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APPENDIX A

X-ray Photoelectron Spectra

X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB Mk II spectrometer using an Al anode at 260 watts (13 kV and 20 mA). Samples were mounted on the sample holders of 10 mm in diameter, and photoelectrons were collected from a central area of $4 \times 7 \text{ mm}^2$ at $5-8 \times 10^{-10}$ Torr.

The wide scan spectrum shows that only carbon and oxygen were present in the sample whose concentrations are higher than 0.3% on the surfaces of 5 polymers. The peak area of C1s and O1s and the ratio of O1s/C1s for each sample are summarized in Table A-1.

As shown in Table A-1, the O1s/C1s ratio decreases with an increase in the styrene feed ratio. The MMA/Sty ratios on the polymer surface reflect the bulk ratios under a hypothesis that oxygen detected in the polystyrene homopolymer is most probably a uniformly adsorbed component.

Table A-1 Peak area of C1s, O1s and O1s/C1s

Sample	C1s (Kcps.eV)	O1s (Kcps.eV)	O1s/C1s
PMMA	21.550	22.135	1.03
Copolymer(sty 25%)	31.191	25.253	0.810
Copolymer(sty 50%)	26.966	17.724	0.657
Copolymer(sty 75%)	36.279	23.192	0.639
PS	28.460	11.441	0.402

The amount of O1s found in the PS indicated that there was some concentration of the PMVE matrix polymer still remained on the surface of the PS. However, the NMR and FT-IR spectra of PS did not indicate the presence of oxygen. This implied that, the remaining PMVE was only found on the surface of the PS.

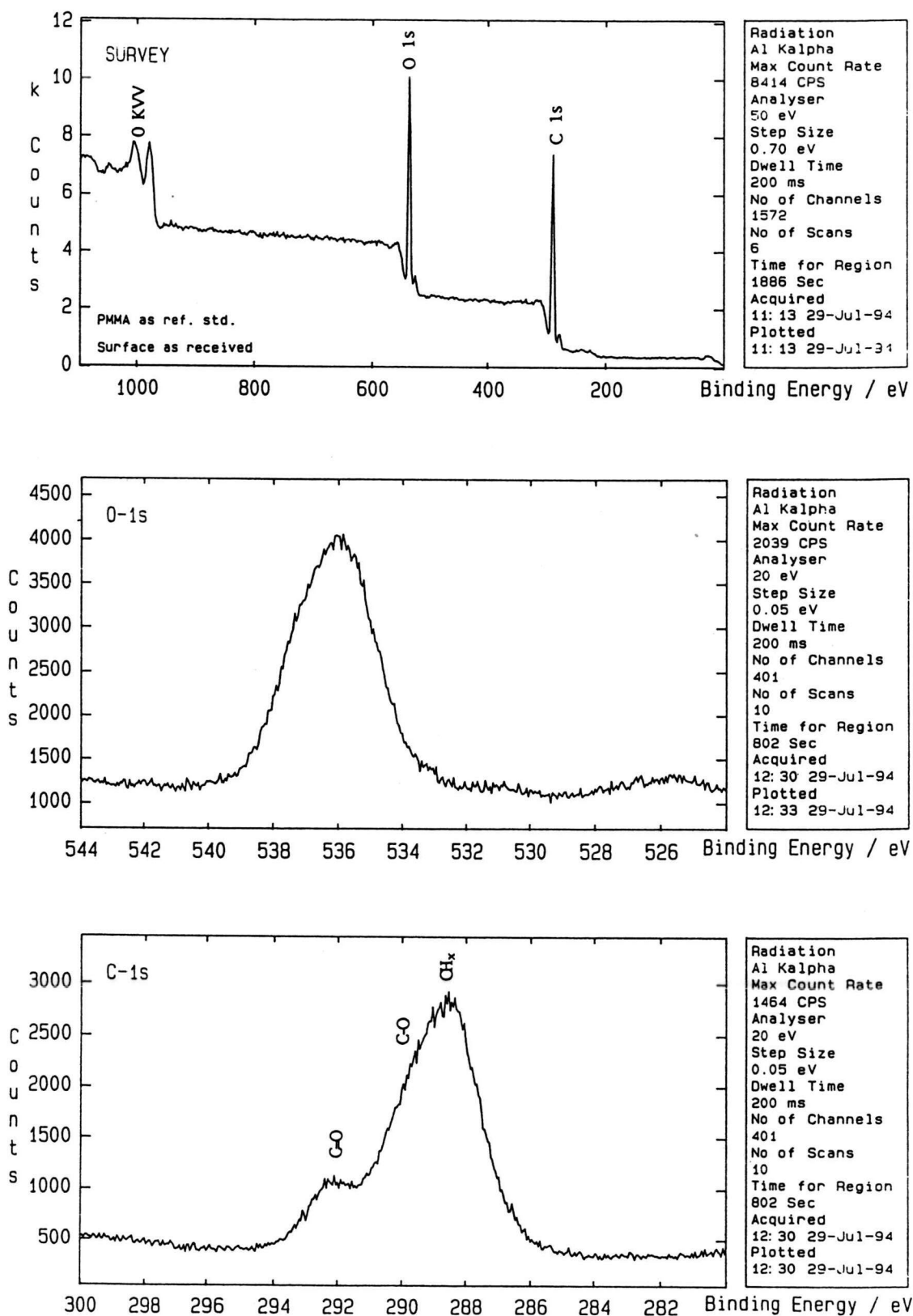


Figure A-1 XPS spectra of PMMA homopolymer

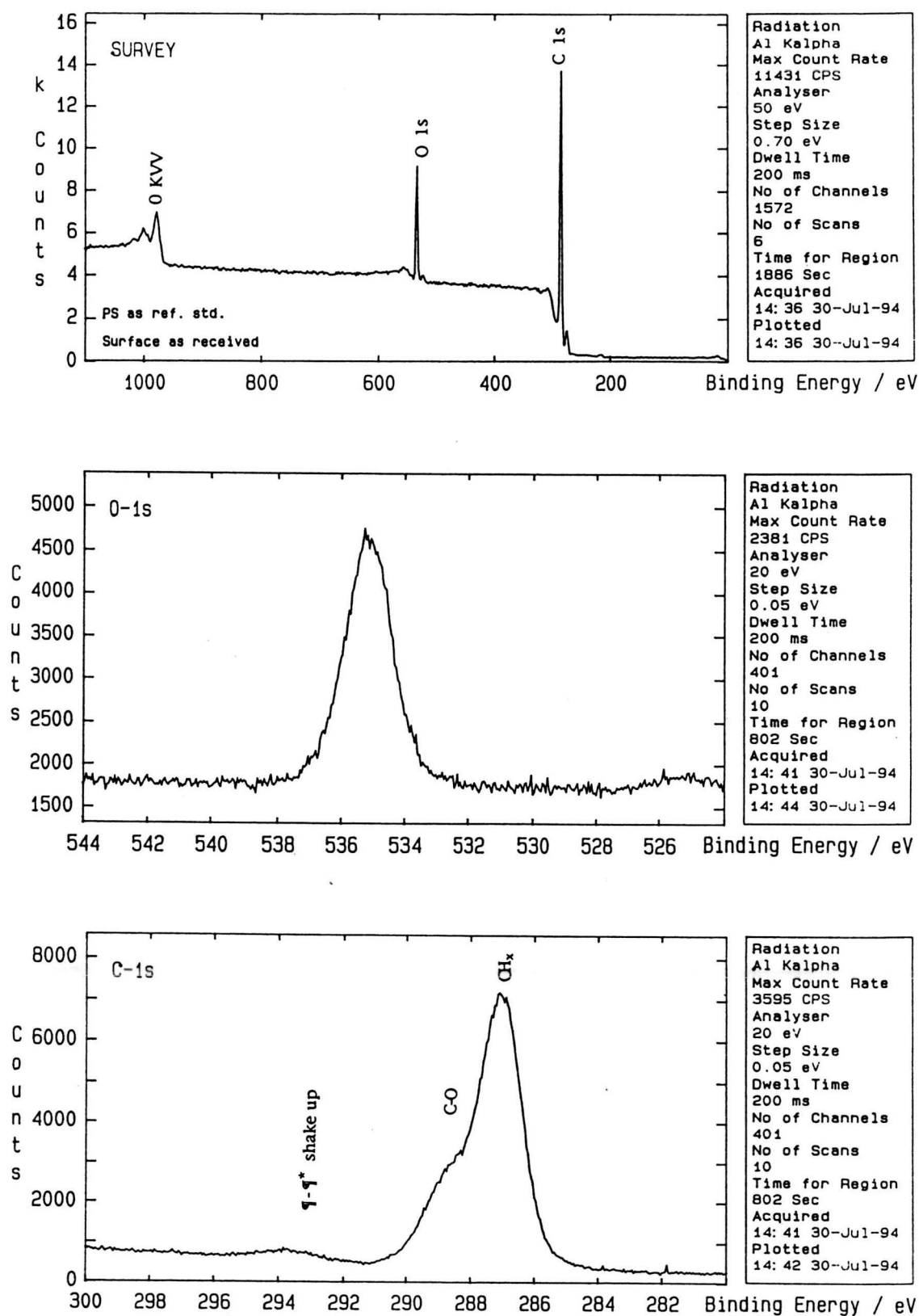


Figure A-2 XPS spectra of PS homopolymer

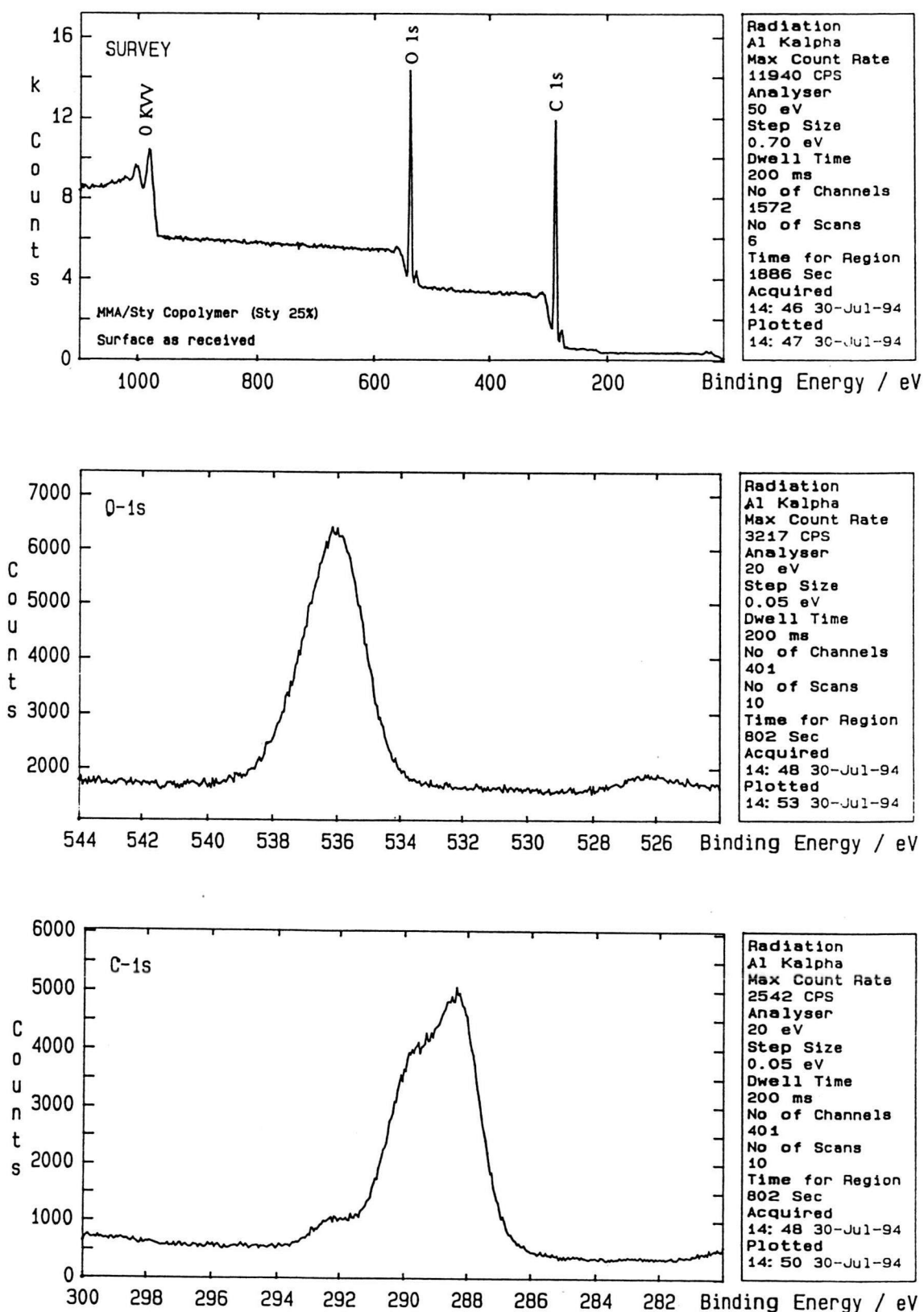


Figure A-3 XPS spectra of poly(St-co-MMA): St feed 25 %

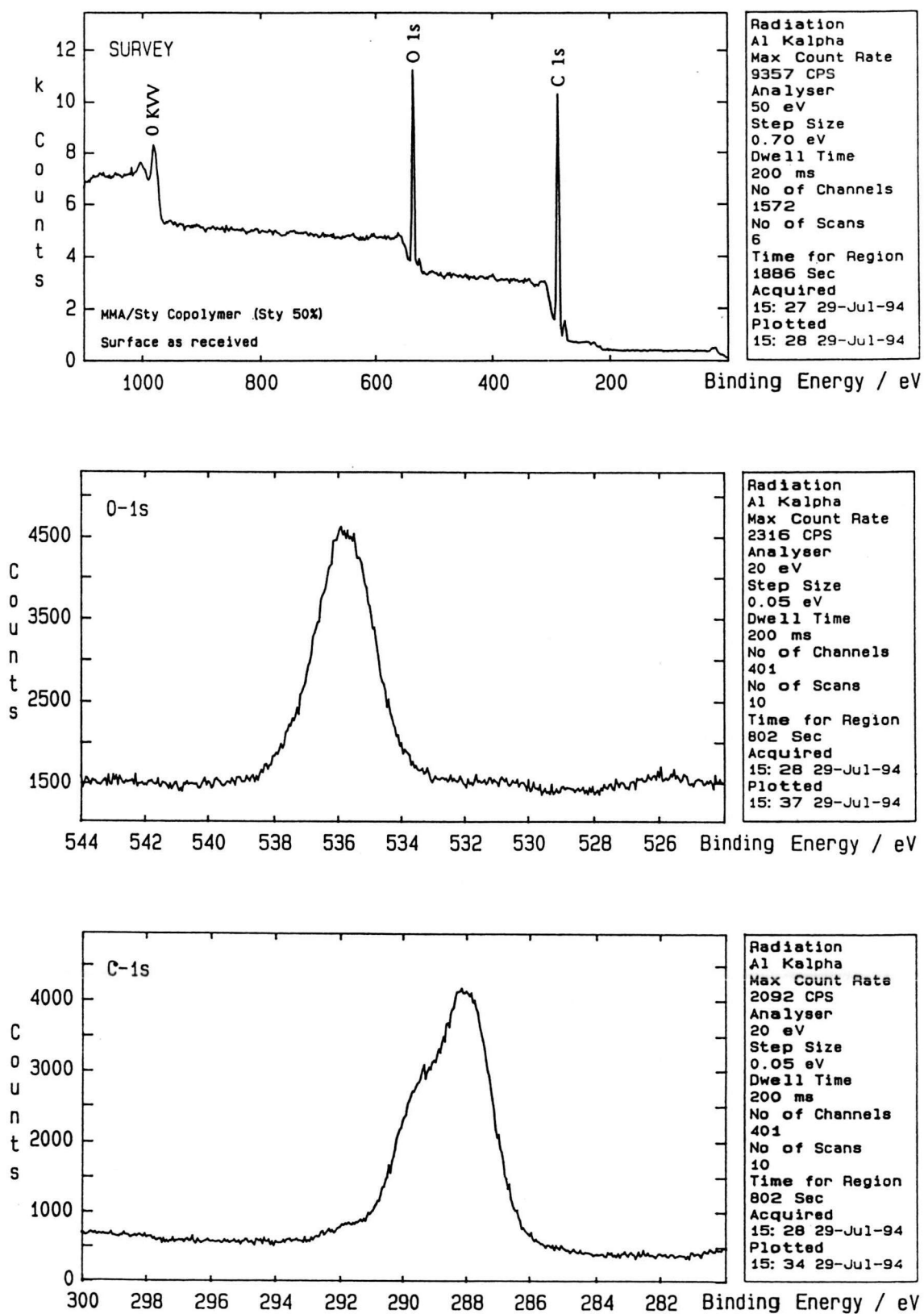


Figure A-4 XPS spectra of poly(St-co-MMA): St feed 50 %

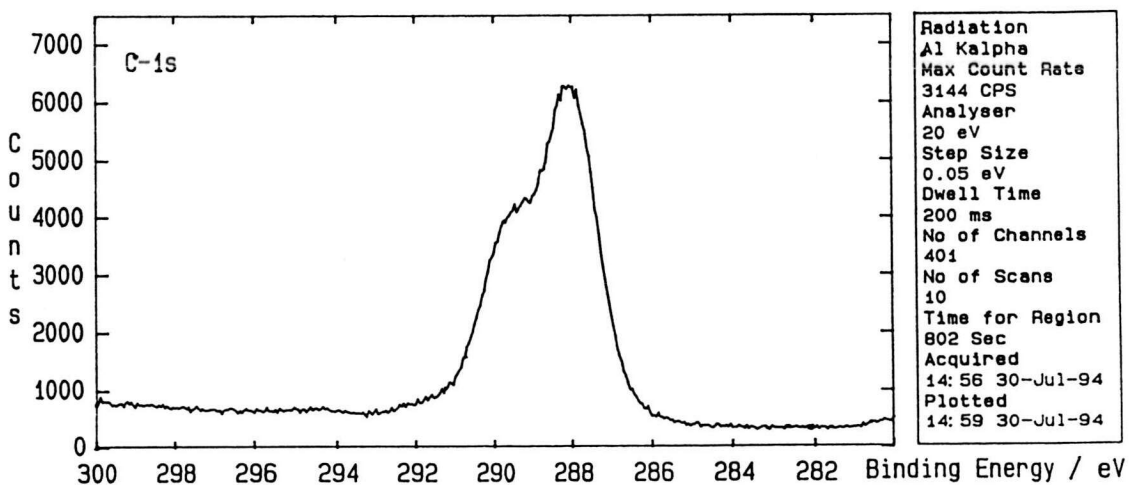
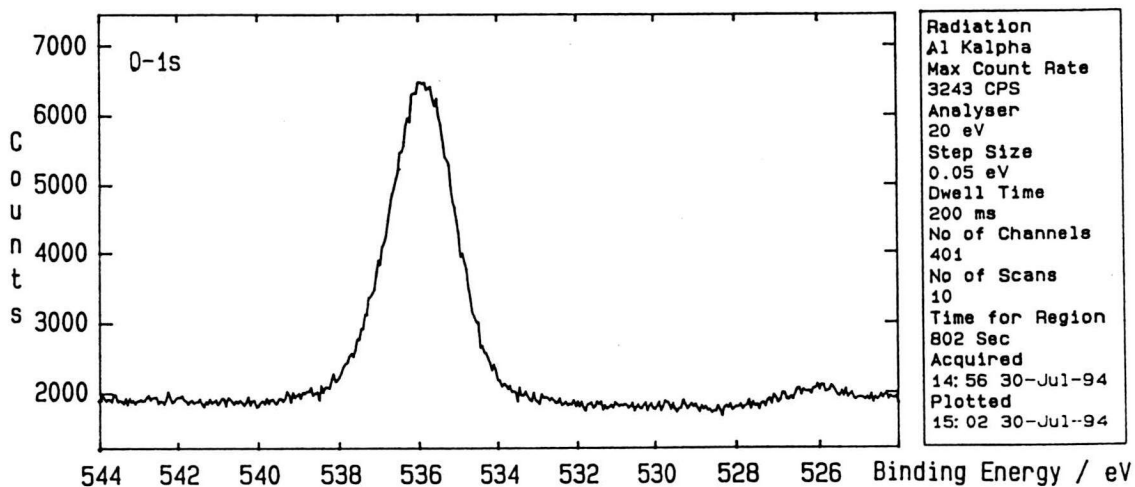
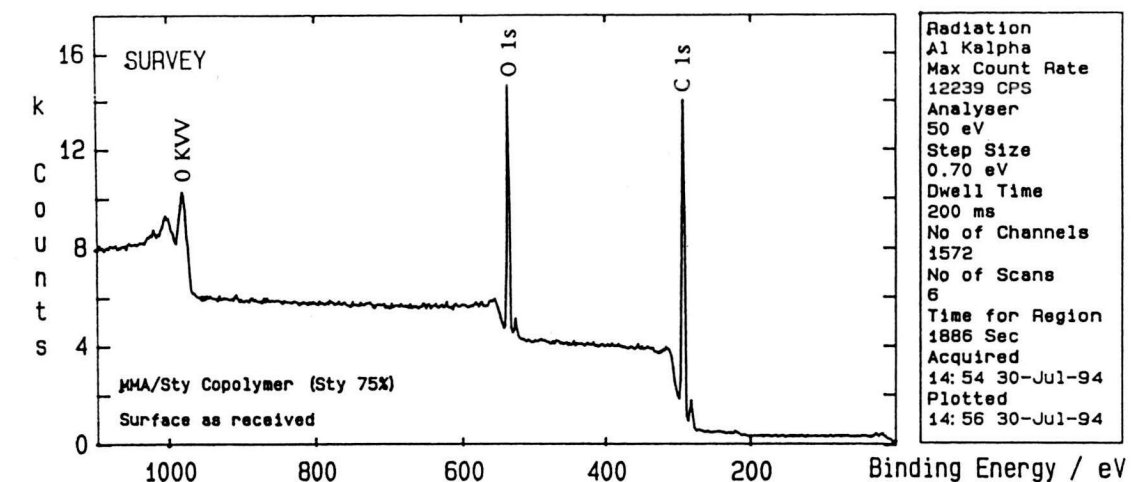


Figure A-5 XPS spectra of poly(St-co-MMA): St feed 75 %

APPENDIX B

Nuclear Magnetic Resonance Spectra

Measurements of H^1 NMR and C^{13} NMR spectra were operated on a Japan Electron Optics Laboratory(JEOL) model JNM-GX270, 270 MHz at 45°C for all copolymers using 4% solution in deuteriochloroform ($CDCl_3$). Tetramethylsilane (TMS) was used as an internal reference standard.

The assignments of the H^1 NMR and C^{13} NMR spectrum were shown in Tables B-1 to B-2, respectively. The copolymers of the various styrene feeds were analysed by using the H^1 NMR technique (Figures B-a to B-c) while only the copolmer of 75% styrene feed was analysed by using the C^{13} NMR(Figure B-2) in order to obtain the information of poly(styrene-co-methyl methacrylate) formation.

Determination of the copolymer composition from a high resolution H^1 NMR spectrum was done by comparing the peak areas of the methyl proton($-C-CH_3$; $\delta = 0.1-1.1$ ppm) of MMA and the phenyl proton($-C_6H_5$; $\delta = 6.6-7.5$ ppm) of Sty, the peak area was measured by weighting the paper weight under the peak. The detailed method of the determination was shown by an example of calculation. The results of the calculation were shown in the Tables B-a, B-b amd B-c for the solution, bulk and dispersion copolymerizations, respectively.

It should be noted that, the resonance of the methoxy proton of the MMA($-O-CH_3$; $\delta = 2.2-3.6$ ppm) was shown to be resolved into three peaks in the copolymer of Sty-co-MMA resulted from a diamagnetic shielding by the phenyl ring, neighboring to the methyl methacrylate group.

Table B-1 Assignments of the H^1 NMR spectrum of poly(styrene-co-methyl methacrylate)

Assignments	Chemical Shift(ppm)
MMA O- CH_3 methoxy proton	2.2-3.6
C- CH_3 methyl proton	0.1-1.1
Sty C_6H_5 phenyl proton	6.6-7.5

An example of calculation

Dispersion copolymer: 25 mole% Sty feed, 80 weight% EtOH in the mixed solvent

$$\begin{aligned} \text{Weight of the methyl proton peak} &= 80.04 \text{ mg} \\ \text{Weight of the phenyl proton peak} &= 71.93 \text{ mg} \\ \text{Ratio of MMA:Sty} &= 80.04/3 : 71.93/5 \\ &= 26.68 : 14.39 \end{aligned}$$

$$\% \text{Sty in copolymer} = 14.39 / (14.39 + 26.68) = 35$$

Table B-a Copolymer composition of the solution copolymer

Sty in feed (mole %)	wt.of phenyl peak(mg)	wt.of methyl peak(mg)	Sty: MMA in copolymer	F (%Sty)
25	65.4	69.2	13.08 : 23.07	36
38	97.9	58.2	19.58 : 19.40	50
50	81.2	43.0	16.24 : 14.33	53
62	65.6	24.2	13.12 : 8.07	62
75	56.6	12.3	11.32 : 4.10	73

F: copolymer composition

Table B-b Copolymer composition of the bulk copolymer

Sty in feed (mole %)	wt.of phenyl peak(mg)	wt.of methyl peak(mg)	Sty: MMA in copolymer	F (%Sty)
25	29.7	33.2	5.94 : 11.07	35
38	46.2	31.8	9.24 : 10.60	47
50	41.5	19.8	8.30 : 6.60	56
62	61.5	19.8	12.30 : 6.60	65
75	123.5	21.9	24.70 : 7.30	77

F: copolymer composition

Table B-c Copolymer composition of the dispersion copolymer

Sty in feed (mole %)	wt. of phenyl peak(mg)	wt. of methyl peak(mg)	Sty: MMA in copolymer	F (%Sty)
25	71.9	80.0	14.39 : 26.68	35
38	74.5	72.7	14.90 : 24.24	38
50	42.7	21.0	8.53 : 6.99	55
62	45.4	17.5	9.08 : 5.82	61
75	71.7	17.7	14.34 : 5.90	71

F: copolymer composition

Table B-2 Assignments of the C^{13} NMR spectrum of poly(styrene-co-methyl methacrylate)

Assignments	Chemical Shift(ppm)
MMA C*=O carbonyl carbon	174-178
C*H ₂ methylene carbon	47-54
>C*< tertiary carbon	43-47
C-C*H ₃ α-methyl carbon	16-22
Sty aromatic ring carbon(1)	142-147
aromatic ring carbon(2-6)	125-130
C*H ₂ methylene carbon	47-50
C*H methine carbon	36-40

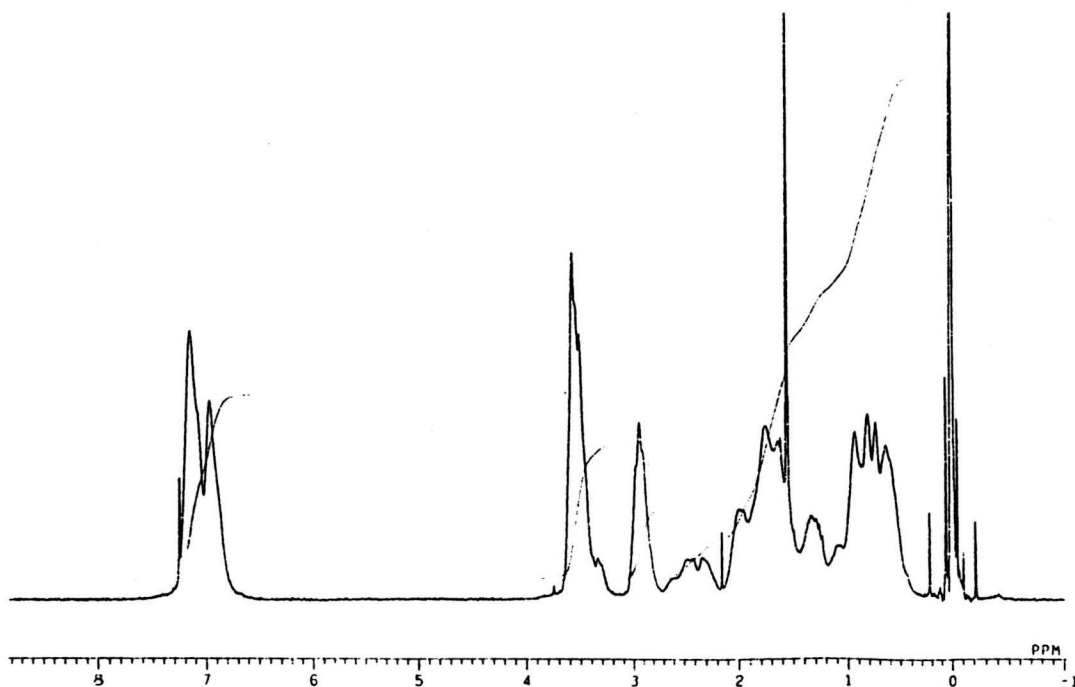


Figure B-a1 ^1H NMR spectrum of the solution copolymer
(Styrene 25 mole% feed)

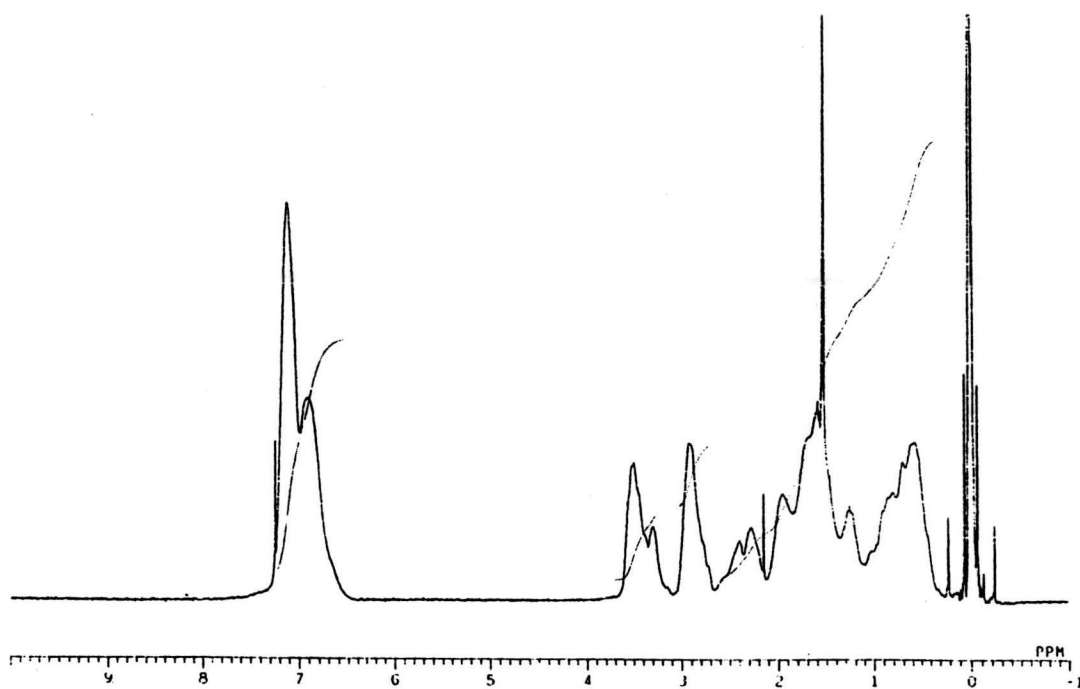


Figure B-a2 ^1H NMR spectrum of the solution copolymer
(Styrene 38 mole% feed)

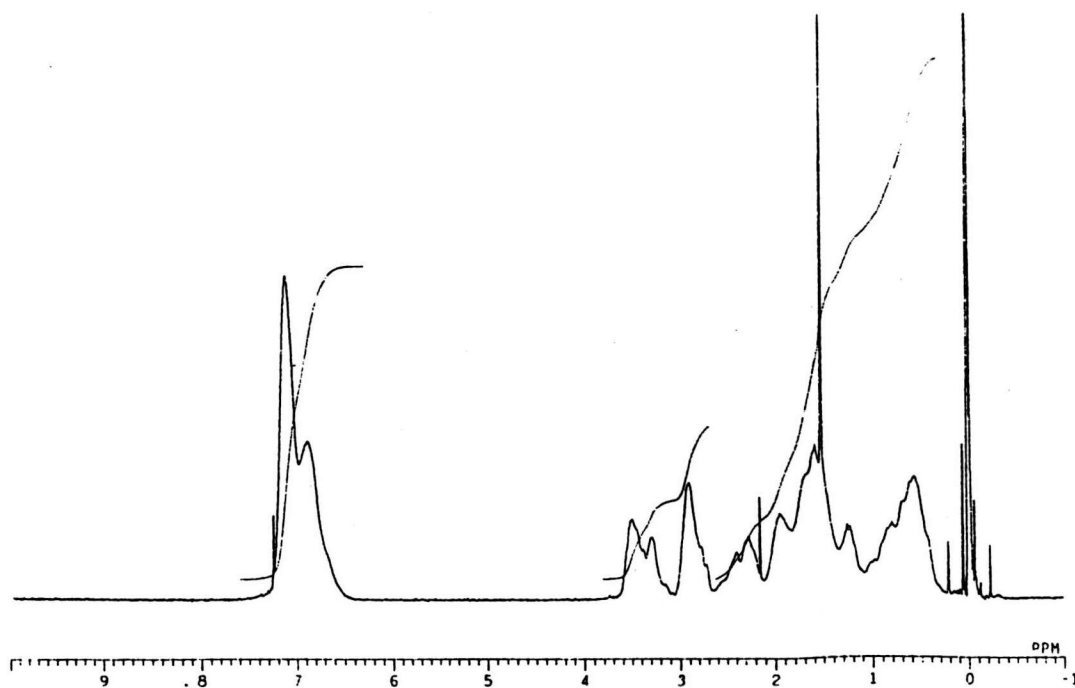


Figure B-a3 ^1H NMR spectrum of the solution copolymer
(Styrene 50 mole% feed)

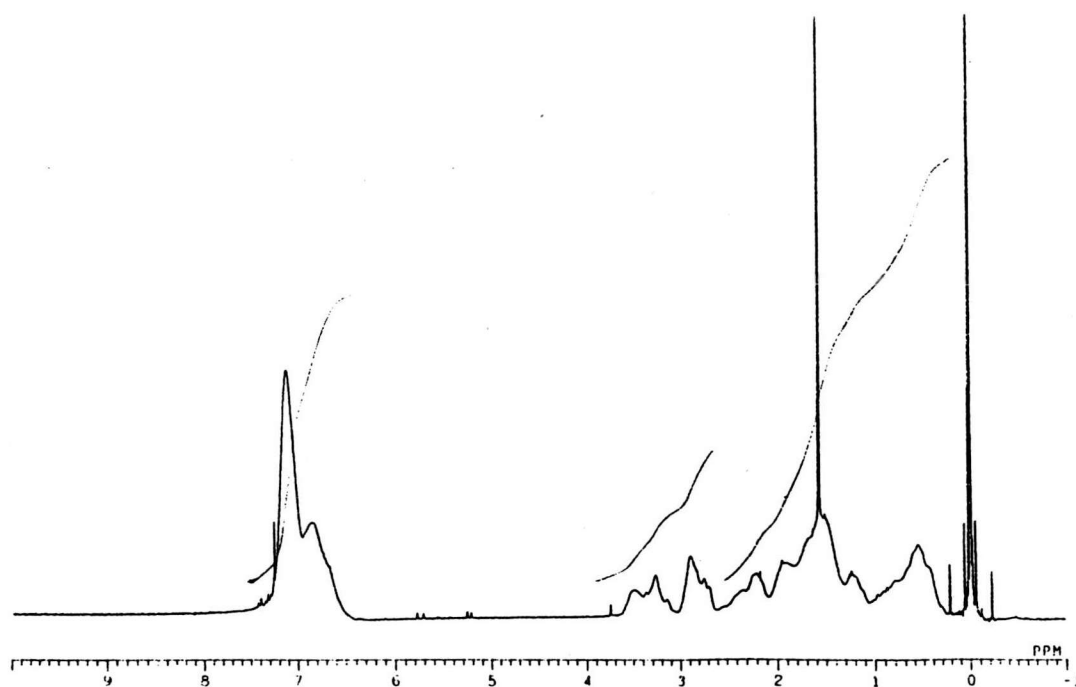


Figure B-a4 ^1H NMR spectrum of the solution copolymer
(Styrene 62 mole% feed)

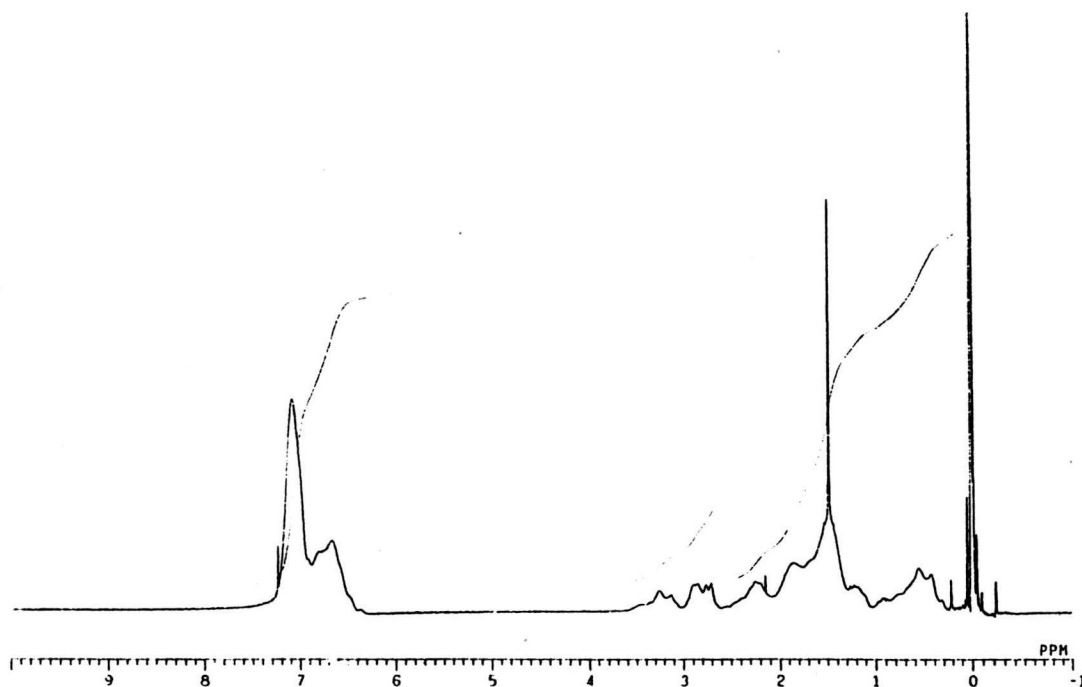


Figure B-a5 ^1H NMR spectrum of the solution copolymer
(Styrene 75 mole% feed)

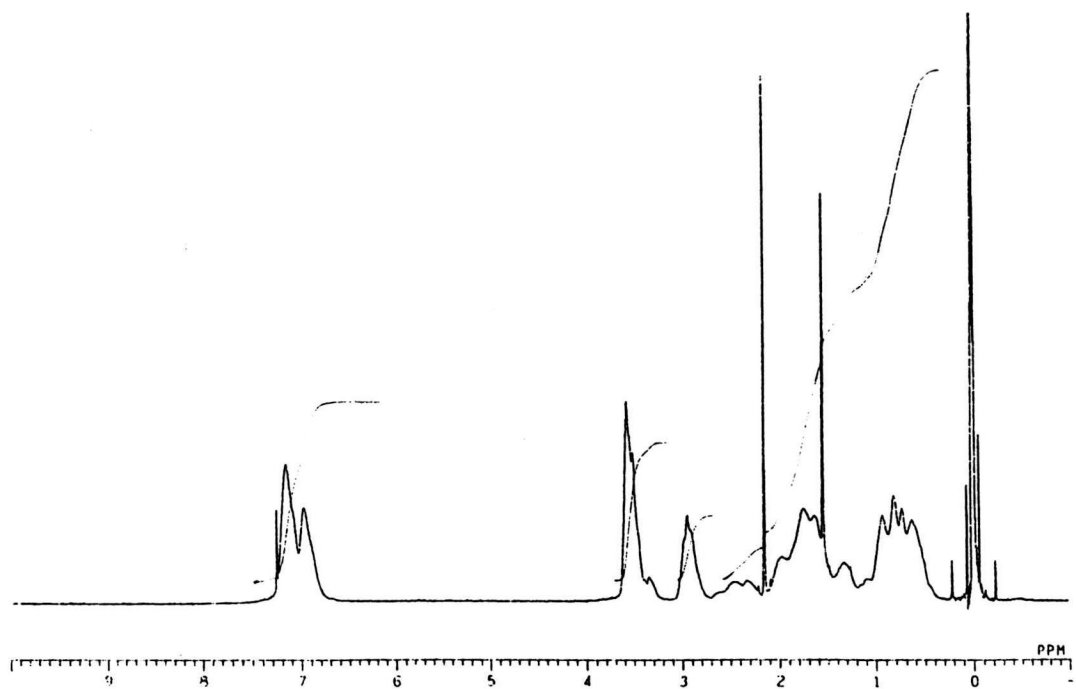


Figure B-b1 ^1H NMR spectrum of the bulk copolymer
(Styrene 25 mole% feed)

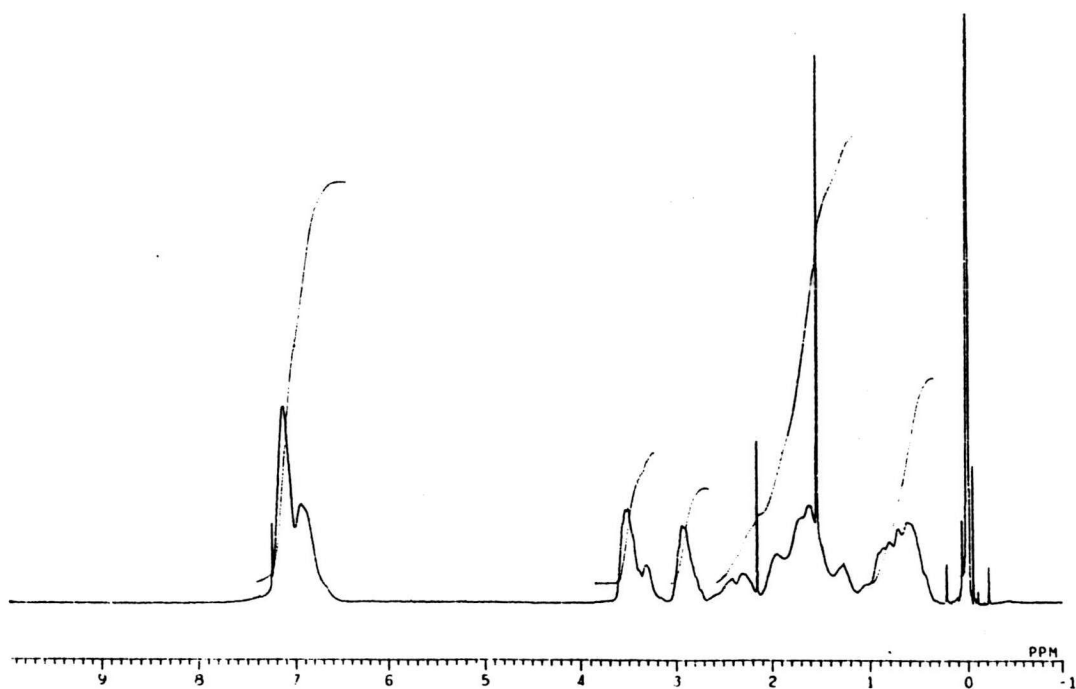


Figure B-b2 ^1H NMR spectrum of the bulk copolymer
(Styrene 38 mole% feed)

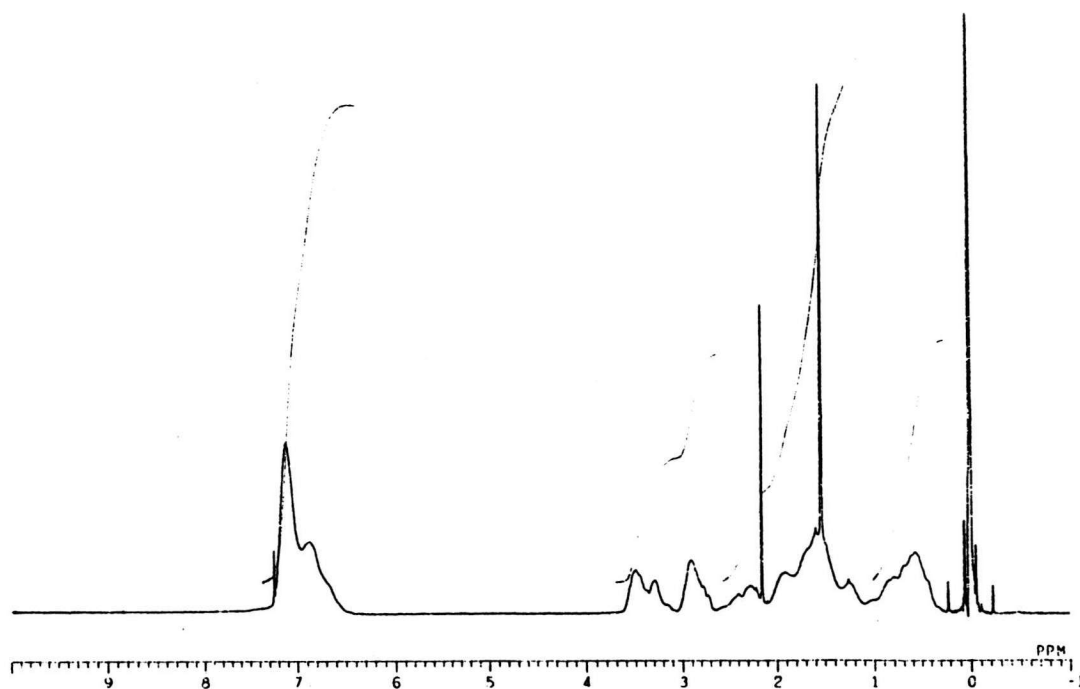


Figure B-b3 ^1H NMR spectrum of the bulk copolymer
(Styrene 50 mole% feed)

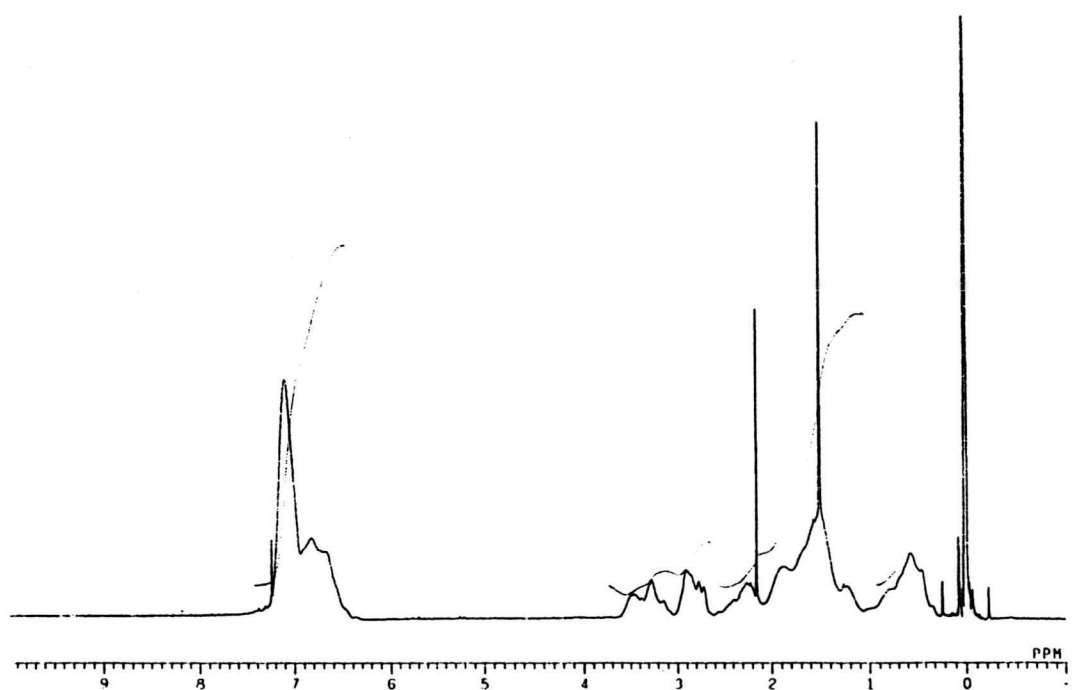


Figure B-b4 ^1H NMR spectrum of the bulk copolymer
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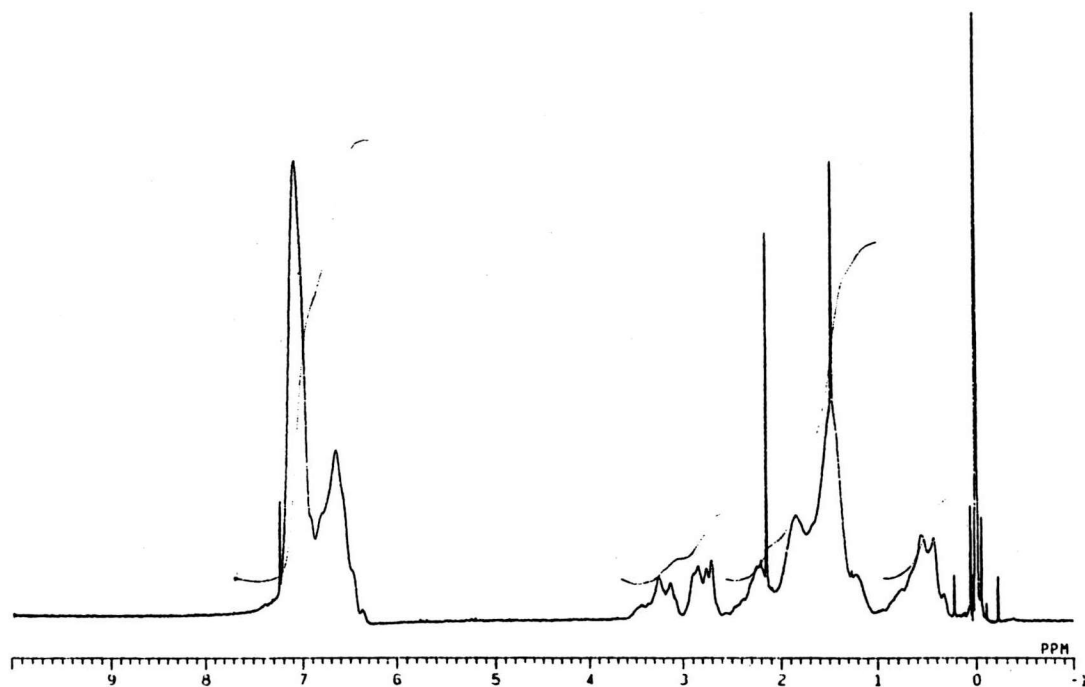


Figure B-b5 ^1H NMR spectrum of the bulk copolymer
(Styrene 75 mole% feed)

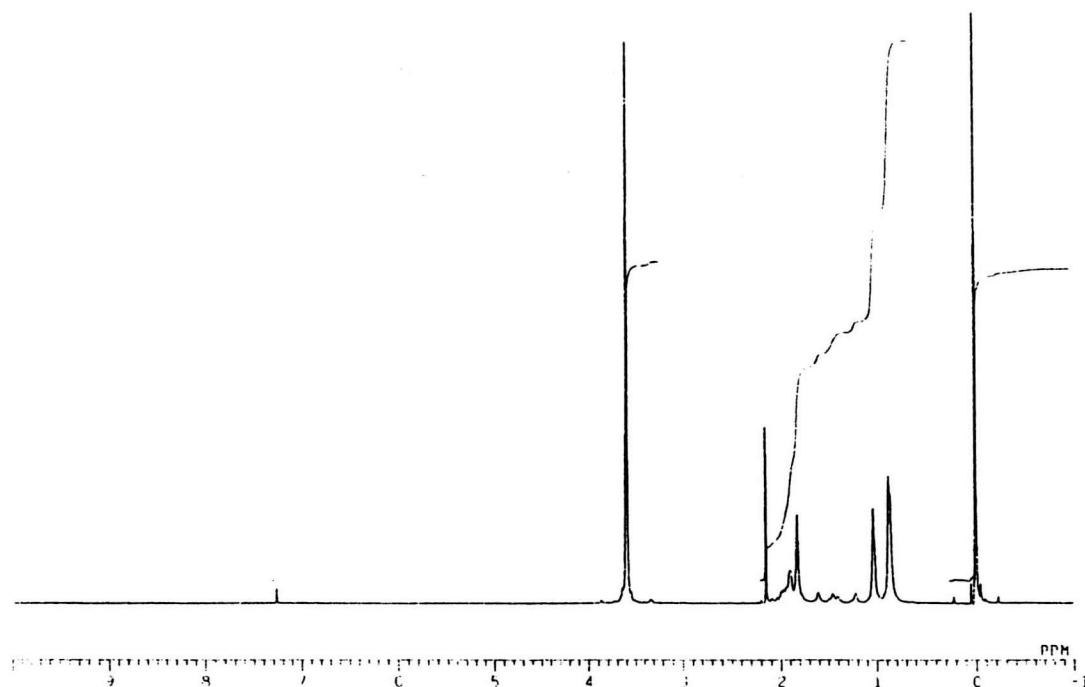


Figure B-c1 ^1H NMR spectrum of the dispersion homopolymer
(Styrene 0 mole% feed (PMMA))

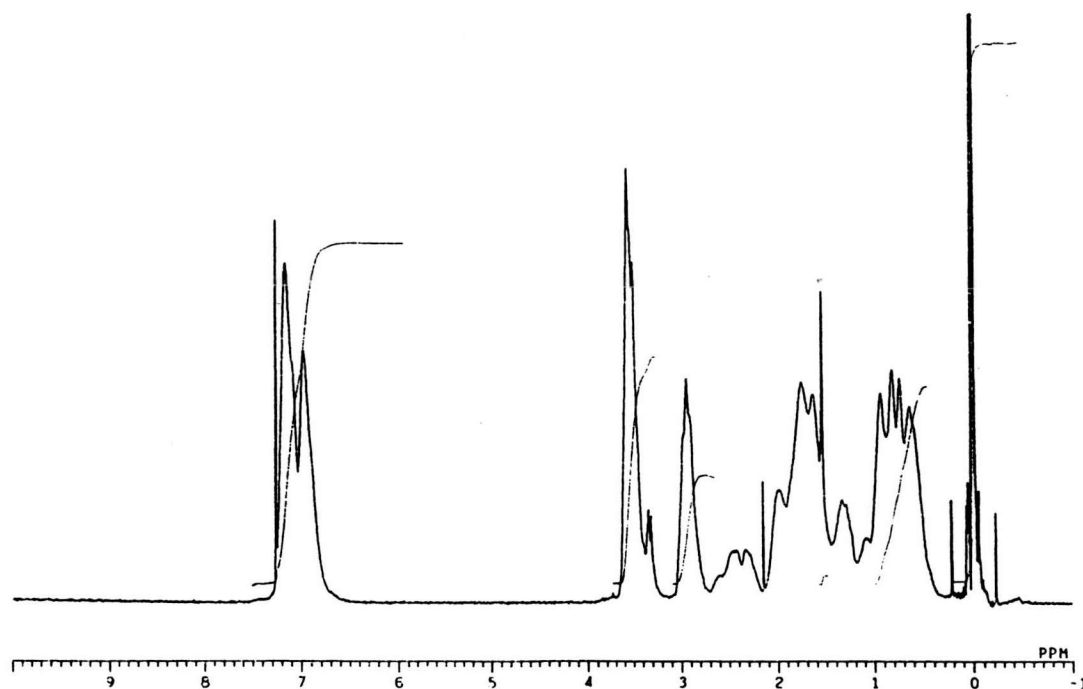


Figure B-c2 ^1H NMR spectrum of the dispersion copolymer
(Styrene 25 mole% feed)

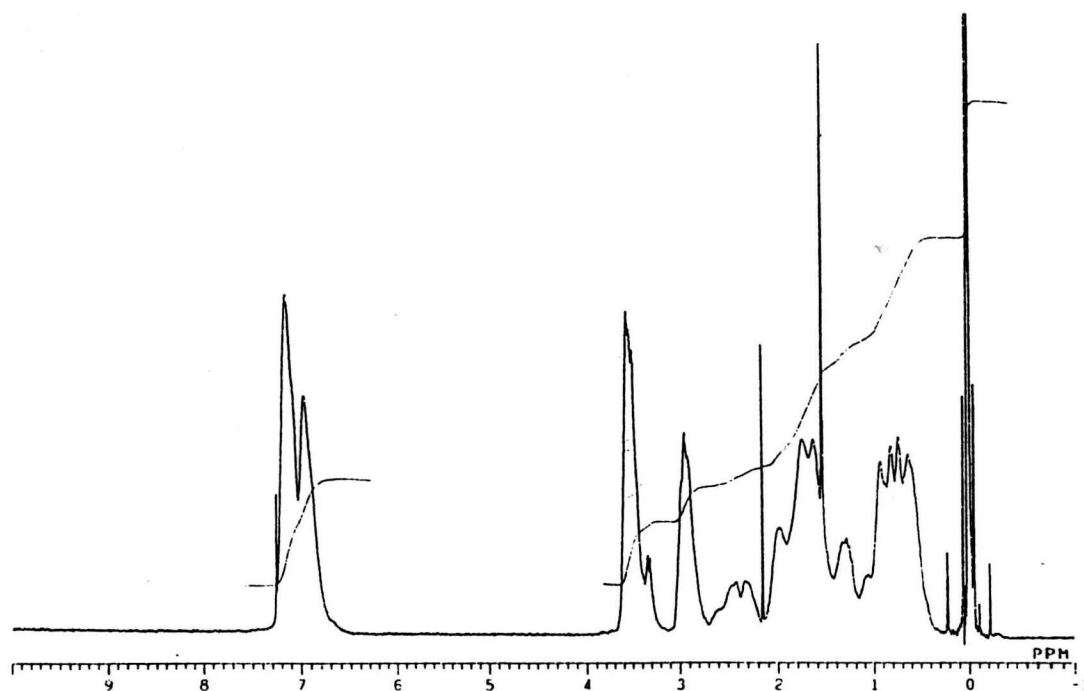


Figure B-c3 ^1H NMR spectrum of the dispersion copolymer
(Styrene 38 mole% feed)

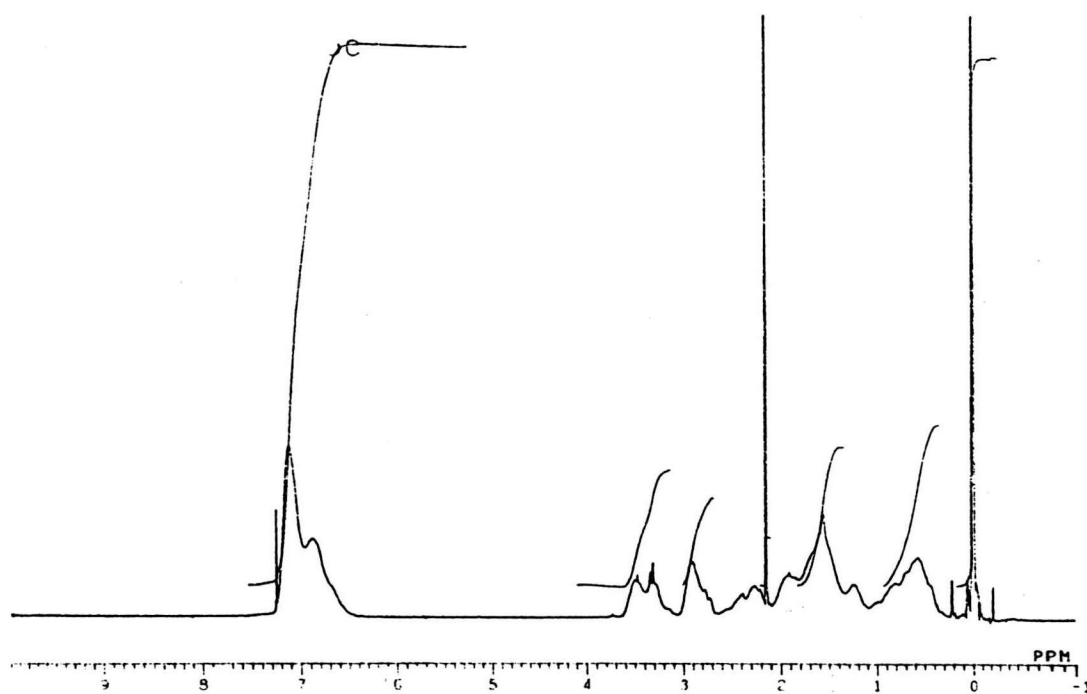


Figure B-c4 ^1H NMR spectrum of the dispersion copolymer
(Styrene 50 mole% feed)

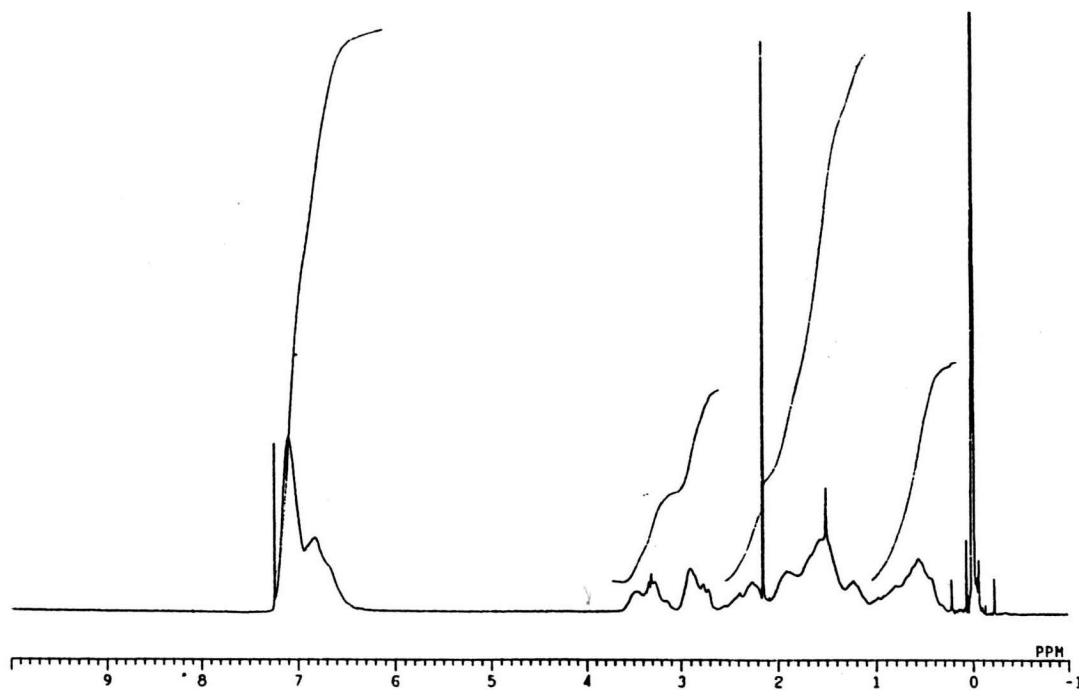


Figure B-c5 ^1H NMR spectrum of the dispersion copolymer
(Styrene 62 mole% feed)

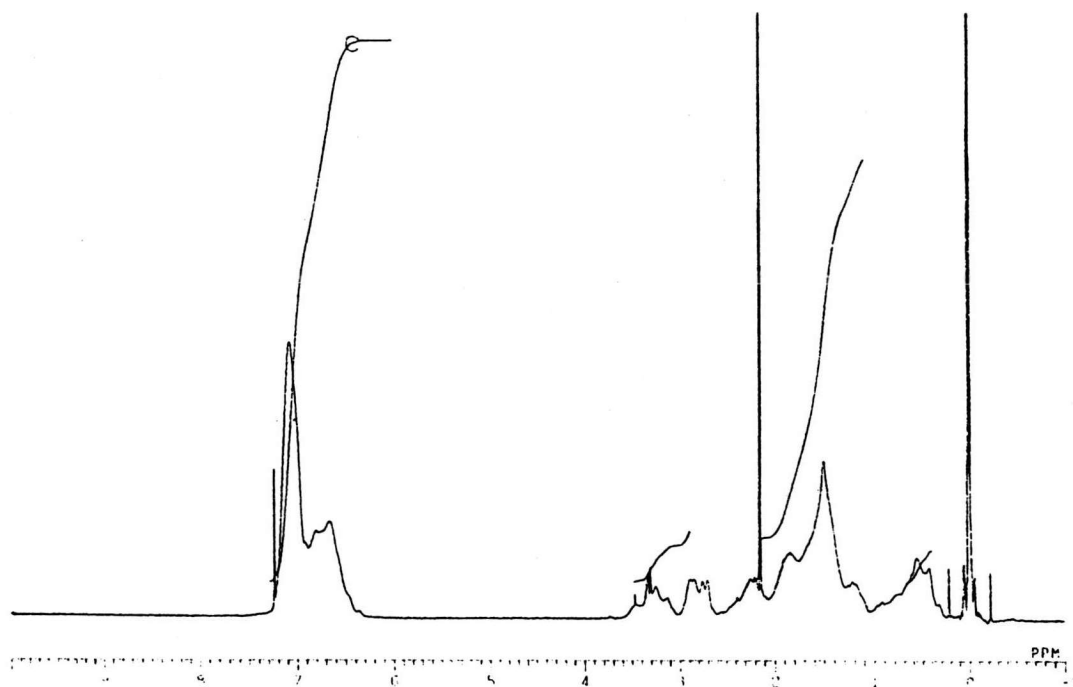


Figure B-c6 ^1H NMR spectrum of the dispersion copolymer
(Styrene 75 mole% feed)

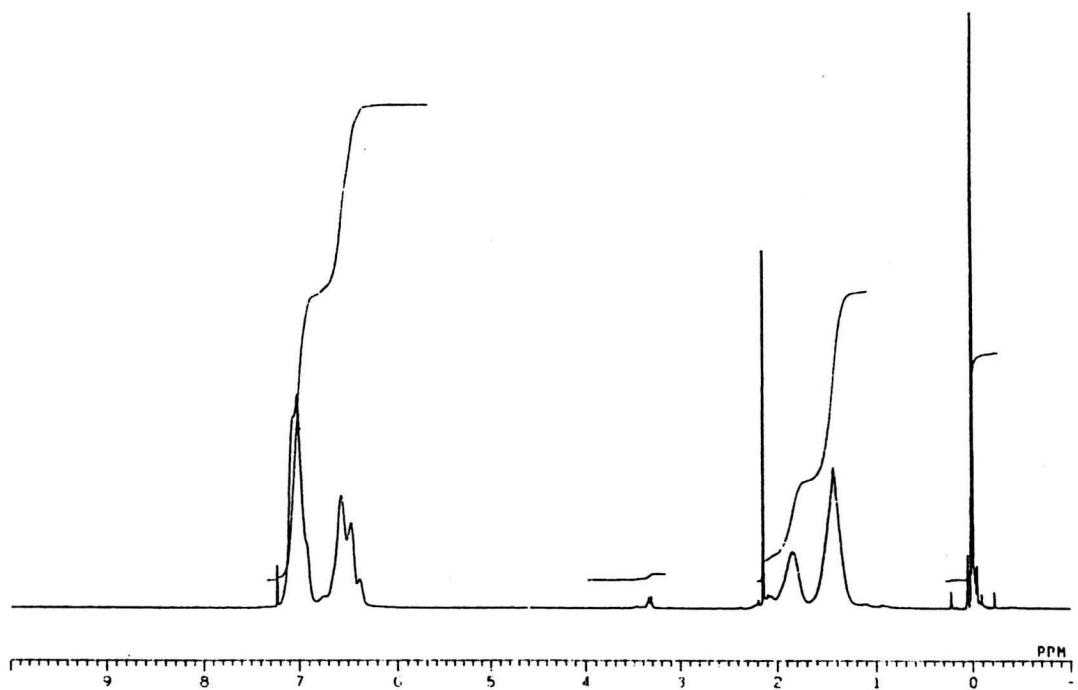


Figure B-c7 ^1H NMR spectrum of the dispersion homopolymer
(Styrene 100 mole% feed (PS))

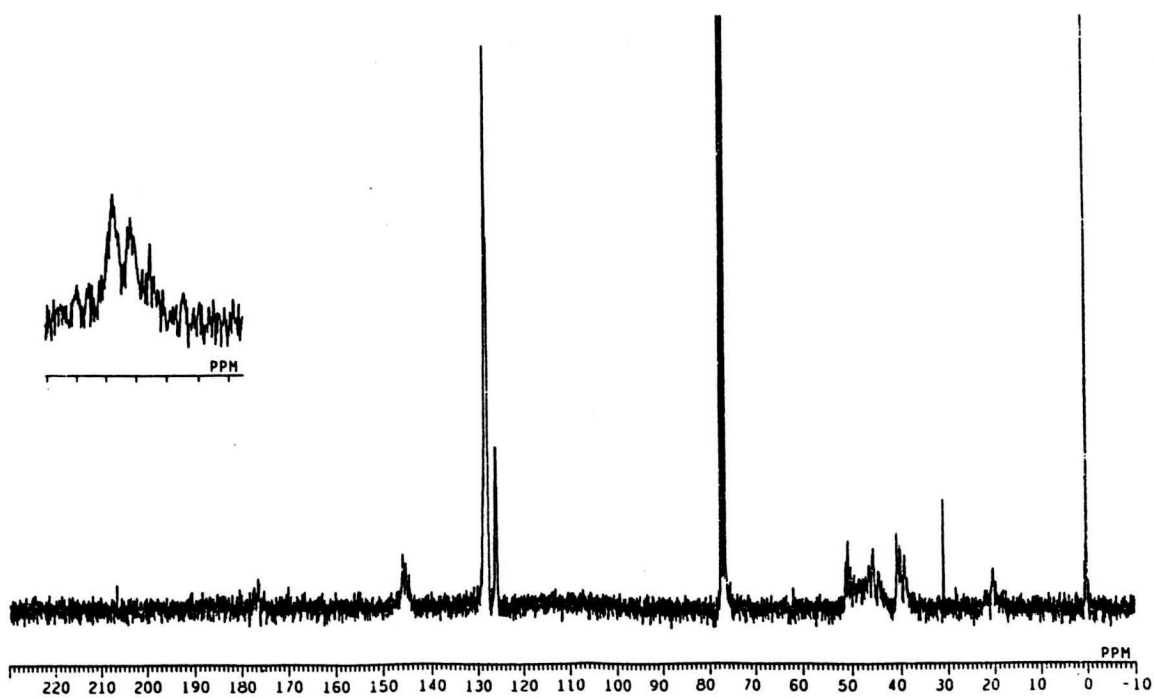


Figure B-2 ^{13}C NMR spectrum of the dispersion copolymer
(Styrene 75 mole% feed, ethanol 80 weight%)

APPENDIX C

Fourier-Transform Infrared Spectra

The FT-IR spectra of all copolymers were operated on the NICOLET 740 with the TGS detector. The product samples were prepared by using the method of KBr pellet; the standard samples, on the other hand, were prepared by using the solution method of chloroform (CHCl_3) as a solvent.

Table C-1 shows the assignments of the FT-IR spectrum. The FT-IR spectrum of PMMA product (Figure C-b1) shows the C=O stretch at 1728 cm^{-1} , and the PS product shows the C-H benzene ring stretch at 698 cm^{-1} (Figure C-b7). Both of the C=O and C-H benzene ring stretches were obtained in all the poly(styrene-co-methyl methacrylate) spectra. By considering these two stretching vibrations, a calibration curve was made by finding the relationship between the mole% styrene in the standard and the ratio of absorbance (A_{698}/A_{1728}) that was obtained from the FT-IR spectrum (Figures C-a1 to C-a5 and Table C-2). The calibration curve was shown in Figure C-1.

Figures C-b2 to C-b6 show the FT-IR spectra of the copolymer products. From these spectra, the ratios of the absorbance at 698 cm^{-1} to the absorbance at 1728 cm^{-1} (A_{698}/A_{1728}) of all the copolymers were calculated (Table C-3). The copolymer compositions were therefore, measured by using the above calibration curve (Table C-4).

Table C-1 Assignments of the FT-IR spectrum of poly(styrene-co-methyl methacrylate)

	Assignments	Wave Number(cm^{-1})
MMA	C=O stretch	1728
	C-O stretch	1250-1100
	COOCH ₃ stretch	990, 755
Sty	C-H benzene ring stretch	3061, 3029
	C-H aliphatic stretch	2923, 2851
	C=O benzene ring stretch	1602, 1493
	C-H benzene ring stretch	760, 700

Table C-2 The ratios of the absorbance of the standard

Sty wt%	25.0	33.3	50.0	66.7	75.0
Sty mole%	24.3	32.5	49.0	65.8	74.3
A_{698}/A_{1728}	0.36	0.48	0.76	1.11	1.45

Table C-3 The ratios of the absorbance of the products

Sty% feed	25	38	50	62	75
A_{698}/A_{1728}	0.43	0.55	0.72	0.81	1.04

Table C-4 The copolymer composition of the products

f (mole% Sty)	25	38	50	62	75
F (% Sty)	29	37	47	52	63

f: monomer feed composition F: monomer composition in the copolymer

FT-IR

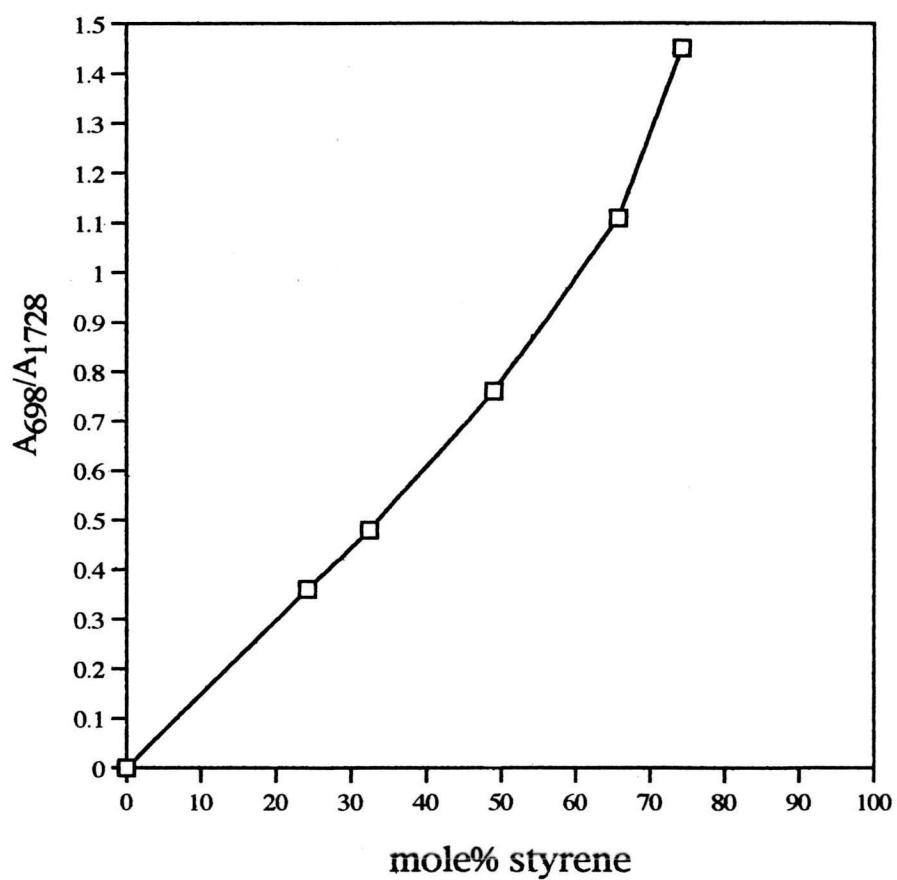


Figure C-1 FT-IR calibration curve

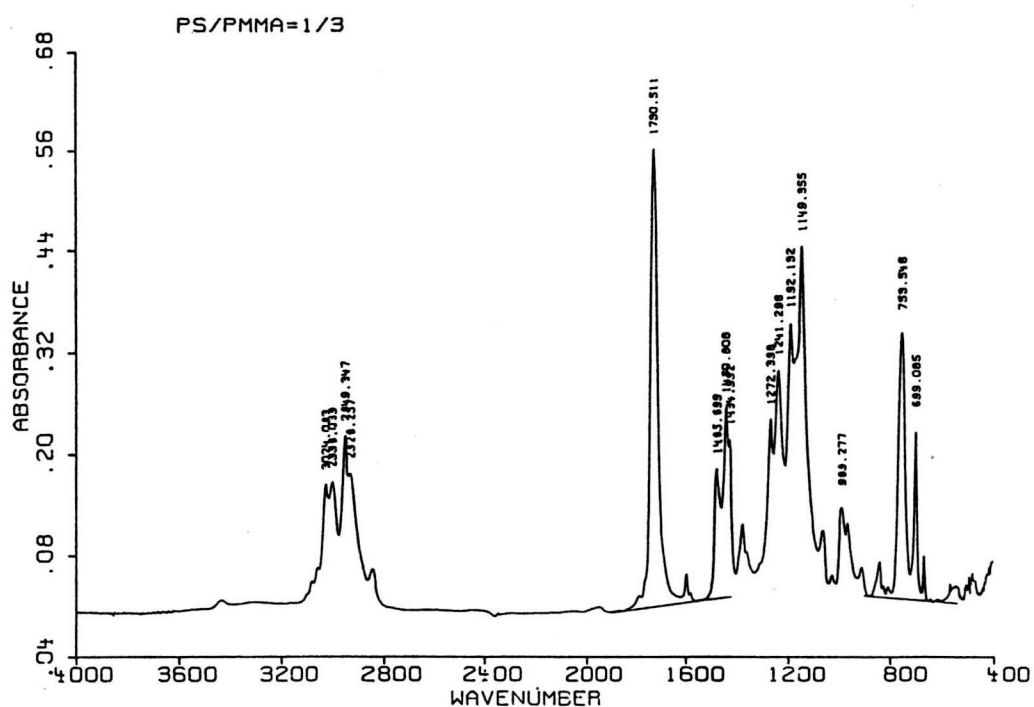


Figure C-a1 FT-IR spectrum of the standard copolymer at 25.0 weight% styrene/methyl methacrylate

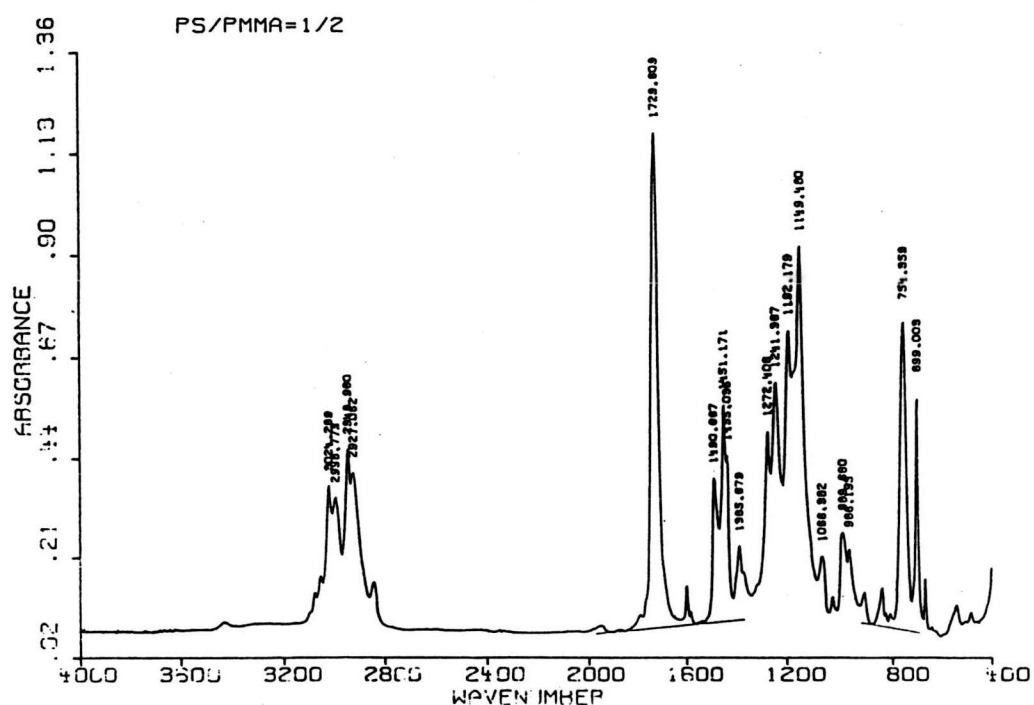


Figure C-a2 FT-IR spectrum of the standard copolymer at 33.3 weight% styrene/methyl methacrylate

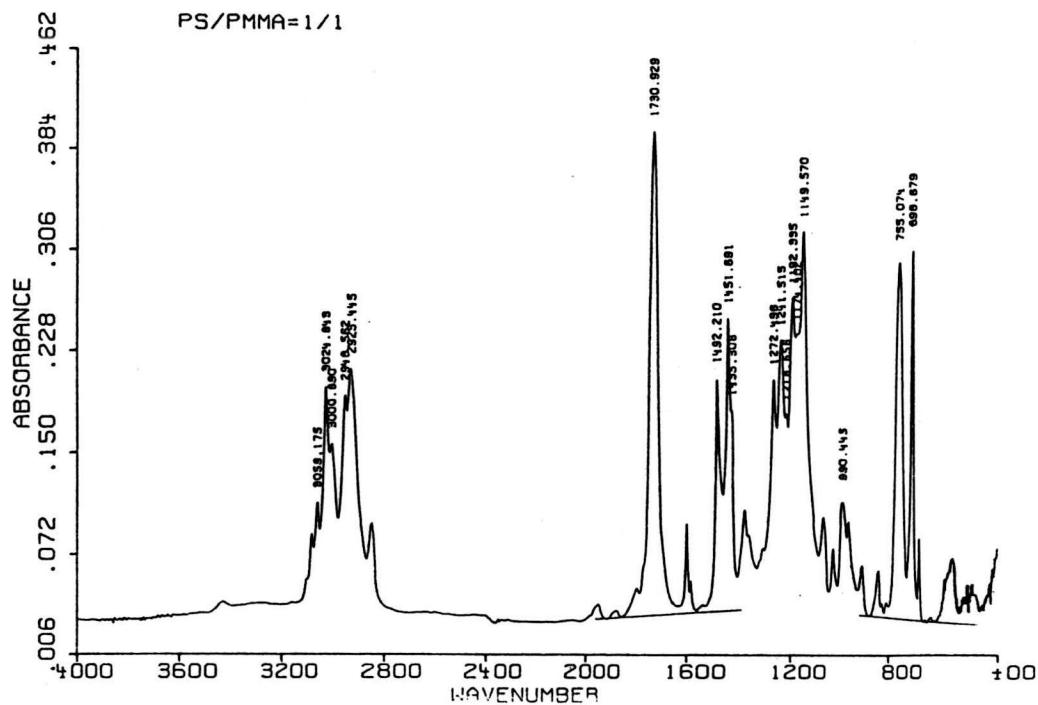


Figure C-a3 FT-IR spectrum of the standard copolymer at 50.0 weight% styrene/methyl methacrylate

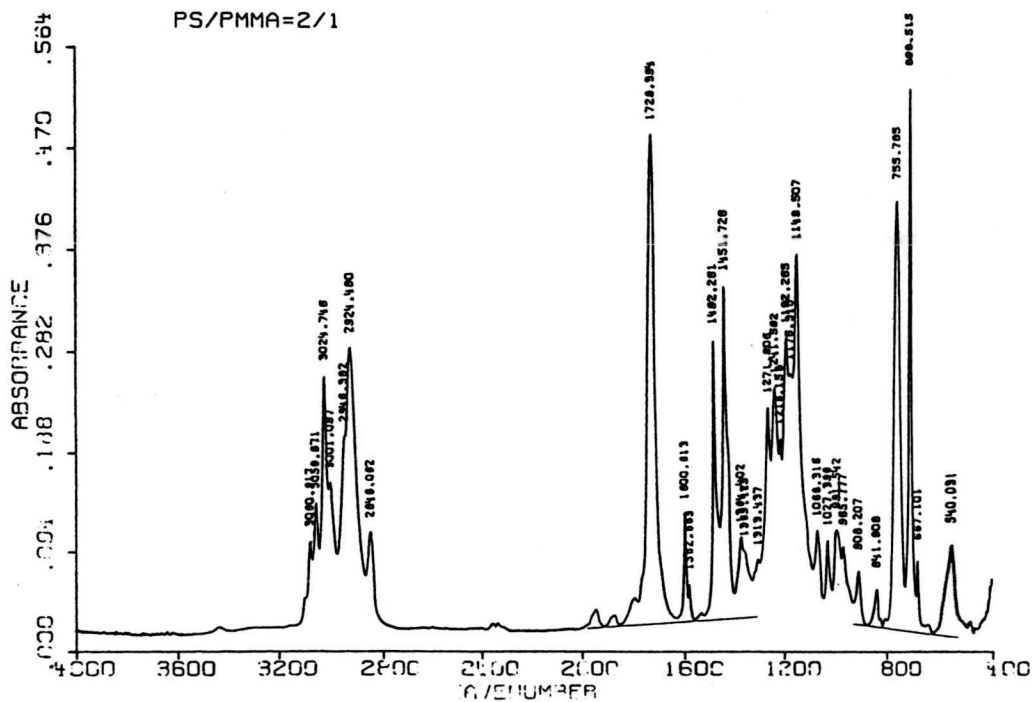


Figure C-a4 FT-IR spectrum of the standard copolymer at 66.7 weight% styrene/methyl methacrylate

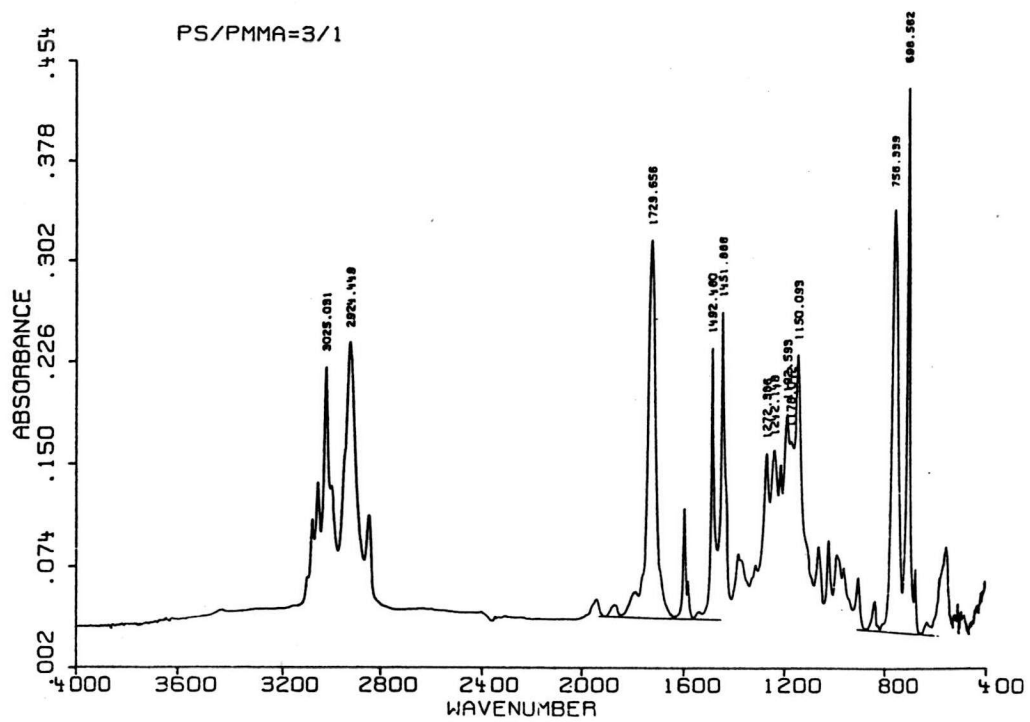


Figure C-a5 FT-IR spectrum of the standard copolymer at 75.0 weight% styrene/methyl methacrylate

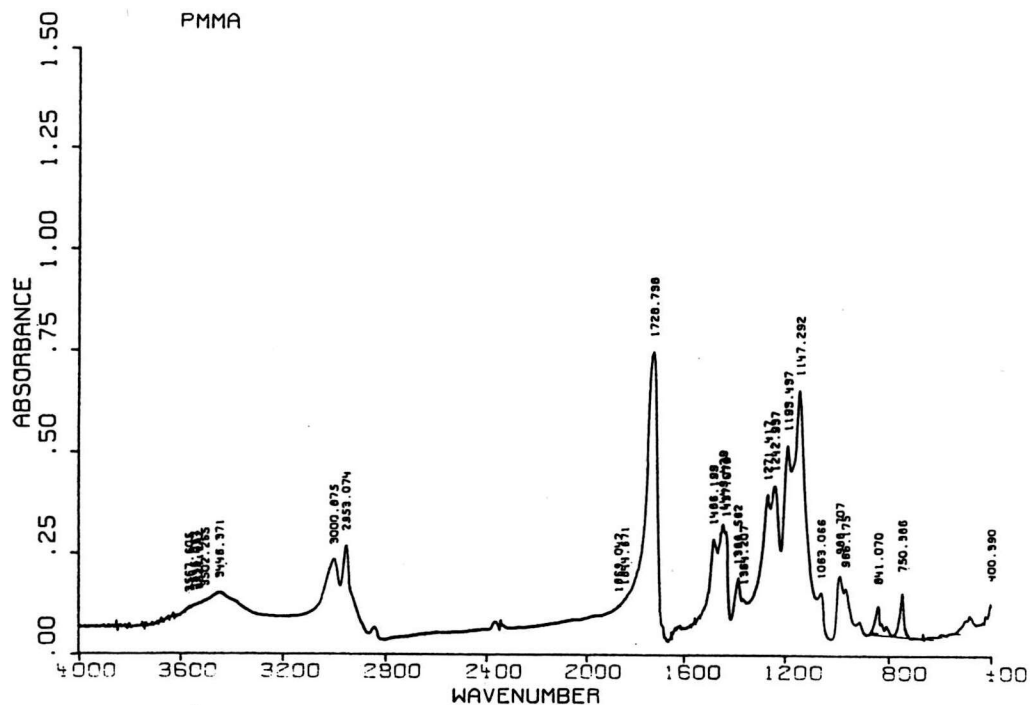


Figure C-b1 FT-IR spectrum of the product homopolymer at 0 mole% styrene or 100% methyl methacrylate feed (PMMA)

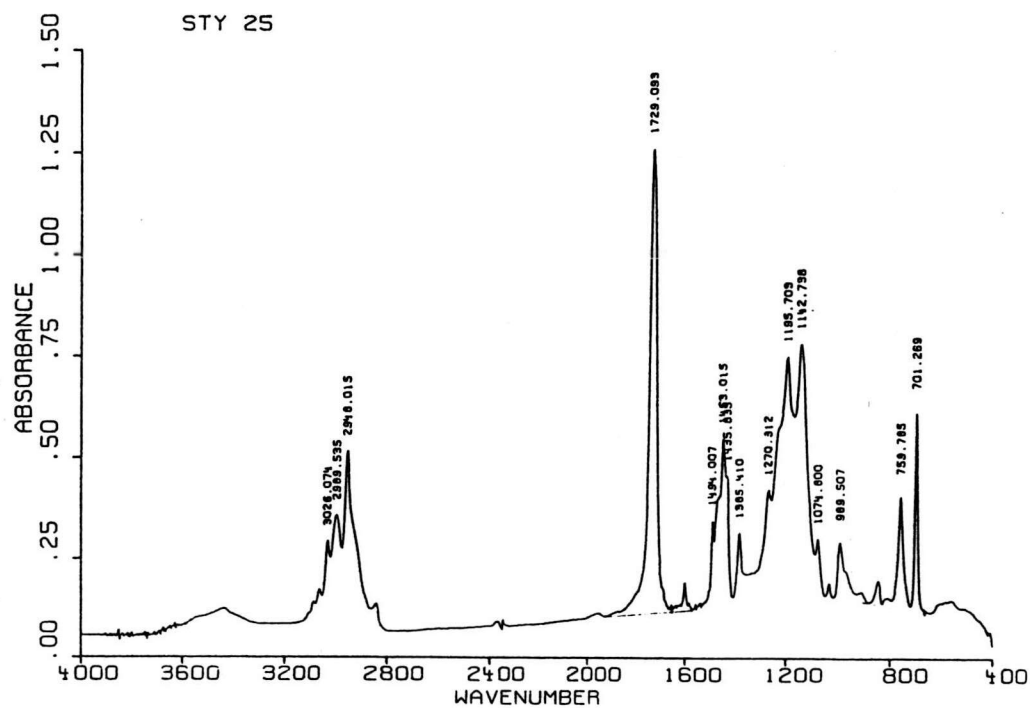


Figure C-b2 FT-IR spectrum of the product copolymer at 25.0 mole% styrene/methyl methacrylate feed

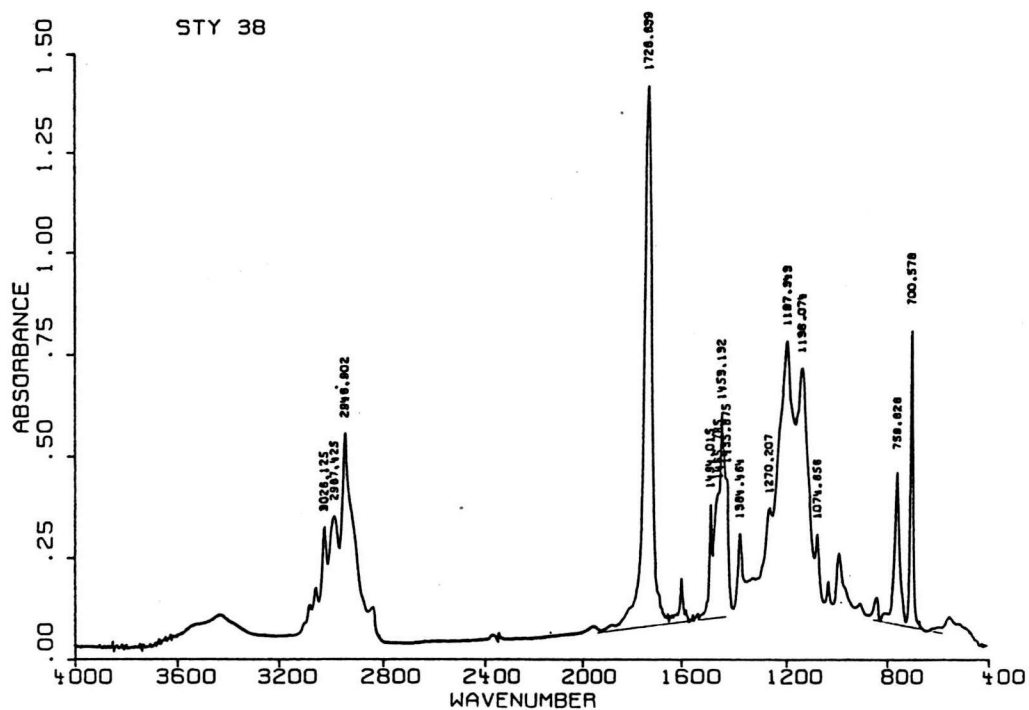


Figure C-b3 FT-IR spectrum of the product copolymer at 38.0 mole% styrene/methyl methacrylate feed

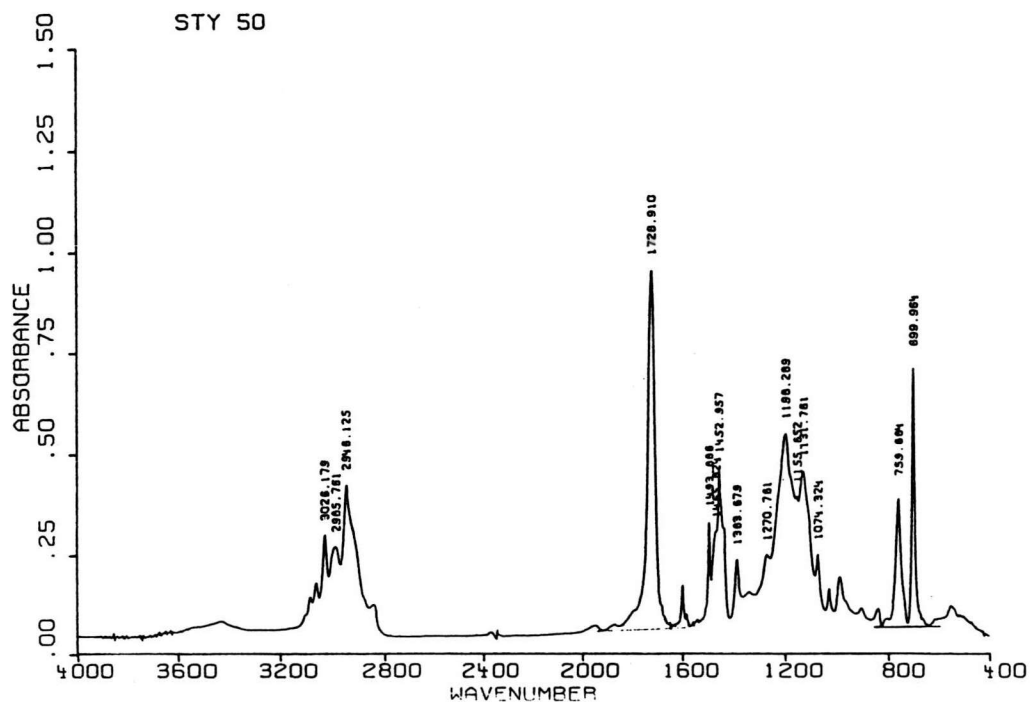


Figure C-b4 FT-IR spectrum of the product copolymer at 50.0 mole% styrene/methyl methacrylate feed

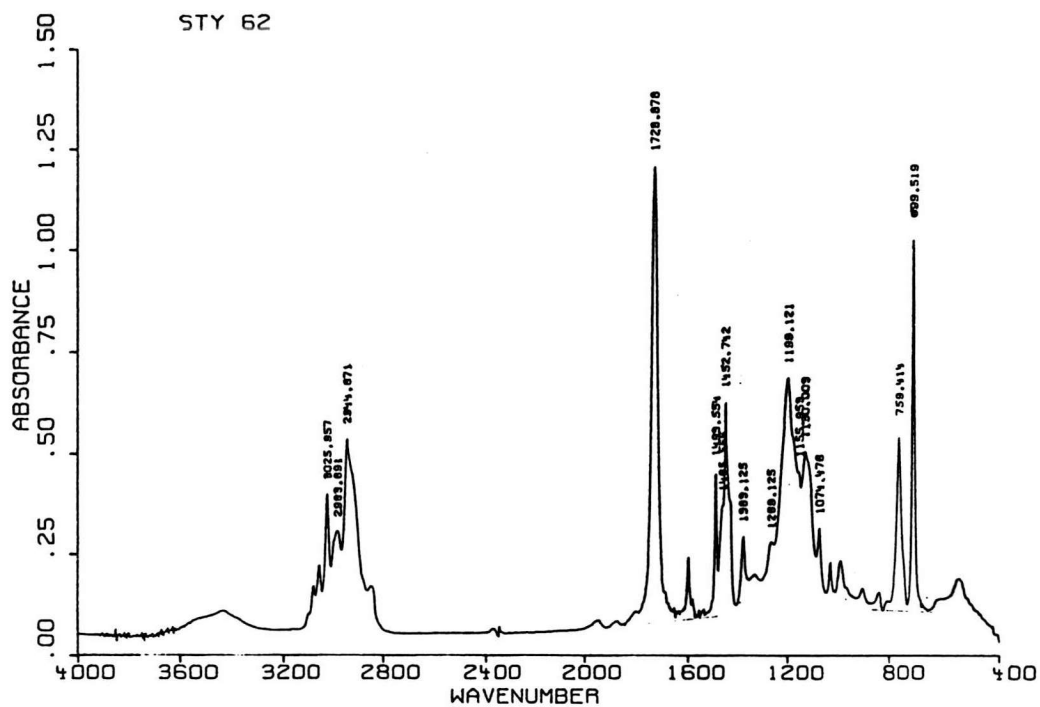


Figure C-b5 FT-IR spectrum of the product copolymer at 62.0 mole% styrene/methyl methacrylate feed

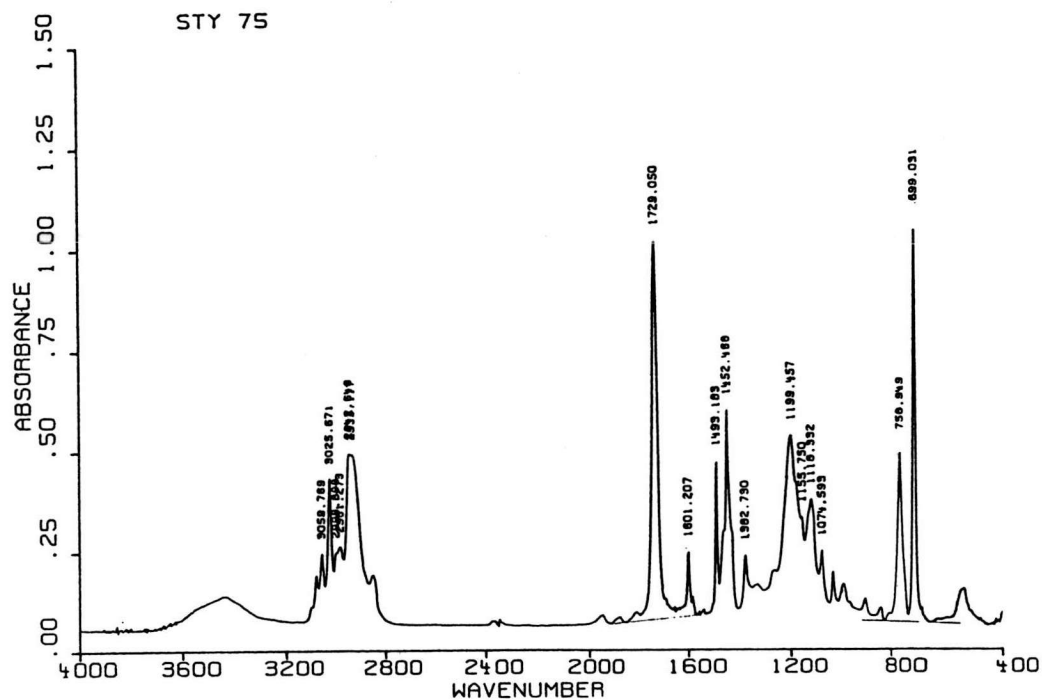


Figure C-b6 FT-IR spectrum of the product copolymer at 75.0 mole% styrene/methyl methacrylate feed

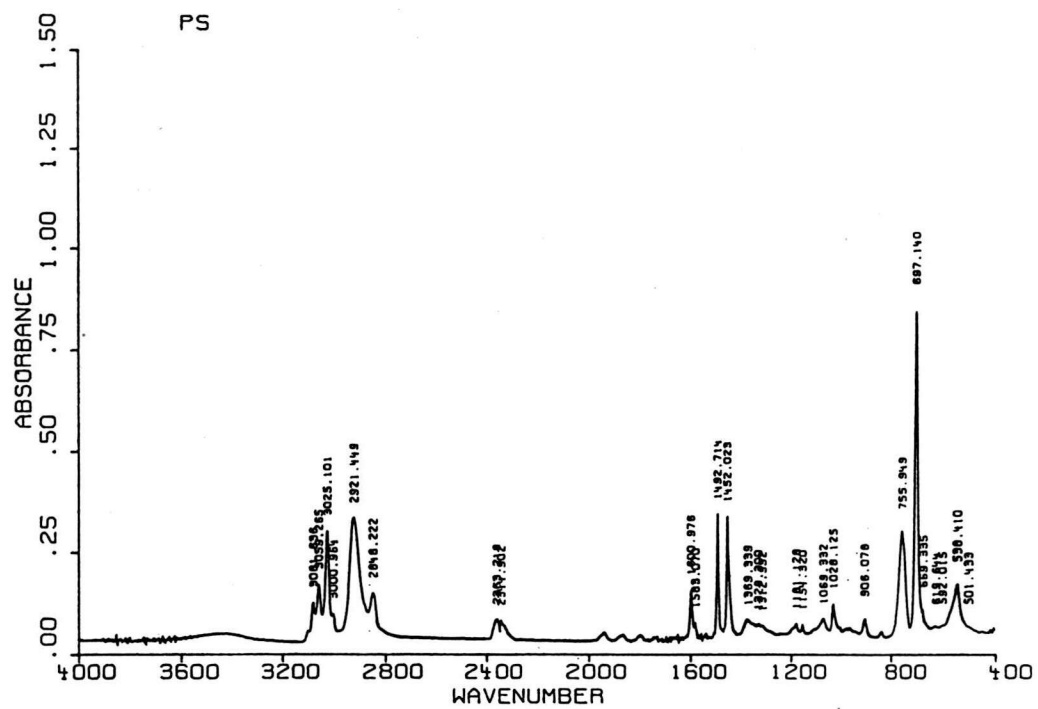


Figure C-b7 FT-IR spectrum of the product homopolymer at 100 mole% styrene or 0% methyl methacrylate feed (PS)

APPENDIX D

SEM Micrographs and Particle Size Distributions

The SEM micrographs of all copolymer were operated on a HITACHI model S430 at various magnification powers : 800, 1.2k, 2.5k and 5k. The particle size was measured by the direct size measurement of particle on the micrograph in comparison with the scale showed that was set by the microscopic magnification. On a particle size distribution, the frequency of each particle size range was counted and the standard deviation for each sample was also calculated from the respective frequency.

Figures D-1 to D-4 show the scanning electron micrographs of the copolymer by solution and dispersion copolymerizations.

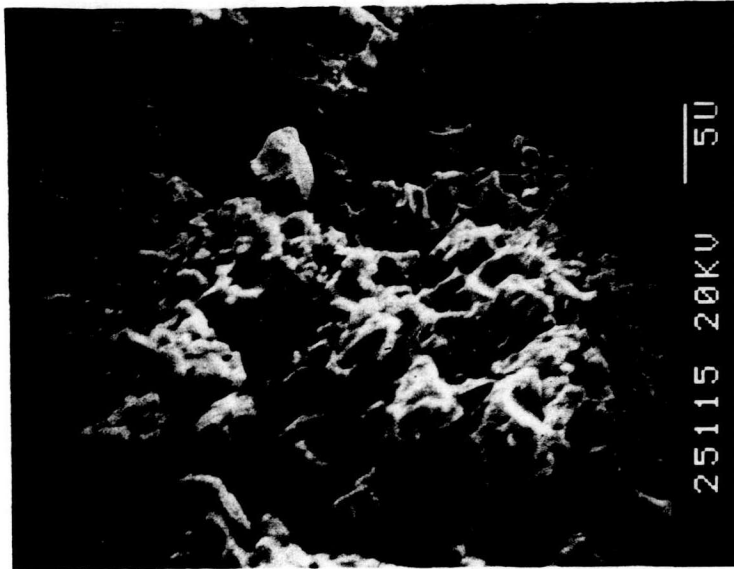
Figure D-a1 to D-a7 show the particle size distribution of the dispersion copolymer at various styrene feeds.

Figure D-b1 to D-b7 show the particle size distribution of the dispersion copolymer at various percents of ethanol in the mixed solvent.

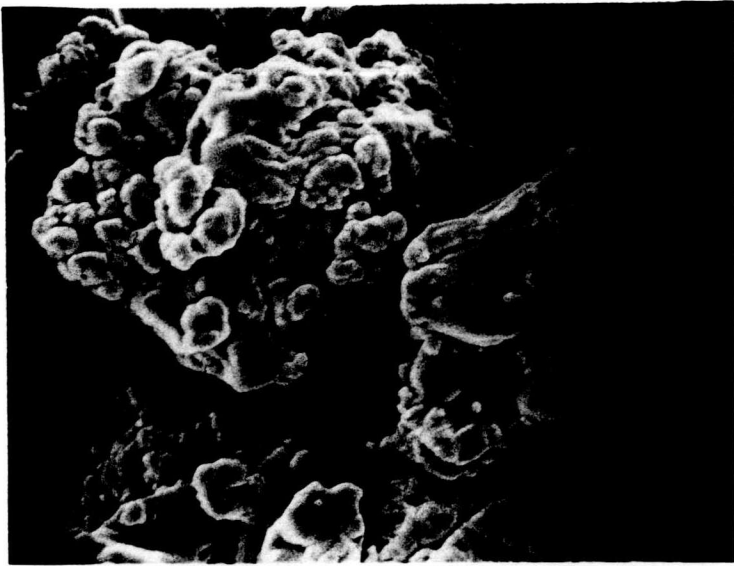
Figure D-c1 to D-c3 show the particle size distribution of the dispersion copolymer at various temperatures.



St 25% feed



St 38% feed



St 62% feed

Figure D-1 Scanning electron micrographs of the copolymers by solution copolymerization in the mixed solvent content of 80:20 weight% ethanol/n-hexane

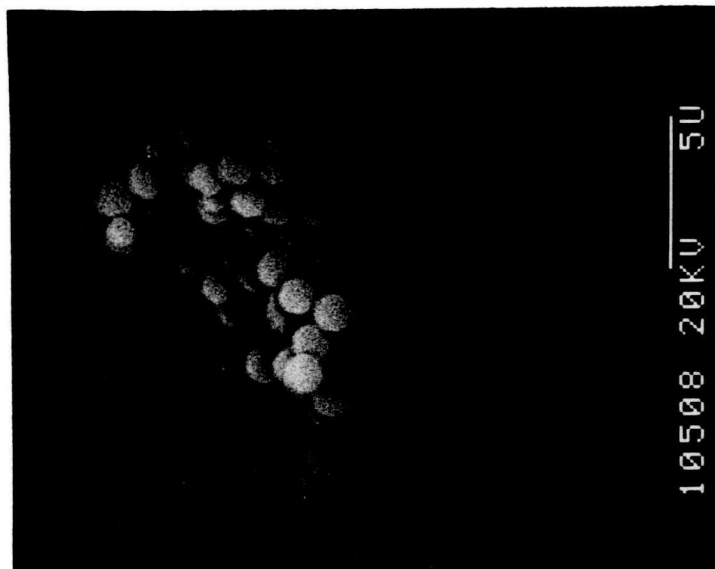
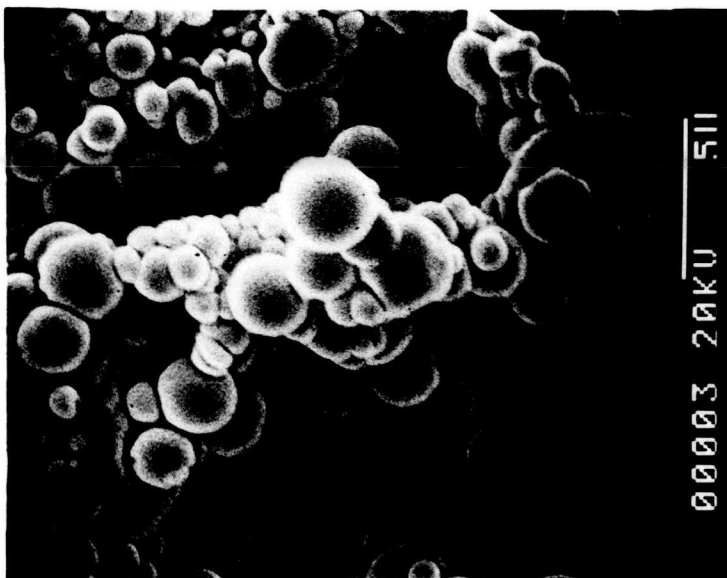
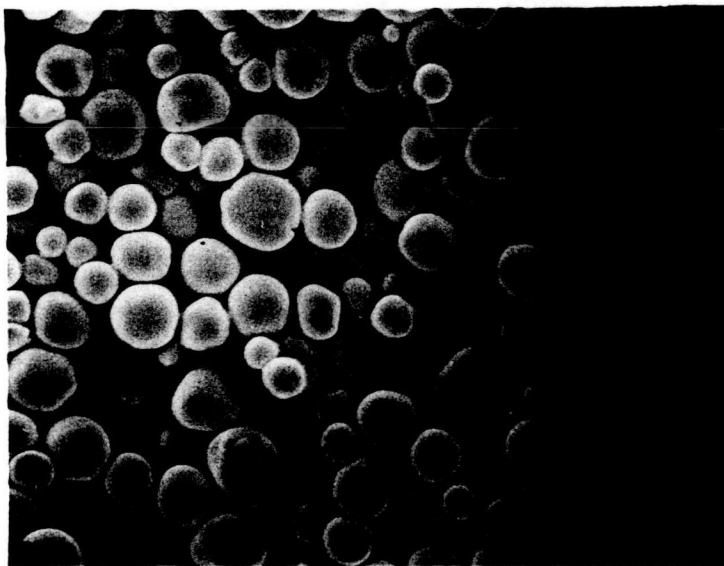
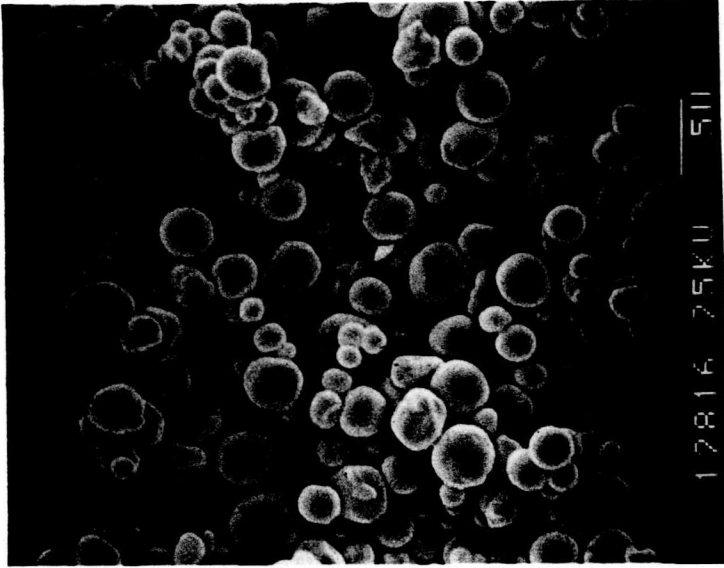


Figure D-2 Scanning electron micrographs of the PMMA (left) and PS (right) by dispersion polymerization in the mixed solvent content of 80:20 weight% ethanol/n-hexane

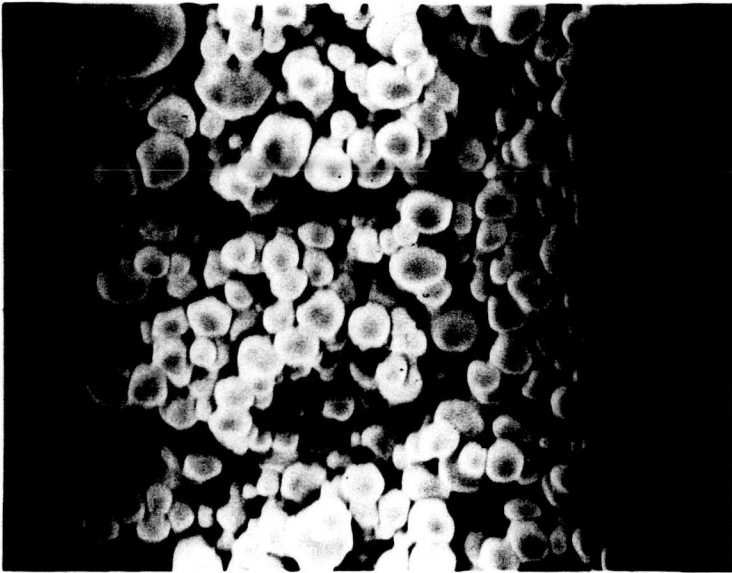


St 38% feed

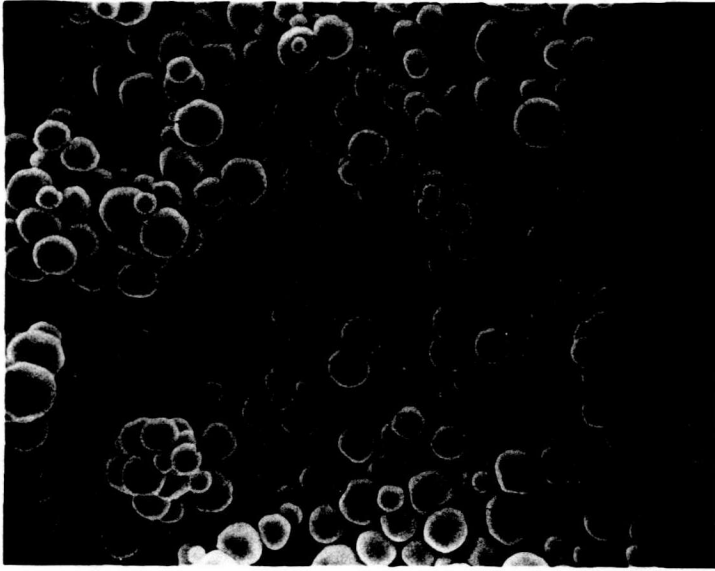


St 62% feed

Figure D-3 Scanning electron micrographs of the copolymers by dispersion copolymerization in the mixed solvent content of 80:20 weight% ethanol/n-hexane



EtOH 80% feed



EtOH 100% feed

Figure D-4 Scanning electron micrographs of the copolymers by dispersion copolymerization in the feed content of 25:75 mole% St/MMA in the homogeneous system

St 0% feed (PMMA)

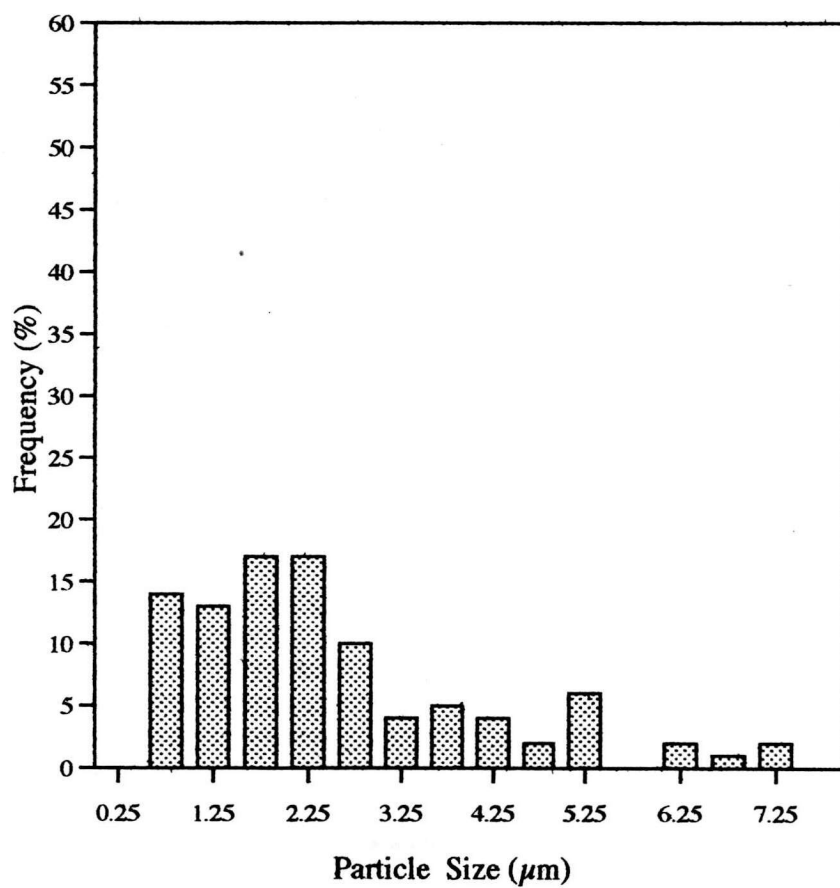


Figure D-a1 Particle size distribution of the dispersion copolymer (MMA 100% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 25 % feed

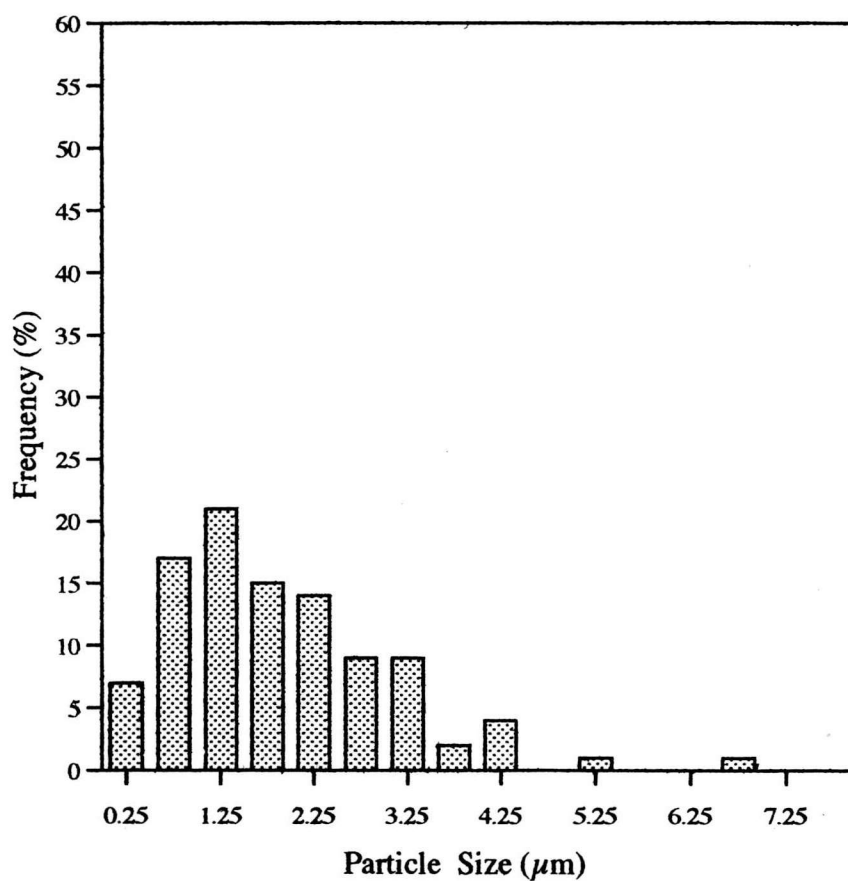


Figure D-a2 Particle size distribution of the dispersion copolymer (St 25% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 38 % feed

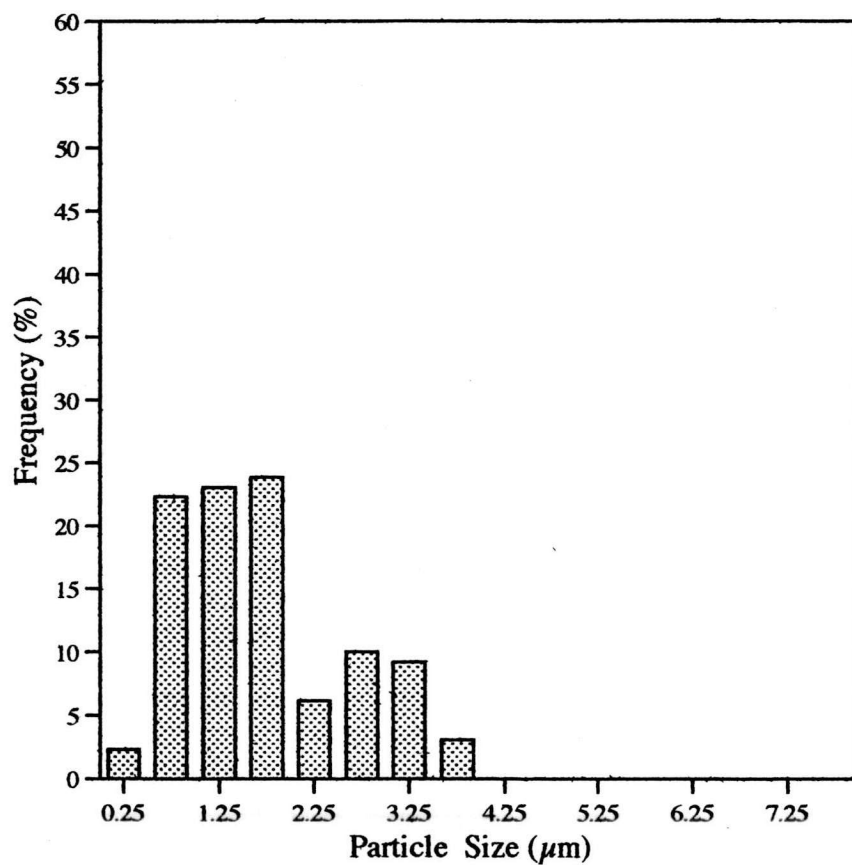


Figure D-a3 Particle size distribution of the dispersion copolymer(St 38% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 50 % feed

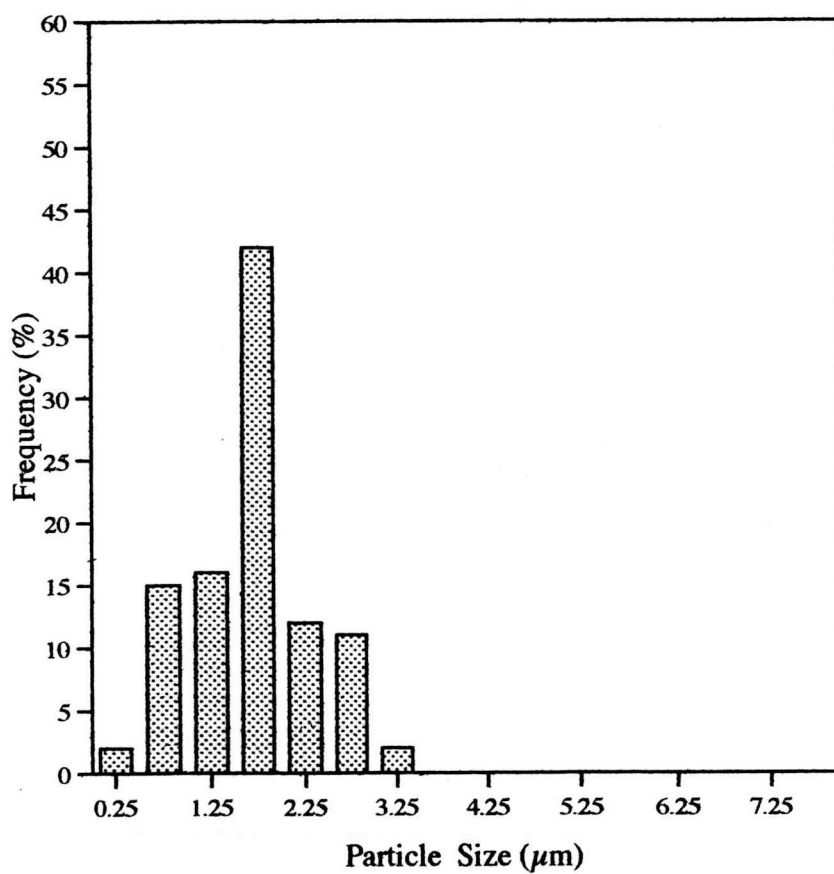


Figure D-a4 Particle size distribution of the dispersion copolymer(St 50% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 62 % feed

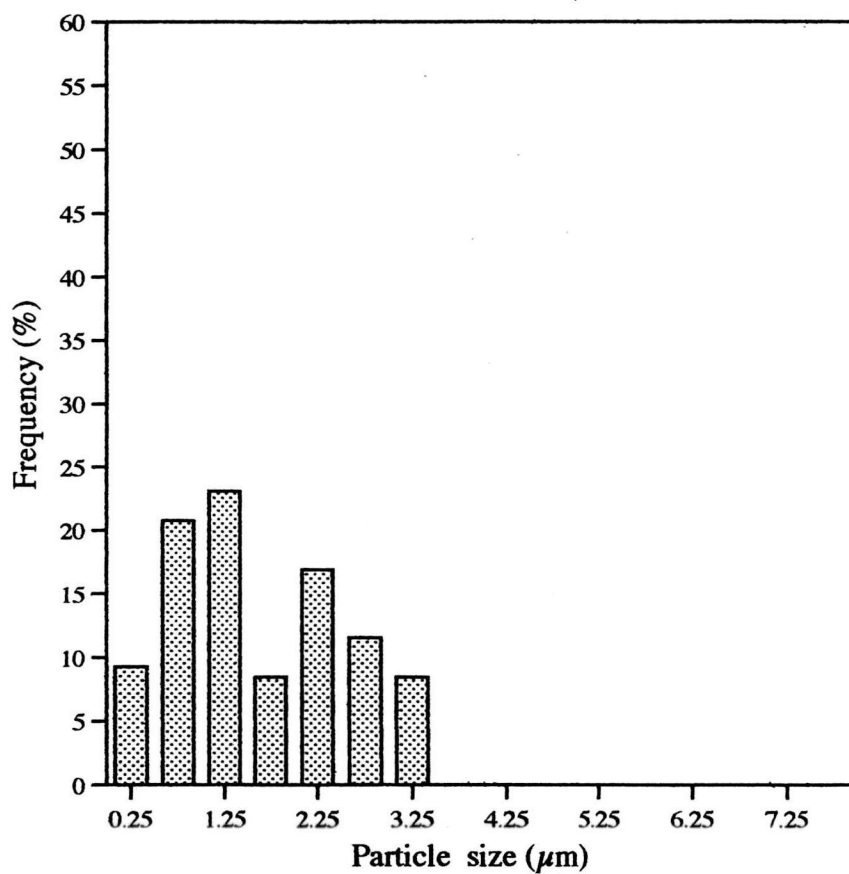


Figure D-a5 Particle size distribution of the dispersion copolymer(St 62% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 75 % feed

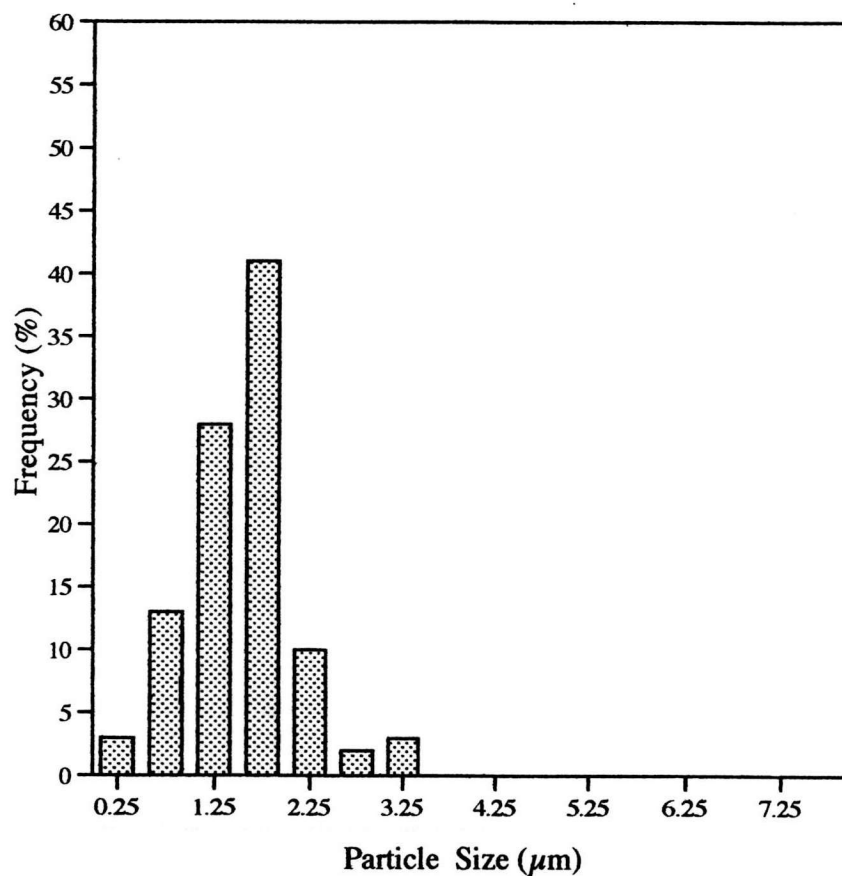
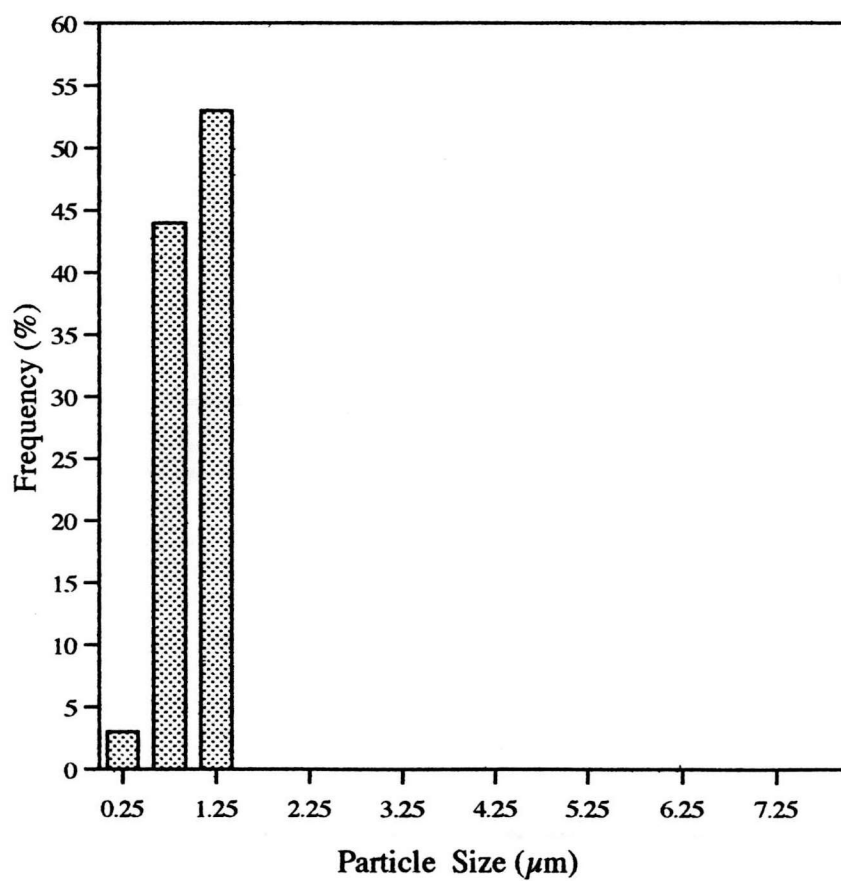


Figure D-a6 Particle size distribution of the dispersion copolymer (St 75% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

St 100% feed (PS)



FigureD-a7 Particle size distribution of the dispersion copolymer(St 100% feed) in the mixed solvent of 80:20 weight% ethanol/n-hexane

EtOH 0 %

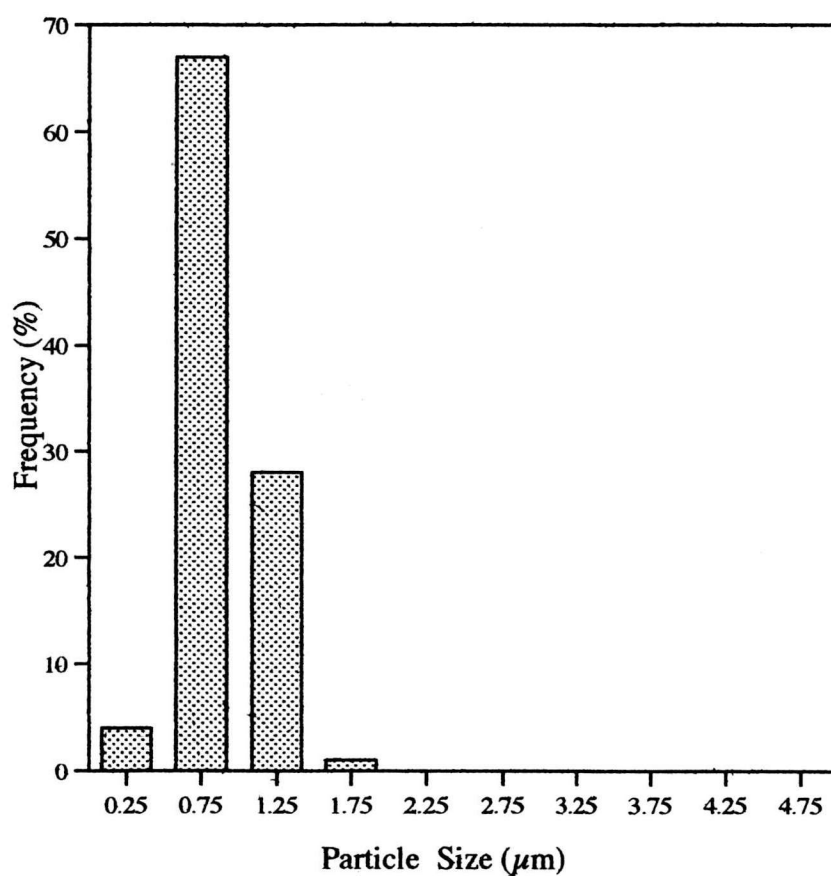


Figure D-b1 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% St/MMA in homogeneous system (100 weight% n-hexane)

EtOH 20 %

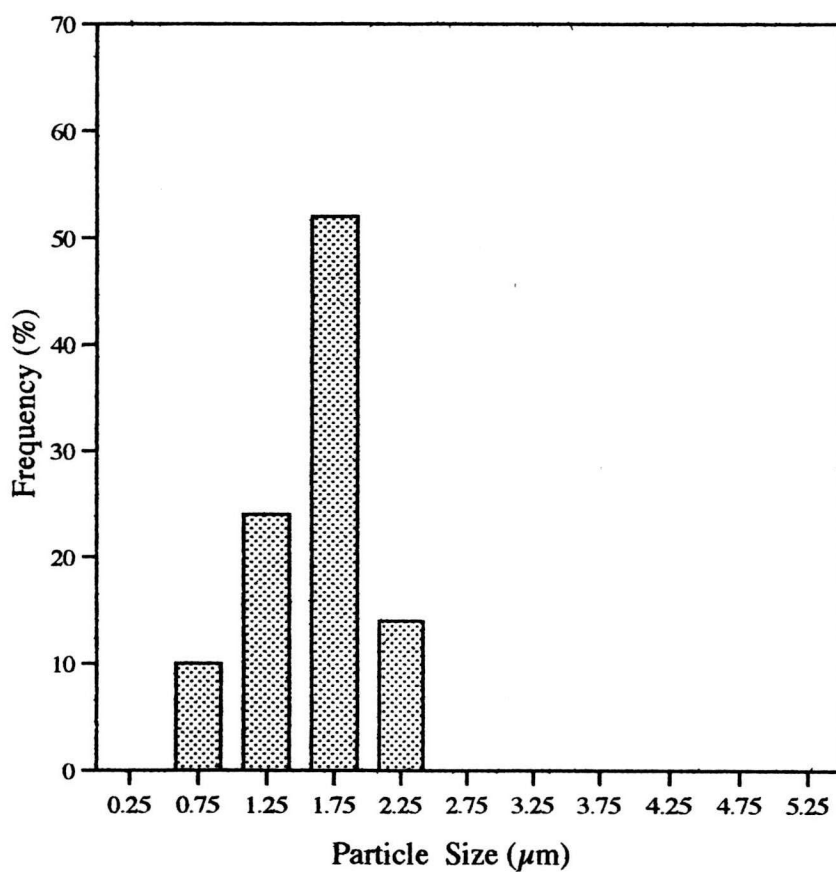


Figure D-b2 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% St/MMA in homogeneous system (EtOH 20 weight%)

EtOH 35 %

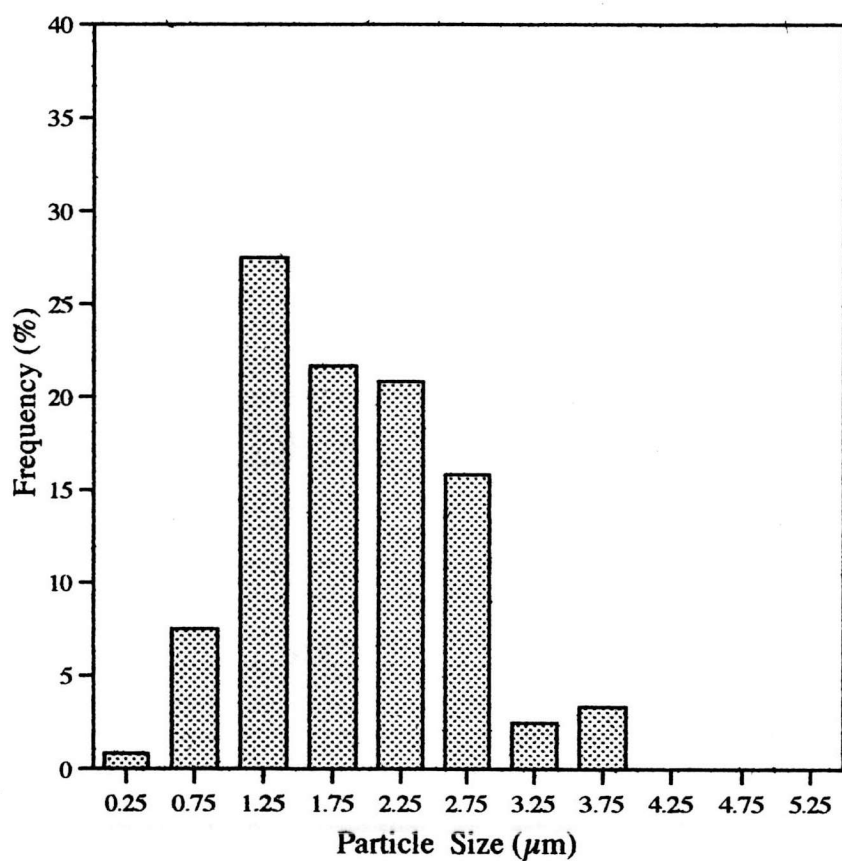


Figure D-b3 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole % St/MMA in homogeneous system (EtOH 35 weight%)

EtOH 50 %

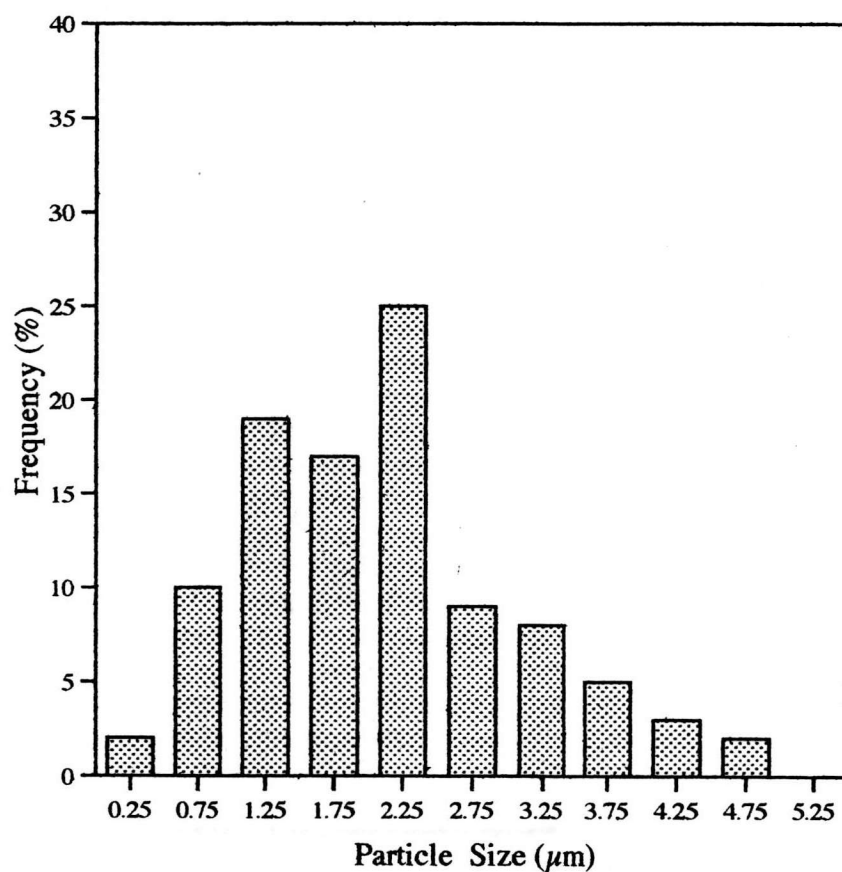


Figure D-b4 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% St/MMA in heterogeneous system (EtOH 50 weight%)

EtOH 65 %

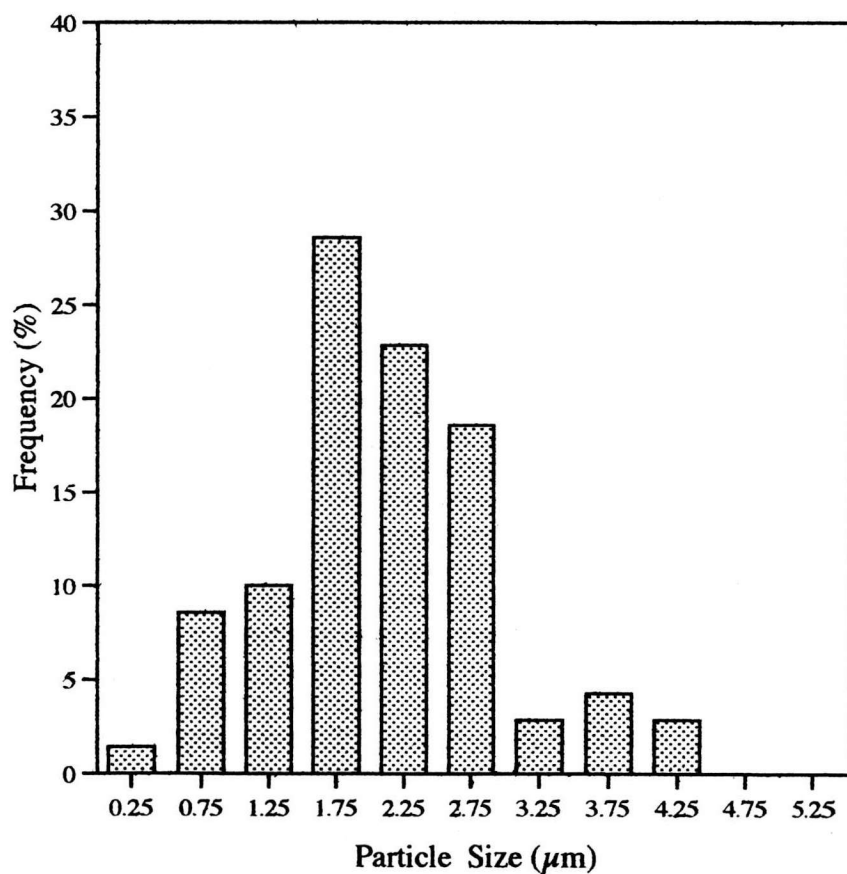


Figure D-b5 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% St/MMA in heterogeneous system (EtOH 65 weight%)

EtOH 80 %

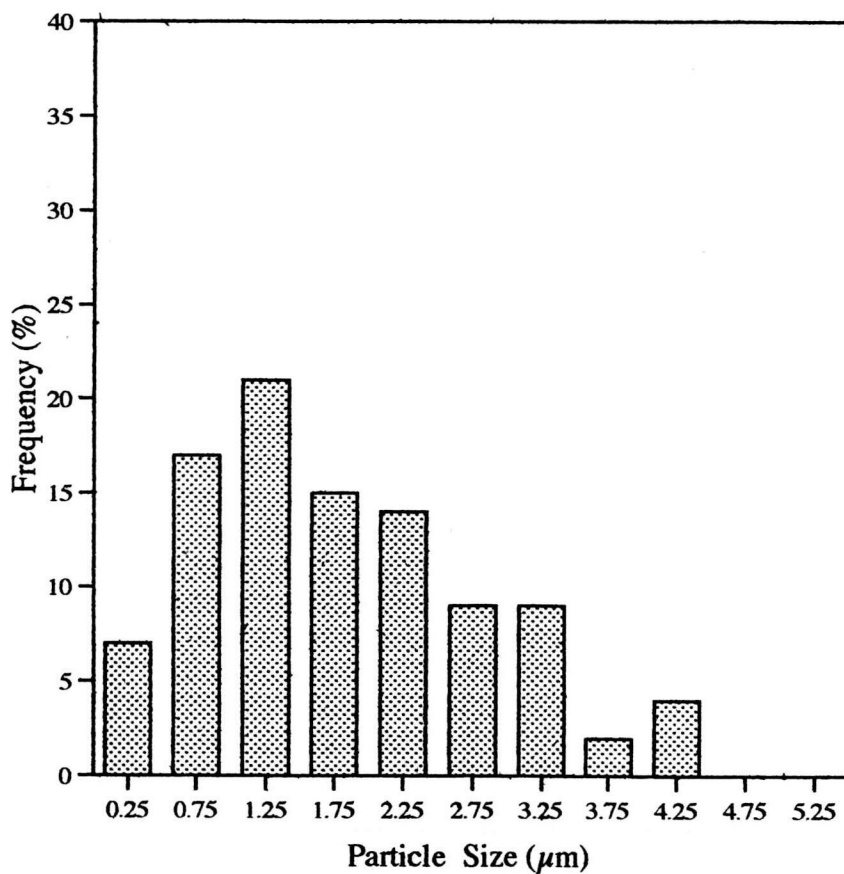


Figure D-b6 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% mole% St/MMA in homogeneous system (EtOH 80 weight%)

EtOH 100 %

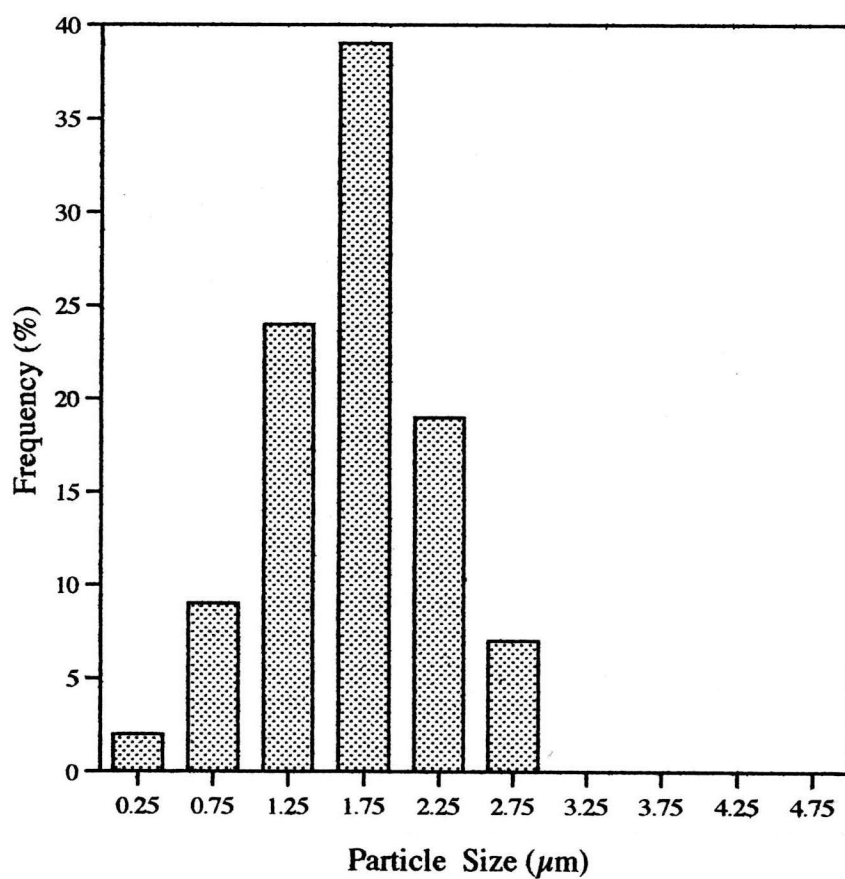


Figure B-b7 Particle size distribution of the dispersion copolymer in the feed content of 25:75 mole% St/MMA in homogeneous system (EtOH 100 weight%)

Temperature 50°C

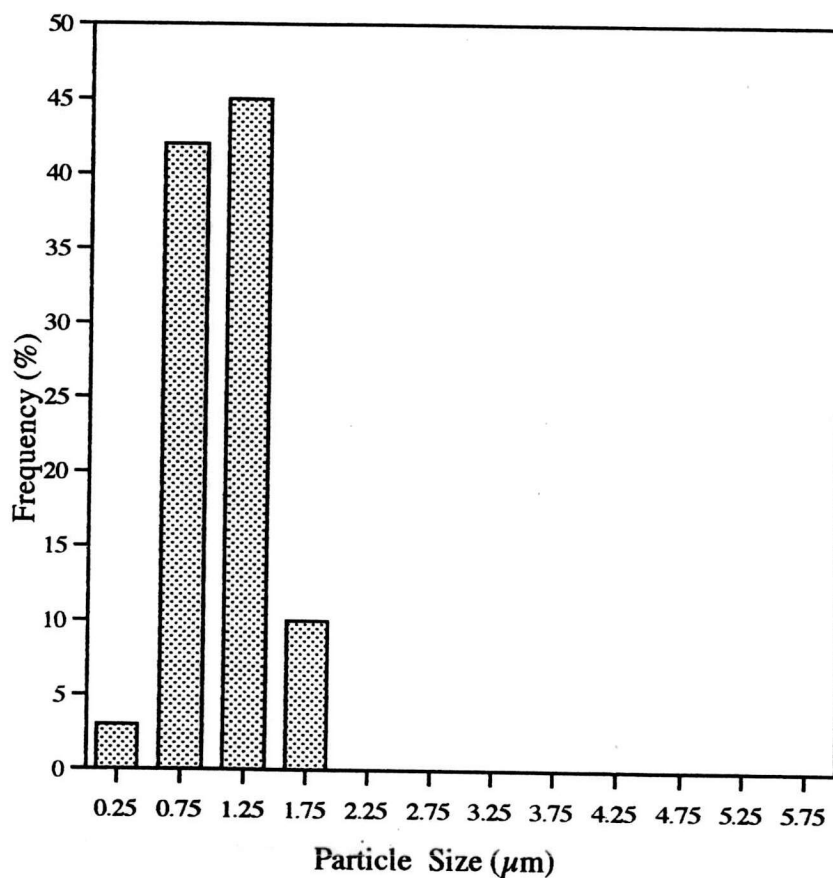


Figure D-c1 Particle size distribution of the dispersion copolymer in the feed of 75:25 mole% St/MMA and mixed solvent content of 80:20 weight% ethanol/n-hexane at 50° C of the reaction temperature

Temperature 55°C

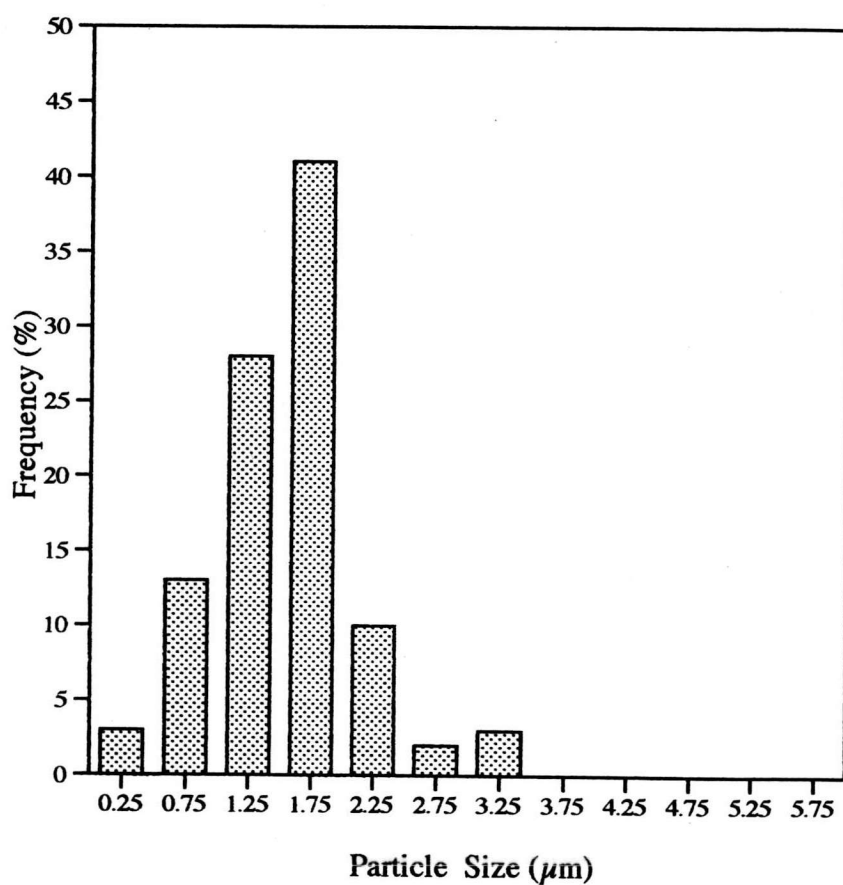


Figure D-c2 Particle size distribution of the dispersion copolymer in the feed of 75:25 mole% St/MMA and mixed solvent content of 80:20 weight% ethanol/n-hexane at 55°C of the reaction temperature

Temperature 64°C

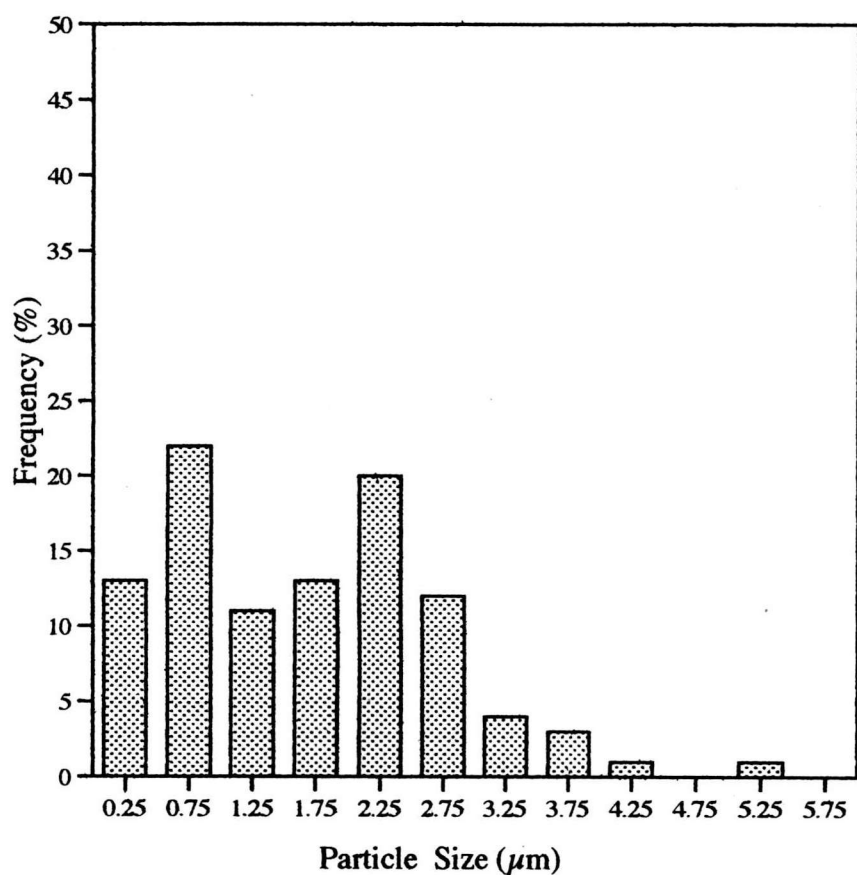


Figure D-c3 Particle size distribution of the dispersion copolymer in the feed of 25:75 mole% St/MMA and mixed solvent content of 80:20 weight% ethanol/n-hexane at 64°C of the reaction temperature

Appendix E

Calculated-Glass Transition Temperature

T_g of the copolymer was calculated from the following (1):

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2) \quad E(1)$$

T_{g1} and T_{g2} are the glass transition temperatures of homopolymers 1 and 2
w₁ and w₂ are the weight fractions of constituents 1 and 2 in the copolymer.
K is calculated from the ratio of α_r-α_g of homopolymer 1 to homopolymer 2

when α_r is the thermal expansion coefficient of the rubber state.

α_g is the thermal expansion coefficient of the glass state.

α_r-α_g is about 2x10⁵ for polystyrene and poly(methyl methacrylate).

The relation between T_g of the homopolymer and the copolymer is therefore transformed into

$$T_g = (w_1 T_{g1} + w_2 T_{g2}) / (w_1 + w_2) = w_1 T_{g1} + w_2 T_{g2} \quad E(2)$$

as w₁+w₂ = 1

An example of calculation

Dispersion copolymerization of 25:75 mole% styrene/methyl methacrylate feed and 80:20 weight % ethanol/n-hexane in mixed solvent.

Let styrene be the constituent 1,

w₁ be the weight fraction of styrene in copolymer = 35.9%,

w₂ be the weight fraction of methyl methacrylate in copolymer = 64.1%,

T_{g1} be the glass transition temperature of homopolystyrene = 96°C,

T_{g2} be the glass transition temperature of homopoly(methyl methacrylate) = 111°C.

$$\begin{aligned} T_g \text{ of the 25 mole\% styrene feed copolymer} &= (0.359 \times 96) + (0.641 \times 111) \\ &= 105.2^\circ\text{C} \end{aligned}$$

Reference

1. Billmeyer, F.W. Textbook of Polymer Science. 3rd ed. New York: John Wiley & Sons., 1984:337-339.

APPENDIX F

Gel Permeation Chromatography

The GPC chromatograms were obtained on a Shimadzu (LC-10A) with a Showa Denko (KF-80M) chromatography column at the maximum temperature of 60°C. Both of refractive index (RI) and ultraviolet (UV) spectrophotometer were used as detectors. UV detector was used at 277 nm for PS and copolymers and at 246 nm for PMMA. The GPC column was packed with poly(styrene-co-divinylbenzene) with the minimum number of theoretical plates 10,000. Tetrahydrofuran (THF) was used as a solvent and carrier.

For GPC analysis, 2 mg of dried sample was dissolved into 2 ml of THF. The solution was then filtered by using 0.45 μm syringe filter. 10 microliter of the filtered polymer solution was injected into the GPC (using THF as the carrier fluid) for each analysis.

- Figures F-a1 to F-a7 show the GPC chromatograms of solution copolymers
- Figures F-b1 to F-b5 show the GPC chromatograms of bulk copolymer
- Figures F-cs1 to F-cs7 show the GPC chromatograms of dispersion copolymers at various styrene feeds
- Figures F-ce1 to F-ce7 show the GPC chromatograms of dispersion copolymers at various ethanol contents
- Figures F-ct1 to F-ct4 show the GPC chromatograms of dispersion copolymers at various reaction temperatures

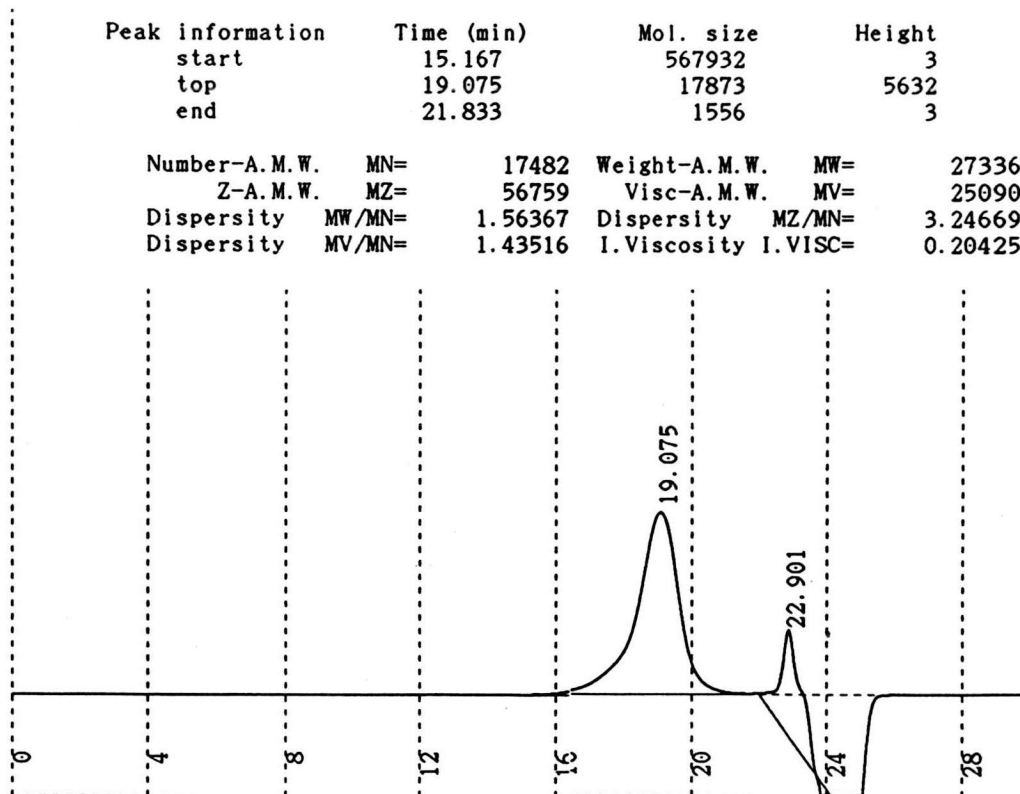


Figure F-a1 GPC chart of solution homopolymer: St feed 0 mole%

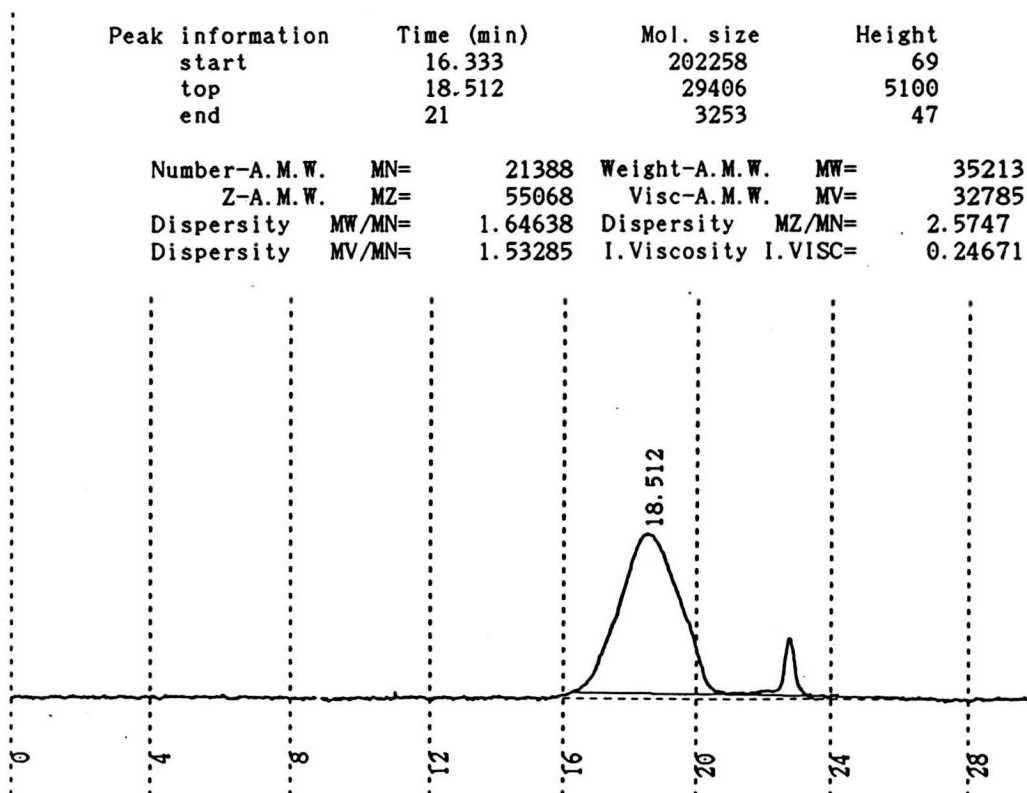


Figure F-a2 GPC chart of solution copolymer: St feed 25 mole%

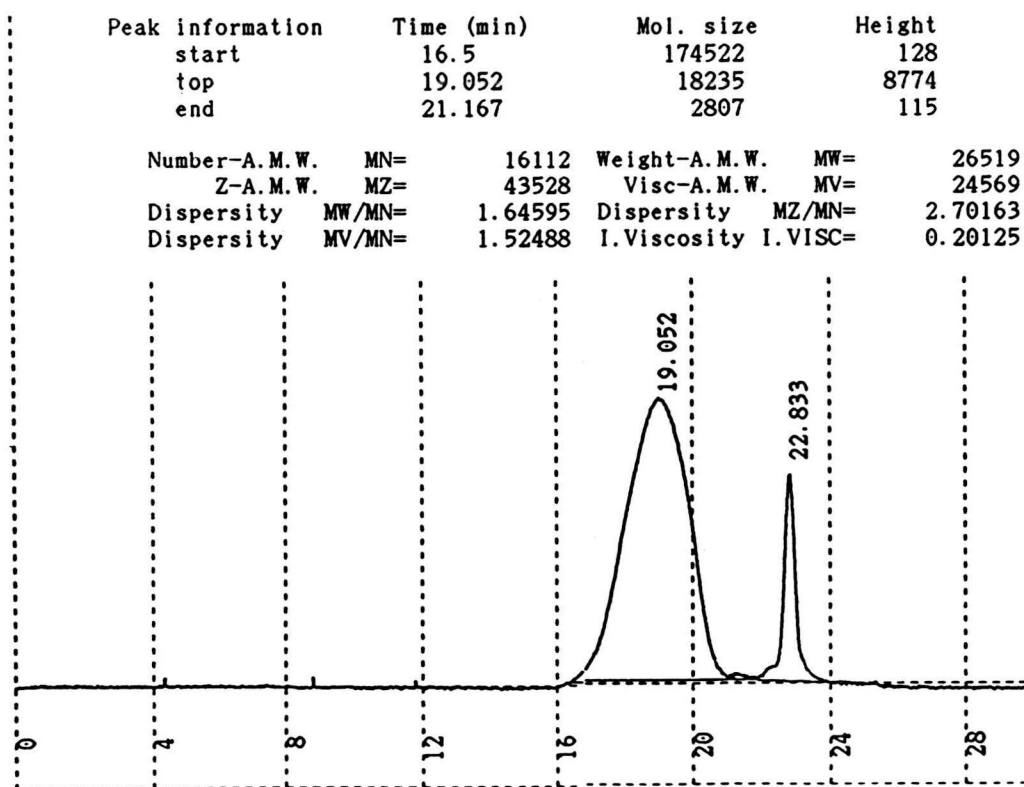


Figure F-a3 GPC chart of solution copolymer: St feed 38 mole%

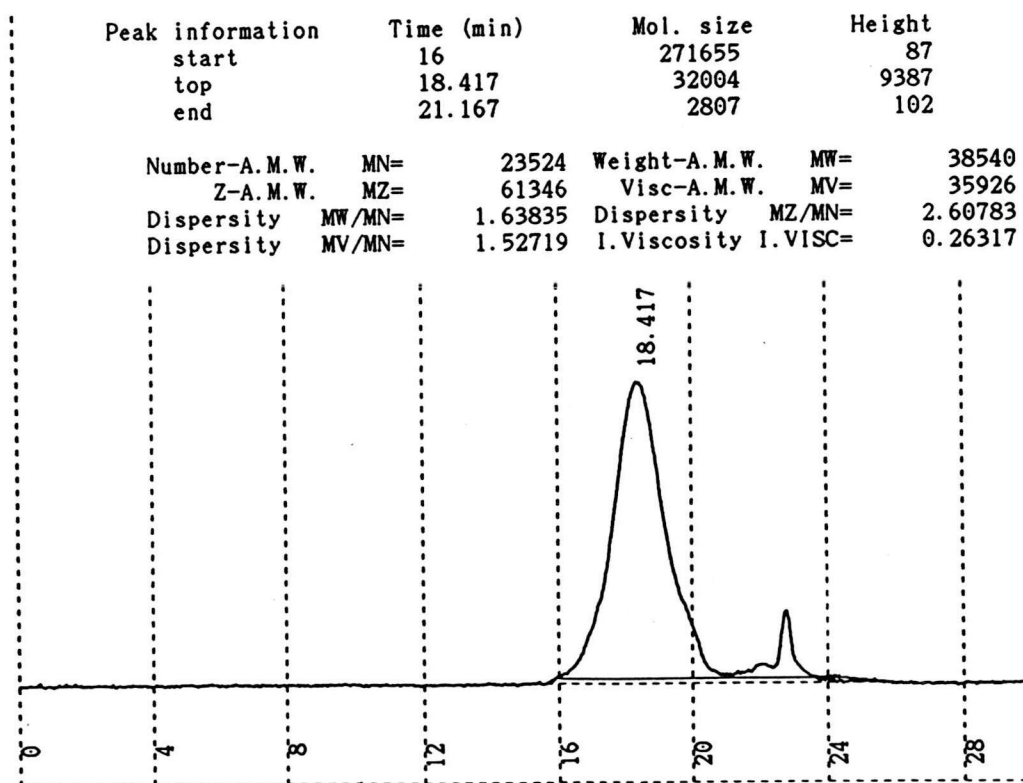


Figure F-a4 GPC chart of solution copolymer: St feed 50 mole%

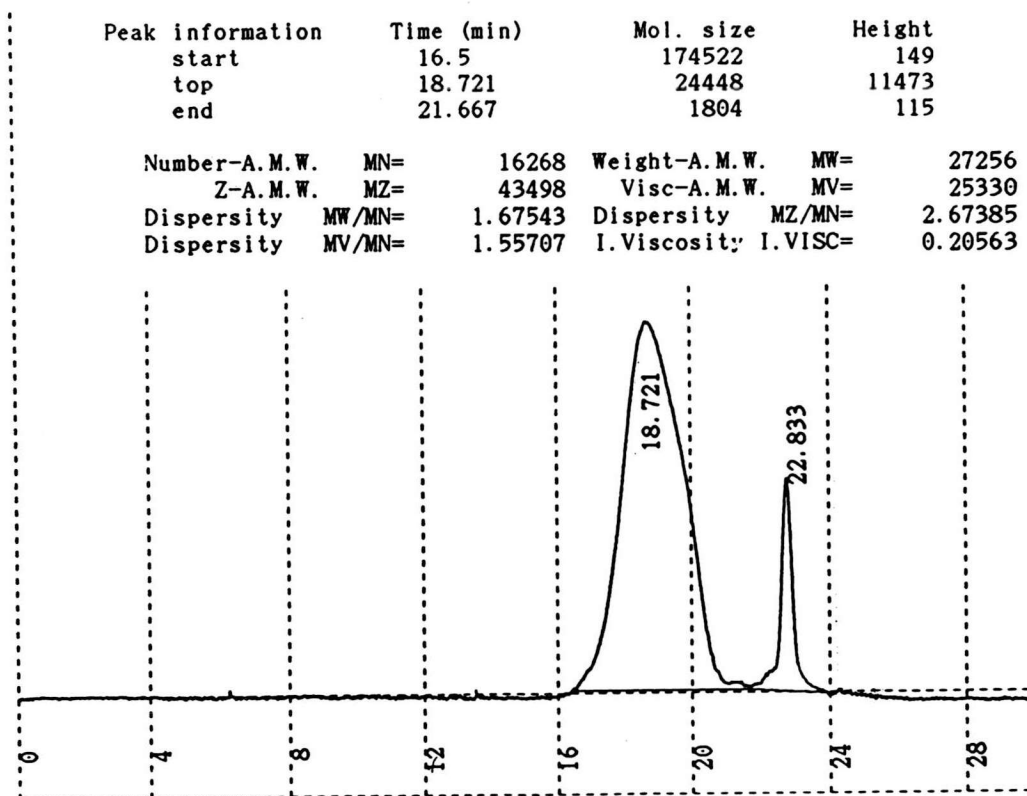


Figure F-a5 GPC chart of solution copolymer: St feed 62 mole%

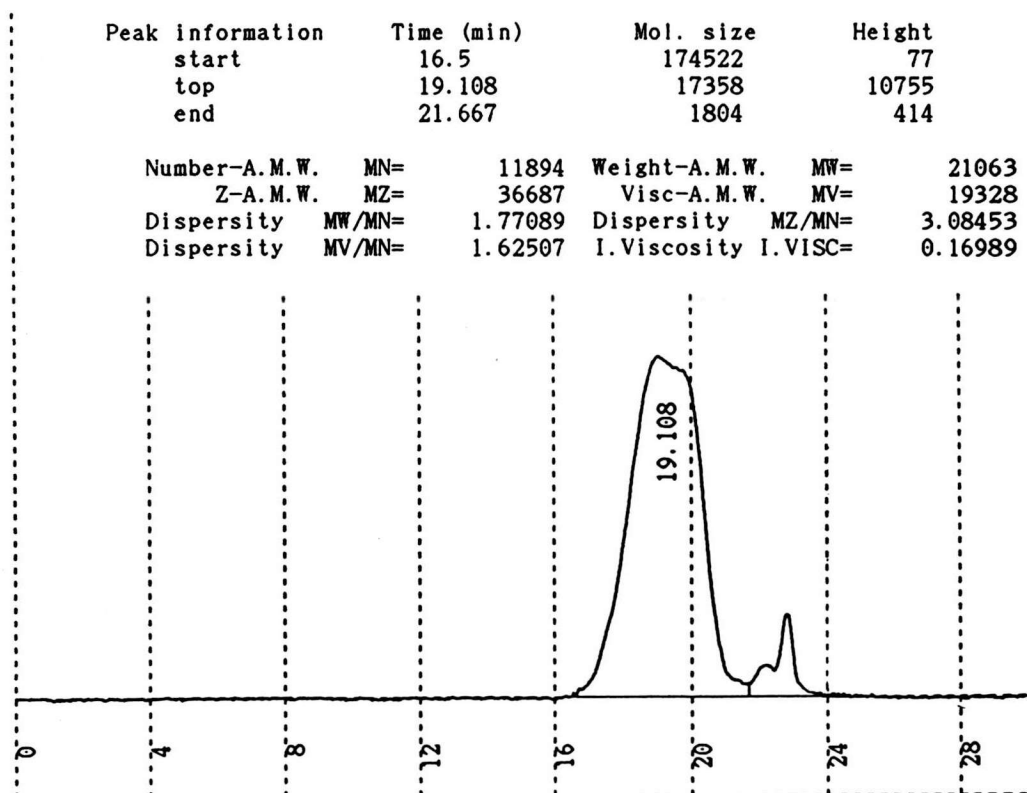


Figure F-a6 GPC chart of solution copolymer: St feed 75 mole%

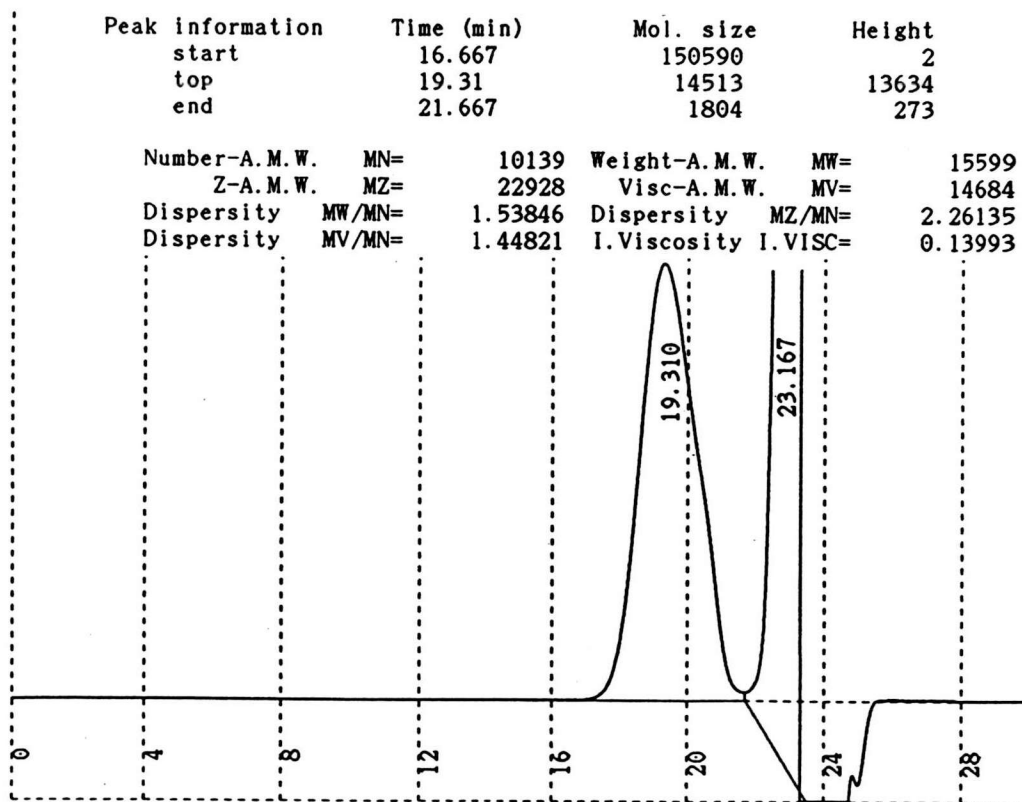


Figure F-a7 GPC chart of solution homopolymer: St feed 100 mole%

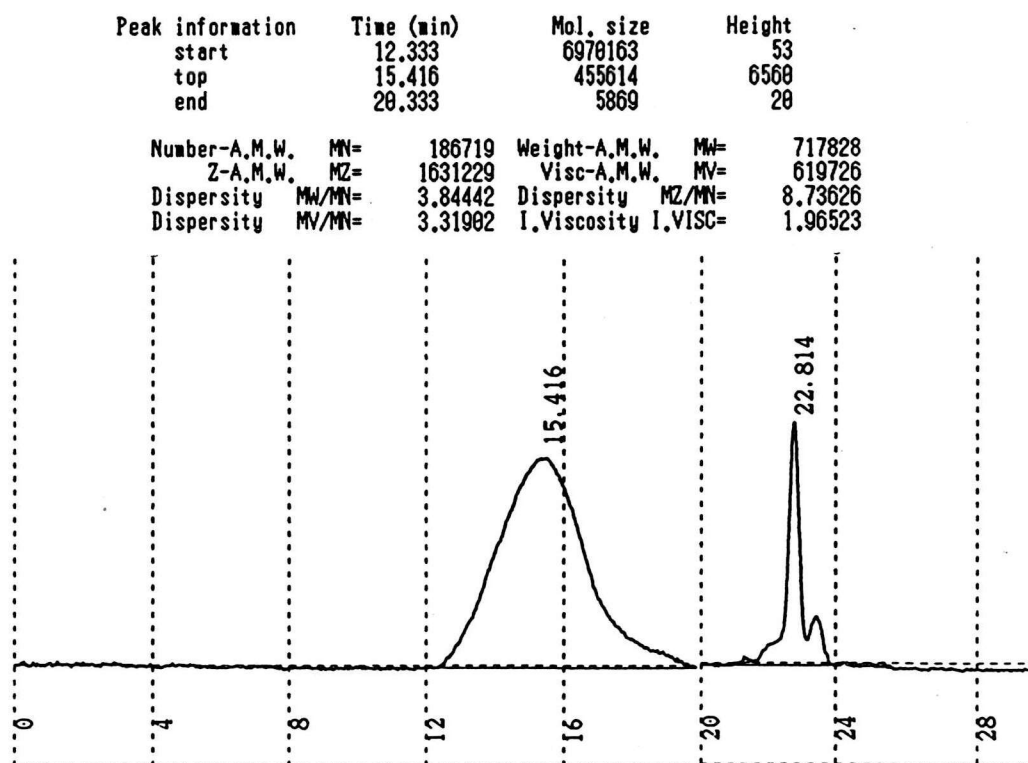


Figure F-b1 GPC chart of bulk comopolymer: St feed 25 mole%

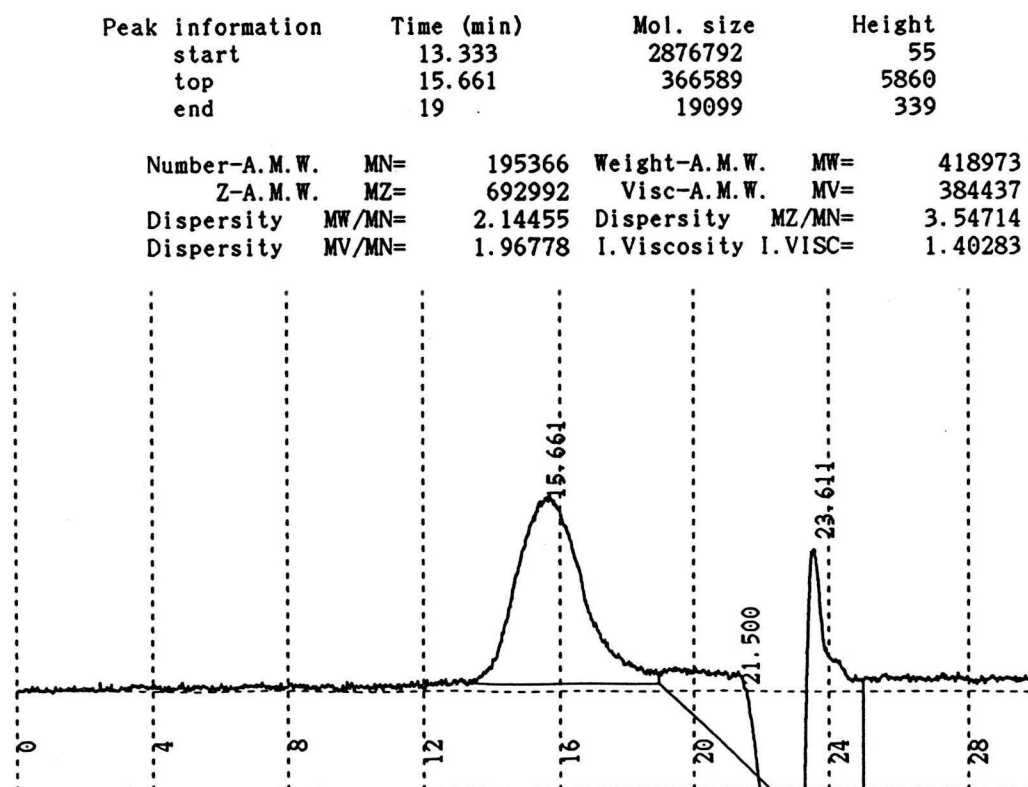


Figure F-b2 GPC chart of bulk comopolymer: St feed 38 mole%

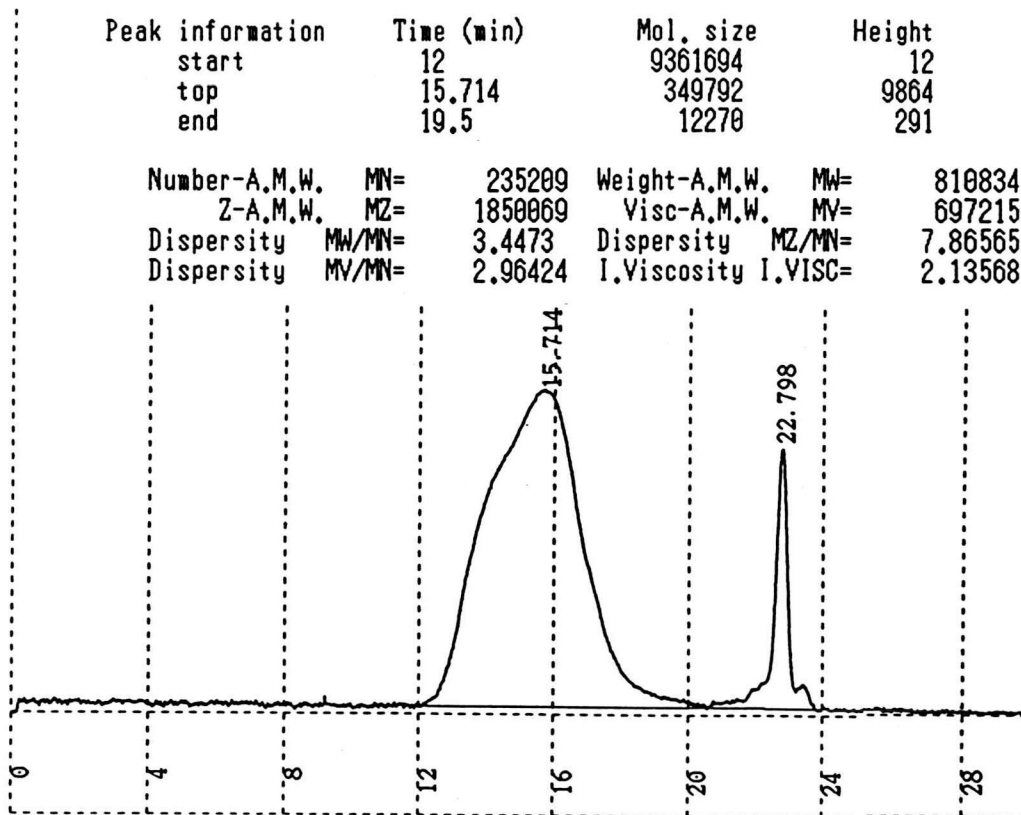


Figure F-b3 GPC chart of bulk comopolymer: St feed 50 mole%

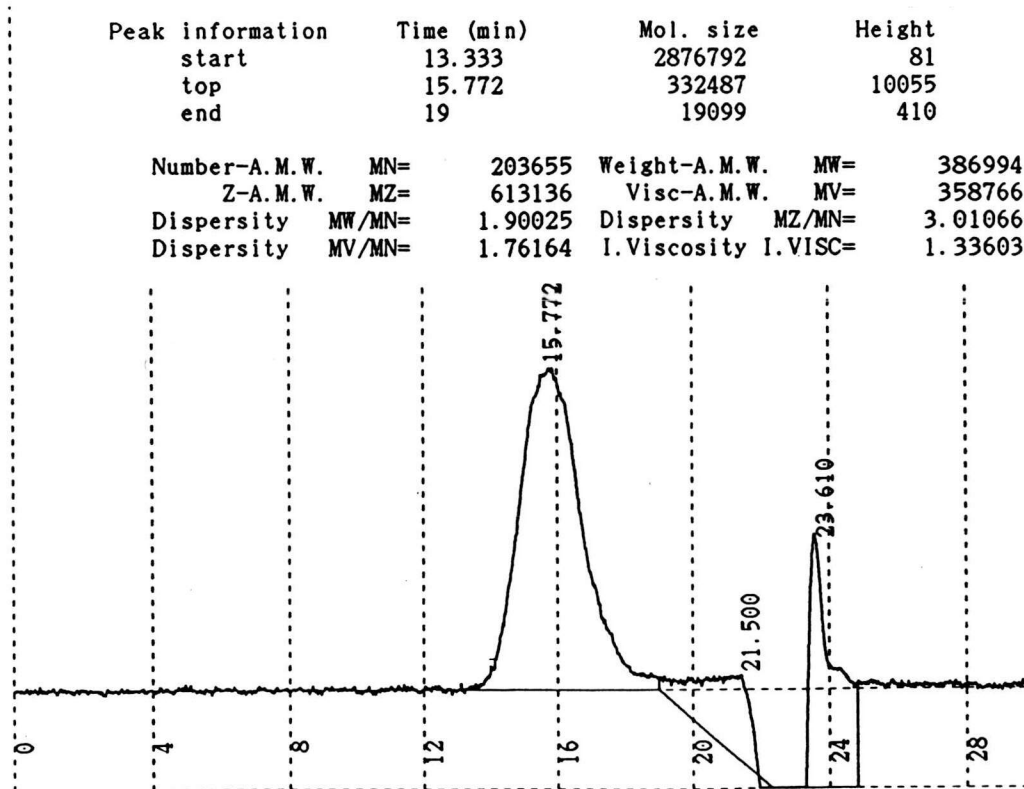


Figure F-b4 GPC chart of bulk comopolymer: St feed 62 mole%

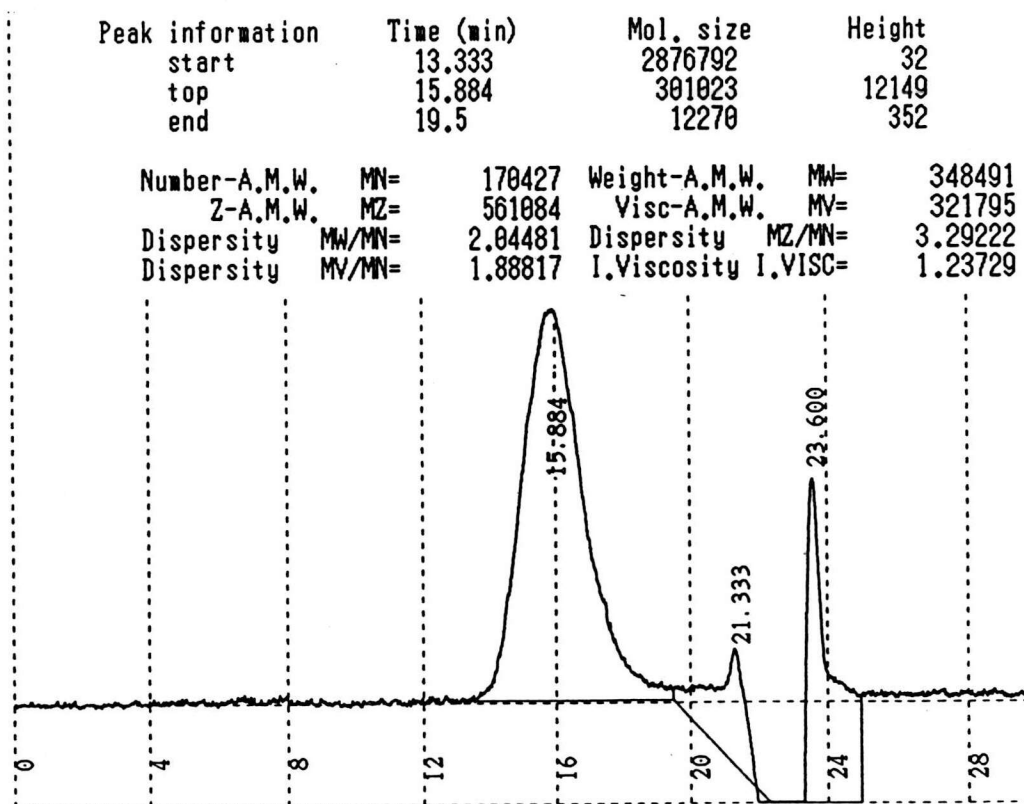


Figure F-b5 GPC chart of bulk comopolymer: St feed 75 mole%

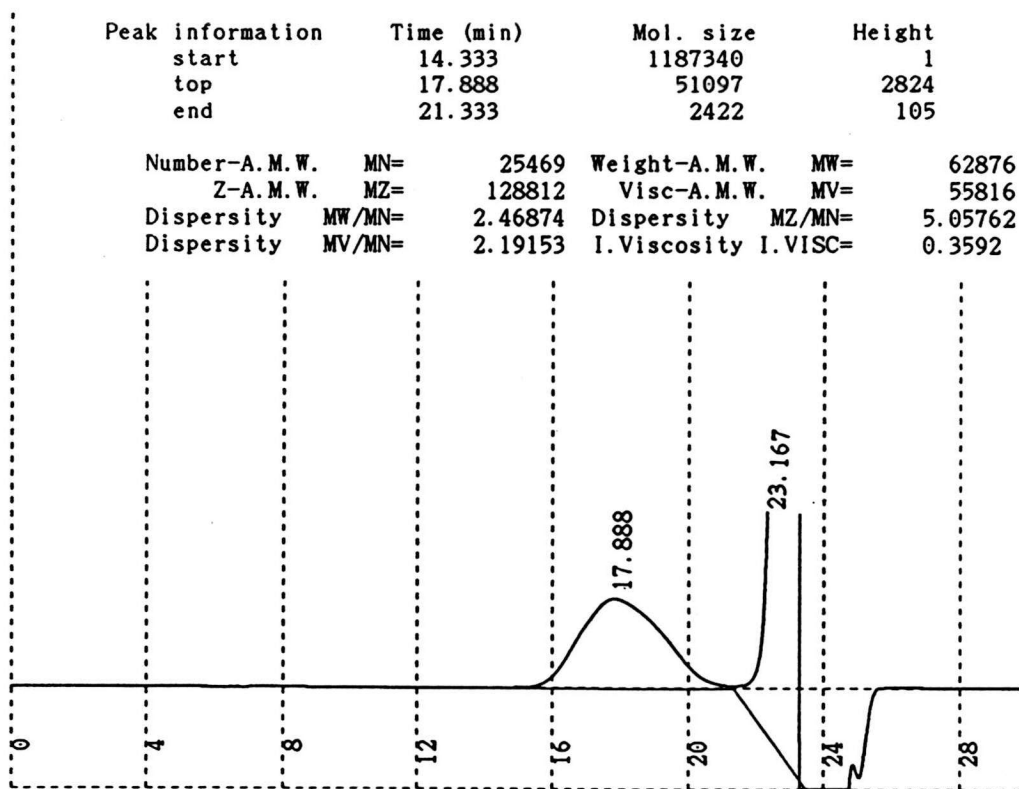


Figure F-cs1 GPC chart of dispersion homopolymer: St feed 0 mole%

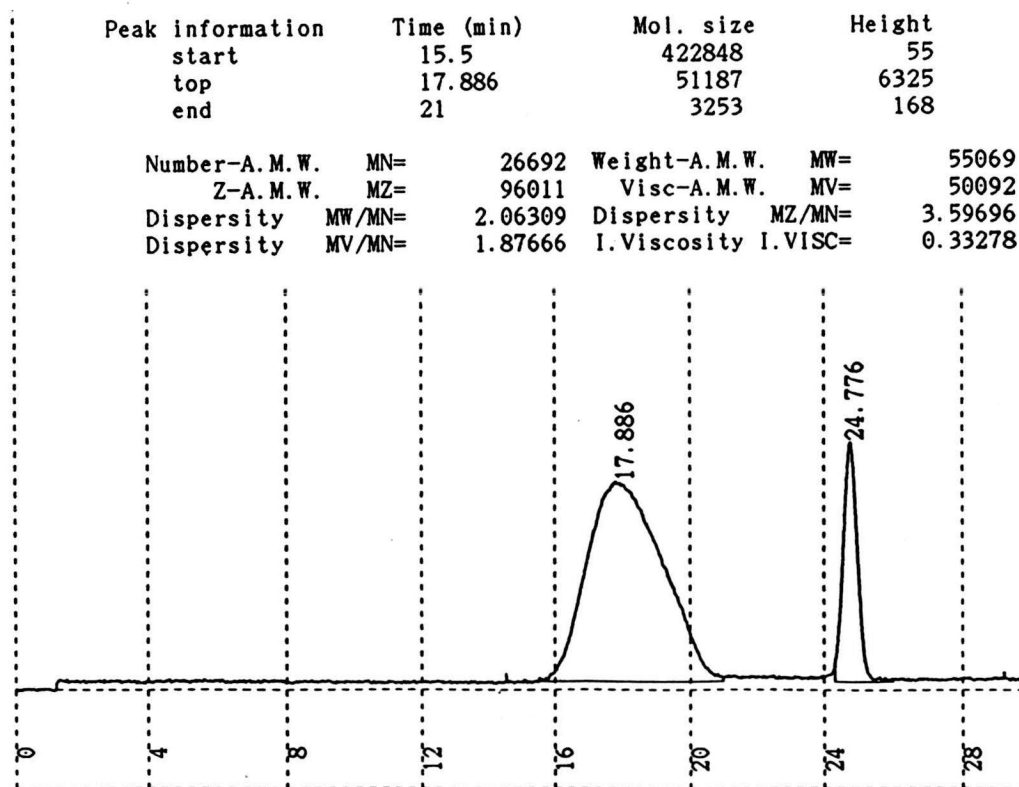


Figure F-cs2 GPC chart of dispersion copolymer: St feed 25 mole%,

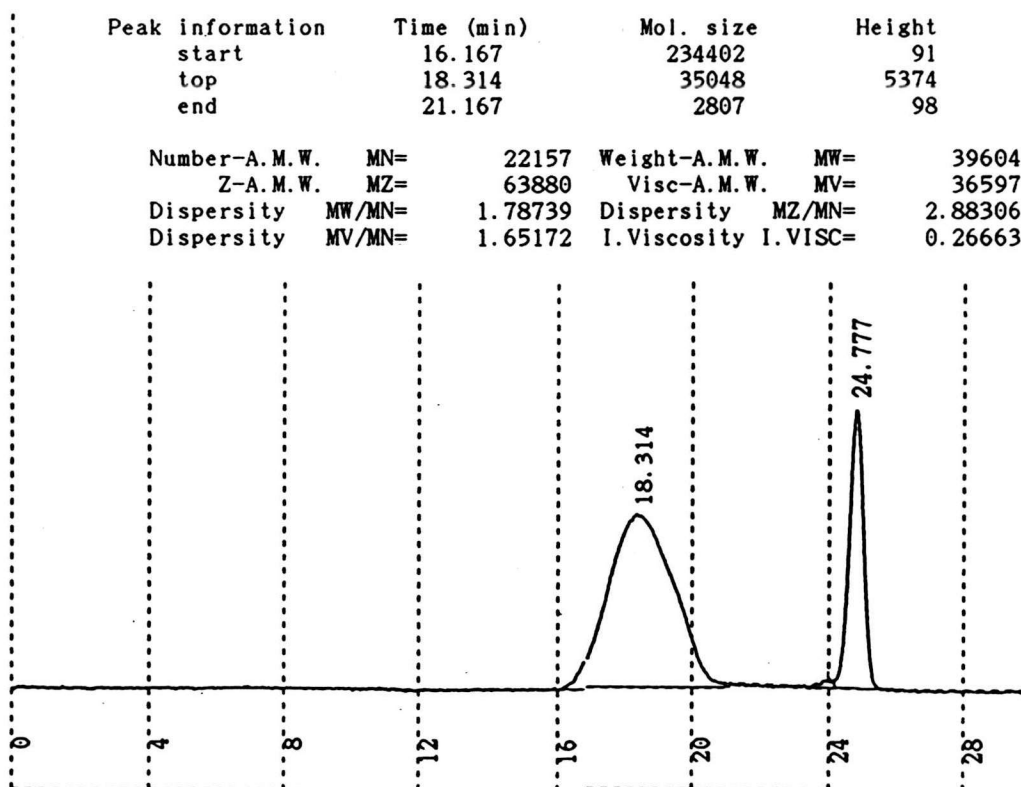


Figure F-cs3 GPC chart of dispersion copolymer: St feed 38 mole%,

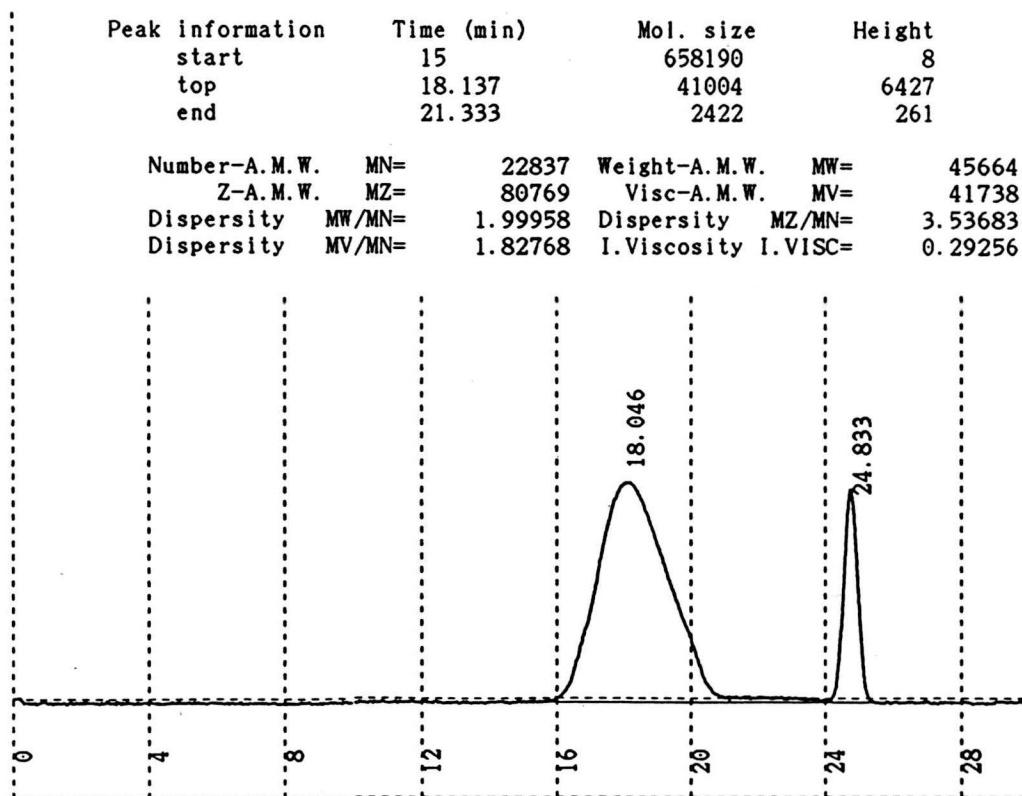


Figure F-cs4 GPC chart of dispersion copolymer: St feed 50 mole%,

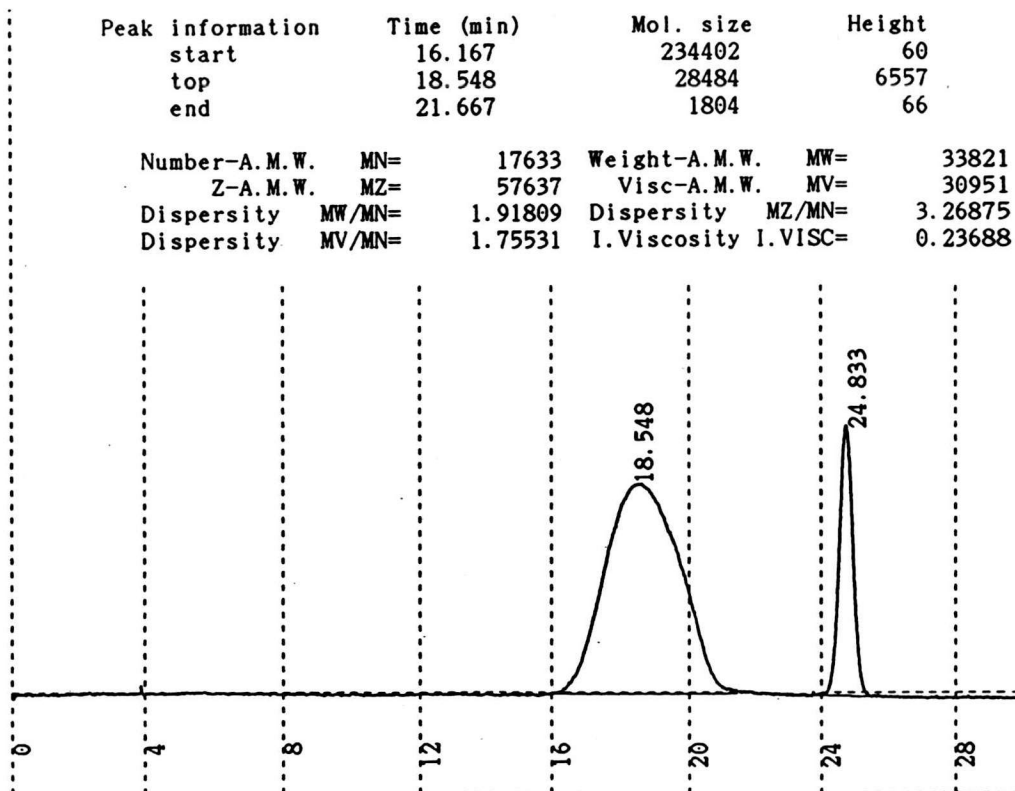


Figure F-cs5 GPC chart of dispersion copolymer: St feed 62 mole%,

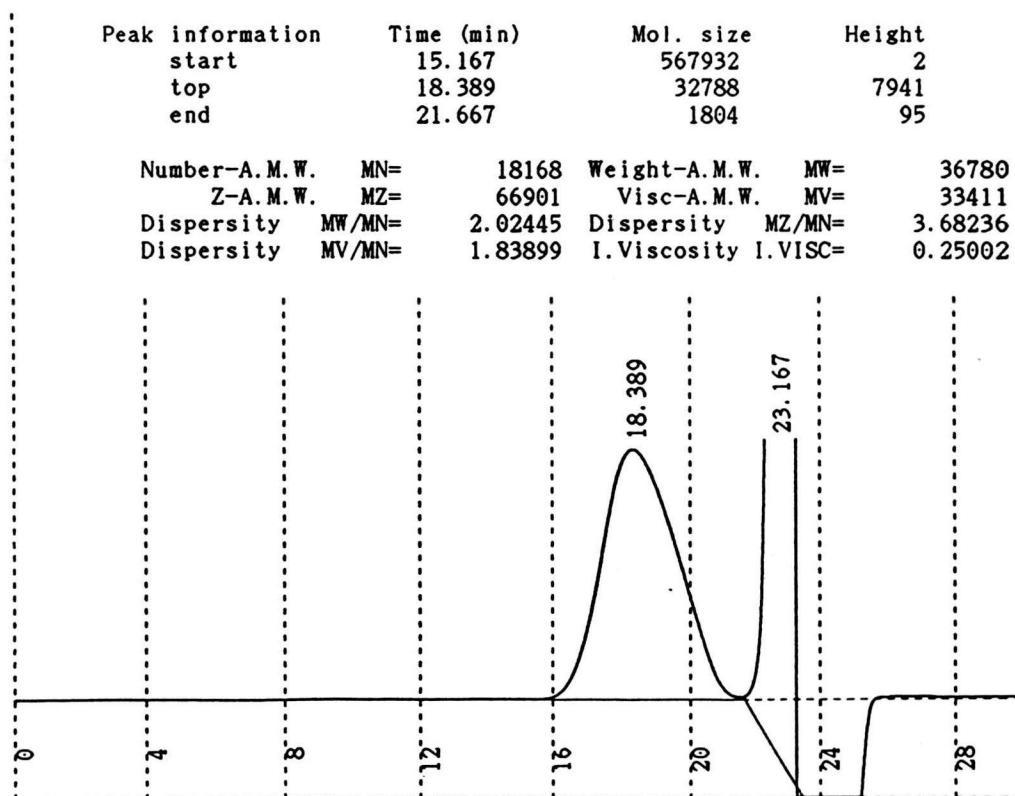


Figure F-cs6 GPC chart of dispersion copolymer: St feed 75 mole%,

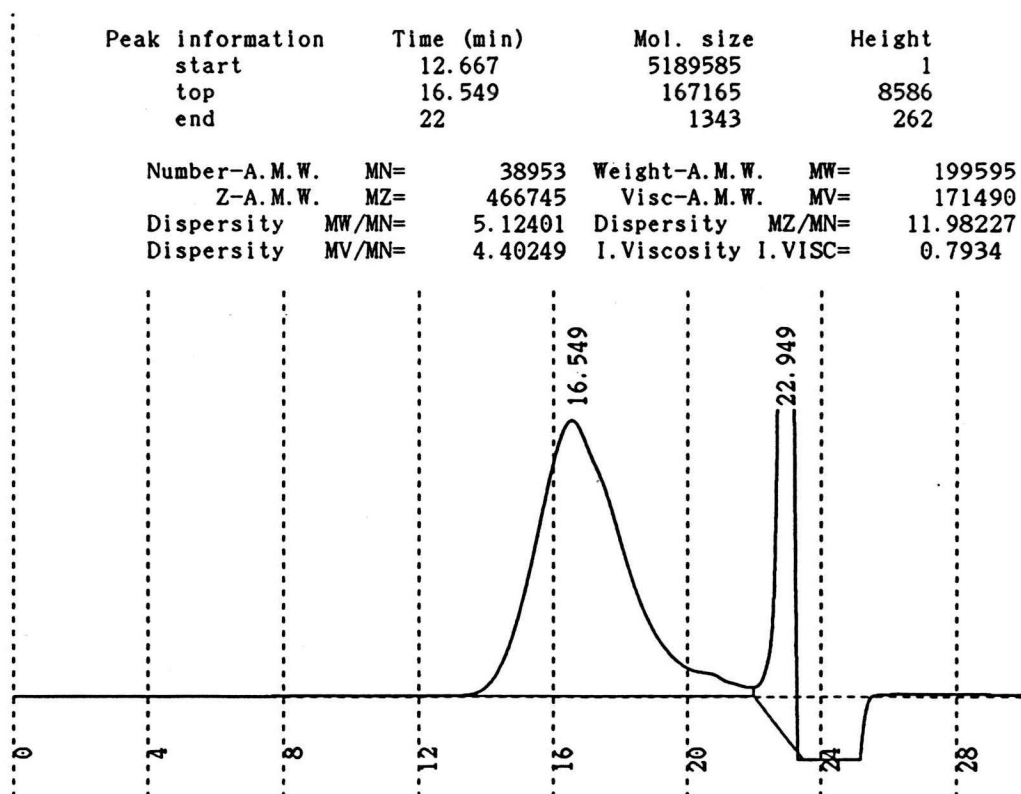


Figure F-cs7 GPC chart of dispersion homopolymer: St feed 100 mole%

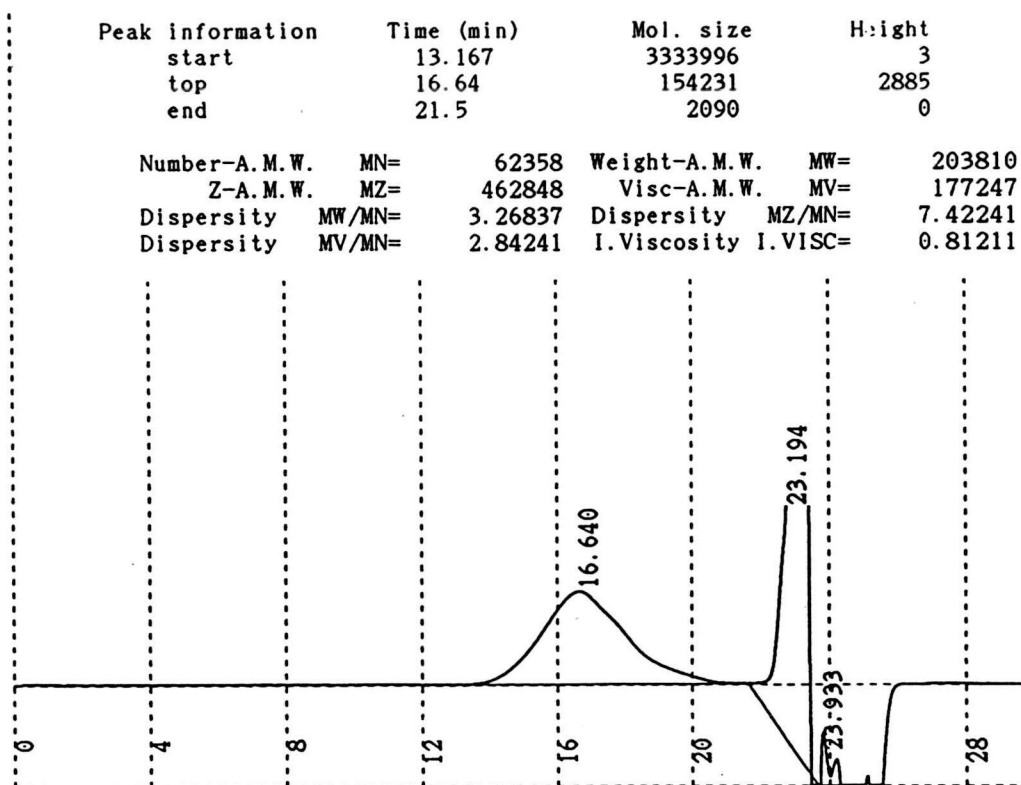


Figure F-ce1 GPC chart of dispersion copolymer: EtOH 0 weight%

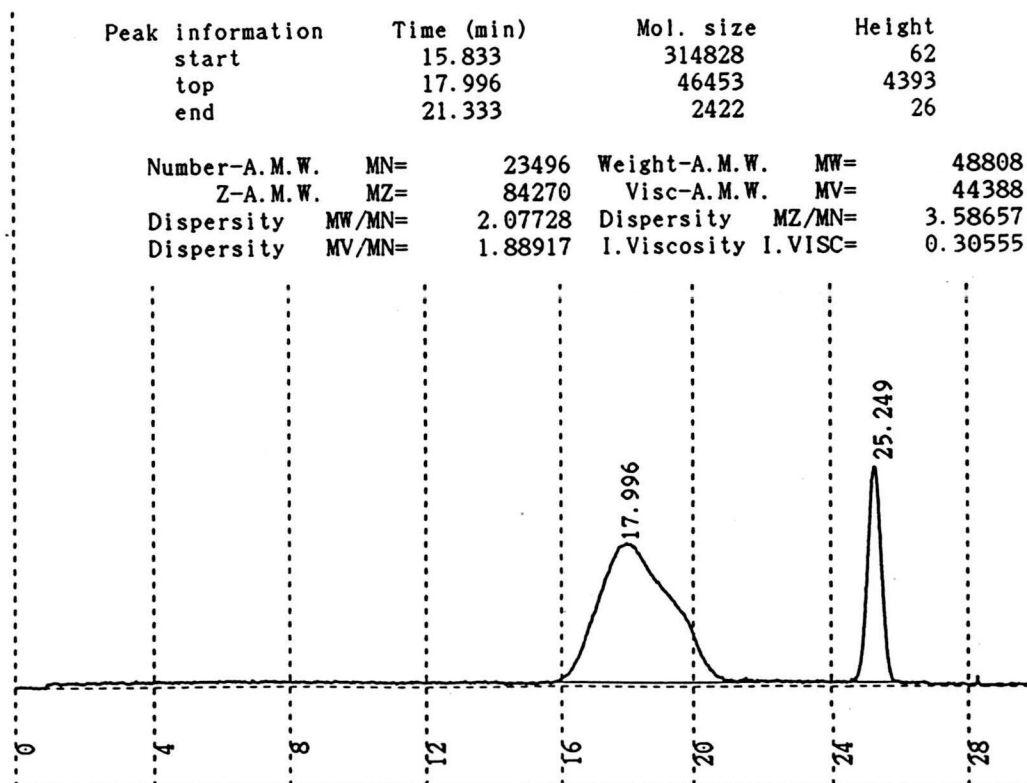


Figure F-ce2 GPC chart of dispersion copolymer: EtOH 20 weight%

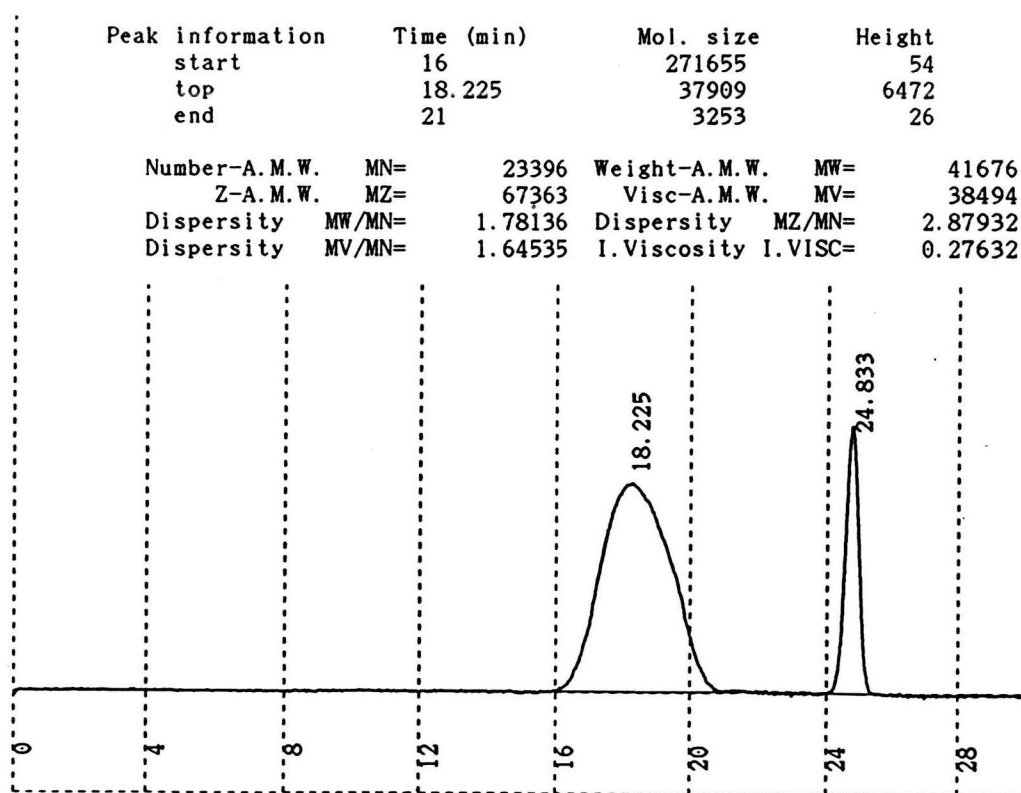


Figure F-ce3 GPC chart of dispersion copolymer: EtOH 35 weight%

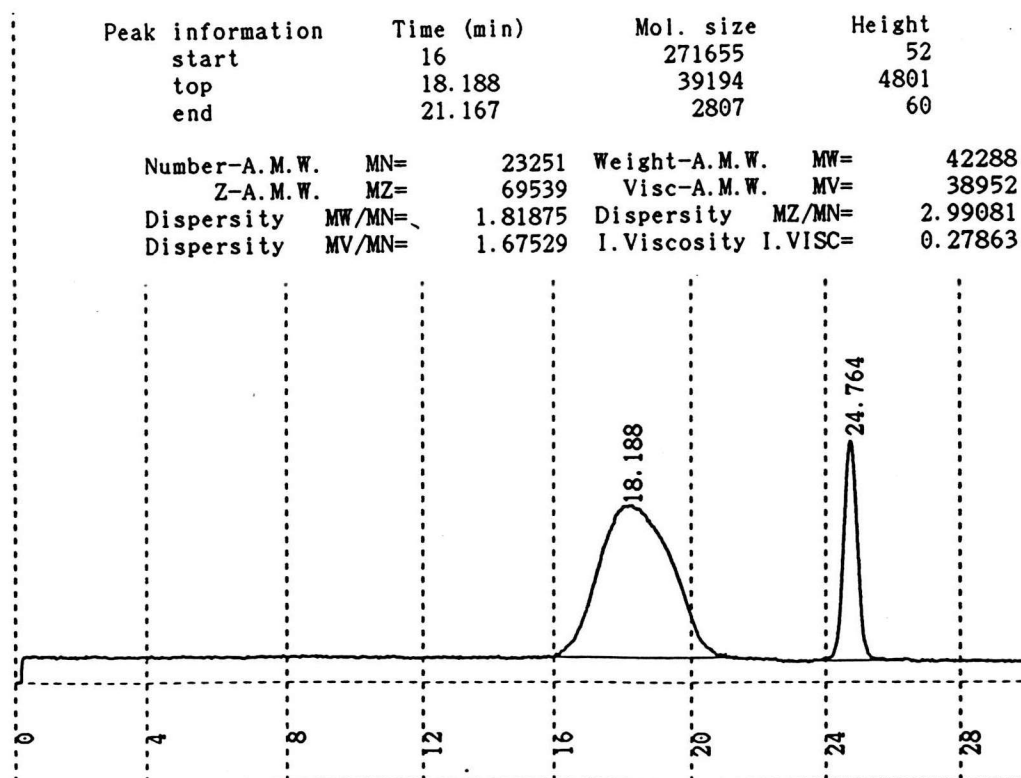


Figure F-ce4 GPC chart of dispersion copolymer: EtOH 50 weight%

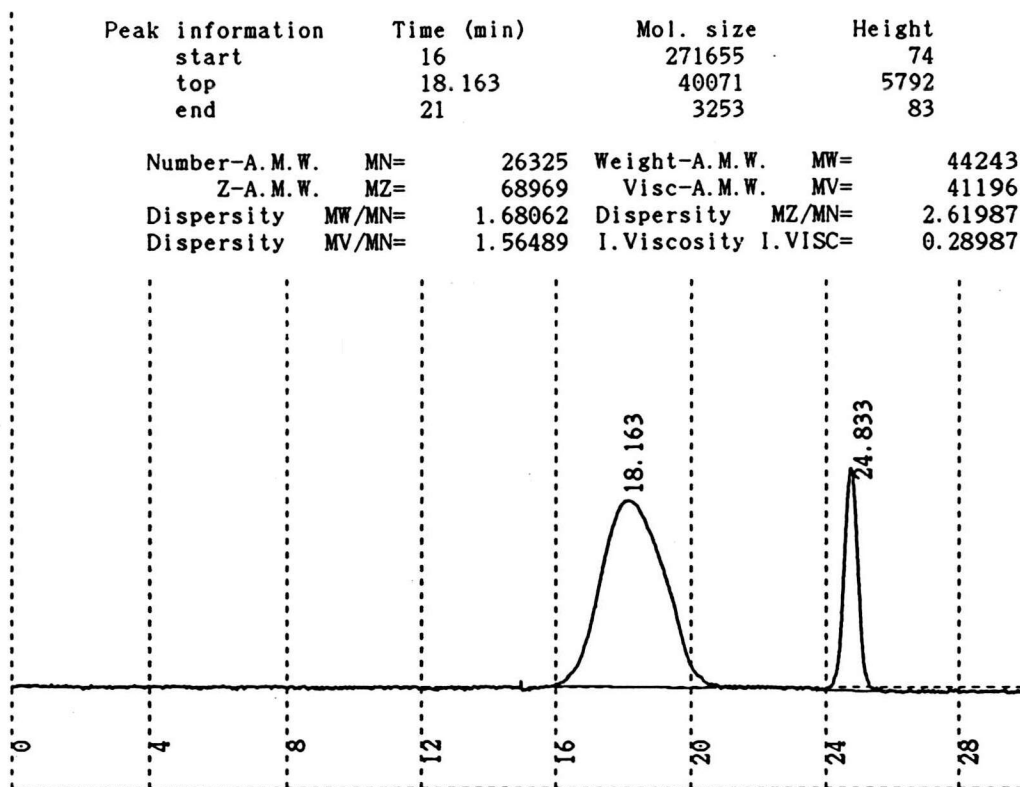


Figure F-ce5 GPC chart of dispersion copolymer: EtOH 65 weight%

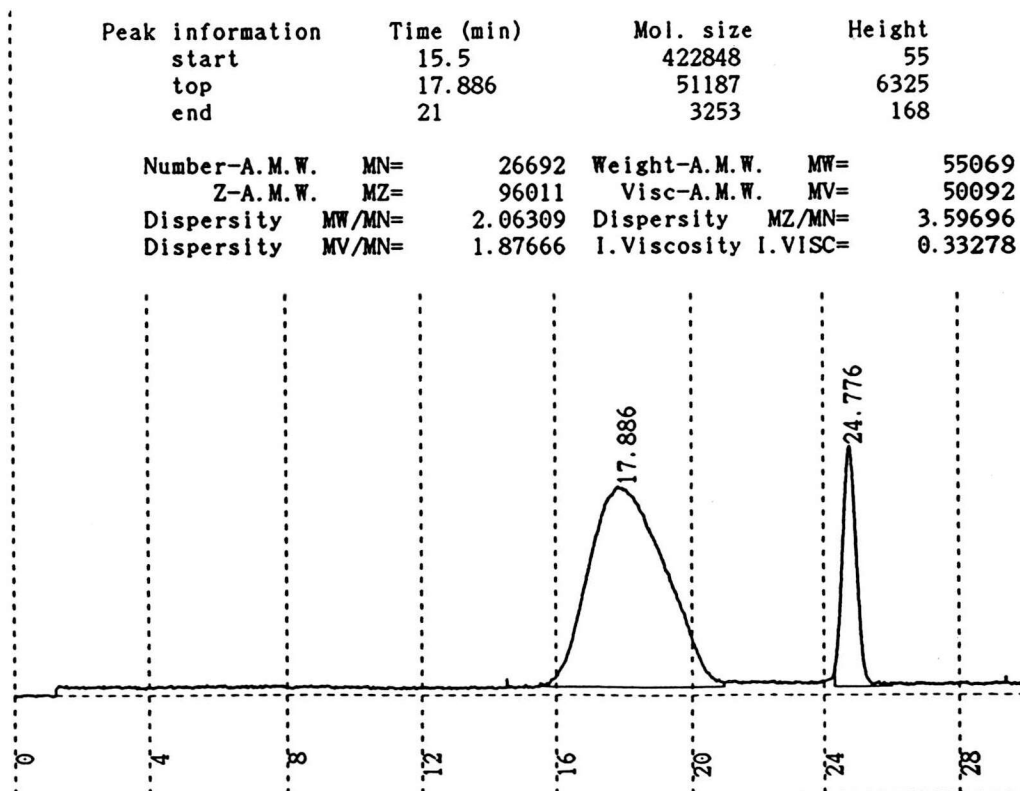


Figure F-ce6 GPC chart of dispersion copolymer: EtOH 80 weight%

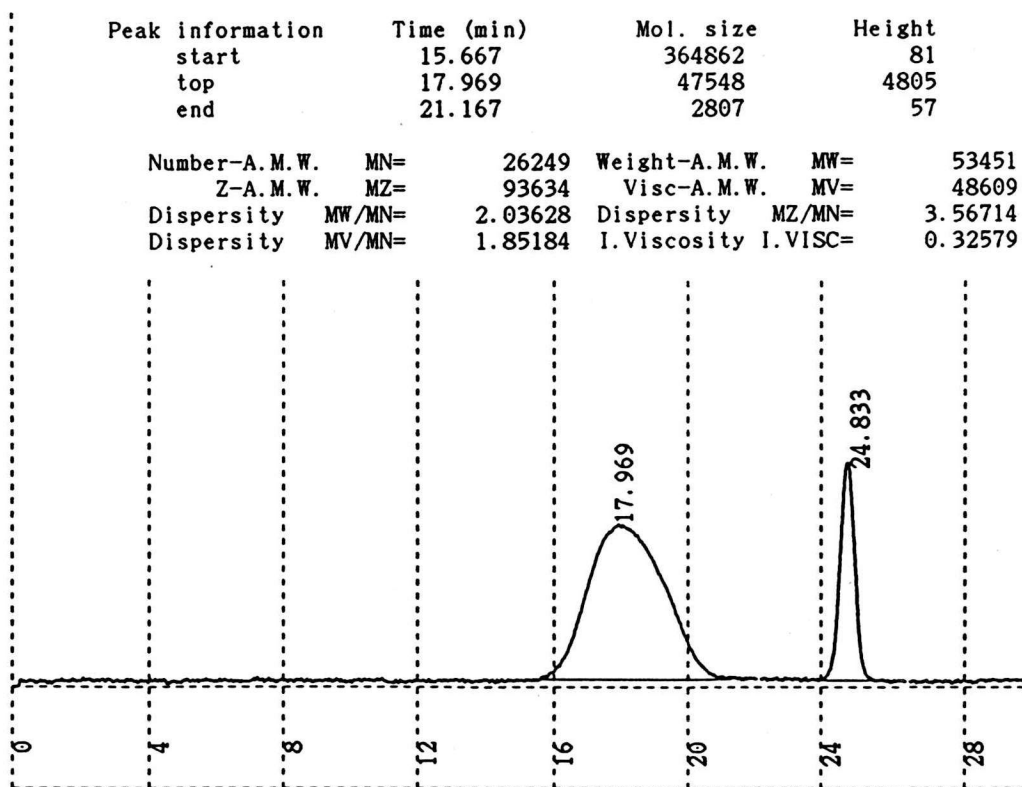


Figure F-ce7 GPC chart of dispersion copolymer: EtOH 100 weight%

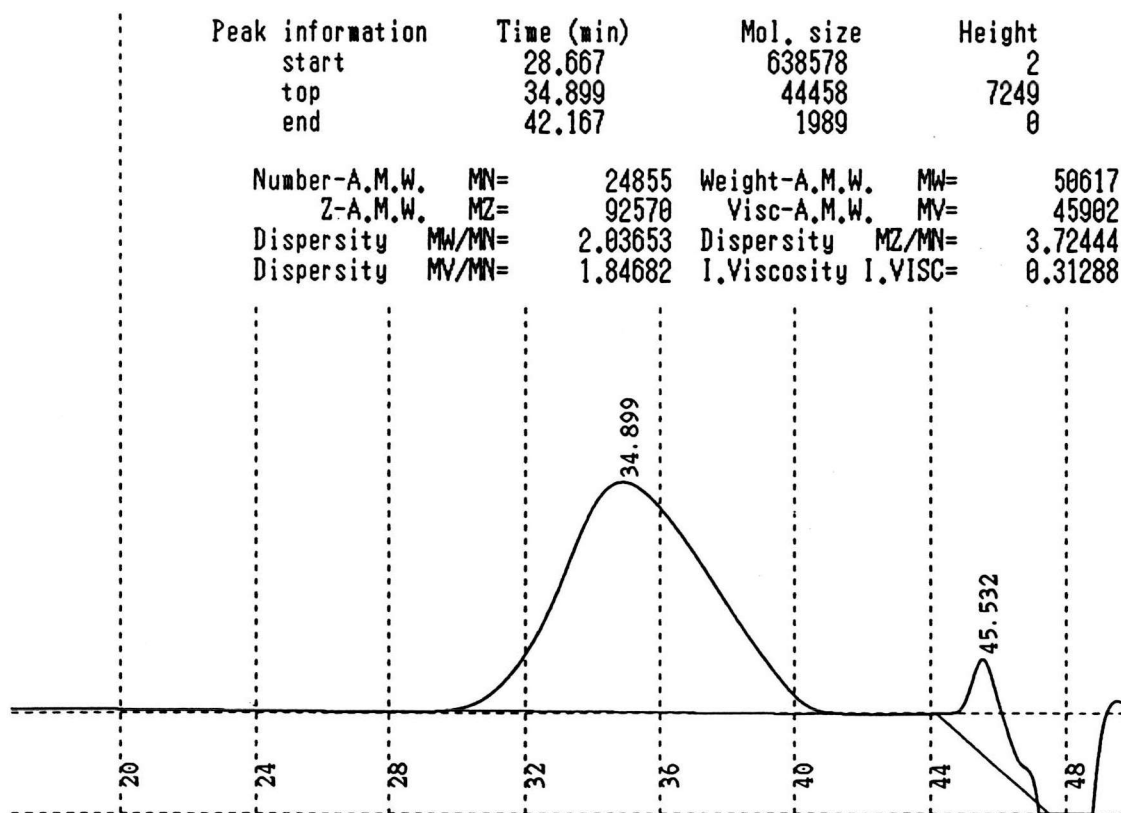


Figure F-ct1 GPC chart of dispersion copolymer: 50°C

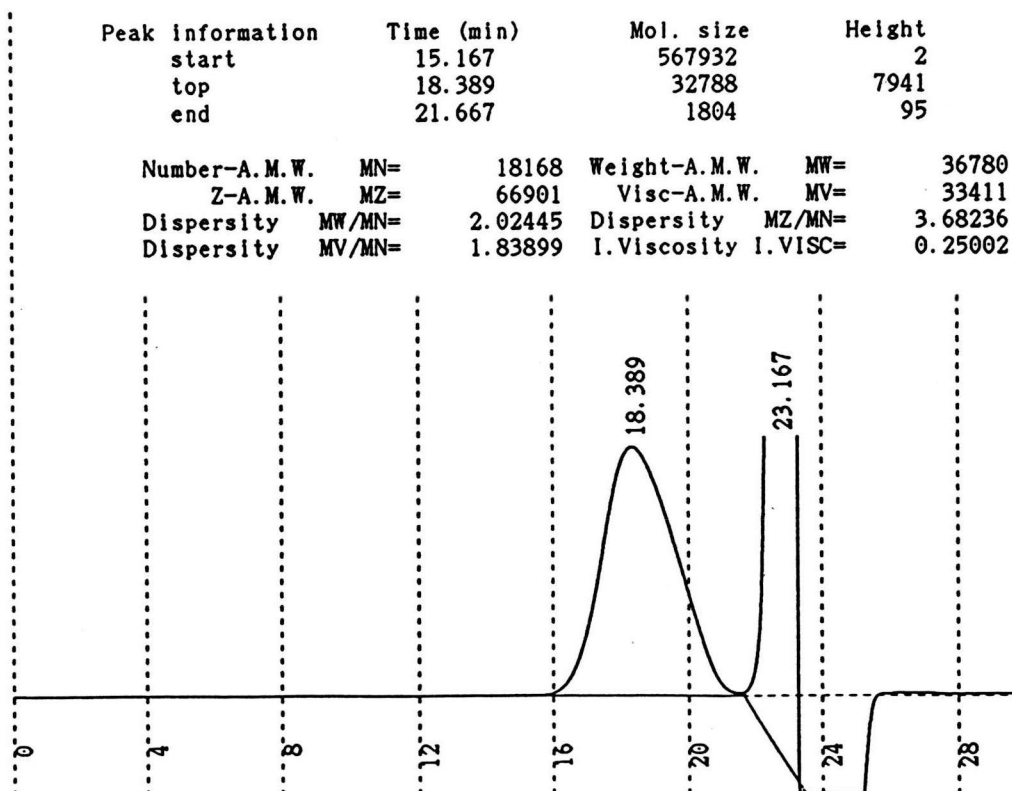


Figure F-ct2 GPC chart of dispersion copolymer: 55°C

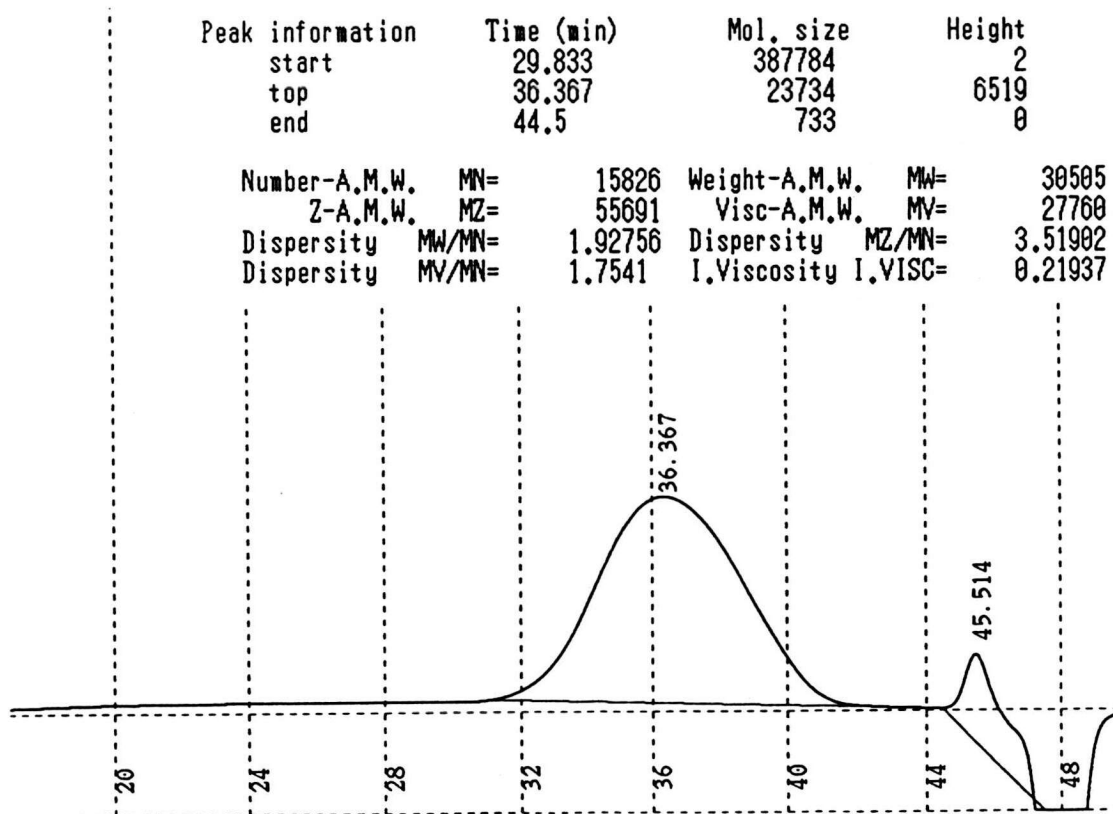


Figure F-ct3 GPC chart of dispersion copolymer: 64°C

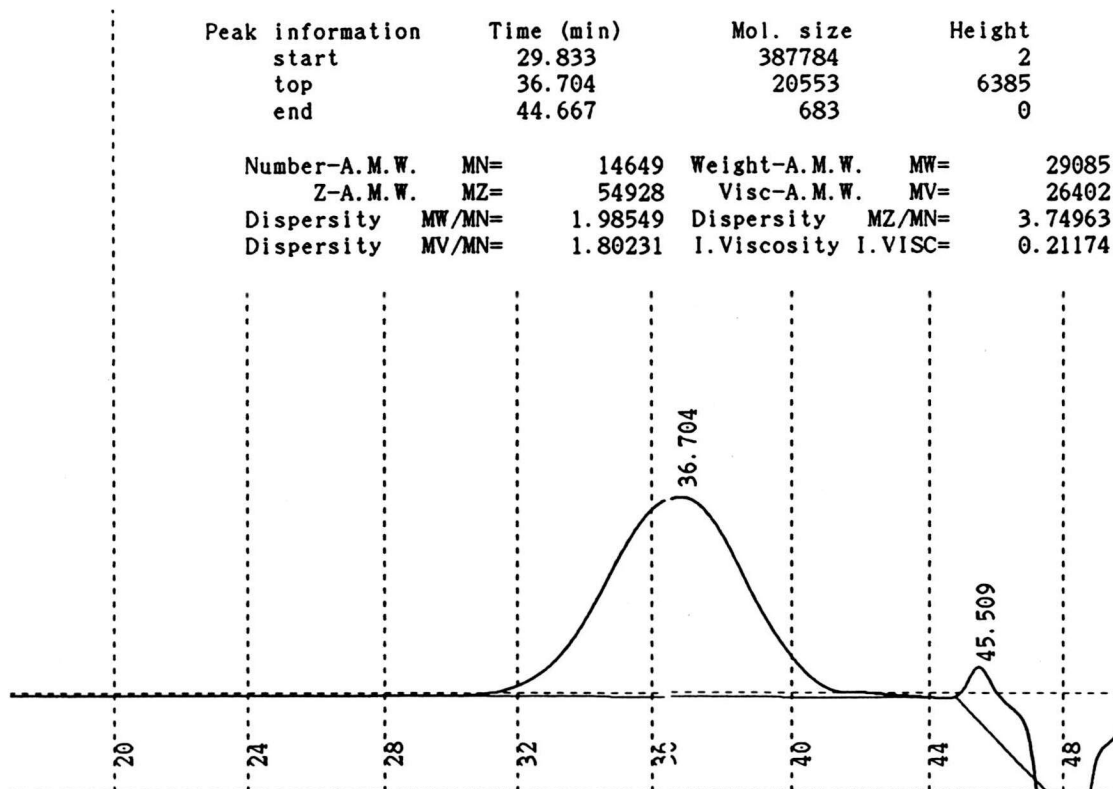


Figure F-ct4 GPC chart of dispersion copolymer: 73°C

APPENDIX G

Elemental Analysis

Elemental analysis was operated on a Perkin-Elmer model PE2400II. Analytical data showed %C, %H and %N. Percent carbon was used to calculate the styrene composition in the poly(styrene-co-methyl methacrylate).

An example of calculation

St	C_8H_8	$M_w = 104.15$	$\%C = 12 \cdot 8 / 104.15 = 92.17$
MMA	$C_5H_8O_2$	$M_w = 100.12$	$\%C = 12 \cdot 5 / 100.12 = 59.93$

Dispersion copolymer ; 25 mole% St feed, 80 weight% EtOH in the mixed solvent

%C found (1 st expt)	=	71.15	
%C found (2 nd expt)	=	70.82	
Average %C found	=	$(71.15+70.82)/2$	= 70.985
Ratio of MMA:St	=	$(92.17-70.985) : (70.985-59.93)$	
	=	21.185 : 11.055	
% St in copolymer	=	$11.055 / (21.185+11.055)$	= 34

Table G-1 Analytical data of solution copolymers

Copolymer (%St)		%C	%H	%N
25	1st	70.86	8.05	2.05
	2nd	70.87	8.09	2.07
38	1st	74.83	8.09	0.84
	2nd	74.81	8.10	0.65
50	1st	77.38	8.01	0.66
	2nd	77.20	7.99	0.96
62	1st	80.42	8.14	0.92
	2nd	79.95	8.09	0.47
75	1st	83.70	8.15	1.45
	2nd	83.20	8.08	1.60

Table G-2 Analytical data of dispersion copolymers

Copolymer (%St)		%C	%H	%N
PMMA (0)	1st	59.93	8.54	0
	2nd	60.24	8.56	0
25	1st	71.15	8.17	1.75
	2nd	70.82	8.14	1.91
38	1st	72.60	8.22	0.44
	2nd	71.76	8.11	0.51
50	1st	77.60	7.99	0.42
	2nd	77.23	7.94	0.38
62	1st	77.84	7.97	0.54
	2nd	79.14	8.09	0.64
75	1st	82.37	8.17	1.23
	2nd	82.90	8.23	1.27
PS (100),	1st	91.95	7.95	0.48
	2nd	92.35	8.01	1.19

APPENDIX H

Differential Scanning Calorimeter

Glass transition temperatures (T_g) of the dispersion copolymers were measured on a differential scanning calorimeter model Seiko DSC 200-SSC5000. For each operation, a portion of dried copolymer (weight ca. 10 mg) was placed in the sample can that was sealed and weighed. The sample can was placed on the sensor at room temperature, together with an empty container to assist output balance. They were and rapidly heated (heat rate $10^\circ\text{C}/\text{min}$) to the required temperature (400°C). The heating step was divided into 3 steps, from room temperature to 140°C then cooling by the use of liquid N_2 to -100°C and finally, heated the sensor to 400°C . The T_g was observed in the final heat step.

Figures H-1 to H-7 show the DSC curves of the PS, PMMA homopolymers and poly(St-co-MMA) copolymer.

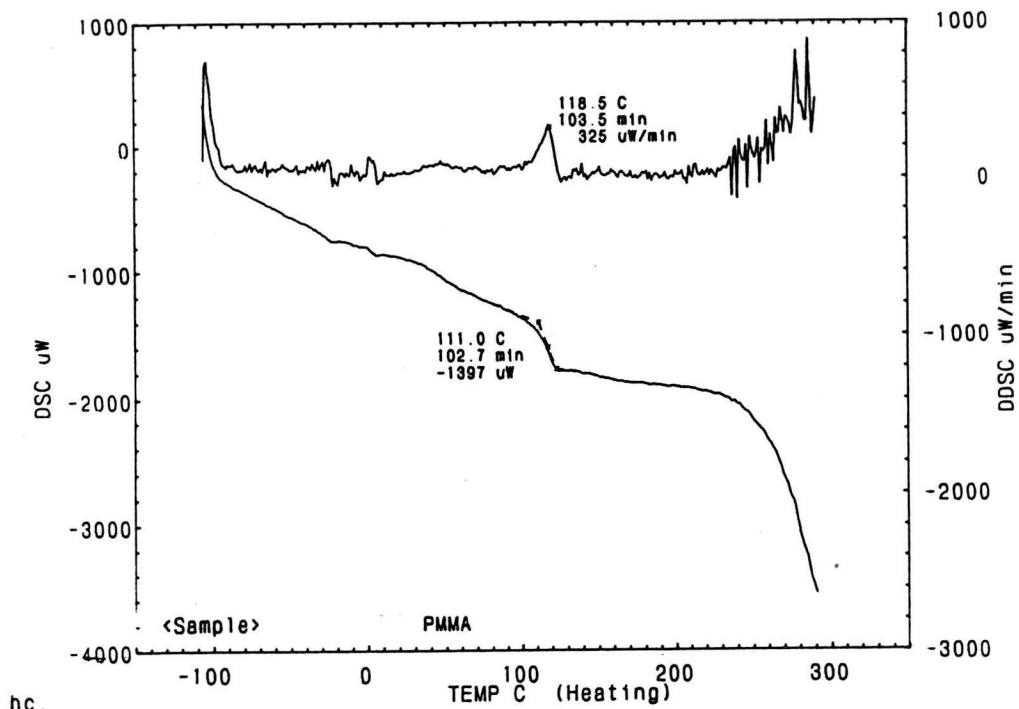


Figure H-1 DSC curve of dispersion PMMA homopolymer

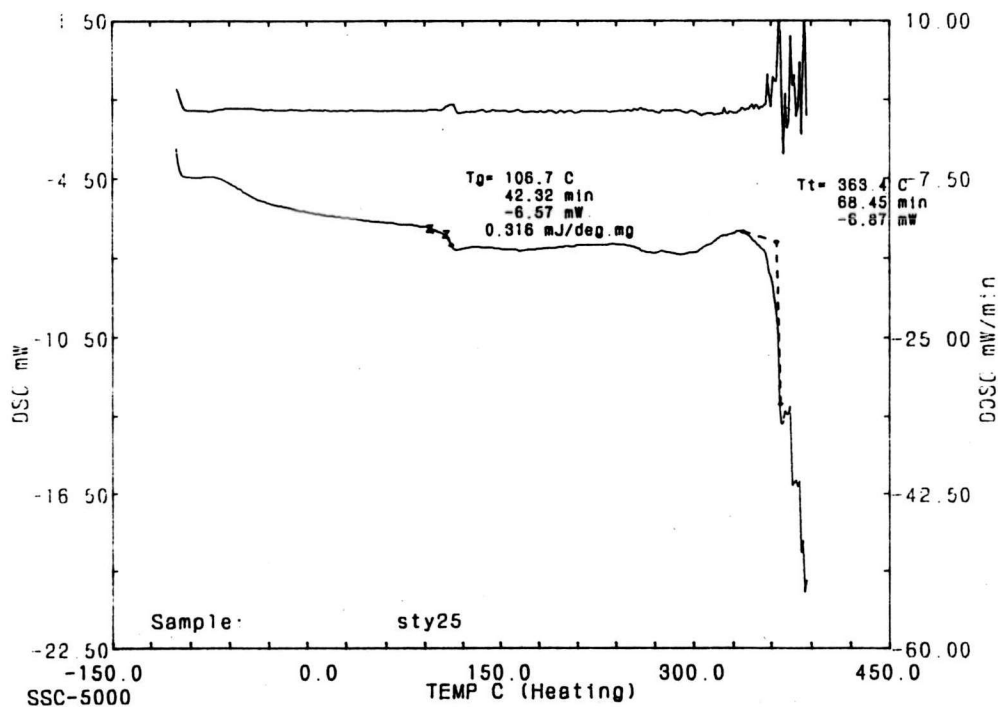


Figure H-2 DSC curve of dispersion poly(St-co-MMA): St feed 25 %

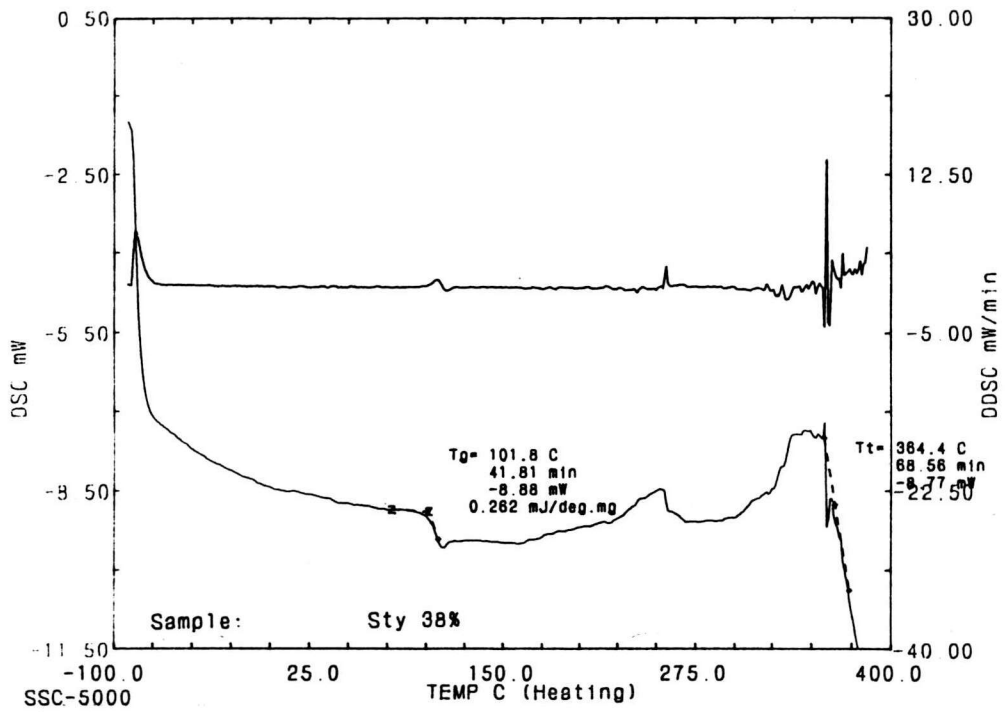


Figure H-3 DSC curve of dispersion poly(St-co-MMA): St feed 38 %

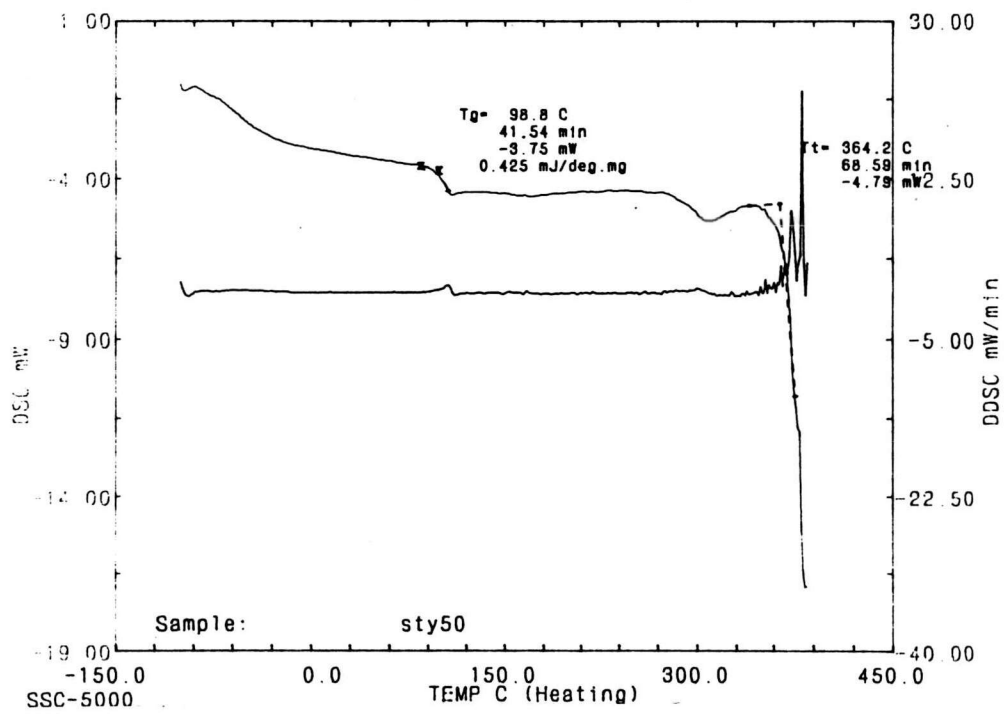


Figure H-4 DSC curve of dispersion poly(St-co-MMA): St feed 50 %

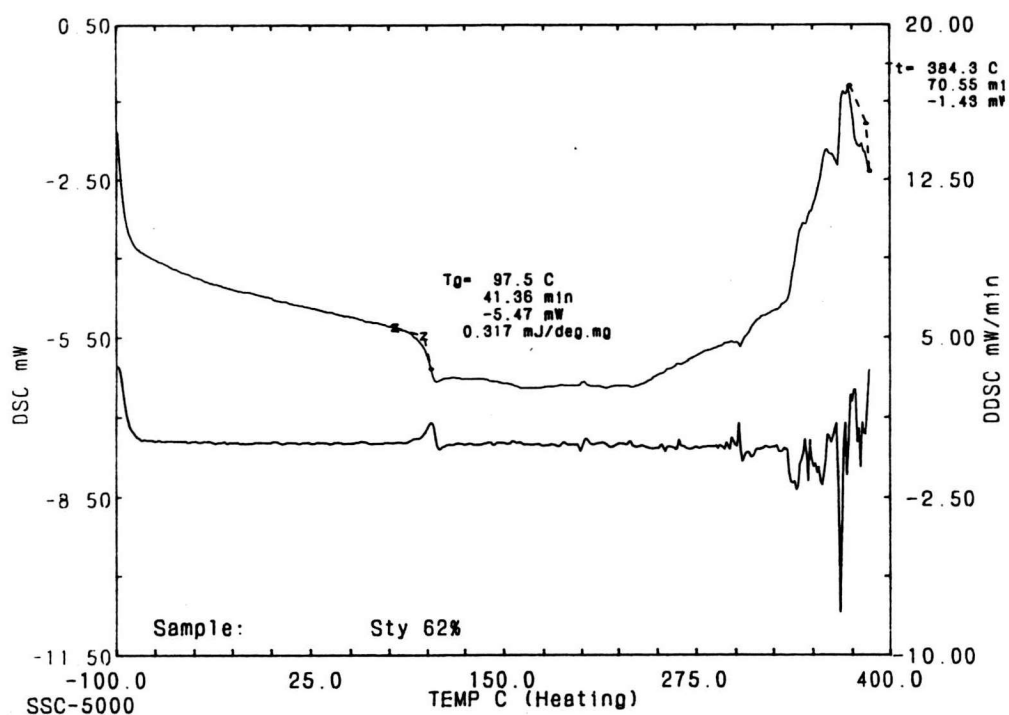


Figure H-5 DSC curve of dispersion poly(St-co-MMA): St feed 62 %

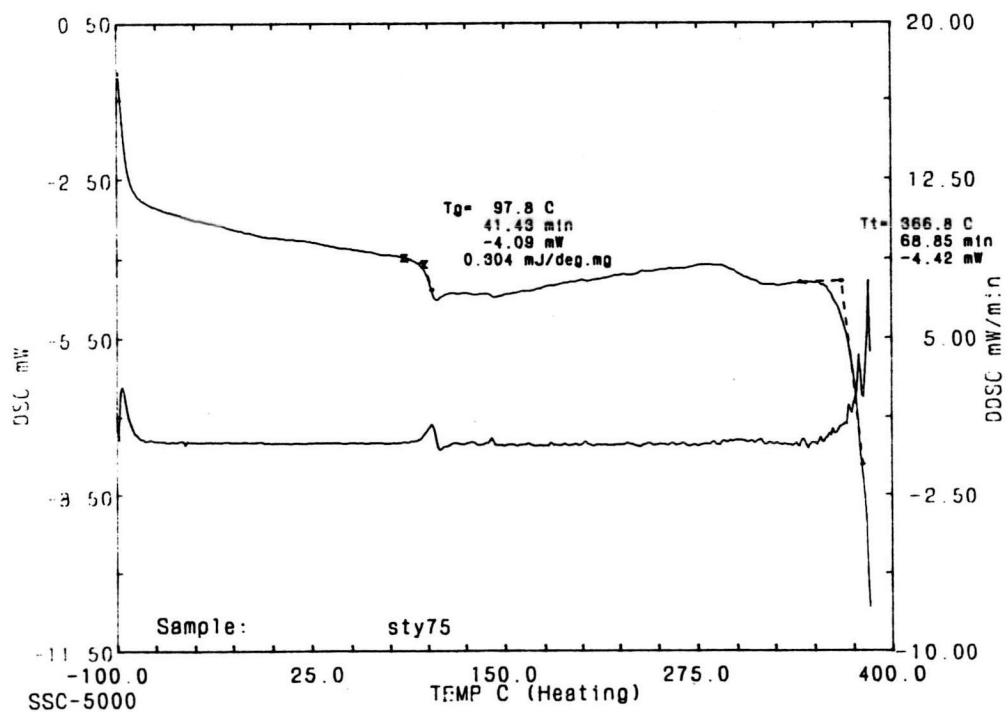


Figure H-6 DSC curve of dispersion poly(St-co-MMA): St feed 75 %

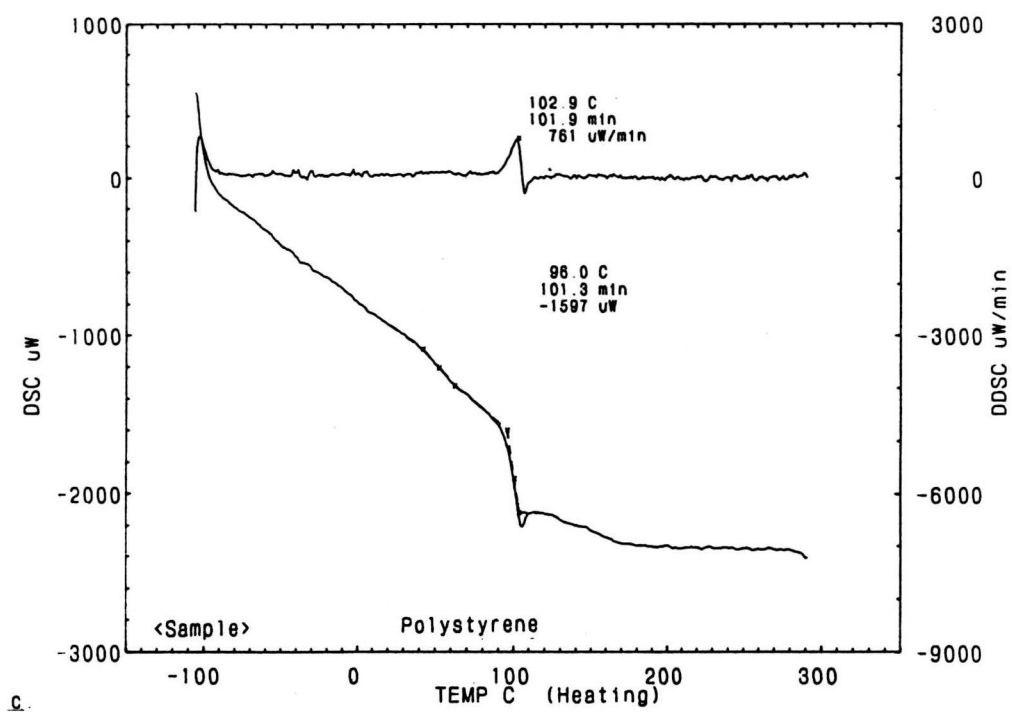


Figure H-7 DSC curve of dispersion PS homopolymer

APPENDIX I

Thermal Gravimetry/Differential Thermal Analysis

Decomposition temperatures (T_d) of the dispersion copolymers were measured on a thermal gravimetry/differential thermal analysis model Seiko TG/DTA 200-SSC5000). For each operation, a portion of dried copolymer (weight ca. 10 mg) was placed in an aluminium pan and placed on the sensor at room temperature, together with an empty container to assist output balance. They were heated at the heat rate of $5^\circ\text{C}/\text{min}$ to 500°C .

Figures I-1 to I-7 show the TG/DTA curves of the PS, PMMA homopolymers and poly(St-co-MMA) copolymer.

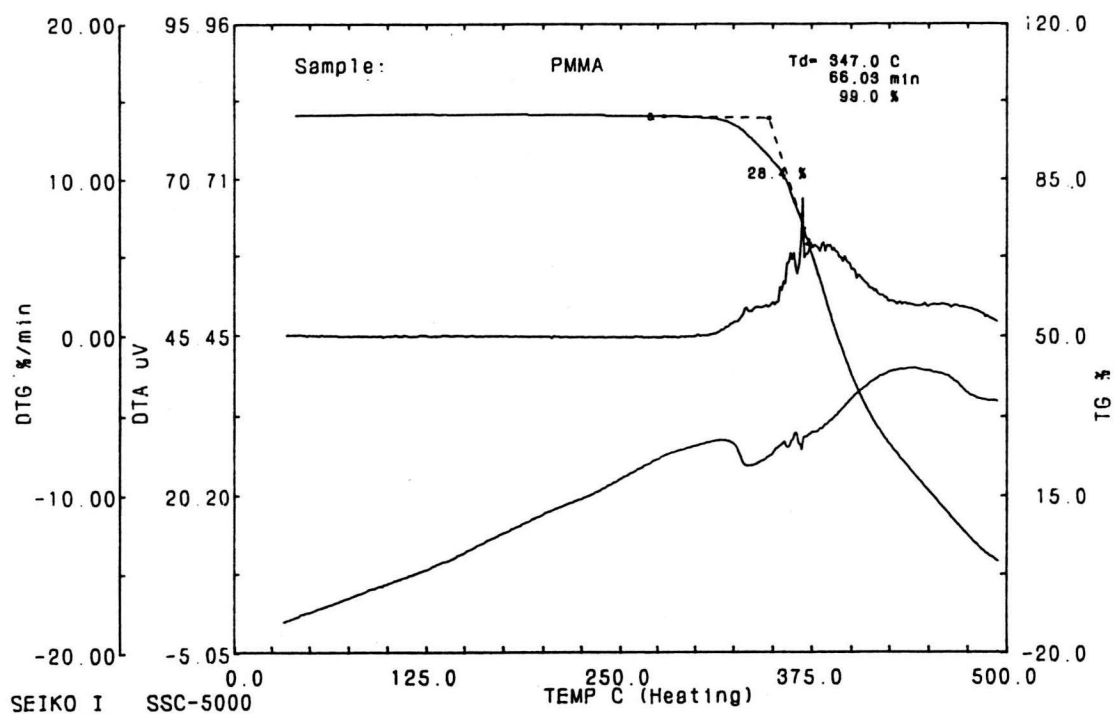


Figure I-1 TG/DTA curve of dispersion PMMA homopolymer

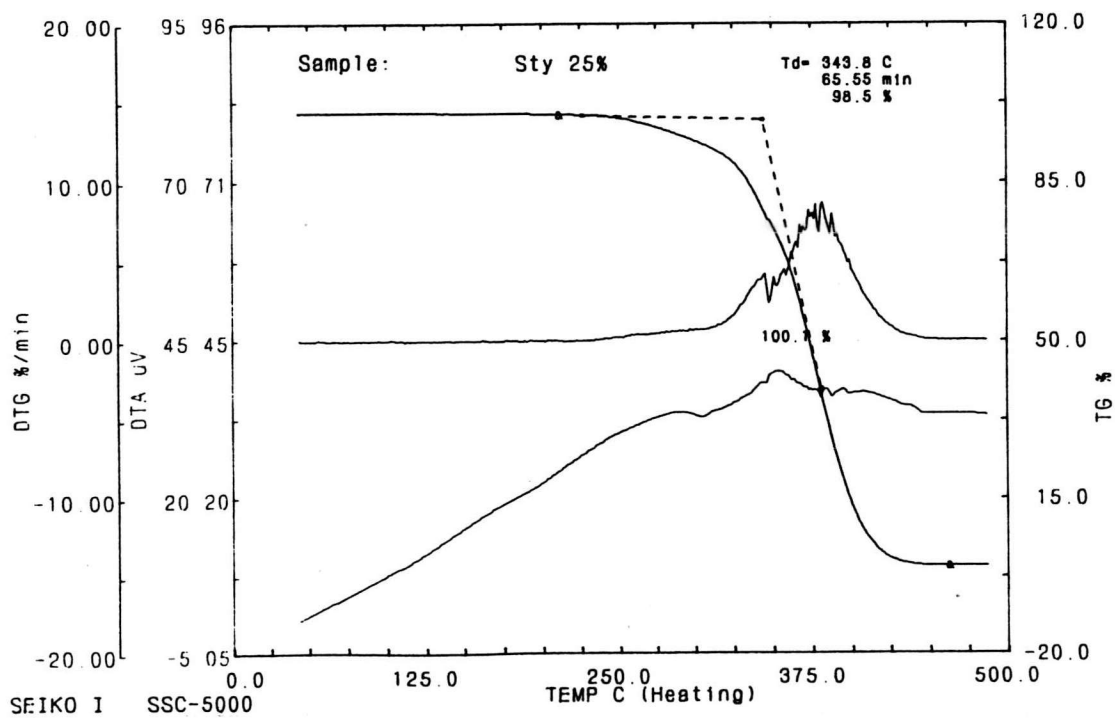


Figure I-2 TG/DTA curve of dispersion poly(St-co-MMA): St feed 25%

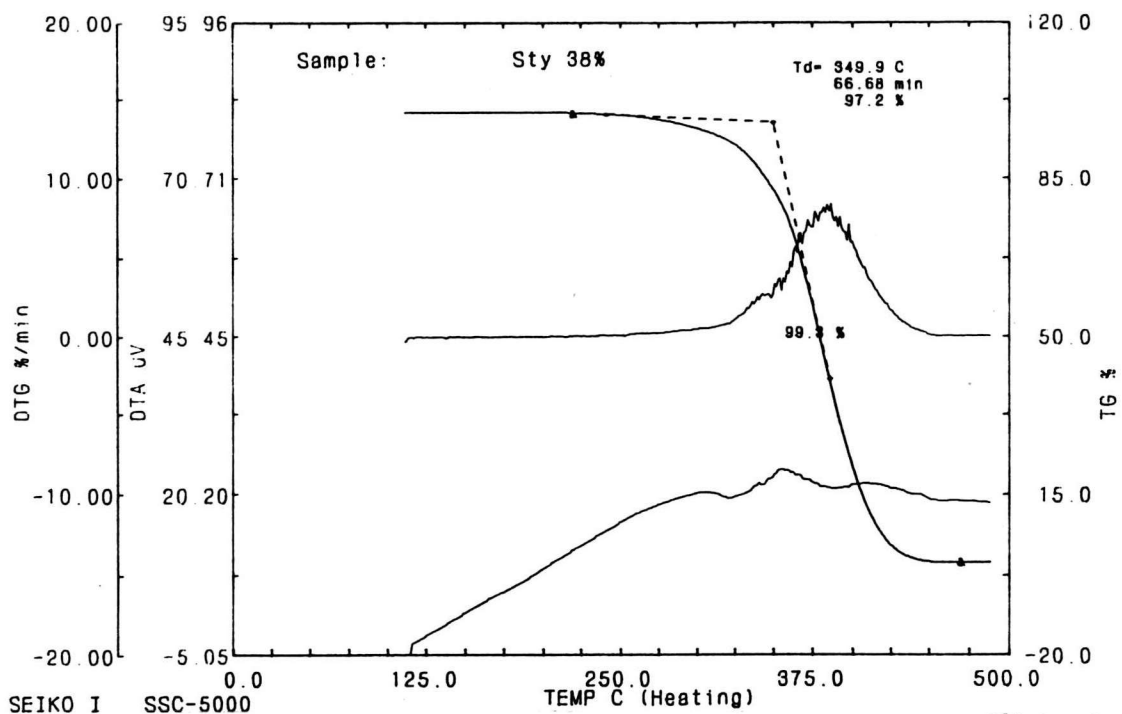


Figure I-3 TG/DTA curve of dispersion poly(St-co-MMA): St feed 38%

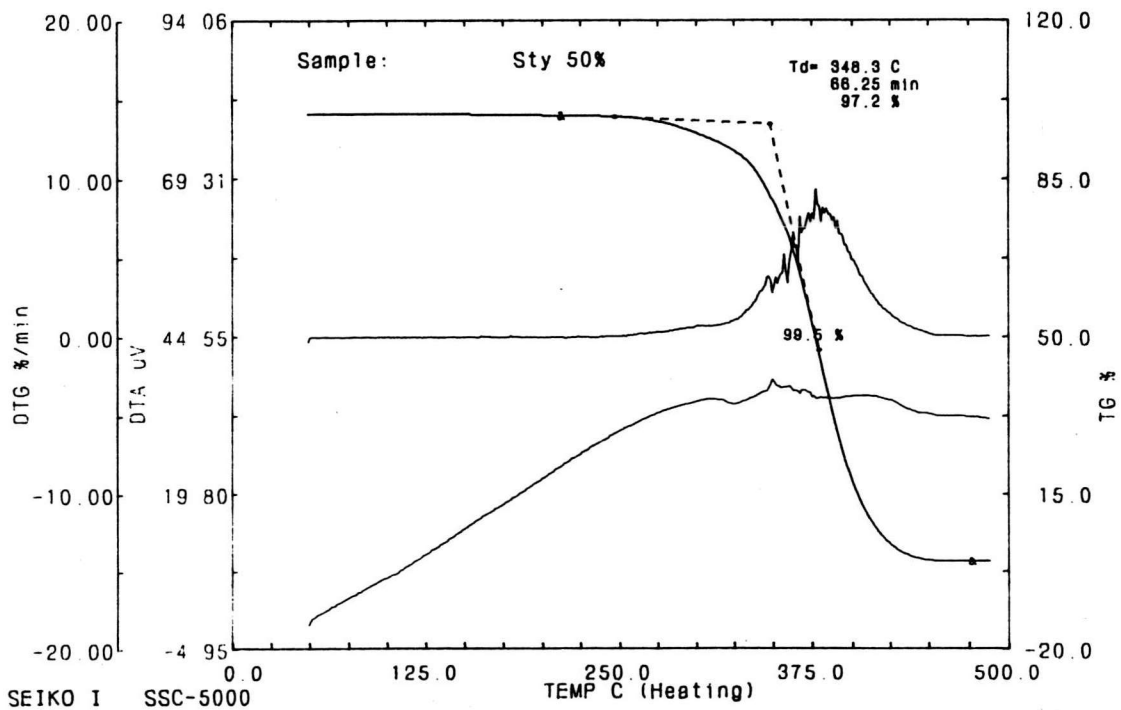


Figure I-4 TG/DTA curve of dispersion poly(St-co-MMA): St feed 50%

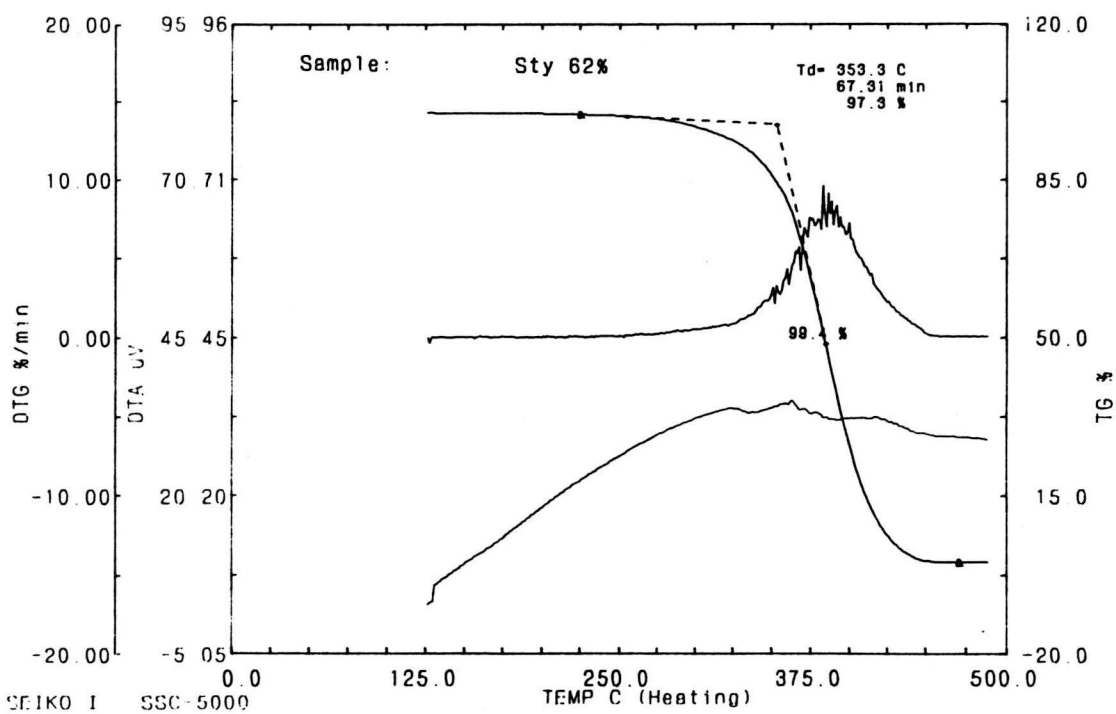


Figure I-5 TG/DTA curve of dispersion poly(St-co-MMA): St feed 62%

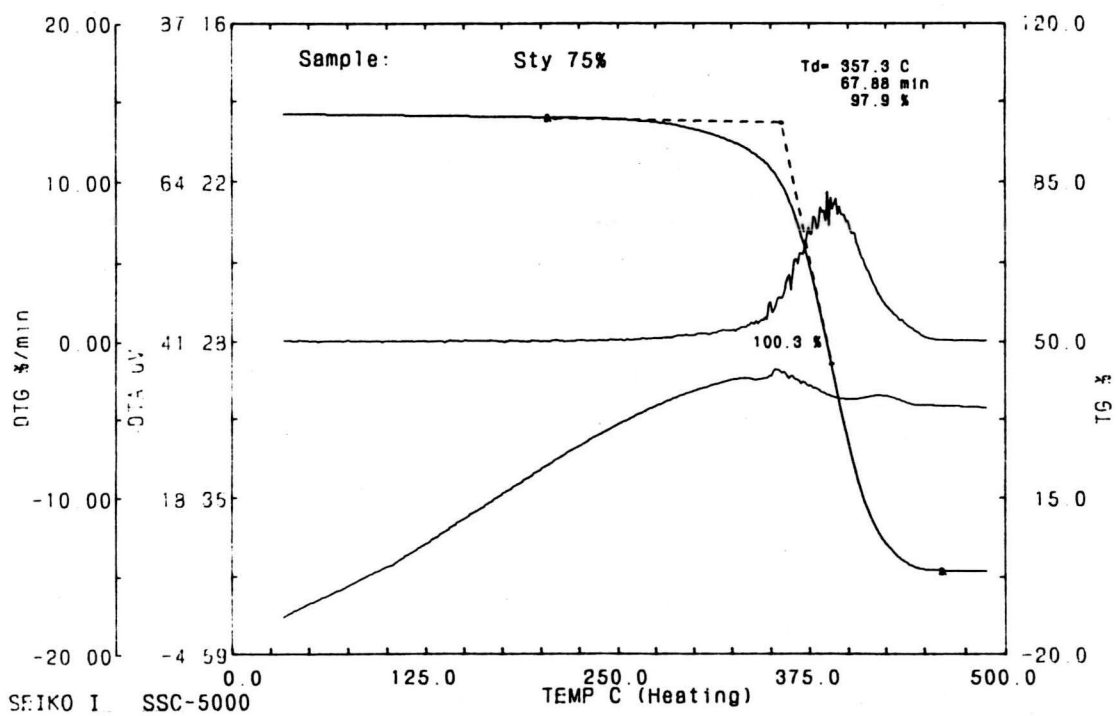


Figure I-6 TG/DTA curve of dispersion poly(St-co-MMA): St feed 75%

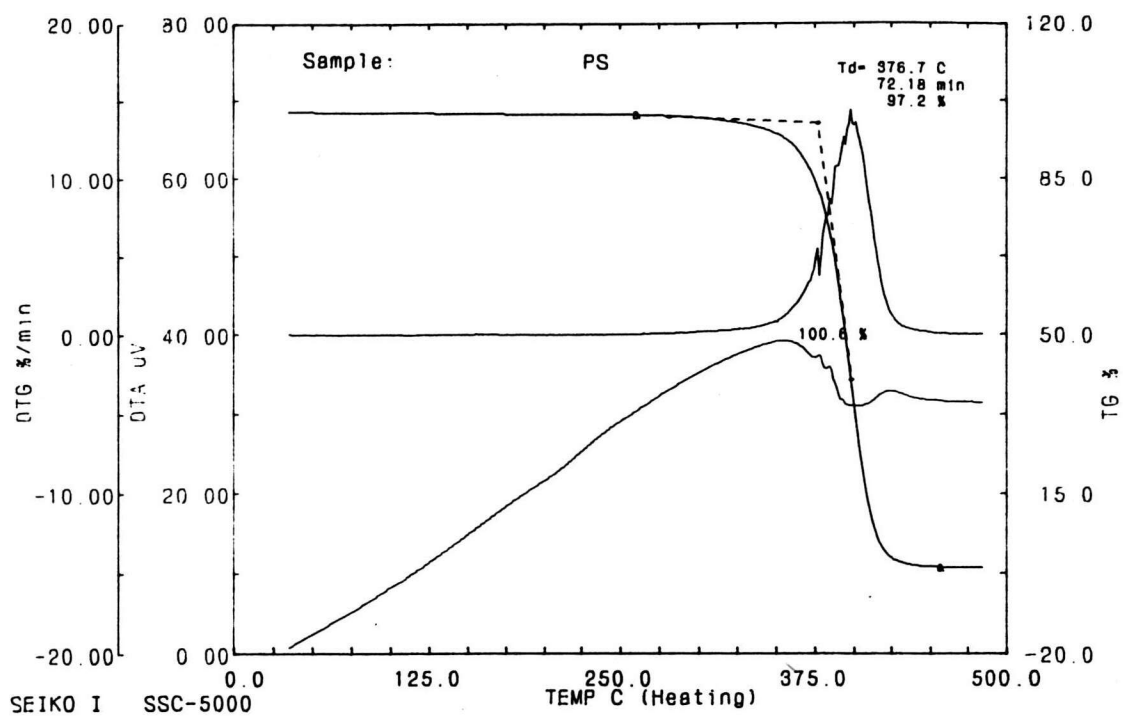


Figure I-7 TG/DTA curve of dispersion PS homopolymer

VITA

Miss Saowaluk Apiwattananon was born on September 5, 1970 in Rayong, Thailand. She received her B.Sc. degree in Chemical Technology from the Faculty of Science, Chulalongkorn University in 1992 and she has been a graduate student in the Multidisciplinary Program of Petrochemistry-Polymer, Petrochemistry Division, Graduate School, Chulalongkorn University since 1992.