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APPENDICES

APPENDIX A

Estimation of solubility parameters of polymers

The solubility parameter of a solvent (δ_{solv}) is a readily accessible quantity. The solubility parameter of a polymer (δ_{pol}) cannot be determined directly because polymers cannot be vaporized without decompositions. Therefore δ_{pol} is defined as the same as that of a solvent in which the polymer will mix in all proportions without heat effect and without volume change and of course without reaction.

Experimental determination of δ_{pol} is possible from solubility measurements (midpoint of solubility range within a solvent group) or from swelling values of sparsely crosslinked polymers.

In 1953, Small [45] has published a table of molar attraction constants which allows the estimation of the solubility parameter merely from the structural formula of the substance and its density. The molar constants (F) are additive and related to the solubility parameter by the equation:

$$\sum_i F_i = \delta \frac{M}{\rho} \tag{A-1}$$

The additive method should not be used for strongly hydrogen-bonded compounds unless such functional groups constitute only a small part of the molecule. Table A-1 shows Small's values. In 1970, Hoy published a number of group contributions for the calculation of F, slightly different from those of Small. They are also shown in Table A-1.

Van Krevelen [45] derived a similar set of atom- and group contributions for the calculation of ΣF as shown in Table A-2.

The molar volume of group contributions is shown in Table A-3. Following are some examples of estimation of the solubility parameter of polymer.

Example 1

Estimate the solubility parameter of poly(butyl methacrylate).

$CH_3CH_2CH_2CH_2OOCCH(CH_3)CH_2$

Solution

From Tables A-1 and A-3 we obtain:

Group	F_{small}	V
4(-CH_2)	532	65.8
1(-C-)	-93	4.75
2(CH_3)	428	45.6
1(-COO-)	310	21.0
total	1177	137.15

$$\delta = \frac{1177}{137.15} = 8.6\ (cal/cm^3)^{1/2}$$

$$= 17.6\ MPa^{1/2}\quad ((cal/cm^3)^{1/2} = 2.046\ MPa^{1/2})$$

In the same way, using Table A-2 we get:

Atom	$F_{Van\ Krevelen}$	V
8(C)	0	65.8
14(H)	959	4.75
2(O_{ester})	250	45.6
total	1209	137.15

$$\delta = \frac{1209}{137.15} = 8.8 \quad (cal/cm^3)^{1/2}$$

$$= 18\ MPa^{1/2}$$

Example 2

Estimate the solubility parameter of poly(lauryl acrylate).

$CH_3(CH_2)_{11}OOCCH_2CH_2$

Solution

From Tables A-1 and A-3 we obtain:

Group	F_{small}	V
13(-CH_2)	1729	213.85
1(CH_3)	214	22.8
1(-COO-)	310	21.0
total	2039	257.65

$$\delta = \frac{2039}{257.65} = 7.9 \quad (cal/cm^3)^{1/2}$$

$$= 16.1\ MPa^{1/2}$$

Table A-1 Molar attraction constants (at 25°C) according to Small and Hoy

Group		F $(cal.cm^3)^{1/2}/mol$ Small	Hoy
$-CH_3$	single bonded	214	148.3
$>CH_2$	single bonded	133	131.5
$>CH-$	single bonded	28	86.0
$>C<$	single bonded	−93	32.0
$=CH_2$	double bonded	190	126.5
$=CH-$	double bonded	111	121.6
$=C<$	double bonded	19	84.5
CH (aromatic)			117.1
C– (aromatic)			98.1
HC≡C–		285	
–C≡C–		222	
Phenyl		735	
Phenylene		658	
Naphthyl		1146	
Ring	5 membered	105–115	21.0
Ring	6 membered	95–105	−23.4
Conjugation		20– 30	23.3

Group		F $(cal.cm^3)^{1/2}/mol$ Small	Hoy
–H (variable)		80–100	
–O– (ether)		70	115.0
$>C=O$ (ketone)		275	263.0
–C(=O)O– (ester)		310	326.6
–C≡N		410	354.6
–F			41.3
–Cl	(mean)	260	207
	single	270	
	twinned ($>CCl_2$)	260	
	triple ($-CCl_3$)	250	
–Br single		340	258
–I single		425	
$>CF_2$	fluorocarbons only	150	
$-CF_3$	fluorocarbons only	274	
–S– (sulphides)		225	209.4
–SH (thiols)		315	
$-ONO_2$ (nitrates)		440	
$-NO_2$ (aliphatic)		440	
$>PO_4$		500	
–CO–O–CO–			567.3
–NH–			180.0

Table A-2 Atomic attraction constants at 25°C according to Van Krevelen (1995)

Atom (or group)	F_i *(cal. cm³)½/mol*	*Atom (or group)*	F_i *(cal. cm³)½/mol*
C	0	N	
H	68·5	*aliph. primary amine*	100
O		*aliph. secondary amine*	140
ether-	125	*arom. primary amine*	65
ester-	125	*heterocyclic*	115
ketonic	335	*nitril*	480
alcoholic (primary)	360	N + O *in*	
alcoholic (secondary)	300	*nitro aliphatic*	460
phenolic	250	*nitro aromatic*	325
S		*acid amide*	
thioether	225	$-C(=O)NH-$	600
thiol	(250)		
F	80	$-C(=O)N<$	400
Cl	230		
Br	300		
I	420		
Double bond (non-aromatic)	80	*non-aromatic ring*	60
Double bond (aromatic)	133	*ramification in chain*	−20
Triple bond	215	*conjugation of double bonds*	25
		2 OHs on adjacent C atom	−190

Table A-3 Group contributions for V (cm³/mol)

Groups		V_r
bivalent	$-CH_2-$	16.45
	$-CH(CH_3)-$	32.65
	$-C(CH_3)_2-$	50.35
	$-CH=CH-$	27.75
	$-CH=C(CH_3)-$	42.8
	$-C_6H_4-$	61.4
	$-CH(C_6H_5)-$	74.5
	$-O-$	8.5
	$-COO-$ (general)	24.6
	$-COO-$ (acrylic)	21.0
	$-S-$	15.0
	$-CHF-$	19.85
	$-CHCl-$	28.25
tetravalent	$>C<$	4.75
trivalent	$>CH-$	9.85
	$-CH=C<$	20.0
monovalent	$-CH_3$	22.8
	$-C_6H_5$	64.65
	$-F$	10.0
	$-Cl$	18.4

Conversion factor to S.I.
1 cm³/mol = 10^{-3} m³/kmol

APPENDIX B

Estimation of solubility parameters of mixtures

In the case of diluent mixtures, the solubility parameter (δ_{mix}) can be considered as an average value of the solubility parameters of the pure diluents and is given by the equation [1]:

$$\delta_{mix} = \frac{X_1V_1\delta_1 + X_2V_2\delta_2}{X_1V_1 + X_2V_2} \qquad \text{(B-1)}$$

Where X_1 is molar fraction of the component 1

X_2 is molar fraction of the component 2

V_1 is molar volume of the component 1

V_2 is molar volume of the component 2

δ_1 is solubility parameter of the component 1

δ_2 is solubility parameter of the component 2

Example 1

Estimate δ_{mix} of the mixed solvent between toluene and heptane with ratio of 0.5g: 0.5g.

Solution

Table B-1 The property of heptane and toluene [41]

Property	Heptane	Toluene
δ ($MPa^{1/2}$)	15.1	18.2
Molecular weight	100.21	92.14
Density (g/cm^3)	0.867	0.684

$$n_T = \frac{0.5}{92.14} = 0.0054$$

$$n_H = \frac{0.5}{100.21} = 0.0050$$

$$X_H = \frac{0.0050}{0.0050 + 0.0054} = 0.479$$

$$X_T = \frac{0.0054}{0.0050 + 0.0054} = 0.521$$

$$V_H = \frac{100.21}{0.684} = 146.51$$

$$V_T = \frac{92.14}{0.867} = 106.27$$

From eq.(1)

$$\delta_{mix} = \frac{(0.479)(146.51)(15.1) + (0.521)(106.27)(18.2)}{(0.479)(146.51) + (0.521)(106.27)}$$

$= 16.5\ MPa^{1/2}$

Example 2

Estimate δ_{mix} of the poly(2-EHA-EGDMA) with a ratio of 2-EHA: EGDMA, is 7g: 3g.

Solution

Table B-2 The property of 2-EHA and EGDMA

Property	2-EHA	EGDMA
δ ($MPa^{1/2}$)	15.9	17.5
Molecular weight	184.28	198.22
Density (g/cm^3)	0.885	1.051

$$n_{2\text{-}EHA} = \frac{7}{184.28} = 0.038$$

$$n_{EGDMA} = \frac{3}{198.22} = 0.015$$

$$X_{EGDMA} = \frac{0.015}{0.038 + 0.015} = 0.285$$

$$X_{2\text{-}EHA} = \frac{0.038}{0.038 + 0.015} = 0.72$$

$$V_{EGDMA} = \frac{198.22}{1.051} = 188.60$$

$$V_{2\text{-}EHA} = \frac{184.28}{0.885} = 208.226$$

$$\delta_{mix} = \frac{(0.72)(208.66)(15.9) + (0.285)(188.60)(17.5)}{(0.72)(208.66) + (0.285)(188.60)}$$

$$= 16.3\ MPa^{1/2}$$

APPENDIX C

FOURIER-TRANSFORM INFRARED SPECTRA

Confirmation of comonomers in the crosslinked polymer

The IR spectra of the crosslinked (meth)acrylate polymers are shown in Figure 4.21. The absorption bands of the resulted polymer appeared at about 700 cm^{-1}, 900-1250 cm^{-1}, 1450 cm^{-1}, 1740 cm^{-1} and 2800-2960 cm^{-1}. The carbonyl groups of MMA and acrylate comonomers are overlapped at 1730-1740 cm^{-1} [43]. Besides, the other bands of the straight chain aliphatic compounds are as following [44].

1. The carbon-hydrogen stretching band appears at 2855-2940 cm^{-1}.
2. The carbon-hydrogen bending band appears at 1470 cm^{-1}.
3. The symmetric carbon-hydrogen bending band of the $-CH_3$ group appears at 1380 cm^{-1}.
4. The CH_2 rocking band absorbs at 725 cm^{-1} when the number of CH_2's increases in the chain.
5. The branching of the chain and the saturated cyclic members absorb between 910-1250 cm^{-1}.

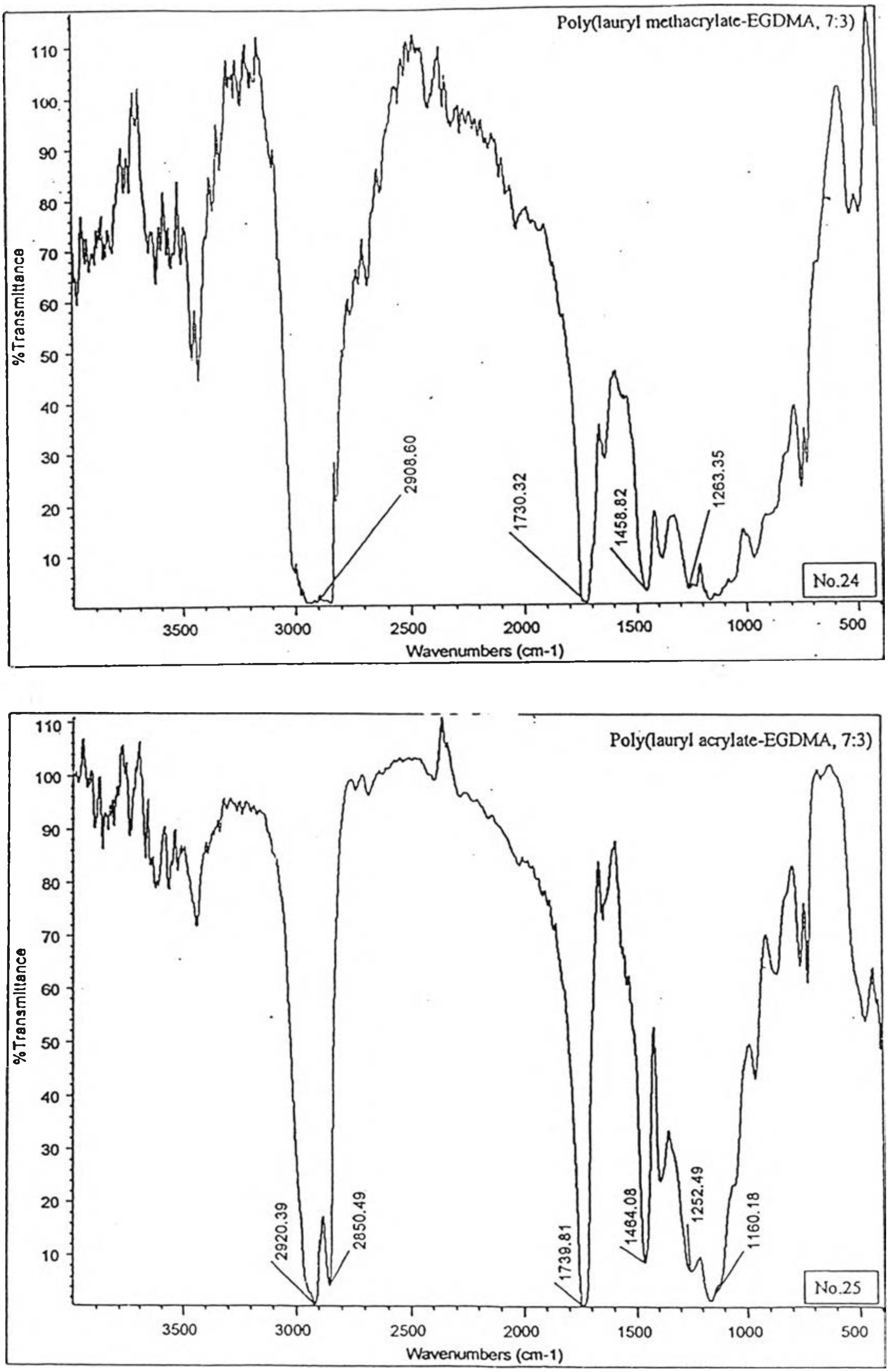
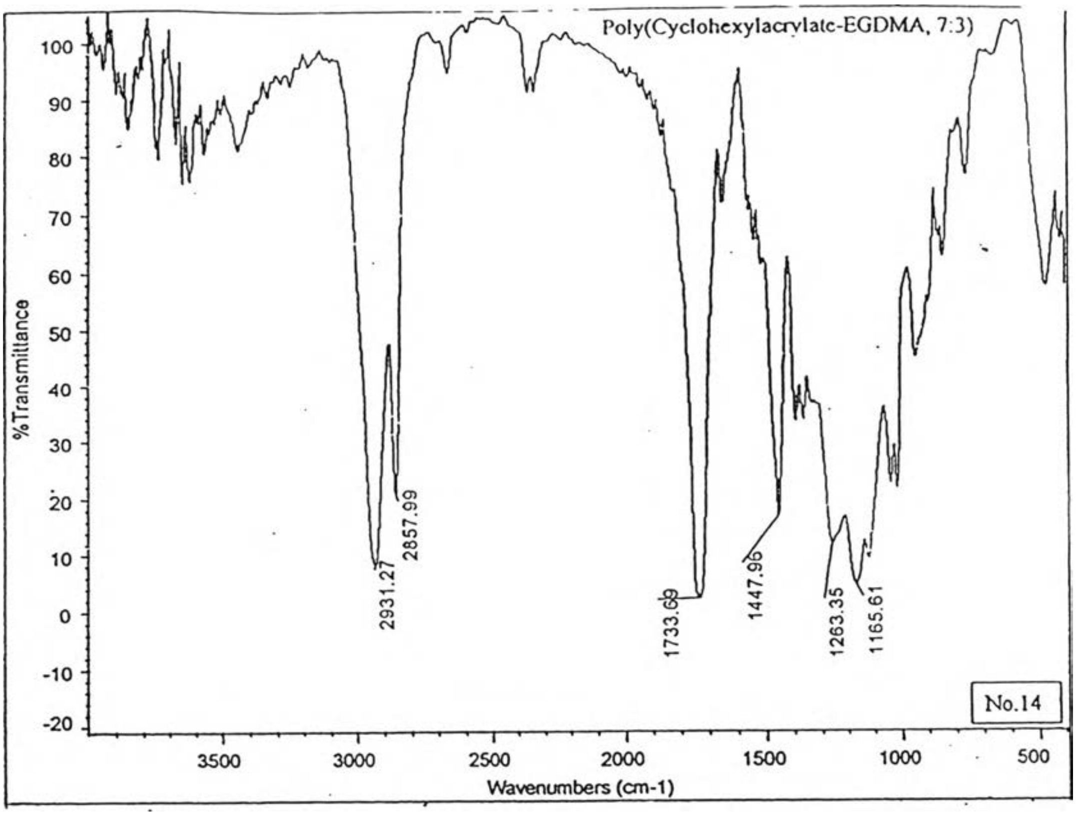


Figure C-1 The IR spectra of crosslinked polymer: (1) the upper figure is poly(lauryl methacrylate-co-EGDMA) particles, (2) the lower figure is poly(lauryl acrylate-co-EGDMA) particles.



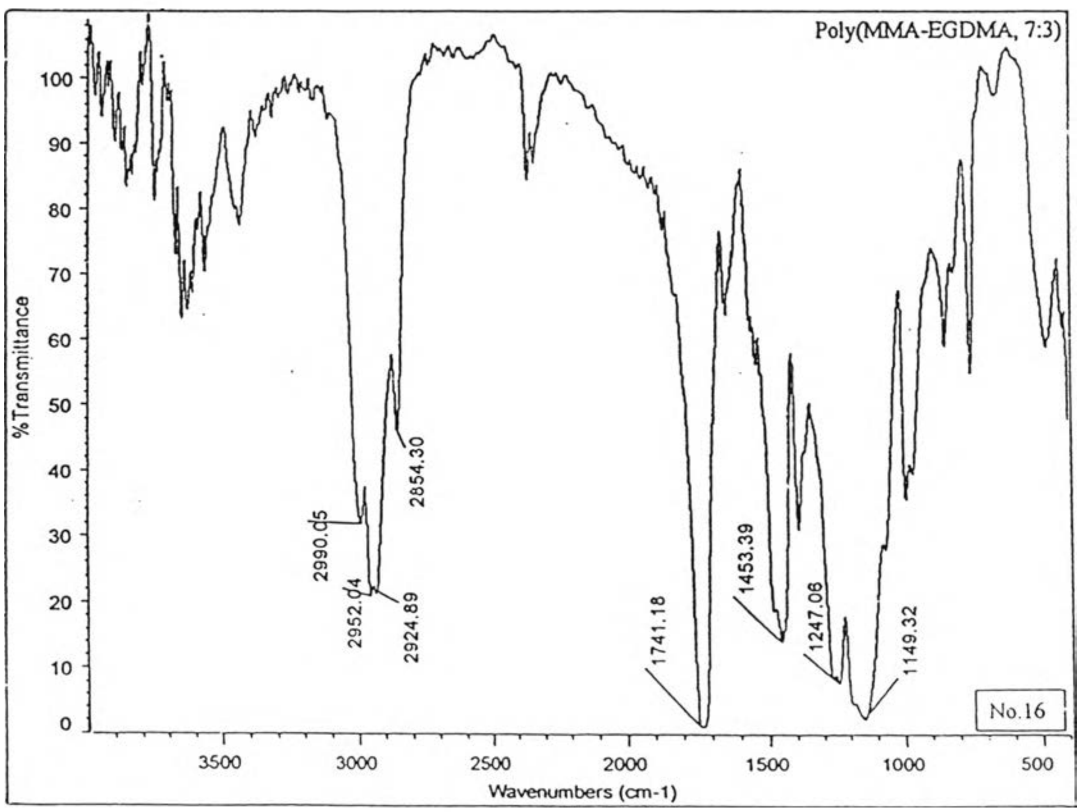
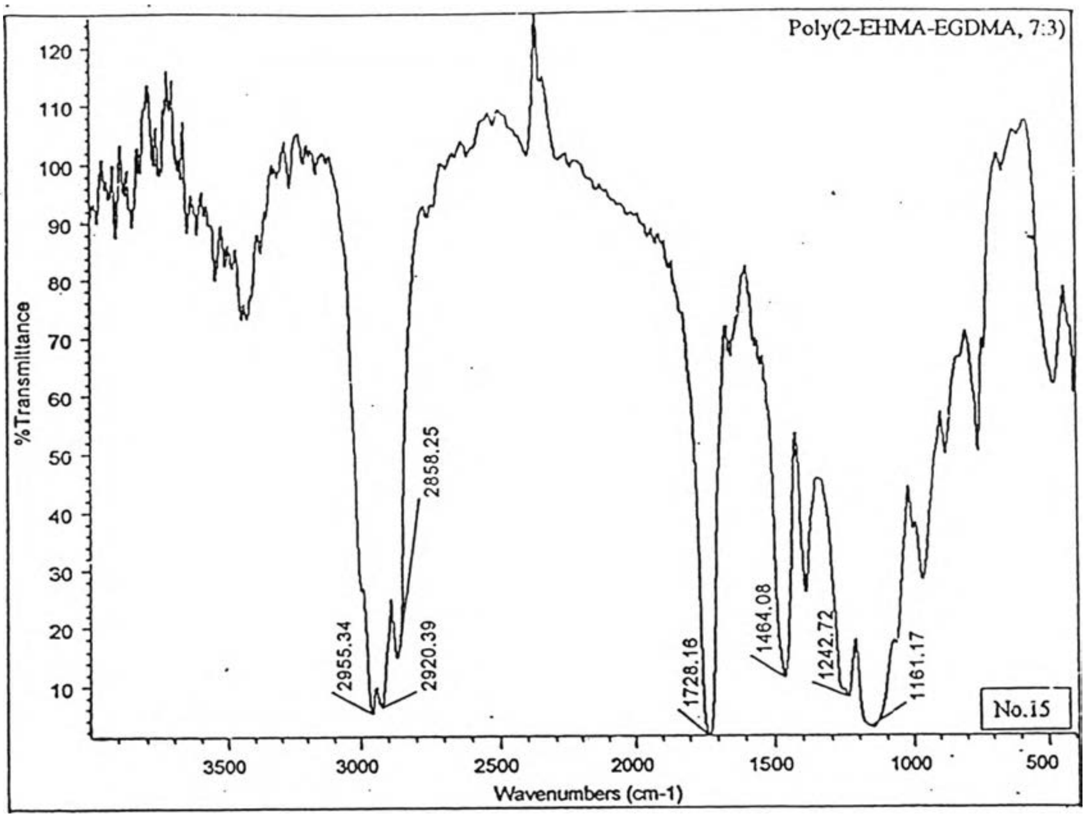


Figure C-2 The IR spectra of crosslinked polymer: (1) the upper figure is poly(cyclohexylacrylte-co-EGDMA) particles, (2) the lower figure is poly(MMA-co-EGDMA) particles.



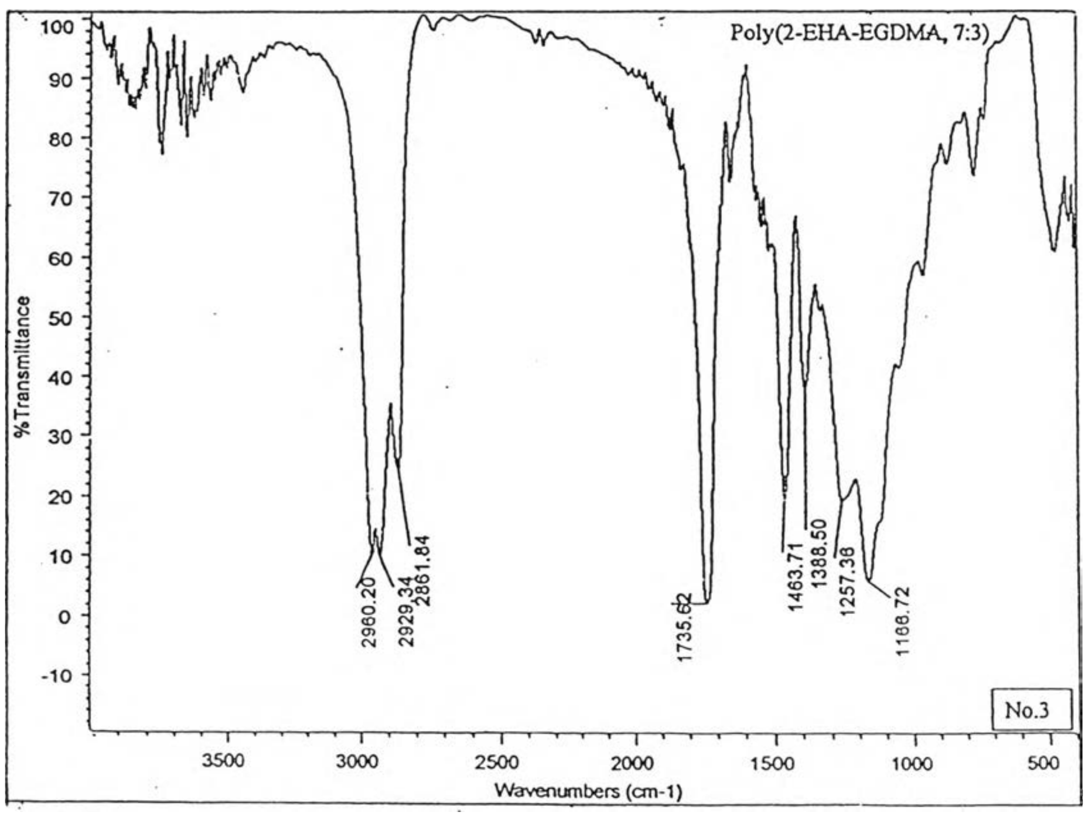
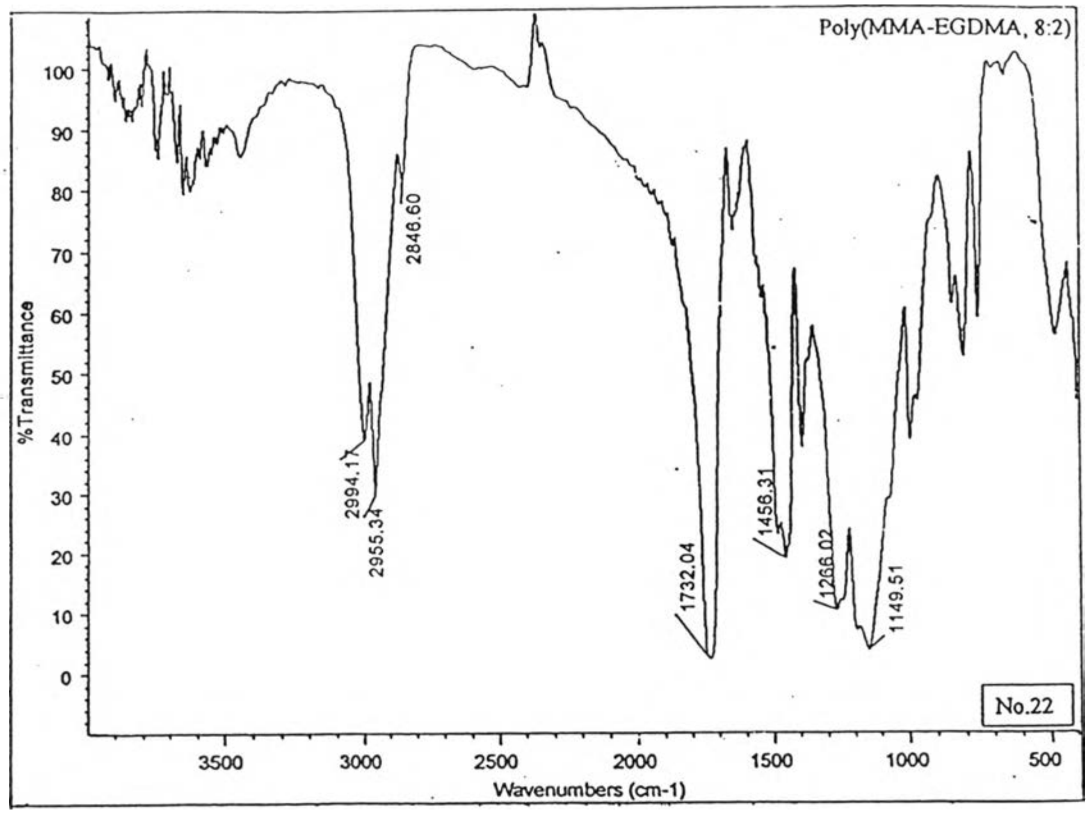


Figure C-3 The IR spectra of crosslinked polymer: (1) the upper figure is poly(2-EHMA-co-EGDMA) particles, (2) the lower figure is poly(2-EHA-co-EGDMA) particles.



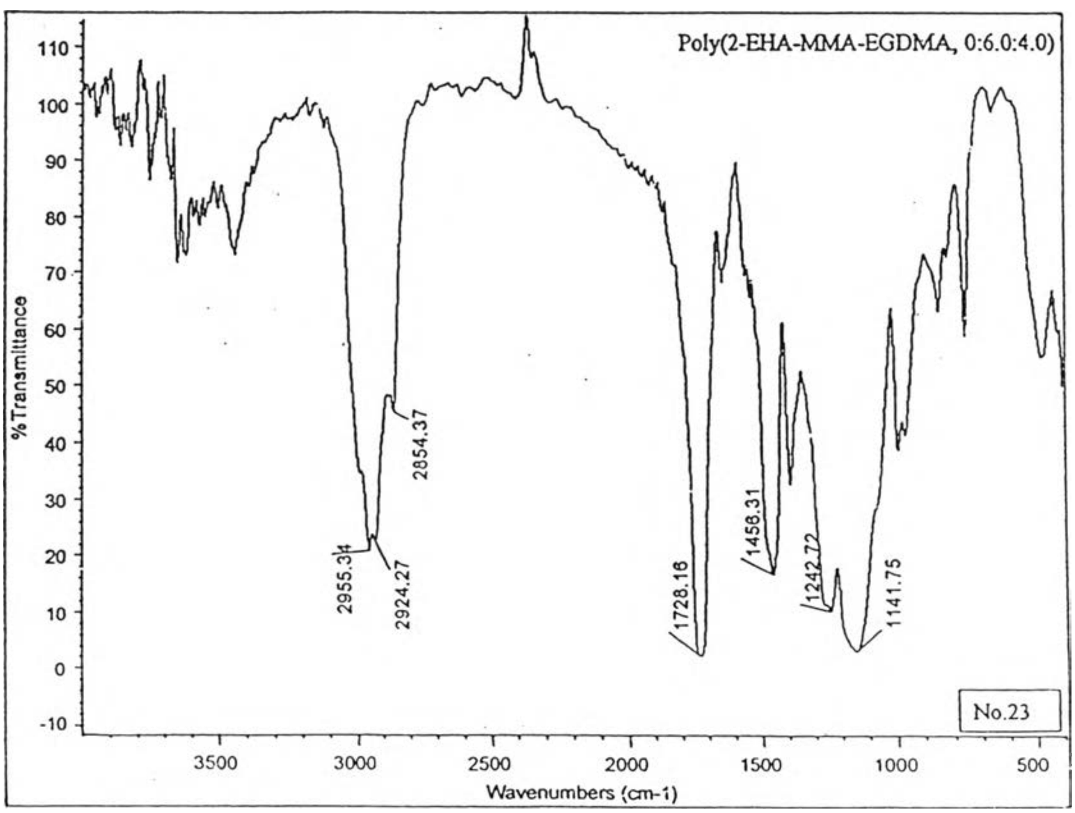
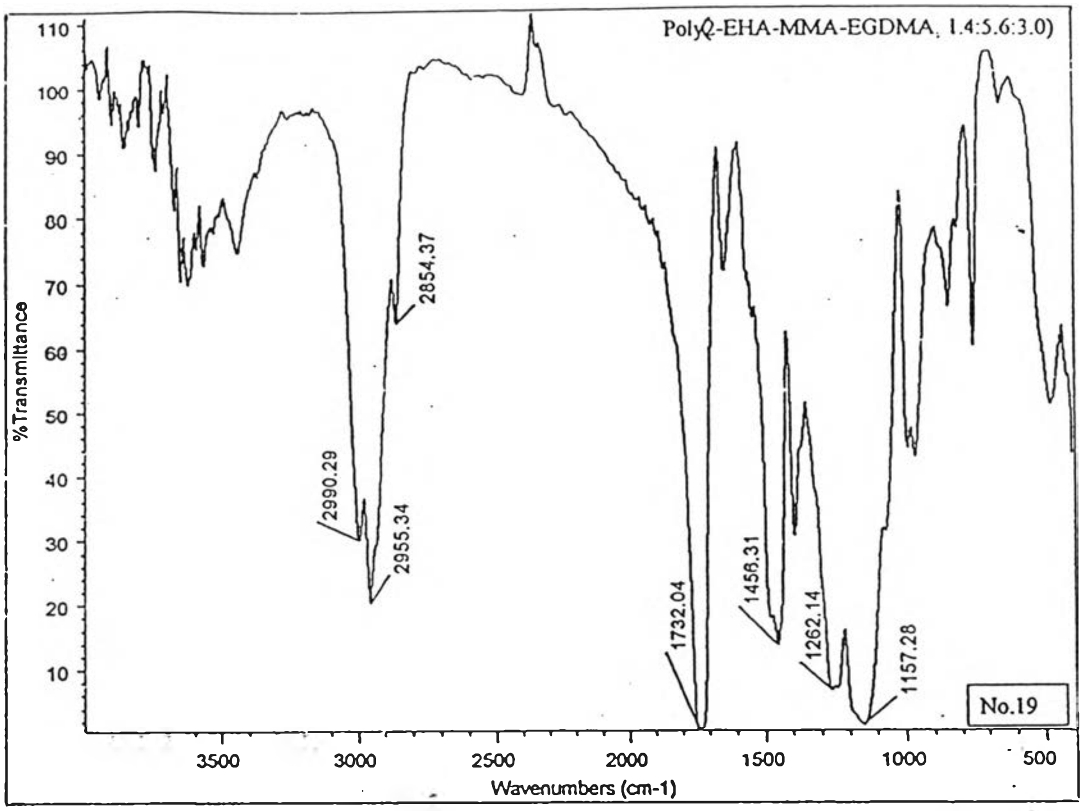


Figure C-4 The IR spectra of crosslinked polymers; (1) the upper figure is poly (MMA-co-EGDMA, 8 g: 2 g) particles, the lower figure is poly (MMA-co-EGDMA, 6 g: 4 g) particles



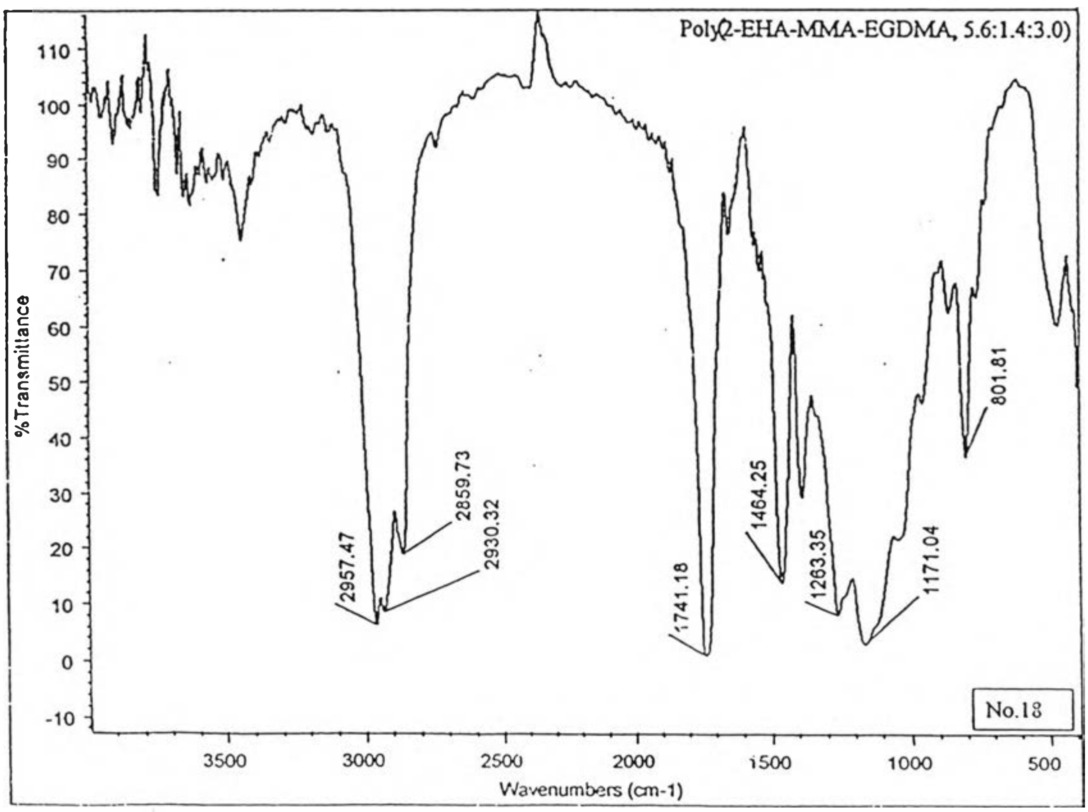


Figure C-5 The IR spectra of crosslinked polymers; (1) the upper figure is poly (2-EHA-co-MMA-co-EGDMA, 1.4: 5.6: 3.0 g) particles, the lower figure is poly (MMA-co-2-EHA-co-EGDMA, 5.6: 1.4: 3.0 g) particles.

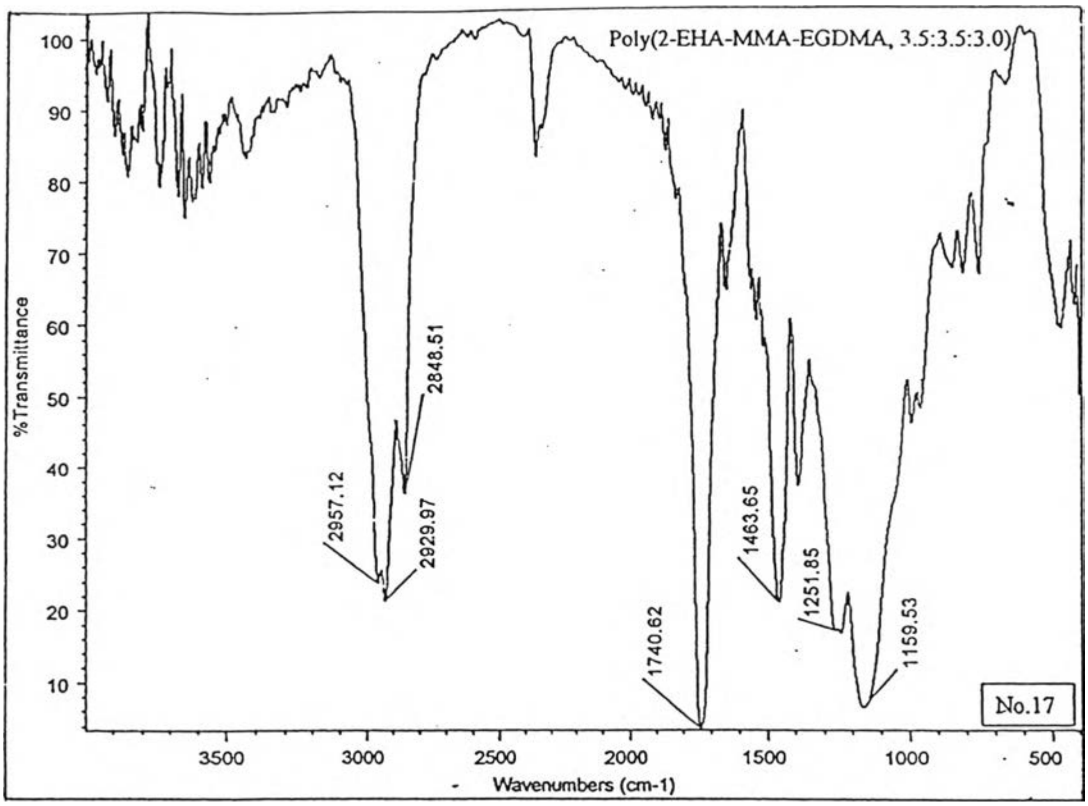


Figure C-6 The IR spectra of crosslinked polymers; poly (2-EHA-co-MMA-co-EGDMA, 3.5: 3.5: 3.0 g) particles.

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