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APPENDIX A

CHAIN COPOLYMERIZATION

Chain copolymerization, the mixture of two monomers is able to produce the polymeric products with two different structures in the polymer chain. As shown in eq. 1, copolymer molecule contains both monomers. The chain polymerization process is termed as a copolymerization in which the product is a copolymer. The random copolymer of different monomer can be carried out with mixtures of two or more monomer. The two monomers incorporated into the copolymer can be determined by the relative concentrations and reactivities [37].

$$M_1 + M_2 \longrightarrow M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_2M_1M_1M_2M_1M_1M_1M_1 \qquad (1)$$

A-1. Type of copolymers

A statistical copolymer has a distribution of the two monomer units along the copolymer chain which follows the statistical law. Where the two monomer units distributed randomly follow zero-order Markov process are referred as random copolymer. There are three types of particular copolymer structures as follows other than the random copolymer (1).

a. $M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$ alternating

b. $M_1M_1M_1M_2M_2M_2M_1M_1M_1M_2M_2M_2$ block

c. $M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1$ graft

M_2
M_2
M_2
M_2
M_2
M_2
M_2
M_2

A-2. Copolymer composition

A-2 a. Copolymerization equation

The different type of monomers has specific tendencies to copolymerization. The composition of copolymer is usually different from that of comonomers in feed, as referred to *the first-order Markov or terminal model of copolymerization*. In case of two monomers M_1 and M_2 without any specificity in type of initiation, the copolymerization of two monomers lead to two types of propagating species; one with M_1* at the propagating end and the other with M_2*. The radical will be represented as M_1* and M_2*. It is assumed that the reactivity of the propagating species is only depending on the monomer unit at the end of the chain. The four propagation reactions are as follows.

$$M_1 * + M_1 \xrightarrow{k_{11}} M_1 * \tag{2}$$

$$M_1 * + M_2 \xrightarrow{k_{12}} M_2 * \tag{3}$$

$$M_2 * + M_1 \xrightarrow{k_{21}} M_1 * \tag{4}$$

$$M_2 * + M_2 \xrightarrow{k_{22}} M_2 * \tag{5}$$

Where k_{11} is the rate constant for a propagating chain ending in M_1 adding monomer M_1, and so on.

Monomer M_1 disappears by Eq. 2 and 4 and monomer M_2 disappears by Eq. 3 and 5. The rate of disappearance of radical species or the rate of entry of monomers to the copolymers are given by

$$\frac{-d[M_1]}{dt} = k_{11}[M_1*][M_1] + k_{22}[M_2*][M_1] \tag{6}$$

$$\frac{-d[M_2]}{dt} = k_{12}[M_1*][M_2] + k_{22}[M_2*][M_2] \tag{7}$$

Equation 6 divided by 7 yields the copolymer composition as the ratio of rate in which two monomers enter the copolymer

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{k_{11}[\mathrm{M}_1{*}][\mathrm{M}_1] + k_{21}[\mathrm{M}_2{*}][\mathrm{M}_1]}{k_{12}[\mathrm{M}_1{*}][\mathrm{M}_2] + k_{22}[\mathrm{M}_2{*}][\mathrm{M}_2]} \tag{8}$$

The reactive species of M_1* and M_2* were assumed to be in *a steady state concentration.* Then, the rate of reaction expressed in Eq.3 and 4 are equal,

$$k_{21}[\mathrm{M}_2{*}][\mathrm{M}_1] = k_{12}[\mathrm{M}_1{*}][\mathrm{M}_2] \tag{9}$$

Equation 9 rearranged and combined with Eq. 8 yields to

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{\dfrac{k_{11}k_{21}[\mathrm{M}_2{*}][\mathrm{M}_1]^2}{k_{12}[\mathrm{M}_2]} + k_{21}[\mathrm{M}_2{*}][\mathrm{M}_1]}{k_{22}[\mathrm{M}_2{*}][\mathrm{M}_2] + k_{21}[\mathrm{M}_2{*}][\mathrm{M}_1]} \tag{10}$$

Let us define,

$$r_1 = \frac{k_{11}}{k_{12}} \text{ and } r_2 = \frac{k_{22}}{k_{21}} \tag{11}$$

Using the parameter in Eq. 11, the Eq. 10 can be rearranged to,

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1](r_1[\mathrm{M}_1] + [\mathrm{M}_2])}{[\mathrm{M}_2]([\mathrm{M}_1] + r_2[\mathrm{M}_2])} \tag{12}$$

Equation 12 is the copolymerization composition equation. Where $\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]}$ is the molar ratio of two monomer units incorporated in copolymer at any instant. The parameter r_1 and r_2 represent the monomer reactivity ratios as function of rate constants in adding other monomer.

The instantaneous copolymer composition equation can be expressed in terms of mole fraction as,

$$f_1 = 1 - f_2 = \frac{[\mathrm{M}_1]}{[\mathrm{M}_1]+[\mathrm{M}_2]} \tag{13}$$

$$F_1 = 1 - F_2 = \frac{d[\mathrm{M}_1]}{d[\mathrm{M}_1]+d[\mathrm{M}_2]} \tag{14}$$

Where f_1 and f_2 are the mole fraction of monomers M_1 and M_2 in unreacted monomers and F_1 and F_2 are the mole fraction of monomers in the copolymer.

Eq.13 combined with Eq. 14 together with Eq. 12 yields

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{15}$$

A-2 b. Copolymerization equation: statistical derivation

By ignoring the steady-state assumption, the determination of number-average sequence lengths will be considered.

$\overline{n_1}$ and $\overline{n_2}$ are the average number of monomer 1 and 2 in a sequence, respectively. Each other is uninterupted by the other one.

The conditional probability p_{11} of forming a M_1M_1 dyad in the copolymer chain is given by a ratio between the rate for M_1* add M_1 and the total rate, that is

$$p_{11} = \frac{R_{11}}{R_{11} + R_{12}} \tag{16}$$

Substitute R_{11} and R_{12} into eq.16, then,

$$p_{11} = \frac{r_1}{r_1 + ([\mathrm{M}_2]/[\mathrm{M}_1])} = \frac{r_1[\mathrm{M}_1]}{r_1[\mathrm{M}_1]+[\mathrm{M}_2]} \tag{17}$$

Similarly, for p_{12}, p_{21}, and p_{22} for forming the dyads M_1M_2, M_2M_1 and M_2M_2 respectively, are given,

$$p_{12} = \frac{R_{12}}{R_{11} + R_{12}} = \frac{[M_2]}{r_1[M_1] + [M_2]} \tag{18}$$

$$p_{21} = \frac{R_{21}}{R_{21} + R_{22}} = \frac{[M_1]}{r_2[M_2] + [M_1]} \tag{19}$$

$$p_{22} = \frac{R_{22}}{R_{21} + R_{22}} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]} \tag{20}$$

The each summation of probabilities for addition to M_1* and M_2* are equal to 1

$$p_{11} + p_{12} = 1 \tag{21-1}$$

$$p_{21} + p_{22} = 1 \tag{21-2}$$

Then, the number-average sequence length $\overline{n_1}$ of monomer M_1 is

$$\overline{n_1} = \sum_{x=1}^{x=\infty} x(\underline{N}_1)_x = (\underline{N}_1)_1 + 2(\underline{N}_1)_2 + 3(\underline{N}_1)_3 + 4(\underline{N}_1)_4 + \ldots\ldots\ldots \tag{22}$$

Where $(\underline{N}_1)_x$ is the mole fraction of a sequence of M_1 units of length x which have value of overall size from 1 to infinity. $(\underline{N}_1)_x$ can be obtained from the consideration of forming such sequence as given by

$$(\underline{N}_1)_x = (p_{11})^{(x-1)} p_{12} \tag{23}$$

In forming sequence such as $M_1M_1M_1$ can be calculated from the probability of M_1 adding M_1 multiplied by the probability p_{11} for a third addition of M_1 multiplied by the probability of p_{12} of addition of M_2 or $p_{11}^2p_{12}$

$$\overline{n_1} = p_{12}(1+2p_{11}+3p_{11}^{\;2}+4p_{11}^3+......) \tag{24}$$

For $p_{11}<1$, which holds in any copolymerization, the expansion series in Eq. 24 is $1/(1-p_{11})^2$ and Eq. 24 becomes,

$$\overline{n_1} = \frac{p_{12}}{(1-p_{11})^2} = \frac{1}{p_{12}} = \frac{r_1[M_1]+[M_2]}{[M_2]} \tag{25}$$

Similarly, $\overline{n_2}$ can be obtained,

$$\overline{n_2} = \frac{p_{21}}{(1-p_{22})^2} = \frac{1}{p_{21}} = \frac{r_2[M_2]+[M_1]}{[M_1]} \tag{26}$$

The ratio of two number-average sequence lengths yields,

$$\frac{\overline{n_1}}{\overline{n_2}} = \frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])} \tag{27}$$

Equation 27 describes the *first-order Markov model of copolymerization*

A-2 c. Variation of copolymer composition with conversion

From the copolymerization equation as shown in Eq. 1 to 15, the copolymerization assumed as instantaneous copolymer composition which may be assumed as that of the copolymer formed at low degrees of conversion. In a particular case, the composition of comonomer stays unchanged from the initial feed. Such copolymerization are termed azeotropic copolymerization. This condition can be obtained by substituting $d[M_1]/d[M_2] = [M_1][M_2]$ to Eq. 12 or 27, is

$$\frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)} \tag{28}$$

or $$F_1 = f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \tag{29}$$

At this particular composition no composition drift occurs and theoretically very homogeneous copolymer is produced until the end of polymerization. All copolymerizations except azeotropic copolymerization, the comonomer composition and copolymer compositions are different. The differential, a drift of comonomer composition occurs on the less reactive monomer as a degree of conversion increases.

In order to determine the copolymer composition as a function of conversion is developed by Skeist. By considering a system initially containing a total of M moles of two monomers and in which the copolymer formed is richer in monomer M_1 than in the comonomer; $F_1 > f_1$. Where dM moles of monomer have been copolymerized, the polymer will contain $F_1 d$M moles of monomer 1 and the unreacted monomer will contain $(M - dM)(f_1 - df_1)$ moles of monomer 1. The moles of M_1 copolymerized equal the difference in the moles of M_1 in the comonomer before and after the reaction. By using a material balance, then

$$Mf_1 - (M - dM)(f_1 - df_1) = F_1 dM \tag{30}$$

Eq. 30 can be rearranged and converted to the integral form (term $df_1 dM$ is neglected)

$$\int_{M_0}^{M} \frac{dM}{M} = \ln\frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)} \tag{31}$$

Where M_0 and $(f_1)_0$ are the initial value of M and f_1 in the feed.

Referred to eq. 15, the calculation of F_1 as a function of f_1 for a given set of r_1 and r_2 values can be carried out. These can be employed as $(F_1 - f_1)$ to allow the numerical integration of eq. 31 between $(f_1)_0$ and f_1. The variation in the comonomer and copolymer composition with the degree of conversion (defined as 1-M/M$_0$) can be obtained.

Integration of Eq. 1 yields,

$$1-\frac{\mathrm{M}}{\mathrm{M}_0}=1-\left[\frac{f_1}{(f_1)_0}\right]^{\alpha}\left[\frac{f_2}{(f_2)_0}\right]^{\beta}\left[\frac{(f_1)_0-\delta}{f_1-\delta}\right]^{\gamma} \tag{32}$$

The equation represents the relationship of degree of conversion with the comonomer composition. The zero subscripts indicates initial quantities and symbol α, β, γ, and δ are given,

$$\alpha=\frac{r_2}{(1-r_2)} \qquad \beta=\frac{r_1}{(1-r_1)} \tag{33}$$

$$\gamma=\frac{(1-r_1r_2)}{(1-r_1)(1-r_2)} \qquad \delta=\frac{(1-r_2)}{(2-r_1-r_2)}$$

Eq. 32 has been used to correlate the drift in comonomer and copolymer composition with conversion for a number of different copolymerizations.

A-3. Microstructure of copolymer

The microstructure of a copolymer is defined by the distribution of the various lengths of the M$_1$ and M$_2$ sequence, or else the sequence-length distribution. The probabilities $(\underline{N}_1)_x$ and $(\underline{N}_2)_x$ of forming M$_1$ and M$_2$ sequences of length x are given by

$$(\underline{N_1})_x=(p_{11})^{(x-1)}p_{12} \tag{23}$$

$$(\underline{N_2})_x=(p_{22})^{(x-1)}p_{21} \tag{34}$$

Eq. 23 and 34 are used to calculate the mole fraction of different lengths of M_1 and M_2 sequences. The analysis of copolymer microstructure can be done form interpreting a NMR spectrum.

A-4. Multicomponent copolymerization

The simultaneous polymerization of three monomers or to produce terpolymer was represented in nine propagation reactions,

Reaction	Rate	
$M_1{}^* + M_1 \rightarrow M_1{}^*$	$R_{11} = k_{11}[M_1{}^*][M_1]$	
$M_1{}^* + M_2 \rightarrow M_2{}^*$	$R_{12} = k_{12}[M_1{}^*][M_2]$	
$M_1{}^* + M_3 \rightarrow M_3{}^*$	$R_{13} = k_{13}[M_1{}^*][M_3]$	
$M_2{}^* + M_1 \rightarrow M_1{}^*$	$R_{21} = k_{21}[M_2{}^*][M_1]$	
$M_2{}^* + M_2 \rightarrow M_2{}^*$	$R_{22} = k_{22}[M_2{}^*][M_2]$	(35)
$M_2{}^* + M_3 \rightarrow M_3{}^*$	$R_{23} = k_{23}[M_2{}^*][M_3]$	
$M_3{}^* + M_1 \rightarrow M_1{}^*$	$R_{31} = k_{31}[M_3{}^*][M_2]$	
$M_3{}^* + M_2 \rightarrow M_2{}^*$	$R_{32} = k_{32}[M_3{}^*][M_2]$	
$M_3{}^* + M_3 \rightarrow M_3{}^*$	$R_{33} = k_{33}[M_3{}^*][M_3]$	

And six sets of the reactivity ratio of monomers can be written,

$$r_{12} = \frac{k_{11}}{k_{12}},\ r_{13} = \frac{k_{11}}{k_{13}},\ r_{21} = \frac{k_{22}}{k_{21}},\ r_{23} = \frac{k_{22}}{k_{23}},\ r_{31} = \frac{k_{33}}{k_{31}},\ r_{32} = \frac{k_{33}}{k_{32}} \tag{36}$$

Using the steady-state or statistical approach, the rates of disappearance of the three monomers are given by,

$$-\frac{d[M_1]}{dt} = R_{11} + R_{21} + R_{31} \tag{37-a}$$

$$-\frac{d[\mathrm{M}_2]}{dt} = R_{12} + R_{22} + R_{32} \tag{37-b}$$

$$-\frac{d[\mathrm{M}_3]}{dt} = R_{13} + R_{23} + R_{33} \tag{37-c}$$

By steady- state assumptions for the concentrations of M_1*, M_2* and M_3* radicals the following relationships are given,

$$R_{12} + R_{13} = R_{21} + R_{31} \tag{38-a}$$

$$R_{21} + R_{23} = R_{12} + R_{32} \tag{38-b}$$

$$R_{31} + R_{32} = R_{13} + R_{23} \tag{38-c}$$

Eq. 37 combined with Eq. 38 and the use of the appropriate rate expressions from Eq. 36 for each R term yields the terpolymer composition

$$\begin{aligned}
&d[\mathrm{M}_1] : d[\mathrm{M}_2] : d[\mathrm{M}_3] = \\
&[\mathrm{M}_1]\left\{\frac{[\mathrm{M}_1]}{r_{31}r_{21}} + \frac{[\mathrm{M}_2]}{r_{21}r_{32}} + \frac{[\mathrm{M}_3]}{r_{31}r_{23}}\right\}\left\{[\mathrm{M}_1] + \frac{[\mathrm{M}_2]}{r_{12}} + \frac{[\mathrm{M}_3]}{r_{13}}\right\} \\
&: [\mathrm{M}_2]\left\{\frac{[\mathrm{M}_1]}{r_{12}r_{31}} + \frac{[\mathrm{M}_2]}{r_{12}r_{32}} + \frac{[\mathrm{M}_3]}{r_{32}r_{13}}\right\}\left\{[\mathrm{M}_2] + \frac{[\mathrm{M}_1]}{r_{21}} + \frac{[\mathrm{M}_3]}{r_{23}}\right\} \\
&: [\mathrm{M}_3]\left\{\frac{[\mathrm{M}_1]}{r_{13}r_{12}} + \frac{[\mathrm{M}_2]}{r_{23}r_{12}} + \frac{[\mathrm{M}_3]}{r_{13}r_{23}}\right\}\left\{[\mathrm{M}_3] + \frac{[\mathrm{M}_1]}{r_{31}} + \frac{[\mathrm{M}_2]}{r_{32}}\right\}
\end{aligned} \tag{39}$$

If the following simplified relationships hold, Eq. 39 may be simplified as follows.

$$R_{12} = R_{21} \tag{40-a}$$

$$R_{23} = R_{32} \tag{40-b}$$

$$R_{31} = R_{13} \tag{40-c}$$

Combination of Eq. 40 and 39 yields the terpolymer composition as

$$
\begin{aligned}
& d[\mathrm{M}_1]:d[\mathrm{M}_2]:d[\mathrm{M}_3]=[\mathrm{M}_1]\left\{[\mathrm{M}_1]+\frac{[\mathrm{M}_2]}{r_{12}}+\frac{[\mathrm{M}_3]}{r_{13}}\right\} \\
& :[\mathrm{M}_2]\frac{r_{21}}{r_{12}}\left\{\frac{[\mathrm{M}_1]}{r_{21}}+[\mathrm{M}_2]+\frac{[\mathrm{M}_3]}{r_{23}}\right\} \qquad (41) \\
& :[\mathrm{M}_3]\frac{r_{31}}{r_{13}}\left\{\frac{[\mathrm{M}_1]}{r_{31}}+\frac{[\mathrm{M}_2]}{r_{32}}+[\mathrm{M}_3]\right\}
\end{aligned}
$$

APPENDIX B

GLASS TRANSITION TEMPERATURE OF RANDOM COPOLYMERS

The glass transition temperature of random copolymer varies corresponding to those of corresponding homopolymers. To predict the Tg of random copolymer, generally used is Fox's equation as given,

$$\frac{1}{Tg_{12}} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} \tag{42}$$

The copolymer's Tg is correlated with the Tg of homopolymer.

In this equation, Tg is expressed as a function of dyad distribution which are closely related to the flexibility of chain. Johnson's equation takes the sequence length distribution in consideration.

$$\frac{1}{Tg_{12}} = \frac{W_1 p_{11}}{Tg_1} + \frac{W_2 p_{22}}{Tg_2} + \frac{W_1 p_{12}}{Tg_{12}} \tag{43}$$

where W_1 and W_2 are the weight fractions of monomer 1 and 2, and Tg_1 and Tg_2 are the glass transition temperatures of homopolymer

APPENDIX C

NUCLEAR MAGNETIC RESONANCE SPECTRA

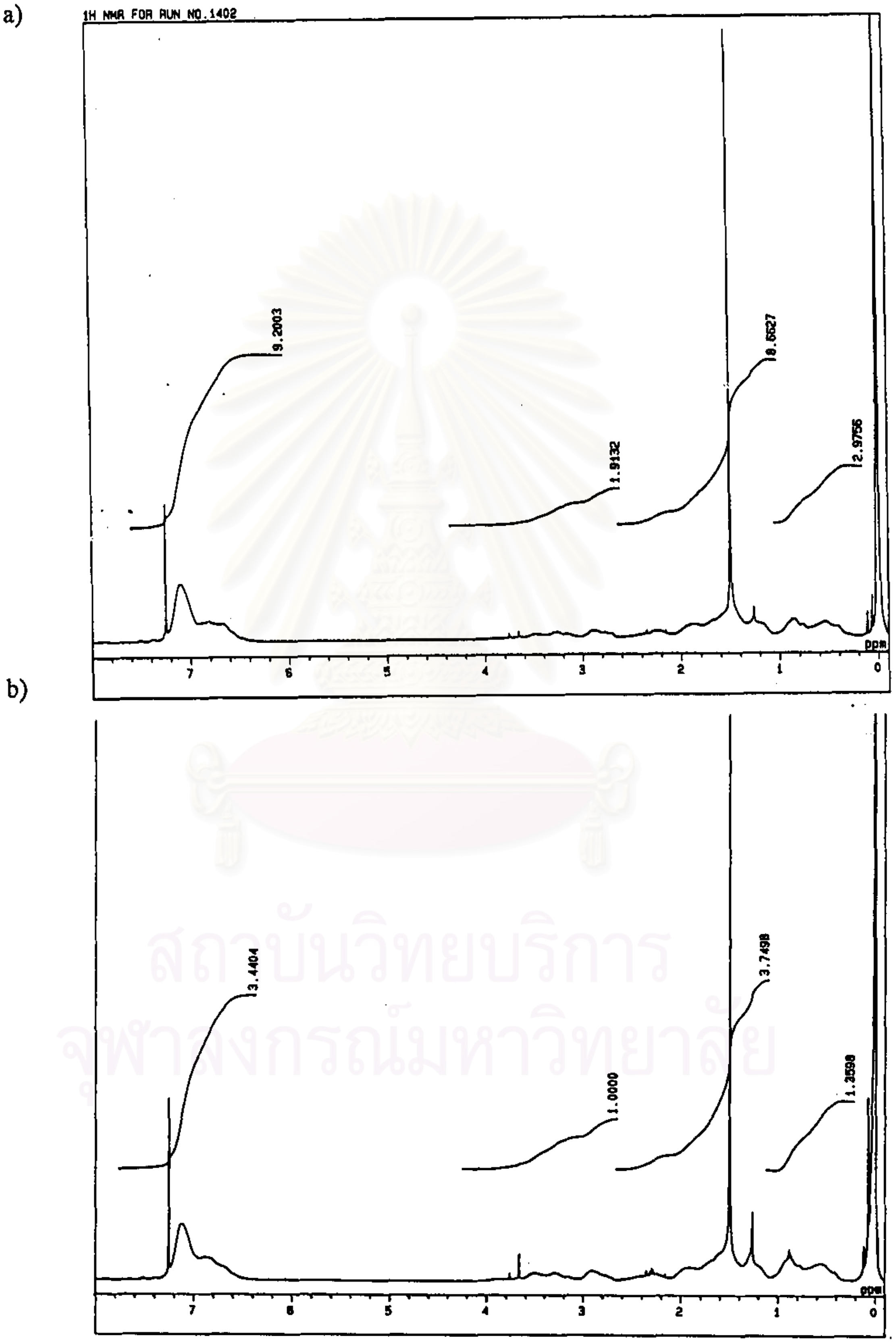


Figure C-1 ^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: a) 50:40:10, b) 50:35:15

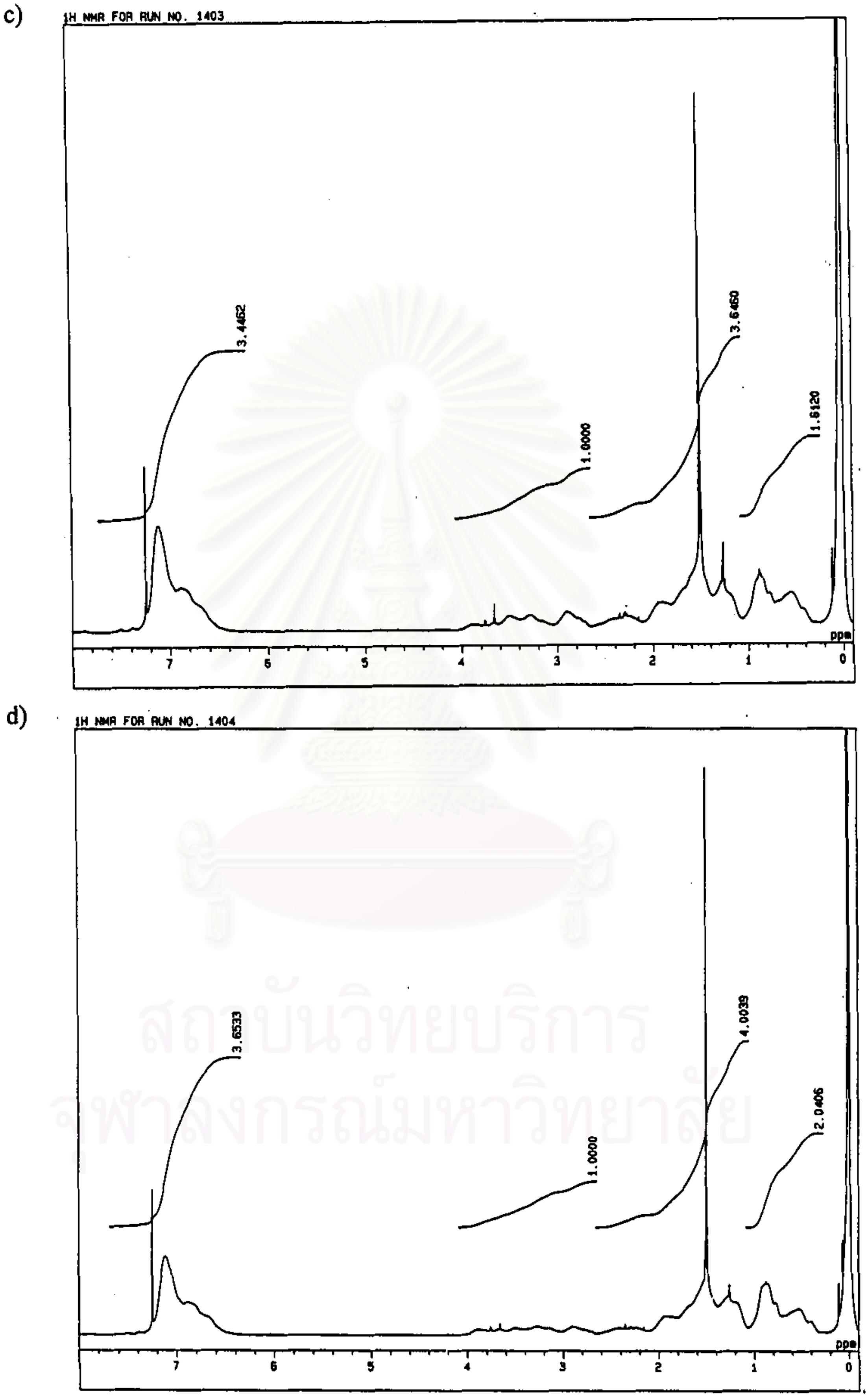


Figure C-1 (continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: c) 50:30:20, d) 50:20:30

e)

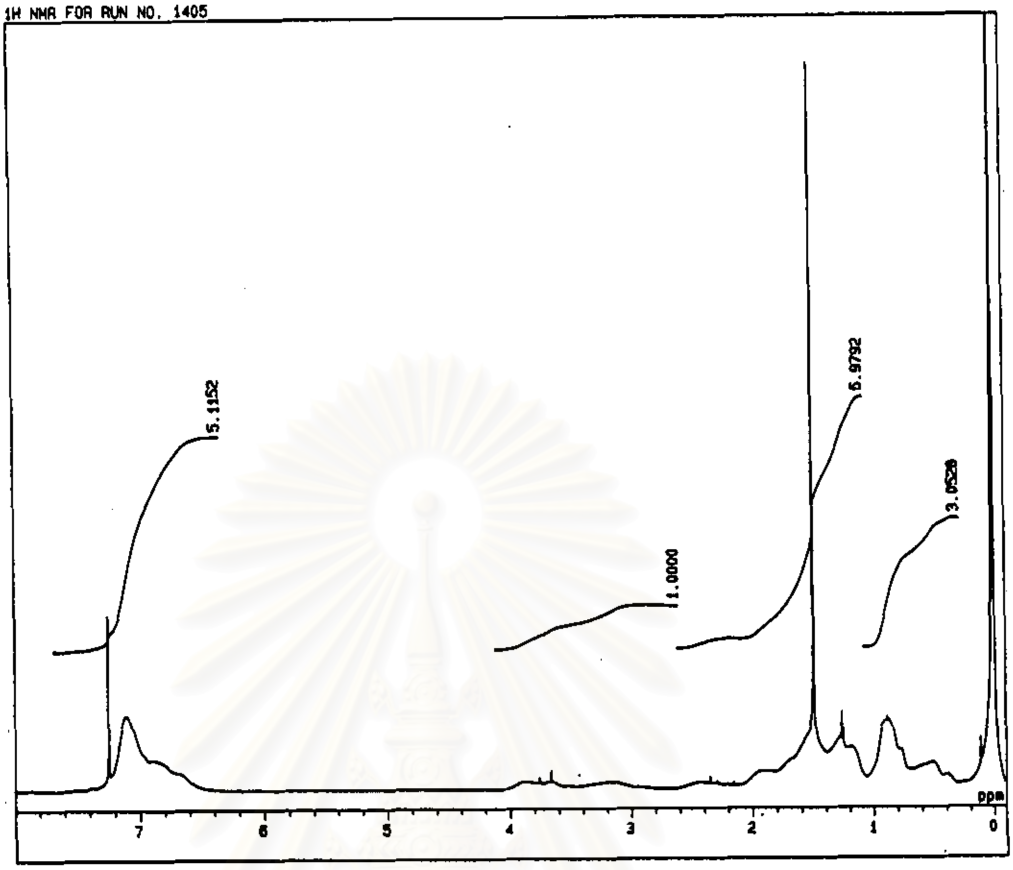


Figure C-1 (continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: e) 50:10:40

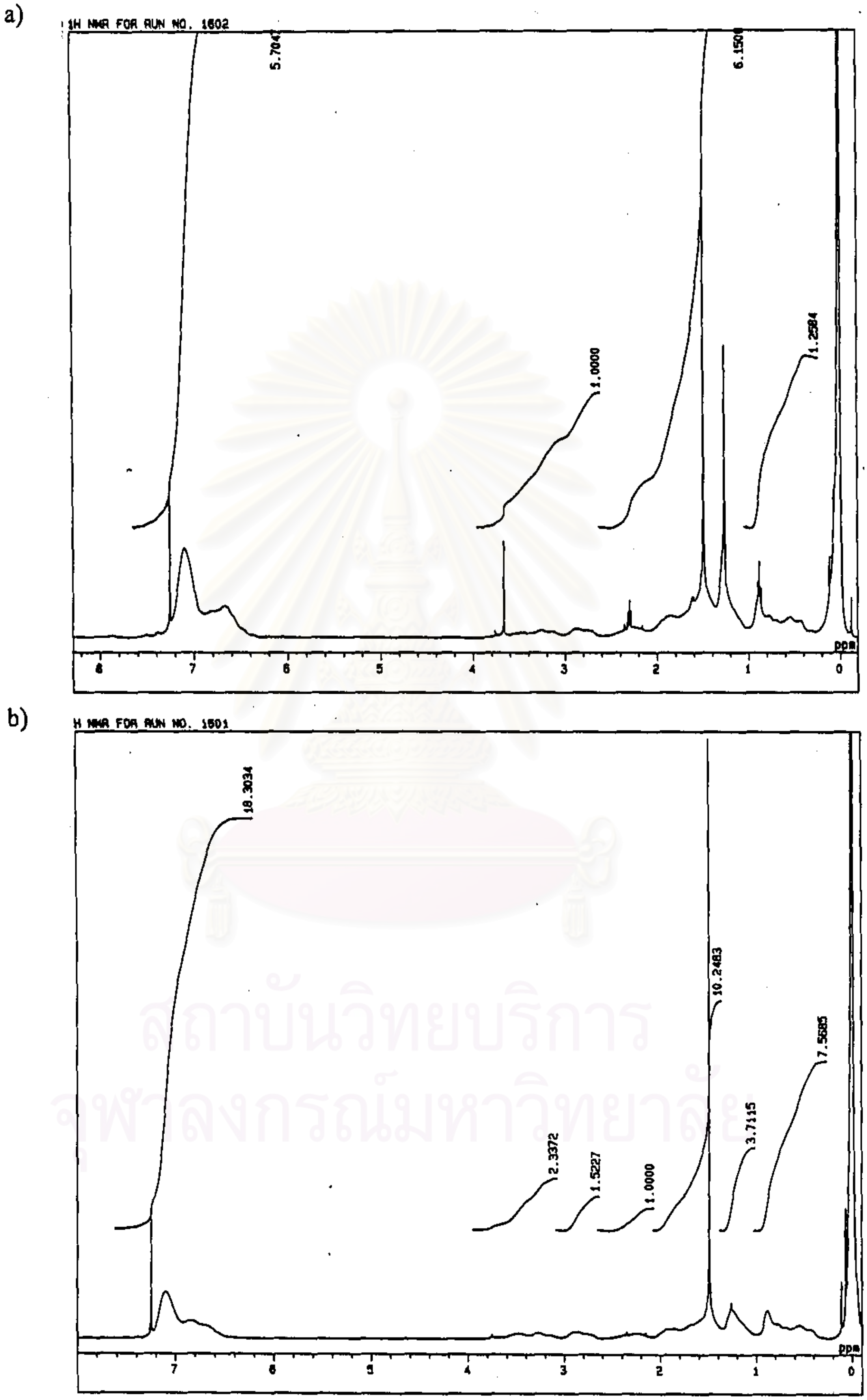


Figure C-2 ^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: a) 50:40:10, b) 50:35:15

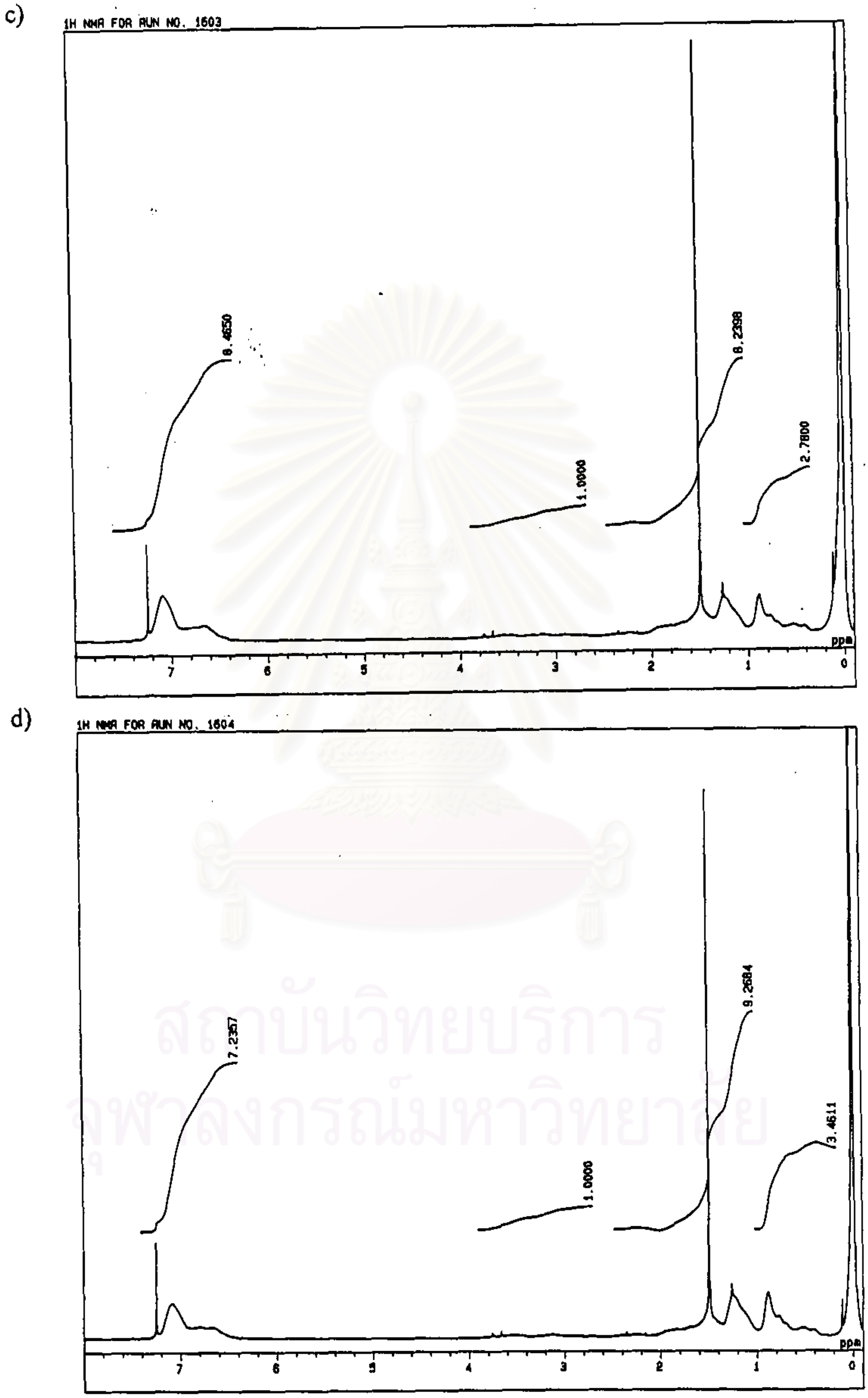


Figure C-2 (continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: c) 50:30:20, d) 50:20:30

e)

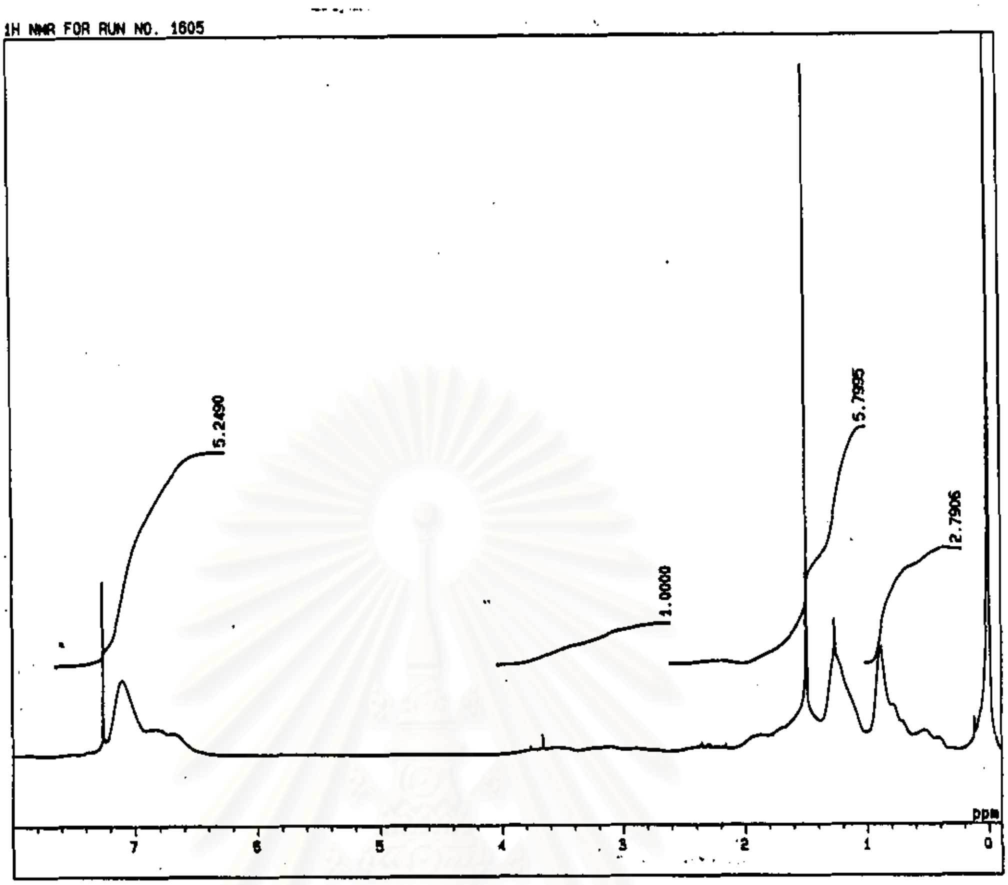


Figure C-2 (continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: e) 50:10:40

APPENDIX D

DIFFERENCIAL SCANNING CALORIMETER

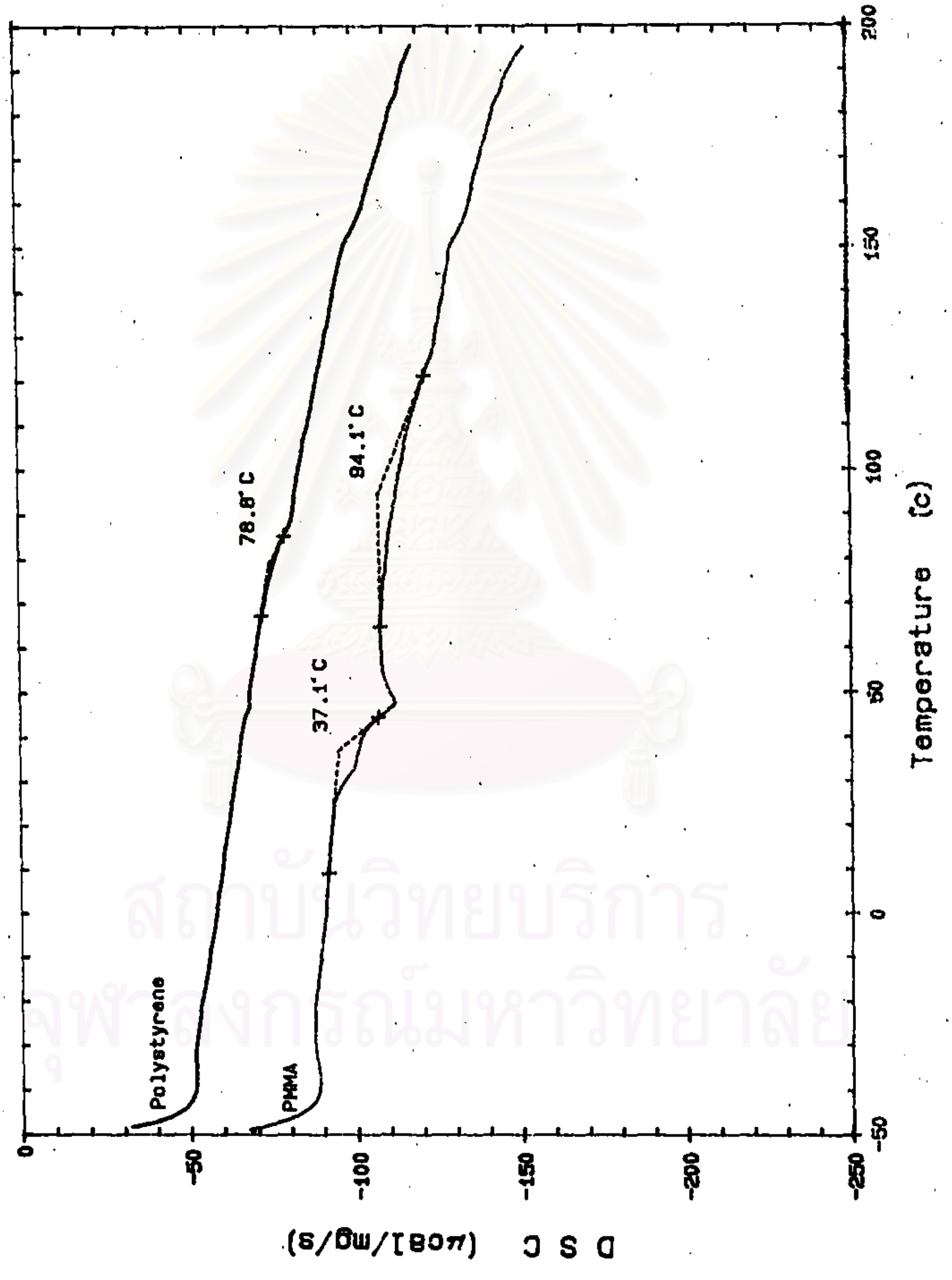


Figure D-1 DSC curves of: a) polystyrene, b) poly(methyl methacrylate) homopolymer

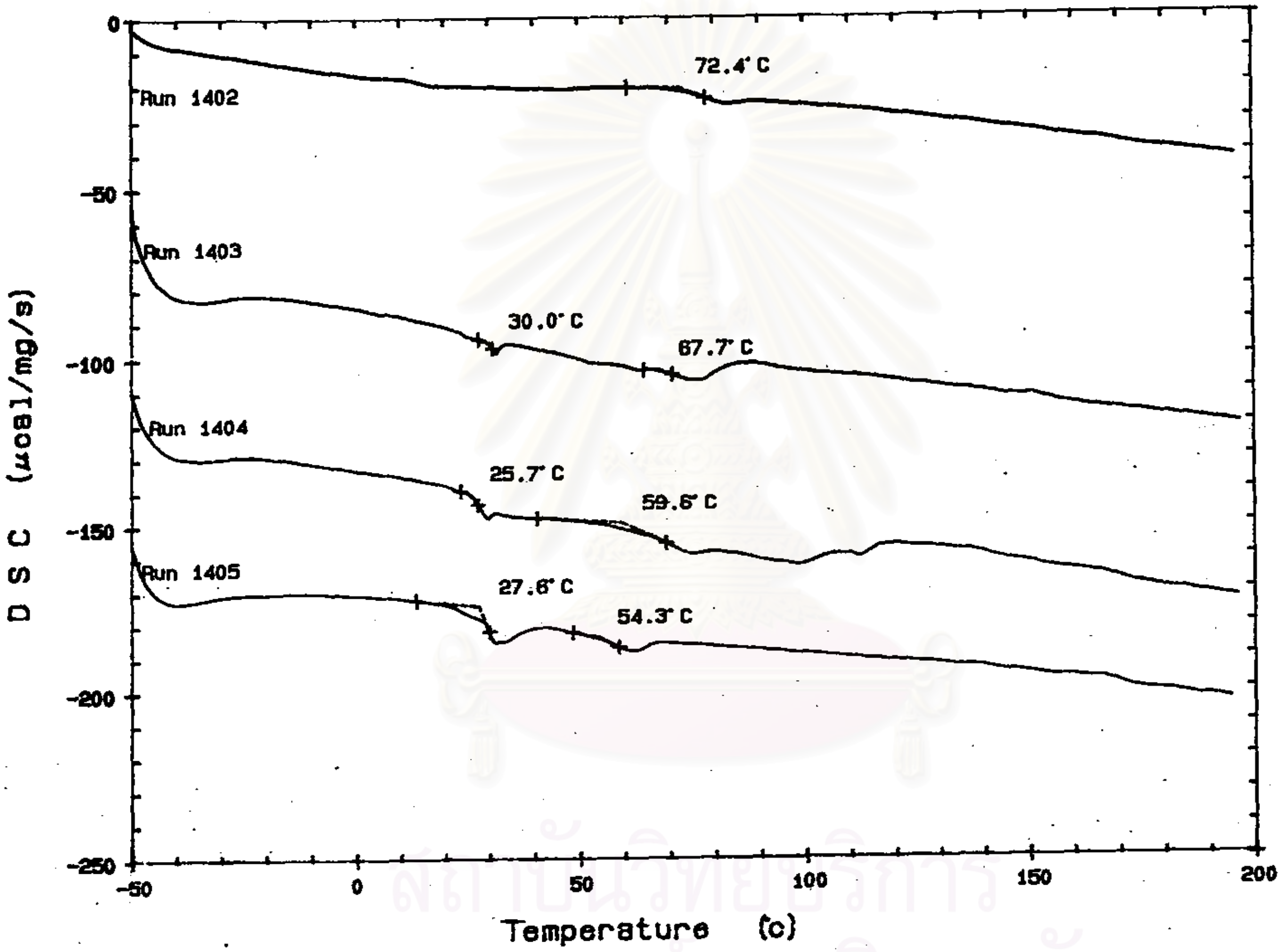


Figure D-2 DSC curves of non-crosslinked poly(styrene-co-MMA-co-n-BMA) weight fractions of St/MMA/n-BMA in the feed: a) 50:40:10

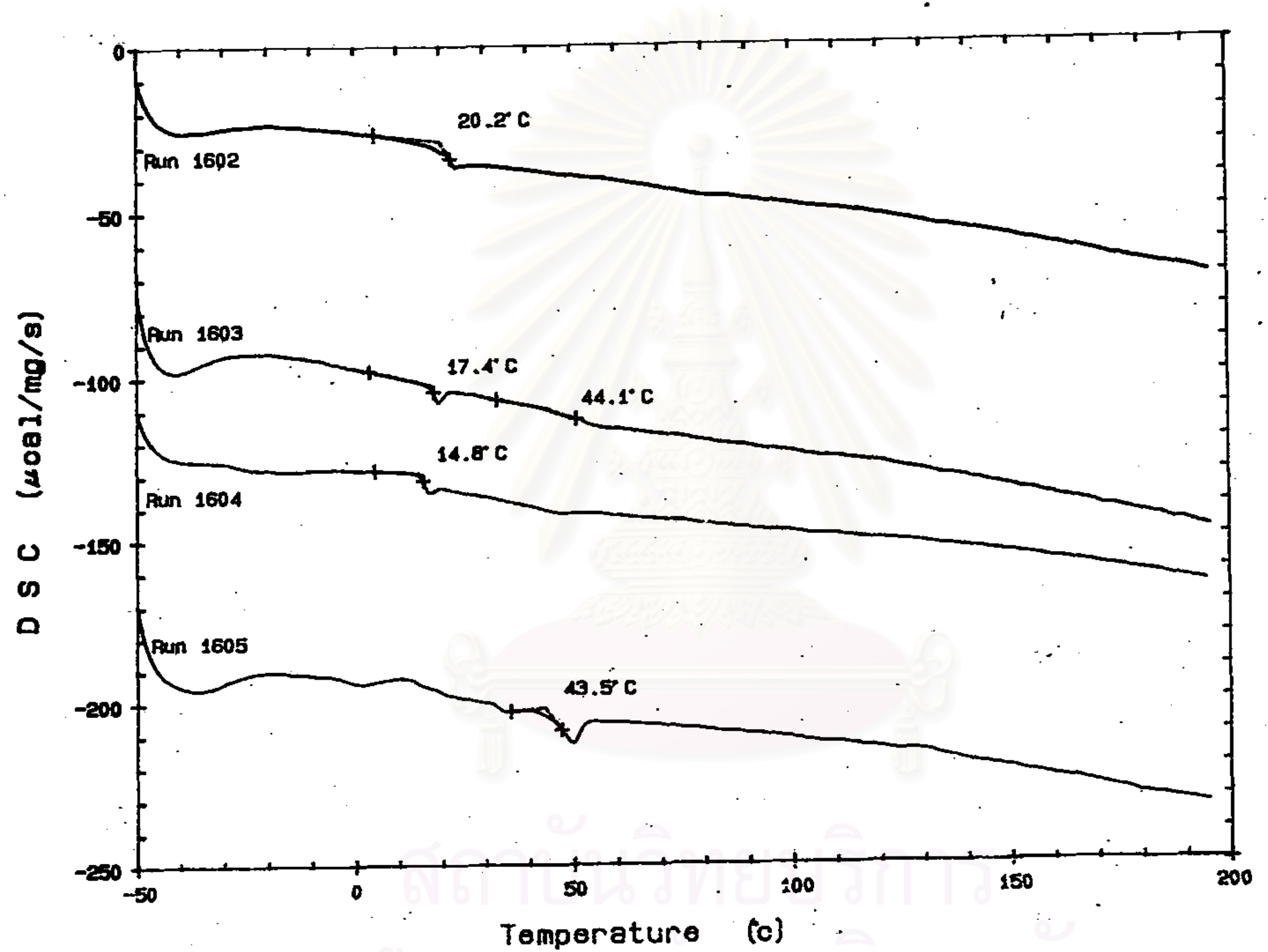


Figure D-3 DSC curves of non-crosslinked poly(styrene-co-MMA-co-2-EHMA) weight fractions of St/MMA/2-EHMA in the feed: a) 50:40:10 (Run 1602), b) 50:30:20 (Run 1603), c) 50:20:30 (Run 1604), and d) 50:10:40 (Run 1605), respectively.

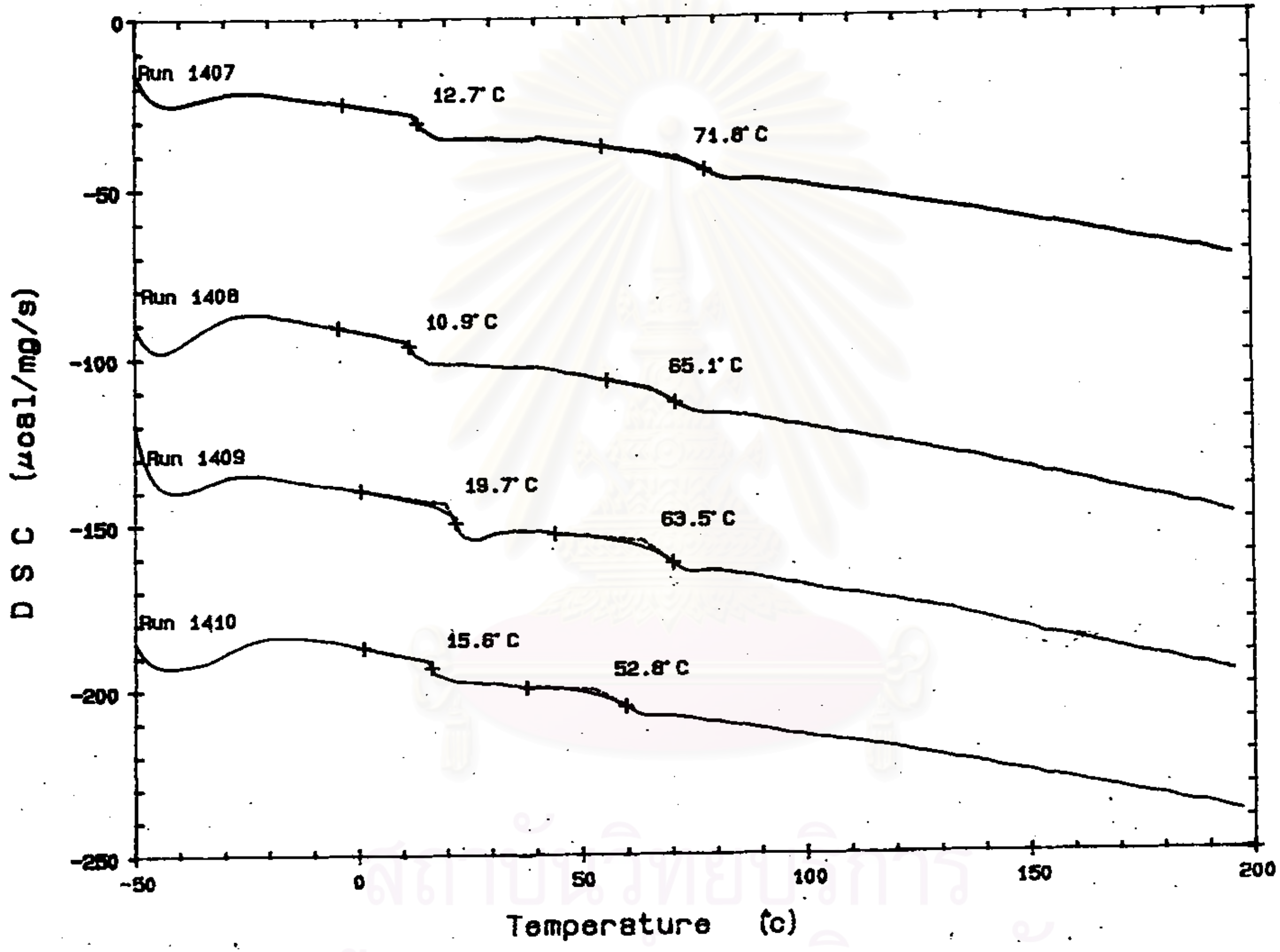


Figure D-4 DSC curves of crosslinked poly(styrene-co-MMA-co-n-BMA) weight fraction of St/MMA/n-BMA in the feed a) 50:40:10 (Run 1407), b) 50:30:20 (Run 1408), c) 50:20:30 (Run 1409), and d) 50:10:40 (Run 1410), respectively.

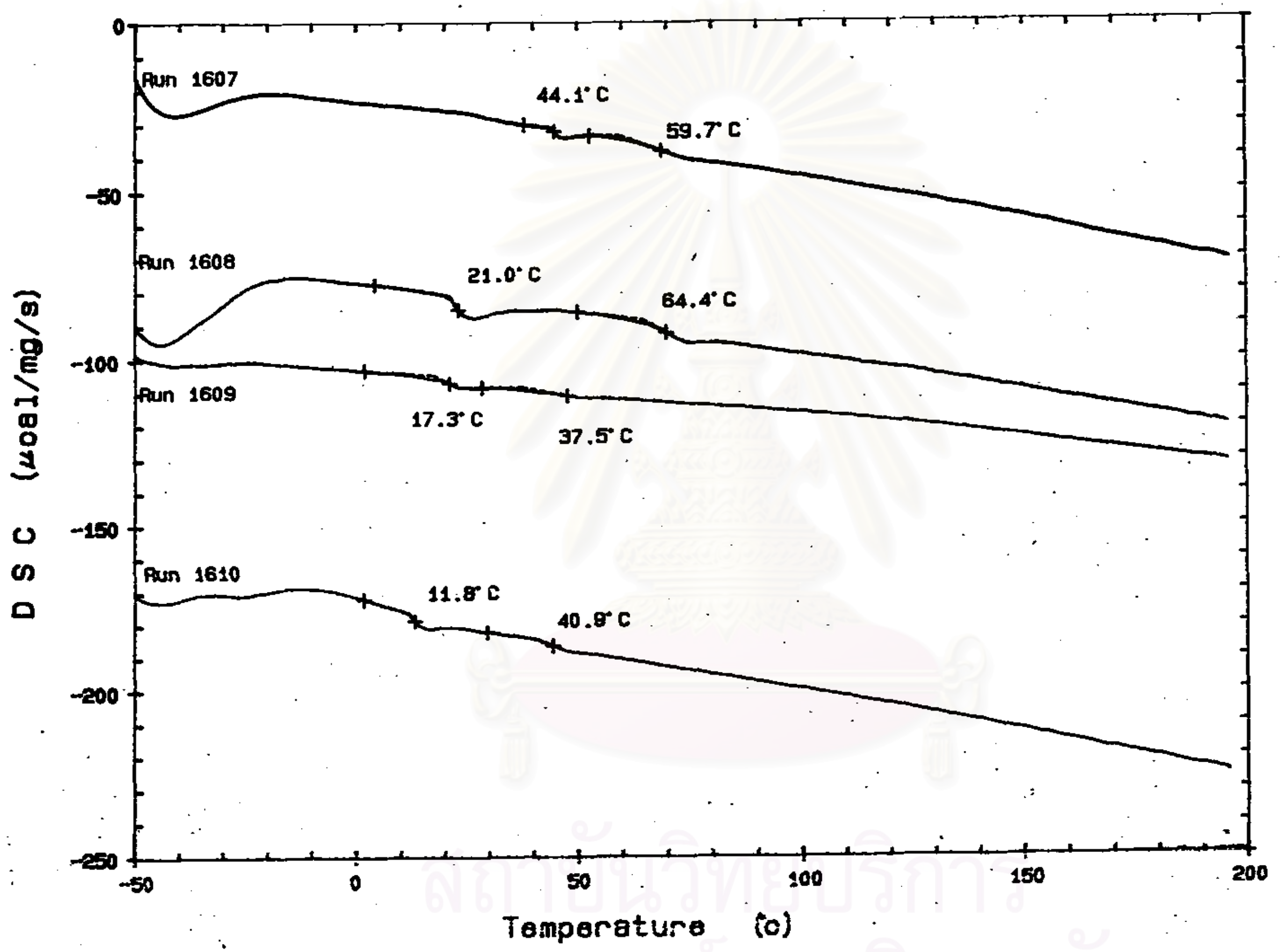


Figure D-5 DSC curves of crosslinked poly(styrene-co-MMA-co-2-EHMA) weight fraction of St/MMA/2-EHMA in the feed: a) 50:40:10 (Run 1607), b) 50:30:20 (Run 1608), c) 50:20:30 (Run 1609), and d) 50:10:40 (Run 1610), respectively

APPENDIX E

FOURIER-TRANSFORM INFRARED SPECTRA

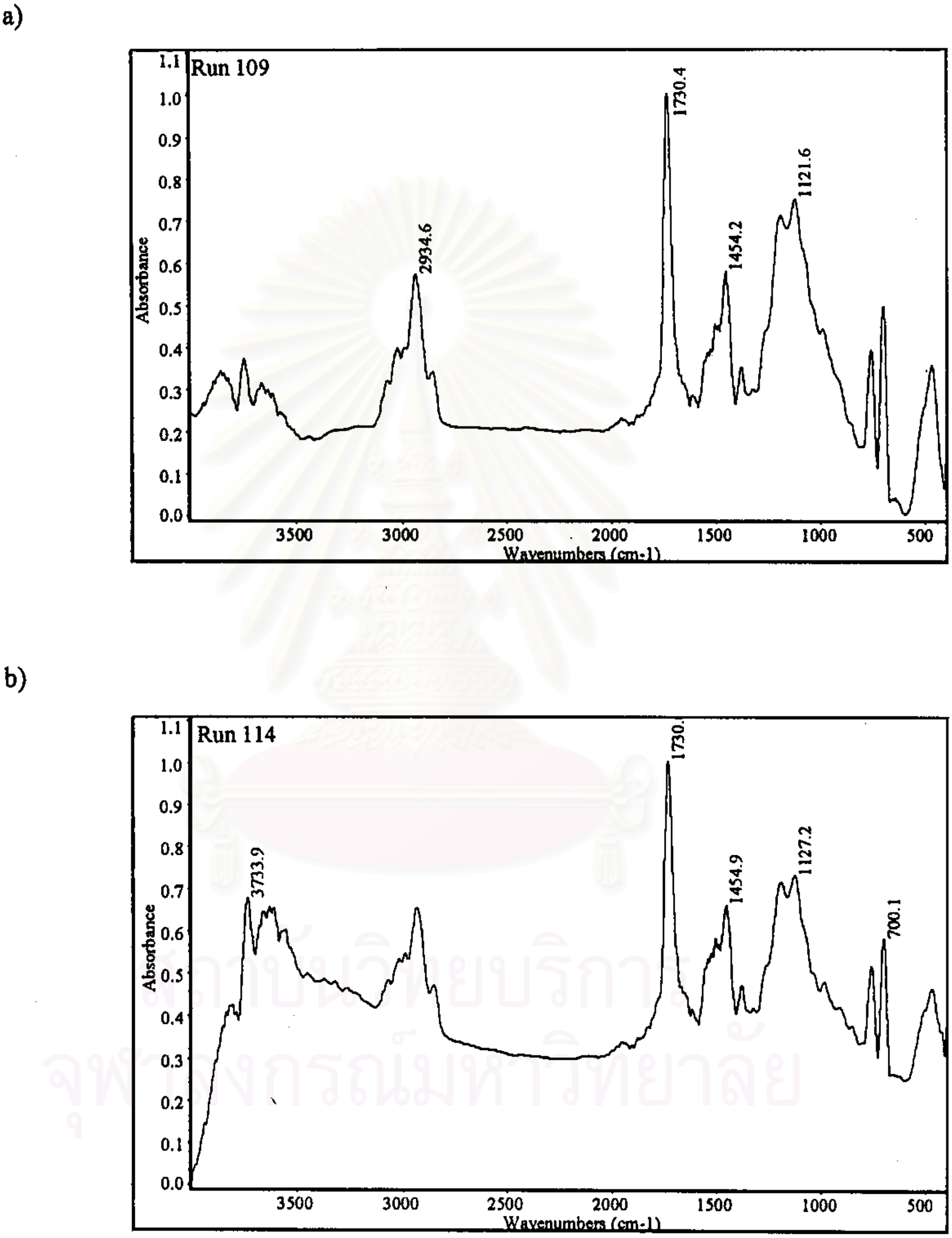
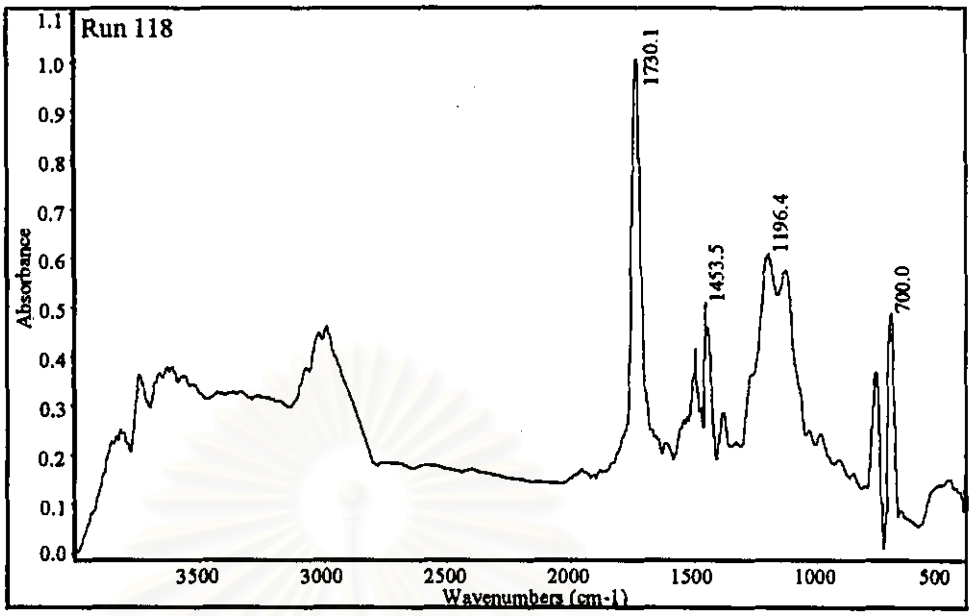


Figure E-1 FT-IR spectrum of poly(styrene-co-MMA) weight% ratio of St/MMA in the feed 50:50 with various additives: a) Hexadecane, b) 1-Hexadecanol c)



d)

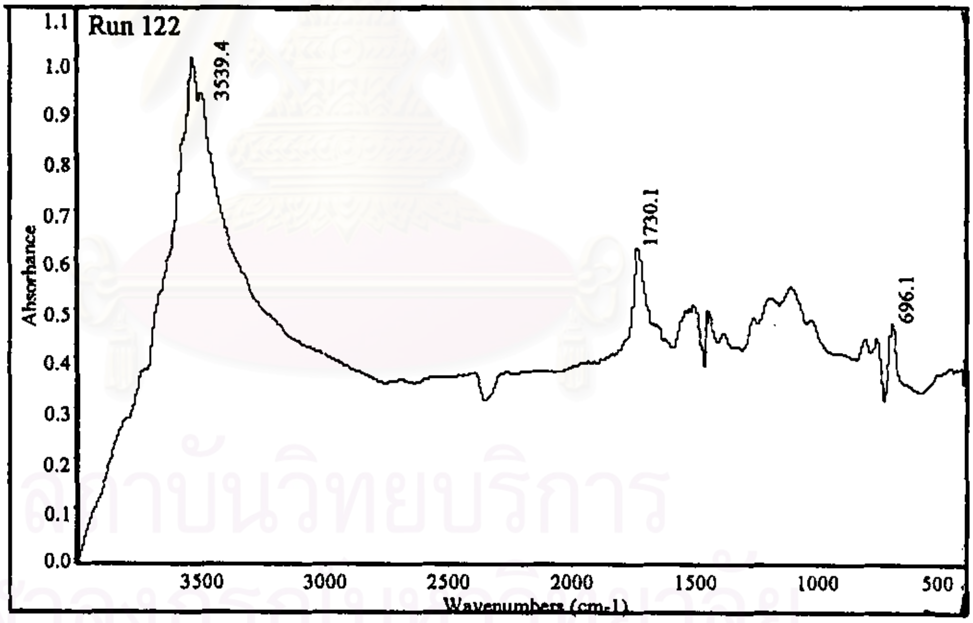


Figure E-1 (continued) FT-IR spectrum of poly(styrene-co-MMA) weight ratio of St/MMA in the feed 50:50 with various additives: c) Methyl palmitate, d) Bees wax

VITA

Miss Roongkan Nuisin was born on October 26, 1974 in Chiang Rai, Thailand. She received her B.Sc. degree in Chemistry from the Faculty of Science, Chiang Mai University in 1996 and she has been a graduate student in the Multidisplinary Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University since 1996. During her masters degree study (1998), she was granted a fellowship from the King Prajadhipok and Queen Rambhai Barni Memorial foundation; and AIEJ Short-term student Exchange Promotion Program to the Graduate school of BASE, Tokyo University of Agriculture and Technology.