

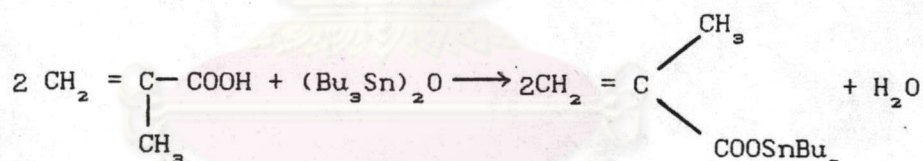
CHAPTER III

RESULTS AND DISCUSSION

3.1 Preparation of the Organotin Monomers

3.1.1 Tri-n-butyltin methacrylate (TBTM)

The method (sec.2.3) involved a condensation reaction between bis(tri-n-butyltin) oxide (TBTO) and methacrylic acid in refluxing toluene under reduced pressure.



where Bu = n-butyl

The reaction was considered as completed when the calculated quantity of water was collected.

This process gave a good yield of TBTM (~ 90% by wt.). The transparent monomer was a liquid at room temperature, melting point 18-19°C. TBTM monomer polymerized spontaneously in the absence of the catalysts at temperature higher than 30°C giving an elastomeric product that was insoluble in methanol.

The results of elemental analysis were agree well with the formular,

meaned TBTM was prepared.

Spectroscopic technics were used to characterize the structures. From IR spectra, the 1645 cm^{-1} peak (in this case shifted down to 1620 cm^{-1} due to α, β unsaturation effect) is the characteristic peak of $-\text{COOSn}$ group. (28). However, this peak superimposed on the absorbance of vinyl double bond. The IR spectra of both TBTM and TBTO in the region about $1100\text{-}700\text{ cm}^{-1}$ are quite similar as well as to the spectra of TBTA with minor modifications.(27).

The IR spectra of TBTO and TBTM are shown in Fig.3.1 and 3.2

^1H NMR and ^{13}C NMR spectra are shown in Fig. 3.3 and 3.4
The signals of ^{13}C NMR at $124.5\text{-}137.9$ ppm refered to $\text{C}=\text{C}$.

$^{119\text{m}}\text{Sn}$ Moessbauer spectroscopy data, isomer shift (δ) mms^{-1} and quadrupole splitting (ΔE_{q} mms^{-1}), are two important parameters of organotin compounds. The isomer shift of monomer and quadrupole splitting of TBTM were 1.38 and 2.98 (Table 3.2).

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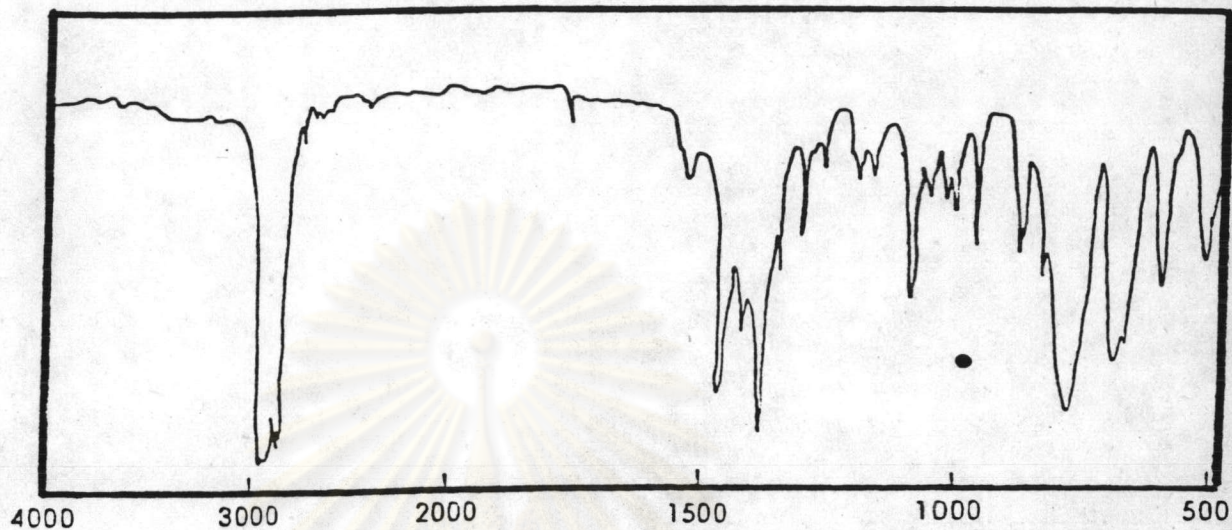


FIG.3.1 IR spectrum of BIS (tributyltin oxide).

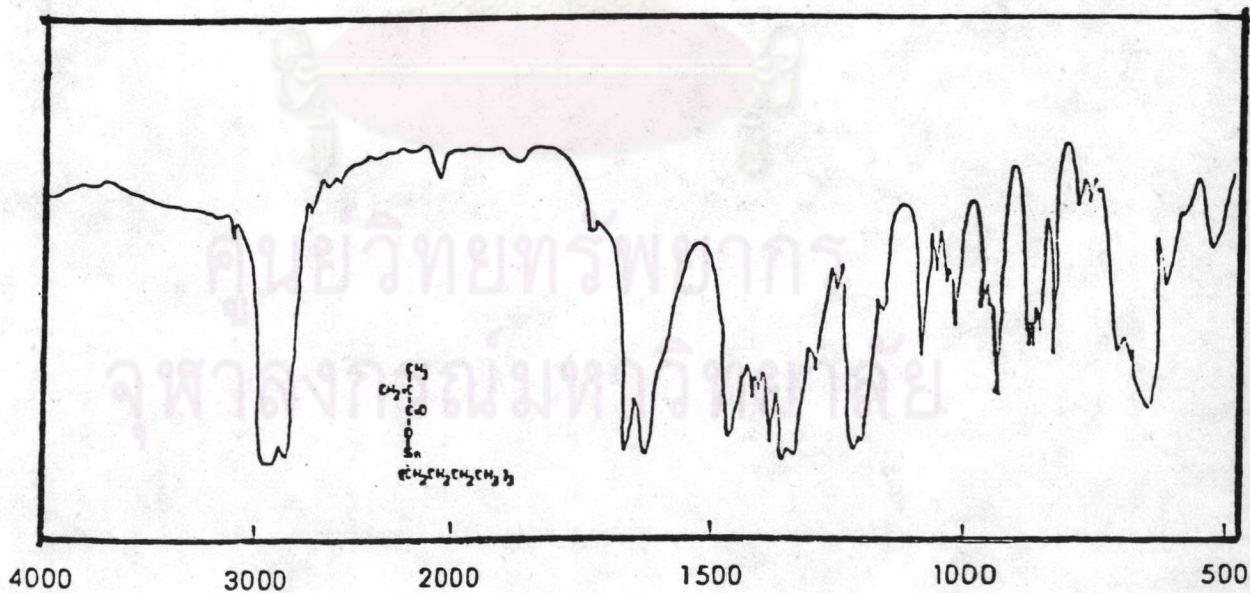


FIG.3.2 IR spectrum of tri-n-butyltin methacrylate.

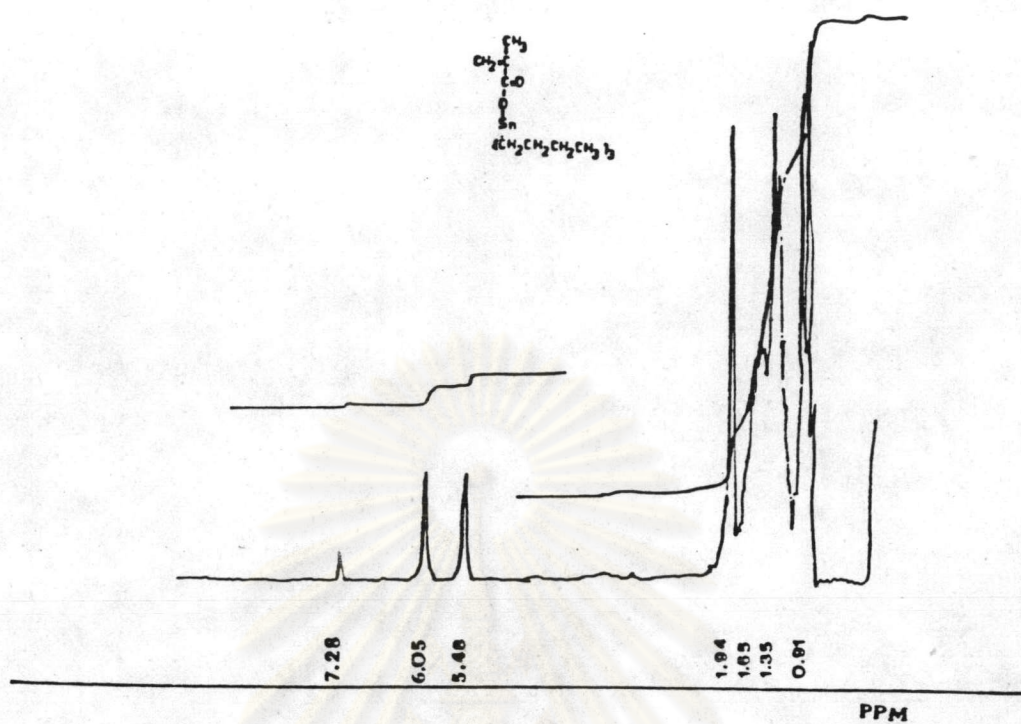


FIG.3.3 ^1H NMR spectrum (CDCl_3) of TBTM monomer.

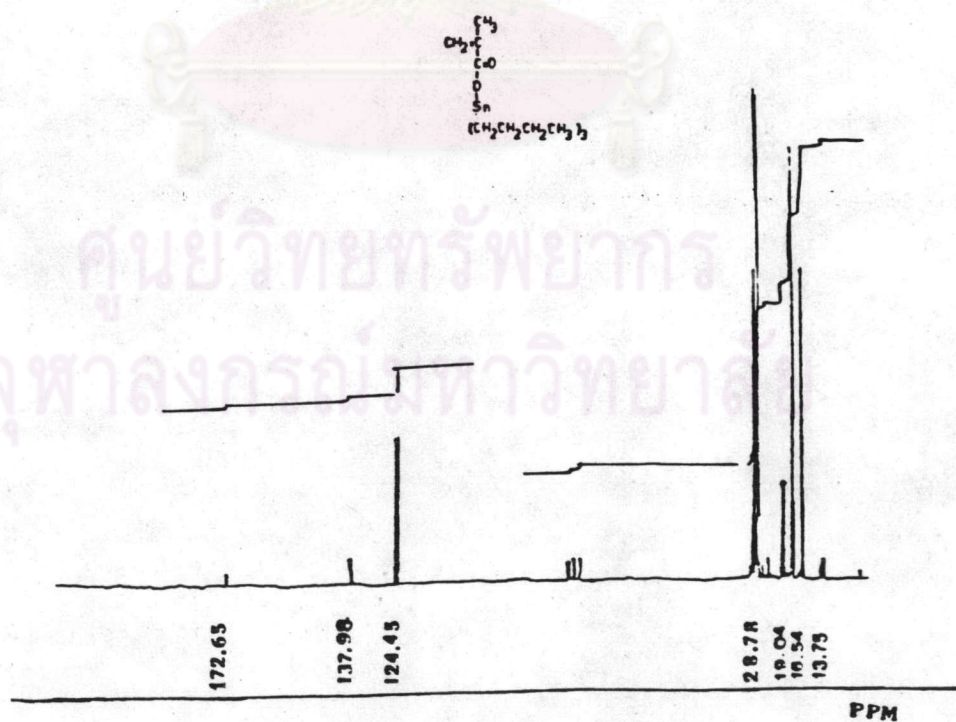
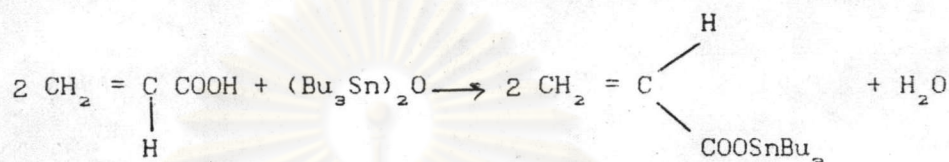


FIG.3.4 ^{13}C NMR spectrum (CDCl_3) of TBTM monomer.

3.1.2 Tri-n-butyltin acrylate (TBTA)

The method of preparation of TBTM (3.1.1) were repeated, but acrylic acid was used instead of methacrylic acid. TBTA monomer is transparent-needle like crystals, melting point 74-75°C.



where Bu = n-butyl

Both TBTA and TBTM were soluble in common organic solvents. The TBTA monomer, in the absence of added catalysts, is stable from homopolymerization except upon long exposure to much higher temperature than 30°C. IR spectrum see Fig. 3.5. IR (KBr) ν (cm^{-1}) (C=O) of carboxylic tin of this monomer is lower than that of TBTM, because of electronic releasing of methyl group adjacent to vinyl bond in the structure of TBTM. However, C=O absorption of both TBTM and TBTA monomers were shifted to lower frequencies due to α , β unsaturation of the monomer.

IR spectra of TBTM and TBTA monomers in the 1500-1700 cm^{-1} region are similar to the spectra of other tributyltin carboxylates with minor modifications due to the conjugation between the C=C bond and the C=O bond.

^1H NMR and ^{13}C NMR spectra are shown in Fig. 3.6, 3.7

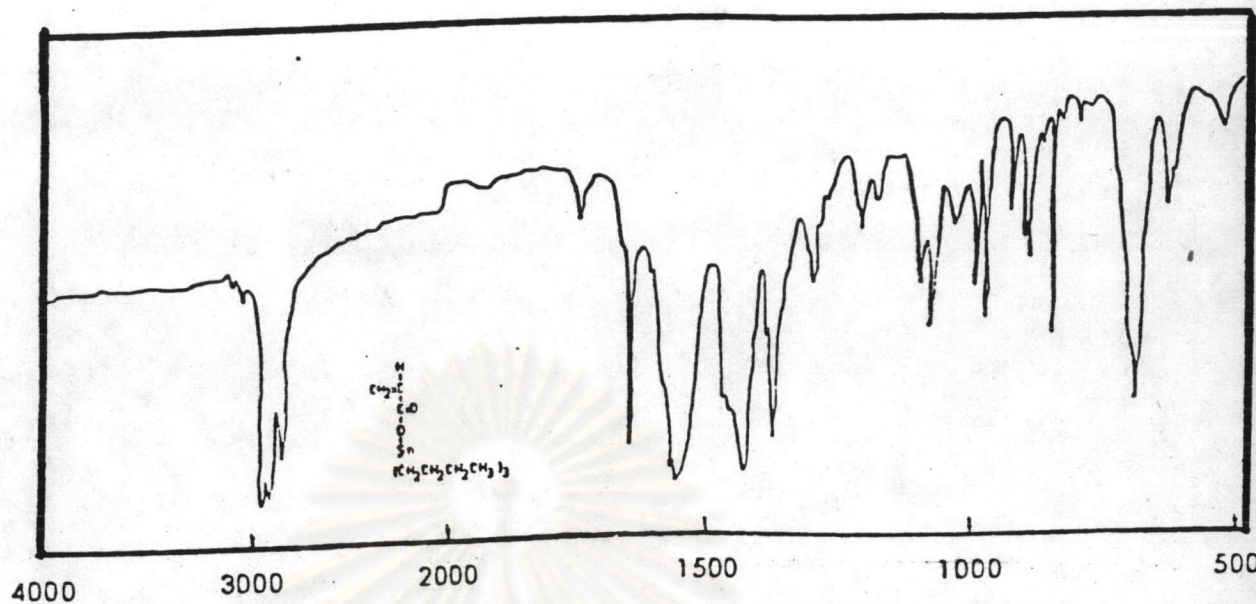


FIG.3.5 IR spectrum of tri-n-butyltin acrylate.

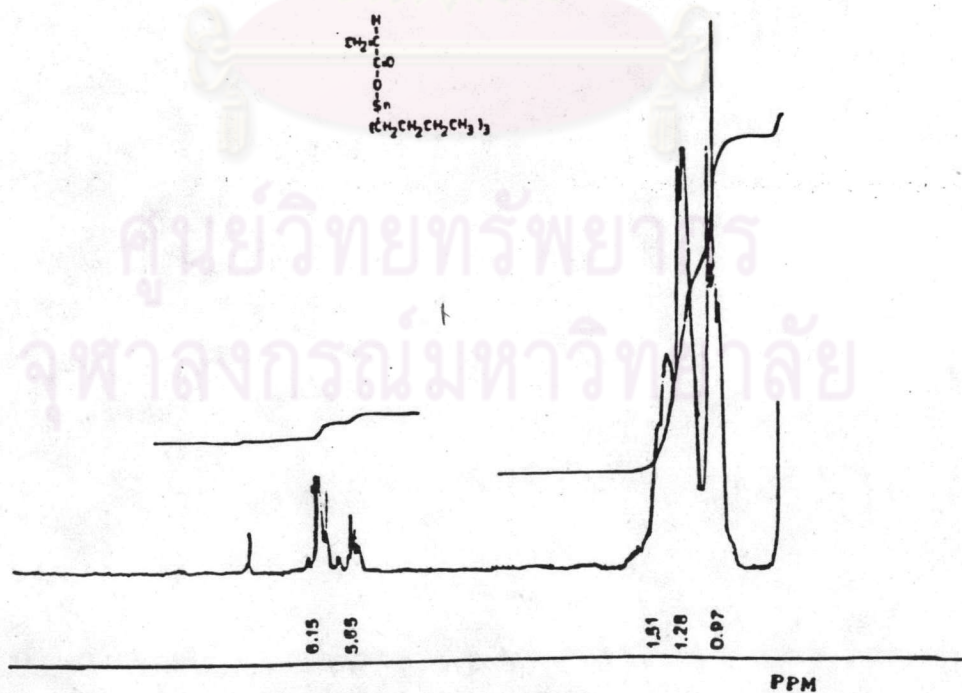


FIG.3.6 ^1H NMR spectrum (CDCl_3) of TETA monomer.

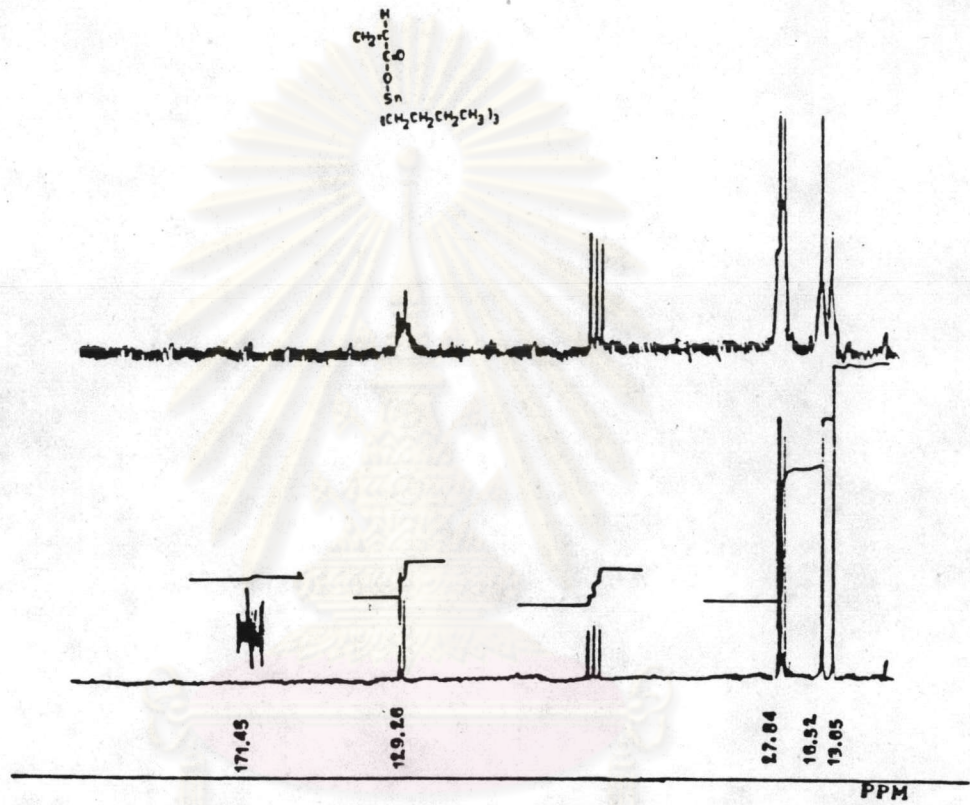


FIG.3.7 ^{13}C NMR spectrum (CDCl₃) of TBTA monomer.

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^{119m}Sn Moessbauer spectroscopy data : the isomer shift (δ) mms^{-1} and quadrupole splitting ($\Delta E_q \text{ mms}^{-1}$) of TBTA are 1.43 and 3.52. See Table 3.2 (Fig. 3.8).

The isomer shift value of TBTA is closed to TBTM and fall in the range $1.35 - 1.50 \text{ mms}^{-1}$. This indicated that the alkyl groups, tri-n-butyl, which are electron donating group, are attached to tin atom (29). Generally speaking, the isomer shift values are dependent upon the S-electron density at the ^{119}Sn nucleus with a positive δ corresponding to an increase in nucleus S-electron density at the tin atom. Since the electron density at tin nucleus is related to the S-electron density in the valence shell of the tin atom, δ should vary with the polarity of the tin-ligand bonds. For example, in the series of organotin derivatives which contain no inorganic radicals, e.g. R_4Sn , or in which the anionic group remains constant such as triorganotin hydroxides R_3SnOH , the isomer shift increases with the electron donating power of the alkyl group (Table 3.1). The strongly electron-withdrawing nature of a phenyl group attached to tin is reflected in the isomer shift values of the phenyltin derivatives which are usually lower than their alkyltin counter-parts.

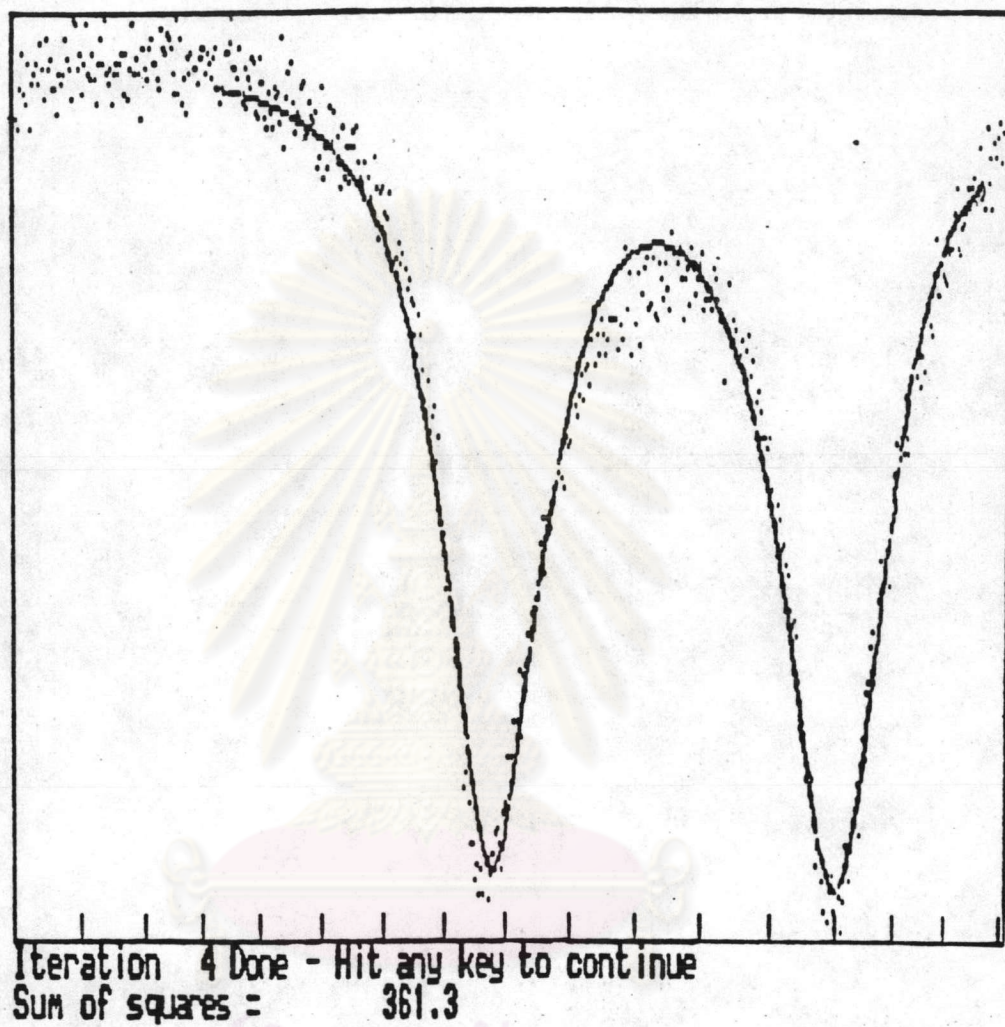
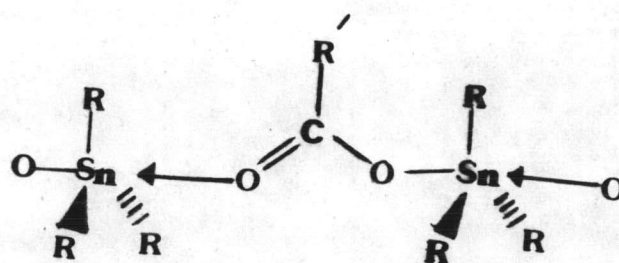


FIG.3.8 ^{119}mSn Moessbauer spectrum of TBTA monomer.

TABLE 3.1 Variation of δ with R in $R_4\text{Sn}$ and $R_3\text{SnOH}$ derivatives (30)

R	($R_4\text{Sn}$) (mms^{-1})	($R_3\text{SnOH}$) (mms^{-1})
Me	1.20	1.20
Et	1.30	1.30
Pr	1.30	1.34
Bu	1.35	1.37
Ph	1.15	1.16

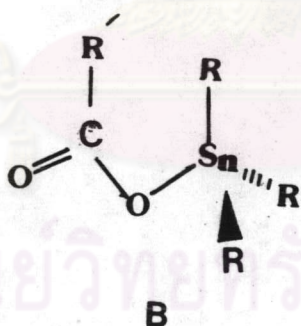
The quadrupole splitting values (Eq) in mms^{-1} are associated with a particular tin atom stereochemistry, particularly for di- and tri- organotin compounds. It is a measure of the asymmetry in the ^{119}Sn nuclear charge and results from an imbalance in tin atom's 5p valence electrons. This is affected mainly by the spatial arrangements of the ligands or atoms about the metal and is manifested as a two-line quadrupole split Moessbauer spectrum. For regular tetrahedral triorganotin compounds, eg. $(\text{Bu}_3\text{Sn})_2\text{O}$ and di organotin compounds $R_2\text{SnX}_2$, the Eq values usually fall within the range $1.00 - 2.40 \text{ mms}^{-1}$. For TBTM and TBTA monomer, Eq values were larger and fall in the range $2.89-3.50$ which existed in penta coordination (36). Tin atoms were in trigonal bipyramidal arrangement with the three butyl groups located in equatorial positions.



A

Fig. (A) Structures of tributyltin (meth) acrylate in solid state

From Fig.(A), tin atoms were in a self-associated polymeric form in which the anionic group, $R'COO^-$ acted as an intermolecular bridging ligand. When these monomers that had the structure A are diluted in organic solvents, the polymeric chain dissociated, to produce the tetrahedral monomer (structure B).



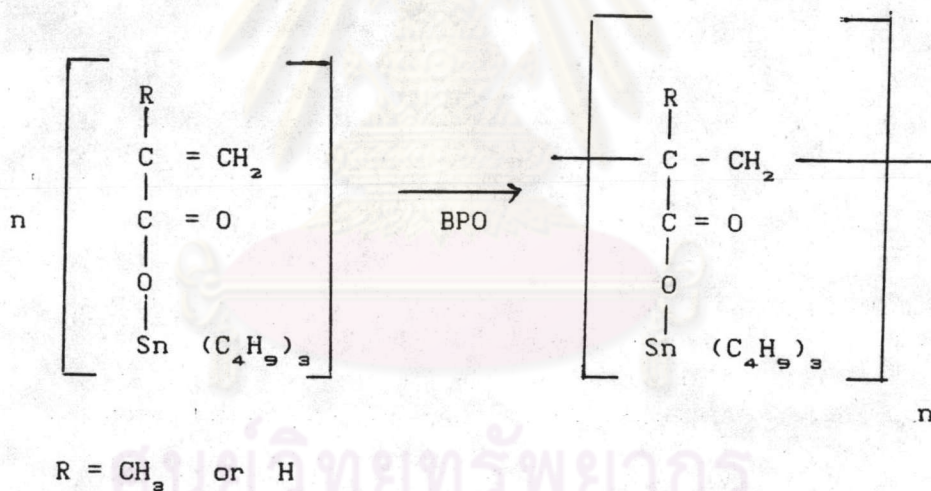
B

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3.2 Preparation of Homopolymers

3.2.1 Preparation of poly TBTM and poly TBTA

TBTM and TBTA monomers can be polymerized either by solution (toluene) or emulsion (water) method, which polymerize into rubbery or elastomeric products. Since TBTM monomer was liquid at room temperature, it could also be polymerized by bulk technic. In this thesis, solution polymerization technic was used. Polymerization mechanism was a free radical chain polymerization and accomplished according to the following reaction.



The products were a typical chain-type vinyl polymers with carbon to carbon links . The carboxyl-tin group was attached in pendant position to the polymer chain. After washing the products with methanol-water mixture (9:1) several times, poly TBTM was obtained as a white, tough , semisolid material with rubbery texture , While poly TBTA was a very soft rubbery material and less tough than poly TBTM. These homopolymers were soluble in aromatic, chlorinated hydrocarbons; partially soluble in ketonic solvents and insoluble in

alcohols and water. The glass transition temperature of poly TBTM was 0°C and was higher than that of poly TBTA (-22°C).

IR spectra of both homopolymers were quite identical. See Fig. 3.9 and 3.10. The carbonyl stretching frequencies of the carboxyl ($\text{C}=\text{O}$) group of the polymers (Poly TBTM & Poly TBTA) were higher than in monomers form (from 1620 to 1645 in TBTM and 1580 to 1645 in TBTA).

The ^1H NMR and ^{13}C NMR spectra of both homopolymers were also similar. See Fig. 3.11 and 3.12. The signal at $\delta \sim 5.5-6.2$ ppm of ^1H NMR due to ethylenic proton was disappeared as well as the signal at $\delta \sim 124.5-130.4$ ppm of ^{13}C NMR. This indicated that TBTM and TBTA monomers were polymerized.

The polymer films of these triorganotin homopolymers were transparent, soft, tender, and had poor thermal stability, indicating that they were not suitable for use as binder in antifouling marine paints. It is wellknown that polyacrylates and polymethacrylates have excellent properties for use in surface coating industries. Thus, copolymers from triorganotin monomers and methyl methacrylate or tertiary butyl acrylate were prepared to accommodate the more suitable properties of the latter compound.

The acrylates and methacrylates are thermoplastic in nature and many grades soften considerably at temperatures below 100°C . The esters of poly acrylic acid are susceptible to hydrolysis by strong acids and alkalis. However, the hydrolysis does not occur at the polymer chain. The methacrylates are considerably more resistant to hydrolysis, with particularly good alkali resistance. This may be

ascribed to the fact that the carboxyl group is attached to a tertiary carbon atom, which is known to diminish its reactivity. Hence, MMA and t-BA were chosen to copolymerize with tri-n-butyltin acrylate and tri-n-butyltin methacrylate.



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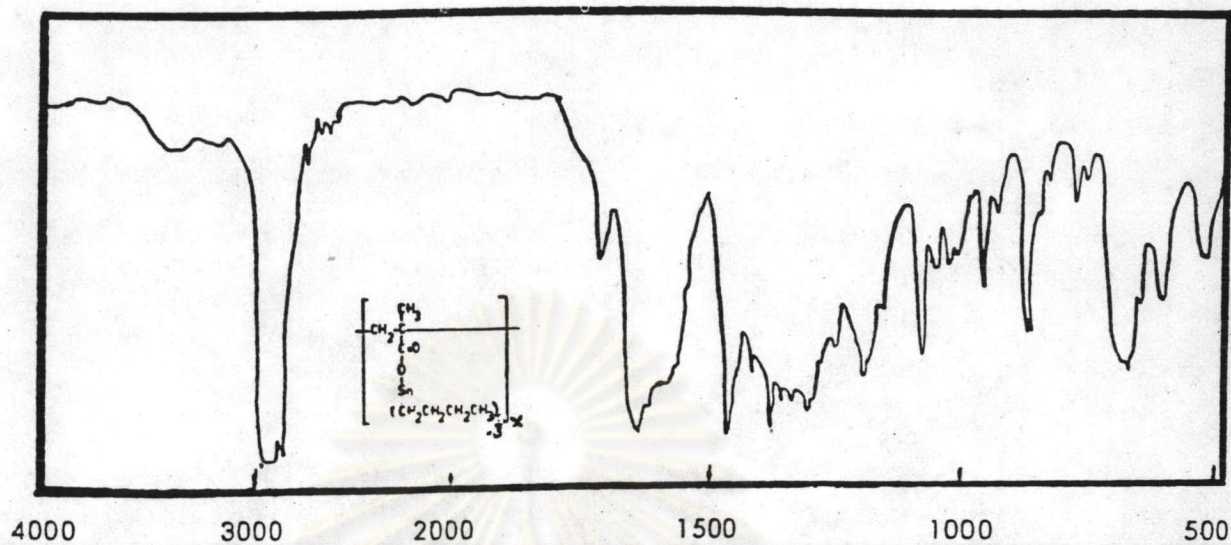


FIG.3.9 IR spectrum of poly (tri-n-butyltin methacrylate).

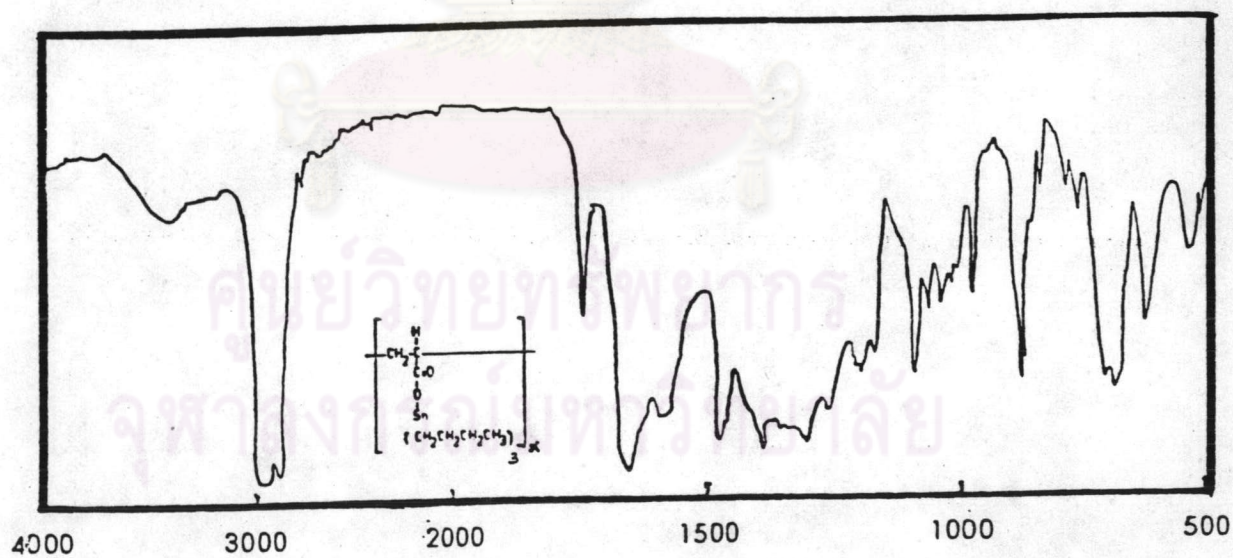


FIG.3.10 IR spectrum of poly (tri-n-butyltin acrylate).

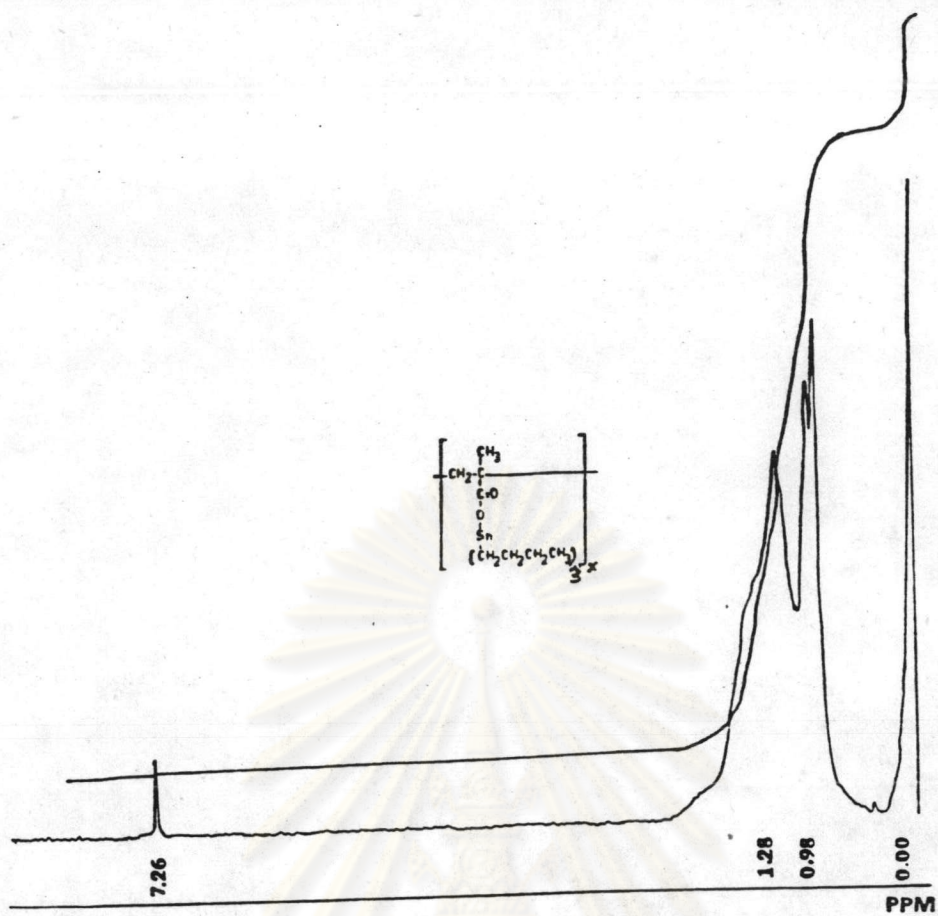


FIG.3.11 ¹H NMR spectrum (CDCl₃) of poly TBTM.

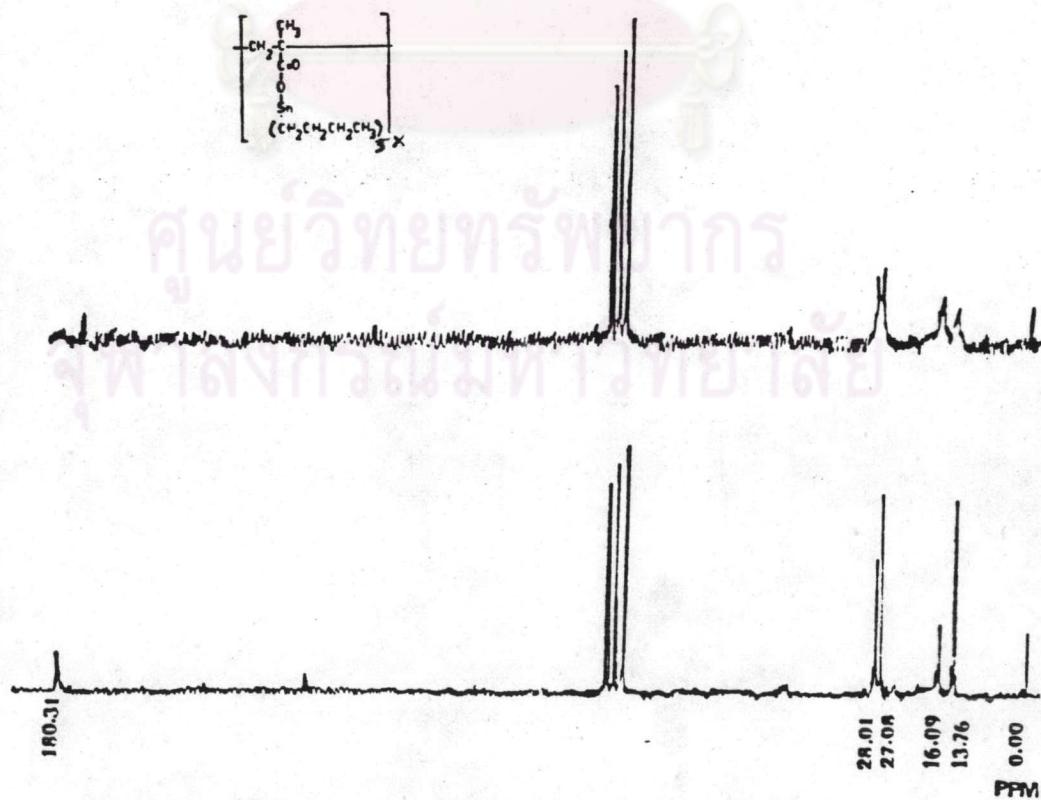
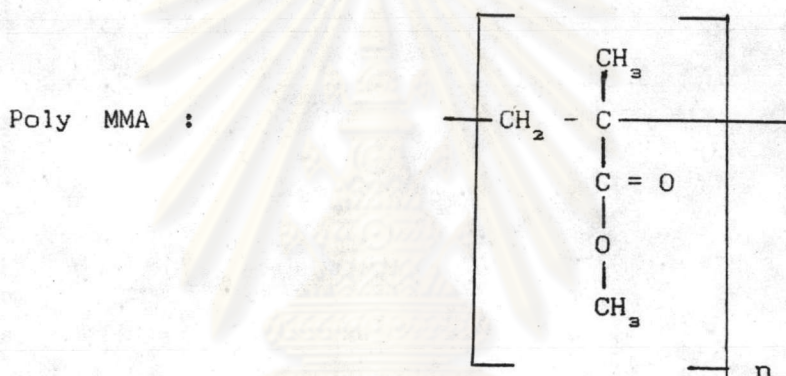


FIG.3.12 ¹³C NMR spectrum (CDCl₃) of poly TBTM.

3.2.2 Preparation of poly MMA and poly t-BA

Polymethyl methacrylate (poly MMA) and poly tertiary-butyl acrylate (poly t-BA) were prepared to compare their physical properties with tributyltin copolymers.

Poly MMA and poly t-BA were prepared by in solution polymerization.

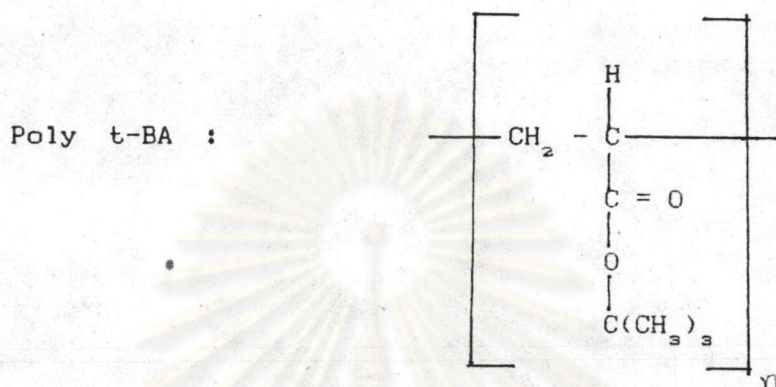


Poly MMA was soluble in common organic solvents : THF, ethanol/water, CCl_4 , esters, aromatic hydrocarbons. It gave a hardest product with glass transition temperature (T_g) of 105°C .

IR spectrum of Poly MMA shows a strong peak of carbonyl stretching vibration at 1725 cm^{-1} , ν (C-C-O) vibration coupled with that of ν (C-O) at 1268 and 1240 cm^{-1} . The skeletal stretching coupled with C-H deformation vibration at 1188 and 1145 cm^{-1} . (see Fig. 3.13). All these bands indicates the characteristic of poly MMA.

The ^1H NMR spectrum of poly MMA shows the signals at 3.60 ppm ($\text{CH}_3\text{-OC=O}$) which refers to ester methyl proton of poly MMA. (Fig.

3.14). Comparison to MMA monomer, the ^1H NMR spectrum was quite the same excepting the signal at 5.48-6.15 ppm due to $(\text{CH}_2=\text{C})$ in monomer which disappeared in the polymer. (Fig. 3.15)



This polymer was soluble in esters, aromatic hydrocarbons, chlorinated hydrocarbons, THF, ketones. Poly t-BA gave soft and tough polymer with T_g about 47.4°C (31). It was observed that T_g of poly t-BA was inferior to that of poly MMA but superior to those of poly TBTM and poly TBTA homopolymers.

IR spectrum of poly t-BA is shown in Fig. 3.16. The absorption frequency (cm^{-1}) of tertiary butyl group $\begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ at 1395-1385 (m), 1370-1360 (S) shows $-\text{CH}_3$ symmetry, bending as doublet. Generally, a lower frequency band is more intense. The strong band at 1730 cm^{-1} was due to the stretching frequency of the carboxyl ($\text{C}=\text{O}$) group.

^1H NMR and ^{13}C NMR spectra are shown in Fig. 3.17 & 3.18

POLY(METHYL METHACRYLATE)

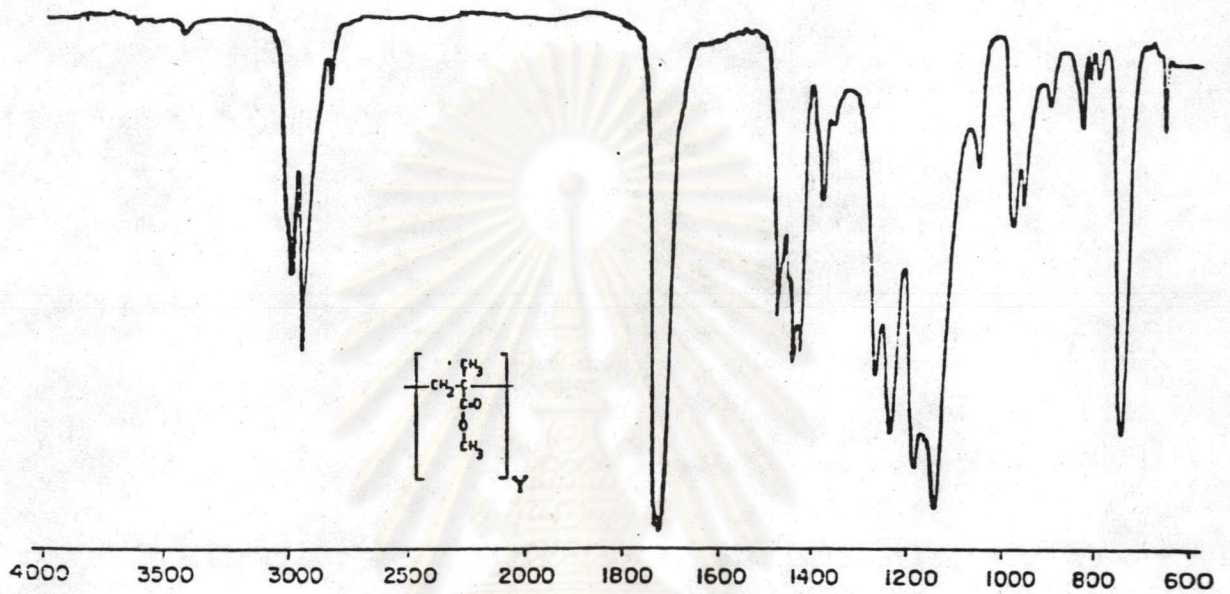


FIG.3.13 IR spectrum of poly methyl methacrylate.

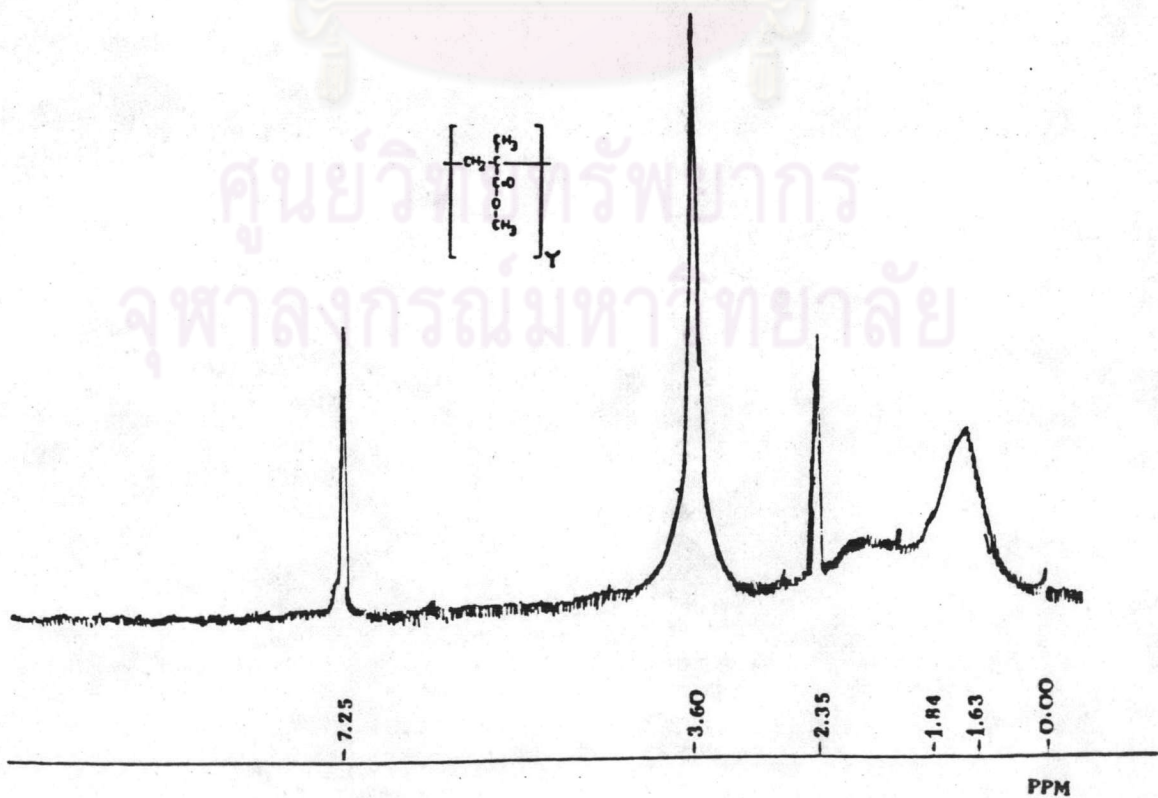


FIG.3.14 ¹H NMR spectrum (CDCl₃) of poly MMA.

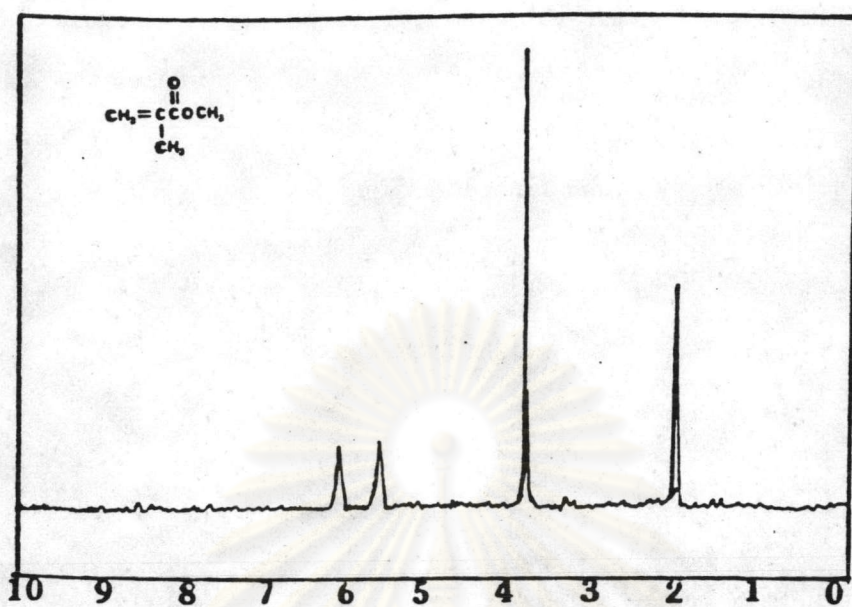


FIG.3.15 ^1H NMR spectrum (CDCl_3) of MMA monomer.

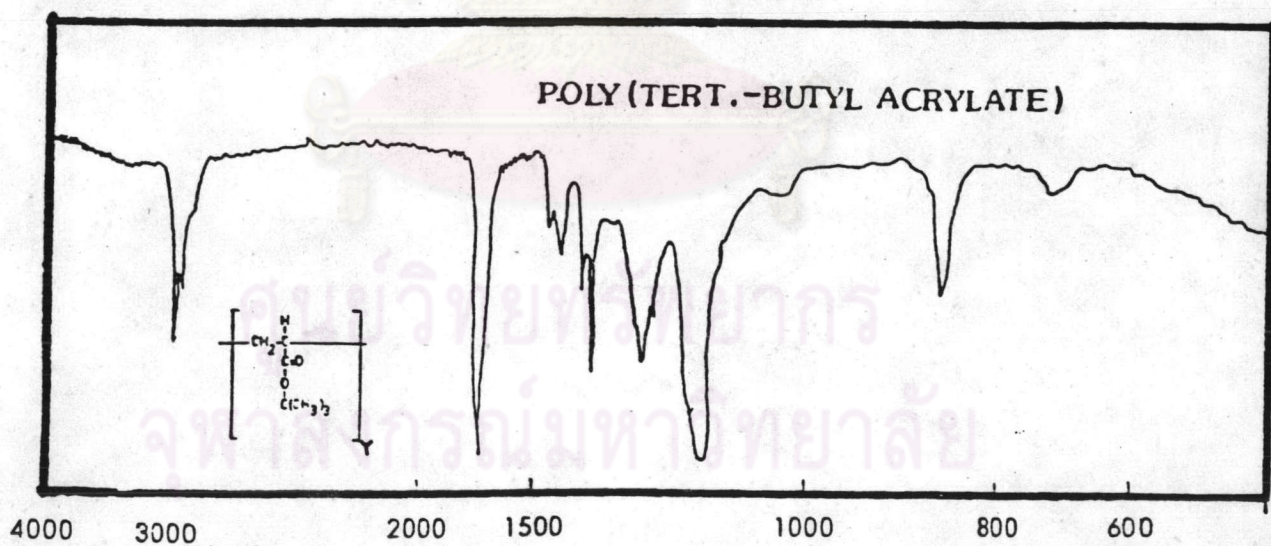


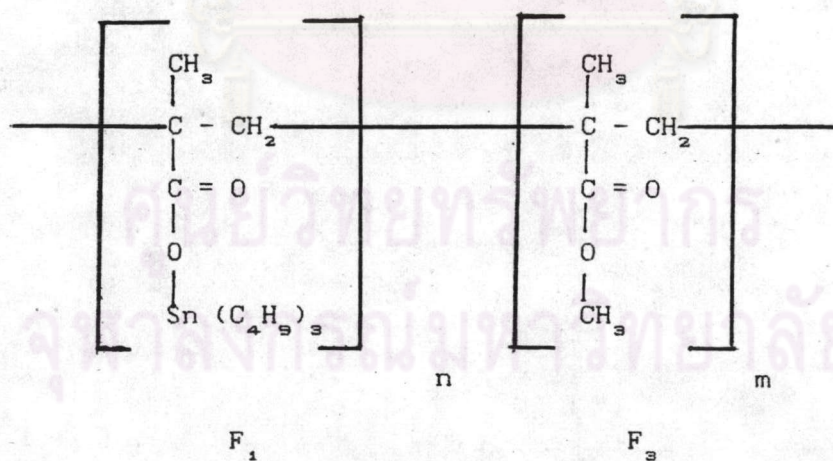
FIG.3.16 IR spectrum of poly (tert-butyl acrylate).

3.3 Study on TBTM and TBTA Copolymers

All the triorganotin copolymers in this thesis were prepared at the same condition, except TBTA-copolymers which the reaction temperature was increased from $75 \pm 1^\circ\text{C}$ to 80°C . The polymerizations were carried out with thermostatically controlled in order to control the molecular weight (Mw) and molecular weight distribution (MWD) of the copolymers.

3.3.1 Characterization of the Copolymers

Four copolymer systems were prepared from TBTM with MMA, TBTM with t-BA, TBTA with MMA and TBTA with t-BA from various mole ratio compositions. The structures of these four copolymers can be illustrated as follow :



TBTM-MMA copolymer

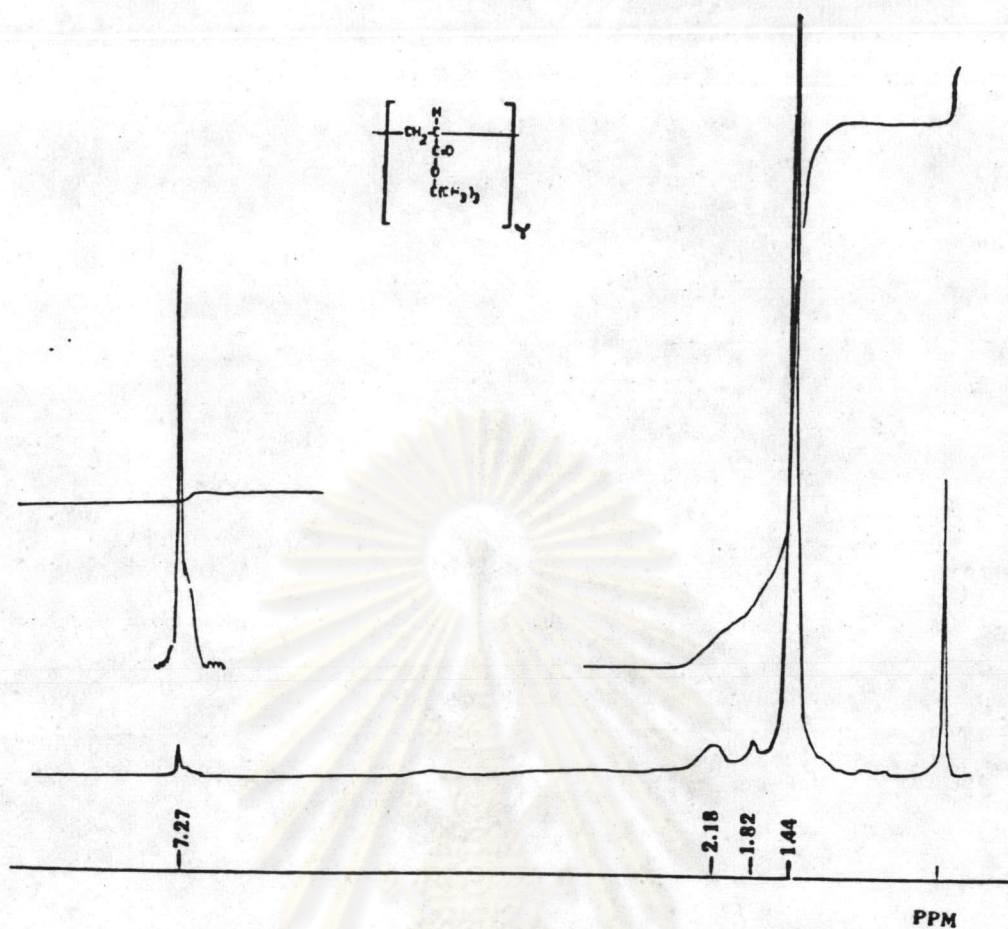


FIG.3.17 ^1H NMR spectrum (CDCl_3) of poly tertiary butyl acrylate.

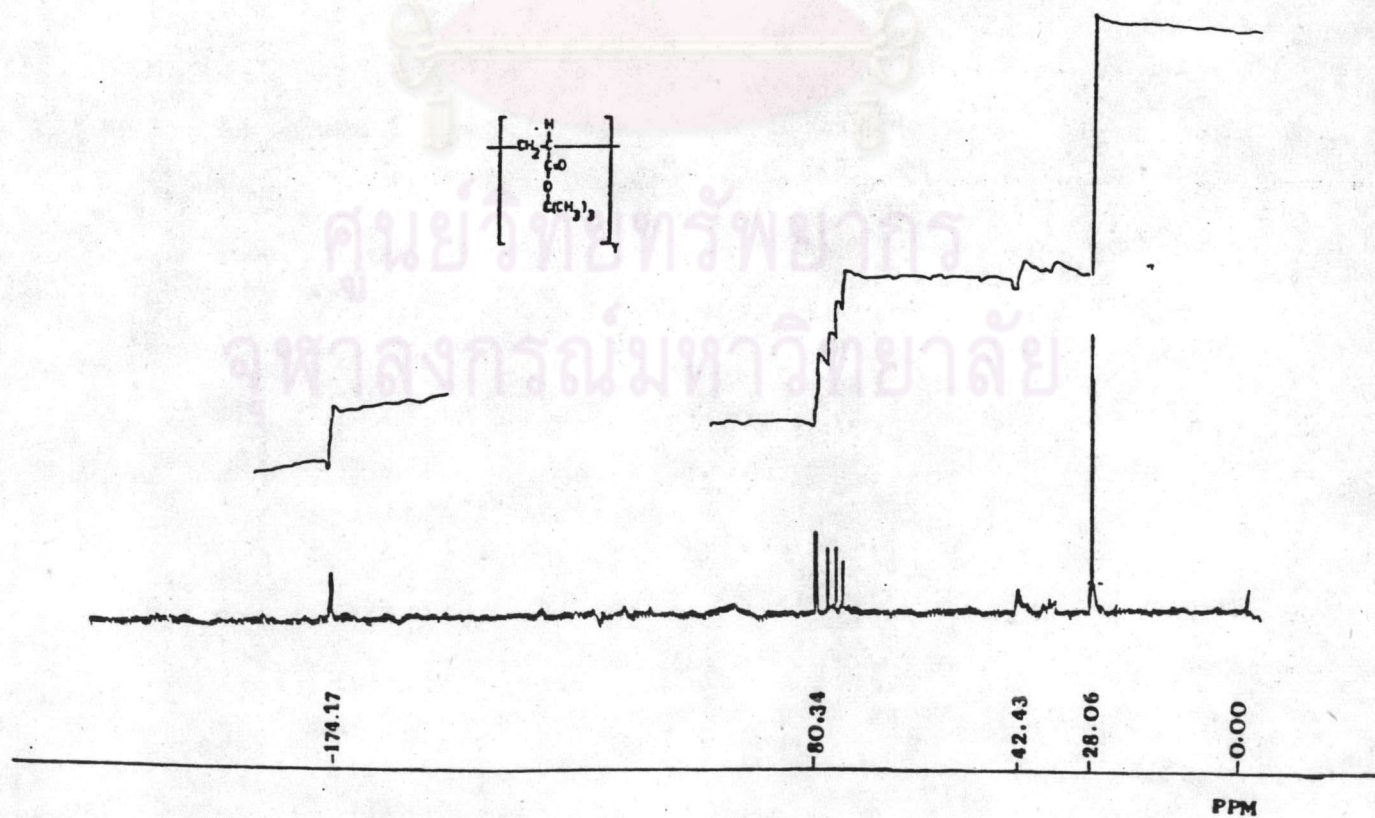
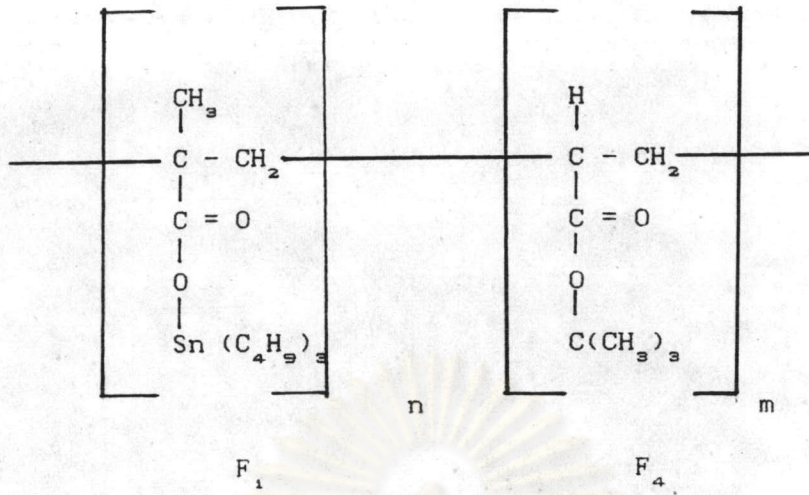
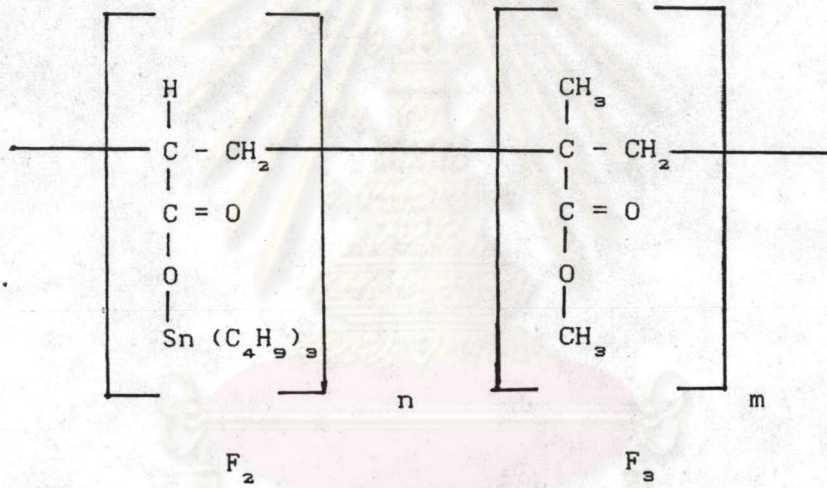


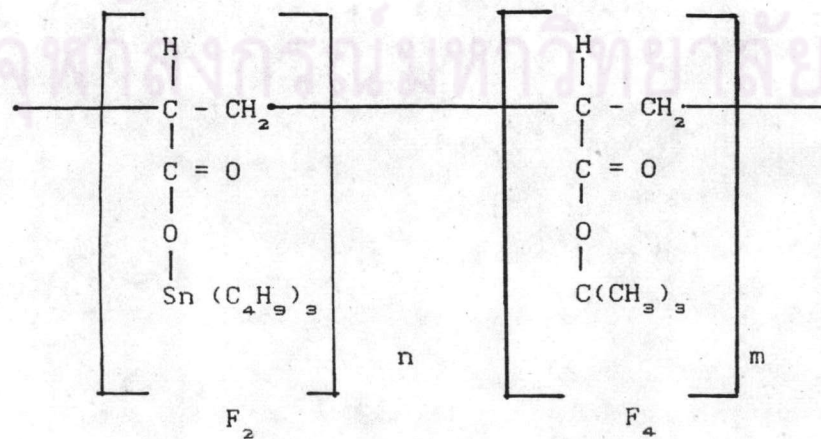
FIG.3.18 ^{13}C NMR spectrum (CDCl_3) of poly tertiary butyl acrylate.



TBTM-t-BA copolymer



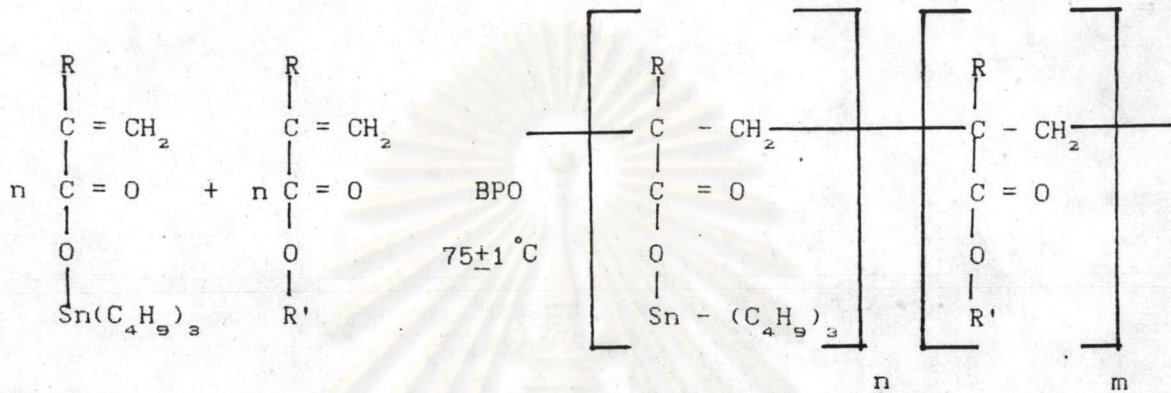
TBTA-MMA copolymer



TBTA-t-BA copolymer

Where $F_1 = \text{TBTM}$, $F_2 = \text{TBTA}$, $F_3 = \text{MMA}$, $F_4 = t\text{-BA}$

The polymerization reaction could be represented in the equation below :



where $\text{R} = \text{H}$ or CH_3

$\text{R}' = \text{CH}_3$ or $\text{C}(\text{CH}_3)_3$

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All the copolymers were characterized by IR, ^1H NMR, ^{13}C NMR and $^{119\text{m}}\text{Sn}$, Moessbauer spectroscopy technics.

The infrared spectra of TBTM-MMA and TBTA-MMA copolymers were quite similar and were characterized by two strong bands at 1645 and 1740 cm^{-1} due to the stretching frequencies of the carboxyl (C=O) group of tributyltin carboxylate and methacrylic ester respectively. The spectra of copolymers from t-BA with TBTM and TBTA were also identical and showed two carboxyl (C=O) bands at 1740 and 1645 cm^{-1} from tertiary butyl acrylate and tributyltin monomers respectively. The strong bands at $1375\text{--}1370\text{ cm}^{-1}$ were characteristic peaks of $-\text{CH}_3$ symmetry bending in the tertiary butyl group $(\text{CH}_3-\text{C}-\text{CH}_3)$

$$\begin{array}{c} | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

appeared as doublet according to Cummins et. al. [28]. The tributyltin carboxylates bands at 1640 cm^{-1} which were typical of carbonyl groups rather than carboxylate groups due to the influence of tin atom, suggesting that organotin esters were chelated covalent compounds involving a five-coordinated tin atom.

The IR spectra of these copolymers are shown in Fig. 3.19, 3.20, 3.21, and 3.22.

It was obvious that the relative intensity of the band at 1645 cm^{-1} increased by increasing the mole fraction of tri-n-butyltin monomer, suggesting that the band at 1645 cm^{-1} was the actual band for carbonyl group of tributyltin carboxylate. (see Fig. 3.23, 3.24, 3.25 and 3.26)

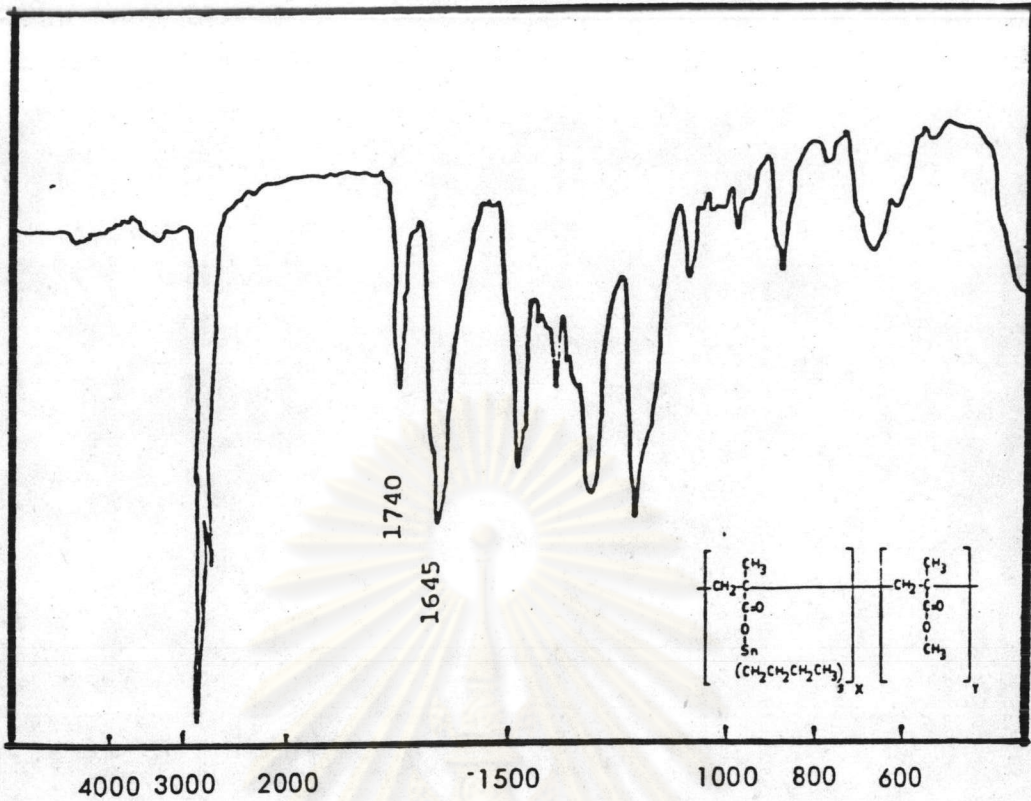


FIG.3.19 IR spectrum of TBTM-MMA copolymer (0.08:0.02 mole).

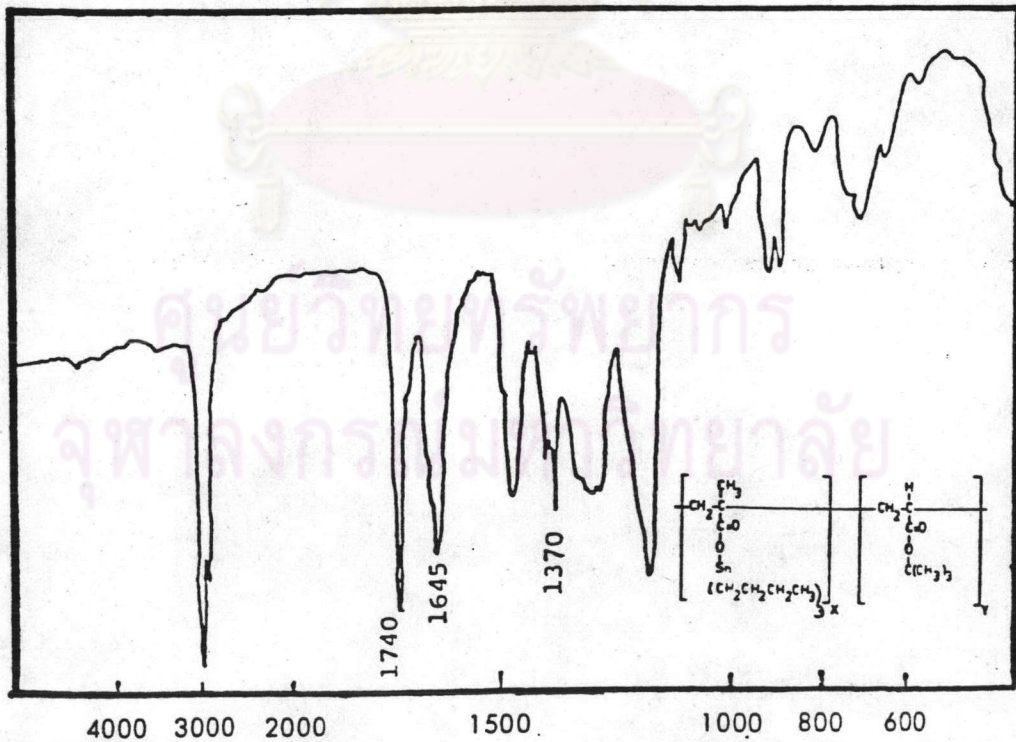


FIG.3.20 IR spectrum of TBTM-t-BA copolymer (0.04:0.06 mole).

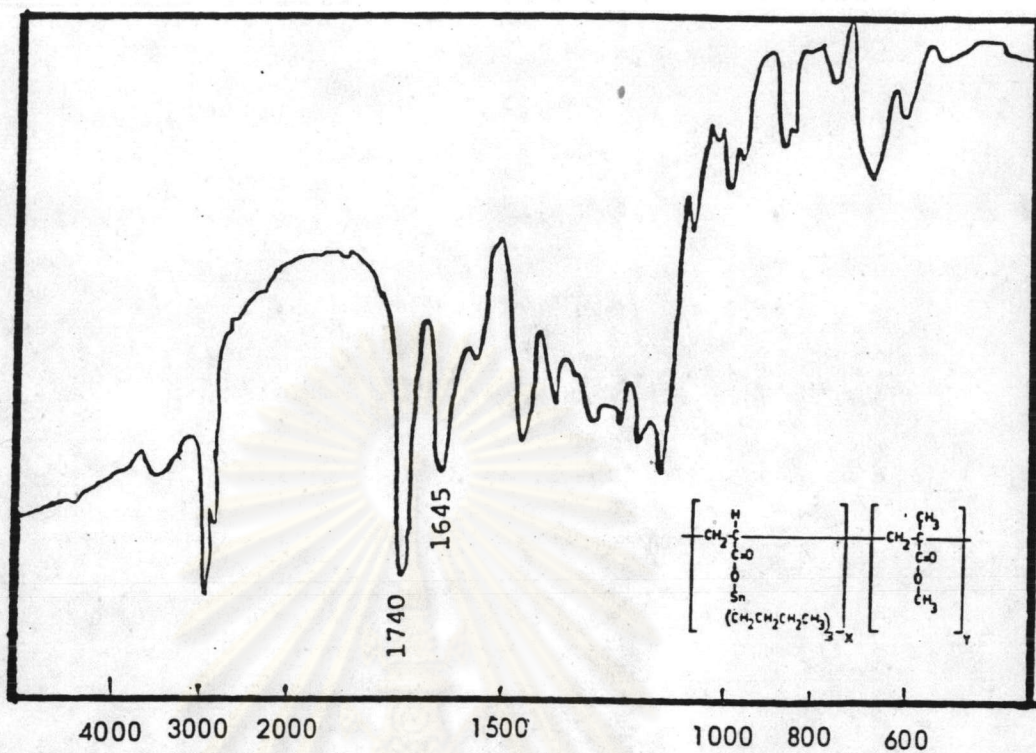


FIG.3.21 IR spectrum of TBTA-MMA copolymer (0.03:0.07 mole).

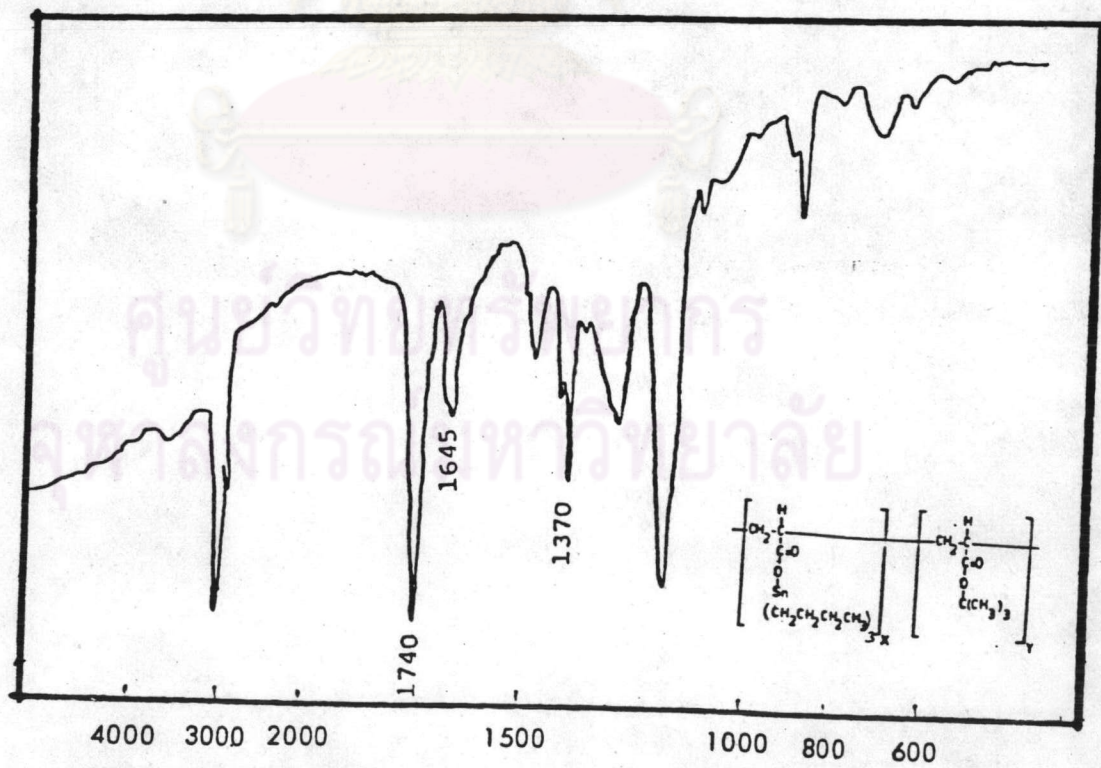


FIG.3.22 IR spectrum of TBTA-t-BA copolymer (0.03-0.07 mole).

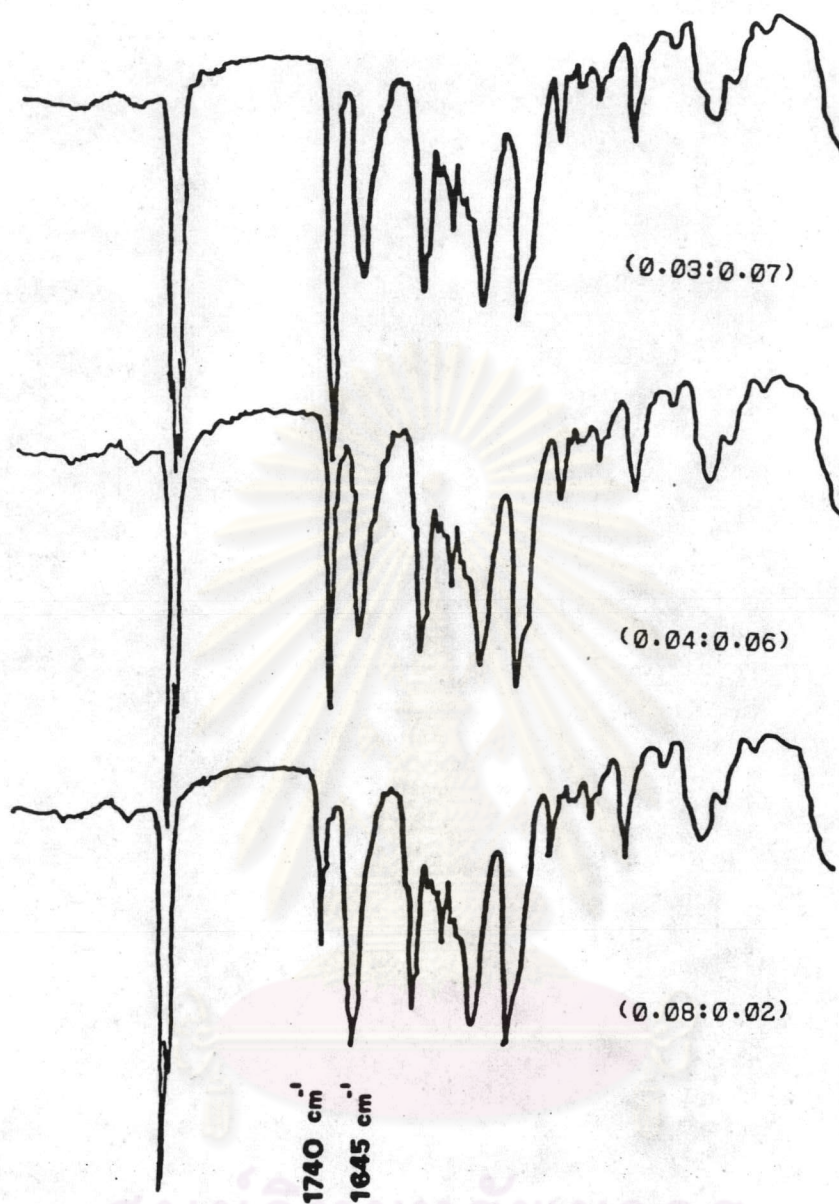


FIG.3.23 Comparison of IR spectra of TBTM-MMA at various mole ratio (0.03:0.07), (0.04:0.06), (0.08:0.02).

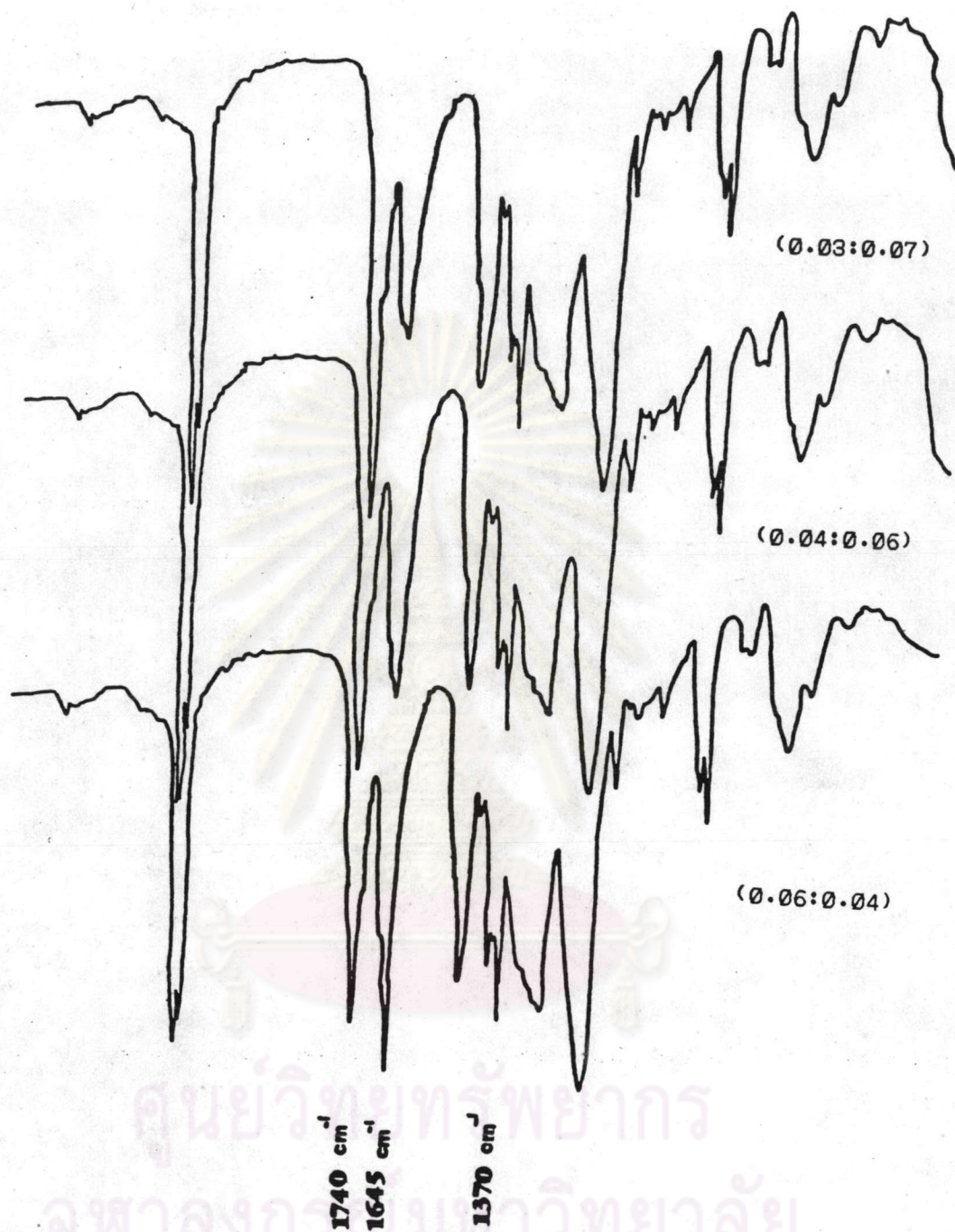


FIG.3.24 Comparison of IR spectra of TBTM-t-BA at various mole ratio (0.03:0.07), (0.04:0.06), (0.06:0.04).

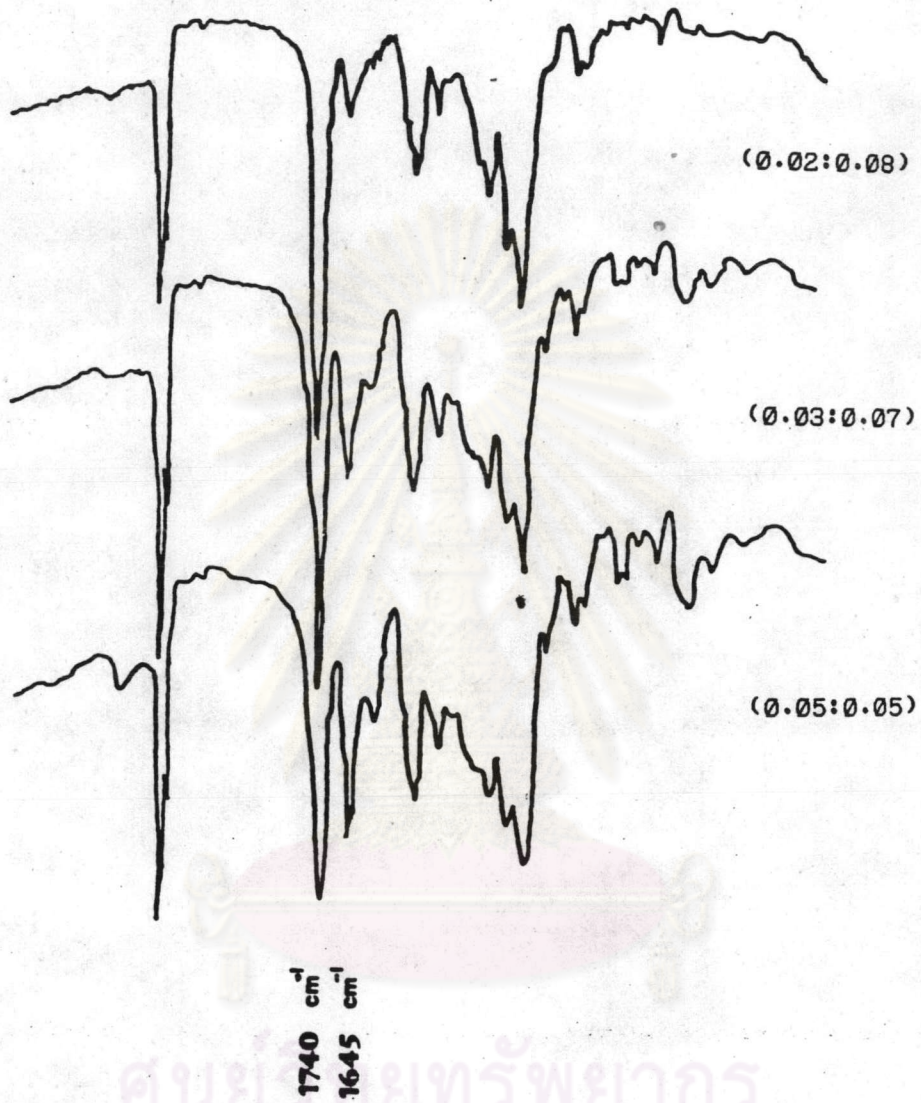


FIG.3.25 Comparison of IR spectra of TBTA-MMA at various mole ratio (0.02-0.08), (0.03-0.07), (0.05:0.05).

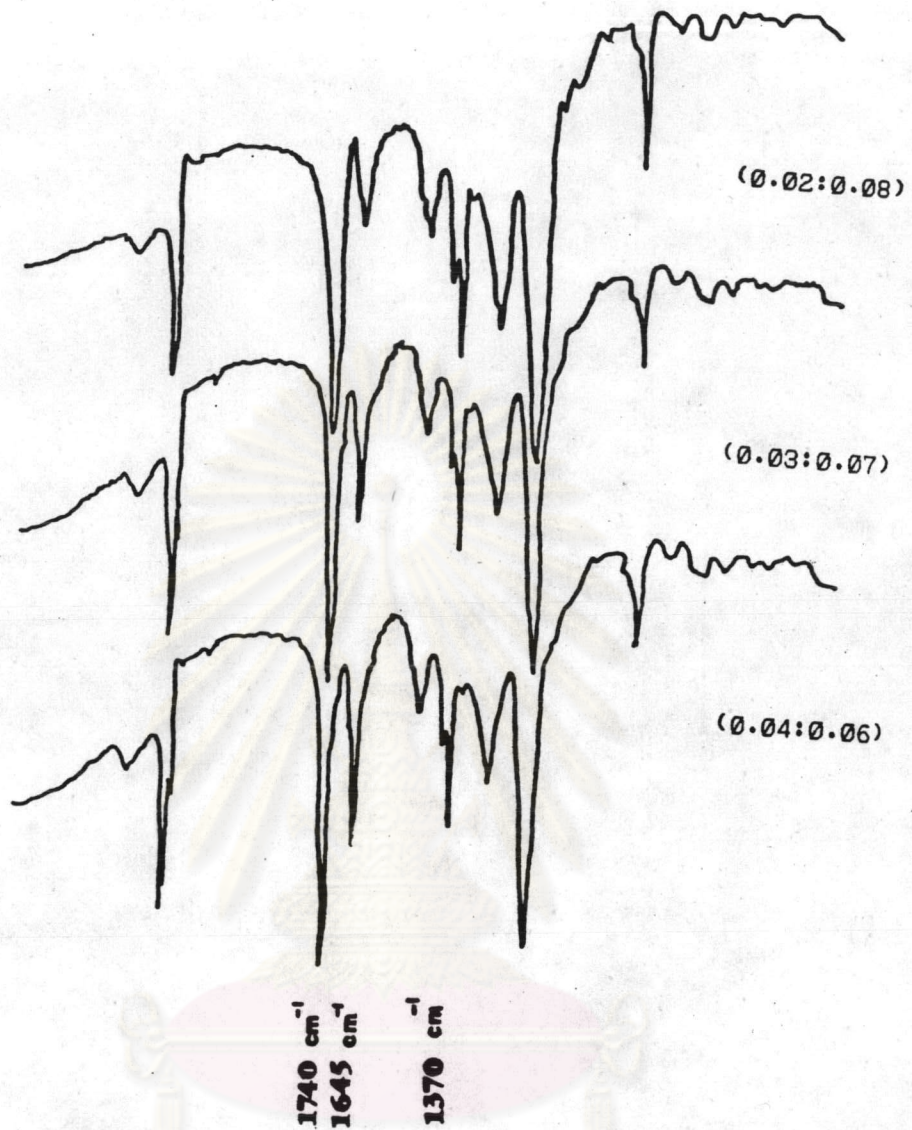


FIG.3.26 Comparison of IR spectra of TBTA-t-BA at various mole ratio $(0.02:0.08)$, $(0.03:0.07)$, $(0.04:0.06)$.

The ^1H NMR and ^{13}C NMR spectroscopy of TBTM-MMA :

^1H NMR, the signal at 3.56 ($\text{CH}_3\text{-O-C=O}$, in MMA) due to methoxy proton of poly MMA. See Fig. 3.27 and for ^{13}C NMR, the signals at 51.63 and 178.85 ppm showed that TBTM-MMA was copolymerized. See Fig. 3.28.

The ^1H NMR and ^{13}C NMR spectroscopy of TBTM-t-BA :

The ^1H NMR, chemical shift at 1.43 ppm due to proton in tert-butyl group of t-BA. For ^{13}C NMR, the signals at 79.85 ppm of tert-carbon and two carbonyl signals indicated that TBTM-t-BA was copolymerized. See Fig. 3.29 and 3.30.

^1H NMR and ^{13}C spectra of TBTA-MMA were quite identical to TBTM-MMA (see Fig. 3.31 and 3.32). Similarly, the ^1H NMR and ^{13}C NMR spectra of TBTA-t-BA were quite identical to TBTM-t-BA spectra (see Fig. 3.33 and 3.34).

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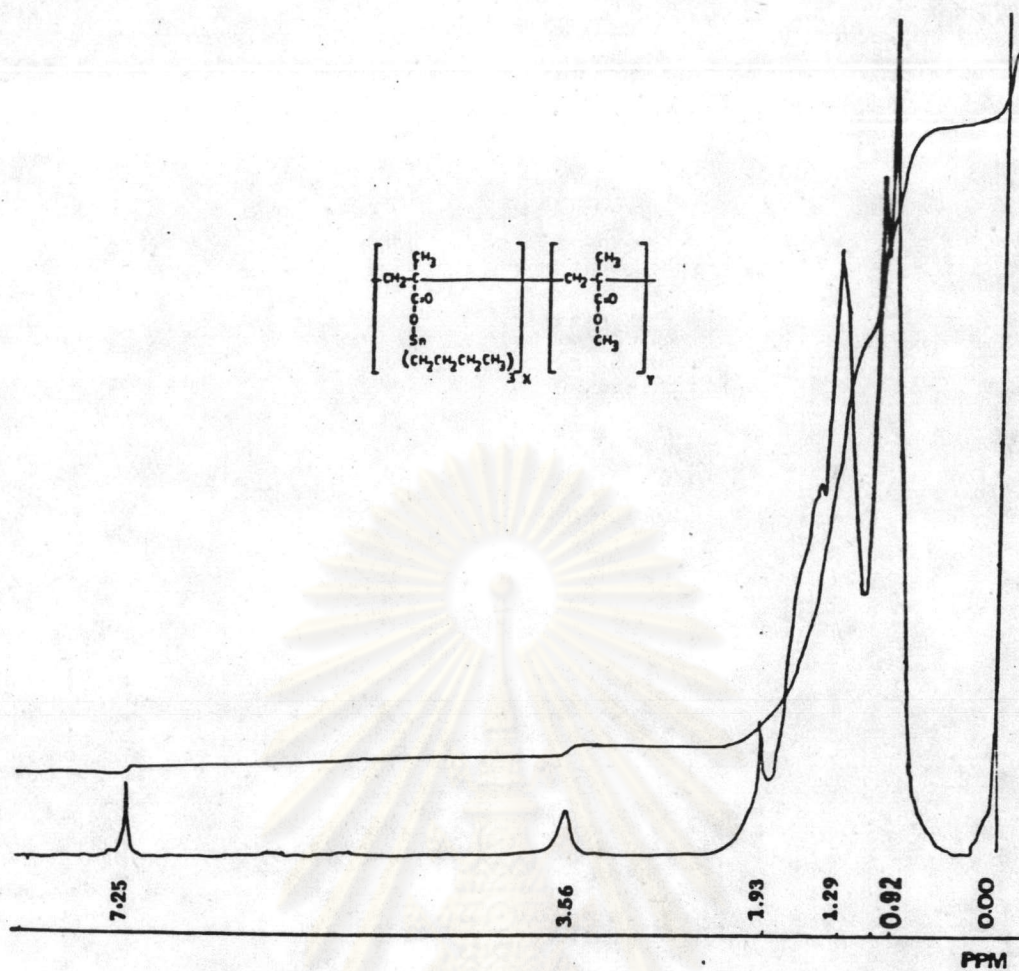


FIG.3.27 ^1H NMR spectrum (CDCl₃) of poly TBTM-MMA.

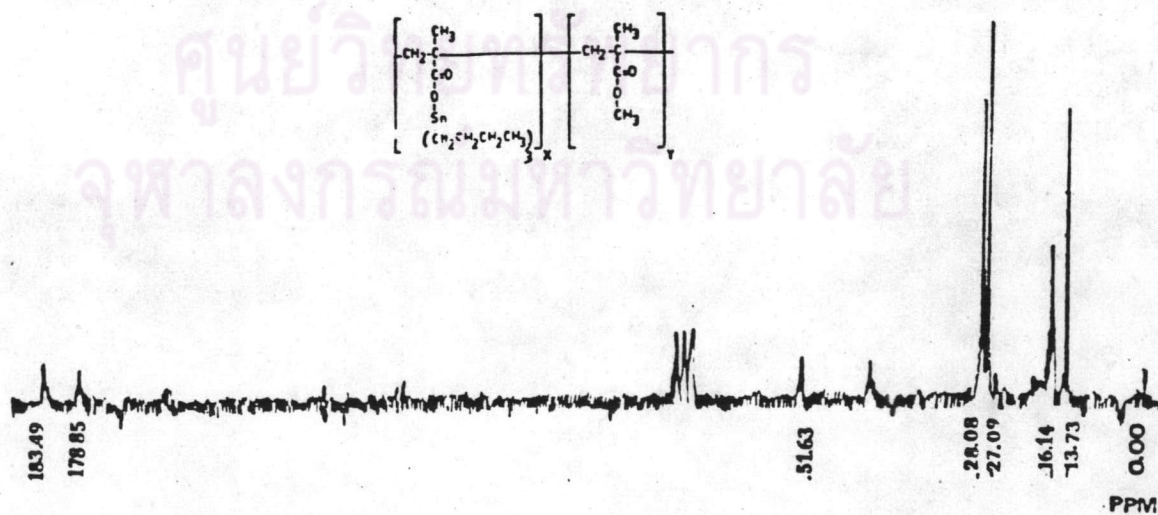


FIG.3.28 ^{13}C NMR spectrum (CDCl₃) of poly TBTM-MMA.

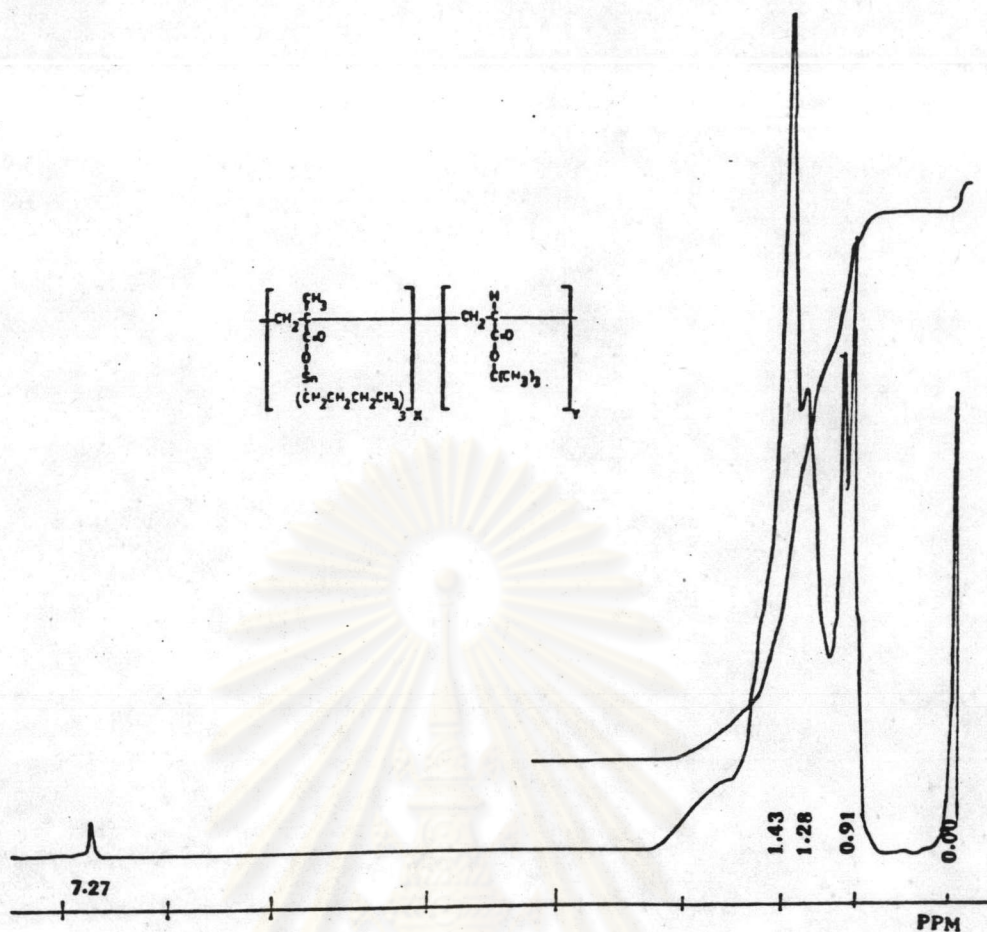


FIG.3.29 ^1H NMR spectrum (CDCl_3) of poly TBTM-t-BA.

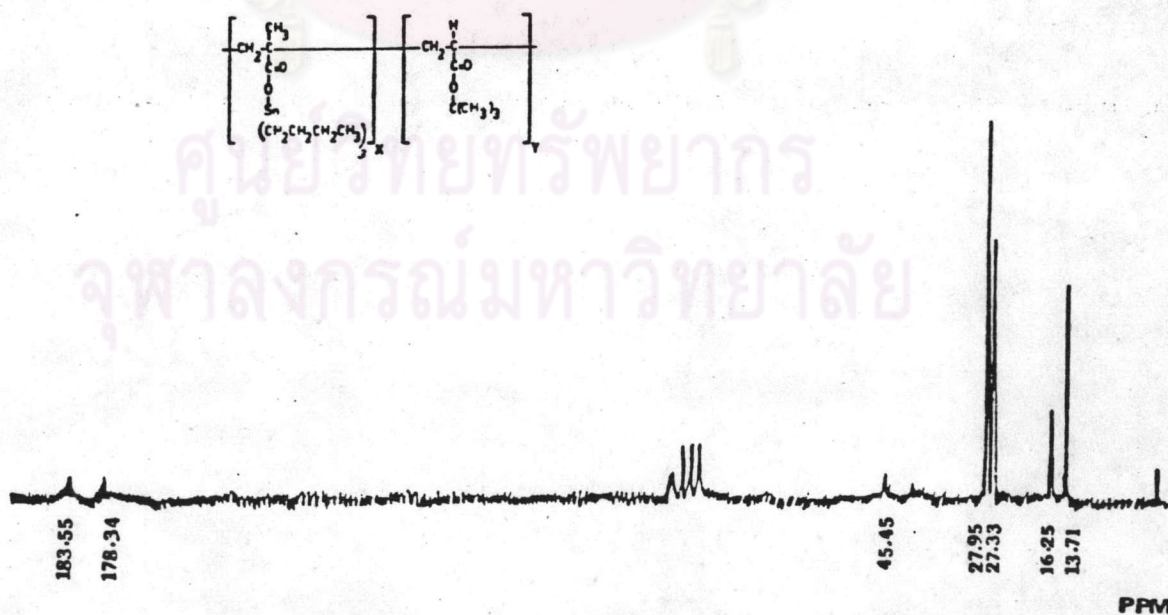


FIG.3.30 ^{13}C NMR spectrum (CDCl_3) of poly TBTM-t-BA.

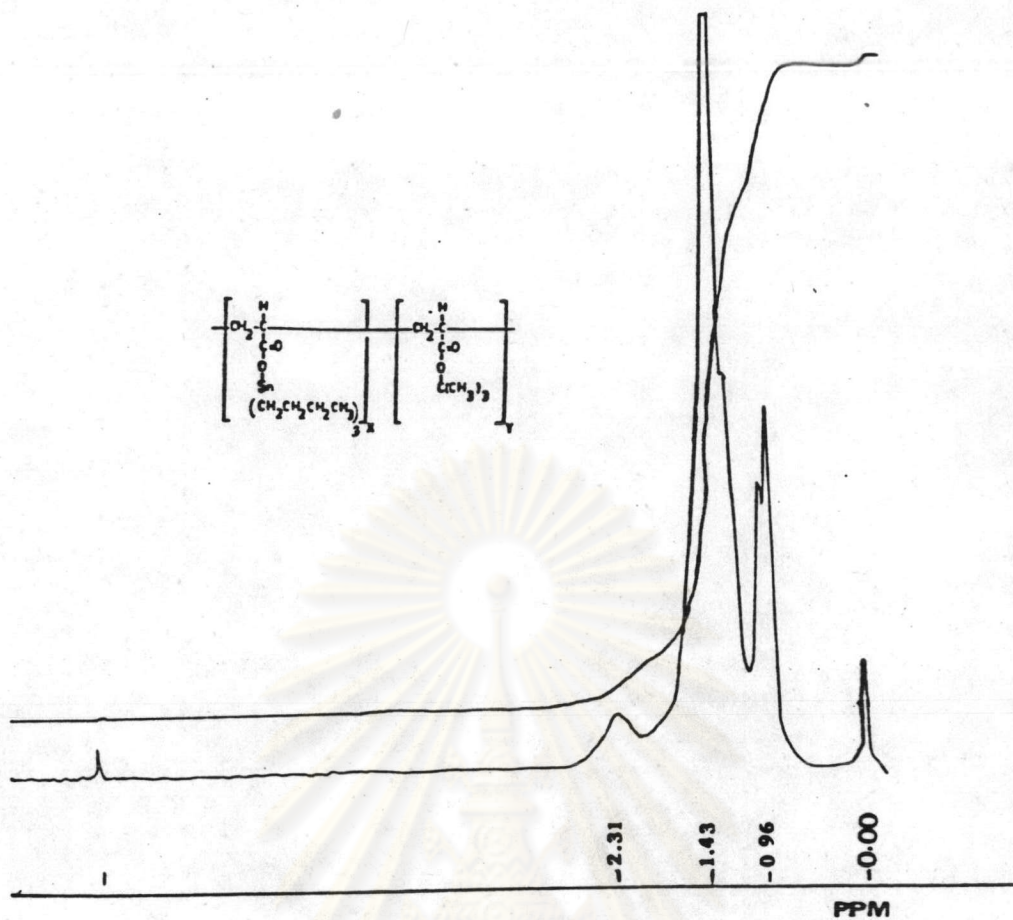


FIG.3.33 ^1H NMR spectrum (CDCl_3) of poly TBTA-t-BA.

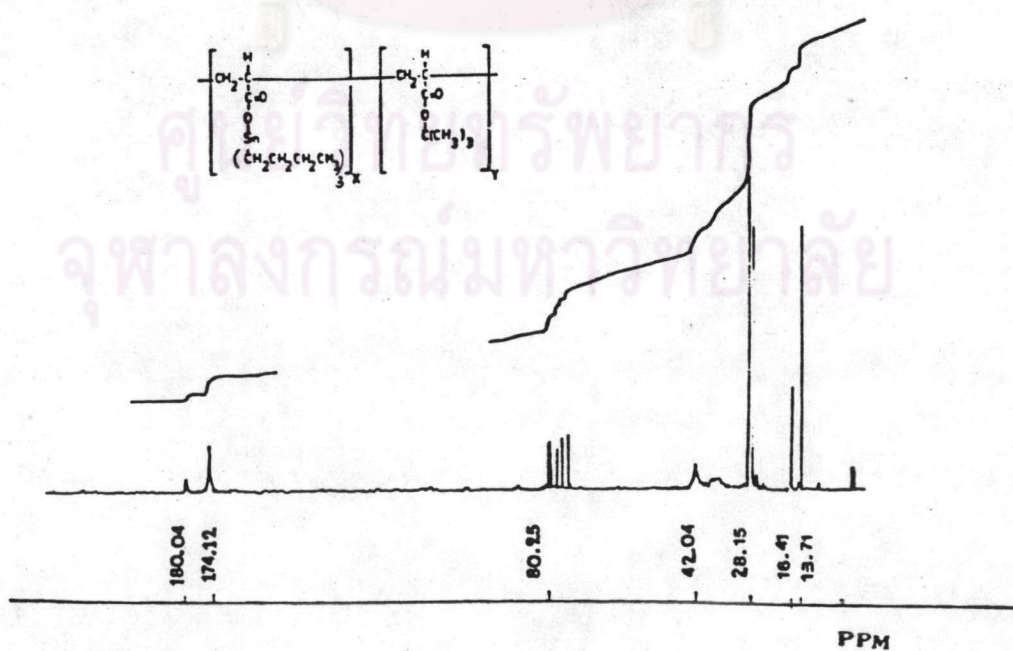
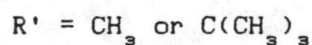
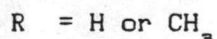
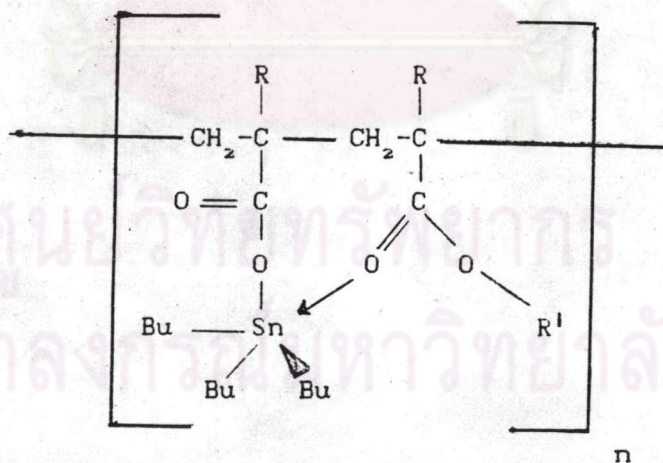


FIG.3.34 ^{13}C NMR spectrum (CDCl_3) of poly TBTA-t-BA.

The moessbauer spectroscopy data are listed in table 3.2 and spectra of some polymers are shown in Fig. 3.35 and 3.36. The isomer shift values (δ) observed for TBTM copolymers ($1.37-1.44 \text{ mms}^{-1}$) were a little higher than TBTM monomer (1.38 mms^{-1}) and these effect were similar to those of TBTA copolymers ($1.44-1.47 \text{ mms}^{-1}$) compared to TBTA monomer (1.43 mms^{-1}). The higher δ value reflected a little greater s-electron density at the tin nucleus in polymers than in monomers. However, δ values of copolymers were in the same range as their organotin monomers. This indicated that tin bonding in copolymers was the same as that in monomers or the tin nucleus was in tri-n-butyltin ester form.

The quadrupole splitting values of tri-n-butyltin copolymers were in the range expected for a trigonal bipyramidal tin atom geometry, with bridging carboxylate groups (OC=O) as the figure below:



This structure showed the pentacoordination of organotin polymers.

TABLE 3.2 The ^{119}mSn Moessbauer data of monomers and copolymers

Compounds	δ mm s^{-1}	ΔEq mm s^{-1}	Γ_1	Γ_2
TBTM monomer	1.38	2.98	1.12	1.06
TBTA monomer	1.43	3.52	1.34	1.41
TBTM-MMA II	1.42	2.93	1.09	1.06
TBTM-MMA III	1.38	2.83	1.23	1.36
TBTM-MMA IV	1.37	2.80	1.20	1.29
TBTM-t-BA II	1.42	2.91	1.14	1.15
TBTM-t-BA III	1.44	2.87	1.30	1.39
TBTM-t-BA IV	1.41	2.86	1.19	1.24
TBTA-MMA II	1.46	3.11	1.25	1.26
TBTA-MMA IV	1.44	3.07	1.26	1.32
TBTA-t-BA II	1.47	3.08	1.23	1.37
TBTA-t-BA IV	1.47	3.02	1.20	1.40
TBTM-BA III	1.37	2.75	1.17	1.34

δ = Isomer shifts

ΔEq = Quadrupole splitting

Note : II = Mole fraction (0.30:0.70)

III = " " (0.40:0.60)

IV = " " (0.50:0.50)



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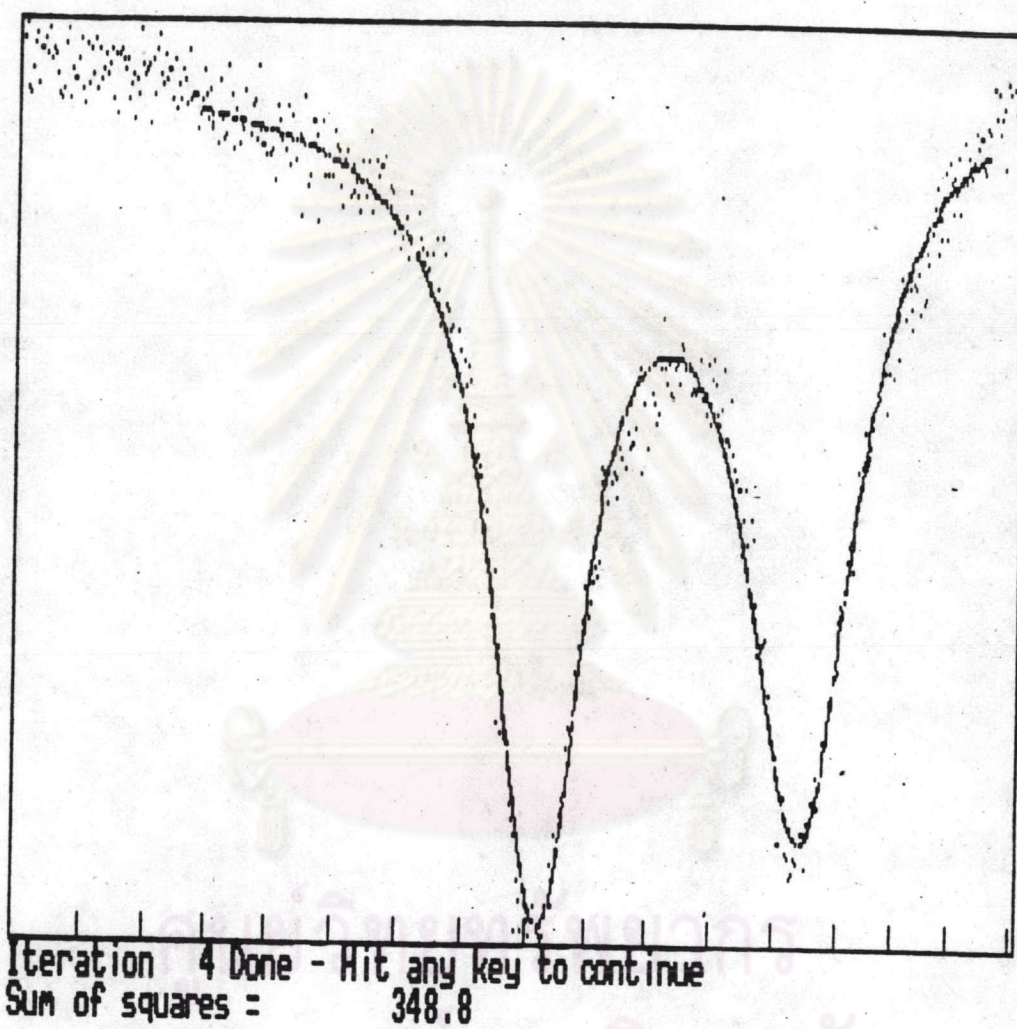


FIG.3.35

 ^{119}mSn Mossbauer spectrum of TBTM-MMA copolymer.

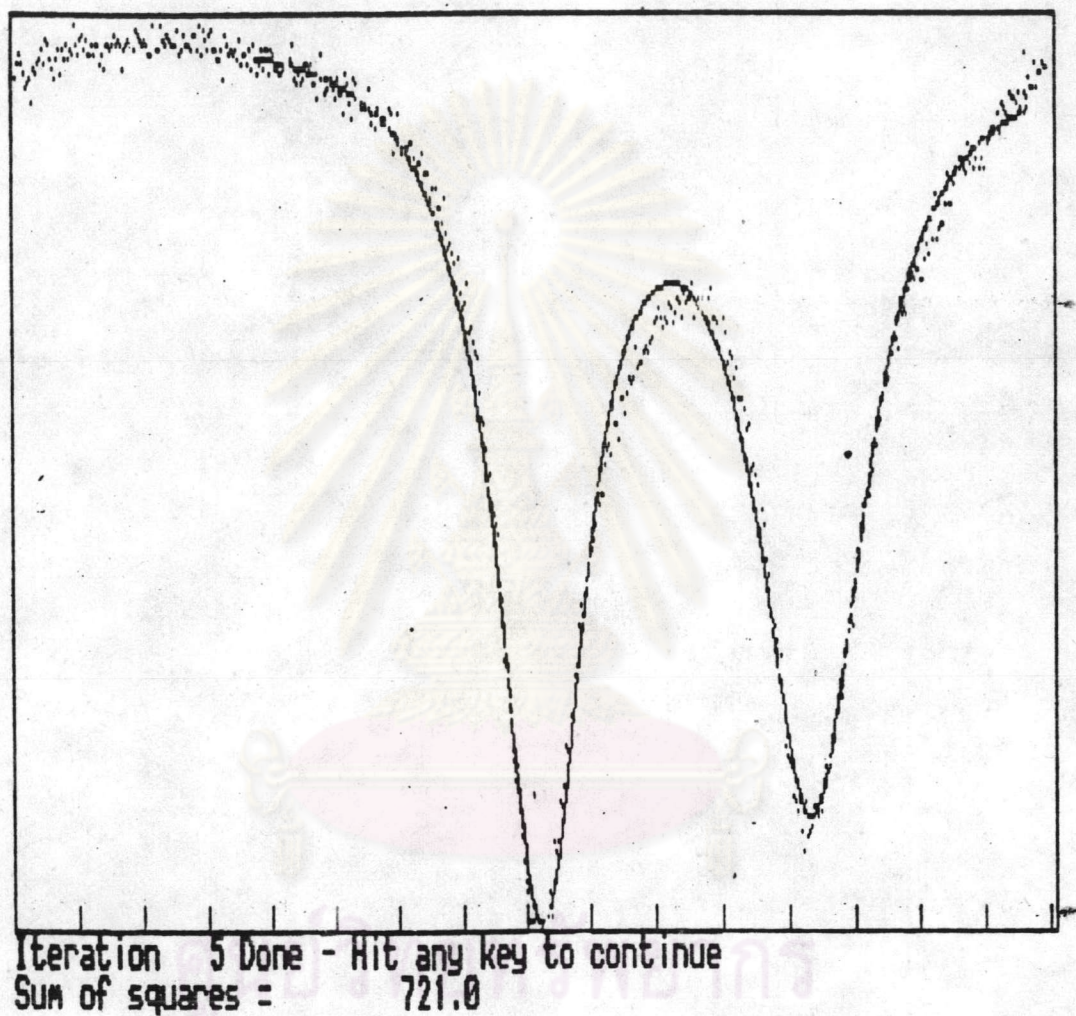


FIG.3.36 ^{119}mSn Moessbauer spectrum of TBTM-t-BA copolymer.

3.3.2 Analysis of copolymer compositions

It is well known that molecular heterogeneity has a direct effect on the physical properties of polymers. The antifouling efficiency of the tin-containing copolymers might also be affected by the distribution of the organotin monomer in the copolymer chain. Thus, the feed compositions of each polymer system were varied to produce organotin polymers with variable tin contents. Table 3.3, 3.4, 3.5, 3.6 illustrate the feed compositions, results of tin analysis and copolymer compositions (mole fraction in copolymer).

The copolymer compositions were determined from tin analysis by the equation of T. Otsui and M. Kinoshita (see Appendix). The elemental analysis of copolymers including C, H and Sn are shown in Table 3.7.

From Table 3.3, 3.4, 3.5 and 3.6, the composition curves of copolymer systems are plotted by mole fractions of M_1 in feed (f_1) versus mole fractions of M_1 in the copolymer (F_1). See Fig. 3.37, 3.38, 3.39 and 3.40.

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TABLE 3.3 Copolymerization of TBTM (M_1) with MMA (M_2)

Polymer System	Mole fraction in feed		Tin content of Copolymer(%by wt.)	Mole fraction in copolymer	
	$M_1 (f_1)$	$M_2 (f_2)$		$M_1 (f_1)$	$M_2 (f_2)$
TBTM-MMA ₁	0.20	0.80	15.30	0.20	0.80
TBTM-MMA ₂	0.30	0.70	19.13	0.29	0.71
TBTM-MMA ₃	0.40	0.60	22.60	0.40	0.60
TBTM-MMA ₄	0.50	0.50	25.18	0.51	0.49
TBTM-MMA ₅	0.60	0.40	26.34	0.57	0.43
TBTM-MMA ₆	0.80	0.20	30.00	0.83	0.17

TABLE 3.4 Copolymerization of TBTM (M_1) with t-BA (M_2)

Polymer System	Mole fraction in Feed		Tin content of Copolymer(%by wt.)	Mole fraction in copolymer	
	$M_1 (f_1)$	$M_2 (f_2)$		$M_1 (f_1)$	$M_2 (f_2)$
TBTM-t-BA ₁	0.20	0.80	13.17	0.20	0.80
TBTM-t-BA ₂	0.30	0.70	18.40	0.32	0.68
TBTM-t-BA ₃	0.40	0.60	19.35	0.35	0.65
TBTM-t-BA ₄	0.50	0.50	24.28	0.53	0.47
TBTM-t-BA ₅	0.60	0.40	26.35	0.63	0.37
TBTM-t-BA ₆	0.80	0.20	30.85	0.93	0.07

TABLE 3.5 Copolymerization of TBTA (M_1) with MMA (M_2)

Polymer : Mole fraction in Feed			Tin content of Copolymer(%by wt.).	Mole fraction in copolymer	
System	$M_1(f_1)$	$M_2(f_2)$		$M_1(f_1)$	$M_2(f_2)$
TBTA-MMA ₁	0.20	0.80	8.64	0.09	0.91
TBTA-MMA ₂	0.30	0.70	13.39	0.16	0.84
TBTA-MMA ₃	0.40	0.60	17.05	0.23	0.77
TBTA-MMA ₄	0.50	0.50	19.19	0.28	0.72
TBTA-MMA ₅	0.60	0.40	24.04	0.43	0.57
TBTA-MMA ₆	0.80	0.20	28.60	0.65	0.35

TABLE 3.6 Copolymerization of TBTA (M_1) with t-BA (M_2)

Polymer : Mole fraction in Feed			Tin content of Copolymer(%by wt.).	Mole fraction in Copolymer	
System	$M_1(f_1)$	$M_2(f_2)$		$M_1(f_1)$	$M_2(f_2)$
TBTA-t-BA ₁	0.20	0.80	14.07	0.21	0.79
TBTA-t-BA ₂	0.30	0.70	19.10	0.33	0.67
TBTA-t-BA ₃	0.40	0.60	21.76	0.41	0.59
TBTA-t-BA ₄	0.50	0.50	24.00	0.49	0.51
TBTA-t-BA ₅	0.60	0.40	25.70	0.56	0.44
TBTA-t-BA ₆	0.80	0.20	29.88	0.78	0.22

TABLE 3.7 Elemental microanalysis

Polymer System Feed mole fraction	Element (%by wt.)		
	H	C	Sn
TBTM-MMA (0.20-0.80)	8.32	55.75	15.30
TBTM-MMA (0.30-0.70)	8.38	54.69	19.13
TBTM-MMA (0.40-0.60)	8.44	53.73	22.60
TBTM-MMA (0.50-0.50)	8.49	53.02	25.18
TBTM-MMA (0.60-0.40)	8.51	52.70	26.34
TBTM-MMA (0.80-0.20)	8.57	51.68	30.00
TBTM-t-BA (0.20-0.80)	9.08	59.53	13.17
TBTM-t-BA (0.30-0.70)	8.95	57.27	18.40
TBTM-t-BA (0.40-0.60)	8.92	56.81	19.35
TBTM-t-BA (0.50-0.50)	8.79	54.57	24.28
TBTM-t-BA (0.60-0.40)	8.74	53.63	26.35
TBTM-t-BA (0.80-0.20)	8.62	51.59	30.85

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(continue)

Polymer system feed mole fraction	Element (% by wt.)		
	H	C	Sn
TBTA-MMA (0.20-0.80)	8.14	57.33	8.64
TBTA-MMA (0.30-0.70)	8.18	55.88	13.39
TBTA-MMA (0.40-0.60)	8.22	54.75	17.05
TBTA-MMA (0.50-0.50)	8.24	54.09	19.19
TBTA-MMA (0.60-0.40)	8.29	52.61	24.04
TBTA-MMA (0.80-0.20)	8.33	49.20	28.60
TBTA-t-BA (0.20-0.80)	8.98	58.87	14.07
TBTA-t-BA (0.30-0.70)	8.82	56.47	19.10
TBTA-t-BA (0.40-0.60)	8.73	55.20	21.76
TBTA-t-BA (0.50-0.50)	8.66	54.13	24.00
TBTA-t-BA (0.60-0.40)	8.61	53.32	25.70
TBTA-t-BA (0.80-0.20)	8.47	51.32	29.88

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The copolymerization composition curve of TBTM-MMA showed almost ideal behaviour. The theoretical curve, F_1 vs f_1 , was very close to the line representing $f_1 = F_1$. This suggested that copolymerization of TBTM with MMA gave azeotropic copolymers which had the same composition as the monomer feed mixtures. The polymeric products of constant composition were formed throughout the copolymerization reactions. (Fig. 3.37). The results suggested that reactivity ratio of TBTM might be equal to MMA.

The composition curves of TBTM-t-BA and TBTA-t-BA (Fig. 3.38 and 3.40) were very close to the line representing $F_1 = f_1$ for a wide range of mole fractions, from 0.20-0.58 mole of TBTM-t-BA and at 0.20-0.36 mole of TBTA-t-BA. These ranges might be azeotropic compositions (only for this case). On the other hand, composition curve of TBTA-MMA in Fig. 3.39 gave no azeotropic copolymer compositions as could be seen from the deviation of the curve F_1 vs f_1 from ideal behavior. The TBTM-t-BA composition curve showed that reactivity ratio of t-BA monomer might be less than TBTM (compared to TBTM-MMA system). It was probably due to steric effect of t-BA monomer.

For TBTA-MMA and TBTA-t-BA copolymer systems, the results were not clearly understood. The electronic effects might operate in these cases. Detail investigations would be helpful to make any conclusion.

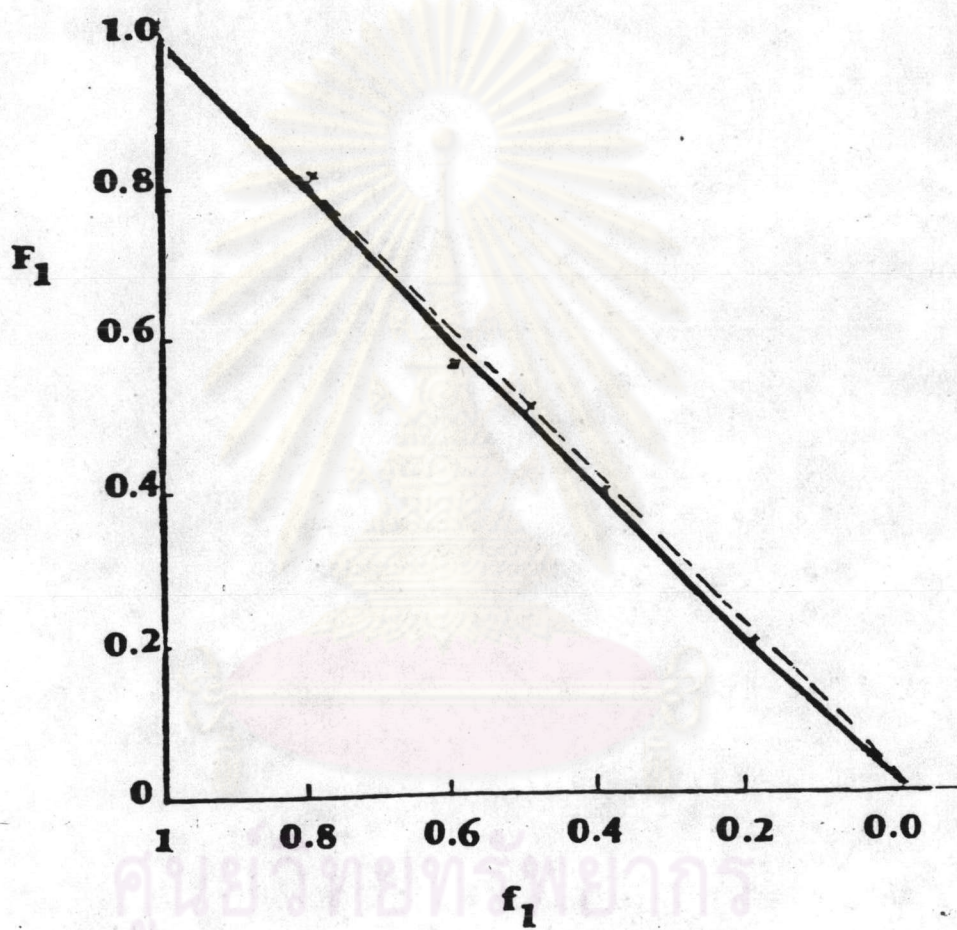


FIG.3.37 Copolymer compositions (F_1) as the function of feed compositions (f_1) for the copolymerization of TBTM with MMA.

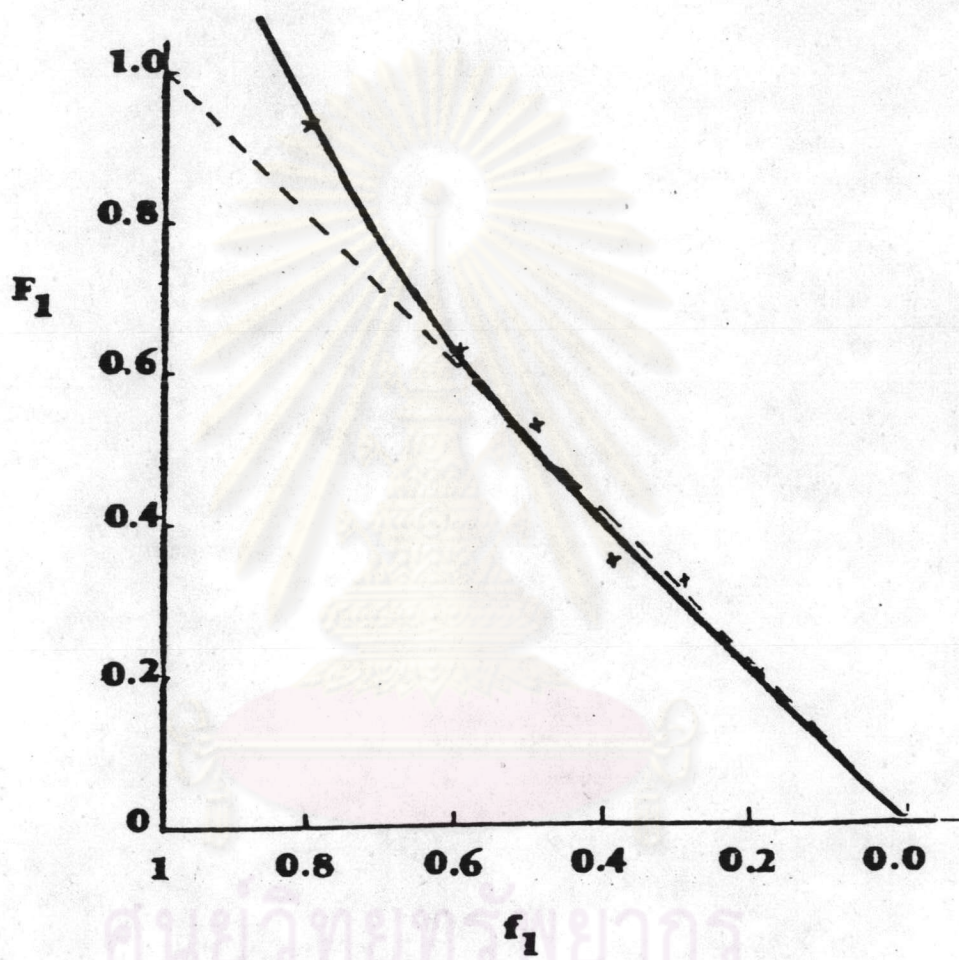


FIG.3.38 Copolymer compositions (F_1) as the function of feed compositions (f_1) for the copolymerization of TBTM with t-BA.

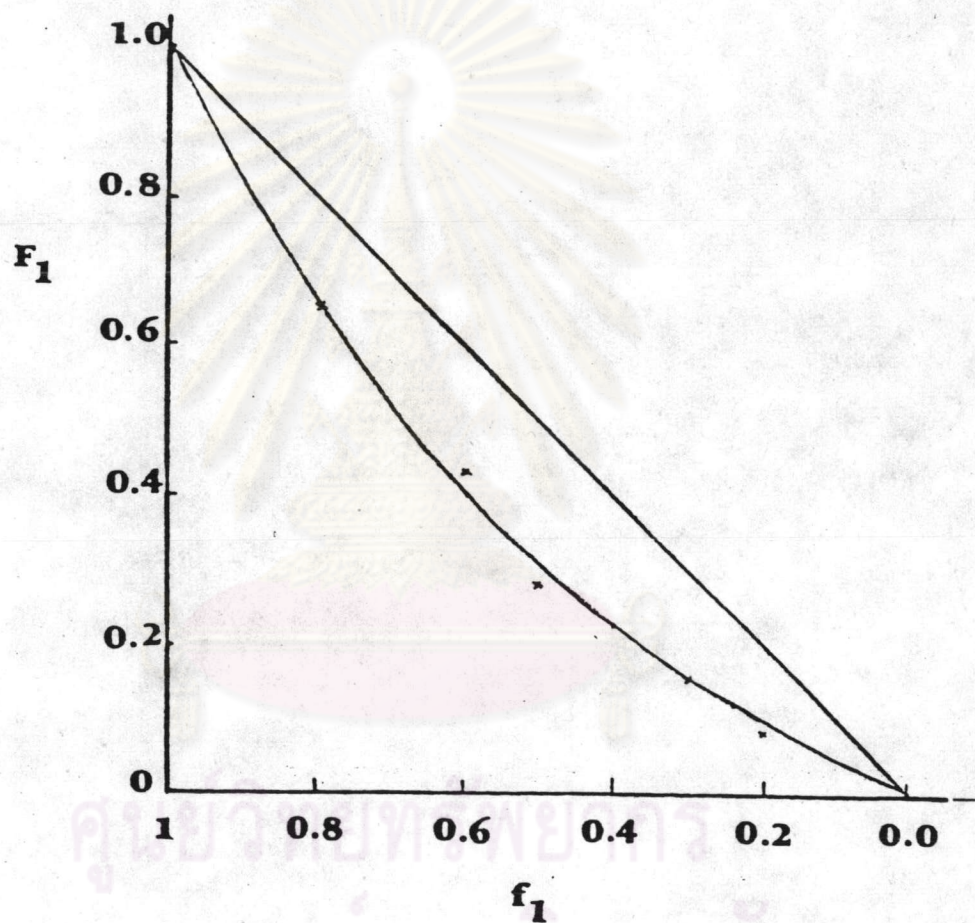


FIG.3.39 Copolymer compositions (F_1) as the function of feed compositions (f_1) for the copolymerization of TBTA with MMA.

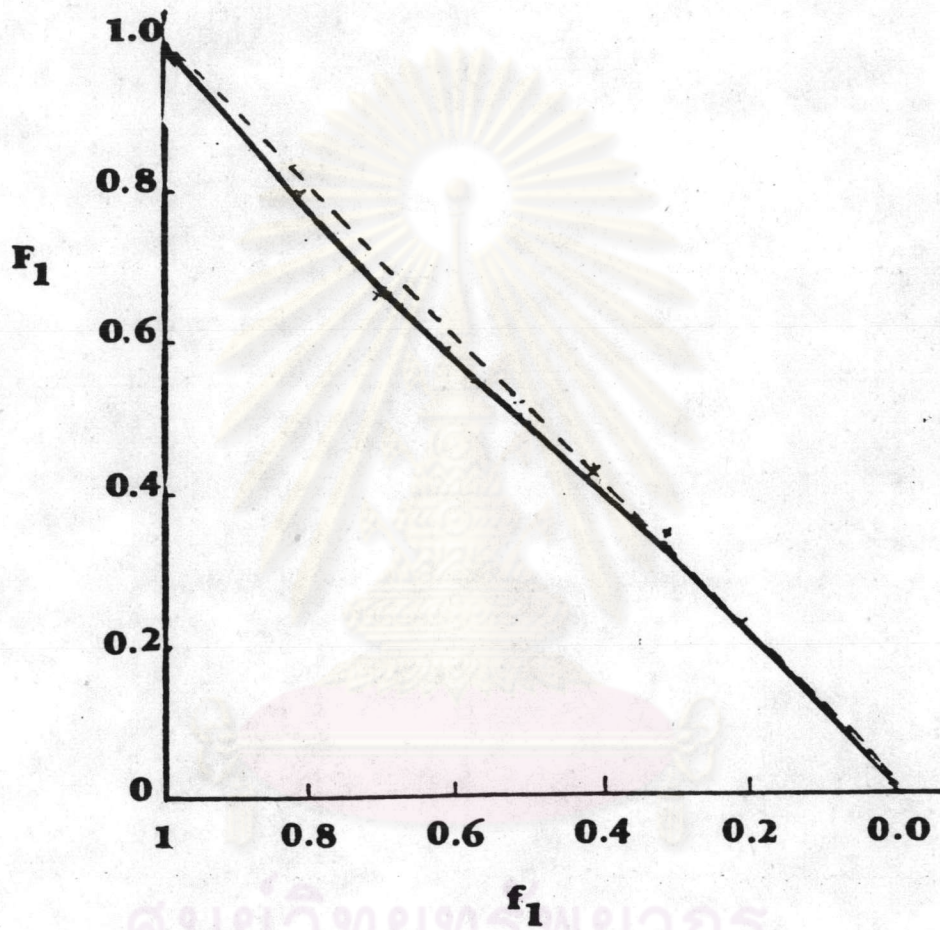


FIG.3.40 Copolymer compositions (F_1) as the function of feed compositions (f_1) for the copolymerization of TBTA with t-BA.

3.3.3 Physical Properties and Film Testing of Copolymers

Certain physical properties, such as molecular weights (both number and weight, M_n & M_w), molecular weight distribution (MWD) and glass transition temperature (T_g) of the copolymers of different mole fractions were determined. The prepared copolymers were solids, hard or soft rubbery materials depending on their T_g values. They were colorless, transparent and soluble in common organic solvents. Some of them were suitable for film forming but the others were not.

A. Effect of organotin monomer content on T_g

To study the effect of organotin monomer contents on T_g , the copolymer obtained from different feed compositions of each system was selected for measurement. The ratios of tri-n-butyltin monomer : comonomer (MMA/t-BA) were 0.30:0.70, 0.50:0.50 and 0.60:0.40 (see Table 3.8). DSC thermograms of each copolymer system at mole ratio 0.30 : 0.70 are shown in Fig. 3.41.

It was obvious that T_g values of the copolymers decreased while the mole fraction of the organotin monomers increased. For the copolymers with the same organotin monomer and feed composition, T_g values were found to be decreased if the organotin comonomer was t-BA, for example, TBTM-MMA (11) $T_g = 54.96^\circ\text{C}$ whereas TBTM t-BA (11) $T_g = 21.02^\circ\text{C}$ and TBTA-MMA (11) $T_g = 35.67^\circ\text{C}$ whereas TBTA-t-BA (11) $T_g = 12.66^\circ\text{C}$.

This could be summarized that, polymers with longer side chain

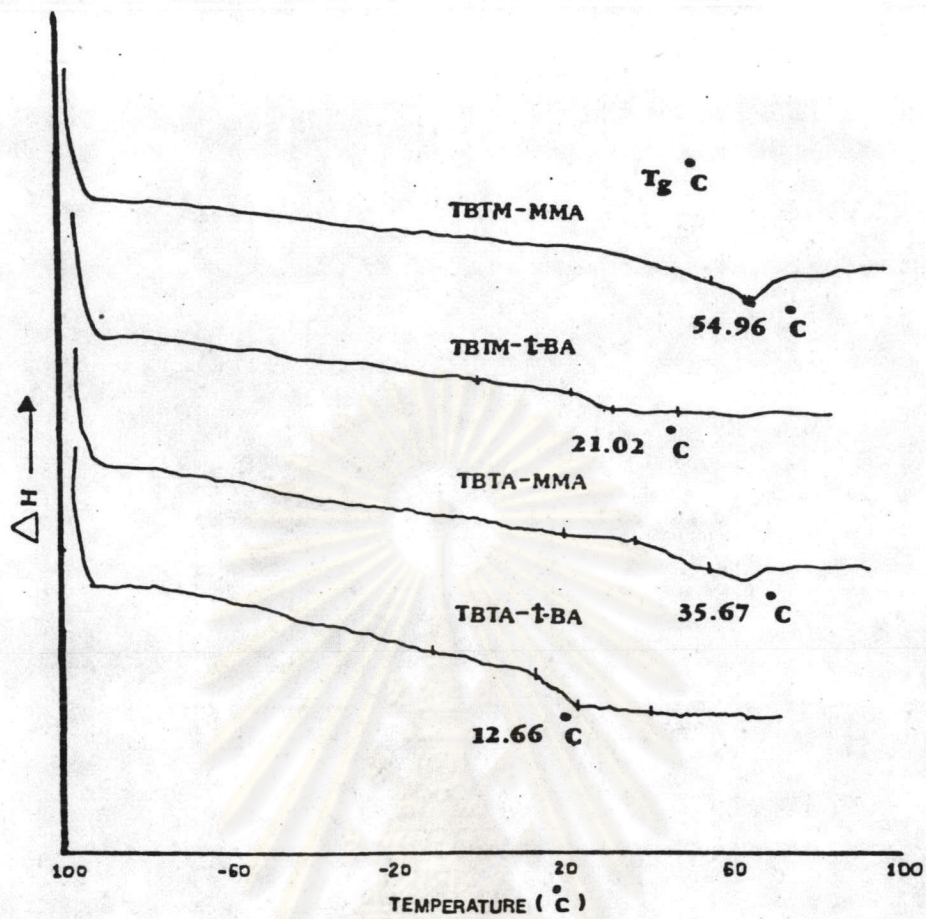
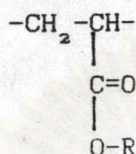


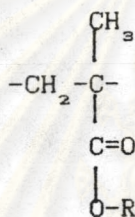
FIG.3.41 DSC thermogram of triorganotin copolymers (mole fraction of organotin monomer : comonomer = 0.30 : 0.70)

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would have lower Tg values , for example , Tg of poly MMA is 105 °C while Tg of poly t-BA is 47.4 °C. From literature review, the effect of pendant groups on the glass transition temperature of an amorphous polymer system was exhibited in the series of acrylates.



and methacrylates



Tg decreased with increasing length of the side chain until the length reached 8 carbons for the acrylate series and 12 carbons for the methacrylate series. (31).

It was found that, the methacrylates had higher Tg values than the corresponding acrylates because of the stiffening effect produced in the former by the α -methyl group (see Table 3.9).

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TABLE 3.8 Molecular weight and Tg of copolymers

Copolymers : Feed mole fraction	Mn	Mw	MWD	Tg °C
TBTM-MMA ₂ (0.30:0.70)	2,785	2,889	1.04	54.96
TBTM-MMA ₄ (0.50:0.50)	2,978	3,001	1.00	47.52
TBTM-MMA ₅ (0.60:0.40)	3,155	3,176	1.00	23.31
TBTM-t-BA ₂ (0.30:0.70)	2,653	2,772	1.04	21.02
TBTM-t-BA ₄ (0.50:0.50)	2,961	2,994	1.01	na*
TBTM-t-BA ₅ (0.60:0.40)	2,852	2,881	1.01	na*
TBTA-MMA ₂ (0.30:0.70)	2,662	2,758	1.04	35.67
TBTA-MMA ₄ (0.50:0.50)	2,939	2,965	1.00	28.41
TBTA-MMA ₅ (0.60:0.40)	3,078	3,154	1.02	17.53
TBTA-t-BA ₂ (0.30:0.70)	2,596	2,729	1.05	12.66
TBTA-t-BA ₄ (0.50:0.50)	2,874	2,904	1.01	-2.79
TBTA-t-BA ₅ (0.60:0.40)	2,804	2,834	1.01	-4.98

NOTE : na* = Data were not available because the DSC instrument was out of order.

TABLE 3.9

The effect of side chain lengths on Tg values for acrylate & methacrylate polymers

side chain - length	Tg of acrylate (°K)	Tg of methacrylate (°K)
methyl	279	378
ethyl	249	338
propyl	225	308
butyl	218	293

A graph plotted between Tg(°C) and mole fraction of MMA and t-BA in each copolymer system showed the same trend. The Tg values increased with increasing methyl methacrylate contents in the copolymers. Tg values for TBTM-MMA were higher than TBTA-MMA resulted from the lower Tg of poly TBTA (see Fig. 3.42).

Tg values also increased with increasing t-BA contents in the copolymers, for the same reason as stated above (see Fig. 3.43).

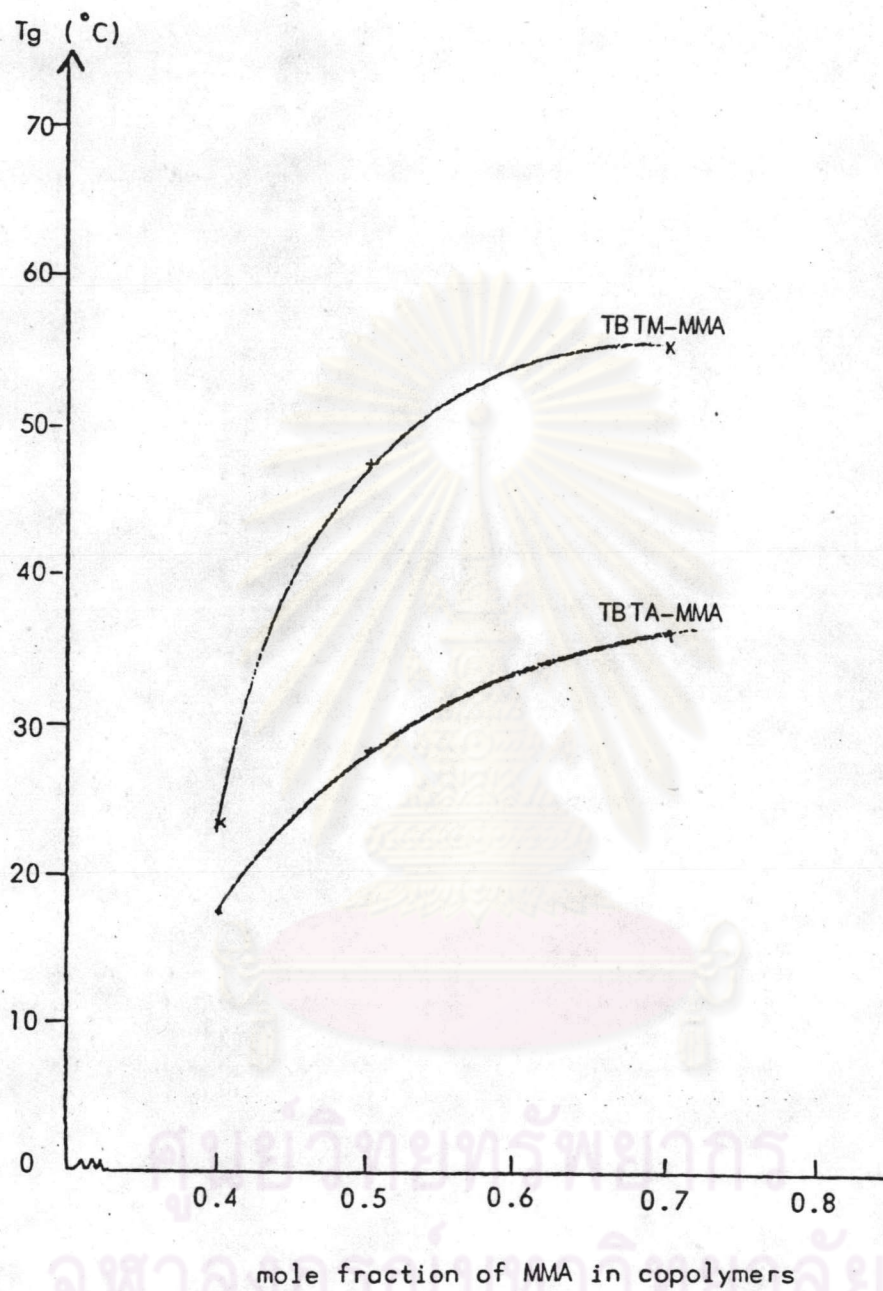


FIG.3.42 T_g of TBTM-MMA and TBTA-MMA copolymers at various mole ratio of MMA.

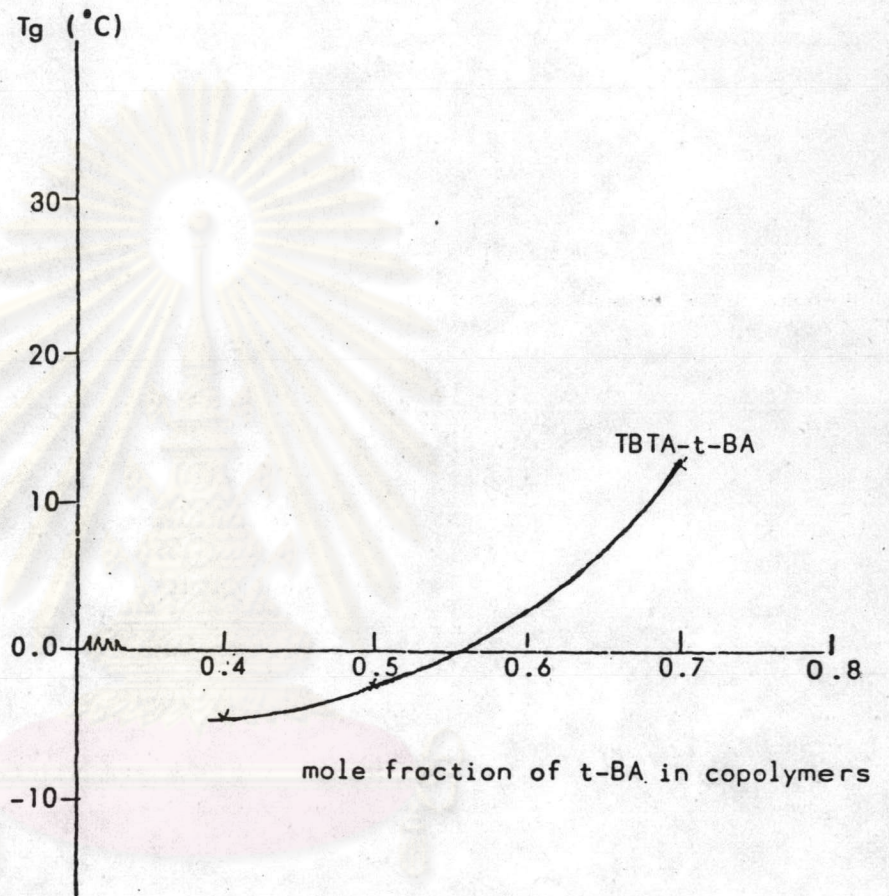


FIG.3.43 T_g of TBTA-t-BA copolymers at various mole ratio of t-BA.

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B. Determination of Molecular Weight and Molecular Weight Distribution of Copolymers

The molecular weight (M_w, M_n) and molecular weight distribution (MWD) of copolymers were analyzed by gel permeation chromatography (GPC) and are shown in Table 3.8.

$$\text{MWD} = M_w/M_n$$

Where M_w = weight average molecular weight

M_n = number average molecular weight

These data showed that the molecular weights of the copolymer products were in a medium range which can easily be reprocessed into films or coatings. The MWD of each copolymer was close to 1, indicating that the polymers were almost homogeneous.

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C. Effect of organotin monomer contents on the physical properties of polymer films

According to paint technology, antifouling compositions are considered to be a separate group of paints. Rapid air drying, good adhesion and reasonable hardness are the important physical characteristics needed for antifouling coatings. Copolymers for each system were prepared for varnishing by dissolving them in xylene (50% by weight). The varnishes were applied on standard steel panel for adhesion test and on glass to study the drying time of the films. The hardness of polymer films were not measured in this work because the instrument was not available.

All copolymers gave transparent coating on the surface of metal and glass. The films were elastic or tacky depending on the organotin contents.

1. Effect on Adhesion Test

The adhesion of films were better when organotin contents in the copolymer were increased. Only organotin-t-BA copolymers provided slightly better film adhesion than organotin-MMA copolymers.

All of the copolymer films had good adhesion (see Table 3.10). The assessment "go" in table 3.10 had the same meaning as "pass" for practical use in the paint industry. The results suggest the relation between T_g and adhesion power. A low T_g of polymer seemed to give a good adhesion power. However, the exact reason was under investigated.

TABLE 3.10 Adhesion test of polymer film (dry film thickness 50 μm)

Polymer system	Classification	Assessment ,go/no go
TBTM-MMA (Ia)	1-2	go
TBTM-MMA (IIa)	1-2	go
TBTM-MMA (IIIa)	1	go
TBTM-MMA (IVa)	1-0	go
TBTM-MMA (Va)	1-0	go
TBTM-MMA (VIa)	0	go
TBTM-t-BA (Ib)	1	go
TBTM-t-BA (IIb)	1	go
TBTM-t-BA (IIIb)	1-0	go
TBTM-t-BA (IVb)	1-0	go
TBTM-t-BA (Vb)	0	go
TBTM-t-BA (VIb)	0	go
TBTA-MMA (Ic)	1-2	go
TBTA-MMA (IIc)	1	go
TBTA-MMA (IIIc)	1	go
TBTA-MMA (IVc)	1-0	go
TBTA-MMA (Vc)	1-0	go
TBTA-MMA (VIc)	0	go

(continue)

Polymer system	Classification	Assessment ,go/no go
TBTA-t-BA (I _d)	1-0	go
TBTA-t-BA (II _d)	1-0	go
TBTA-t-BA (III _d)	0	go
TBTA-t-BA (IV _d)	0	go
TBTA-t-BA (V _d)	0	go
TBTA-t-BA (VI _d)	0	go

Note : I = Mole fraction (0.20:0.80)

II = " " (0.30:0.70)

III = " " (0.40:0.60)

IV = " " (0.50:0.50)

V = " " (0.60:0.40)

VI = " " (0.80:0.20)

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2. Effect on drying time

The varnish of each copolymer was applied on the standard long strip glass to obtain a film with thickness ranging from 37 to 45 microns. The polymer films of TBTM-MMA dried within a few hours (1-7.5 hrs.). For TBTM-t-BA films as well as TBTA-MMA at mole ratio (0.20 : 0.80 - 0.60 : 0.40), their drying times were in the range of 3-9 hr. excepting the film of mole ratio 0.80 : 0.20 that gave softness, tackiness and long drying time. TBTA-t-BA films took time more than 12 hr. to be dried and gave tackiness also (see table 3.11).

It showed that the drying time of films decreased with increasing organotin contents in the copolymers . The drying time of polymer films were also affected by Tg of the polymers. Organotin-MMA copolymer exhibited rapid film drying while organotin-t-BA copolymers exhibited slow film drying due to lower Tg of t-BA. Among copolymers consisting of the same comonomer , the tri-n-butyltin methacrylate systems seemed to dry faster than the tri-n-butyltin acrylate systems. This was because Tg of poly TBTM was higher than that of poly TBTA. However, the problem of film drying was not critical and could be solved by adding a suitable drier during the formulation of paints.

TABLE 3.11 Drying time test (wet film thickness 37 μm)

Polymer system	Time(hr.)	Assessment ,go/no go	Remarks
TBTM-MMA (Ia)	1.00	go	
TBTM-MMA (IIa)	2.50	go	
TBTM-MMA (IIIa)	3.00	go	
TBTM-MMA (IVa)	3.25	go	
TBTM-MMA (Va)	5.00	go	
TBTM-MMA (VIa)	7.50	go	
TBTM-t-BA (Ib)	3.00	go	
TBTM-t-BA (IIb)	4.25	go	
TBTM-t-BA (IIIb)	5.00	go	
TBTM-t-BA (IVb)	7.00	go	
TBTM-t-BA (Vb)	8.00	go	
TBTM-t-BA (VIb)	>12.00	no go	tacky film
TBTA-MMa (Ic)	3.00	go	
TBTA-MMA (IIc)	3.25	go	
TBTA-MMA (IIIc)	4.50	go	
TBTA-MMA (IVc)	6.00	go	
TBTA-MMA (Vc)	9.00	go	
TBTA-MMA (VIc)	>12.00	no go	tacky film

(continue)

Polymer system	Time(hr.)	Assessment ,go/no go	Remarks
TBTA-t-BA (Id)	>12.00	no go	tacky film
TBTA-t-BA (IId)	>12.00	no go	tacky film
TBTA-t-BA (IIId)	>12.00	no go	tacky film
TBTA-t-BA (IVd)	>12.00	no go	tacky film
TBTA-t-BA (Vd)	>12.00	no go	tacky film
TBTA-t-BA (VI d)	>12.00	no go	tacky film

Note : I = Mole fraction (0.20:0.80)

II = " " (0.30:0.70)

III = " " (0.40:0.60)

IV = " " (0.50:0.50)

V = " " (0.60:0.40)

VI = " " (0.80:0.20)

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