CHAPTER (III)

Results and Discussion

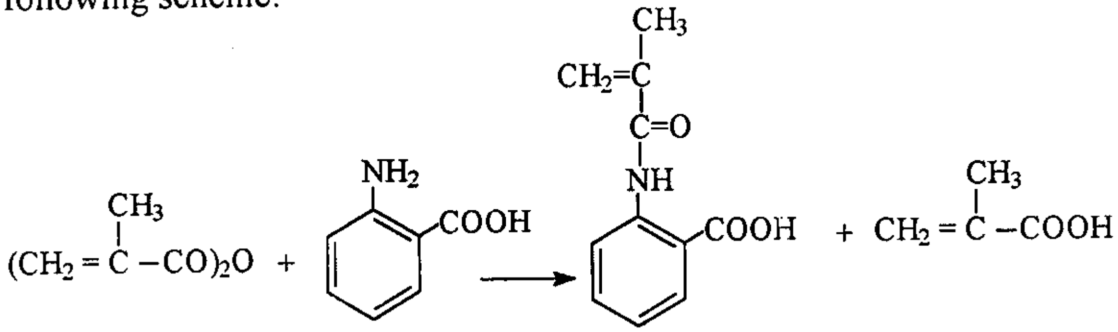
CHAPTER III

A-Synthesis and Polymerization of the Monomer

1- Synthesis of o-Methacrylamidobenzoic acid (o-MAB):

a-Acid anhydride method:

o-Methacrylamidobenzoic acid was prepared by the reaction of methacrylic anhydride with o-amino benzoic acid in the presence of N,N-dicyclohexylcarbdiimide (DCCI) as a condensing agent according to the following scheme:

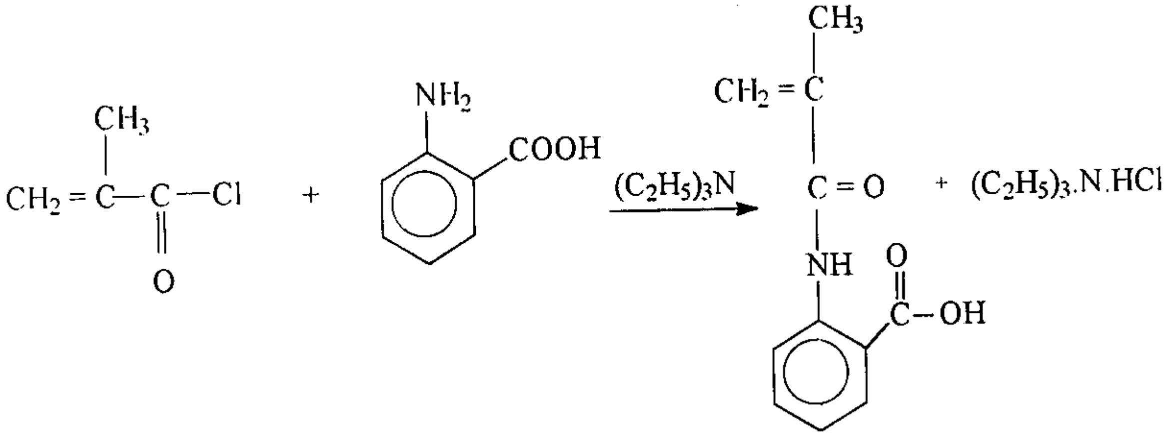


The structure of o-methacrylamidobenzoic acid (o-MAB) was esablished from its IR spectrum (Fig. 1) which shows the following bands: $\nu_{OH, NH}$ (3600-3300) cm^{-1} , ν_{CH} aromatic (3100) cm^{-1} , ν_{CH} aliphatic (2900-2850) cm^{-1} , $\nu_{C=o}$ of acid at (1700) cm^{-1} and amidic carbonyl at (1650) cm^{-1}.

On the other hand, Fig.(2) showed ^{1}HNMR of o-methacryl-amidobenzoic acid which gave the following characteristics peaks; δ 2.2 ppm (s, $3H_2$, CH_3), two distinguished signals of two olefinic protons ($\rangle C=CH_2$) at δ (5.6, 6.1) ppm. Four different aromatic protons between δ (7.2-8.2) ppm, carboxylic proton appears at δ 10.4 ppm (s, 1H, OH) and amidic proton at δ 11.4 ppm (s, 1H, NH).

b-Acid Chloride method

o-Methacrylamidobenzoic acid was prepared by the reaction of methacryloylchloride with o-aminobenzoic acid in the presence of triethylamine according to method described in page (43)



The resulting o-methacrylamidobenzoic acid was obtained as white crystals and was recrystalized from benzene. The yield of rerystalized product was 90% and the m.p 163 °C.

The IR and ^{1}H-NMR spectra of the product was found to be identical with that prepared by DCCI method.

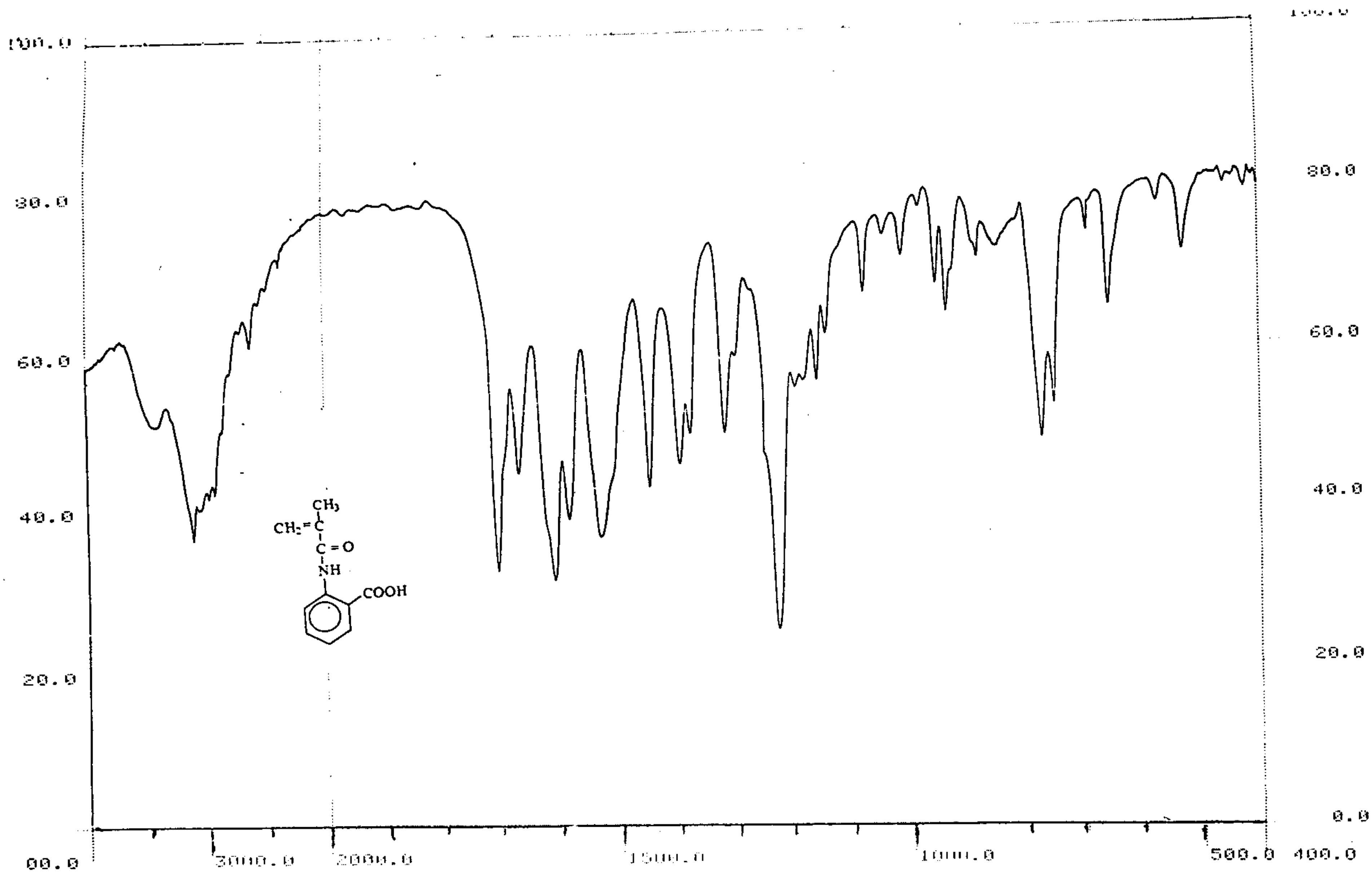


Fig. (1) : IR spectrum of o-methacrylamidobenzoic acid (o-MBA)

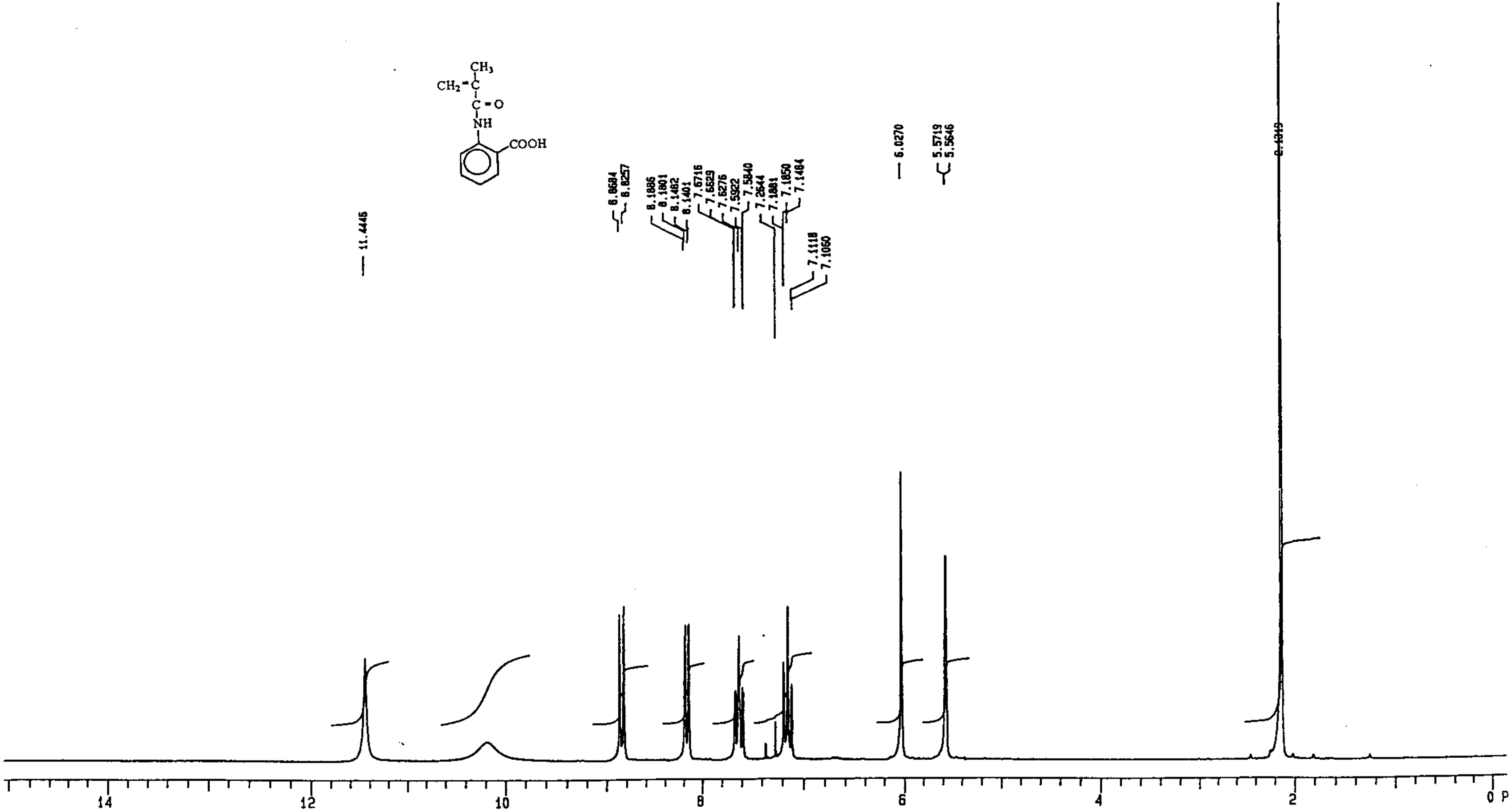
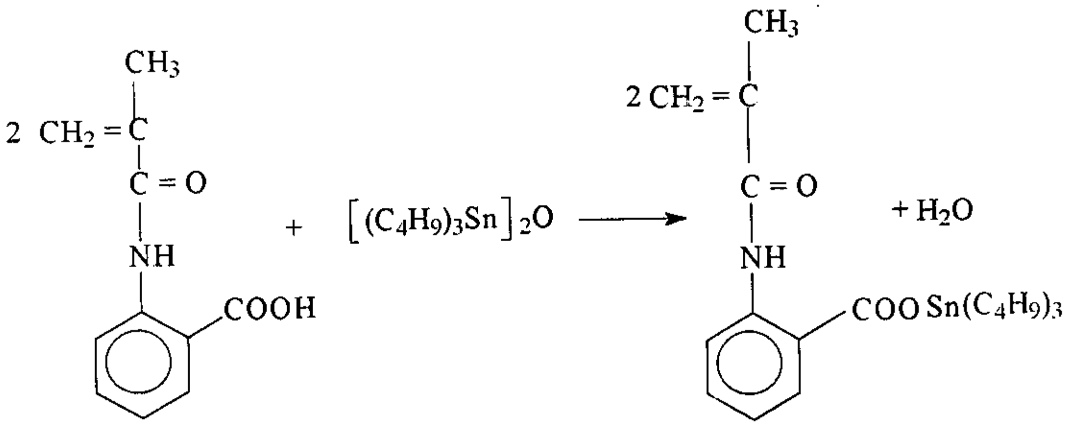


Fig. (2) : ^{1}H NMR spectrum of o-methacrylamidobenzoic acid (o-MBA)

2- Preparation of o-methacrylamido-tri-n-butyl tin benzoate (o-MTBTB)

o-methacrylamido-tri-n-butyltin benzoate was prepared by esterification of o-methacrylamdiobenzoic acid with bis (tri-n-butytin) oxide according to the method described in page (44).



Its tin content was found to be 23.78% against a calculated value 24.1%.

The structure of o-methacrylamido-tri-n-butyltin benzoate was established via spectral data; the IR spectrum (Fig.3) show the following bands; ν_{NH} at 3500 cm^{-1} , ν_{CH} aromatic 3150 cm^{-1}, ν_{CH} olefinic at (2950-2850) cm^{-1} , $\nu_{C=O}$ acidic at 1700 cm^{-1} , $\nu_{C=O}$ aromatic 1650 cm^{-1}.

The ^{1}H-NMR spectrum of o-methacrylamido tri-n-butyltin benzoate (Fig. 4) shows the following signals; δ (0.78-2.00) for the aliphatic protons (tri-n-butyl + CH_3) to distinguish olefinic protons (=CH_2) δ S 5.45, 5.96, for single aromatic protons, δ 6.6, finally signal at 12.15 for amidic proton (s, 1H, NH).

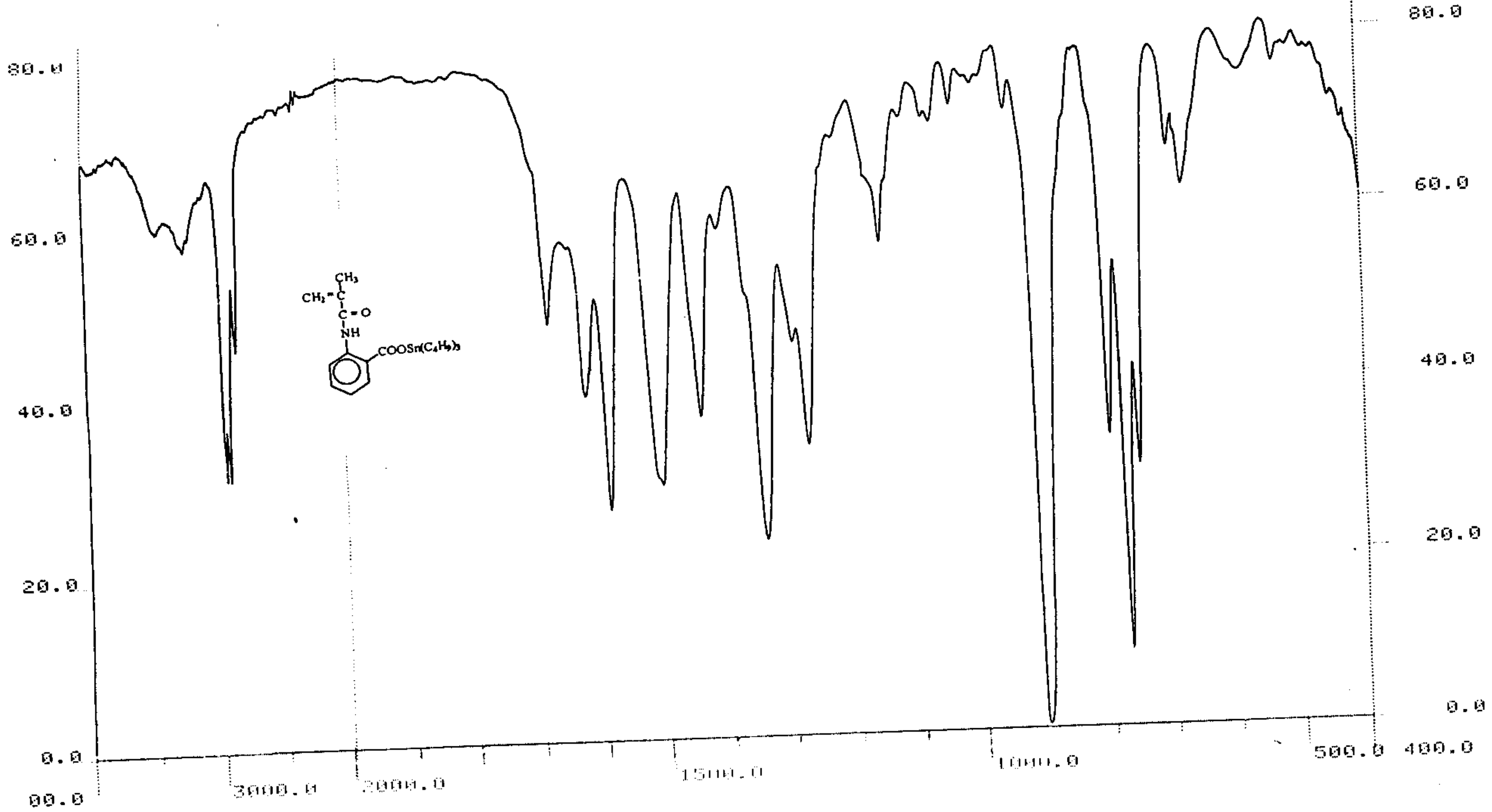


Fig. (3) : IR spectrum of o-methacrylamido-tri-n-butyl tin benzoate.

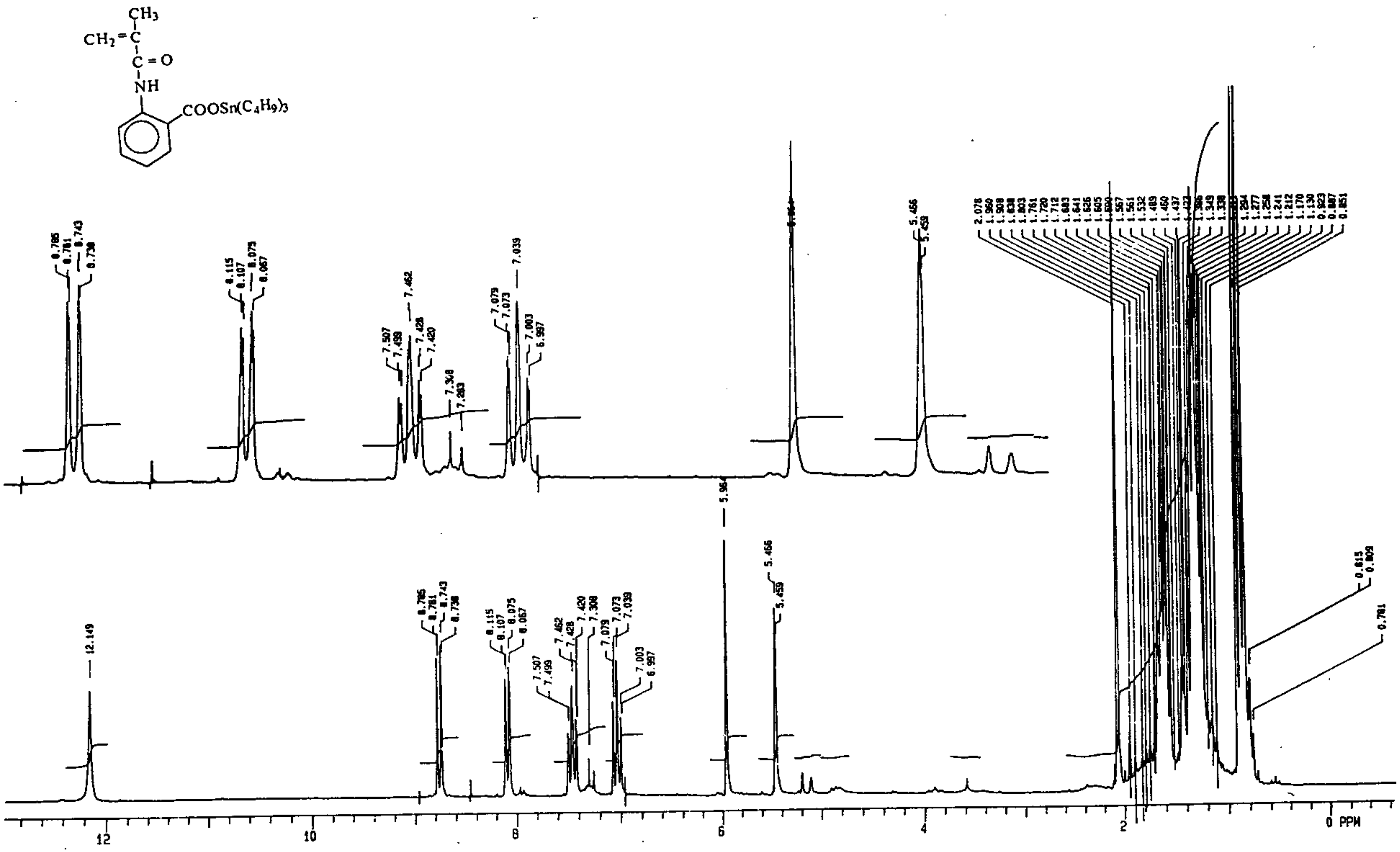
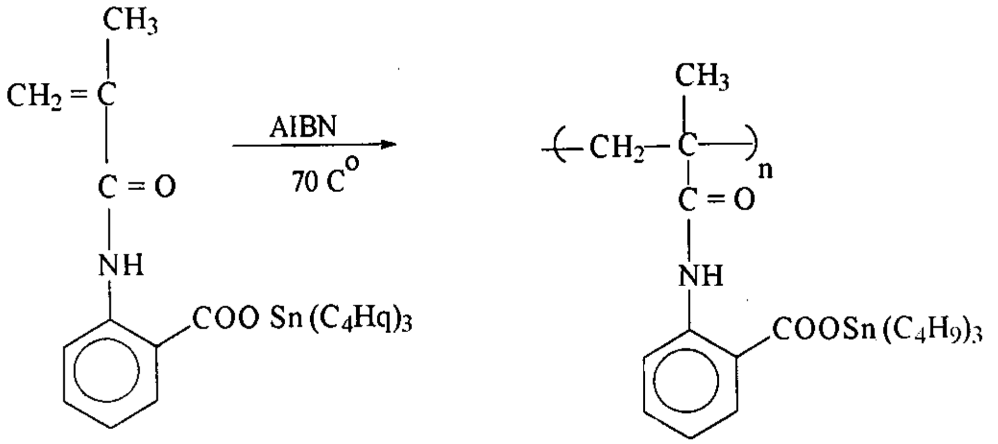


Fig. (4) : ^{1}HNMR spectrum of o-methocrylamido-tri-n-butyl tin benzoate.

3- Polymerization of o-methacrylamido-tri-n-butyltin benzoate

o-Methacrylamido-tri-n-butyltin benzoate was polymerized in DMF solution at 70°C using AIBN as a free radical initiator according to the method described in page (44) to give poly o-methacrylamido-tri-n-butyltin benzoate:



o-methacrylamido-tri-n-butyltin benzoate Poly(o-methacrylamido-tri-n-butyltin benzoate)

The poly (o-methacrylamido-tri-n-butyltin benzoate) was obtained as a viscous material by reprecipitation from methanol (85%). The yield was 88%.

The structure of the prepared polymer was investigated by the tin content and it was found to be 23.7 % but the calculated value was found to be 24.1% for $C_{23}H_{39}O_3Sn$.

The IR spectrum of poly (o-methacryl-amindo-tri-n-butyltin benzoate) (Fig.5) gave the following characteristic bands, ν_{NH} at 3400 cm^{-1}, ν_{CH} aromatic at 3100 cm^{-1}, $\nu_{C\text{-}H}$ aliphitic at (2900-2850) cm^{-1}, $\nu_{C=O}$ amidic at 1640 cm^{-1} and $\nu_{C=O}$ carboxylic at 1680 cm^{-1}.

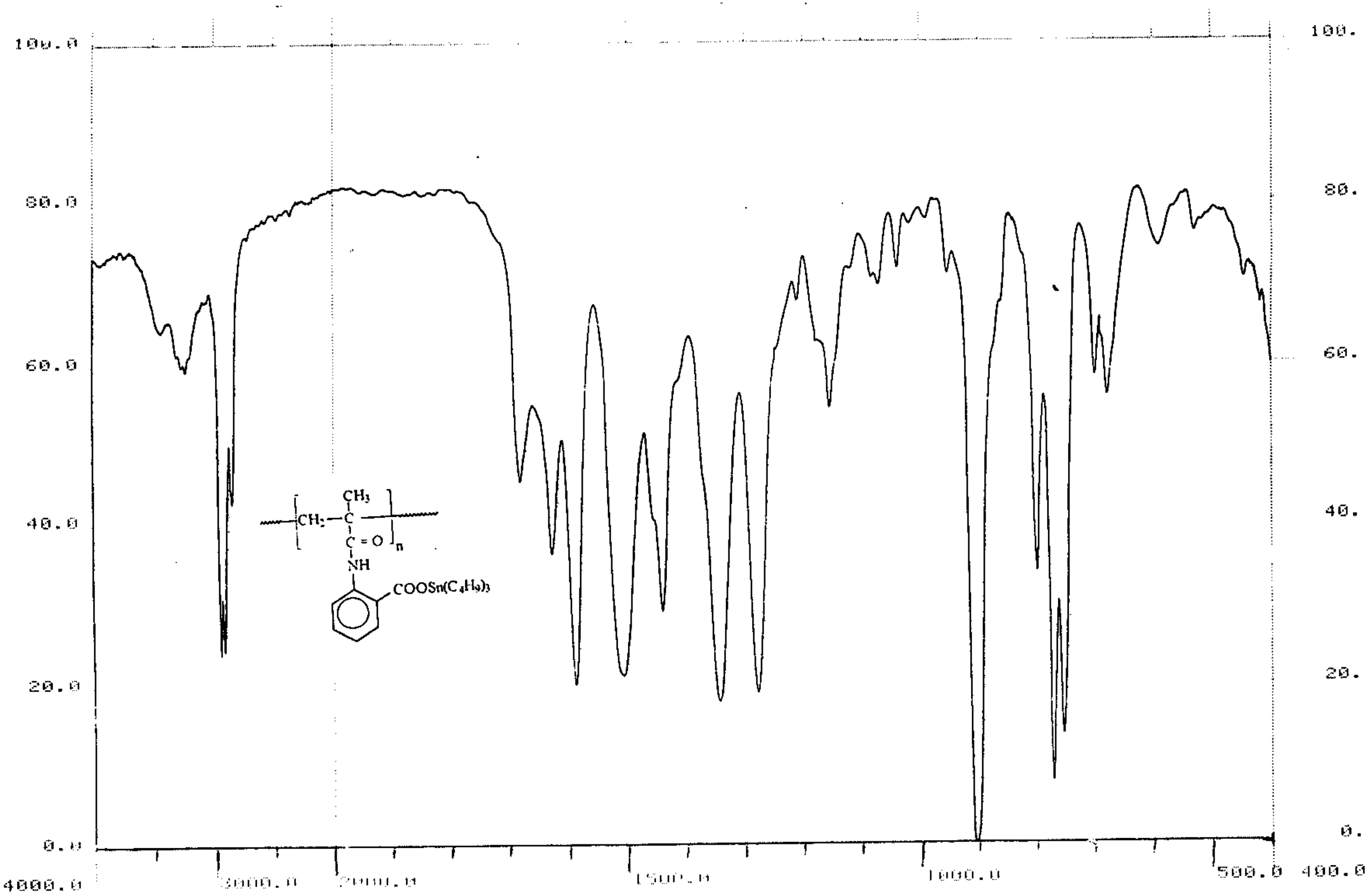
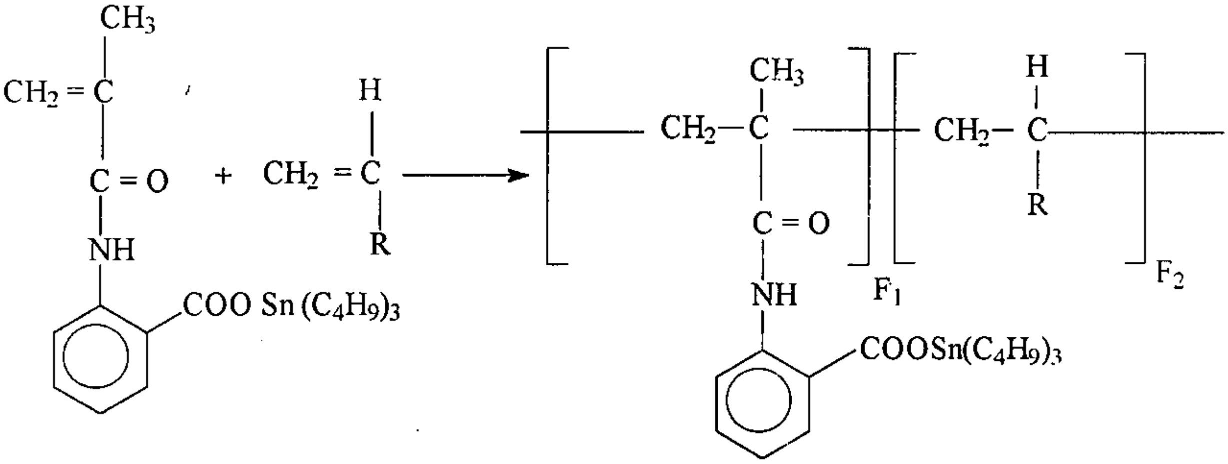


Fig. (5): IR spectrum of poly o- methocrylamido-tri-n-butyl tin benzoate.

B-Binary copolymerization reactions

a- Copolymerization of o-methacrylamido-tri-n-butyltin benzoate (o-MTBTB) with acrylic acid esters:

Copolymerization of o-methacrylamdio-tri-n-butyltin benzoate with methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) was carried out by copolymerization technique in DMF (1.5 mole /l) at 70°C in the presence of 1 mole of AIBN and the reaction can be represented as the follows:



Where :

M_1 – M_2	R`
MTBTB-MA	- $COOCH_3$
MTBTB-EA	- $COOC_2H_5$
MTBTB-BA	- $COOC_4H_9$

The prepared copolymers are solids soluble in most organic solvents, their structure was investigated by IR and ^{1}H-NMR spectroscopy.

The IR spectra Fig. (6,10) of the prepared polymers are quite similar and show broad bands attributed to ν_{NH} and ν_{CH} aliphatic (3400-3100) cm^{-1}; $\nu_{C=O}$ of acrylate esters (1720-1710) cm^{-1} and $\nu_{C=O}$ of amidic at 1640 cm^{-1}.

The ^{1}H-NMR spectra of (o-MTBTB-MA), (o-MTBTB-EA) and (o-MTBTB-BA) Fig. (7,9,11) are similar and show signals at δ (0.86 – 1.6) ppm aliphatic protons ($-CH_2$, $-CH_3$) δ at 2.09 ppm (s, 1H, -CH) methine proton, δ (7.0-8.6) of aromatic protons and δ 11.6 (s, 1H, NH).

The results of the copolymerization reaction are illustrated in the tables (1-3). The monomer reactivity ratios for each system were calculated by both Finemon-Ross and Kelen-Tudos methods described in page (16) and the standard deviation of the results were calculated by regression analysis Fig. (12,13,14) illustrate the Kelen-Tudos plots of the three systems which give r_1 and $-r_2/\alpha$, both as intercepts. The results are summarized in table (4) which show that there is a good agreement between the values of the reactivity ratios calculated by the two methods. Also, the range of experimental error in r_1 and r_2 is quite small. Table (4) shows that the monomer reactivity ratio value of (o-MTBTB) (r_1) for all systems studied are very low values which indicates that the growing radical ending with o-MTBTB unit prefers M_2 monomers than M_1 monomer in propagation stage.

Fig. (15) illustrates the composition curves of the binary systems and it is clear that all systems studied didn't give azeotropic compositions and also show that the copolymers produced have a lower content of F_1 than the comonomer mixtures.

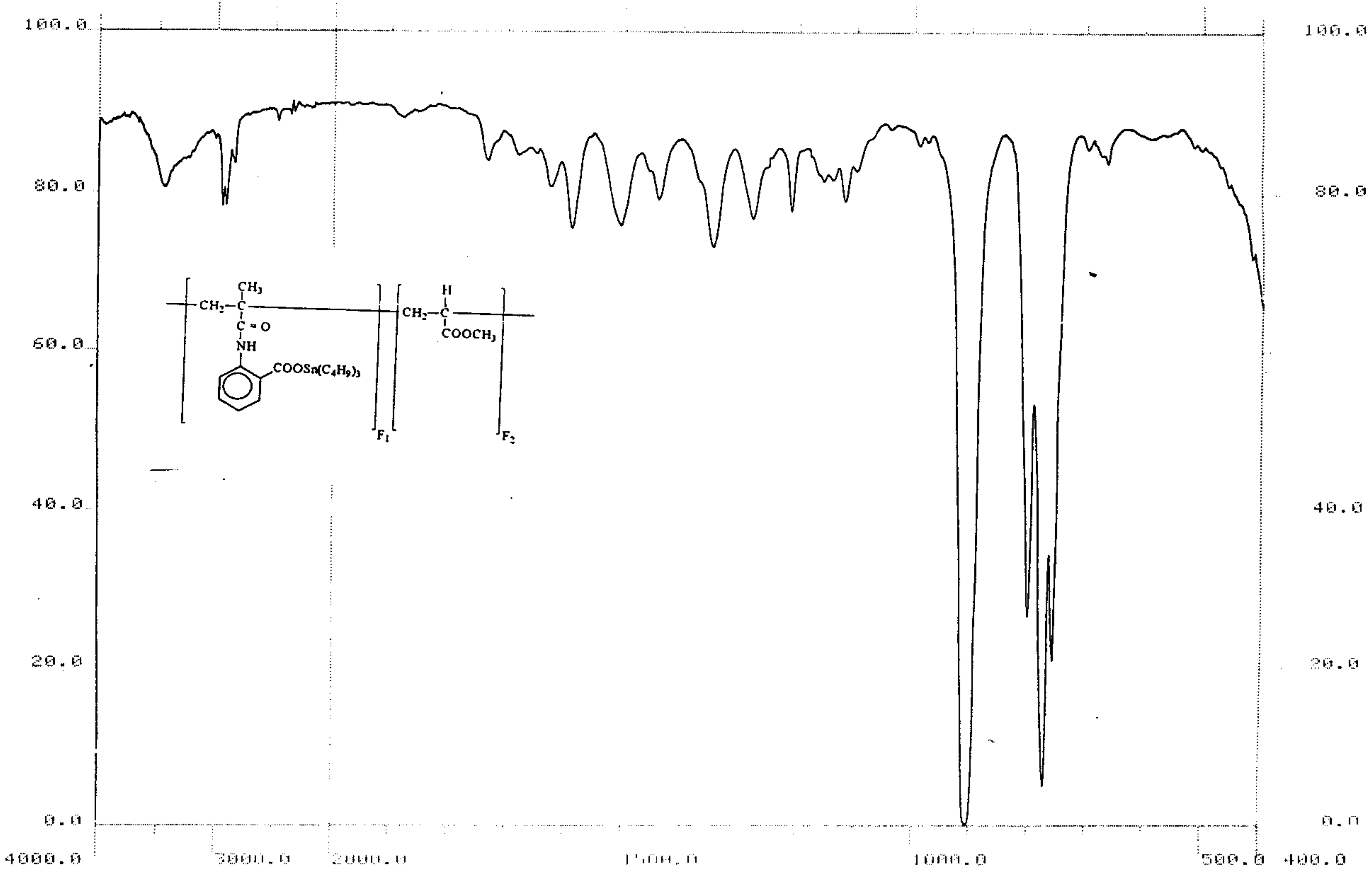


Fig. (6) : IR spectrum of o-MTBTB -MA copolymer.

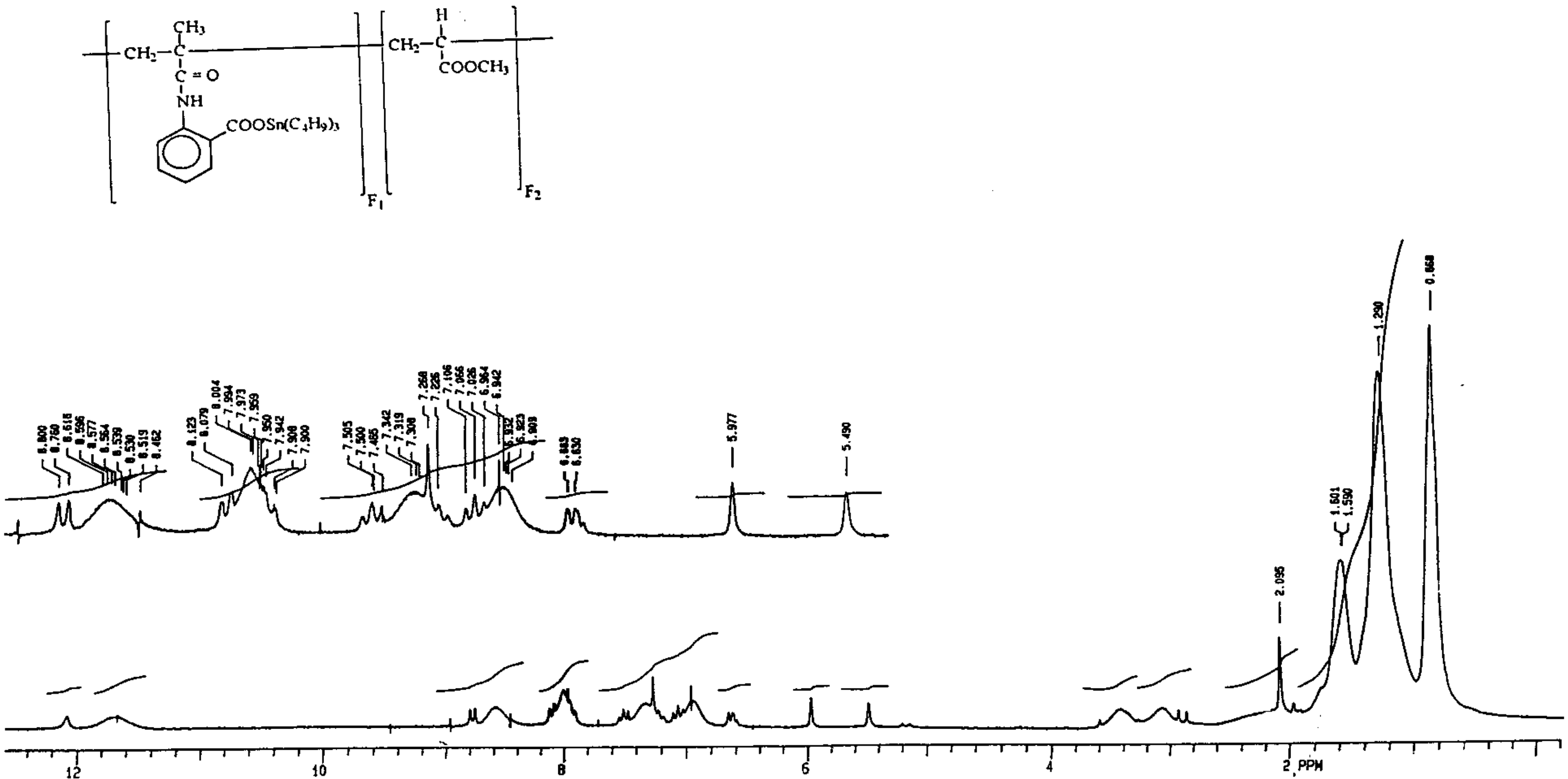


Fig. (7): ^{1}HNMR spectrum of o-MTBTB-MA copolymer.

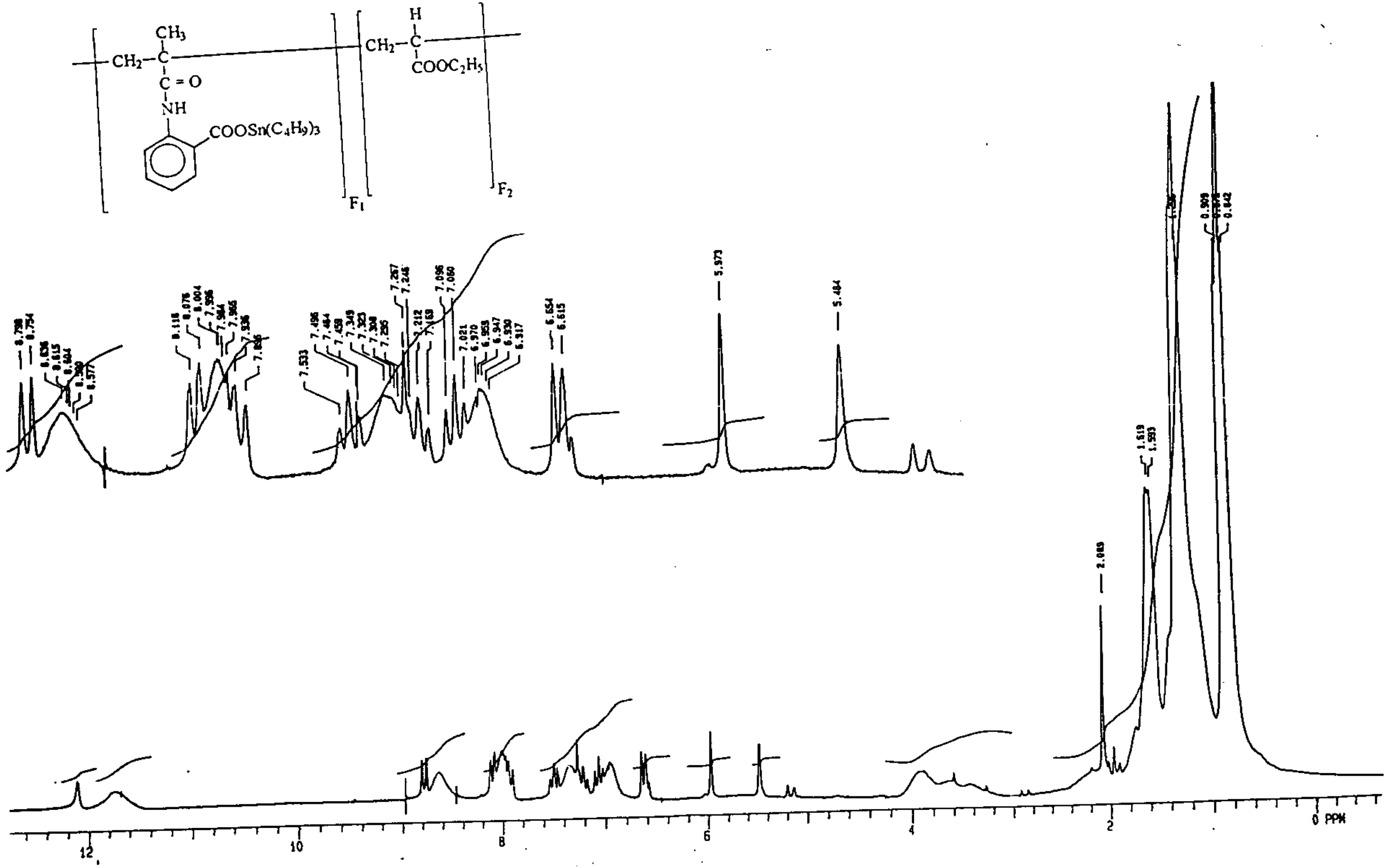


Fig. (9): ^{1}HNMR spectrum of o-MTBTB-EA copolymer.

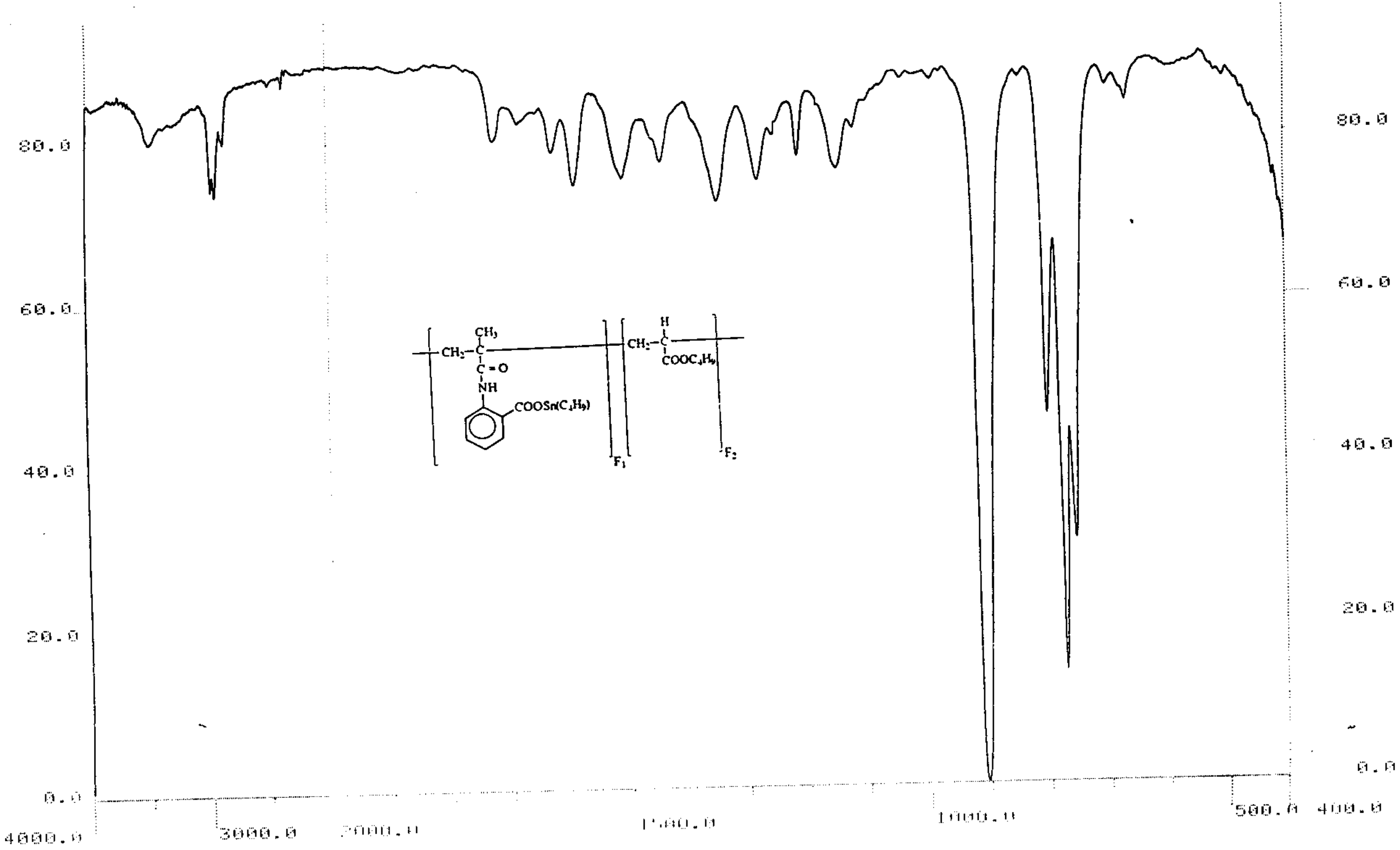


Fig. (10): IR spectrum of o-MTBTBA-BA copolymer.

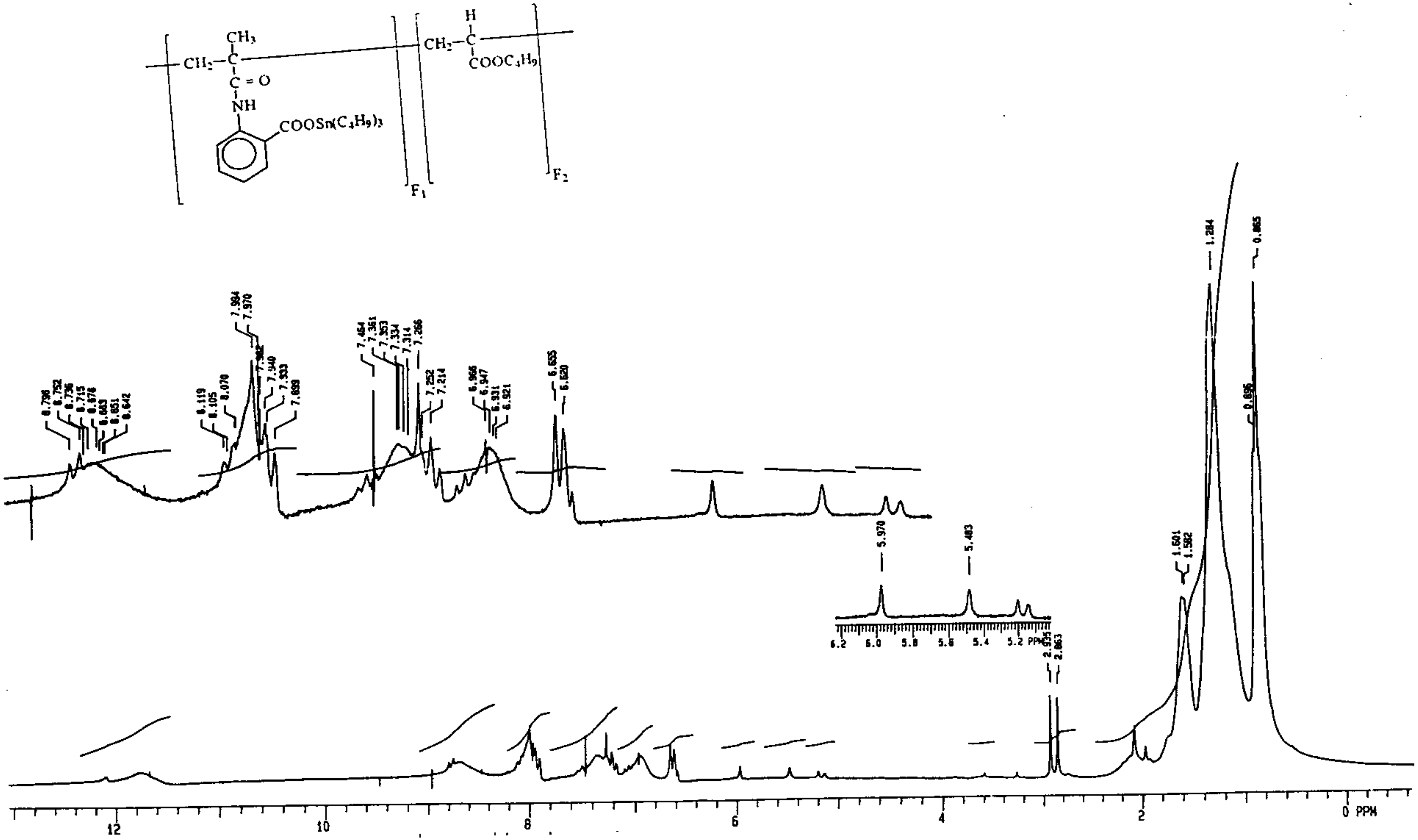


Fig. (11): ^{1}HNMR spectrum of o-MTBTA BA copolymer.

Table (1) : Copolymerization of o-MTBTB (M_1) with MA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tudos method	
a*	f_1^o			b*	F_1^o	a-a/b	a^2/b	η	ξ
2.3333	0.6999	6.2210	17.2900	0.4647	0.3172	- 2.6884	11.7173	- 0.1489	0.6492
1.8909	0.6500	7.3120	16.1000	0.3636	0.2666	- 3.3090	9.8325	- 0.2047	0.6083
1.5000	0.6000	8.2110	14.9100	0.2931	0.2266	- 3.6163	7.6748	- 0.2582	0.5479
1.2223	0.5500	7.2200	13.7200	0.2379	0.1921	- 3.9163	6.2808	- 0.3105	0.4979
1.0000	0.4997	5.6110	12.5300	0.1942	0.1626	- 4.1478	5.1478	- 0.3613	0.4484
0.8367	0.4500	8.2210	11.3400	0.1589	0.1371	- 4.4258	4.4030	- 0.4122	0.4101
0.6667	0.4364	7.2210	10.1500	0.1298	0.1148	- 4.4662	3.4219	- 0.4579	0.3508

* Molar ratio

o Mole fraction

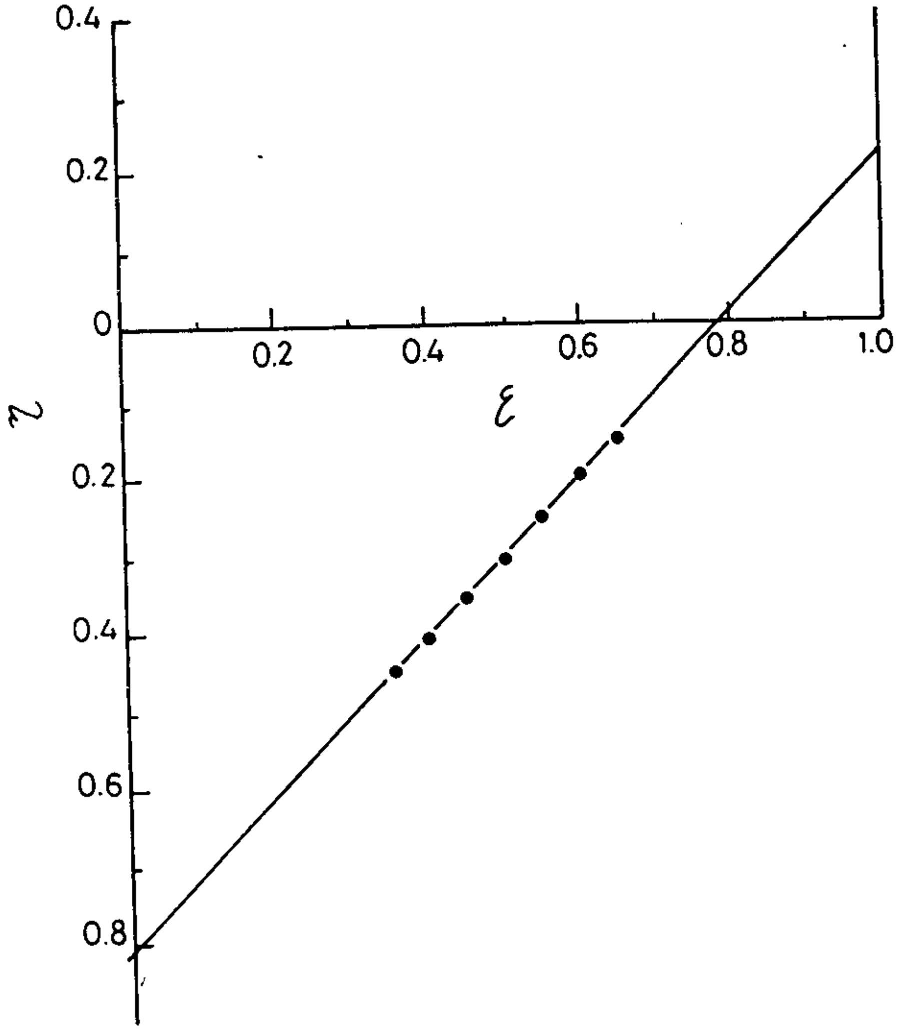


Fig. (12): Kelen-Tudos plot for copolymerization of o-MTBTB with MA.

$$\xi = \frac{a^2}{\alpha b + a^2} \text{ and } \eta = \frac{a\,(b-1)}{\alpha b + a^2}$$

Where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer respectively and

$$\alpha = \frac{a_{min.} \cdot a_{max.}}{(b_{min.} \cdot b_{max.})^{1/2}}$$

Table (2) : Copolymerization of o-MTBTB (M_1) with EA (M_2).

Initial monomer Composition		**Conversion**	**% Sn**	**Copolymer Composition**		**Fineman- Ross method**		**Kelen-Tudos method**	
a*	**f_1^o**	**%**		**b***	**F_1^o**	**a-a/b**	**a^2/b**	**λ**	**ξ**
2.3330	0.7000	7.0410	16.640	0.4730	0.3211	-2.5987	11.5082	- 0.1471	0.6516
1.8909	0.6320	7.0320	15.260	0.3765	0.2735	- 3.1313	9.4962	- 0.2000	0.6068
1.5000	0.6000	6.8210	14.260	0.3040	0.2331	- 3.4330	7.3995	- 0.2532	0.5459
1.2223	0.5500	8.3210	13.070	0.2477	0.1985	- 3.7118	6.0309	- 0.3046	0.4949
1.0000	0.4997	6.4210	11.880	0.2026	0.1684	- 3.9344	4.9344	- 0.3548	0.4450
0.8367	0.5452	7.3110	10.690	0.1658	0.1422	- 4.2120	4.2227	- 0.4057	0.4069
0.6667	0.3357	6.2210	9.0000	0.1350	0.1189	- 4.2699	3.2900	- 0.4520	0.3484

* Molar ratio

o Mole fraction

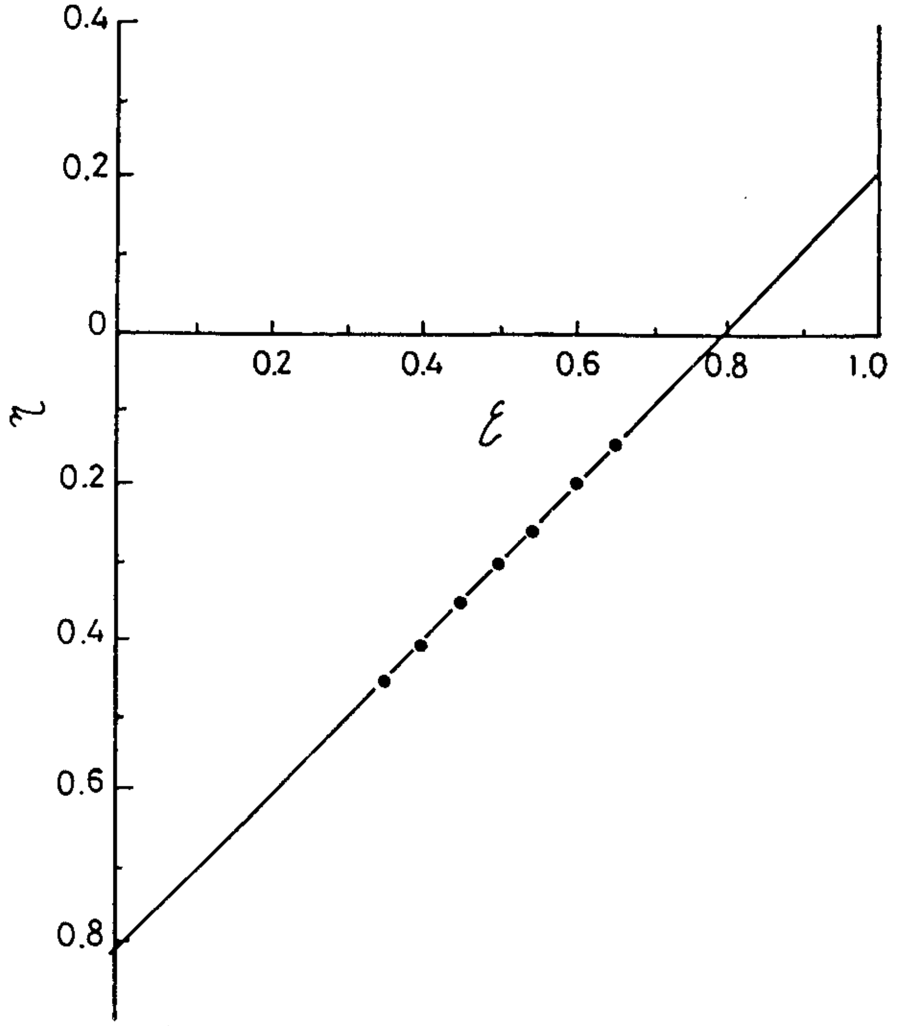


Fig. (13): Kelen-Tüdös plot for copolymerization of o-MTBTB with EA.

Table (3): Copolymerization of o-MTBTB (M_1) with (BA) M_2

Initial monomer composition		**Conversion**	**Sn%**	**Copolymer composition**		**Fineman-Ross method**		**Kelen-Tudos method**	
a*	**f_1^o**	**%**		**b***	**F_1^o**	**a-a/b**	**a^2/b**	**η**	**ξ**
2.3333	0.7000	7.2230	13.8010	0.3590	0.2641	-4.1652	15.1633	- 0.1785	0.6499
1.8909	0.6500	8.2130	12.6101	0.2931	0.2267	- 4.5558	12.1898	- 0.2238	0.5989
1.5000	0.6000	6.2670	11.4200	0.2399	0.1435	- 4.7521	9.3782	- 0.2708	0.5344
1.2223	0.5500	8.2210	10.2311	0.1960	0.1639	- 5.0127	7.6211	- 0.3174	0.4826
1.0000	0.5000	8.1670	9.0410	0.1593	0.1374	- 5.2793	6.2793	- 0.3654	0.4346
0.8367	0.4550	7.0140	7.8501	0.1279	0.1134	- 5.7020	5.4708	- 0.4180	0.4011
0.6667	0.3999	7.4211	6.6610	0.1010	0.0917	- 5.9330	4.3998	- 0.4720	0.3500

* Molar ratio

o Mole fraction

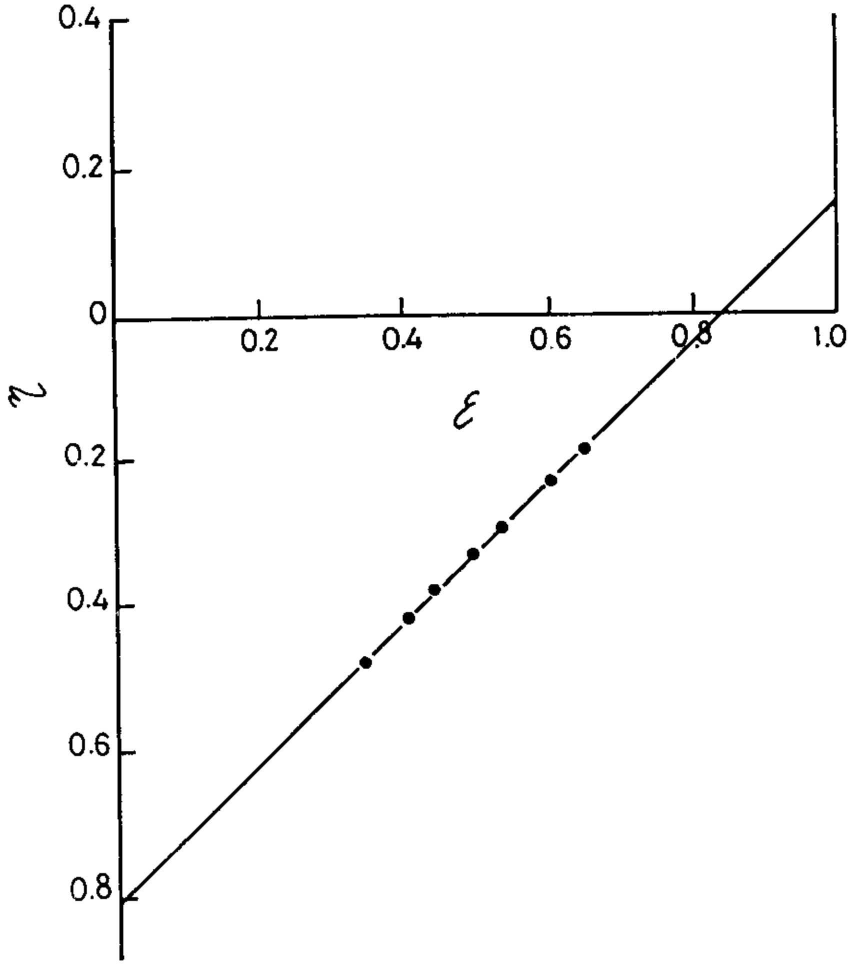


Fig. (14): Kelen-Tudos plot for copolymerization of o-MTBTB with BA.

Table (4) : Monomer reactivity ratio for copolymerization of o-MTBTB with MA, EA and BA.

$M_1 - M_2$	Fineman-Ross Method		Kelen-Tudos Method			
	r_1	r_2	r_1	r_2	r_1r_2	α
MTBTB – MA	0.252 ± 0.06	5.011 ± 0.05	0.250 ± 0.05	5.050 ± 0.04	1.2625	6.332
MTBTB –EA	0.241 ± 0.40	5.101 ± 0.03	0.210 ± 0.05	5.084 ± 0.04	1.0676	6.154
MTBTB-BA	0.175 ± 0.03	6.850 ± 0.03	0.150 ± 0.03	6.779 ± 0.04	1.01685	8.167

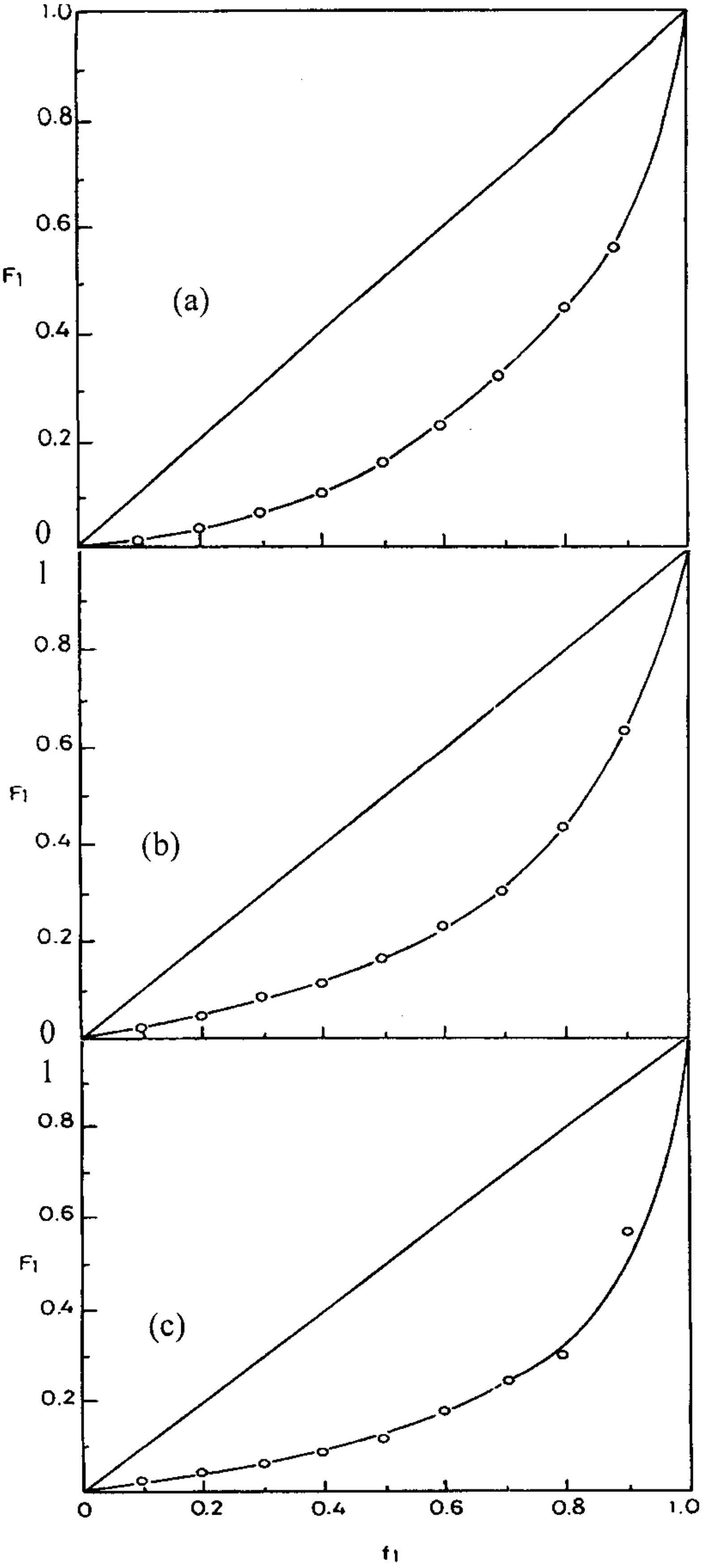


Fig. (15): Composition curves for copolymerization of (a) o-MTBTB monomer with MA, (b) o-MTBTB monomer with EA, and (c) o-MTBTB monomer with BA. Line represents calculated values and points correspond to experimental values

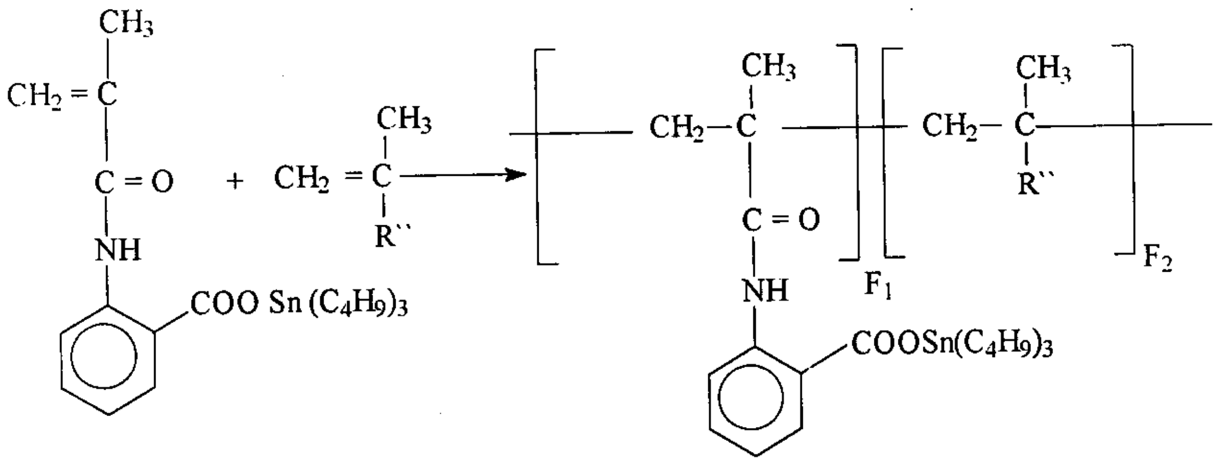
F_1 = molar fraction of M_1 in feed and

F_1 = molar fraction of M_1 in copolymer .

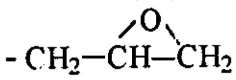
b-Copolymerization Reaction of o-Methacrylamido-tri-n-butyltin benzoate (MTBTB) with methacrylic esters.

Copolymerization of o-methacrylamido-tri-n-butyltinbenzoate with methyl methacrylate (MMA), butyl methacrylate (BMA) and glycidyl methacrylate (GMA).

The copolymerization of (o-MTBTB) with each MMA, BMA and GMA were carried out in DMF (1.5-mole/l) at 70°C in the presence of 1 mole of AIBN, the reaction can be represented as follows:



Where :

M_1 — M_2	R``
MTBTB-MMA	- $COOCH_3$
MTBTB-BMA	- $COOC_4H_9$
MTBTB-GMA	 $-CH_2-\overset{O}{CH-CH_2}$

The prepared copolymers were solids, soluble in most organic solvents, the structures of the copolymers (o-MTBTB-MMA, o-MTBTB-BMA and o-MTBTB–GMA) were studied and investigated by IR and ^{1}H-NMR.

Thus, the IR spectra Fig. (16) of the prepared copolymers are quite similar and show signals at ν_{CH} aliphatic in region (2900-2850) cm^{-1}, ν_{NH} at 3400 cm^{-1}, ν_{CH} aromatic at 3150 cm^{-1}, strong absorption band at 1720 cm^{-1} attributable to the carbonyl group of butyl ester and band at 1640 for the carbonyl amide.

The ^1H NMR spectra of o-MTBTB-MMA, o-MTBTB-BMA, and o-MTBTB-GMA [Fig. (17)] is similar and show the following signals aliphatic protons for CH_2, CH_3 appears δ (0.87-1.6) ppm in case of o-MTBTB-BMA.OCH_3 appears at δ 3.8, aromatic protons appear δ (7.1-8.8) ppm and amidic proton appears at δ 12.1.

The results of the copolymerization reaction (o-MTBTB-MMA), (o-MTBTB-BMA) and (o-MTBTB-GMA) were illustrated in tables (5-7). The monomer reactivity ratios for each system were calculated by both Finemon-Ross and Kelen-Tudos described in page (16) and the standard deviation of the results were calculated by regression analysis Figs. (19, 20) illustrate the Kelen-Tudos plots of three systems which give r_1 and $-r_2 / \alpha$, both as intercepts and the results are summarized in Table (8) which show that there is a good agreement between the value of the reactivity ratios calculated by the two methods. Also, the range of experimental error in r_1 and r_2 is quite small. Table (8) shows that the monomer reactivity ratio value of (o-MTBTB) (r_1) for all systems studied are nearly equal to zero which indicates that the growing radical ending with MTBTB unit prefer M_2 monomers than M_1 monomer in propagation stage.

Fig (21) illustrates the composition curves of the binary systems and that all systems studied don't give azeotropic compositions and also show that the copolymers produced have a lower content of F_1 than the commoner mixtures.

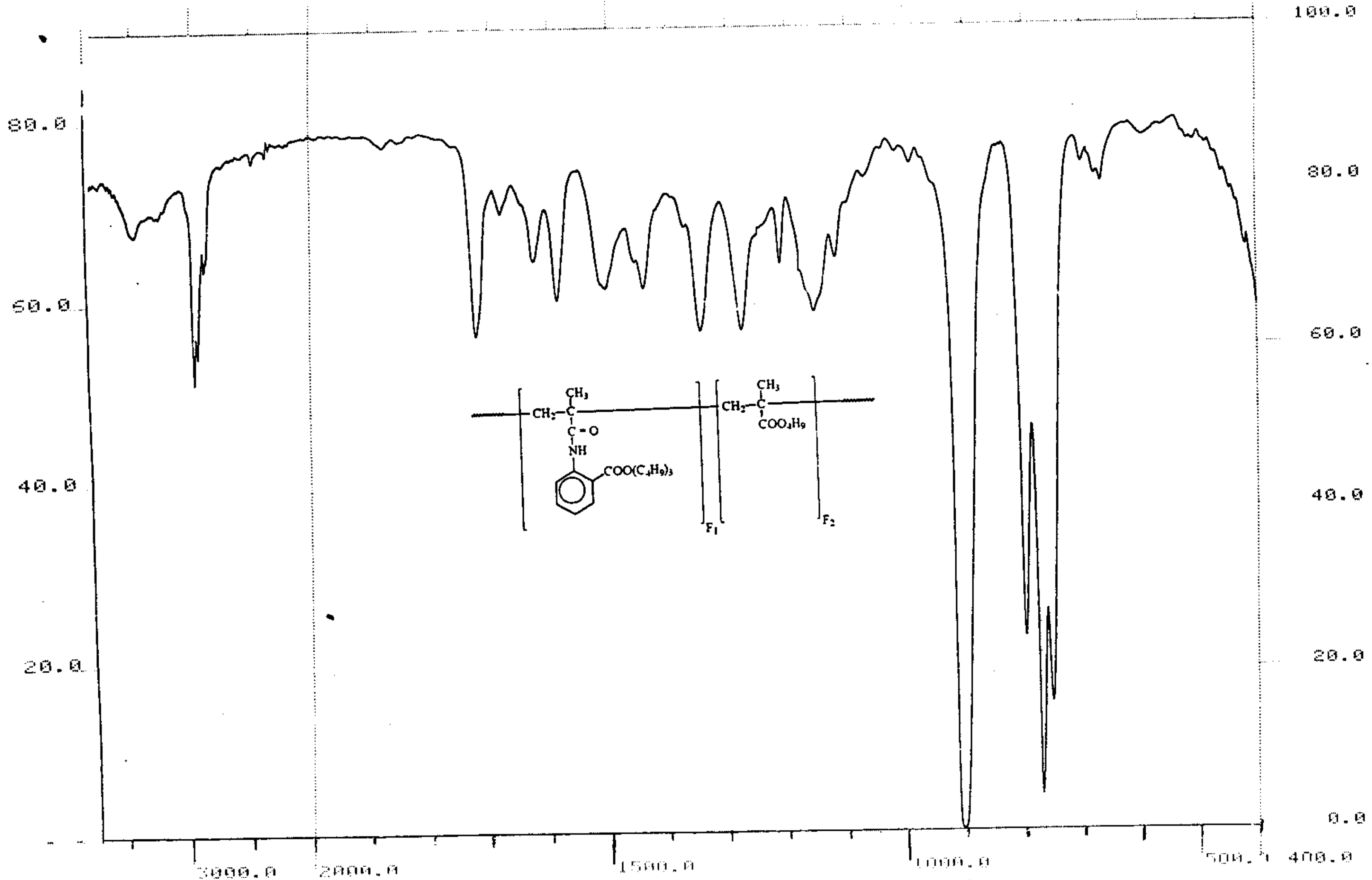


Fig.(16): IR spectrum of o-MTBTB-BMA copolymer.

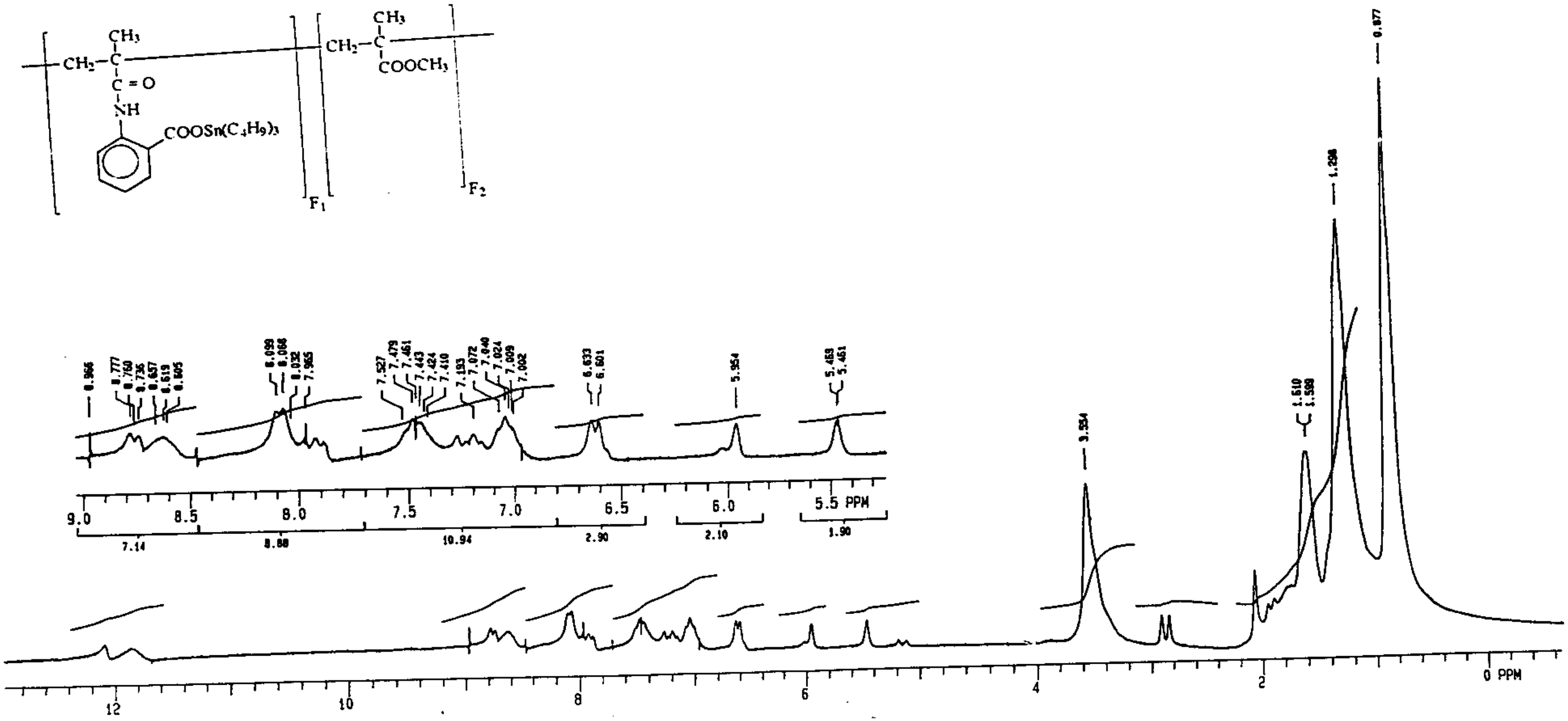


Fig. (17): ^{1}HNMR spectrum of o-MTBTB-MMA copolymer.

Table (5) : Copolymerization of o-MTBTB (M_1) with MMA (M_2)

Initial monomer composition		**Conversion**	**Sn%**	**Copolymer composition**		**Fineman-Ross method**		**Kelen-Tudos method**	
a*	**f_1^o**	**%**		**b***	**F_1^o**	**a-a/b**	**a^2/b**	**η**	**ξ**
2.3333	0.7000	7.3310	15.1001	0.3528	0.2608	- 4.2793	15.4295	- 0.1811	0.6530
1.8909	0.6500	6.2310	13.9110	0.2859	0.2223	- 4.7230	12.5076	- 0.2281	0.6040
1.5000	0.6000	7.2410	12.7200	0.2332	0.1891	- 4.9300	9.6450	- 0.2763	0.5406
1.2223	0.5499	7.3310	11.5310	0.1909	0.1603	- 5.1801	7.8258	- 0.3230	0.4884
1.0000	0.5000	8.2110	10.4311	0.1560	0.1350	- 5.4081	6.4081	- 0.3703	0.4388
0.8367	0.4500	7.2410	9.1501	0.1269	0.1126	- 5.7870	5.5182	- 0.4148	0.4023
0.6667	0.3999	7.5610	7.9602	0.1020	0.0926	- 5.8654	4.3548	- 0.4673	0.3469

* Molar ratio

o Mole fraction

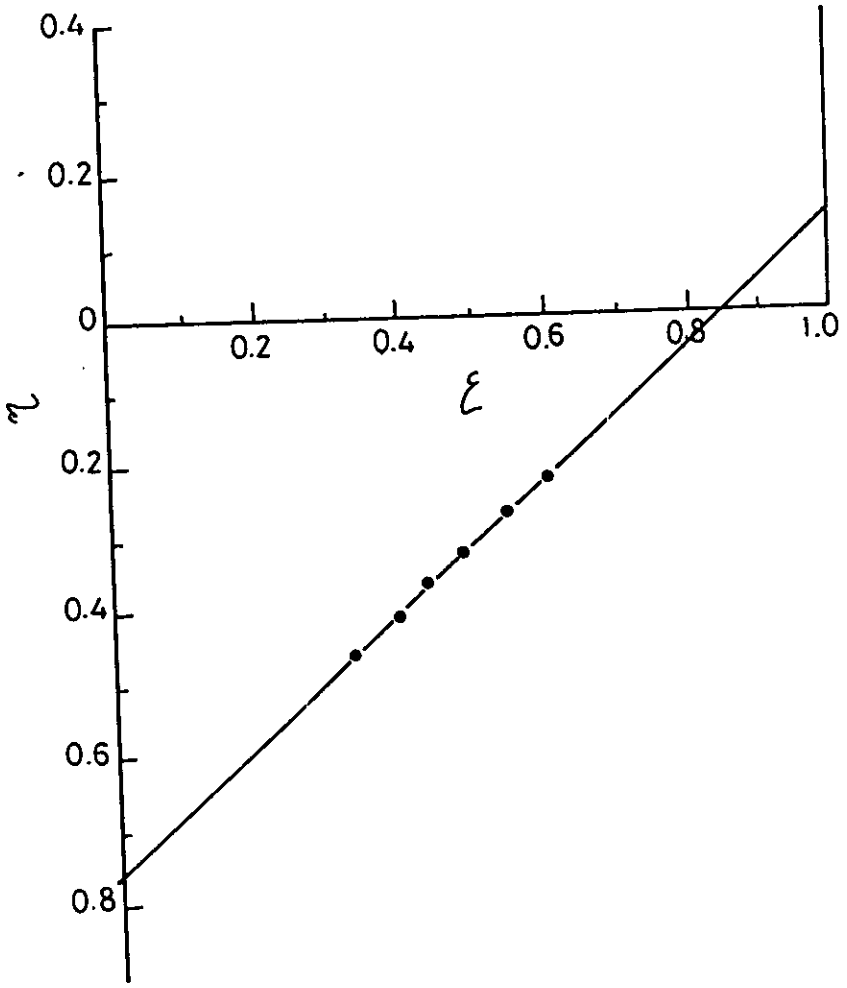


Fig. (19): Kelen-Tudos plot for copolymerization of o-MTBTB with MMA.

Table (6) : Copolymerization of o-MTBTB (M_1) with GMA (M_2).

Initial monomer Composition		**Conversion**	**Sn%**	**Copolymer composition**		**Fineman-Ross method**		**Kelen-Tudos method**	
A*	**F_1^o**	**%**		**b***	**F_1^o**	**a-a/b**	**a^2/b**	**λ**	**ξ**
2.3330	0.7000	8.3210	13.9011	0.4051	0.2883	- 3.4568	13.4377	- 0.1656	0.6498
1.8909	0.6500	7.5110	12.7100	0.3306	0.2485	- 3.8278	10.8133	- 0.2119	0.5988
1.5000	0.600	6.2310	11.5201	0.2706	0.2130	- 4.0432	8.3147	- 0.2590	0.5344
1.2223	0.5500	6.7210	10.3000	0.2211	0.1810	- 4.3039	6.7544	- 0.3074	0.4825
1.0000	0.5000	7.2110	9.1410	0.1798	0.1524	- 4.5619	5.5619	- 0.3562	0.4343
0.8367	0.4500	7.2110	7.9300	0.1440	0.1259	- 4.9702	4.8585	- 0.4108	0.4014
0.6667	0.4000	6.3120	6.7612	0.1144	0.1026	- 5.1617	3.8856	- 0.4638	0.3491

* Molar ratio

o Mole fraction

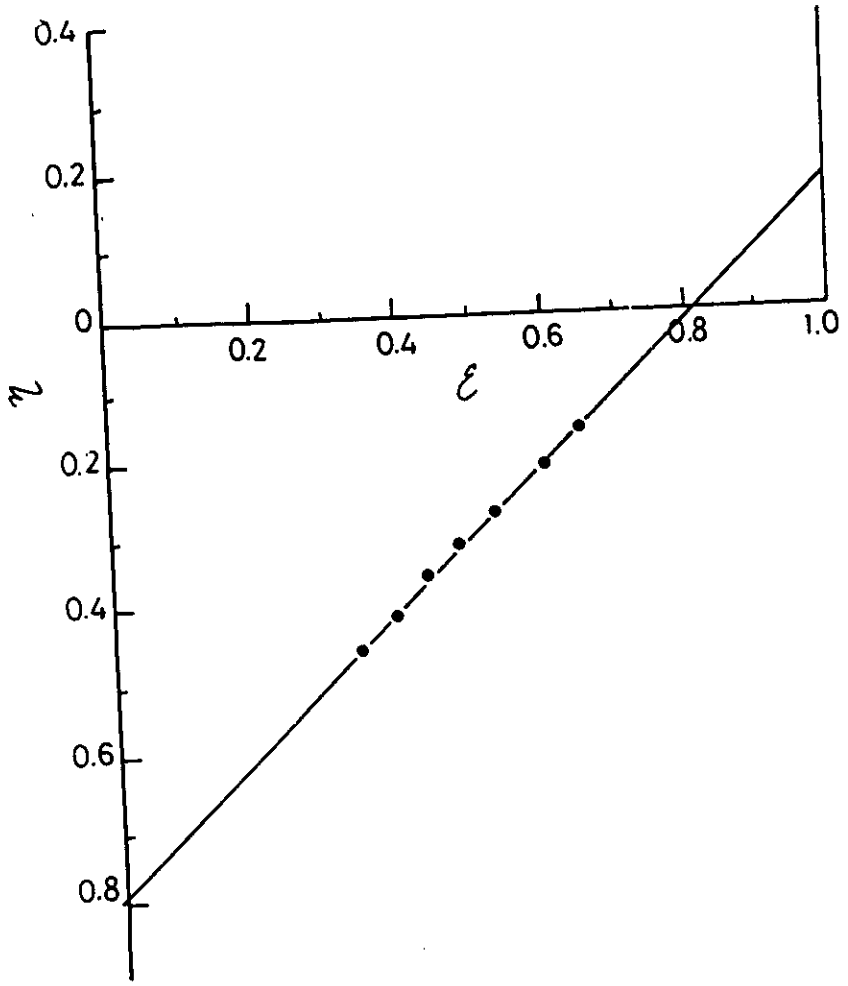


Fig. (20): Kelen-Tudos plot for copolymerization of o-MTBTB with GMA.

Table (7): Copolymerization of o-MTBTB (M_1) with B MA(M_2)

Initial monomer composition		Conversion %	%Sn	Copolymer composition		Fineman-Ross method		Kelen-Tudos method	
a*	F_1^o			b*	F_1^o	a-a/b	a^2/b	λ	ξ
2.3330	0.7000	8.3210	14.6200	0.4598	0.3150	- 2.7412	11.8408	- 0.1510	0.6538
1.8909	0.6320	7.7120	13.4310	0.3781	0.2743	- 3.1674	9.5646	- 0.1995	0.6025
1.5000	0.600	6.4220	12.2400	0.3055	0.2340	- 3.4089	7.3634	- 0.2493	0.5385
1.2223	0.5500	6.1590	11.0500	0.2500	0.2000	- 3.6656	5.9746	- 0.2984	0.4863
1.0000	0.4997	5.3110	9.8600	0.2040	0.1694	- 3.8529	4.8529	- 0.3479	0.4371
0.8367	0.5452	7.3410	8.6710	0.1653	0.1416	- 4.2248	4.2348	- 0.4006	0.4016
0.6667	0.3357	6.5510	7.4800	0.1322	0.1168	- 4.3761	3.3618	- 0.4500	0.3476

* Molar ratio

o Mole fraction

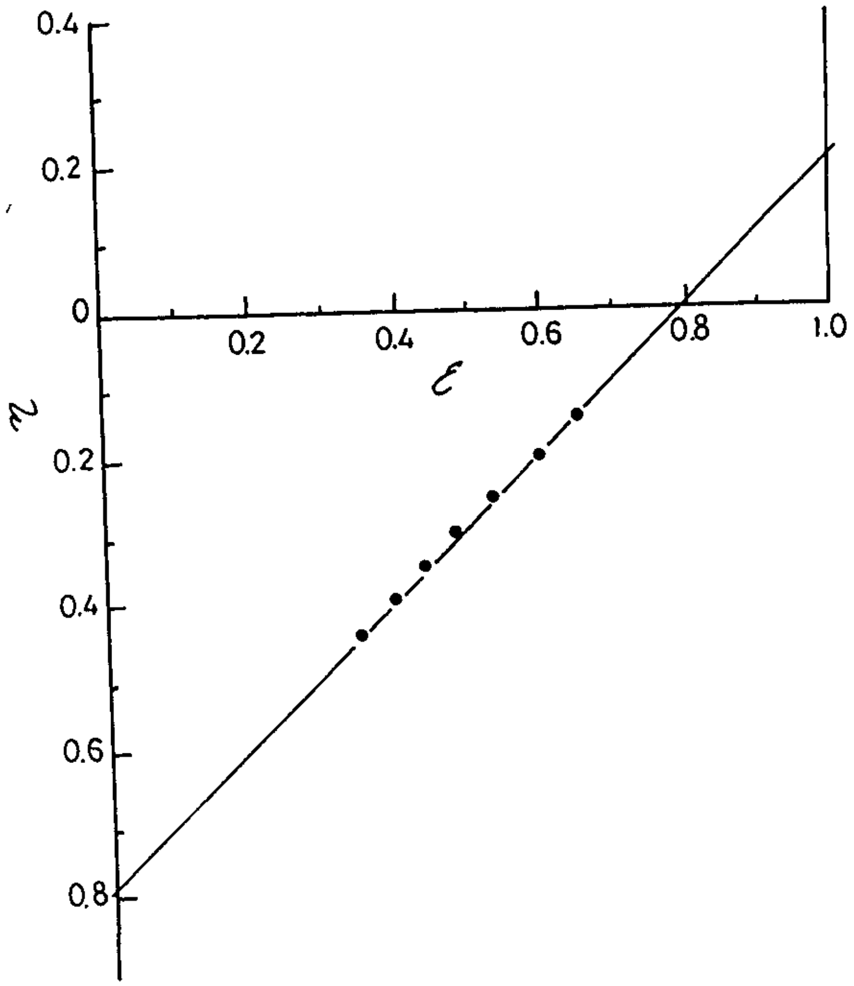


Fig. (21): Kelen-Tudos plot for copolymerization of o-MTBTB with BMA.

Table (8) : Monomer reactivity ratio for copolymerization of o-MTBTB with MMA, BMA and GMA.

$M_1 - M_2$	Fineman-Ross Method		Kelen-Tudos Method			
	r_1	R_2	r_1	r_2	$r_1\ r_2$	α
MTBTB – MMA	0.160 ± 0.05	6.311 ± 0.06	0.140 ± 0.07	6.223 ± 0.04	0.871	8.197
MTBTB –GMA	0.191 ± 0.40	5.801 ± 0.03	0.170 ± 0.04	5.722 ± 0.03	0.972	4.243
MTBTB-BMA	0.240 ± 0.03	5.010 ± 0.02	0.200 ± 0.03	4.921 ± 0.04	0.984	6.309

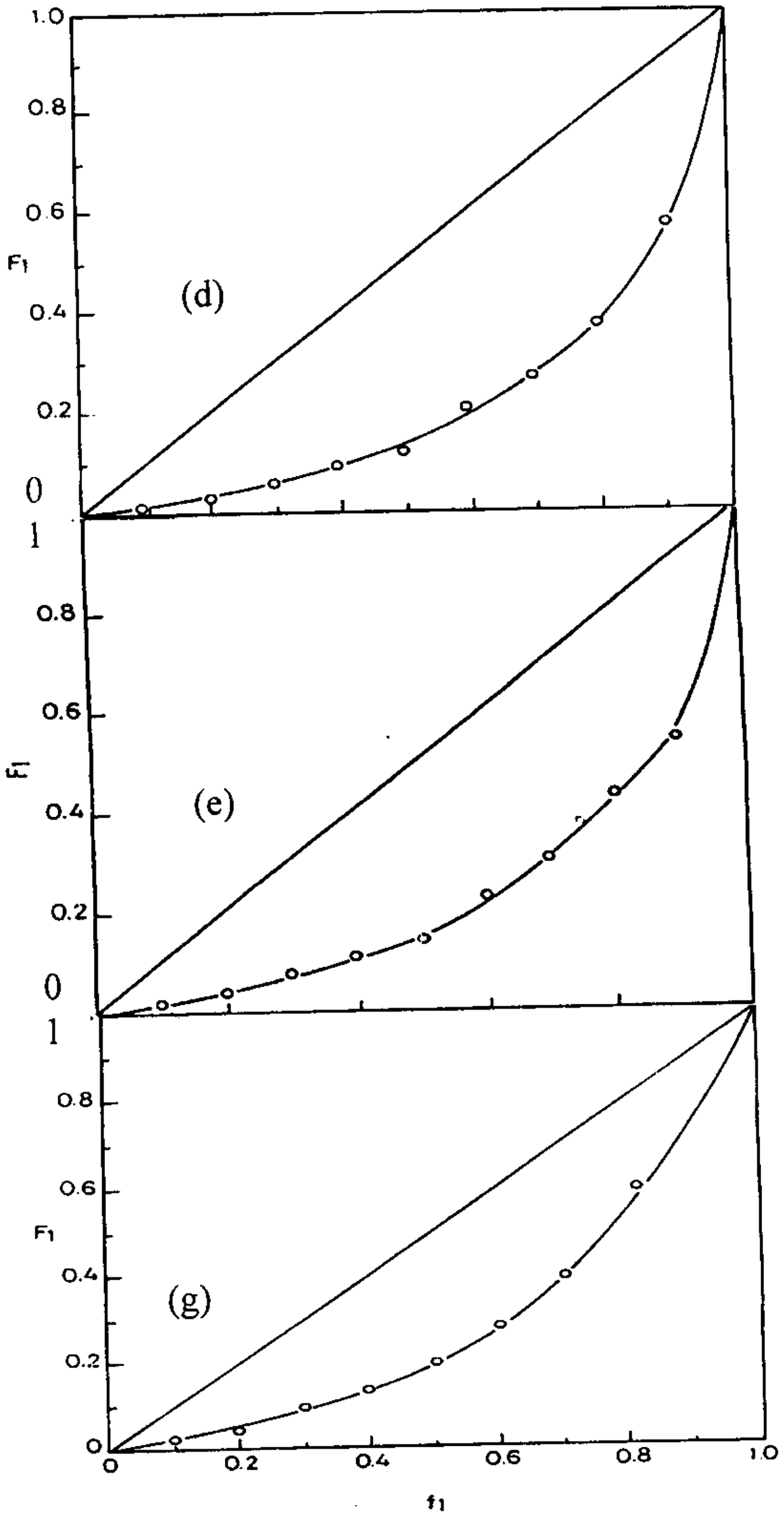


Fig. (21): Composition curves for copolymerization of

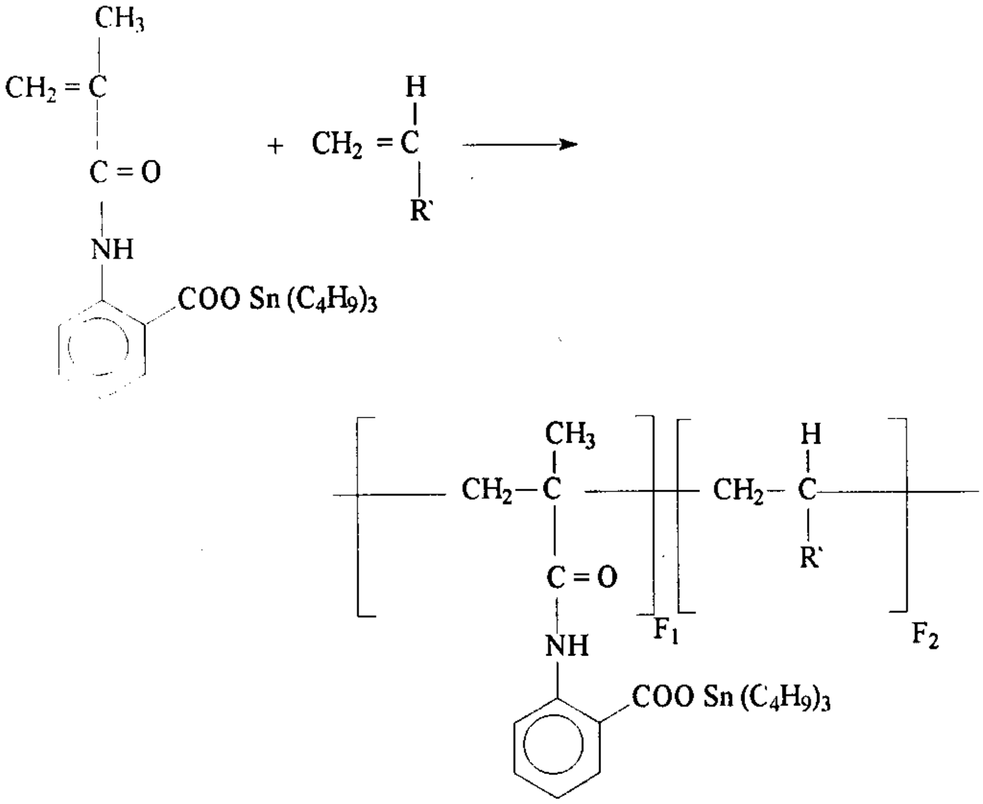
(d) o-MTBTB monomer with MMA, (e) o-MTBTB monomer with BMA, and (g) o-MTBTB monomer with GMA. Line represents calculated values and points correspond to experimental values

F_1 = molar fraction of M_1 in feed and

F_1 = molar fraction of M_1 in copolymer .

C-Copolymerization Reaction of o-methacrylamido-tri-n-butyltin benzoate (O-MTBTB) with different monomers:

Copolymerization of o-methacrylamido-tri-n-butyltinbenzoate with Styrene (ST), Acrylnitryle (AN) and vinylacetate (VA) was carried out in DMF (1.5 mole/l) at 70°C in the presence of AIBN, and the reaction can be represented as:



Where:

M_1 — M_2	R`
o-MTBTB-ST	- C_6H_5
o-MTBTB-AN	- $C \equiv N$
o-MTBTB-VA	- $O\text{-}CO\text{-}CH_3$

The prepared copolymers were solid, soluble in most organic solvents and the structure of the copolymers produced was investigated by IR and ^{1}H-NMR.

Thus, the IR spectra Figs. (22,24) show the following characteristic bands ν_{NH} amide and ν_{CH} aromatic between (3400-3200) cm^{-1}, ν_{CH} aliphatic (2900-2850), $\nu_{C=O}$ amide at 1640 cm^{-1} and there is an additional signal at 2230 cm^{-1} due to $\nu_{C=N}$.

The ^{1}H-NMR spectra of o-MTBTB-ST, o-MTBTB-AN and o-MTBTB-VA [Figs (23, 25)] are similar and show the following signals at δ (0.8-1.8) of aliphatic protons, for tri-n-butyle, 2CH$_2$ and CH$_3$, δ 2.1 (S, 1H, CH) for methine proton, δ (6.6-8.8) for aromatic protons and amide proton appear at δ 12.1 (S, 1H, NH).

Results of the copolymerization reactions are illustrated in Tables (9-11). The monomer reactivity ratios for each copolymer system were calculated by both Fineman-Ross and Kelen-Tudos described in page (16) and the standard deviation of the results were calculated by regression analysis. Figs. (26-28) illustrate the Kelen-Tudos plots of the three systems studied which give r_1 and $-r_2 / \alpha$, both as intercepts. The results are summarized in Table (12) which show that there is a good agreement between the values of the reactivity ratios calculated by the two methods. Also the range of experimental error in r_1 and r_2 is quite small. Table (12) shows that the monomer reactivity ratio value of (o-MTBTB), r_1 for all systems studied are very low which indicates that the growing radical ending with o-MTBTB unit prefers M_2 monomer than M_1 in propagation stage. Fig. (29) illustrates the composition curves of the binary systems which don't give any azeotropic compositions and also shows that the copolymer produced have a lower content of F_1 than the comonomer mixture.

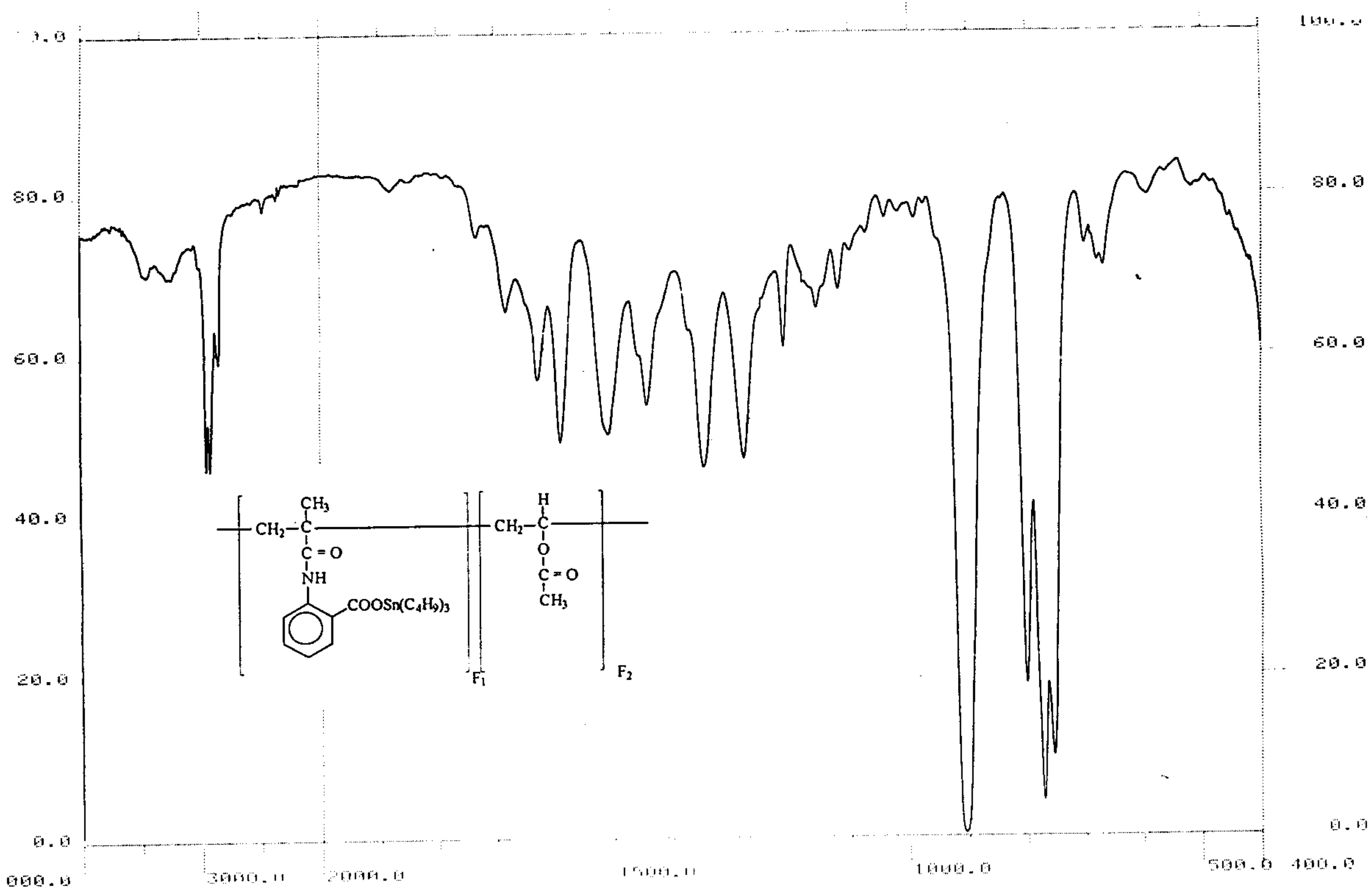


Fig. (24): IR spectrum of o-MTBTB-VA copolymer.

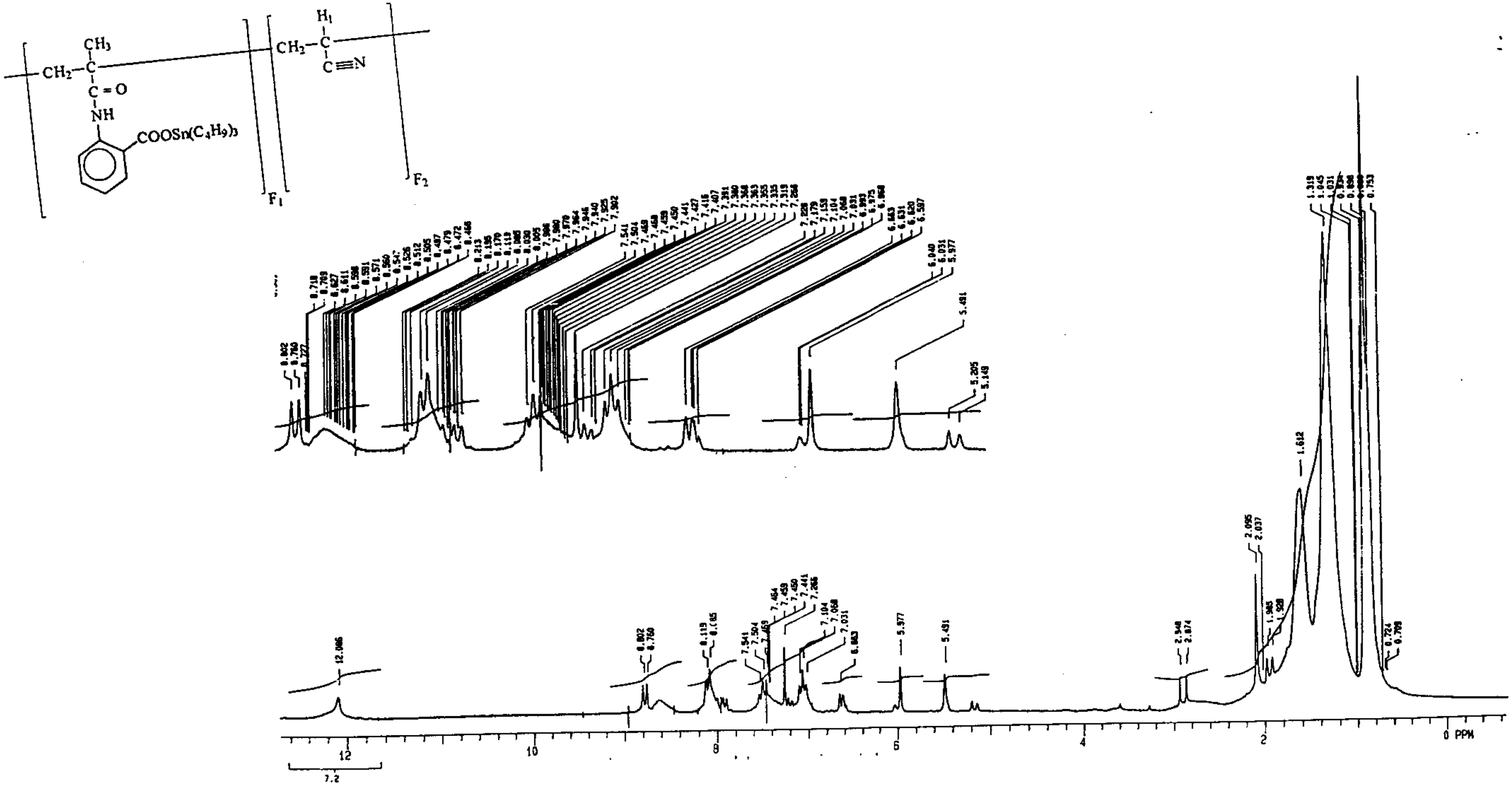


Fig (25) : ^{1}HNMR spectrum of o-MTBTB-AN copolymer.

Table (9) : Copolymerization of o-MTBTB (M_1) with ST (M_2)

Initial monomer Composition		**Conversion**	**Sn%**	**Copolymer composition**		**Fineman-Ross method**		**Kelen-Tudos method**	
a*	**f_1^o**	**%**		**b***	**F_1^o**	**a-a/b**	**a^2/b**	**η**	**ξ**
2.3333	0.6999	7.3451	16.2300	0.4535	0.3120	- 2.8109	12.0033	- 0.1528	0.6525
1.8909	0.6500	7.3122	15.0401	0.36301	0.2663	- 3.3168	9.8471	- 0.2042	0.6063
1.5000	0.6049	8.1111	13.8511	0.2942	0.2273	- 3.5964	7.4536	- 0.2562	0.5446
1.2223	0.5714	6.2312	12.6601	0.2402	0.1937	- 3.8659	6.2145	- 0.3065	0.4932
1.0000	0.500	7.3413	11.4700	0.1967	0.1644	- 4.0839	5.0839	- 0.3559	0.4430
0.8367	0.450	6.5214	10.2902	0.1607	0.1385	- 4.3707	4.3569	- 0.4066	0.4053
0.6667	0.3999	7.4511	9.0901	0.1306	0.1155	- 4.4393	3.4040	- 0.4532	0.3432

* Molar ratio

o Mole fraction

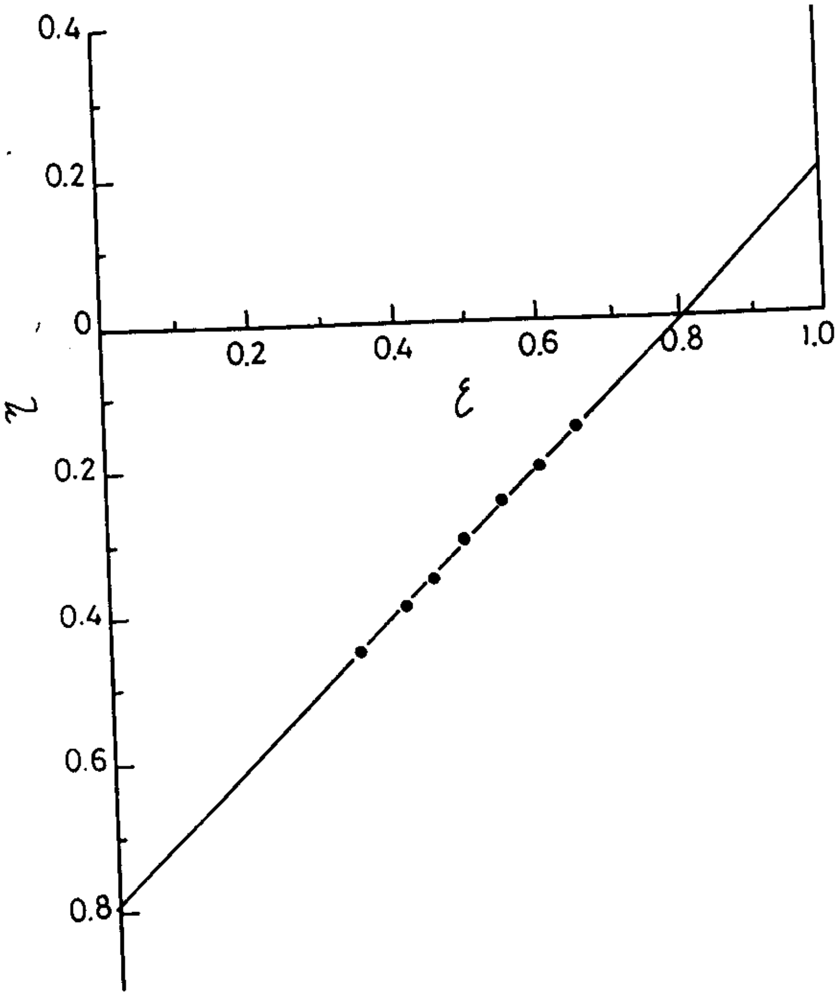


Fig. (26): Kelen-Tudos plot for copolymerization of o-MTBTB with ST.

Table (10) : Copolymerization of o-MTBTB (M_1) with AN (M_2)

Initial monomer composition		Converion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tudos method	
a*	f_1^o			b*	F_1^o	a-a/b	a^2/b	η	ξ
2.3333	0.7000	8.3111	18.4010	0.3676	0.2688	- 4.0134	14.8090	- 0.1740	0.6421
1.8909	0.6547	6.8911	17.2100	0.2815	0.2197	- 4.8242	12.6976	- 0.2302	0.6061
1.5000	0.6021	7.3421	16.0202	0.2219	0.1816	- 5.2593	10.1389	- 0.2859	0.5513
1.0000	0.5499	7.4411	14.8301	0.1781	0.1512	- 5.6439	8.3879	- 0.3392	0.5041
1.2223	0.5000	6.3412	13.6412	0.1446	0.1263	- 5.9156	6.9156	- 0.3900	0.4559
0.8367	0.4500	7.6781	12.4500	0.1181	0.1056	- 6.2465	5.9264	- 0.4406	0.4180
0.6667	0.4000	8.1234	11.2610	0.0967	0.0882	- 6.2290	4.5972	- 0.4848	0.3578

* Molar ratio

o Mole fraction

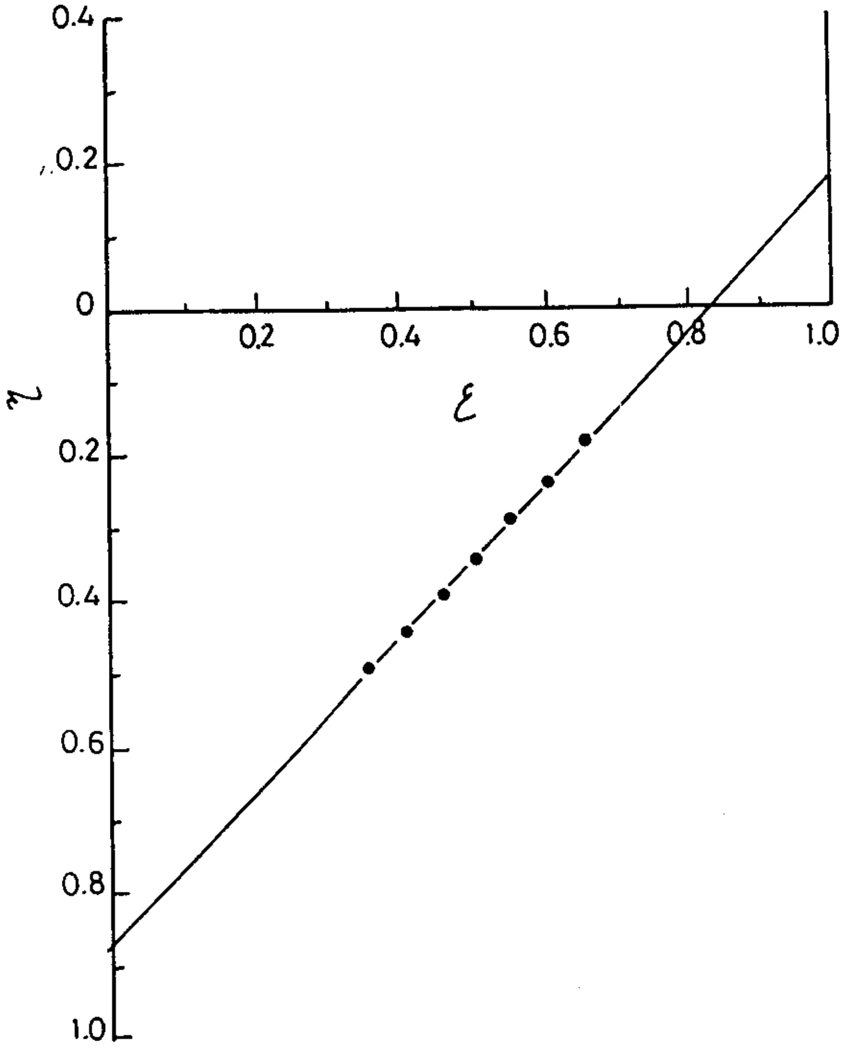


Fig. (27): Kelen-Tudos plot for copolymerization of o-MTBTB with AN.

Table (11) : Copolymerization of o-MTBTB (M_1) with VA(M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tudos method	
a*	f_1^o			b*	F_1^o	a-a/b	a^2/b	η	ξ
2.3333	0.7000	7.3321	16.7010	0.4113	0.2914	- 3.3384	13.2341	- 0.1643	0.6513
1.8909	0.6500	7.8913	15.5100	0.3271	0.2465	- 3.8898	10.9306	- 0.21594	0.6066
1.5000	0.6000	8.5611	14.3201	0.2640	0.2089	- 4.1815	8.5222	- 0.2623	0.5347
1.0000	0.5490	6.7382	13.1311	0.2150	0.1769	- 4.4653	6.9579	- 0.3182	0.4952
1.2223	0.5000	7.3271	11.9410	0.1759	0.1496	- 4.6855	5.6855	- 0.3669	0.4452
0.8367	0.4500	6.8912	10.7501	0.1439	0.1258	- 4.9779	4.8649	- 0.4166	0.4071
0.6667	0.3999	7.3310	9.5600	0.1173	0.1049	- 5.0189	3.7903	- 0.4616	0.3486

* Molar ratio

o Mole fraction

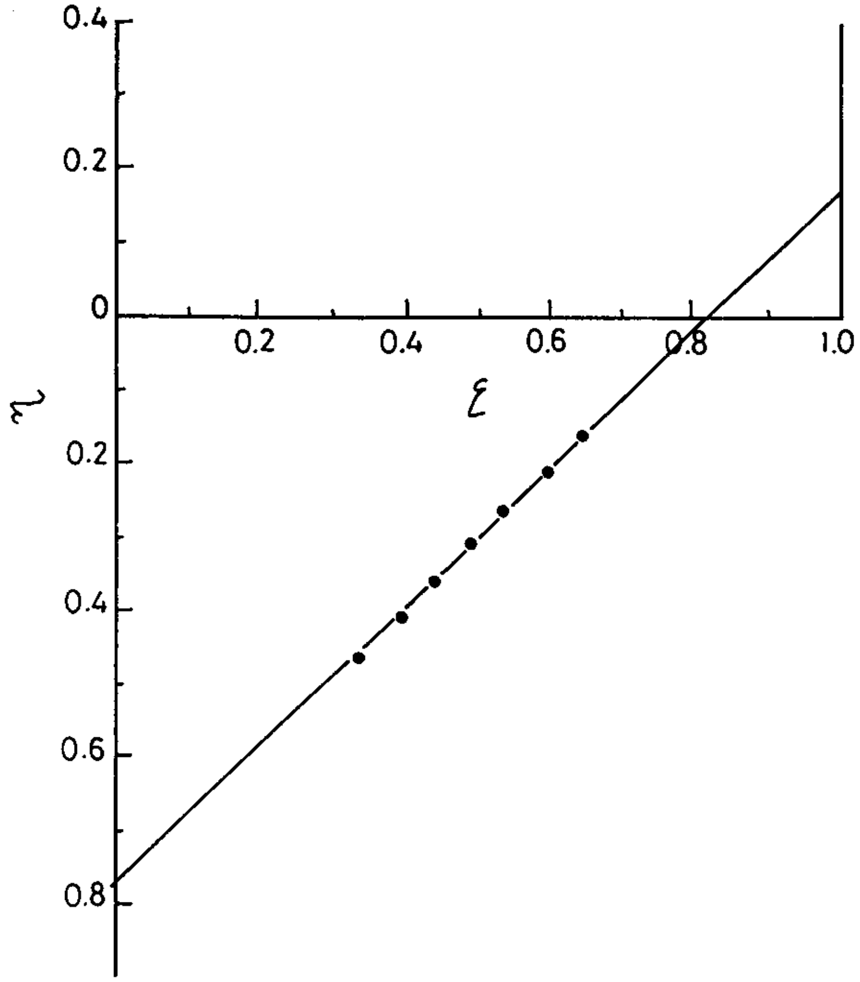


Fig. (28): Kelen-Tudos plot for copolymerization of o-MTBTB with VA.

Table (12) : Monomer reactivity ratio for copolymerization of o-MTBTB with ST, AN and VA.

$M_1 - M_2$	**Fineman-Ross Method**		**Kelen-Tudos Method**			
	r_1	r_2	r_1	r_2	$r_1\ r_2$	α
MTBTB – ST	0.21 ± 0.04	5.06 ± 0.05	0.19 ± 0.05	5.04 ± 0.06	0.96	6.39
MTBTB –AN	0.20 ± 0.03	6.06 ± 0.03	0.18 ± 0.04	6.44 ± 0.04	1.16	8.25
MTBTB-VA	0.17 ± 0.04	5.50 ± 0.02	0.16 ± 0.03	5.45 ± 0.04	0.87	7.08

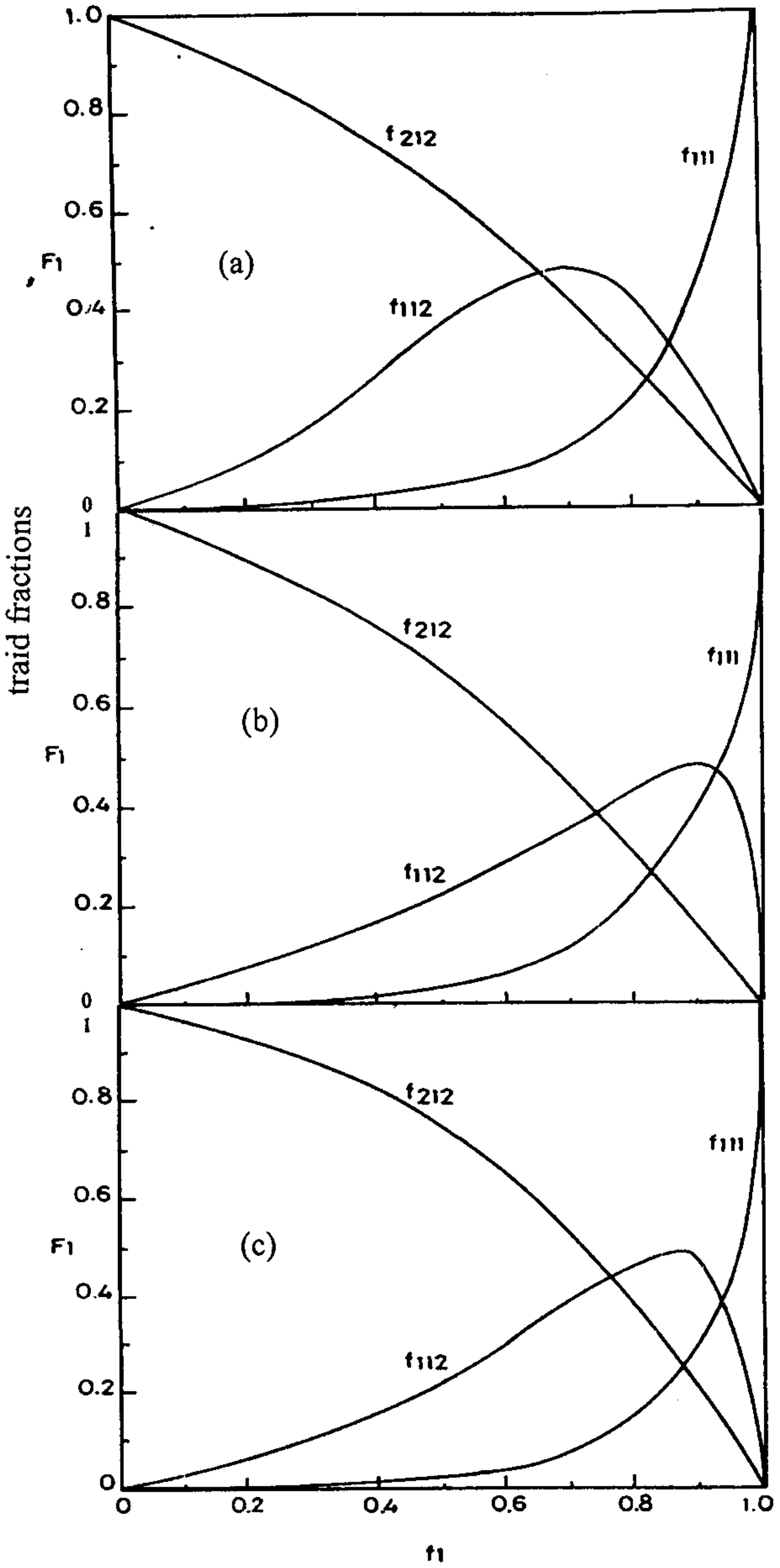


Fig. (30) ; Dependance of traid fraction f_{111}, f_{112} and f_{212} on comonomer composition for
(a) o- MTBT B with MA, (b) o- MTBTB with EA,
(c) o- MTBTB with BA

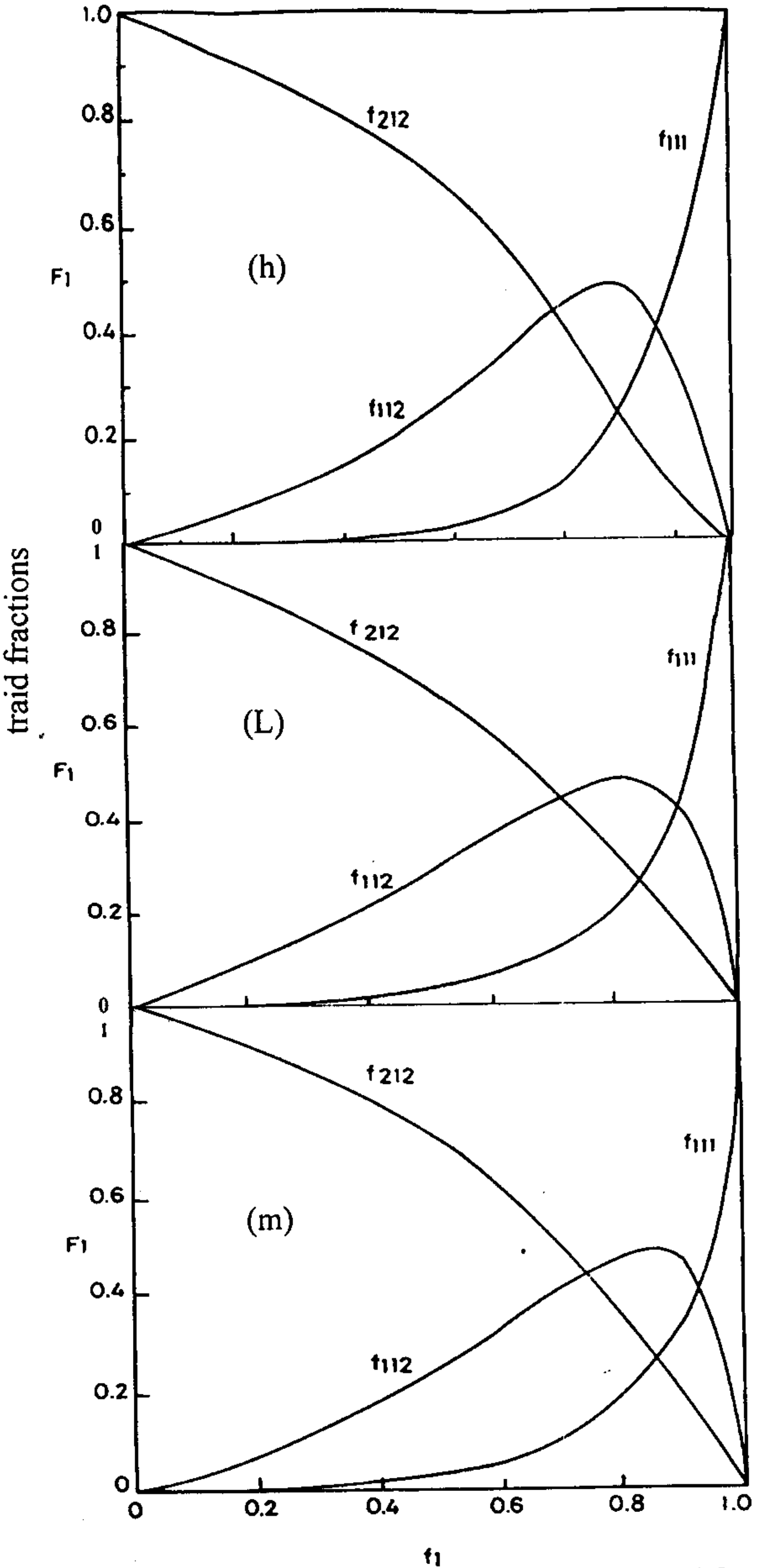


Fig. (31)' : Dependance of traid fraction f_{111}, f_{112} and f_{212} on comonomer composition for
(h) o- MTBT B with MMA, (l) o- MTBTB with BMA,
(m) o- MTBTB with GMA.

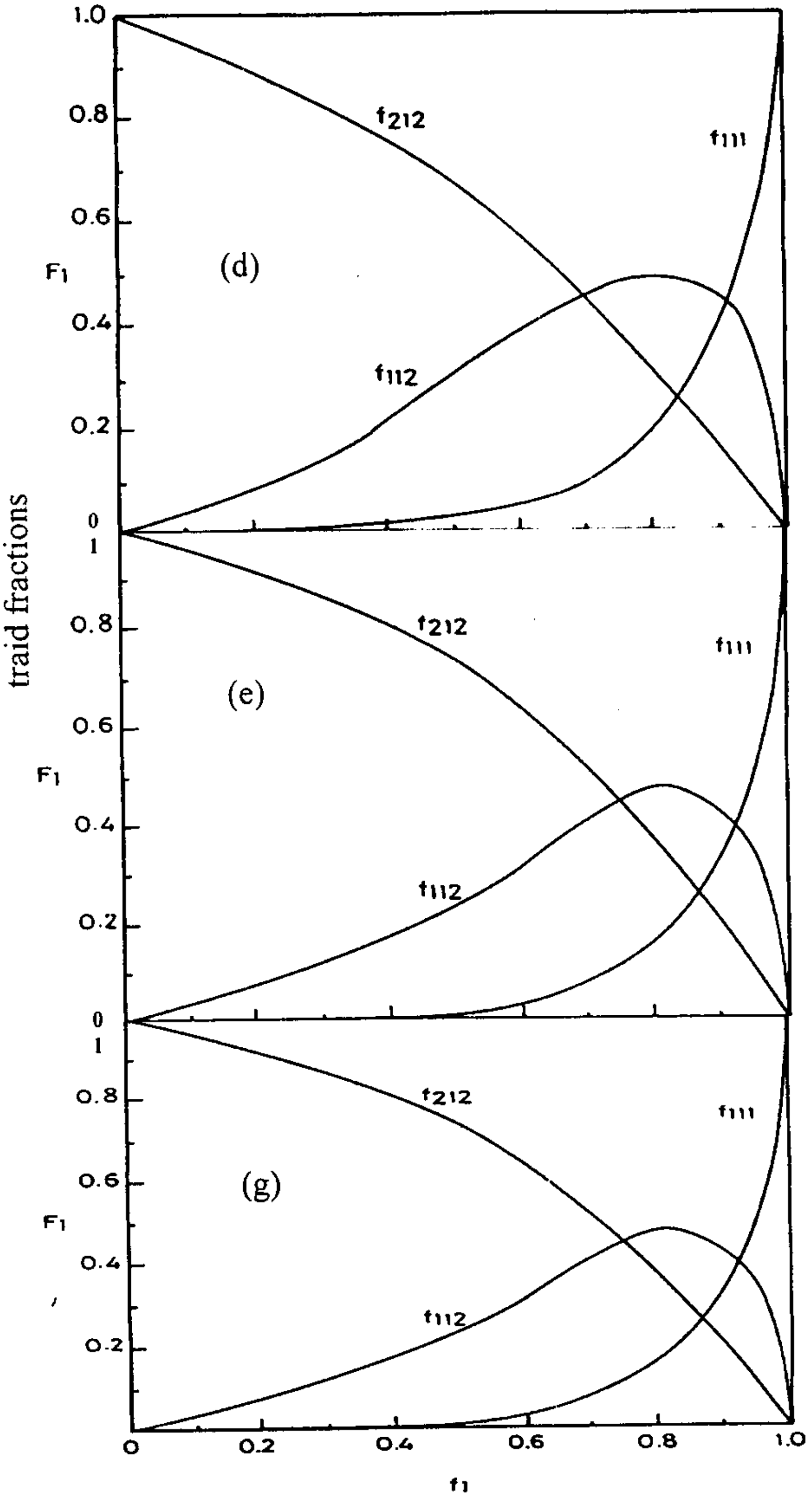


Fig. (32) : Dependance of traid fraction f_{111}, f_{112} and f_{212} on comonomer composition for
(d) o- MTBT B with ST, (e) o- MTBTB with AN,
(g) o- MTBTB with VA