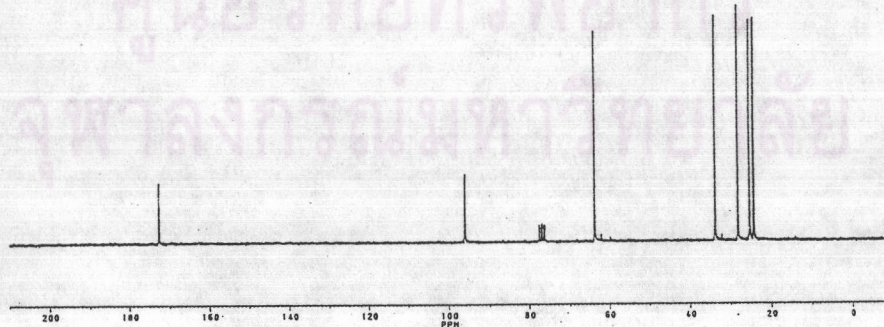
(CDCl$_3$ as solvent)

Figure 3.6 ^{13}C NMR spectrum of poly (∈-caprolactone)

(CDCl$_3$ as solvent)

Poly(-caprolactone) and polymer blends were dissolved in tetrahydrofuran. The solution was filtered through 0.5 μ m Millipore FH filters, and then deaerated for 15 mins. The 100 μ L sample solutions were injected into the gel permeation chromatograph (GPC, Waters model 600 E) at the elution flow rate of 1.0 mL/min. The chromatographic peaks were separated by using linear Ultrastyragel column and detected by differential refractometer (Waters model 470). The chromatographic data were collected by personal computer and analyzed by the Maxima software program. The molecular weight of the polymers were computed based on a calibration curve obtained of polystyrene standard (shown in Appendix C).

3.4 Preparation of cast films as sample specimens

Thin films were prepared by casting 3.00 g of polymers
or polymer mixtures dissolved in the suitable solution with a
simple cast mold shown in Figure 3.11.   The solvent was dried
by oven at 120 °C.   The solvent for poly($\in$-caprolactone) and its
polymer blends films was tetrahydrofuran.   The starch graft
copolymers was seldomly dissolved in any solvents, however,
they could swell and suspend in toluene. The swelling graft
copolymers suspending in toluene were casted by the same method.
The data of films are shown in Table 3.16.
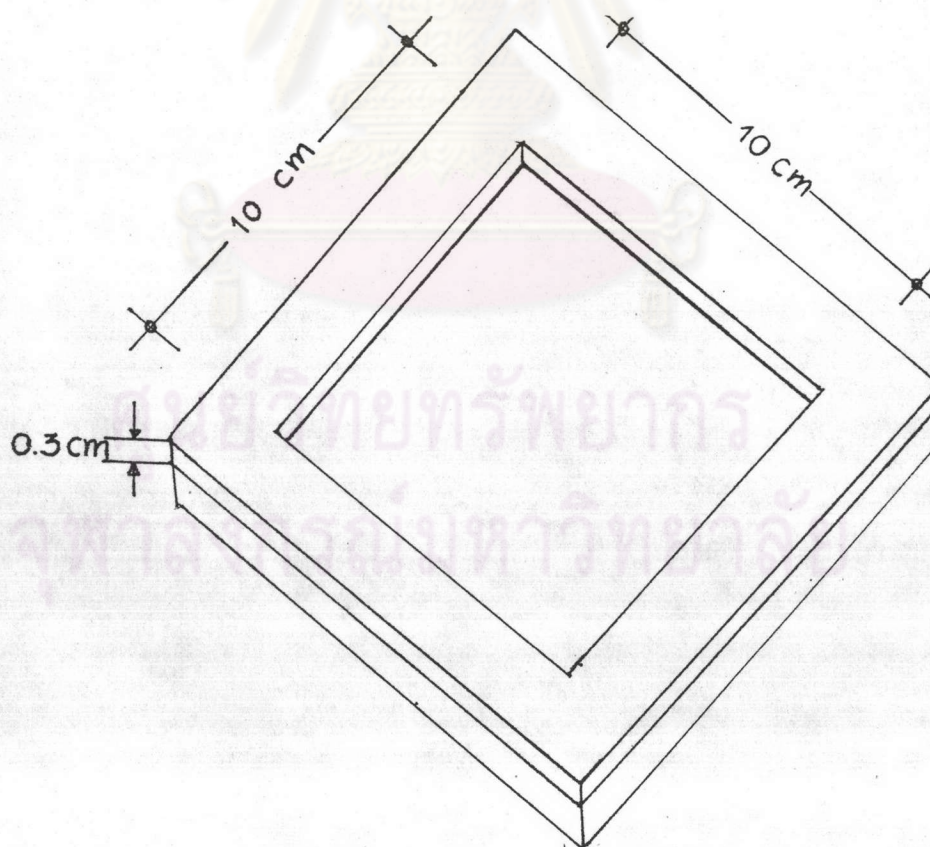
Figure 3.7   A simple mold for casting polymers into films

Table 3.16 Preparation of polymer films

Sample No.	Constituents				Average thickness (cm)
	% PCL	% PVAc	% PVC	% Starch -g-PMA	
F1	100	–	–	–	0.037 ± 0.002
F2	90	10	–	–	0.038 ± 0.002
F3	80	20	–	–	0.035 ± 0.001
F4	70	30	–	–	0.038 ± 0.004
F5	60	40	–	–	0.038 ± 0.003
F6	90	–	10	–	0.036 ± 0.003
F7	80	–	20	–	0.036 ± 0.002
F8	70	–	30	–	0.035 ± 0.003
F9	60	–	40	–	0.034 ± 0.002
F10	–	–	–	100	0.034 ± 0.002
F11	–	30	–	70	0.034 ± 0.002
F12	–	40	–	60	0.035 ± 0.002
F13	–	–	30	70	0.034 ± 0.002
F14	–	–	40	60	0.035 ± 0.002

3.5 Preliminary biodegradation study of polymer films

In this study, the films were inoculated with five fungi as follows;

Penicillium	funiculosum	ATCC No. 3386
Aspergillus	flavus	ATCC No. 3366
Aspergillus	niger	ATCC No. 3390
Gliocladium	virens	ATCC No. 3388
Chaetomium	globosum	ATCC No. 3340

The study followed the ASTM No. G 21 and composed of the following steps.

(1) Preparation of fungal spore

The procedure for preparation of fungal spore is shown in Appendix B.

(2) Specimen Inoculation

A 0.1 ml of fungal spore solution was spreaded on the Petri dishes containing BMS medium. Three pieces of each polymer film samples were placed on each dish. The controlled dishes did not contain polymer films but 5 % glucose was added instead.

(3) Incubation

The inoculated test and controlled specimens were covered and incubated at room temperture and not less than 85 % relative

humidity for 50 days.

(4) Observations for visible effects

Observe the growth of fungi on polymer films every 5 day-range and judge them as follows:

Observed growth on specimens	Rating
None	0
Traces of growth (less than 10 %)	1
Light growth (10 to 30 %)	2
Medium growth (30 to 60 %)	3
Heavy growth (60 % to complete coverage)	4

The observations of fungal growth of the incubated films are shown in Tables 3.17-3.21. The figures of the observed growth rating are shown in Appendix D.

(5) Determination of the molecular weight loss

The gel permeation chromatography was used to measure the molecular weights of the incubated and unincubated films. The molecular weight loss of the incubated films were calculated with respect to that of the unincubated. The percentages of molecular weight loss of some films are shown in Table 3.22.

Table 3.17 The observed growth of Penicillium funiculosum
on specimens

Specimens	Incubation time (day)							
	3	5	10	15	20	25	30	50
F1	1	2	2	3	4	4	4	4
F2	0	1	1	2	2	2	2	3
F3	0	1	1	2	2	2	2	2
F4	0	1	1	1	2	2	2	2
F5	0	0	0	0	0	0	0	0
F6	0	1	1	2	2	3	3	3
F7	0	0	1	1	1	1	1	1
F8	0	0	1	1	1	1	1	1
F9	0	0	1	1	1	1	1	1
F10	1	2	3	3	4	4	4	4
F11	0	1	1	2	2	3	3	3
F12	0	1	1	2	2	3	3	3
F13	0	1	1	1	2	2	2	2
F14	0	0	0	1	1	1	1	1

Table 3.18 The observed growth of _Aspergillus flavus_
on specimens

Specimens	Incubation time (day)							
	3	5	10	15	20	25	30	50
F1	1	2	3	3	4	4	4	4
F2	1	1	2	2	3	3	3	3
F3	1	1	2	2	3	4	4	4
F4	1	1	2	2	3	4	4	4
F5	1	1	1	2	2	2	2	2
F6	0	0	1	1	1	1	1	1
F7	0	0	1	1	1	1	1	1
F8	0	0	1	1	1	1	1	1
F9	0	0	1	1	1	1	1	1
F10	1	2	3	3	4	4	4	4
F11	0	1	1	2	2	2	2	2
F12	0	1	1	2	2	2	2	2
F13	1	1	2	2	3	3	3	3
F14	1	1	2	2	3	3	3	3

Table 3.19   The observed growth of _Aspergillus_ _niger_ on specimens

Specimens	Incubation time (day)							
	3	5	10	15	20	25	30	50
F1	1	1	2	2	2	2	2	2
F2	0	1	1	2	2	2	2	2
F3	0	1	1	2	2	2	2	2
F4	0	1	1	1	2	2	2	2
F5	0	0	1	1	2	2	2	2
F6	1	1	2	2	3	3	3	3
F7	1	1	2	2	3	3	3	3
F8	1	1	2	2	3	3	3	3
F9	1	1	2	2	3	3	3	3
F10	1	2	3	3	4	4	4	4
F11	0	1	1	2	2	2	2	2
F12	0	1	1	2	2	2	2	2
F13	0	0	1	1	1	1	1	1
F14	0	1	1	1	2	2	2	3

Table 3.20 The observed growth of <u>Gliocladium</u> <u>virens</u>

Specimens	Incubation time (day)							
	3	5	10	15	20	25	30	50
F1	1	1	2	2	3	3	3	3
F2	0	0	1	1	2	2	2	2
F3	0	0	1	1	2	2	2	2
F4	0	0	1	1	2	2	2	2
F5	0	0	1	2	2	3	3	3
F6	0	0	1	1	1	1	1	1
F7	0	0	1	1	1	1	1	1
F8	0	0	1	1	1	1	1	1
F9	0	0	1	1	1	1	1	1
F10	1	1	2	3	4	4	4	4
F11	1	1	2	2	3	3	3	3
F12	1	1	2	2	3	3	3	3
F13	0	0	1	1	1	1	1	1
F14	0	0	1	1	1	2	2	2

Table 3.21 The observed growth of Chaetomium globosum

Specimens	Incubation time (day)							
	3	5	10	15	20	25	30	50
F1	1	2	3	3	4	4	4	4
F2	1	2	2	3	4	4	4	4
F3	1	1	2	2	3	3	3	3
F4	1	2	3	3	4	4	4	4
F5	1	1	2	2	3	3	3	3
F6	1	1	2	2	3	3	3	3
F7	1	1	2	2	3	3	3	3
F8	1	1	2	2	3	3	3	3
F9	1	1	2	2	3	3	3	3
F10	1	2	3	3	4	4	4	4
F11	1	2	2	3	3	3	3	3
F12	1	2	3	3	3	3	3	3
F13	1	2	3	3	3	3	3	3
F14	1	2	3	3	3	3	3	3

Table 3.22 Percentage molecular weight lose

Fungi	Specimens								
	F1	F2	F3	F4	F5	F6	F7	F8	F9
Penicillium funiculosum	97.11	8.20	9.90	8.85	0.57	30.37	6.91	6.41	9.79
Aspergillus flavus	94.85	3.62	6.00	2.14	9.17	8.73	7.22	5.35	15.08
Gliocladium virens	33.00	14.43	17.73	12.89	25.44	18.35	20.32	4.76	12.35
Chaetomium globosum	29.88	9.25	12.48	21.07	28.74	7.23	8.46	15.77	15.08
Aspergillus niger	10.76	16.39	8.93	6.35	9.18	15.38	9.43	4.10	9.08

Tables 3.17-3.21 showed that the synthetic polymers, PCL and Starch-g-PMA films, strongly supported the growth fungi. The films were found to be covered by the visible fungal spore at rating of 3 (medium growth) within 15 days of fungal exposure or incubation. The two best fungi which could grow on PCL and Starch-g-PMA films as observed were *Aspergillus flavus* and *Chaetomium globosum.*

The polymer blends of PCL/ PVAc and PCL/ Starch-g-PMA films could also support the fungal growth as well or better than the films of PCL/ PVC and PCL/ Starch-g-PMA. For the case of *Aspergillus niger*, the fact that it could grow on PCL/PVC films better than on PCL/ PVAc, was the exception.

Table 3.22 showed that all polymer blends of PCL could support the growth of fungi. However, the molecular weight loss of incubated polymer blend films had no relationship with the weight ratio of PCL in the polymer blends.