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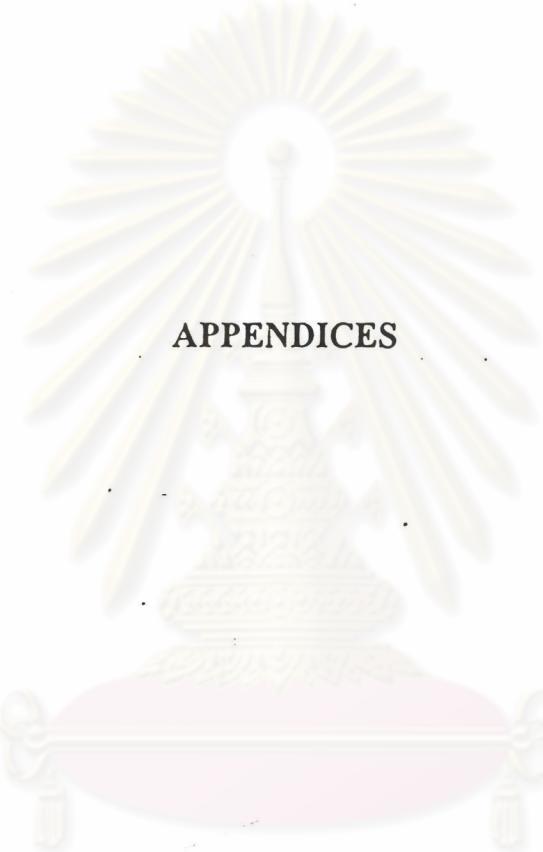
APPENDICES

APPENDIX A

A.1 Calibration Curve for Calculation of Degree of Substitution

Table A.1 The absorbance at λ_{max} 590 nm for plotting calibration curve.

Propylene glycol concentration (μg/25 ml)	Absorbance
25	0.3454
50	0.5259
75	0.7387

*Blank = Native Tapioca Starch
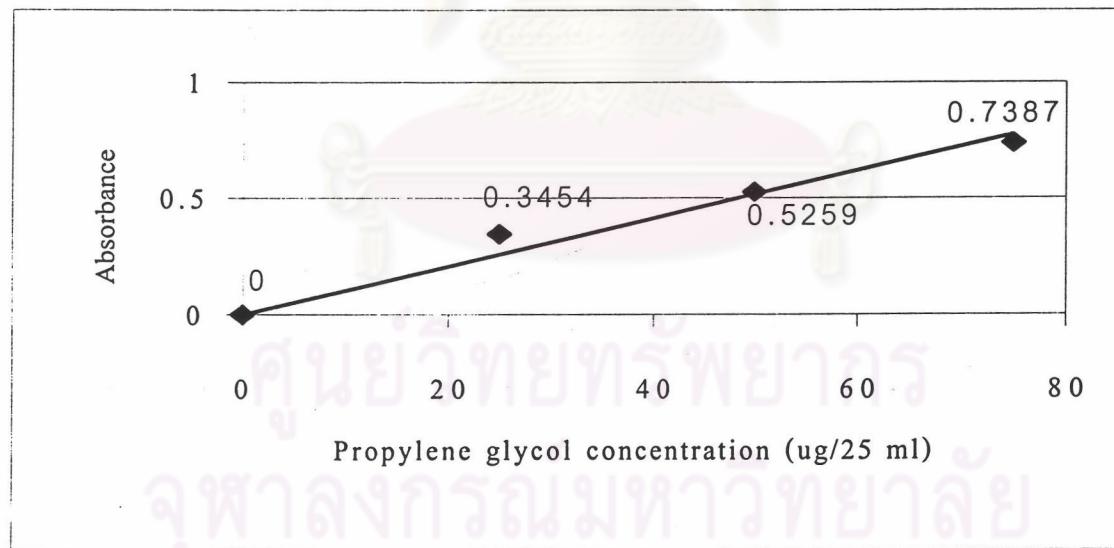
**Figure A.1** The plot of propylene glycol concentration versus absorbance at λ_{max} 590 nm.

From Fig. A.1, the calibration curve is a linear graph. So the equation for calculating concentration of propylene glycol from absorbance is the equation A.1.

$$y = 0.0104x + c \qquad\qquad (A.1)$$

Where y = The absorbance at λ_{max} 590 nm

x = The concentration of propylene glycol (μg/25 ml)

c = 0

APPENDIX B

B. Calculation of Degree of Substitution

From the calculation curve of concentration of propylene glycol versus absorbance, the concentration of propylene glycol produced from hydroxypropyl group is known. The concentration of propylene glycol was then converted to hydroxypropyl group equivalent from which DS was calculated according to the equation B.1.

$$DS = \frac{162W}{100M-(M-1)W} \qquad (B.1)$$

Where W = The percentage by weight of substituent.

M = The molecular weight of monomeric units of the polymeric substitutent.

For propylene oxide treated starch: W is the hydroxypropyl group equivalent in 100 mg of dry starch; M is the molecular weight of propylene oxide. So the equation B.1 is changed to the equation B.2.

$$DS = \frac{162W}{5800-57W} \qquad (B.2)$$

APPENDIX C

C. Effect of Sodium Sulfate on Degree of Substitution

Table C.1 Effect of sodium sulfate on degree of substitution

Batch	Na$_2$SO$_4$ (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	8	0.1005	1	0.2174	0.0458	
			2	0.2478	0.0524	
			3	0.2056	0.0433	
2	8	0.1003	1	0.2301	0.0486	
			2	0.2078	0.0439	0.0475 ± 0.0031
			3	0.2278	0.0482	
3	8	0.0993	1	0.2357	0.0504	
			2	0.2140	0.0457	
			3	0.2318	0.0495	
1	12	0.0992	1	0.2416	0.0517	
			2	0.2850	0.0612	
			3	0.2428	0.0520	
2	12	0.1004	1	0.2660	0.0563	
			2	0.2550	0.0540	0.0549 ± 0.0034
			3	0.2414	0.0510	
3	12	0.1000	1	0.2531	0.0538	
			2	0.2750	0.0585	
			3	0.2597	0.0552	

Batch	Na$_2$SO$_4$ (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	15	0.0992	1	0.2807	0.0601	
			2	0.3297	0.0710	
			3	0.3246	0.0699	
2	15	0.0993	1	0.3143	0.0676	
			2	0.2822	0.0605	0.0664 ± 0.0055
			3	0.3212	0.0691	
3	15	0.0997	1	0.3219	0.0689	
			2	0.3391	0.0727	
			3	0.2701	0.0576	

APPENDIX D

D. Effect of the Sodium Hydroxide on Degree of Substitution

Table D.1 Effect of sodium hydroxide on degree of substitution

Batch	NaOH (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	0.5	0.1046	1	0.1768	0.0357	
			2	0.1832	0.0370	
			3	0.1681	0.0339	
2	0.5	0.1012	1	0.1517	0.0316	
			2	0.1066	0.0221	0.0308 ± 0.0067
			3	0.1957	0.0409	
3	0.5	0.0998	1	0.1345	0.0284	
			2	0.1133	0.0239	
			3	0.1121	0.0236	
1	1.0	0.0992	1	0.2807	0.0602	
			2	0.3297	0.0710	
			3	0.03246	0.0699	
2	1.0	0.0993	1	0.3143	0.0676	
			2	0.2822	0.0605	0.0664 ± 0.0055
			3	0.3212	0.0691	
3	1.0	0.0997	1	0.3219	0.0689	
			2	0.3391	0.0727	
			3	0.2701	0.0576	

Batch	NaOH (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	1.5	0.0999	1	0.3674	0.0788	
			2	0.3480	0.0745	
			3	0.3499	0.0749	
2	1.5	0.0991	1	0.3204	0.0690	
			2	0.3364	0.0726	0.0752 ± 0.0038
			3	0.3723	0.0805	
3	1.5	0.0999	1	0.3480	0.0745	
			2	0.3383	0.0724	
			3	0.3713	0.0797	

APPENDIX E

E. Effect of Propylene Oxide Concentration on Degree of Substitution

Table E.1 Effect of propylene oxide concentration on degree of substitution

Batch	Propylene oxide (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	5	0.0987	1	0.2974	0.0642	
			2	0.2640	0.0569	
			3	0.2454	0.0548	
2	5	0.0997	1	0.2675	0.0571	0.0548 ± 0.0049
			2	0.2456	0.0523	
			3	0.2370	0.0504	
3	5	0.0990	1	0.2723	0.0585	
			2	0.2290	0.0491	
			3	0.2342	0.0502	
1	7	0.0999	1	0.3674	0.0788	
			2	0.3480	0.0745	
			3	0.3499	0.0749	
2	7	0.0991	1	0.3204	0.0690	0.0752 ± 0.0038
			2	0.3364	0.0726	
			3	0.3723	0.0805	
3	7	0.0999	1	0.3480	0.0745	
			2	0.3383	0.0724	
			3	0.3713	0.0797	

Batch	Propylene oxide (% dry starch)	Weight (g)	No.	Absorbance	DS	Average DS
1	9	0.1006	1	0.4550	0.0975	
			2	0.4924	0.1058	
			3	0.4638	0.0995	
2	9	0.1009	1	0.4365	0.0931	
			2	0.4729	0.1012	0.1013 ± 0.0044
			3	0.4705	0.1007	
3	9	0.1004	1	0.4986	0.1075	
			2	0.4810	0.1035	
			3	0.4798	0.1033	

APPENDIX F

F. Effect of Reaction Time on Degree of Substitution

Table F.1 Effect of reaction time on degree of substitution

Batch	Reaction time (hours)	Weight (g)	No.	Absorbance	DS	Average DS
1	6	0.1006	1	0.2506	0.0529	
			2	0.2414	0.0509	
			3	0.2726	0.0576	
2	6	0.0999	1	0.2495	0.0530	
			2	0.2076	0.0440	0.0493 ± 0.0048
			3	0.2314	0.0491	
3	6	0.0998	1	0.2157	0.0457	
			2	0.2008	0.0425	
			3	0.2221	0.0477	
1	12	0.0998	1	0.4271	0.0910	
			2	0.4421	0.0894	
			3	0.4600	0.0926	
2	12	0.1002	1	0.4598	0.0992	
			2	0.4332	0.0955	0.0927 ± 0.0037
			3	0.4315	0.0929	
3	12	0.0997	1	0.4303	0.0863	
			2	0.4570	0.0938	
			3	0.4559	0.0936	

Batch	Reaction time (hours)	Weight (g)	No.	Absorbance	DS	Average DS
1	18	0.1000	1	0.4728	0.1021	
			2	0.4759	0.1028	
			3	0.5021	0.1087	
2	18	0.1004	1	0.4759	0.1024	
			2	0.4486	0.0963	0.1023 ± 0.0037
			3	0.4791	0.1031	
3	18	0.0997	1	0.4761	0.1000	
			2	0.5047	0.1062	
			3	0.4723	0.0991	
1	20	0.1012	1	0.4610	0.0983	
			2	0.4723	0.1008	
			3	0.4695	0.1001	
2	20	0.0999	1	0.4781	0.1033	
			2	0.4832	0.1044	0.1018 ± 0.0019
			3	0.4684	0.1011	
3	20	0.1001	1	0.4711	0.1016	
			2	0.4801	0.1036	
			3	0.4765	0.1028	

Batch	Reaction time (hours)	Weight (g)	No.	Absorbance	DS	Average DS
1	24	0.1006	1	0.4550	0.0975	
			2	0.4924	0.1058	
			3	0.4638	0.0995	
2	24	0.1009	1	0.4365	0.0931	
			2	0.4729	0.1012	0.1013 ± 0.0044
			3	0.4705	0.1007	
3	24	0.1004	1	0.4986	0.1075	
			2	0.4810	0.1035	
			3	0.4798	0.1033	

APPENDIX G

G. Effect of Temperature on Degree of Substitution

Table G.1 Effect of temperature on degree of substitution

Batch	Temperature (^{o}C)	Weight (g)	No.	Absorbance	DS	Average DS
1	30	0.0999	1	0.1934	0.0409	
			2	0.1846	0.0391	
			3	0.1900	0.0402	
2	30	0.0998	1	0.1847	0.0391	0.0408 ± 0.0016
			2	0.2051	0.0435	
			3	0.1911	0.0405	
3	30	0.1050	1	0.1991	0.0401	
			2	0.2005	0.0404	
			3	0.2151	0.0434	
1	40	0.0998	1	0.4271	0.0910	
			2	0.4421	0.0894	
			3	0.4600	0.0926	
2	40	0.1002	1	0.4598	0.0992	0.0927 ± 0.0037
			2	0.4332	0.0955	
			3	0.4315	0.0929	
3	40	0.0997	1	0.4303	0.0863	
			2	0.4570	0.0938	
			3	0.4559	0.0936	

Batch	Temperature (°C)	Weight (g)	No.	Absorbance	DS	Average DS
1	45	0.1000	1	0.4612	0.0949	
			2	0.4468	0.0930	
			3	0.4742	0.0998	
2	45	0.0996	1	0.4130	0.0892	
			2	0.4410	0.0954	0.0948 ± 0.0029
			3	0.4295	0.0928	
3	45	0.1014	1	0.4513	0.0959	
			2	0.4487	0.0954	
			3	0.4554	0.0968	

APPENDIX H

H. Effect of the Reaction Medium on Degree of Substitution

Table H.1 Effect of ethanol concentration on degree of substitution

Batch	Ethanol : Water (°C)	Weight (g)	No.	Absorbance	DS	Average DS
1	30:70	0.0999	1	0.2451	0.0521	
			2	0.2725	0.0586	
			3	0.2461	0.0523	
2	30:70	0.1004	1	0.2313	0.0489	0.0522 ± 0.0031
			2	0.2412	0.0509	
			3	0.2550	0.0539	
3	30:70	0.1019	1	0.2432	0.0507	
			2	0.2590	0.0539	
			3	0.2330	0.0485	
1	70:30	0.1000	1	0.4700	0.1015	
			2	0.4421	0.0953	
			3	0.4583	0.0989	
2	70:30	0.0998	1	0.4702	0.1018	0.1003 ± 0.0029
			2	0.4694	0.1016	
			3	0.4508	0.0974	
3	70:30	0.1001	1	0.4593	0.0991	
			2	0.4777	0.1032	
			3	0.4815	0.1041	

APPENDIX I

I. High Degree of substitution of Hydroxypropylated tapioca starch

Table I.1 Degree of substitution of high hydroxypropylated tapioca starch

Batch	Weight (g)	No.	Absorbance	DS	Average DS
1	0.1016	1	0.9678	0.2038	
		2	0.9770	0.2059	
		3	0.9654	0.2033	
2	0.1012	1	0.9532	0.2101	
		2	0.9643	0.2127	0.2057 ± 0.0062
		3	0.9792	0.2162	
3	0.0998	1	0.9320	0.1987	
		2	0.9359	0.1976	
		3	0.9586	0.2028	

APPENDIX J

J. Calculation of Degree of Substitution from ^{1}H-NMR Spectra

With ^{1}H-NMR spectroscopy, the DS was calculated using the integrated intensities of the signals from methyl protons in the hydroxypropyl groups and the integrated intensities of the signals from the equatorial protons of the anhydroglucose unit of starch. The DS can be calculated directly from the equation J.1.

$$DS = \frac{I_{HP}}{3I_{AGU}} \qquad (J.1)$$

In which I_{HP} = The area of the NMR peak from the hydroxypropyl group of the starch.

I_{AGU} = The area of the NMR peak from the equatorial proton of the anhydroglucose unit of starch. This peak area is multiplied by 3 due to the fact that three reactive sites are present at one anhydroglucose unit.

APPENDIX K

K. Characteristic of Hydroxypropylated tapioca starch

Table K.1 Characteristic of hydroxypropylated tapioca starch

Condition	DS	Gel. Temp. (°C)	Peak Viscosity (BU)	Moisture	Whiteness
Native Starch	-	69.5	625	13.98	93.6
Na_2SO_4 8%, NaOH 1.0%, PO 7%, t24hrs, T40°C	0.0485	65.0	610	15.73	91.1
Na_2SO_4 12%, NaOH 1.0%, P.O 7%, t24hrs, T40°C	0.0558	60.5	730	17.34	91.4
Na_2SO_4 15%, NaOH 1.0%, PO 7%, t24hrs, T40°C	0.0670	60.5	710	14.46	93.0
Na_2SO_4 15%, NaOH 0.5%, PO 7%, t24hrs, T40°C	0.0355	64.3	570	14.48	92.1
Na_2SO_4 15%, NaOH 1.0%, PO 7%, t24hrs, T40°C	0.0670	60.5	710	14.46	93.0
Na_2SO_4 15%, NaOH 1.5%, PO 7%, t24hrs, T40°C	0.0761	60.5	715	16.25 -	94.0
Na_2SO_4 15%, NaOH 1.5%, PO 5%, t24hrs, T40°C	0.0586	62.0	555	13.46	92.1
Na_2SO_4 15%, NaOH 1.5%, PO 7%, t24hrs, T40°C	0.0761	60.5	715	16.25	94.0
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t24hrs, T40°C	0.1048	54.5	730	12.87	93.2
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t6hrs, T40°C	0.0538	65.0	645	14.39	91.1
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t12hrs, T40°C	0.0959	59.0	720	14.93	90.6
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t18hrs, T40°C	0.1018	60.5	670	16.29	91.7
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t24hrs, T40°C	0.1048	54.5	730	12.87	93.2
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t12hrs, T30°C	0.0413	62.8	750	14.50	91.0
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t12hrs, T40°C	0.0959	59.0	720	14.93	90.6
Na_2SO_4 15%, NaOH 1.5%, PO 9%, t12hrs, T45°C	0.0959	59.0	710	15.20	93.2
EtOH 70%, NAOH 2.0%, PO 15%, t24hr, T45°C	0.2130	56.0	650	13.72	93.5

VITA

Miss Pimorn Buachamras was born on October 31, 1977 in Bangkok. She graduated with a Bachelor Degree of Science (Chemistry) form King Mongkut's University of Technology Thonburi in 1999. In 1999, she was accepted as a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University.