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APPENDICES

Appendix A Determination of Degree of Purification of Purified Biopolymer by Fourier Transform Infrared Spectroscopy (FT-IR)

This method was used to analyse the functional groups of the purified biopolymers in order to find out the hydroxyl and amide groups, which are the major functional groups in determining degree of deacetylation. FT-IR result of purified biopolymer is shown in Figure A1.

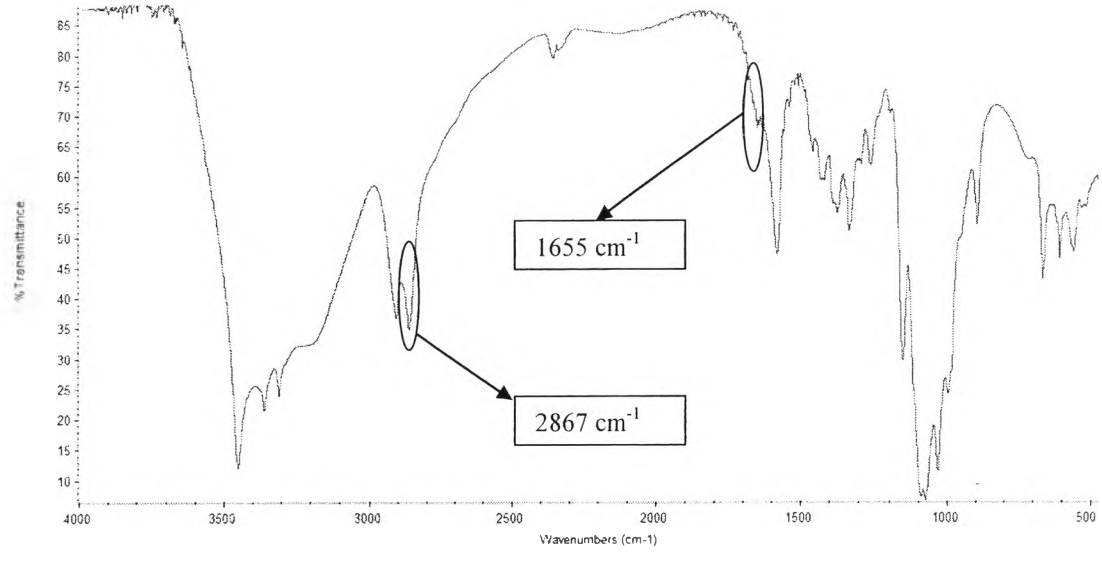

Figure A1 IR spectrum of purified biopolymer used to find degree of purification.

The degree of purified biopolymer can be determined by using the relation of the absorbance ratio of the amide band I at 1655 cm^{-1} to the CH stretching band at 2867 cm^{-1}(Miya *et al.*, 1980).The relation of the ratio of the absorbance against the degree of deacetylation is shown in Figure A2.The absorbance ratio can be calculated by this equation A1-A3,

All values of parameters in these equations are shown in Table A1

Table A1. All values of parameters in equations A1, A2 and A3 and the average of degree of deacetylation of purified biopolymer

No.	Relative intensity		A_{2867}	Relative intensity		A_{1655}	Absorbance ratio	%DD
	AB	AC		DE	DF			
1	57.72	77.54	0.128	74.45	76.12	0.009	0.075	96.99
2	59.85	79.23	0.122	73.23	74.83	0.009	0.077	96.39
3	58.76	81.34	0.141	74.44	76.15	0.009	0.070	97.03
	Average							96.80

Example of No.1:

$$A_{C-H\ stretching,2867\ cm^{-1}} = \log_{10}\left(\frac{AC}{AB}\right) \quad \textbf{(Equation A1)}$$

$$A_{C-H\ stretching,2867\ cm^{-1}} = \log_{10}\left(\frac{77.54}{57.72}\right)$$

$$A_{amide,1655\ cm^{-1}} = \log_{10}\left(\frac{DF}{DE}\right) \quad \textbf{(Equation A2)}$$

$$A_{amide,1655\ cm^{-1}} = \log_{10}\left(\frac{76.12}{74.45}\right)$$

$$Absorbance\ ratio = \frac{A_{amide,1655\ cm^{-1}}}{A_{C-H\ stretching,2867\ cm^{-1}}} \quad \textbf{(Equation A3)}$$

$$= \frac{0.009}{0.128}$$

$$= 0.075$$

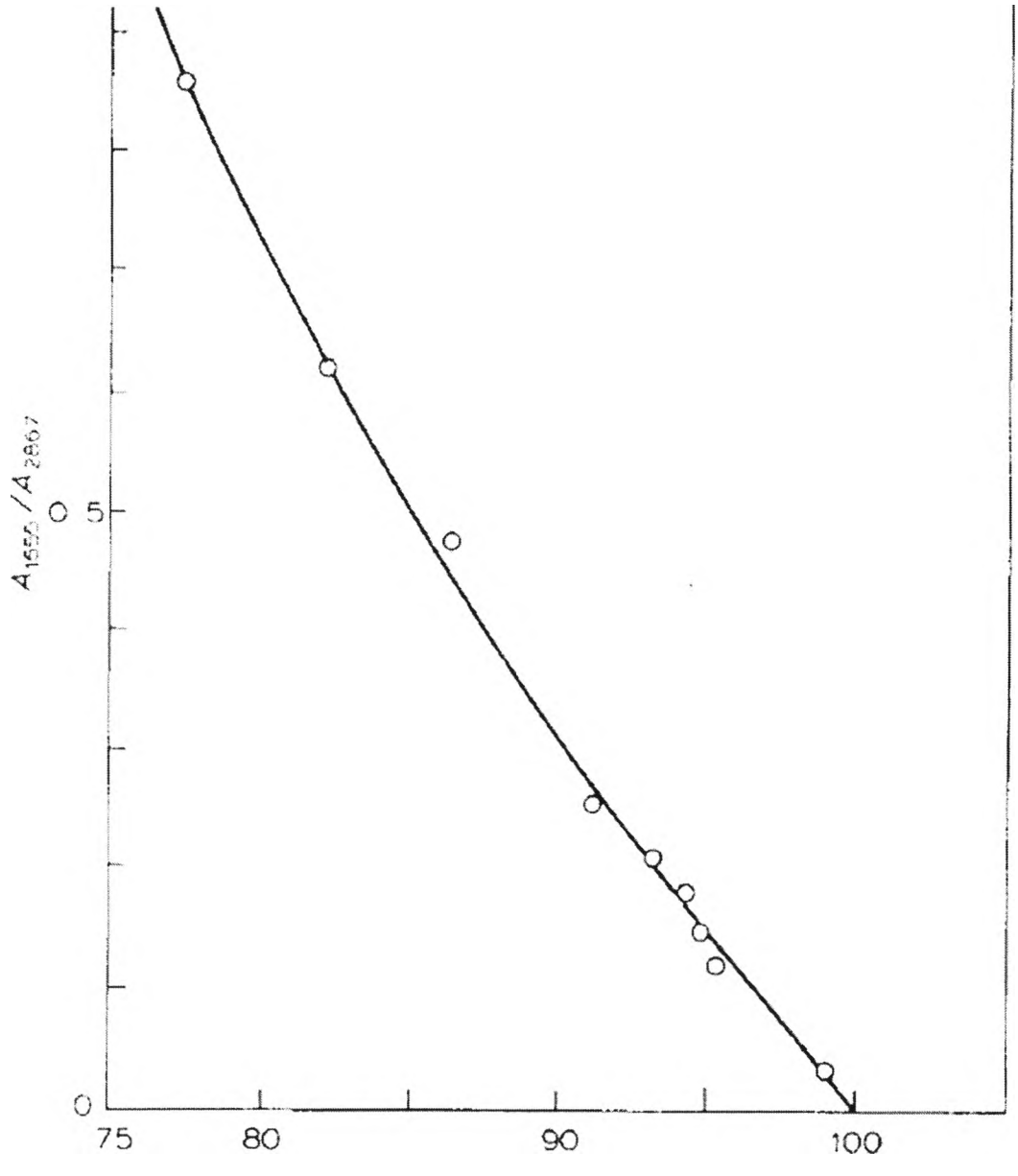

Figure A2 Relation of the ratio of the absorbance of the band at 1655cm to that of the band at 2867cm 1 (A_{1655}/A_{2867}) against the degree of deacetylation.

From Figure A2, the absorbance ratio of the amide band I at 1655 cm^{-1} to the CH stretching band at 2867 cm^{-1} can be determined the degree of purification. From Table A1, The average degree of deacetylation is 96.80 % with 0.358 % standard deviation.

Appendix B Calculation of Degree of Deacetylation from Titration Method

This method used titration curve of 0.1 M NaOH and 0.05 g purified biopolymer dissolved in 0.1 M HCl. The titration curve is shown in Figure B1.

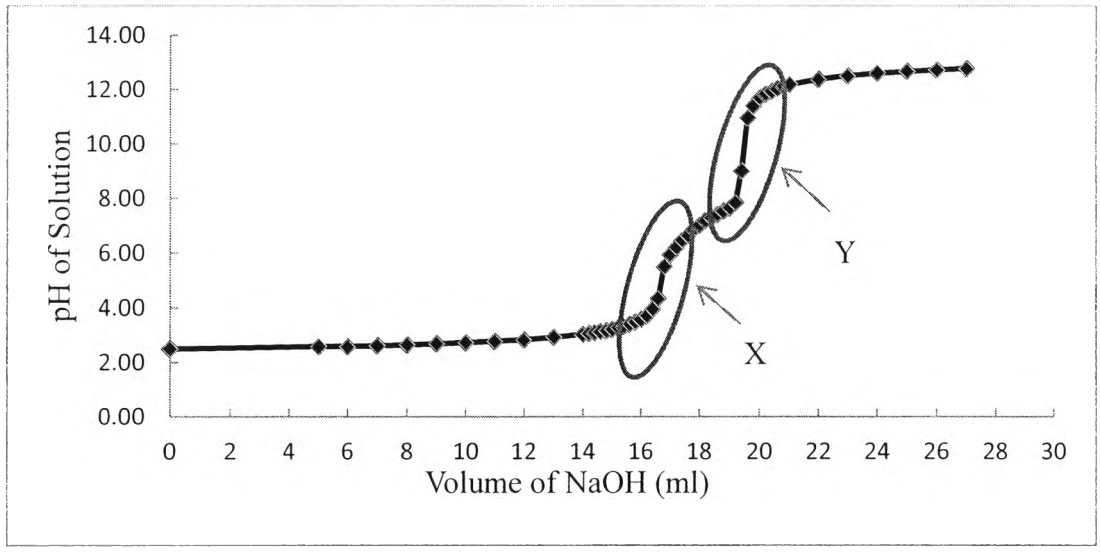

Figure B1 Titration curve for determining degree of deacetylation of purified biopolymer.

A titration curve shows that there are two equivalent points those are related to excess of HCl and protonated amino groups. The first equivalent point is due to neutralization of the excess HCl with NaOH solution and the second equivalent point is due to displacement of HCl bound to the primary amino groups of biopolymer. The correct position of two equivalent points can be determined by linear extrapolation of the adjacent portions of the titration curve. The degree of deacetylation is calculated from the two equivalent points (Avadi *et al.*, 2004).

Degree of deacetylation (DD) observed from equation B1:

$$\%DD = 16.1(Y - X)\frac{f}{W} \qquad \textbf{(Equation B1)}$$

Y is slope of point Y in Figure B1

X is slope of point X in Figure B1

f is concentration of NaOH (molar)

W is the initial purified biopolymer weight (grams)

From this experiment:

$$DD = 16.1(19.5 - 16.505)\frac{0.1}{0.0502}$$

$$DD = 96.05\ \%$$

This calculation also applied to other batches of the purified biopolymer and the results are shown in table B1. The average degree of deacetylation is 96.05 % with 0.066 % standard deviation

Table B1. All values of parameters in equations B1 and the average of degree of deacetylation of purified biopolymer

No.	NaOH consumed at 1st equivalent point (mL)	NaOH consumed at 2nd equivalent point (mL)	the initial purified biopolymer(g)	the molarity of the NaOH (N)	%DD
1	16.505	19.5	0.0502	0.1	96.05
2	15.31488	18.3	0.0500	0.1	96.12
3	15.91303	18.9	0.0501	0.1	95.99
Average					96.05

Appendix C Calculation of Chemical used

Example of chemical used, the relation between mole of reactant and weight of reactant :

Table C1 Effect of coupling agents on purified biopolymer (PB)/arginine (AR)/coupling agents (CA) at mole ratio of 1:1:0, 1:1:1, 1:1:2 and 1:1:3, respectively at reaction time 48 h (3.1)

Mole ratio of PB/AR/CA	Weight of chemical used (g)				Reaction time (h)
	PB	AR	EDC.HCl	Sulfo-NHS	
1:1:0	0.2534	0.2712	-	-	48
1:1:1	0.2518	0.2743	0.3027	0.3391	48
1:1:2	0.2540	0.2775	0.5950	0.6744	48
1:1:3	0.2532	0.2719	0.8932	1.0102	48

For mole ratio of biopolymer (PB)/arginine (AR)/coupling agents (CA) was 1:1:1

Biopolymer : $mole\ of\ biopolymer = \frac{weight\ of\ biopolymer\ (g)}{molecular\ weight\ of\ biopolymer}$ **(Equation B1)**

$$mole\ of\ biopolymer = \frac{0.25\ g}{161\ g/mole}$$

$$mole\ of\ biopolymer = 0.0016\ mole$$

The mole ratio of biopolymer/arginine was 1:1

Arginine : $mole\ of\ arginine = \frac{weight\ of\ arginine\ (g)}{molecular\ weight\ of\ arginine}$

$$0.0016 = \frac{weight\ of\ arginine\ (g)}{174.2\ g/mole}$$

$$mole\ of\ arginine = 0.278\ g$$

The mole ratio of biopolymer/EDC.HCl was 1:1

EDC.HCl : $mole\ of\ EDC.HCl = \frac{weight\ of EDC.HCl\ (g)}{molecular\ weight\ of\ EDC.HCl}$

$$0.0016 = \frac{weight\ of\ EDC.HCl\ (g)}{191.7\ g/mole}$$

$$mole\ of\ EDC.HCl = 0.307\ g$$

The mole ratio of biopolymer/sulfo-NHS was 1:1

EDC.HCl : $mole\ of\ sulfo-NHS = \frac{weight\ of\ sulfo-NHS\ (g)}{molecular\ weight\ of\ sulfo-NHS}$

$$0.0016 = \frac{weight\ of\ sulfo-NHS\ \ (g)}{217.13\ g/mole}$$

$$mole\ of\ sulfo-NHS = 0.347\ \ g$$

Appendix D Calculation of Degree of Substitution of Biopolymer-Arginine from CHN Elemental Analysis Method

D1 Effect of coupling agents to biopolymer (4.2.1)

The products were analyzed by CHN Analyzer for percent carbon (% C), percent hydrogen (% H), and percent nitrogen (% N) to calculate degree of substitution (%DS) through ratio C/N compared with theory as shown in Table D1. The degree of substitution (%DS) was defined as an extent to which arginine could chemically react with NH_2 of glucosamine units in biopolymer.

Table D1 Degree of substitution of arginine in biopolymer-arginine at various ratios of coupling agents to biopolymer while biopolymer/arginine were kept constant at 1:1

PB:AR:CA	Reaction time (h)	%C	%N	C/N	%DS
biopolymer	-	49.33	7.88	6.26	-
1:1:1	48	41.71	8.69	4.80	3.00
1:1:2	48	40.68	8.57	4.75	3.20
1:1:3	48	42.60	7.63	5.58	-

From calculation of %DS, lower ratio C/N gave higher %DS. The ratio of purified biopolymer (PB) to arginine (AR) to coupling agents (CA) of 1:1:2 at reaction time 48 h gave the highest degree of substitution (3.2%) due to give the lowest ratio C/N. whereas at ratio biopolymer/arginine/coupling agents was 1:1:3, degree of substitution were very low and could not calculated from this method because of ratio C/N was out of range from theory. Probably the CHN analyzer was not an appropriate method for this kind of product. Therefore, an alternative method was HPLC due to used only permeate from stirred cell that used small amounts of products.

D2 Effect of reaction time (4.2.2)

The degrees of substitution from CHN Analysis are shown in Table D2.

Table D2 Percent of C, H and N and degree of substitution of biopolymer-arginine at various reaction times

PB/AR/CA	Reaction time (h)	%C	%N	C/N	%DS
biopolymer	-	49.33	7.88	6.26	-
1:1:1	24	41.83	7.53	5.56	-
1:1:1	48	41.71	8.69	4.80	3.00
1:1:1	72	44.05	9.29	4.74	3.20

For CHN method, the experimental result was shown in Table 4.3. The ratio of biopolymer (PB) to arginine (AR) to coupling agents (CA) of 1:1:1 at reaction time 72 h give the highest degree of substitution (3.20%) whereas at reaction time 24 h, degree of substitution was very low and could not calculated from this method.

D3 Effect of arginine to biopolymer (4.2.3)

The results from CHN analyzer indicating degree of substitution are shown in Table D3.

Table D3 Degree of substitution at various ratio of arginine to biopolymer and reaction time 72 h

PB:AR:CA	Reaction time (h)	%C	%N	C/N	%DS
biopolymer	-	49.33	7.88	6.26	-
1:1:1	72	44.05	9.29	4.74	3.20
1:2:1	72	40.72	10.73	3.79	14.50
1:3:1	72	42.61	11.11	3.84	13.70

Arginine in ratio of biopolymer (PB) to arginine (AR) to coupling agents (CA) of 1:2:1 at reaction time 72 h gave the highest degree of substitution (14.50%).

To calculated degree of substitution, ratio C/N was compared with Table D4 to evaluated degree of substitution.

Table D4 Calculation of Degree of Substitution from CHN Elemental Analysis Method

% DS	mole of group			MW of PB	weight of nitrogen in group per mole			Total weight of nitrogen	weight of carbon in group per mole			Total weight of carbon	%N	%C	C/N ratio
	A	B	C		A	B	C		A	B	C				
0	96	4	0	16286	1344	56	0	1400	6912	384	0	7296	8.59634	44.79921	5.211429
1.041667	95	4	1	16442	1330	56	70	1456	6840	384	144	7368	8.85537	44.81207	5.06044
2.083333	94	4	2	16598	1316	56	140	1512	6768	384	288	7440	9.109531	44.82468	4.920635
3.125	93	4	3	16754	1302	56	210	1568	6696	384	432	7512	9.358959	44.83705	4.790816
4.166667	92	4	4	16910	1288	56	280	1624	6624	384	576	7584	9.603785	44.8492	4.669951
5.208333	91	4	5	17066	1274	56	350	1680	6552	384	720	7656	9.844135	44.86113	4.557143
6.25	90	4	6	17222	1260	56	420	1736	6480	384	864	7728	10.08013	44.87284	4.451613
7.291667	89	4	7	17378	1246	56	490	1792	6408	384	1008	7800	10.31189	44.88434	4.352679
8.333333	88	4	8	17534	1232	56	560	1848	6336	384	1152	7872	10.53952	44.89563	4.25974
9.375	87	4	9	17690	1218	56	630	1904	6264	384	1296	7944	10.76314	44.90673	4.172269
10.41667	86	4	10	17846	1204	56	700	1960	6192	384	1440	8016	10.98285	44.91763	4.089796
11.45833	85	4	11	18002	1190	56	770	2016	6120	384	1584	8088	11.19876	44.92834	4.011905
12.5	84	4	12	18158	1176	56	840	2072	6048	384	1728	8160	11.41095	44.93887	3.938224
13.54167	83	4	13	18314	1162	56	910	2128	5976	384	1872	8232	11.61953	44.94922	3.868421
14.58333	82	4	14	18470	1148	56	980	2184	5904	384	2016	8304	11.82458	44.95939	3.802198
15.625	81	4	15	18626	1134	56	1050	2240	5832	384	2160	8376	12.0262	44.9694	3.739286
16.66667	80	4	16	18782	1120	56	1120	2296	5760	384	2304	8448	12.22447	44.97924	3.679443
17.70833	79	4	17	18938	1106	56	1190	2352	5688	384	2448	8520	12.41947	44.98891	3.622449
18.75	78	4	18	19094	1092	56	1260	2408	5616	384	2592	8592	12.61129	44.99843	3.568106
19.79167	77	4	19	19250	1078	56	1330	2464	5544	384	2736	8664	12.8	45.00779	3.516234

Table D4 Calculation of Degree of Substitution from CHN Elemental Analysis Method (Cont'd)

% DS	mole of group			MW of PB	weight of nitrogen in group per mole			Total weight of nitrogen	weight of carbon in group per mole			Total weight of carbon	%N	%C	C/N ratio
	A	B	C		A	B	C		A	B	C				
20.83333	76	4	20	19406	1064	56	1400	2520	5472	384	2880	8736	12.98567	45.01701	3.466667
21.875	75	4	21	19562	1050	56	1470	2576	5400	384	3024	8808	13.16839	45.02607	3.419255
22.91667	74	4	22	19718	1036	56	1540	2632	5328	384	3168	8880	13.34821	45.03499	3.37386
23.95833	73	4	23	19874	1022	56	1610	2688	5256	384	3312	8952	13.52521	45.04378	3.330357
25	72	4	24	20030	1008	56	1680	2744	5184	384	3456	9024	13.69945	45.05242	3.28863
26.04167	71	4	25	20186	994	56	1750	2800	5112	384	3600	9096	13.871	45.06093	3.248571
27.08333	70	4	26	20342	980	56	1820	2856	5040	384	3744	9168	14.03992	45.06931	3.210084
28.125	69	4	27	20498	966	56	1890	2912	4968	384	3888	9240	14.20626	45.07757	3.173077
29.16667	68	4	28	20654	952	56	1960	2968	4896	384	4032	9312	14.3701	45.0857	3.137466
30.20833	67	4	29	20810	938	56	2030	3024	4824	384	4176	9384	14.53148	45.0937	3.103175
31.25	66	4	30	20966	924	56	2100	3080	4752	384	4320	9456	14.69045	45.10159	3.07013
32.29167	65	4	31	21122	910	56	2170	3136	4680	384	4464	9528	14.84708	45.10936	3.038265
33.33333	64	4	32	21278	896	56	2240	3192	4608	384	4608	9600	15.00141	45.11702	3.007519
34.375	63	4	33	21434	882	56	2310	3248	4536	384	4752	9672	15.15349	45.12457	2.977833
35.41667	62	4	34	21590	868	56	2380	3304	4464	384	4896	9744	15.30338	45.13201	2.949153
36.45833	61	4	35	21746	854	56	2450	3360	4392	384	5040	9816	15.45112	45.13934	2.921429
37.5	60	4	36	21902	840	56	2520	3416	4320	384	5184	9888	15.59675	45.14656	2.894614
38.54167	59	4	37	22058	826	56	2590	3472	4248	384	5328	9960	15.74032	45.15369	2.868664
39.58333	58	4	38	22214	812	56	2660	3528	4176	384	5472	10032	15.88188	45.16071	2.843537
40.625	57	4	39	22370	798	56	2730	3584	4104	384	5616	10104	16.02146	45.16764	2.819196

Table D4 Calculation of Degree of Substitution from CHN Elemental Analysis Method (Cont'd)

% DS	mole of group			MW of PB	weight of nitrogen in group per mole			Total weight of nitrogen	weight of carhon in group per mole			Total weight of carbon	%N	%C	C/N ratio
	A	B	C		A	B	C		A	B	C				
41.66667	56	4	40	22526	784	56	2800	3640	4032	384	5760	10176	16.15911	45.17447	2.795604
42.70833	55	4	41	22682	770	56	2870	3696	3960	384	5904	10248	16.29486	45.1812	2.772727
43.75	54	4	42	22838	756	56	2940	3752	3888	384	6048	10320	16.42876	45.18784	2.750533
44.79167	53	4	43	22994	742	56	3010	3808	3816	384	6192	10392	16.56084	45.1944	2.728992
45.83333	52	4	44	23150	728	56	3080	3864	3744	384	6336	10464	16.69114	45.20086	2.708075
46.875	51	4	45	23306	714	56	3150	3920	3672	384	6480	10536	16.8197	45.20724	2.687755
47.91667	50	4	46	23462	700	56	3220	3976	3600	384	6624	10608	16.94655	45.21354	2.668008
48.95833	49	4	47	23618	686	56	3290	4032	3528	384	6768	10680	17.07172	45.21975	2.64881
50	48	4	48	23774	672	56	3360	4088	3456	384	6912	10752	17.19526	45.22588	2.630137
51.04167	47	4	49	23930	658	56	3430	4144	3384	384	7056	10824	17.31718	45.23193	2.611969
52.08333	46	4	50	24086	644	56	3500	4200	3312	384	7200	10896	17.43752	45.2379	2.594286
53.125	45	4	51	24242	630	56	3570	4256	3240	384	7344	10968	17.55631	45.24379	2.577068
54.16667	44	4	52	24398	616	56	3640	4312	3168	384	7488	11040	17.67358	45.24961	2.560297
55.20833	43	4	53	24554	602	56	3710	4368	3096	384	7632	11112	17.78936	45.25536	2.543956
56.25	42	4	54	24710	588	56	3780	4424	3024	384	7776	11184	17.90368	45.26103	2.528029
57.29167	41	4	55	24866	574	56	3850	4480	2952	384	7920	11256	18.01657	45.26663	2.5125
58.33333	40	4	56	25022	560	56	3920	4536	2880	384	8064	11328	18.12805	45.27216	2.497354
59.375	39	4	57	25178	546	56	3990	4592	2808	384	8208	11400	18.23814	45.27762	2.482578
60.41667	38	4	58	25334	532	56	4060	4648	2736	384	8352	11472	18.34689	45.28302	2.468158
61.45833	37	4	59	25490	518	56	4130	4704	2664	384	8496	11544	18.4543	45.28835	2.454082

Table D4 Calculation of Degree of Substitution from CHN Elemental Analysis Method (Cont'd)

% DS	mole of group			MW of PB	weight of nitrogen in group per mole			Total weight of nitrogen	weight of carbon in group per mole			Total weight of carbon	%N	%C	C/N ratio
	A	B	C		A	B	C		A	B	C				
62.5	36	4	60	25646	504	56	4200	4760	2592	384	8640	11616	18.5604	45.29361	2.440336
63.54167	35	4	61	25802	490	56	4270	4816	2520	384	8784	11688	18.66522	45.29881	2.42691
64.58333	34	4	62	25958	476	56	4340	4872	2448	384	8928	11760	18.76878	45.30395	2.413793
65.625	33	4	63	26114	462	56	4410	4928	2376	384	9072	11832	18.8711	45.30903	2.400974
66.66667	32	4	64	26270	448	56	4480	4984	2304	384	9216	11904	18.97221	45.31405	2.388443
67.70833	31	4	65	26426	434	56	4550	5040	2232	384	9360	11976	19.07213	45.319	2.37619
68.75	30	4	66	26582	420	56	4620	5096	2160	384	9504	12048	19.17087	45.3239	2.364207
69.79167	29	4	67	26738	406	56	4690	5152	2088	384	9648	12120	19.26846	45.32875	2.352484
70.83333	28	4	68	26894	392	56	4760	5208	2016	384	9792	12192	19.36491	45.33353	2.341014
71.875	27	4	69	27050	378	56	4830	5264	1944	384	9936	12264	19.46026	45.33826	2.329787
72.91667	26	4	70	27206	364	56	4900	5320	1872	384	10080	12336	19.55451	45.34294	2.318797
73.95833	25	4	71	27362	350	56	4970	5376	1800	384	10224	12408	19.64769	45.34756	2.308036
75	24	4	72	27518	336	56	5040	5432	1728	384	10368	12480	19.73981	45.35213	2.297496
76.04167	23	4	73	27674	322	56	5110	5488	1656	384	10512	12552	19.83089	45.35665	2.287172
77.08333	22	4	74	27830	308	56	5180	5544	1584	384	10656	12624	19.92095	45.36112	2.277056
78.125	21	4	75	27986	294	56	5250	5600	1512	384	10800	12696	20.01001	45.36554	2.267143
79.16667	20	4	76	28142	280	56	5320	5656	1440	384	10944	12768	20.09807	45.36991	2.257426
80.20833	19	4	77	28298	266	56	5390	5712	1368	384	11088	12840	20.18517	45.37423	2.247899
81.25	18	4	78	28454	252	56	5460	5768	1296	384	11232	12912	20.27132	45.37851	2.238558
82.29167	17	4	79	28610	238	56	5530	5824	1224	384	11376	12984	20.35652	45.38273	2.229396

Table D4 Calculation of Degree of Substitution from CHN Elemental Analysis Method (Cont'd)

% DS	mole of group			MW of PB	weight of nitrogen in group per mole			Total weight of nitrogen	weight of carbon in group per mole			Total weight of carbon	%N	%C	C/N ratio
	A	B	C		A	B	C		A	B	C				
83.33333	16	4	80	28766	224	56	5600	5880	1152	384	11520	13056	20.4408	45.38692	2.220408
84.375	15	4	81	28922	210	56	5670	5936	1080	384	11664	13128	20.52417	45.39105	2.21159
85.41667	14	4	82	29078	196	56	5740	5992	1008	384	11808	13200	20.60664	45.39514	2.202937
86.45833	13	4	83	29234	182	56	5810	6048	936	384	11952	13272	20.68824	45.39919	2.194444
87.5	12	4	84	29390	168	56	5880	6104	864	384	12096	13344	20.76897	45.4032	2.186107
88.54167	11	4	85	29546	154	56	5950	6160	792	384	12240	13416	20.84885	45.40716	2.177922
89.58333	10	4	86	29702	140	56	6020	6216	720	384	12384	13488	20.92788	45.41108	2.169884
90.625	9	4	87	29858	126	56	6090	6272	648	384	12528	13560	21.0061	45.41496	2.16199
91.66667	8	4	88	30014	112	56	6160	6328	576	384	12672	13632	21.08349	45.4188	2.154235
92.70833	7	4	89	30170	98	56	6230	6384	504	384	12816	13704	21.16009	45.42261	2.146617
93.75	6	4	90	30326	84	56	6300	6440	432	384	12960	13776	21.2359	45.42637	2.13913
94.79167	5	4	91	30482	70	56	6370	6496	360	384	13104	13848	21.31094	45.43009	2.131773
95.83333	4	4	92	30638	56	56	6440	6552	288	384	13248	13920	21.38521	45.43378	2.124542
96.875	3	4	93	30794	42	56	6510	6608	216	384	13392	13992	21.45873	45.43742	2.117433
97.91667	2	4	94	30950	28	56	6580	6664	144	384	13536	14064	21.5315	45.44103	2.110444
98.95833	1	4	95	31106	14	56	6650	6720	72	384	13680	14136	21.60355	45.44461	2.103571
100	0	4	96	31262	0	56	6720	6776	0	384	13824	14208	21.67488	45.44815	2.096812

Example of 0 % degree of substitution:

A = glucosamine group

B = N–acetyl glucosamine group

C = deacetylated glucosamine

0 %DS, assume 100 mole of biopolymer, there are 96 mole of glucosamine (96 % degree of deacetylation), 4 mole of N–acetyl glucosamine.

To calculate molecular weight of modified biopolymer used Table D5:

$$MW\ of\ biopolymer = (96 * 161) + (4 * 203) + (0 * 317) + 16 + 1 + 1$$

$$MW\ of\ biopolymer = 16286$$

Table D5 Calculated molecular weight of modified biopolymer

Functional group	Molecular weight	Weight of nitrogen per mole	Weight of carbon per mole	Weight of hydrogen per mole
A	161	14	72	11
B	203	14	96	13
C	317	70	144	23

To calculated weight of nitrogen per mole used Table D5:

$$A = (96 * 14)$$

$$A = 1344$$

$$B = (4 * 14)$$

$$B = 56$$

$$C = (0 * 14)$$

$$C = 0$$

$$Total\ weight\ of\ nitrogen = 1344 + 56 + 0$$

$$Total\ weight\ of\ nitrogen = 1400$$

To calculated weight of carbon per mole used Table D5:

$$A = (96 * 72)$$
$$A = 6912$$
$$B = (4 * 72)$$
$$B = 384$$
$$C = (0 * 72)$$
$$C = 0$$
$$Total\ weight\ of\ carbon = 6912 + 384 + 0$$
$$Total\ weight\ of\ carbon = 7296$$

To calculated %N:

$$\%N = \frac{1400}{16286}$$
$$\%N = \frac{1400}{16286} * 100$$
$$\%N = 8.59634\ \%$$

To calculated %C:

$$\%C = \frac{7296}{16286}$$
$$\%C = \frac{7296}{16286} * 100$$
$$\%C = 44.79921\ \%$$

To calculated %DS:

$$\%DS = \frac{0}{96} * 100$$
$$\%DS = 0$$

Appendix E Calculation of Degree of Substitution of Biopolymer-Arginine from HPLC Method

This method calculated area from detected peak of 0.1%, 0.5%, 1%, 2%, 3%, 4%, and 5% (wt/v) arginine standard and the areas under the arginine peak from the standard arginine at retention time of 3.5 sec. The detected peaks of arginine standard showed in Figure E1. The area compared with mole of arginine showed in Table E1.

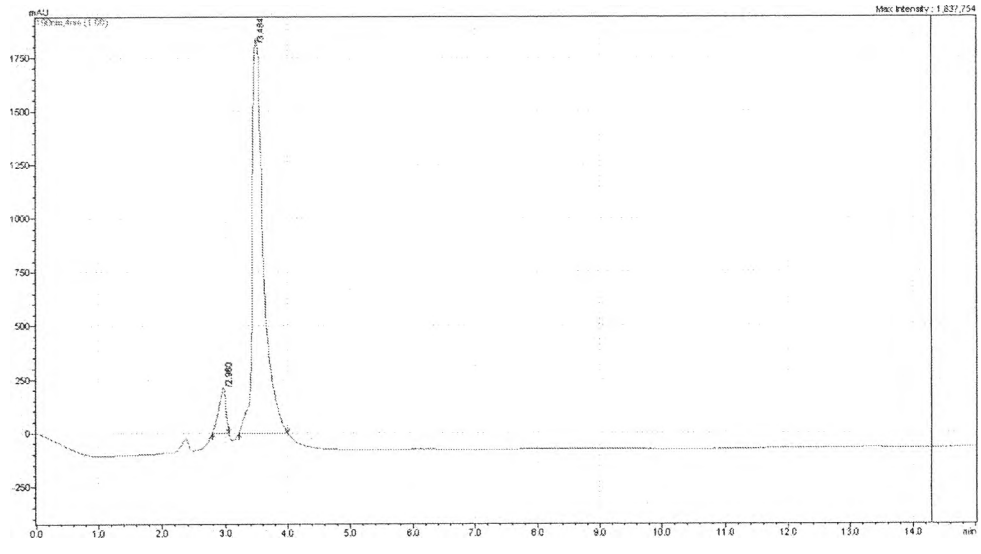

Figure E1 HPLC result of 5% wt/v arginine standard.

Table E1 showed % wt/v of arginine with area from HPLC method

% wt/v of arginine	Mole of arginine	1st Area	2nd Area	3rd Area	$\bar{x}$	SD
0.1 %	0.0000574	10,366	10,381	10,442	10,396	40.253
0.5 %	0.000287	800,121	800,190	800,018	800,110	86.558
1 %	0.000574	2,733,596	2,773,372	2,773,131	2,773,366	232.552
2 %	0.00115	7,596,580	7,597,131	7,596,365	7,596,692	395.091
3 %	0.00172	12,510,858	12,511,472	12,511,798	12,511,798	477.297
4 %	0.00230	19,393,349	19,391,124	19,393,763	19,392,763	1,153.2281
5 %	0.00287	23,115,488	23,113,834	23,114,908	23,114,908	839.205

Example of calculation from %wt/v to mole from equation E1:

5% wt/v arginine standard

$$mole\ of\ arginine = \frac{weight\ of\ arginine\ (g)}{molecular\ weight\ of\ arginine} \quad \textbf{(Equation E1)}$$

$$mole\ of\ arginine = \frac{5}{174.2\ g/mole} * 0.1$$

$$mole\ of\ arginine = 0.00278\ g$$

The peak area of sample from HPLC was compared to the plot of arginine standard curve which is related to equation of standard curve shown in equation E2,

$$Area = (8E+09)\ X \quad \textbf{(Equation E2)}$$

$$X = \frac{Area}{8E+09}$$

X is mole of arginine

The standard curve of arginine is shown in Figure E8 obtained from Table E1. The product results are shown in Figure E9-E15 got area and calculated mole of arginine related with degree of substitution. Degree of substitution which observed from area showed in Table E2. All area of products showed in Table E3.

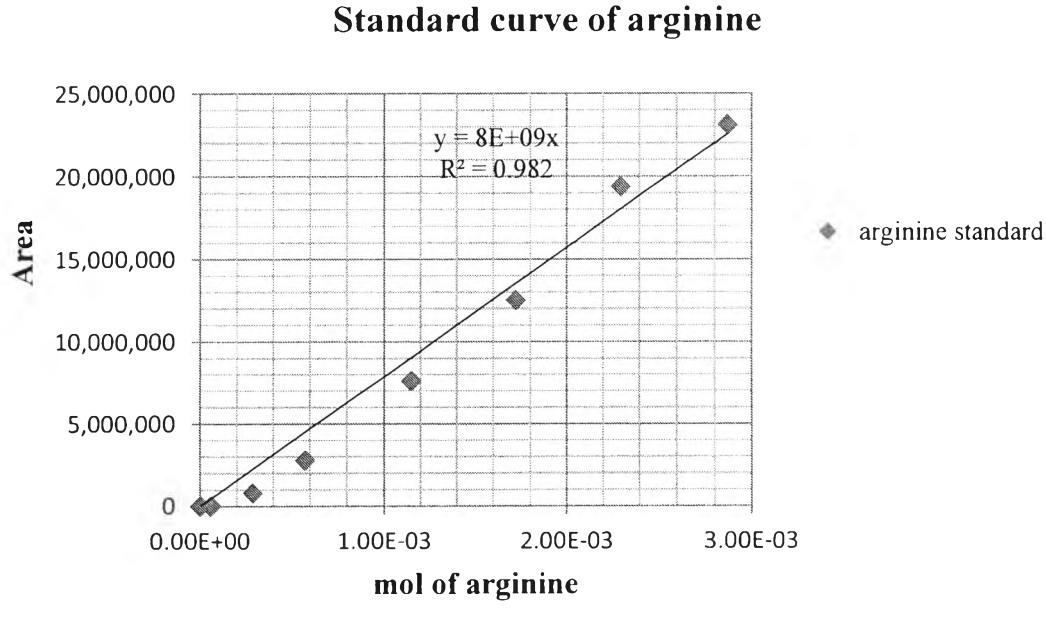

Figure E8 The standard curve of arginine.

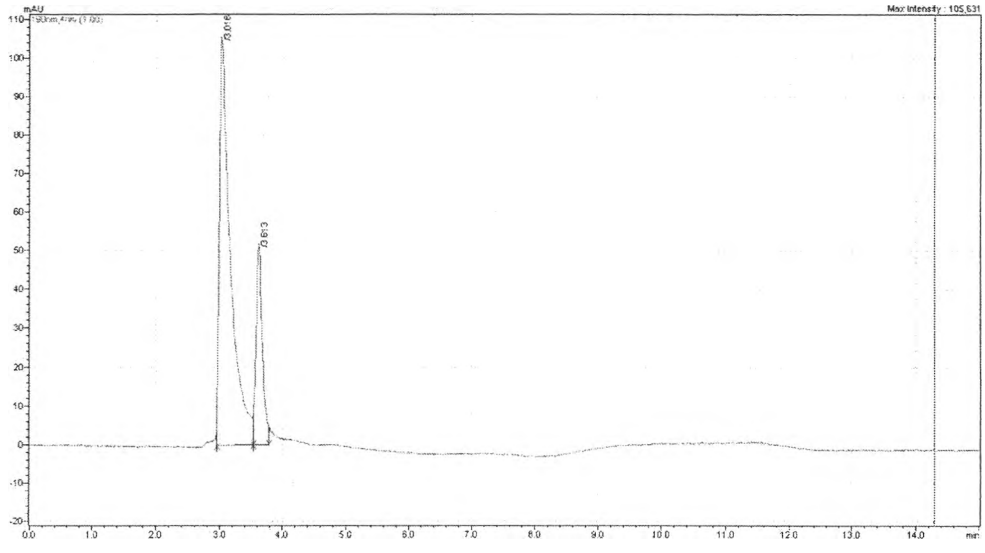

Figure E9 The product at ratio PB/AR/CA = 1:1:1 at reaction time 48 h.

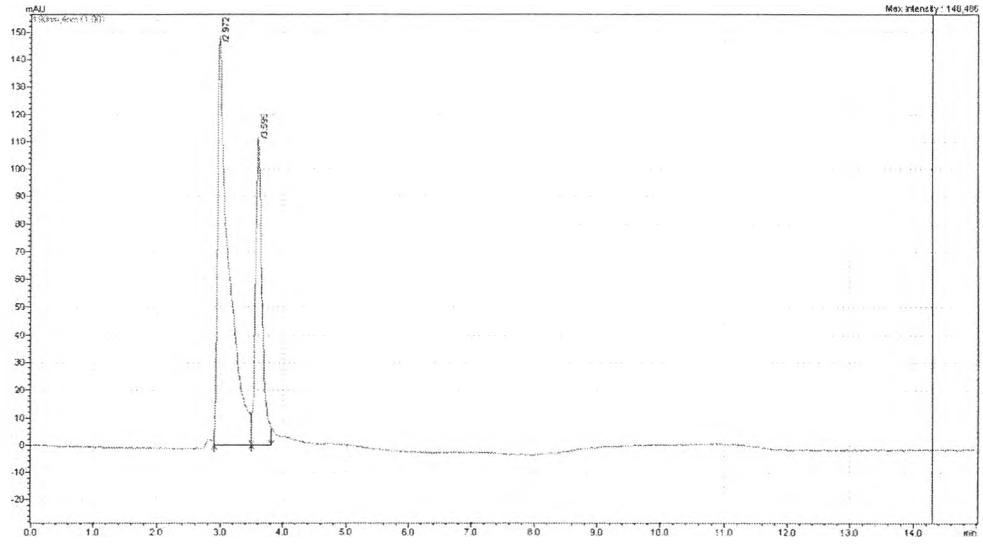

Figure E10 The product at ratio PB/AR/CA = 1:1:2 at reaction time 48 h.

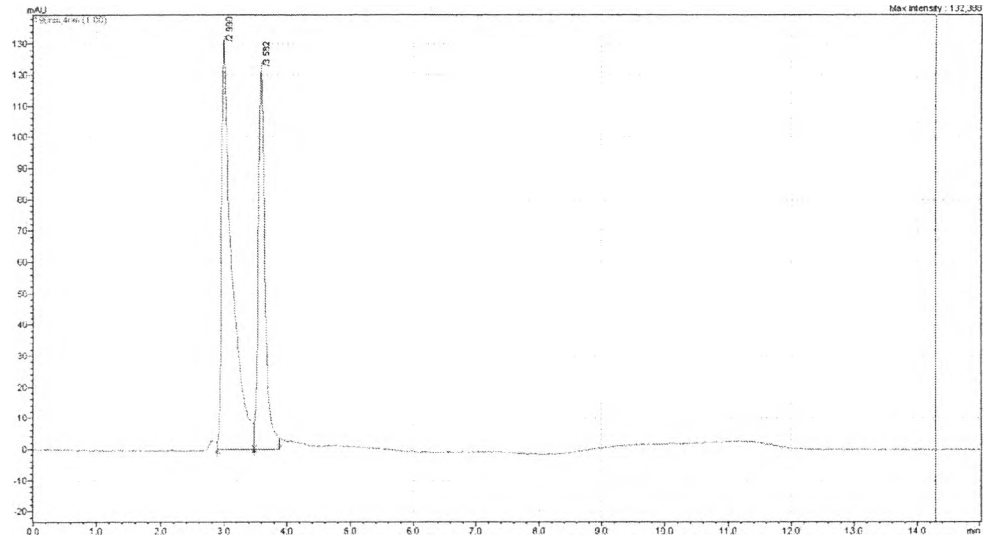

Figure E11 The product at ratio PB/AR/CA = 1:1:3 at reaction time 48 h.

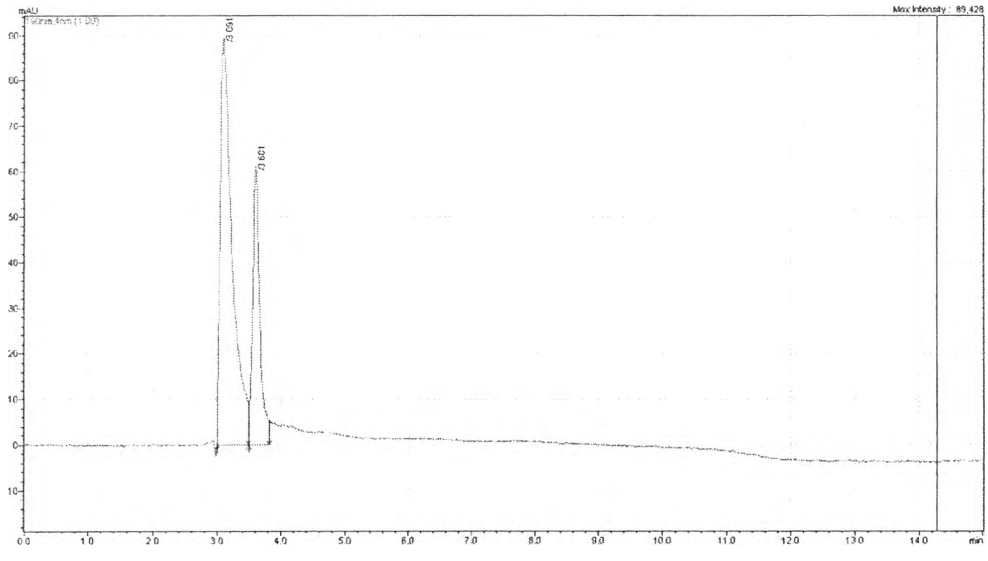

Figure E12 The product at ratio PB/AR/CA = 1:1:1 at reaction time 24 h.

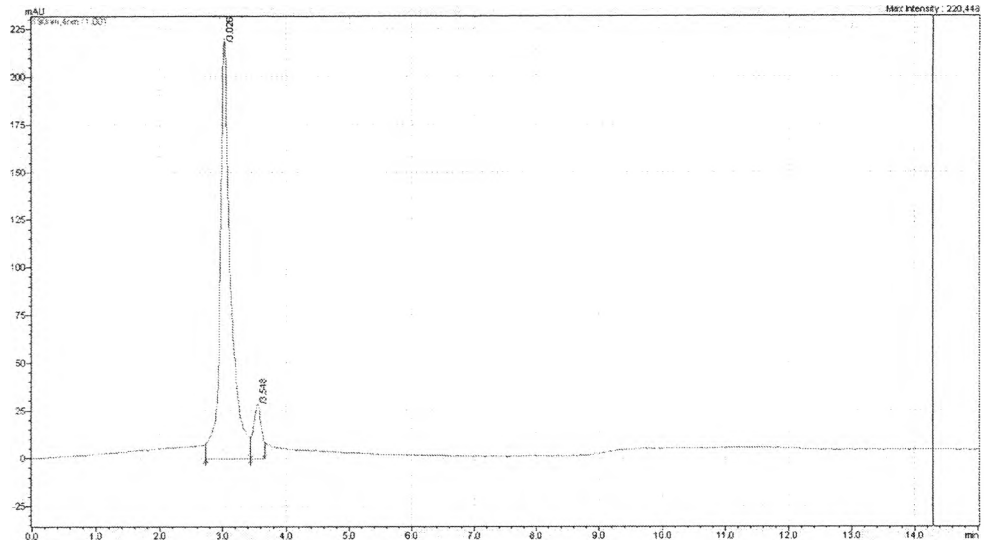

Figure E13 The product at ratio PB/AR/CA = 1:1:1 at reaction time 72 h.

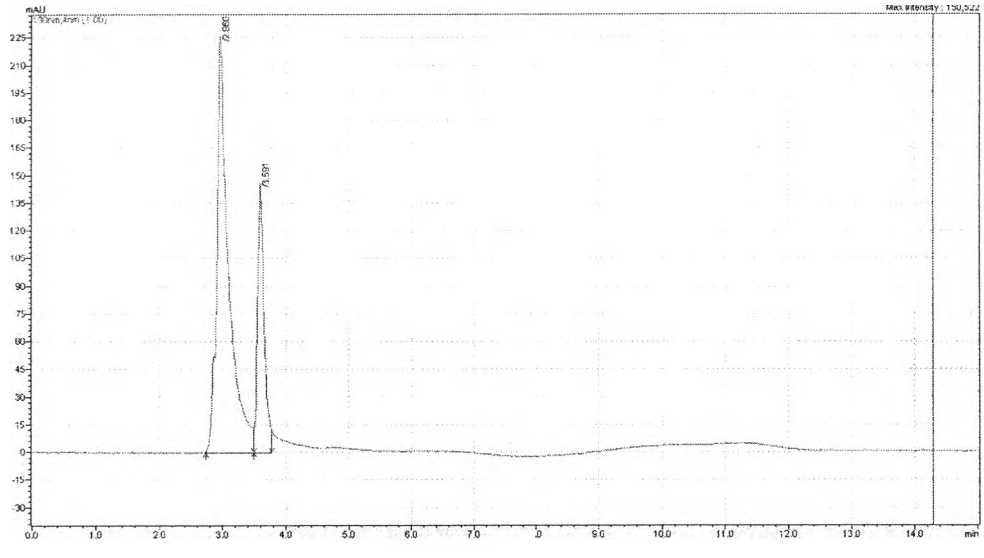

Figure E14 The product at ratio PB/AR/CA = 1:2:1 at reaction time 72 h.

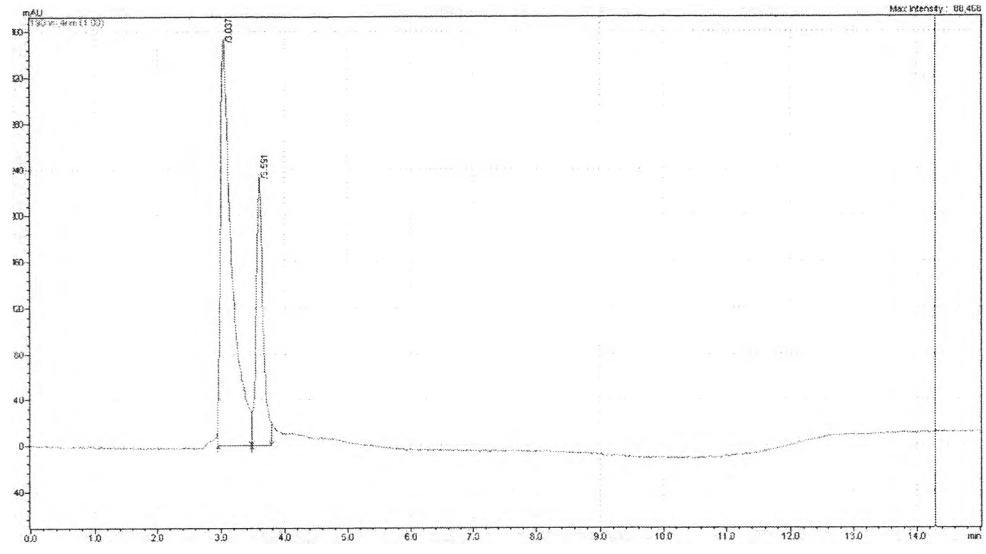

Figure E15 The product at ratio PB/AR/CA = 1:3:1 at reaction time 72 h.

Table E2 Degree of substitution from HPLC method

Ratio of PB/AR/CA	Reaction time (h)	Area	Remaining mole	Mole AR used	Reacted AR mole	%DS
1:1:1	48	3,251,230	0.000406404	0.000621118	0.000215	34.89094
1:1:2	48	4,622,468	0.000577809	0.000621118	0.0000433	7.03777
1:1:3	48	4,712,524	0.000589066	0.000621118	0.0000321	5.208514
1:1:1	24	3,536,490	0.000442061	0.000621118	0.000179	29.09662
1:1:1	72	1,207,350	0.000150919	0.000621118	0.00047	76.4071
1:2:1	72	6,507,162	0.000813395	0.001242236	0.000429	69.68637
1:3:1	72	11,349,894	0.001418737	0.001863354	0.000445	72.25004

Example of calculation degree of substitution:

Ratio biopolymer/arginine/coupling agents is 1:1:1 with reaction time 48 h

From Equation E2:

$$Area = (8E+09)\,X \qquad \textbf{(Equation E2)}$$

$$3{,}251230 = (8E+09)\,X$$

$$X = 0.000406404$$

Remaining mole of arginine is 0.000406404

Mole arginine used is same mole of biopolymer (biopolymer use 0.1 g):

$$mole\ of\ arginine = mole\ of\ biopolymer$$

$$mole\ of\ arginine = \frac{weight\ of\ biopolymer\ (g)}{molecular\ weight\ of\ biopolymer} \quad \textbf{(Equation E1)}$$

$$mole\ of\ arginine = \frac{0.1\ g}{161\ g/mole}$$

$$mole\ of\ arginine = 0.000621118$$

To calculate reacted mole of arginine:

$$mole\ of\ arginine = mole\ of\ arginine\ used - mole\ of\ remaining\ arginine$$

$$mole\ of\ reacted\ arginine = 0.000621118 - 0.000406404$$

$$mole\ of\ reacted\ arginine = 0.000215$$

Mole of biopolymer that can react with arginine with degree of deacetylation = 96.43% (biopolymer use 0.1 g):

Mole of reacted biopolymer =

$$\frac{weight\ of\ biopolymer\ (g)}{(MW\ of\ deacetylated\ PB * \%\ purify) + (MW\ of\ acetylated\ PB * (1 - \%purify))}$$

$$mole\ of\ reacted\ biopolymer = \frac{0.1\ g}{\big((161 * 0.9643) + (203 * 0.0357)\big) g/mole}$$

$$mole\ of\ reacted\ biopolymer = 0.000615387$$

Degree of substitution (%DS):

$$\%DS = \frac{mole\ of\ reacted\ arginine}{mole\ of\ reacted\ biopolymer}$$

$$\%DS = \frac{0.000215}{0.000615387} * 100$$

$$\%DS = 34.89094\ \%$$

Table E3 Area of all products from HPLC method

Ratio of PB/AR/CA	Reaction time (h)	1st Area	2nd Area	3rd Area	$\bar{x}$	SD
1:1:1	48	3,251,230	3,251,142	3,251,346	3,251,239	102.320
1:1:2	48	4,622,468	4,622,399	4,622,522	4,622,463	61.652
1:1:3	48	4,712,524	4,712,120	4,712,542	4,712,395	238.615
1:1:1	24	3,536,490	3,536,764	3,536,319	3,536,524	224.478
1:1:1	72	1,207,350	1,207,783	1,207,557	1,207,563	216.569
1:2:1	72	6,507,162	6,507,887	6,507,006	6,507,352	470.128
1:3:1	72	11,349,894	11,347,273	11,350,194	11,349,120	1606.854

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Krissada, S. and Chintana, S. (2012, April 24) Study of Biopolymer Modified with Arginine for CO_2 Adsorption. Paper presented at the 3rd Research Symposium on Petrochemical and Materials Technology and the 18th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.