

REFERENCES

1. Mayo Smith, W., Manufacture of Plastics, Vol. 1, Reinhold Publishing Corporation, New York, 1957:437-455.
2. International Rubber Study Group, Rubber Statistical Bulletin, Vol. 51, No. 3, December, (1996):11,23.
3. Keith, C.R., Rubber-Toughened Plastics, B.F. Goodrich Company, Washington. DC, (1989):15-64.
3. Miles, D.C., and Briston, J.H., Polymer Technology, Chemical Publishing Corporation, New York, (1989):445-459.
4. Collyer, A.A., Rubber Toughened Engineering Plastics, Chapman & Hall, Cambridge, (1994):136-164.
5. Norman, E.A., South,H., and Michael, B.J., "ABS Graft Polyblends Containing Two Graft Polymers with Different Degree of Grafting", U.S. Pat 3,509,238 (Apr. 28, 1970).
6. Nicholas, P.C., Product Design and Testing of polymeric Materials, Marcel Dekker, Inc., New York, (1990).
7. Roberts, A.D., Natural Rubber Science and technology, Graphicraft Typesetters Ltd., Hong Kong, 2nd ed.(1990):64-98,679-730.
8. Morton, M., Rubber technology, Van Nostrand Reinhold Company, New York, 3rd ed., (1987):179-200.
9. Brydson, J.A., Rubber Chemistry, Applied science Publishers Ltd., Essex, England, (1978):11-24.
10. Richard, M.A., et al., "Emulsion Polymerization Process For ABS Polyblends", U.S. Pat 4,385,157, (May 24, 1983).
11. Karl Zabrocki, et al., "ABS-Moulding Compositions", U.S. Pat 4,520,165, (May 28,1985).

12. Herbert, E.D., Alfred, P.K., and Karl-Heinz, O.P., "Process for The Preparation of Thermoplastic Moulding Compositions", U.S. Pat 4,885,337, (Dec. 5, 1989).
13. George, O., Principles of Polymerization, John Wiley & Sons, Inc., New York, 3Rd ed.(1991):715-720.
14. Gordon Cameron, G., and Younus Qureshi, M., "Free Radical Grafting of Monomers to Polydienes. III. Kinetics and Mechanism of Styrene Grafting to Polyisoprene", Journal of Polymer Science : Polymer Chemistry Edition, John Wiley&Sons,18(1980):2143-2153.
15. Hourston, D.J., and Romaine, J., "Modification of Natural Rubber Latex II. Natural rubber Poly(methyl Methacrylate) Composite Latexes Synthesized Using an Amine-Activated Hydroperoxide",App. Polymer Science, John Wiley&Sons,Inc.,39(1990):1587-1594.
16. Hourston, D.J., and Romaine, J., "Modification of Natural Rubber Latex.III Natural rubber-Polystyrene Composite Latexes Synthesized Using an Azobisisobutyronitrile as initiator", App. Polymer Science, John Wiley&Sons,Inc.,43(1991):2207-2211.
17. Hyungsu, K., Keskkula, H., and Paul, D.R., "Toughening of SAN copolymers by an SAN emulsion grafted rubber", Polymer, Betterworth Heineman Ltd., 31(1990):869-876.
18. Hyungsu, K.,Keskkula, H., and Paul, D.R , "Effect of Acrylonitrile Content on the Toughness of ABS Materials", Polymer, Betterworth Heineman Ltd., 32 (1991):1447-1455.
19. Nui-Jen, H., "A Gel Permeation Chromatography Method to Determine Grafting Efficiency During Graft Copolymerization", Polymer, Betterworth Heineman Ltd., 35(1994), No. 26:5693-5698.
20. Rusdan, D., "Effect of Styrene on Mechanical Stability Time of Natural Rubber Latex before Modification", A Report of the Proceedings of the International Rubber Technology Conference 1993,

- The Rubber Research Institute of Malaysia, (1993):454-460.
21. Perrin, D.D., et al., Purification of Laboratory Chemicals,
A. Wheaton & Co. Ltd., Germany, (1981):87, 416-417.
 22. Faullimmel, J.G., Polymer Laboratory I & II, Multidisciplinary Program
of Petrochemistry-Polymer:46-51.
 23. James, D.I., et al., Spectrochemical Analysis, Prentice-Hall. Inc.,
American,(1988):404-436.
 24. Silverstein, R.M., et al., Spectrometric Identification of Organic
Compounds, John Wiley & Sons. Inc., Singapore, (1991).
 25. Rujinirun, C., "Preparation graft copolymers of styrene and acrylonitrile
onto natural rubber", Master's thesis, Chulalongkorn University,
(1995).
 26. Edith, A.T., Thermal Characterization of polymeric Materials,
Academic Press Limited Inc., London, (1981):365-428.
 27. Dunbrook, R.F.D., and Morris, V.N., The Science of Rubber,
Reinhold Publishing Corporation, New York, (1988):86-89.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX

ศูนย์วิทยทรัพยากร
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APPENDIX A

1) Calculation of Monomers Conversion [19]

The monomers conversion is defined as the mass of SAN formed (graft and free) divided by the initial mass of monomers.

$$\text{Conversion} = \frac{\text{SAN formed}}{\text{initial mass of monomers in sample}}$$

2) Calculation of Grafting Efficiency [19]

The grafting efficiency is readily defined as the mass of the grafted SAN divided by the total SAN produced. The definition of grafting efficiency is

$$\text{grafting efficiency} = \frac{\text{weight of graft SAN}}{\text{weight of free SAN} + \text{weight of grafted SAN}}$$

3) Calculation of Graft Ratio [19]

The graft ratio is defined as the mass of grafted SAN per unit mass of backbone polymer. The definition of graft ratio is

$$\text{graft ratio} = \frac{\text{weight of grafted SAN}}{\text{weight of backbone cis-1,4-polyisoprene}}$$

4) Calculation of Graft Frequency [19]

The graft frequency is the number of backbone polymer repeat units between graft chains. To obtain this we first calculate the number of graft chains per backbone chain. For 17.05 g of grafted SAN at an \bar{M}_n of 90,413 (via Table 4.5) and 69.92 g of grafted *cis*-1,4-polyisoprene at an \bar{M}_n 137,799 (via Table 4.5), one chain of *cis*-1,4-polyisoprene has 2,026.5 (137,799/68) repeat units. Hence the total number of grafted SAN chains is (17.05/90,413) x (Avogadro's number) or 1.89×10^{-4} x (Avogadro's

number). The total number of grafted *cis*-1,4-polyisoprene chains is $(69.92/137,799) \times$ (Avogadro's number) or $5.07 \times 10^{-4} \times$ (Avogadro's number). The number of grafted chains per backbone chains is $(1.89/5.07) = 0.37$. The number of repeat units of rubber backbone per one of grafted chain is $(2,026.5/0.37) = 5,477$.



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Table AI. Effect of initiator concentration, temperature and pressure on the monomers conversion and the grafting efficiency.

Wt. of latex = 150 gm.; Wt. of DRC = 90.75 gm for exp.1-4; wt. of DRC = 91.05 gm for exp.5-13; wt. of monomer = 90 gm.

Experiment	product (g)	% conv.	sample (g)	wt. A*	wt.B*	% graft NR	% free SAN	% free NR	total SAN	free SAN	g-SAN	% grafting efficiency
1	120.019	32.5	2.149	1.501	1.087	50.6	19.3	30.2	29.27	23.12	6.15	26.6
2	135.271	49.5	2.027	1.554	1.045	51.6	25.1	23.3	44.52	33.97	10.55	31.1
3	145.242	60.5	2.120	1.685	1.110	52.4	27.1	20.5	54.49	39.39	15.10	38.3
4	147.979	63.6	2.164	1.712	1.112	51.4	27.7	20.9	57.23	41.03	16.20	39.5
5	145.604	60.6	2.095	1.658	1.102	52.6	26.5	20.9	54.55	38.64	15.91	41.2
6	148.435	63.8	2.079	1.783	1.218	58.6	27.2	14.2	57.39	40.34	17.05	42.3
7	150.192	65.7	2.166	1.895	1.303	60.2	27.3	12.5	59.14	41.05	18.09	44.1
8	154.968	71.0	2.007	1.769	1.208	60.2	28.0	11.9	63.92	43.32	20.60	47.6
9	162.768	79.7	2.124	1.927	1.299	61.2	29.6	9.3	71.72	48.13	23.59	49.0
10	167.779	85.3	2.051	1.892	1.299	63.3	28.9	7.8	76.73	48.51	28.22	58.2
11	171.078	88.9	2.182	2.037	1.397	64.0	29.3	6.6	80.03	50.18	29.85	59.5
12	170.459	88.2	2.013	1.883	1.293	64.2	29.3	6.5	79.41	49.96	29.45	58.9
13	171.042	88.9	2.163	2.047	1.394	64.4	30.2	5.4	79.99	51.64	28.36	54.9
14	174.516	92.7	2.084	1.985	1.348	64.7	30.6	4.8	83.47	53.34	30.12	56.5

Exp.1-4 : 0.5 -2.0 parts by weight of initiator, Exp.5 : 50 °C 0 psig.; Exp.6 : 50 °C 20 psig.; Exp.7 : 50° C 40 psig.

Exp.8 : 60 °C 20 psig.; Exp.9 : 60 °C 40 psig., Exp.10 : 70 °C 20 psig.; Exp. 11 : 70 °C 30 psig.; Exp. 12 : 70 °C 40 psig.

Exp.13 : 80 °C 20 psig.; Exp.14 : 80 °C 40 psig.

*wt A : Graft product were extracted by light petroleum ether at 80 °C for 24 hours.

*wt B : Graft product were extracted by light petroleum ether at 80 °C for 24 hours and extracted by DMF at 140 °C for 24 hours.

Table AII. Effect of initiator concentration, temperature and pressure on graft frequency.

Wt. of latex = 150 gm.; Wt. of DRC = 90.75 gm for exp.1-4; wt. of DRC = 91.05 gm for exp.5-13; wt. of monomer = 90 gm.

Experiment	grafted NR Products	grafted NR	graft ratio	MW of SAN	MW of NR	repeat of NR	no of g-SAN	no of NR	graft per backbone	graft frequency
1	60.71	54.56	0.11	126,015	137,799	2,026.5	2.94E+19	2.38E+20	0.12	16,888
2	69.74	59.18	0.18	98,053	137,799	2,026.5	6.48E+19	2.59E+20	0.25	8,106
3	76.05	60.95	0.25	91,260	137,799	2,026.5	9.96E+19	2.66E+20	0.37	5,477
4	76.04	59.84	0.27	77,046	137,799	2,026.5	1.27E+20	2.61E+20	0.48	4,222
5	76.59	60.68	0.26	92,299	137,799	2,026.5	1.04E+20	2.65E+20	0.39	5,196
6	86.96	69.92	0.24	90,413	137,799	2,026.5	1.13E+20	3.05E+20	0.37	5,477
7	90.35	72.26	0.25	80,222	137,799	2,026.5	1.36E+20	3.16E+20	0.43	4,713
8	93.27	72.67	0.28	85,303	137,799	2,026.5	1.45E+20	3.17E+20	0.46	4,405
9	99.55	75.95	0.31	82,796	137,799	2,026.5	1.72E+20	3.32E+20	0.52	3,897
10	106.26	78.04	0.36	74,071	137,799	2,026.5	2.29E+20	3.41E+20	0.67	3,025
11	109.53	79.68	0.37	61,522	137,799	2,026.5	2.92E+20	3.48E+20	0.84	2,413
12	109.49	80.04	0.37	68,432	137,799	2,026.5	2.59E+20	3.50E+20	0.74	2,739
13	110.23	81.88	0.35	84,737	137,799	2,026.5	2.01E+20	3.58E+20	0.56	3,619
14	112.88	82.76	0.36	82,757	137,799	2,026.5	2.19E+20	3.62E+20	0.61	3,322

Exp.1-4 : 0.5 -2.0 parts by weight of initiator

Exp.5 : 50 °C 0 psig.; Exp.6 : 50 °C 20 psig.; Exp.7 : 50 °C 40 psig.

Exp.8 : 60 °C 20 psig.; Exp.9 : 60 °C 40 psig.

Exp.10 : 70 °C 20 psig.; Exp. 11 : 70 °C 30 psig.; Exp. 12 : 70 °C 40 psig.

Exp.13 : 80 °C 20 psig.; Exp.14 : 80 °C 40 psig.

APPENDIX B

In this research the GPC method was chosen for determination of the molecular weight of free SAN ; in tetrahydrofuran at 30 °C. The details are as follows :

Detector 1 Calibration report

METHOD NAME : DEMO METHOD 1
Calibration Type : Narrow Standards
Curve Type : 6th Order
Equation of Curve : $\log Mw = +2.15E+02 - 1.47E+02*R + 4.33E+01*R^2 - 6.76E-00*R^3 + 5.91E-01*R^4 - 2.73-02*R^5 + 5.21E-04*R^6$
Correlation Coef : $r^2 = 0.99963614$
Std Err of Estimate : 0.02992005
Calibration Points :

Ret time (min.)	Specified Molecular Wt	Calculated Molecular Wt	Valid
5.28	3,840,000	3,575,145	Yes
5.33	2,890,000	3,140,583	Yes
5.78	1,090,000	1,070,769	Yes
6.04	706,000	710,778	Yes
6.66	355,000	351,218	Yes
7.30	190,000	194,714	Yes
8.10	96,400	94,024	Yes
9.00	37,900	38,650	Yes
9.65	18,100	17,902	Yes
10.11	9,100	9,133	Yes

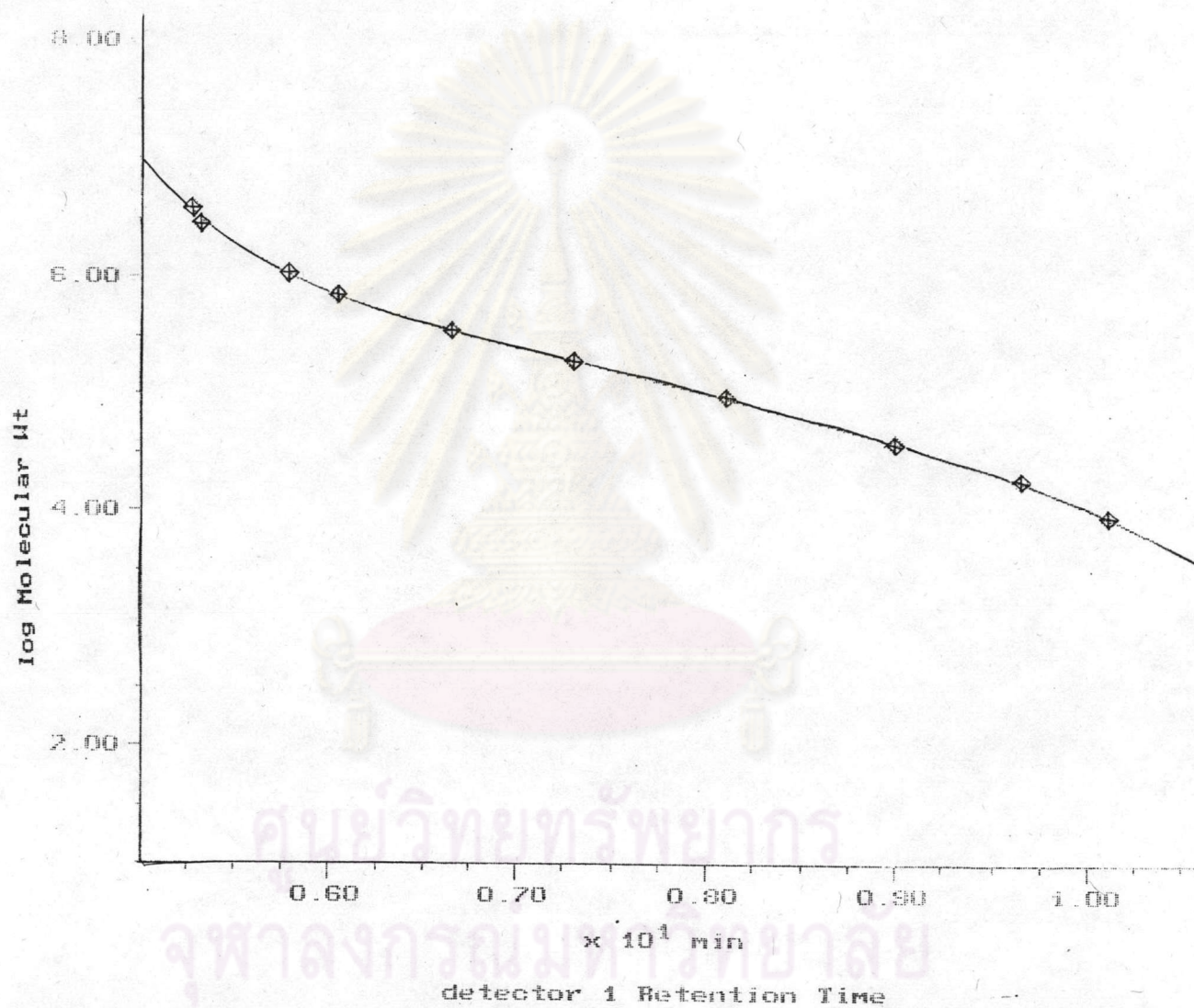
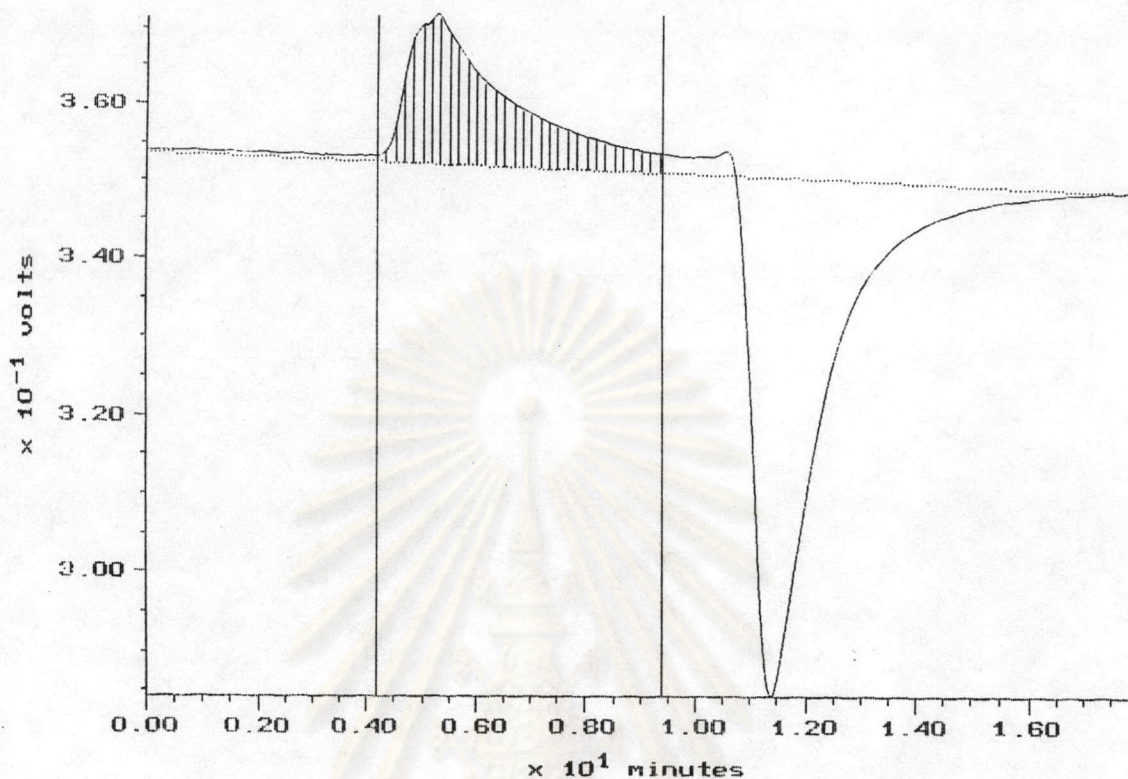


Figure B.1 The calibration curve, standard of polystyrene from GPC chromatograms.



SAMPLE: REVIEW

Method : DEMO METHOD 1
 Acquired : 17-MAR-1997 13:26
 Rate : 2.000 points/sec
 Duration : 18.000 minutes
 Operator : DDV

Instrument : Instrument 1
 Filename : J03171

ANALYSIS PARAMETERS:

Processing Start : 4.21 minutes
 Processing End : 8.90 minutes
 Number of Slices : 29
 Slice Width : 10 seconds

Baseline Start : 0.00 minutes
 Baseline End : 17.99 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 171829	
Weight Average : 1044683	Polydispersity : 6.079799
Viscosity Average : 1044683	Intrinsic viscosity : 0.000000
Z Average : 3198961	Z avg / Wt avg : 3.062136
Z+1 Average : 4787777	Z+1 avg / Wt avg : 4.582995

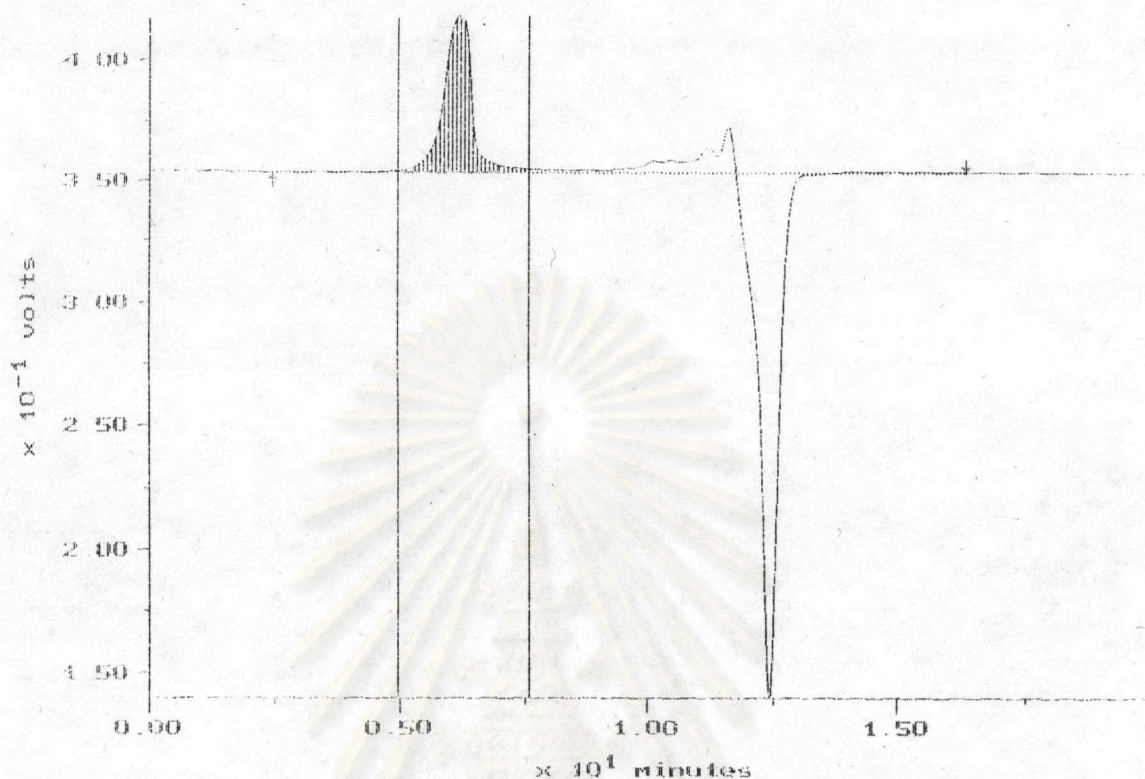
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 137799	
Weight Average : 549795	Polydispersity : 3.989838
Viscosity Average : 549795	Intrinsic viscosity : 0.000000
Z Average : 2050780	Z avg / Wt avg : 3.730082
Z+1 Average : 4139554	Z+1 avg / Wt avg : 7.529450

Peak Maximum:

Slice # : 7
 Molecular Wt : 1081873

Figure B.2 GPC chromatogram of natural rubber.



SAMPLE: REVIEW

Method :
 Acquired : 7-AUG-1996 12:20
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S08071

ANALYSIS PARAMETERS:

Processing Start : 4.95 minutes
 Processing End : 7.63 minutes
 Number of Slices : 33
 Slice Width : 5 seconds

Baseline Start : 2.44 minutes
 Baseline End : 16.43 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 126015	Polydispersity : 6.011183
Weight Average : 757500	Intrinsic viscosity : 0.000000
Viscosity Average : 757500	Z avg / Wt avg : 5.814076
Z Average : 4404163	Z+1 avg / Wt avg : 10.221175
Z-1 Average : 7742541	

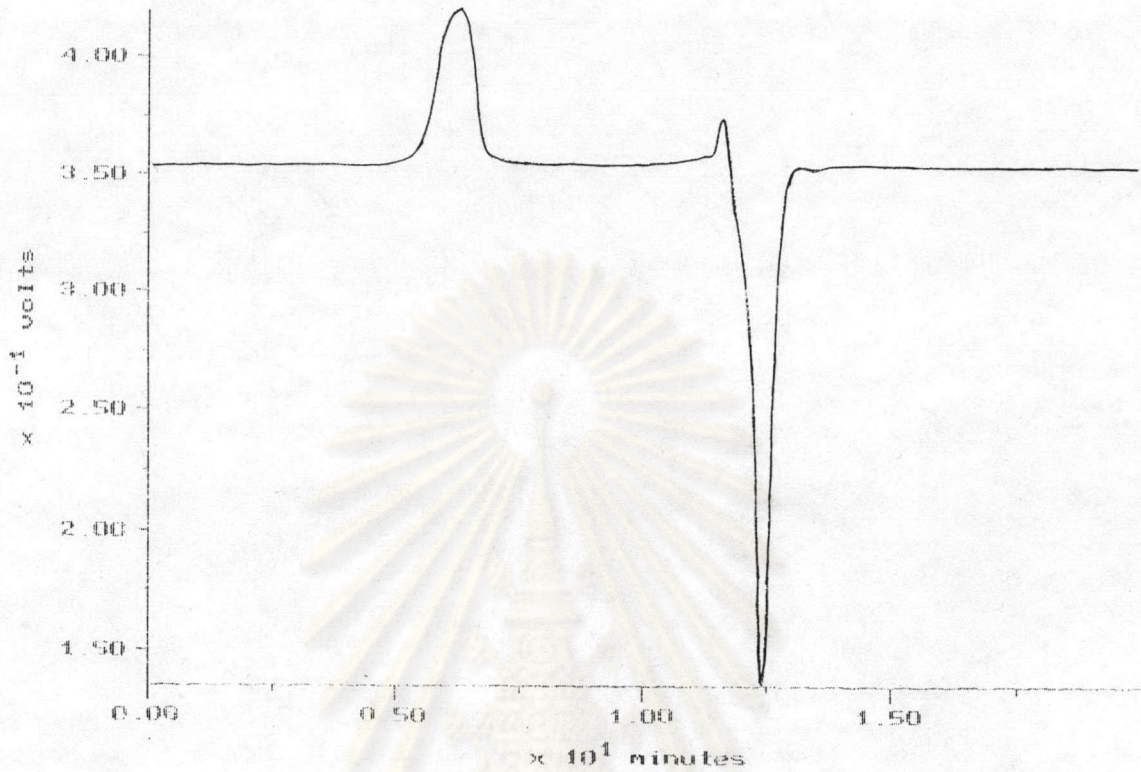
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 55310	Polydispersity : 6.581566
Weight Average : 364028	Intrinsic viscosity : 0.000000
Viscosity Average : 364028	Z avg / Wt avg : 9.696744
Z Average : 3529837	Z+1 avg / Wt avg : 20.448497
Z-1 Average : 7443827	

Peak Maximum:

Slice # : 15
 Molecular Wt : 205365

Figure B.3 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 0.5 % by weight of initiator



SAMPLE: REVIEW

Method :
 Acquired : 7-AUG-1996 13:22
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S28274

ANALYSIS PARAMETERS:

Processing Start : 4.95 minutes
 Processing End : 7.93 minutes
 Number of Slices : 36
 Slice Width : 5 seconds

Baseline Start : 2.44 minutes
 Baseline End : 16.43 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization (Wt%)):

Number Average : 56953	
Weight Average : 839518	Polydispersity : 0.560872
Viscosity Average : 839518	Intrinsic viscosity : 0.036000
Z Average : 4967714	Z avg / Wt avg : 5.917341
Z+1 Average : 7922117	Z+1 avg / Wt avg : 9.436596

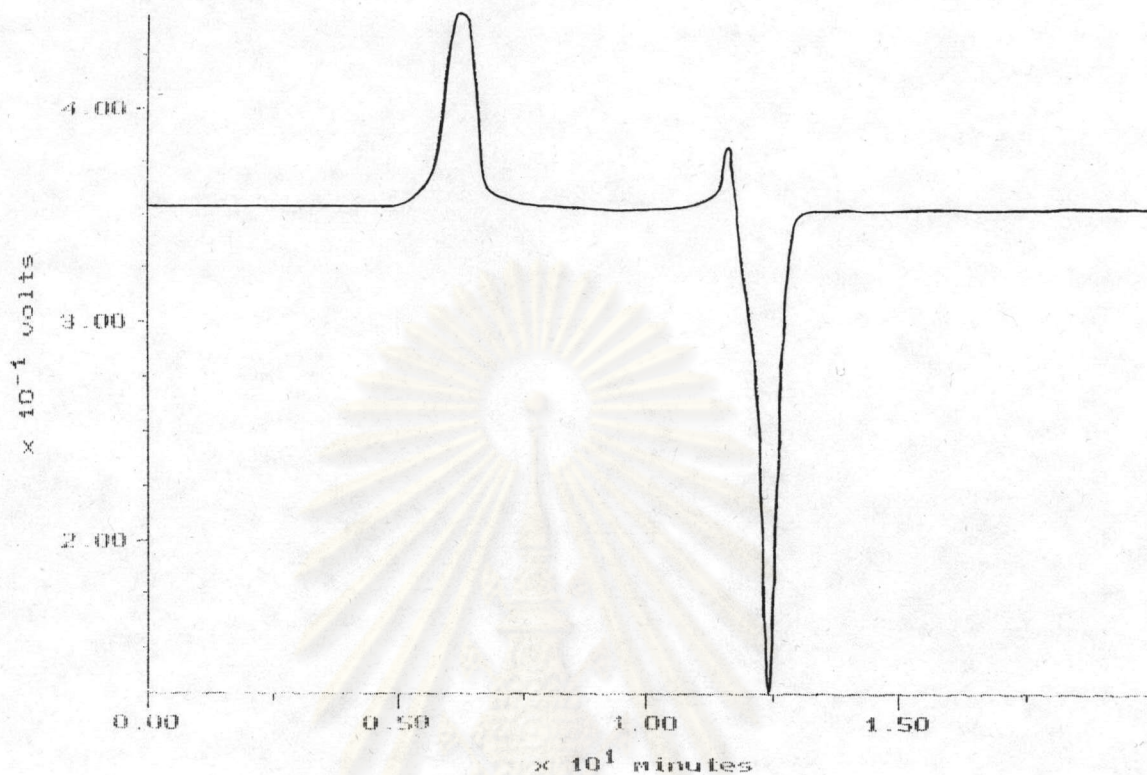
Molecular Weight Distribution Averages (Molecular Weight Normalization (Fit) / -d(log MW)/dt) :

Number Average : 48978	
Weight Average : 354740	Polydispersity : 7.242601
Viscosity Average : 354740	Intrinsic viscosity : 0.100000
Z Average : 4173031	Z avg / Wt avg : 11.491733
Z+1 Average : 7665723	Z+1 avg / Wt avg : 21.617837

Peak Maximum:

Slice # : 16
 Molecular Wt : 136357

Figure B.4 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 1.0 % by weight of initiator



SAMPLE: REVIEW

Method :
 Acquired : 7-AUG-1996 13:01
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S08073

ANALYSIS PARAMETERS:

Processing Start : 4.95 minutes
 Processing End : 7.93 minutes
 Number of Slices : 36
 Slice Width : 5 seconds

Baseline Start : 2.44 minutes
 Baseline End : 16.43 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 91260	Polydispersity : 6.896118
Weight Average : 629338	Intrinsic viscosity : 0.000000
Viscosity Average : 629338	Z avg / Wt avg : 7.034327
Z Average : 4420673	Z+1 avg / Wt avg : 12.336259
Z+1 Average : 7763671	

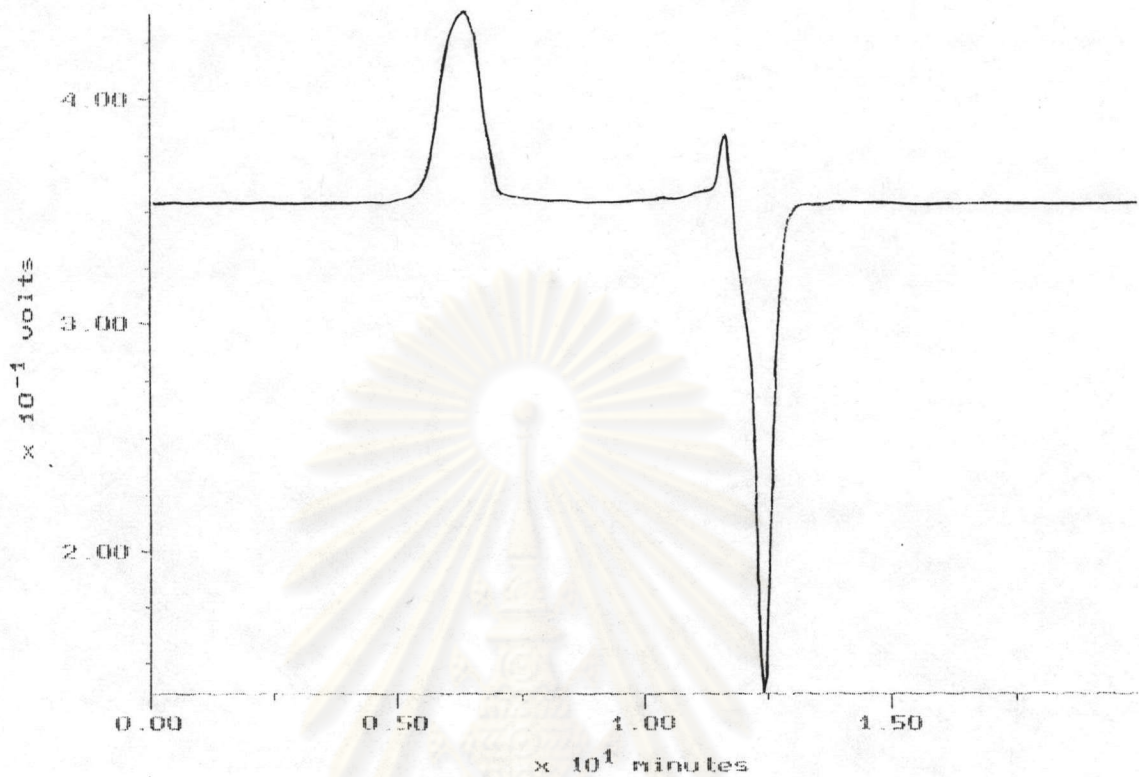
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 46716	Polydispersity : 5.672351
Weight Average : 264989	Intrinsic viscosity : 0.000300
Viscosity Average : 264989	Z avg / Wt avg : 12.96576
Z Average : 3434677	Z+1 avg / Wt avg : 28.186348
Z+1 Average : 7469076	

Peak Maximum:

Slice # : 16
 Molecular Wt : 136350

Figure B.5 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 1.5 % by weight of initiator



SAMPLE: REVIEW

Method :
 Acquired : 7-AUG-1996 12:41
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S03072

ANALYSIS PARAMETERS:

Processing Start : 4.95 minutes
 Processing End : 7.63 minutes
 Number of Slices : 33
 Slice Width : 5 seconds

Baseline Start : 2.44 minutes
 Baseline End : 16.43 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 77046
 Weight Average : 633537
 Viscosity Average : 633587
 Z Average : 4664551
 Z+1 Average : 7835096

Polydispersity : 8.223461
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 7.362136
 Z+1 avg / Wt avg : 12.366259

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

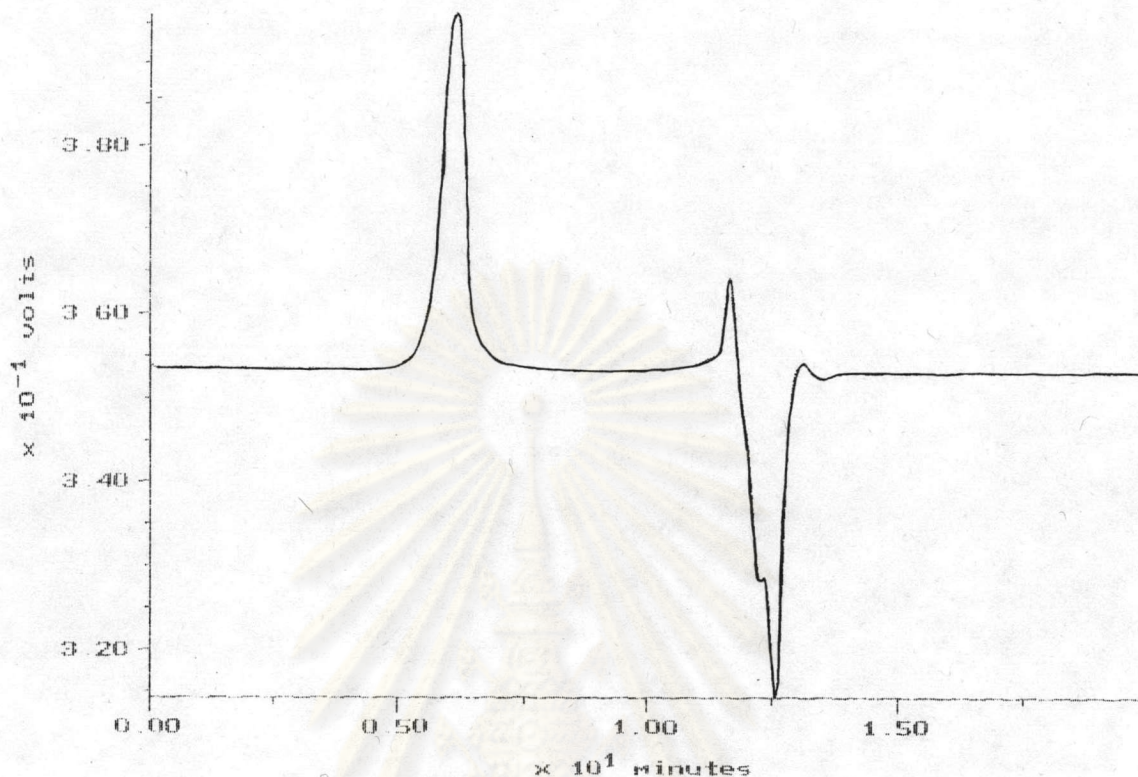
Number Average : 43020
 Weight Average : 237487
 Viscosity Average : 237487
 Z Average : 3625803
 Z+1 Average : 7560329

Polydispersity : 5.520440
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 15.267418
 Z+1 avg / Wt avg : 31.334753

Peak Maximum:

Slice # : 17
 Molecular Wt : 95656

Figure B.6 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 2.0 % by weight of initiator



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 12:54
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S0826R

ANALYSIS PARAMETERS:

Processing Start : 5.08 minutes
 Processing End : 7.66 minutes
 Number of Slices : 16
 Slice Width : 10 seconds

Baseline Start : 2.86 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 92299	
Weight Average : 107290	Polydispersity : 1.162415
Viscosity Average : 107290	Intrinsic viscosity : 0.000000
Z Average : 123349	Z avg / Wt avg : 1.149683
Z+1 Average : 143287	Z+1 avg / Wt avg : 1.335517

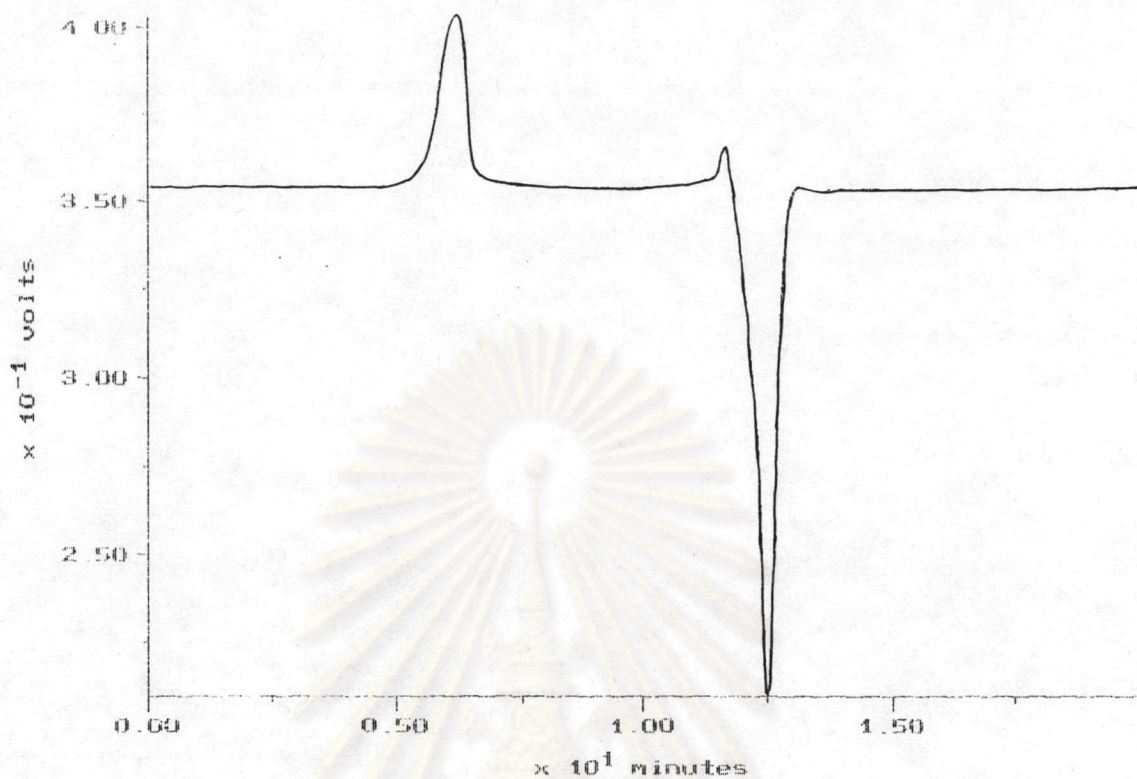
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 92299	
Weight Average : 107290	Polydispersity : 1.162415
Viscosity Average : 107290	Intrinsic viscosity : 0.000000
Z Average : 123349	Z avg / Wt avg : 1.149683
Z+1 Average : 143287	Z+1 avg / Wt avg : 1.335517

Peak Maximum:

Slice # : 7
 Molecular Wt : 90979

Figure B.7 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 50 °C 0 psig..



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 13:15
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S09261

ANALYSIS PARAMETERS:

Processing Start : 4.94 minutes
 Processing End : 7.66 minutes
 Number of Slices : 17
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 90413
 Weight Average : 107030
 Viscosity Average : 107030
 Z Average : 126062
 Z+1 Average : 151545

Polydispersity : 1.183785
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.177828
 Z+1 avg / Wt avg : 1.415920

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

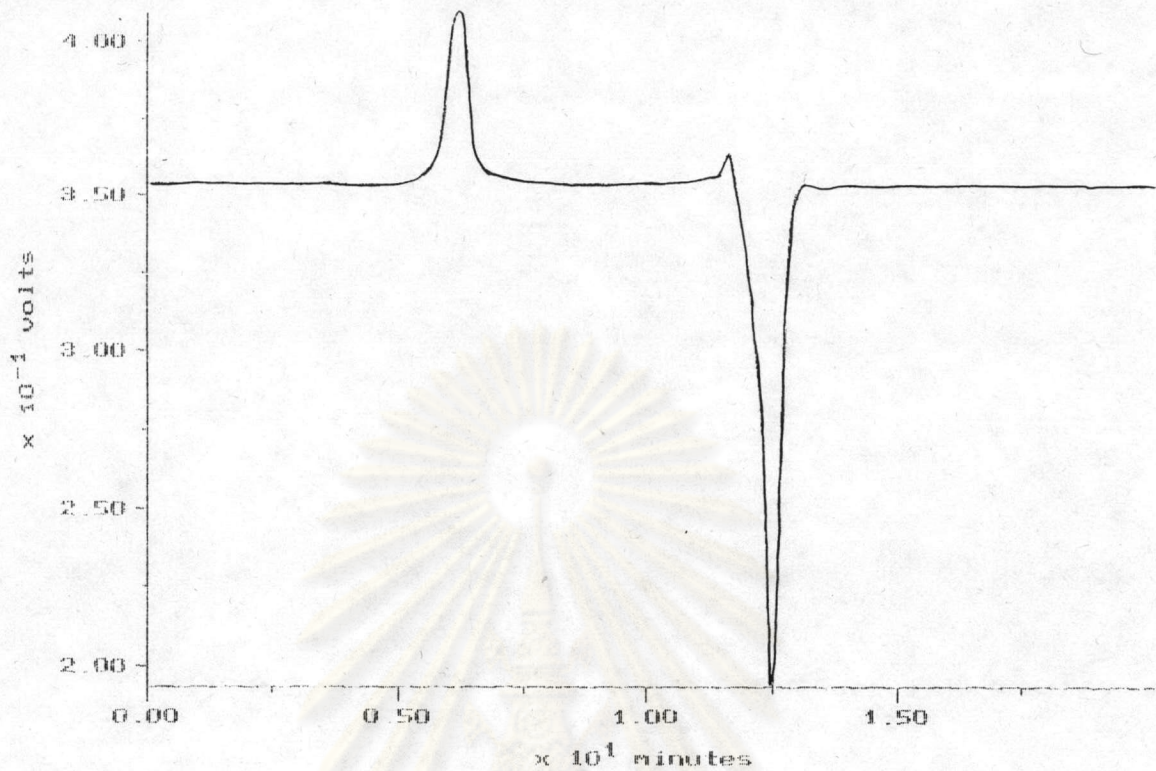
Number Average : 90413
 Weight Average : 107030
 Viscosity Average : 107030
 Z Average : 126062
 Z+1 Average : 151545

Polydispersity : 1.183785
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.177828
 Z+1 avg / Wt avg : 1.415920

Peak Maximum:

Slice # : 8
 Molecular Wt : 87325

Figure B.8 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 50 °C 20 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 12:34
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S0826G

ANALYSIS PARAMETERS:

Processing Start : 5.13 minutes
 Processing End : 7.66 minutes
 Number of Slices : 16
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 80222
 Weight Average : 95291
 Viscosity Average : 95291
 Z Average : 109630
 Z+1 Average : 126742

Polydispersity : 1.187842
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.150436
 Z+1 avg / Wt avg : 1.330058

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log WW)/dt]):

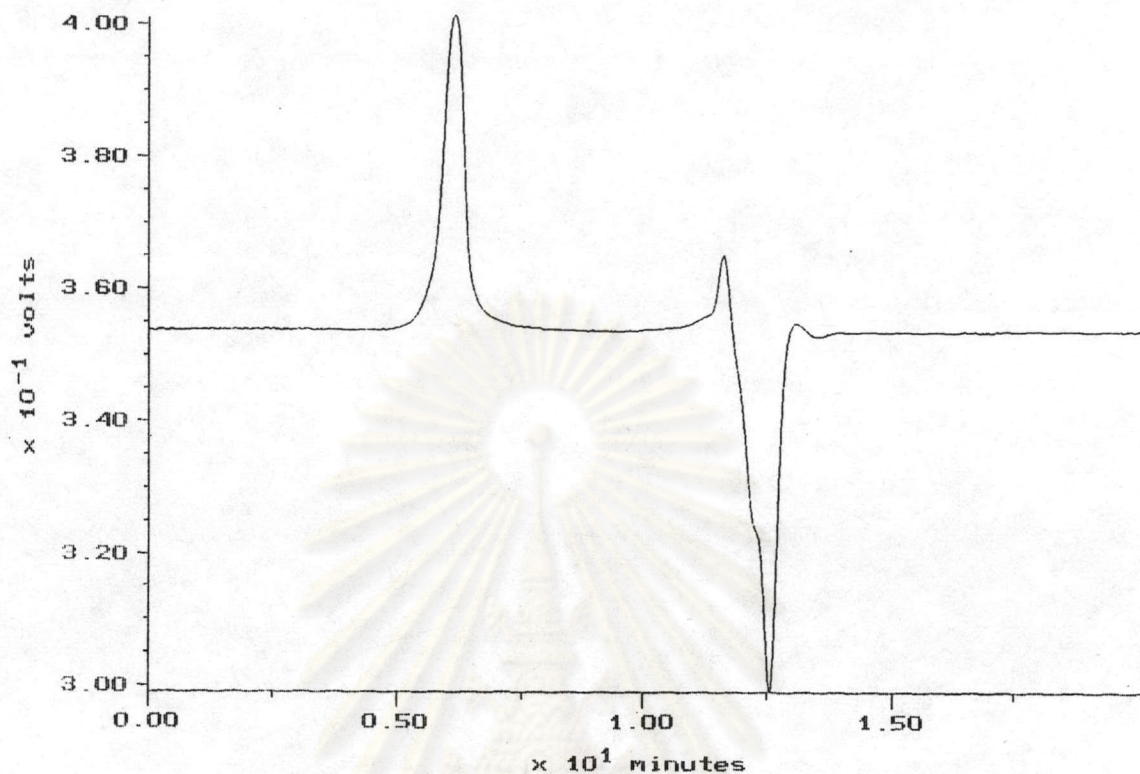
Number Average : 80222
 Weight Average : 95291
 Viscosity Average : 95291
 Z Average : 109630
 Z+1 Average : 126742

Polydispersity : 1.187842
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.150436
 Z+1 avg / Wt avg : 1.330058

Peak Maximum:

Slice # : 7
 Molecular Wt : 84631

Figure B.9 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 50 °C 40 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 13:36
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S08267

ANALYSIS PARAMETERS:

Processing Start : 4.94 minutes
 Processing End : 7.83 minutes
 Number of Slices : 18
 Slice Width : 10 seconds

Baseline Start : 2.98 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 85303
 Weight Average : 101969
 Viscosity Average : 101969
 Z Average : 118887
 Z+1 Average : 141383

Polydispersity : 1.195370
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.165914
 Z+1 avg / Wt avg : 1.386528

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

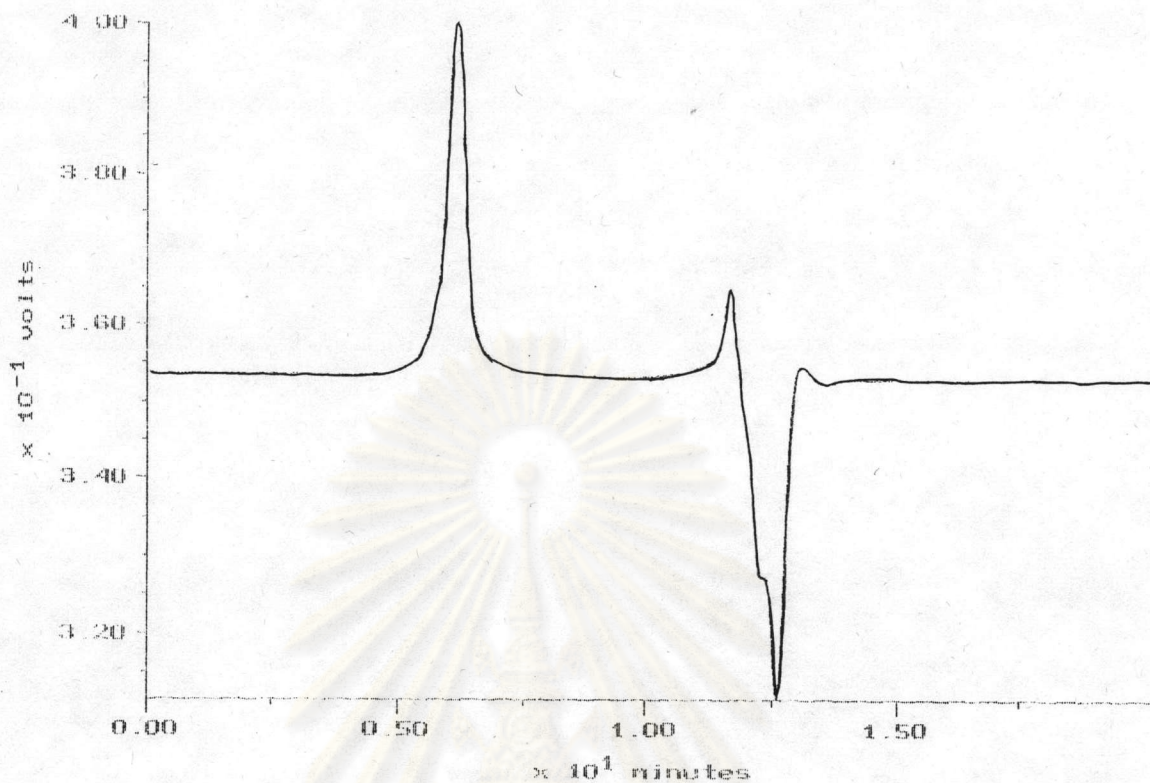
Number Average : 85303
 Weight Average : 101969
 Viscosity Average : 101969
 Z Average : 118887
 Z+1 Average : 141383

Polydispersity : 1.195370
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.165914
 Z+1 avg / Wt avg : 1.386528

Peak Maximum:

Slice # : 8
 Molecular Wt : 87325

Figure B.10 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 60 °C 20 psig.



SAMPLE: REVIEW

Method :
 Acquired : 25-AUG-1996 11:31
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S08250

ANALYSIS PARAMETERS:

Processing Start : 4.99 minutes
 Processing End : 7.88 minutes
 Number of Slices : 18
 Slice Width : 10 seconds

Baseline Start : 2.83 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 82796	Polydispersity : 1.202474
Weight Average : 99561	Intrinsic viscosity : 0.000000
Viscosity Average : 99561	Z avg / Wt avg : 1.187022
Z Average : 118181	Z+1 avg / Wt avg : 1.448648
Z+1 Average : 144228	

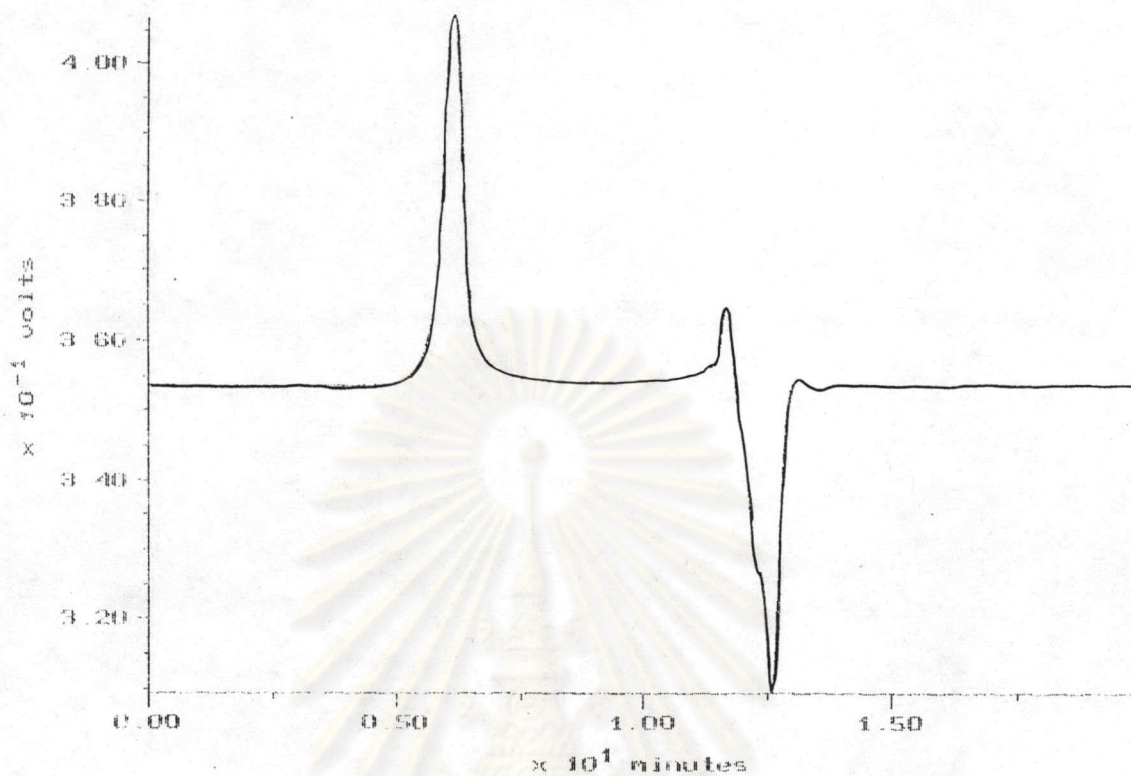
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 82796	Polydispersity : 1.202474
Weight Average : 99561	Intrinsic viscosity : 0.000000
Viscosity Average : 99561	Z avg / Wt avg : 1.187022
Z Average : 118181	Z+1 avg / Wt avg : 1.448648
Z+1 Average : 144228	

Peak Maximum:

Slice # : 8
 Molecular Wt : 82117

Figure B.11 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 60 °C 40 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 10:50
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : 508268

ANALYSIS PARAMETERS:

Processing Start : 5.04 minutes
 Processing End : 8.24 minutes
 Number of Slices : 20
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 74071	Polydispersity : 1.305673
Weight Average : 96712	Intrinsic viscosity : 0.000000
Viscosity Average : 96712	Z avg / Wt avg : 1.185140
Z Average : 114618	Z+1 avg / Wt avg : 1.409554
Z+1 Average : 136321	

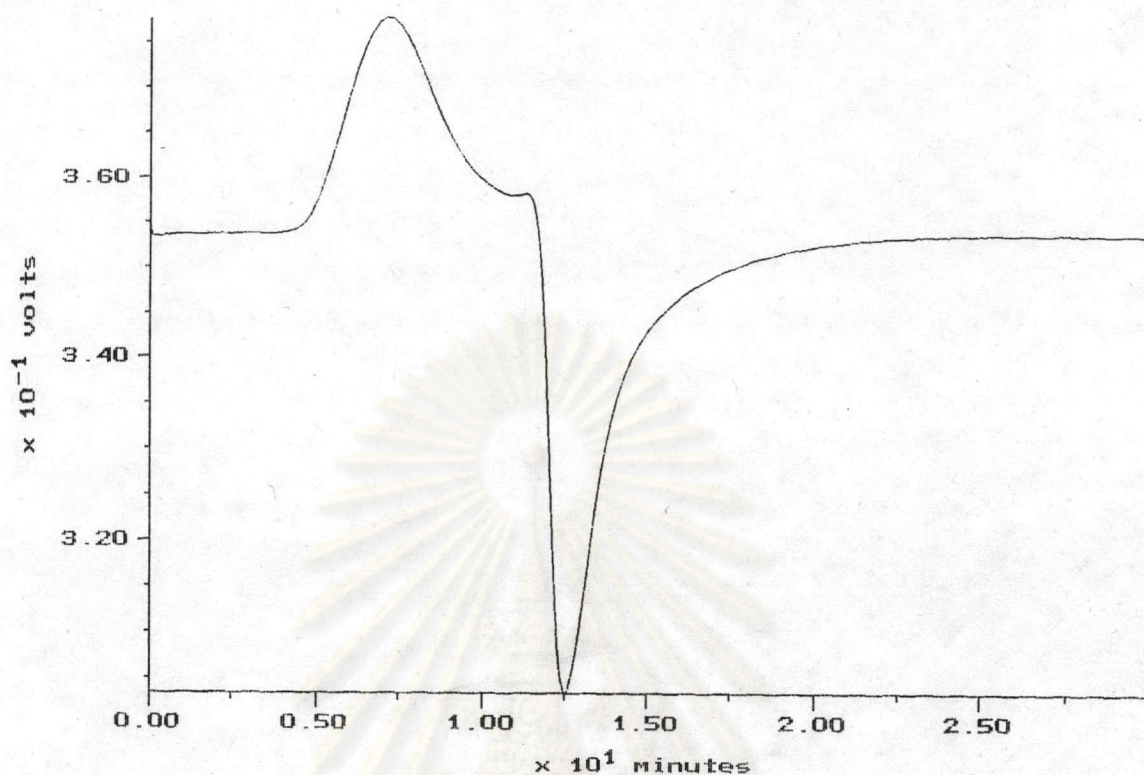
Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 74071	Polydispersity : 1.305673
Weight Average : 96712	Intrinsic viscosity : 0.000000
Viscosity Average : 96712	Z avg / Wt avg : 1.185140
Z Average : 114618	Z+1 avg / Wt avg : 1.409554
Z+1 Average : 136321	

Peak Maximum:

Slice # : 7
 Molecular Wt : 94756

Figure B.12 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 70 °C 20 psig.



SAMPLE: REVIEW

Method :
 Acquired : 31-OCT-1994 14:34
 Rate : 2.000 g/min sec
 Duration : 30.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : J10319 7/20/94

ANALYSIS PARAMETERS:

Processing Start : 4.18 minutes
 Processing End : 10.36 minutes
 Number of Slices : 39
 Slice Width : 10 seconds

Baseline Start : 2.00 minutes
 Baseline End : 25.95 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 61522
 Weight Average : 418679
 Viscosity Average : 418679
 Z Average : 2182647
 Z+1 Average : 4756079

Polydispersity : 6.805403
 Intrinsic viscosity : 0.300000
 Z avg / Wt avg : 5.213172
 Z+1 avg / Wt avg : 11.359720

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

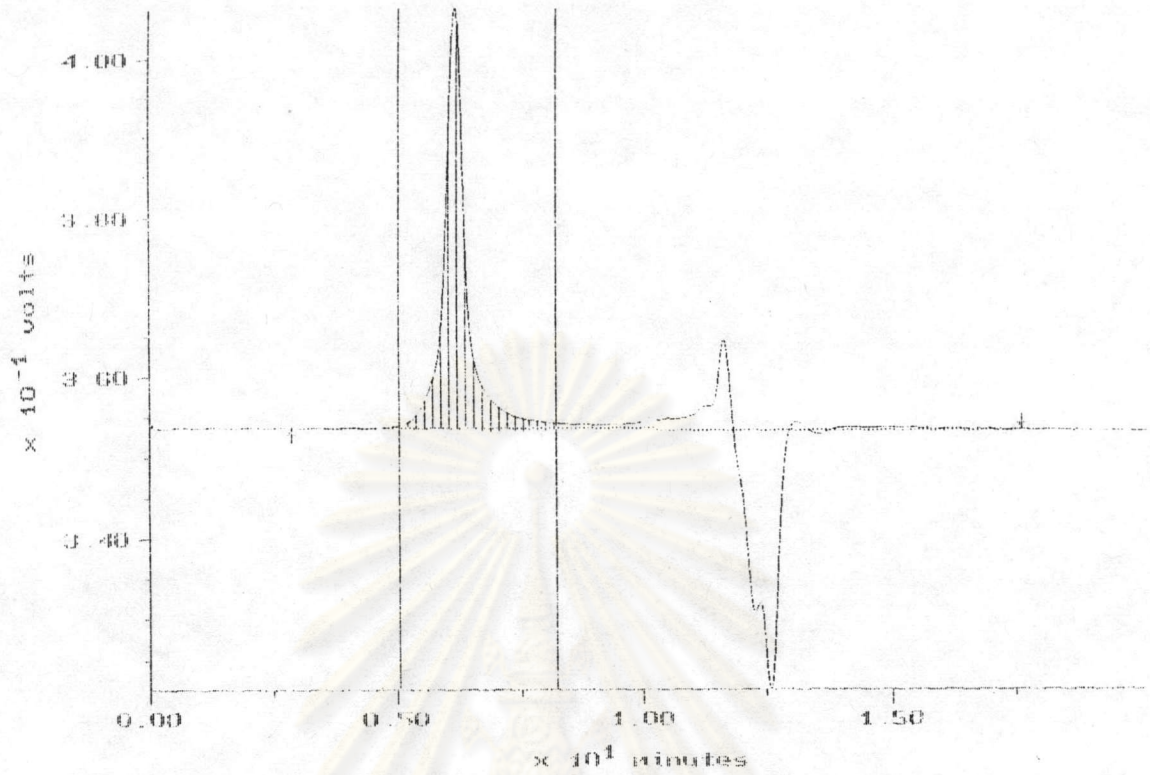
Number Average : 72239
 Weight Average : 255909
 Viscosity Average : 285909
 Z Average : 1205328
 Z+1 Average : 3769330

Polydispersity : 3.957816
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 4.215767
 Z+1 avg / Wt avg : 13.163824

Peak Maximum:

Slice # : 18
 Molecular Wt : 233878

Figure B.13 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 70 °C 30 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1995 10:29
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S3825A

ANALYSIS PARAMETERS:

Processing Start : 5.04 minutes
 Processing End : 8.24 minutes
 Number of Slices : 20
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 68432
 Weight Average : 91572
 Viscosity Average : 91572
 Z Average : 109364
 Z+1 Average : 131010

Polydispersity : 1.338148
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.194288
 Z+1 avg / Wt avg : 1.430669

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log NW)/dt]):

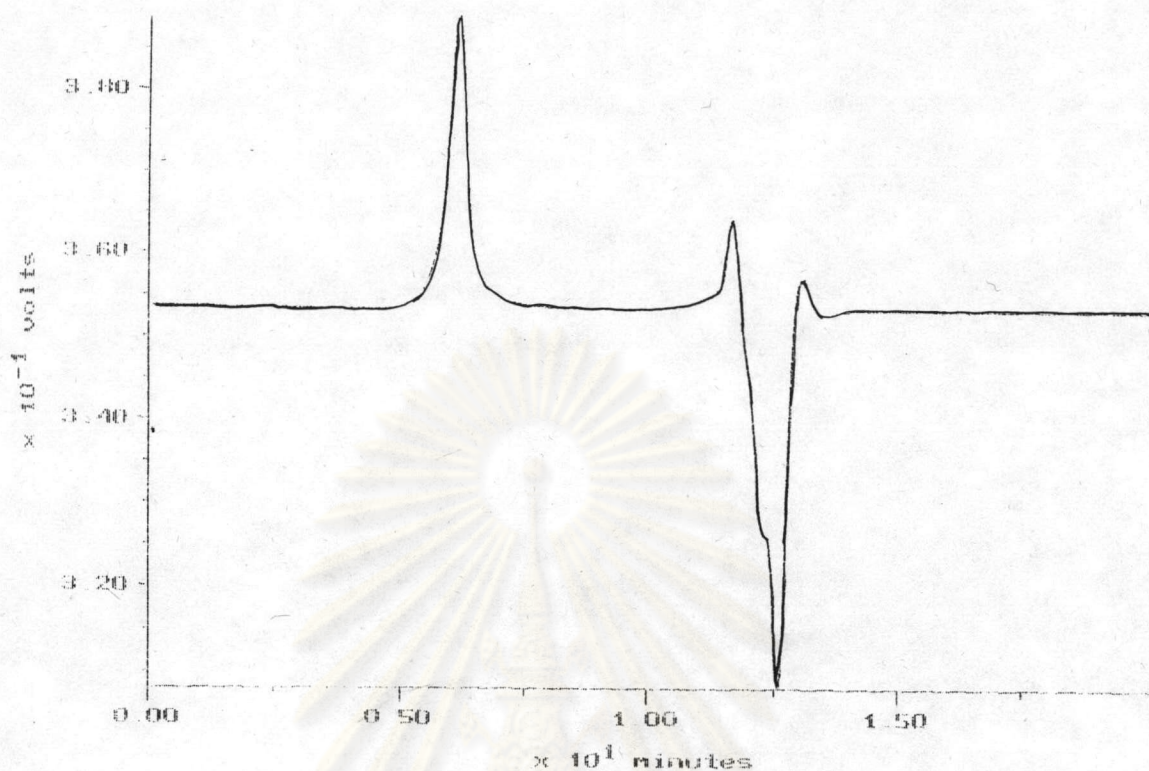
Number Average : 68432
 Weight Average : 91572
 Viscosity Average : 91572
 Z Average : 109364
 Z+1 Average : 131010

Polydispersity : 1.338148
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.194288
 Z+1 avg / Wt avg : 1.430669

Peak Maximum:

Slice # : 7
 Molecular Wt : 94786

Figure B.14 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 70 °C 40 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 12:11
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S0825F

ANALYSIS PARAMETERS:

Processing Start : 4.99 minutes
 Processing End : 7.65 minutes
 Number of Slices : 16
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 84737
 Weight Average : 102241
 Viscosity Average : 102241
 Z Average : 120698
 Z+1 Average : 144605

Polydispersity : 1.236579
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.180516
 Z+1 avg / Wt avg : 1.414357

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

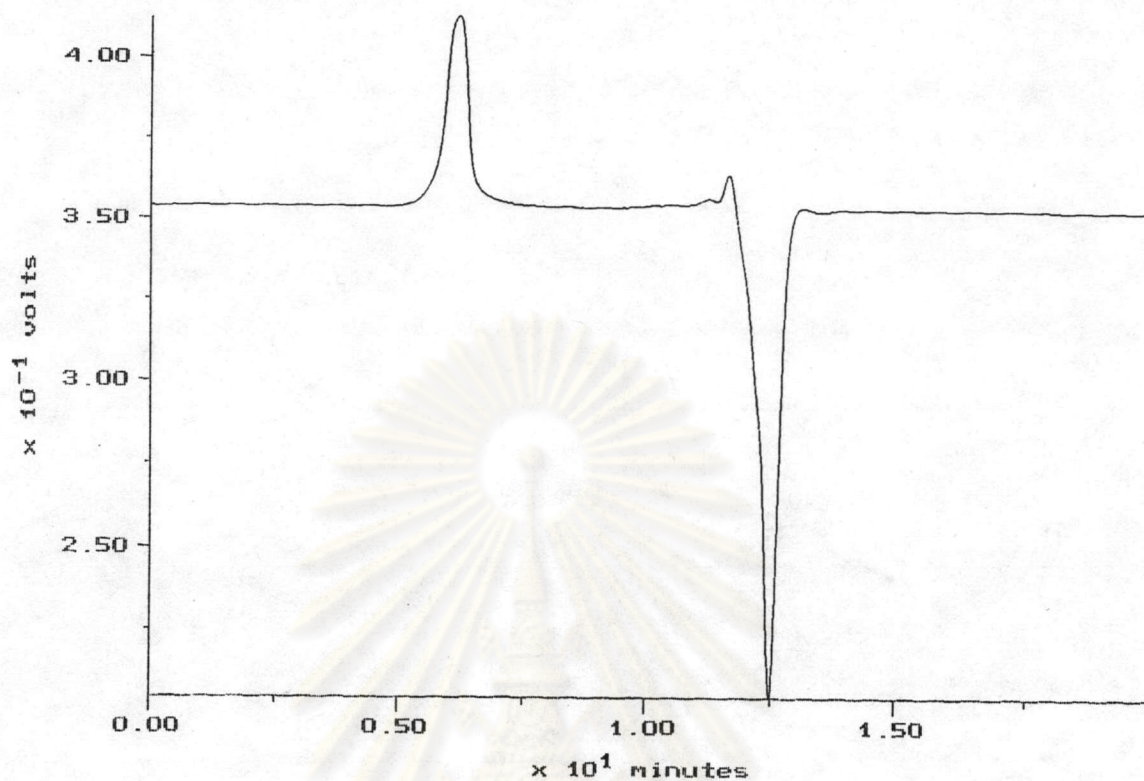
Number Average : 84737
 Weight Average : 102241
 Viscosity Average : 102241
 Z Average : 120698
 Z+1 Average : 144606

Polydispersity : 1.206579
 Intrinsic viscosity : 0.000000
 Z avg / Wt avg : 1.180516
 Z+1 avg / Wt avg : 1.414357

Peak Maximum:

Slice # : 7
 Molecular Wt : 100798

Figure B.15 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 80 °C 20 psig.



SAMPLE: REVIEW

Method :
 Acquired : 26-AUG-1996 14:17
 Rate : 2.000 points/sec
 Duration : 20.000 minutes
 Operator :

Instrument : Instrument 1
 Filename : S0826L

ANALYSIS PARAMETERS:

Processing Start : 5.00 minutes
 Processing End : 8.05 minutes
 Number of Slices : 19
 Slice Width : 10 seconds

Baseline Start : 2.88 minutes
 Baseline End : 17.62 minutes

Calibration : Narrow Standards

DETECTOR: detector 1

Molecular Weight Distribution Averages (Area Normalization [W(t)]):

Number Average : 82757
 Weight Average : 99112
 Viscosity Average : 99112
 Z Average : 114795
 Z+1 Average : 135159

Polydispersity : 1.197618
 Intrinsic viscosity : 0.060000
 Z avg / Wt avg : 1.158244
 Z+1 avg / Wt avg : 1.363705

Molecular Weight Distribution Averages (Molecular Weight Normalization [W(t) / -d(log MW)/dt]):

Number Average : 82757
 Weight Average : 99112
 Viscosity Average : 99112
 Z Average : 114795
 Z+1 Average : 135159

Polydispersity : 1.197618
 Intrinsic viscosity : 0.060000
 Z avg / Wt avg : 1.158244
 Z+1 avg / Wt avg : 1.363705

Peak Maximum:

Slice # : 8
 Molecular Wt : 81280

Figure B.16 GPC chromatogram of free SAN extracted from the products of graft copolymerization at 80 °C 40 psig.

APPENDIX C

Table CI. The ratio of acrylonitrile and styrene in free SAN calculated from the specific peak area of FTIR spectra.

Pressure (psig)	Temp. (°C)	Peak area at		Styrene:Acrylonitrile
		1510 cm ⁻¹	2238 cm ⁻¹	
0	50	292.148	549.093	34.7:65.3
20	50	237.063	301.054	44.1:55.9
	60	238.873	335.202	41.6:58.4
	70	347.098	592.383	36.9:63.1
	80	188.697	294.056	39.1:60.9
30	70	187.474	339.555	35.6:64.4
40	50	166.139	190.391	46.6:53.4
	60	242.187	417.796	36.7:63.3
	70	202.588	395.837	33.9:66.1
	80	265.308	522.072	33.7:66.3

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Table CII. The ratio of acrylonitrile, isoprene and styrene in grafted natural rubber calculated from the specific peak area of FTIR spectra.

Pressure (psig)	Temp. (°C)	Peak area at			Isoprene:Styrene :Acrylonitrile
		810 cm ⁻¹	1510 cm ⁻¹	2238 cm ⁻¹	
0	50	165.892	155.218	82.58	75.5:8.5:16.0
20	50	671.315	134.896	171.309	69.3:13.5:17.2
	60	1197.823	246.935	175.972	73.9:10.9:15.2
	70	410.471	181.844	164.481	58.7:15.3:26.0
	80	255.277	90.372	57.992	63.2:14.4:22.4
30	70	165.892	86.731	47.880	55.1:16.0:28.9
40	50	165.361	107.686	93.969	65.4:16.1:18.5
	60	684.565	140.408	81.39	75.5:9.0:15.5
	70	453.142	245.056	125.419	55.0:15.2:29.8
	80	165.583	78.534	39.910	58.2:14.1:27.7

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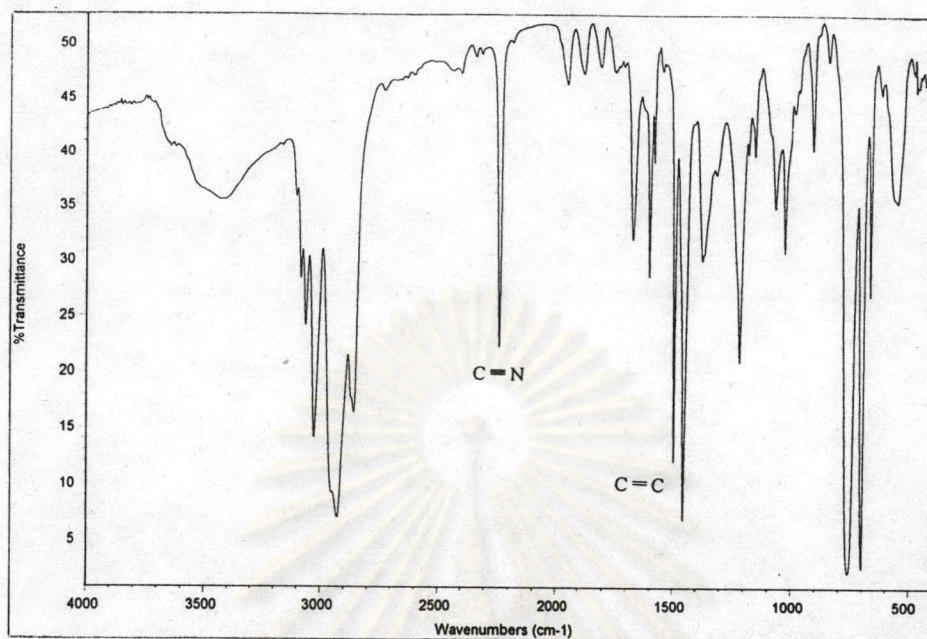


Figure C.1 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 50 °C 0 psig.

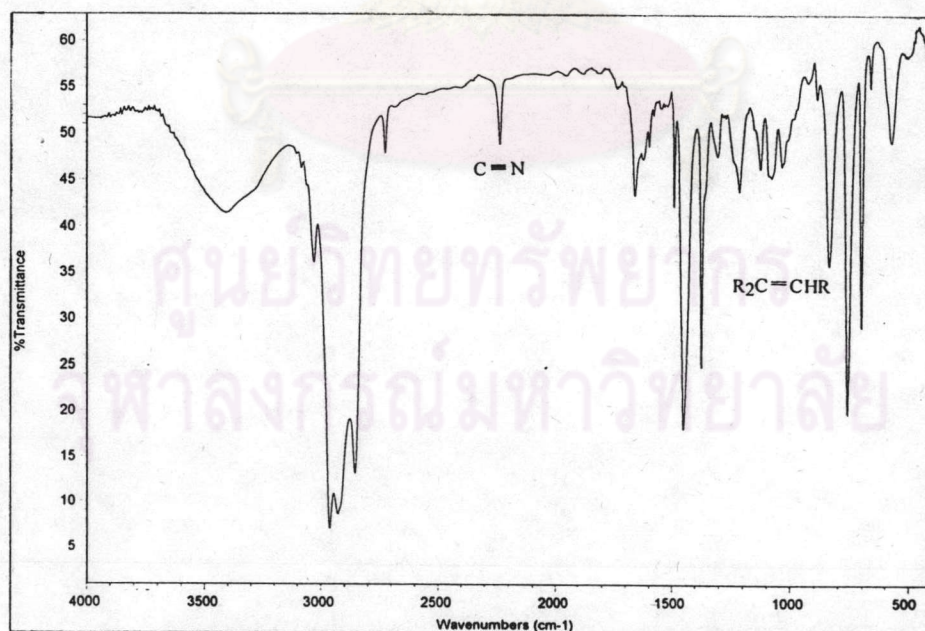


Figure C.2 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 50 °C 0 psig.

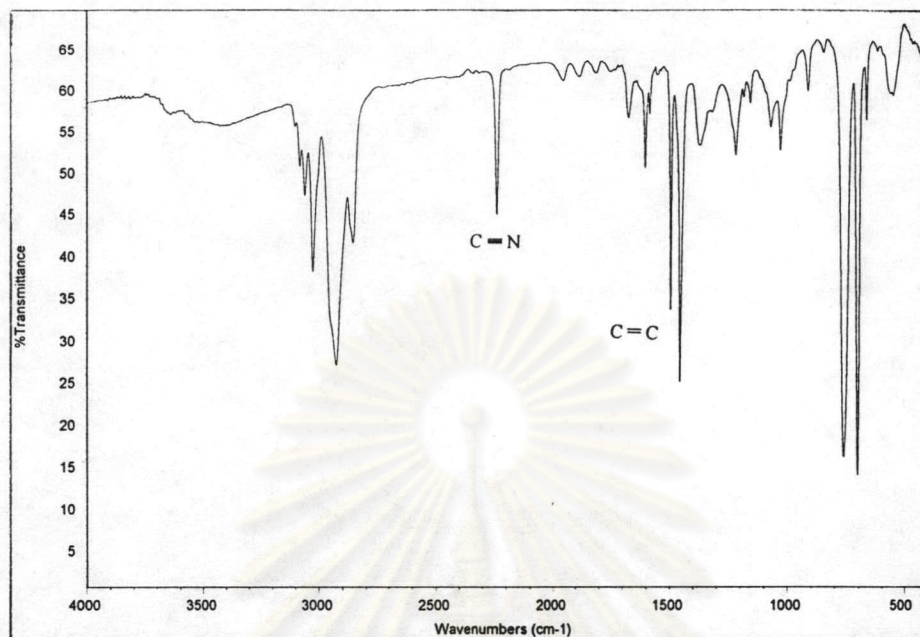


Figure C.3 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 50 °C 20 psig.

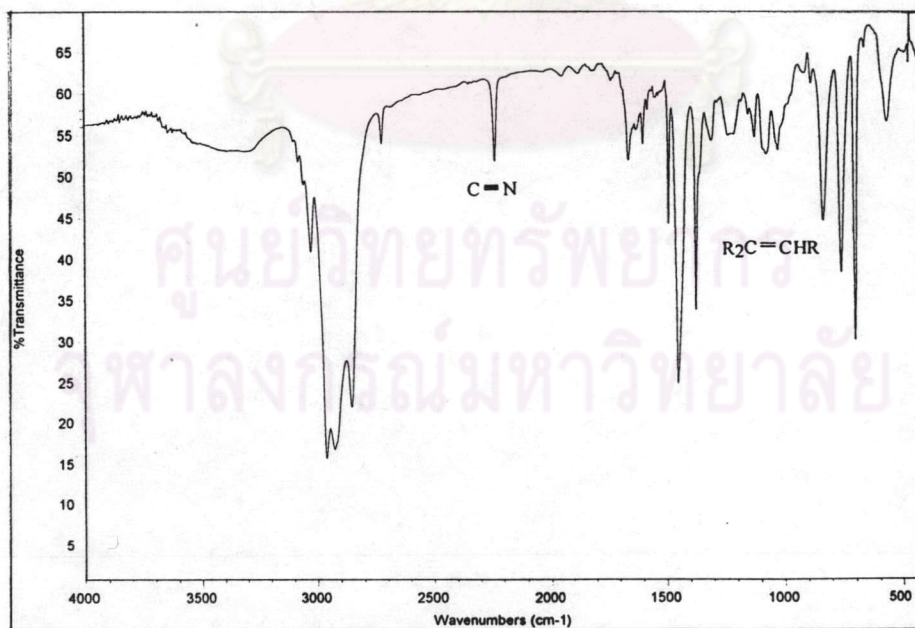


Figure C.4 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 50 °C 20 psig.

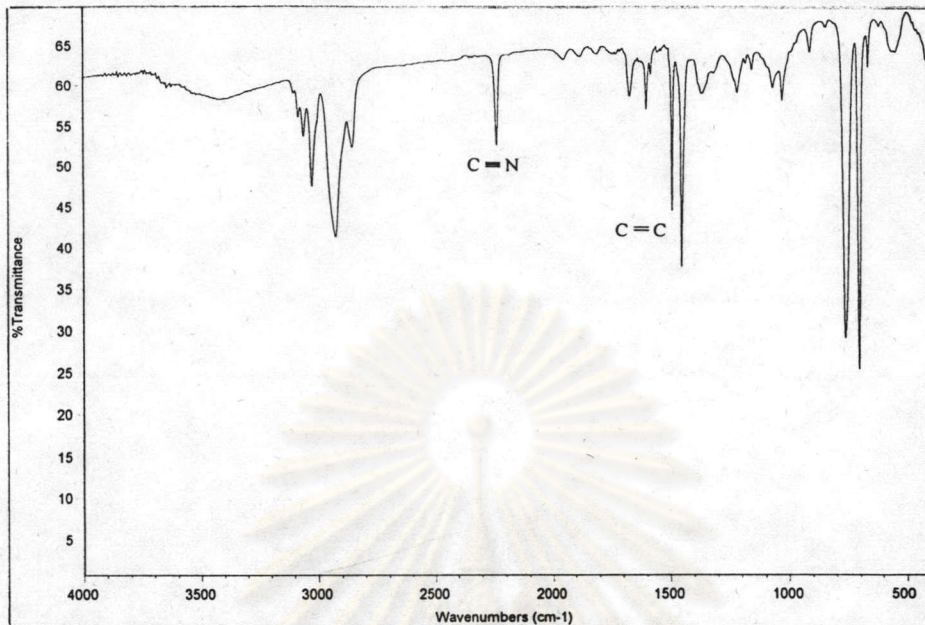


Figure C.5 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 50 °C 40 psig.

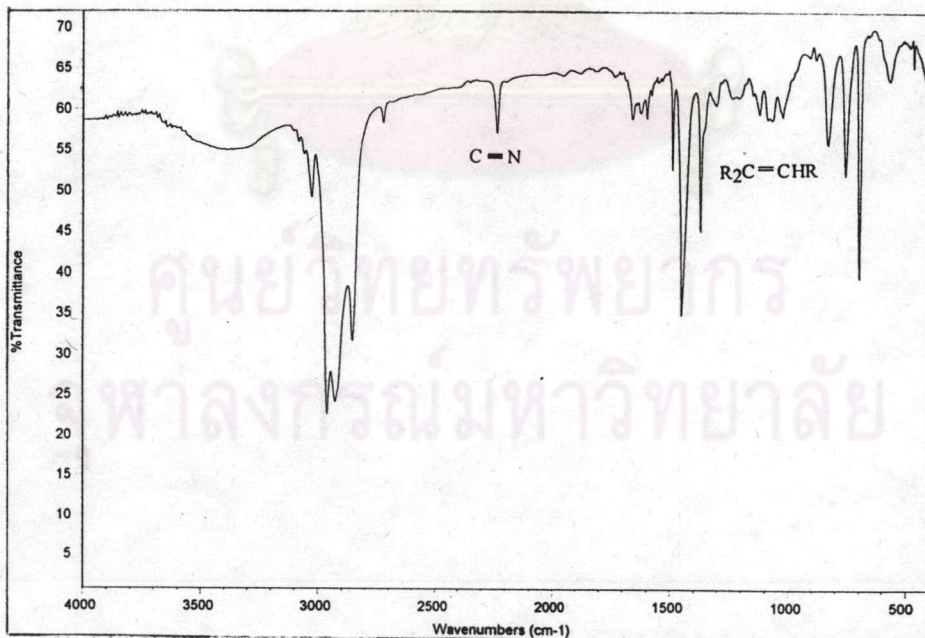


Figure C.6 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 50 °C 40 psig.

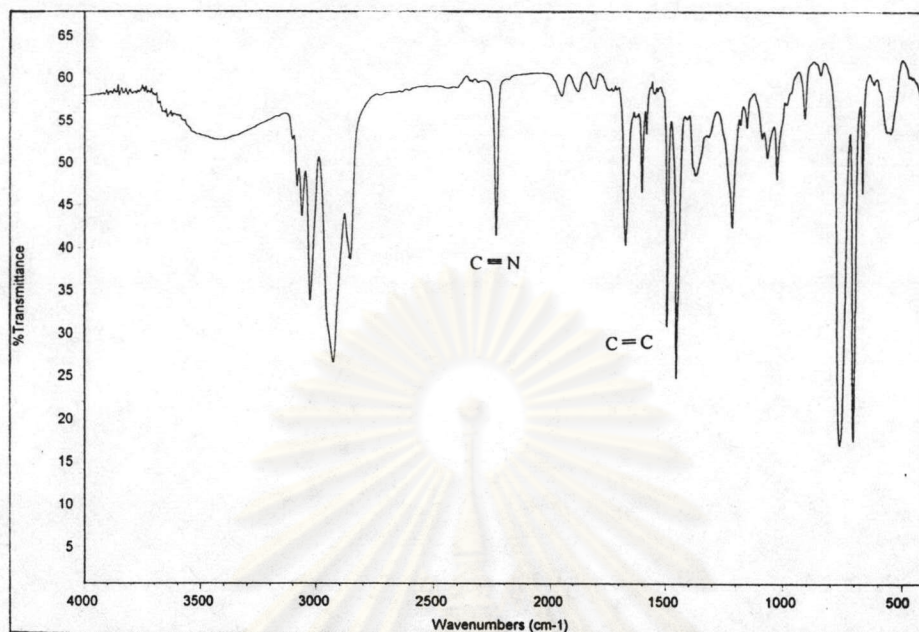


Figure C.7 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 60 °C 20 psig.

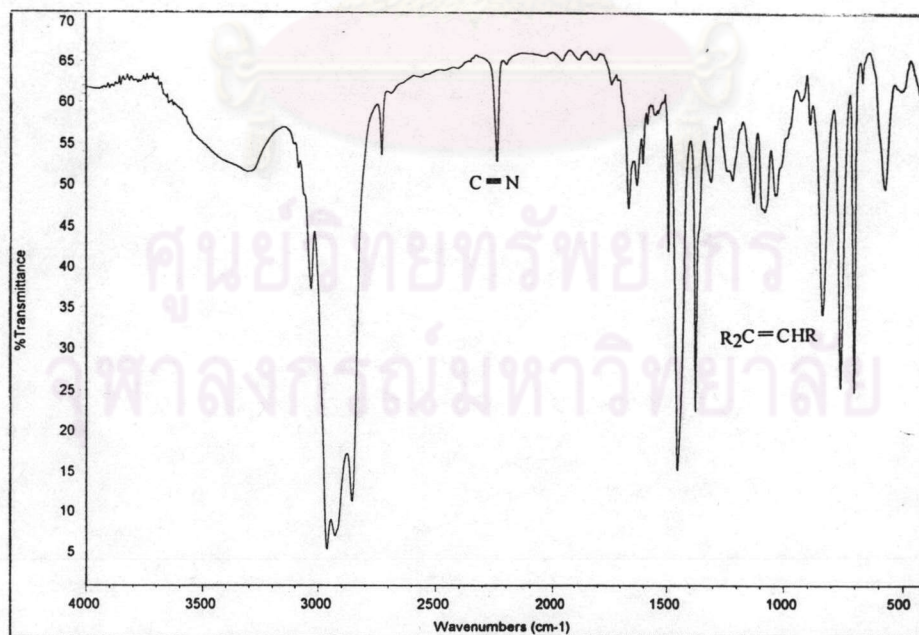


Figure C.8 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 60 °C 20 psig.

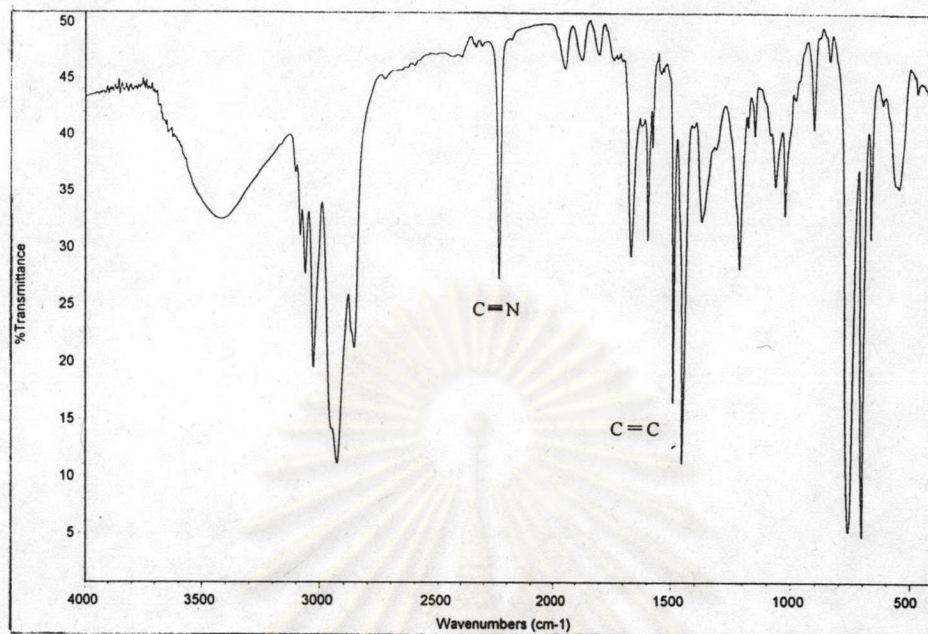


Figure C.9 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 60 °C 40 psig.

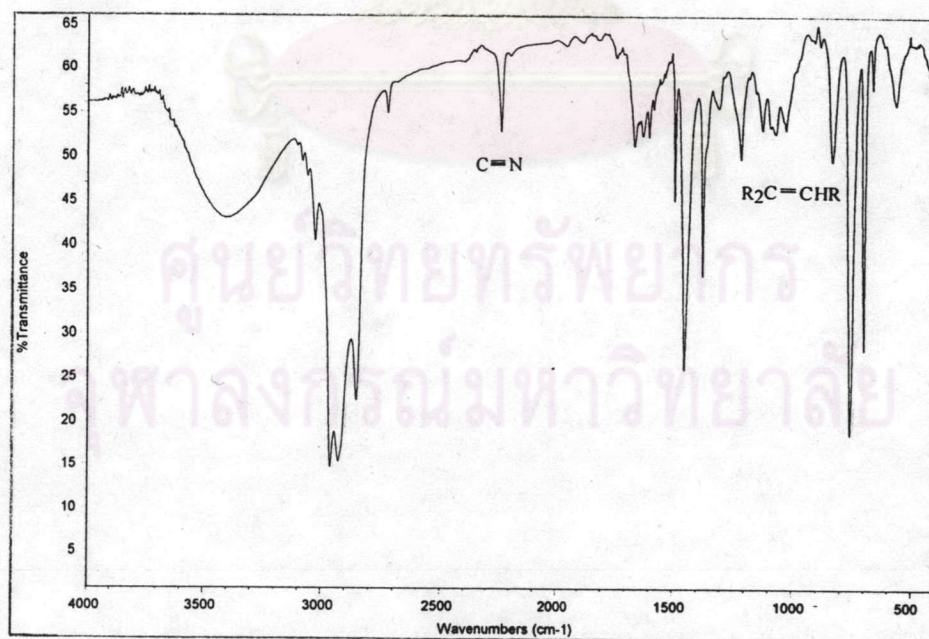


Figure C.10 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 60 °C 40 psig.

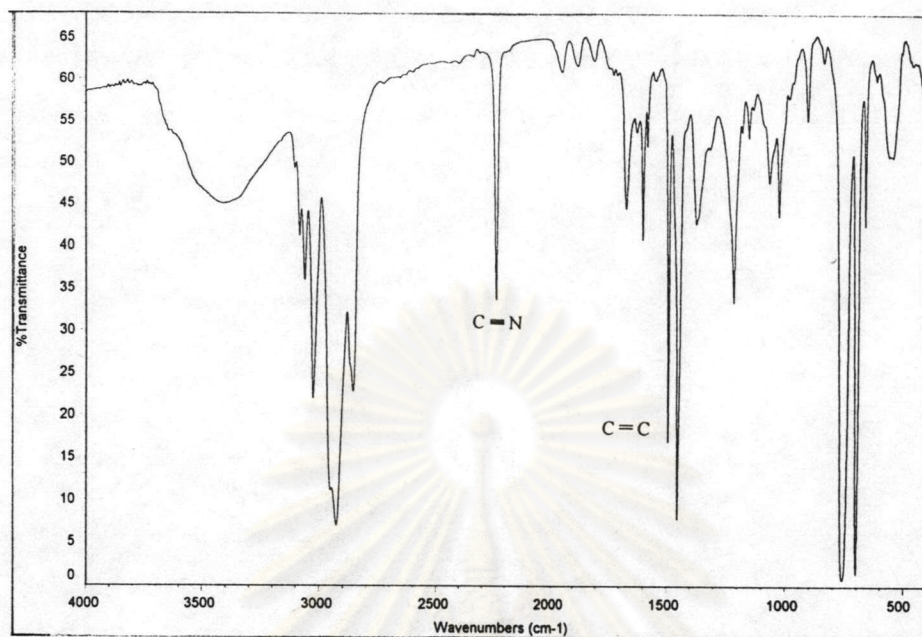


Figure C.11 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 70 °C 20 psig.

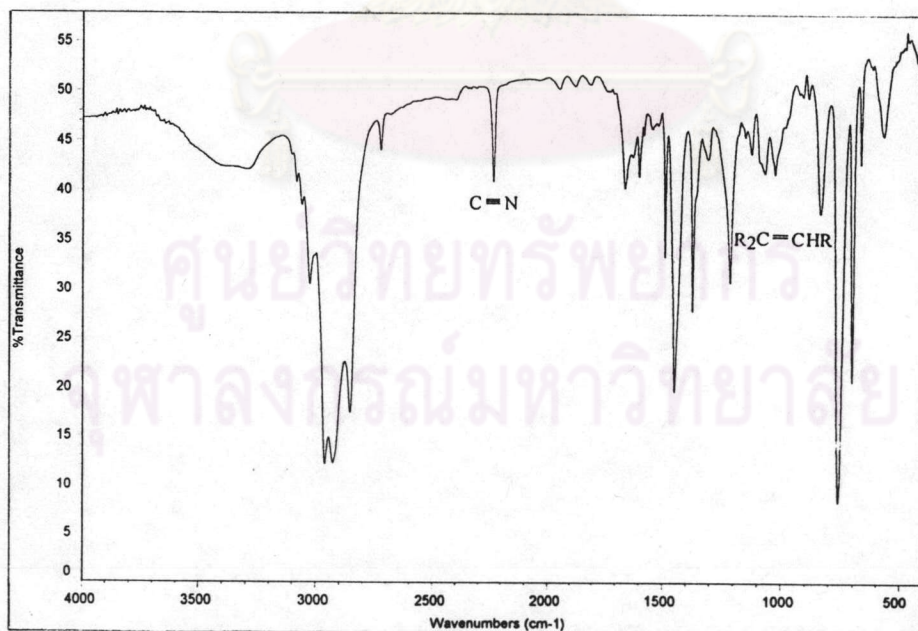


Figure C.12 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 70 °C 20 psig.

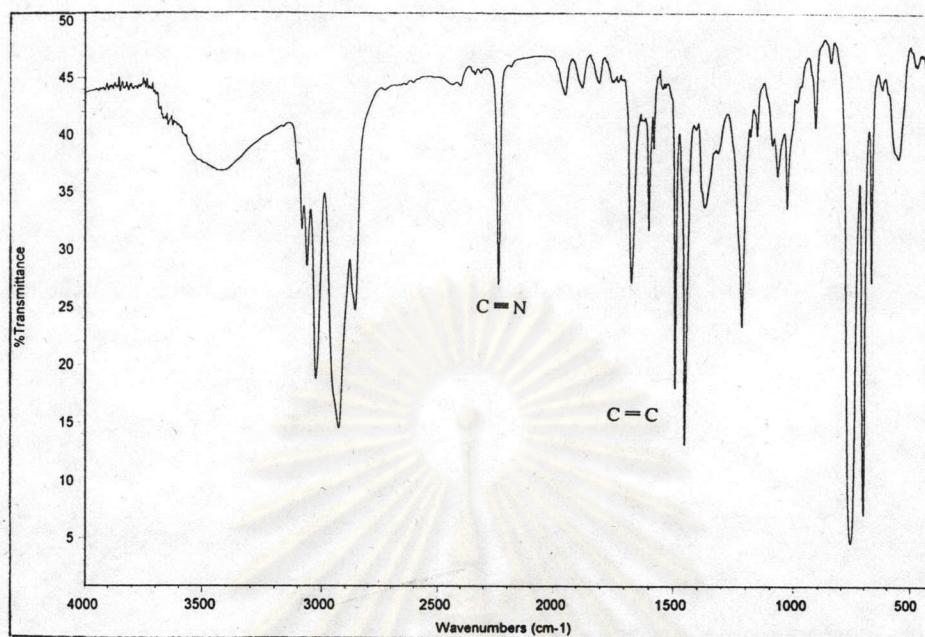


Figure C.13 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 70 °C 30 psig.

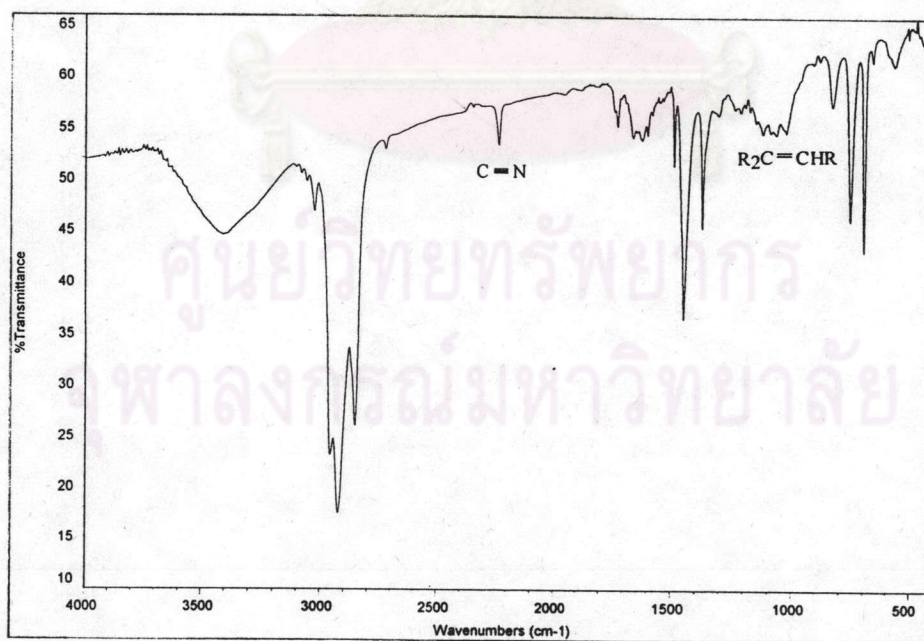


Figure C.14 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 70 °C 30 psig.

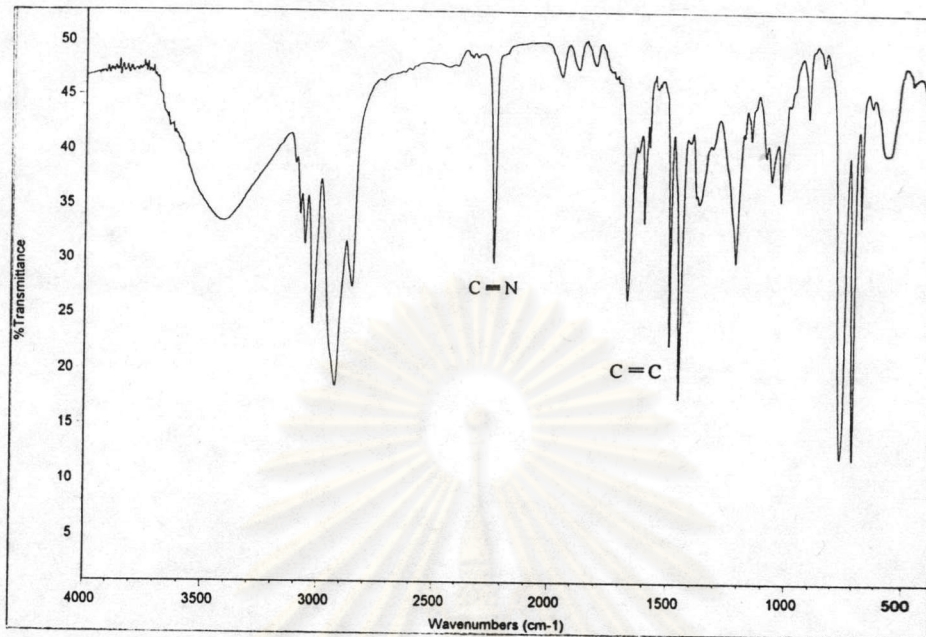


Figure C.15 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 70 °C 40 psig.

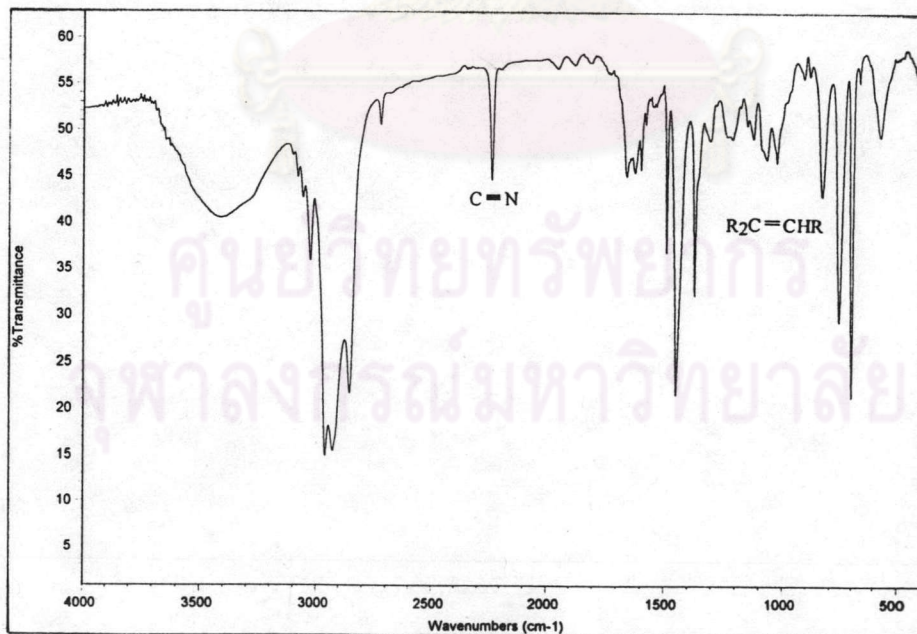


Figure C.16 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 70 °C 40 psig.

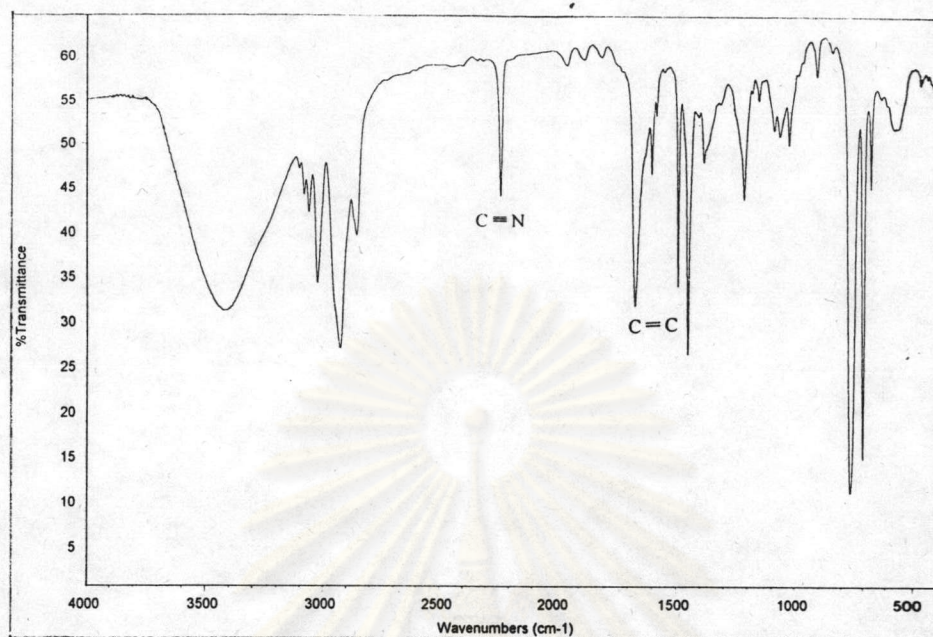


Figure C.17 FTIR spectrum of free SAN extracted from the products of graft copolymerization at 80 °C 20 psig.

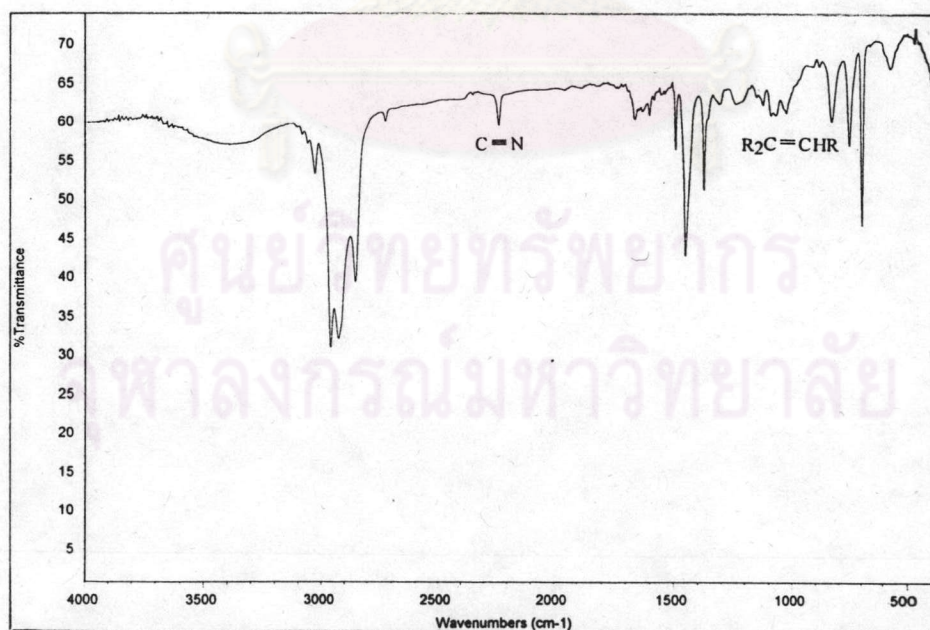


Figure C.18 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 80 °C 20 psig.

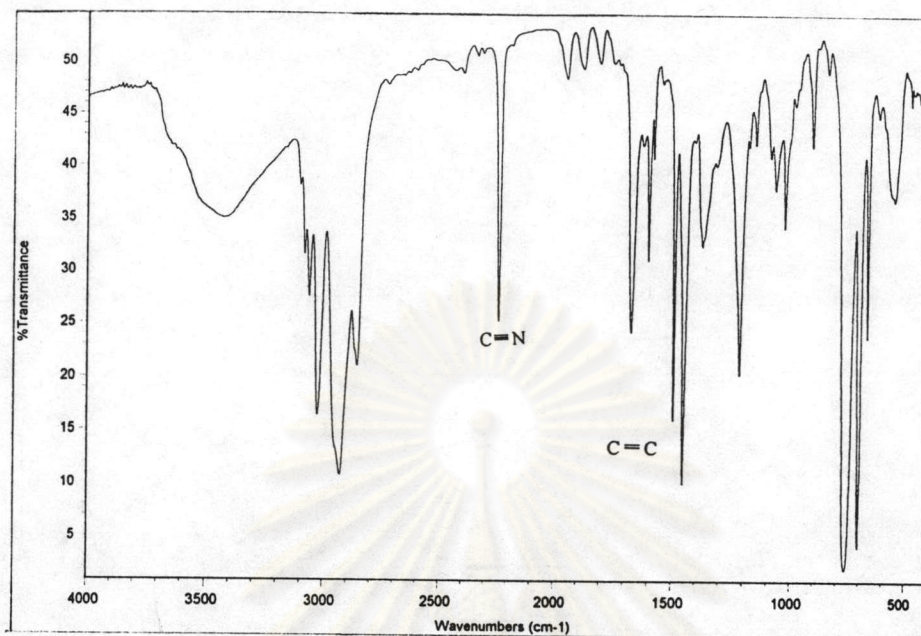


Figure C.19 FTIR spectrum of graft natural rubber extracted from the products of graft copolymerization at 80 °C 40 psig.

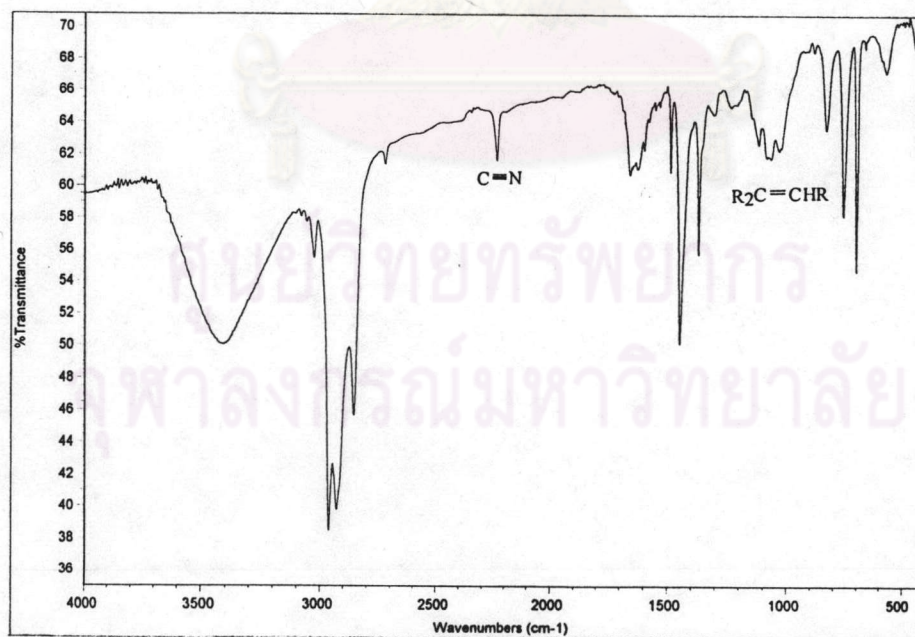


Figure C.20 FTIR spectrum of grafted natural rubber extracted from the products of graft copolymerization at 80 °C 40 psig.

APPENDIX D

Table D. Compositions of grafted natural rubber by CHN\O analyzer.

Pressure (psig)	Temp. (°C)	C : H : N
0	50	84.95 : 10.05 : 3.72
20	50	84.33 : 9.90 : 3.81
	60	83.58 : 9.99 : 3.23
	70	82.27 : 9.54 : 5.38
	80	84.72 : 9.74 : 4.18
30	70	80.78 : 9.23 : 5.52
40	50	85.55 : 10.08 : 3.90
	60	84.38 : 9.86 : 3.45
	70	83.57 : 9.64 : 5.29
	80	81.87 : 9.25 : 5.16

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Determination of Copolymer Compositions of CHN\O Method

Example of Calculation

1) For grafted natural rubber : from graft copolymerization at 50 °C 20 psig.

$$\begin{aligned} \text{Assume } A : I : S &= a : b : c \text{ mole \%} \\ (C_3H_3N) \text{ Acrylonitrile} &= a[C_3H_3N] \\ (C_5H_8) \text{ Isoprene} &= b[C_5H_8] \\ (C_8H_8) \text{ Styrene} &= c[C_8H_8] \end{aligned}$$

$$\begin{aligned} \text{From CHN\O method } C : H : N &= 84.33 : 9.90 : 3.81 \\ \text{Carbon } C &= [3a + 5b + 8c] \times 12 = 84.33 \text{ gm} \quad (1.1) \\ \text{Hydrogen } H &= [3a + 8b + 8c] \times 1 = 9.90 \text{ gm} \quad (1.2) \\ \text{Nitrogen } N &= [a] \times 14 = 3.81 \text{ gm} \quad (1.3) \end{aligned}$$

$$\text{From Eq 1.3} \quad \therefore a = 0.27$$

$$\text{From Eq 1.1} \quad 0.81 + 5b + 8c = 7.03$$

$$\text{From Eq 1.2} \quad 0.81 + 8b + 8c = 9.90$$

$$5b + 8c = 6.22 \quad (1.4)$$

$$8b + 8c = 9.09 \quad (1.5)$$

$$(1.5) - (1.4) \quad 3b = 2.87 \quad (1.6)$$

$$b = 0.96$$

$$\text{Form Eq 1.1} \quad 0.81 + 5(0.96) + 8c = 7.03$$

$$c = 0.18$$

$$a + b + c = 0.27 + 0.96 + 0.18 = 1.41$$

$$a : b : c = 19.1 : 68.1 : 12.8 \text{ mole \%}$$

APPENDIX E

Table EI. Tensile strength of thermoplastic blends at various ratio of grafted NR and SAN.

Graft NR : SAN	Specimen	Width (mm)	Thickness (mm)	Tensile Strength (MPa)	Elongation at Break (%)
20 : 80	1	13	3.37	31.70	2.31
	2	13	3.37	31.89	2.28
	3	13	3.37	30.62	2.42
	4	13	3.37	30.58	2.59
	5	13	3.37	30.33	2.76
	Mean			31.02	2.47
	SD			0.72	0.18
30 : 70	1	13	3.36	30.36	12.04
	2	13	3.36	30.65	13.13
	3	13	3.36	30.88	13.88
	4	13	3.36	31.29	11.48
	5	13	3.36	31.14	10.24
	Mean			30.86	12.15
	SD			0.37	1.27
40 : 60	1	13	3.37	23.10	11.21
	2	13	3.37	23.42	10.31
	3	13	3.37	23.99	9.95
	4	13	3.37	23.49	10.23
	5	13	3.38	23.78	9.84
	Mean			23.56	10.31
	SD			0.34	0.48

Graft NR : SAN	Specimen	Width (mm)	Thickness (mm)	Tensile Strength (MPa)	Elongation at Break (%)
50 : 50	1	13	3.35	21.32	8.45
	2	13	3.37	20.68	8.09
	3	13	3.37	20.05	8.73
	4	13	3.38	20.81	8.20
	5	13	3.36	21.37	8.56
	Mean			20.85	8.41
	SD			0.54	0.23
SAN (120PC)	1	13	3.34	49.72	1.89
	2	13	3.36	52.17	1.41
	3	13	3.37	50.63	1.81
	4	13	3.35	52.16	1.57
	5	13	3.36	52.13	1.63
	Mean			51.36	1.66
	SD			1.13	0.17
ABS (MH-3)	1	13	3.35	32.73	2.34
	2	13	3.35	32.63	2.44
	3	13	3.35	32.80	2.29
	4	13	3.36	32.10	2.53
	5	13	3.35	32.00	2.25
	Mean			32.45	2.44
	SD			0.37	0.11

Table EII. Impact resistance of thermoplastic blends at various ratio of grafted natural rubber and SAN.

Graft NR : SAN	Specimen	Width (mm)	Depth (mm)	Impact Strength (J/m)
20 : 80	1	0.17	10.16	16.73
	2	0.17	10.16	16.73
	3	0.17	10.16	16.73
	4	0.17	10.16	16.73
	5	0.16	10.16	16.24
	Mean			16.63
	S.D.			0.23
30 : 70	1	0.13	10.16	12.79
	2	0.12	10.16	11.81
	3	0.13	10.16	12.79
	4	0.11	10.16	10.83
	5	0.13	10.16	12.79
	Mean			12.20
	S.D.			0.88
40 : 60	1	0.13	10.16	12.79
	2	0.13	10.16	12.79
	3	0.13	10.16	12.30
	4	0.12	10.16	12.79
	5	0.13	10.16	12.79
	Mean			12.69
	S.D.			0.22

Graft NR : SAN	Specimen	Width (mm)	Depth (mm)	Impact Strength (J/m)
50 : 50	1	0.16	10.16	15.75
	2	0.17	10.16	16.73
	3	0.17	10.16	16.73
	4	0.18	10.16	17.72
	5	0.17	10.16	16.73
	Mean			16.73
	S.D.			0.70
SAN (120PC)	1	0.07	10.16	6.89
	2	0.06	10.16	5.91
	3	0.07	10.16	6.89
	4	0.07	10.16	6.89
	5	0.06	10.16	5.91
	Mean			6.50
	SD			0.54
ABS (MH-3)	1	0.50	10.16	49.21
	2	0.55	10.16	54.13
	3	0.54	10.16	53.15
	4	0.50	10.16	49.21
	5	0.55	10.16	54.13
	Mean			51.97
	S.D.			2.55

Table EIII. Hardness (Shore D) of thermoplastic blends at various ratio of grafted NR and SAN.


Specimen No.	Hardness of Graft NR/SAN					
	20:80	30:70	40:60	50:50	SAN (120PC)	ABS (MH-3)
1	75.0	74.5	71.5	69.0	84.0	77.5
2	77.0	73.5	71.0	70.0	84.5	77.0
3	75.0	73.0	70.0	70.0	84.5	77.5
4	75.0	74.5	71.5	69.0	84.0	77.0
5	75.0	73.0	70.5	69.0	85.0	77.0
Mean	75.4	73.7	70.9	69.4	84.4	77.2
SD	0.9	0.8	0.6	0.5	0.4	0.3

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