RESULTS AND DISCUSSION

CHAPTER III

Polymerization Reactions

1. Tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers

The structure of the prepared tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were investigated by their I.R. spectra as shown in Fig. (1). It can be shown that the I.R. spectra of the two tin-containing monomers are quite similar in the region 400-1400 cm^{-1} and are characterized by the presence of a strong band at 1640 cm^{-1} due to the carboxylate carbonyl groups of $-COOSn\lessgtr$. Cummins et al[52] reported that the tributyltin carboxylates exhibit only the 1640 cm^{-1} bands which are typical of a carbonyl rather than a carboxylate group due to the influence of the metal atom, which suggests that organotin esters are covalent and chelated in character rather than ionic compounds. The bands at 2970 cm^{-1} are due to the C-H stretching vibrations of $-CH_2$ and $-CH_3$ groups.

2. Polymerization of tri-n-butyltin acrylate (TBTA)

The polymerization of TBTA initiated by AIBN was carried out in toluene at 70°C. Two series of rate studies of the polymerization of TBTA were carried out in which the initial concentration of AIBN and that of TBTA was varied, while the other was maintained effectively constant, as follows :-

a) Effect of AIBN concentration on the rate of TBTA polymerization

To study the effect of the initiator concentration on the rate of TBTA polymerization, four polymerization reactions were carried out in which the concentration of TBTA was kept constant at 0.7777 mole/l and the AIBN at concentrations varying over 0.0077-0.0311 mole/l. The reaction conditions and results are summarized in Table (1). The time-conversion curves of the four polymerization reactions studied are shown in Fig. (2a), from which the rate of polymerization at each level of initiator concentration was calculated (Table 1).

B) Effect of monomer concentration on the polymerization rate of TBTA

Three polymerization reactions were carried out in which the AIBN concentration was kept at 0.0077 mole/l and the monomer concentration was varied over 0.7777-1.6163 mole/l. The results and experimental conditions are illustrated in Table (2). The time-conversion curves of the polymerization reactions studied are shown in Fig. (3a).

The relation between the rate of the reaction (R_p) as a function of initiator concentration (I), is illustrated logarithmically in Fig. (2b), from which the slope of the obtained straight line is equal to 0.5. This indicates that the order of the reaction with respect to the initiator concentration is a half-order reaction. Also, from Fig. (3b), it is clear that the order of reaction with respect to monomer concentration is equal to one. Accordingly, the rate equation for the radical polymerization of TBTA in toluene at 70°C, using AIBN as initiator could be obtained in the form of ideal polymerization behaviour as follows :

$$R_p = K \left[TBTA\right] \left[AIBN\right]^{1/2}$$

Deb and Samui[60] studied the kinetics of the polymerization of tri-n-butyltin methacrylate and reported that the polymerization showed deviations from ideal behaviour in that the initiator exponent fell below 0.5 at higher initiator concentrations, which may be due to the high viscosity of the monomer.

Table (1)

Effect of AIBN concentration on the rate of polymerization of TBTA (0.7777 mole/l, in toluene, at 70°C).

[AIBN] mole/l	Time min.	Conversion %	$\ln(R_p x10^5)$	$\ln([AIBN]x10^3)$
0.0077	20	9.2	1.7889	2.0412
	40	17.00		
	60	28.1		
	80	35.94		
0.0155	15	10.0	2.1456	2.7408
	20	12.5		
	30	20.0		
	40	26.0		
	50	33.0		
0.0226	10	8.5	2.408	3.1179
	18	16.0		
	28	24.1		
	40	32.5		
0.0311	8	8.5	2.5688	3.4372
	15	14.5		
	20	21.2		
	30	29.5		

Table (2)

Effect of monomer concentration on the rate of polymerization of TBTA (in toluene, at 70°C, in presence of 0.0077 mole/l AIBN)

[TBTA] mole/l	Time min.	Conversion %	$\ln(R_p x10^5)$	ln([TBTA]x 10)
0.7777	20	9.2	1.7889	2.0412
	40	17.0		
	60	28.1		
	80	35.94		
1.2725	27	13.11	2.3448	2.5436
	47	23.08		
	62	30.6		
	77	38.13		
1.6163	25	13.98	2.6966	2.7827
	45	24.37		
	60	32.53		
	75	40.23		

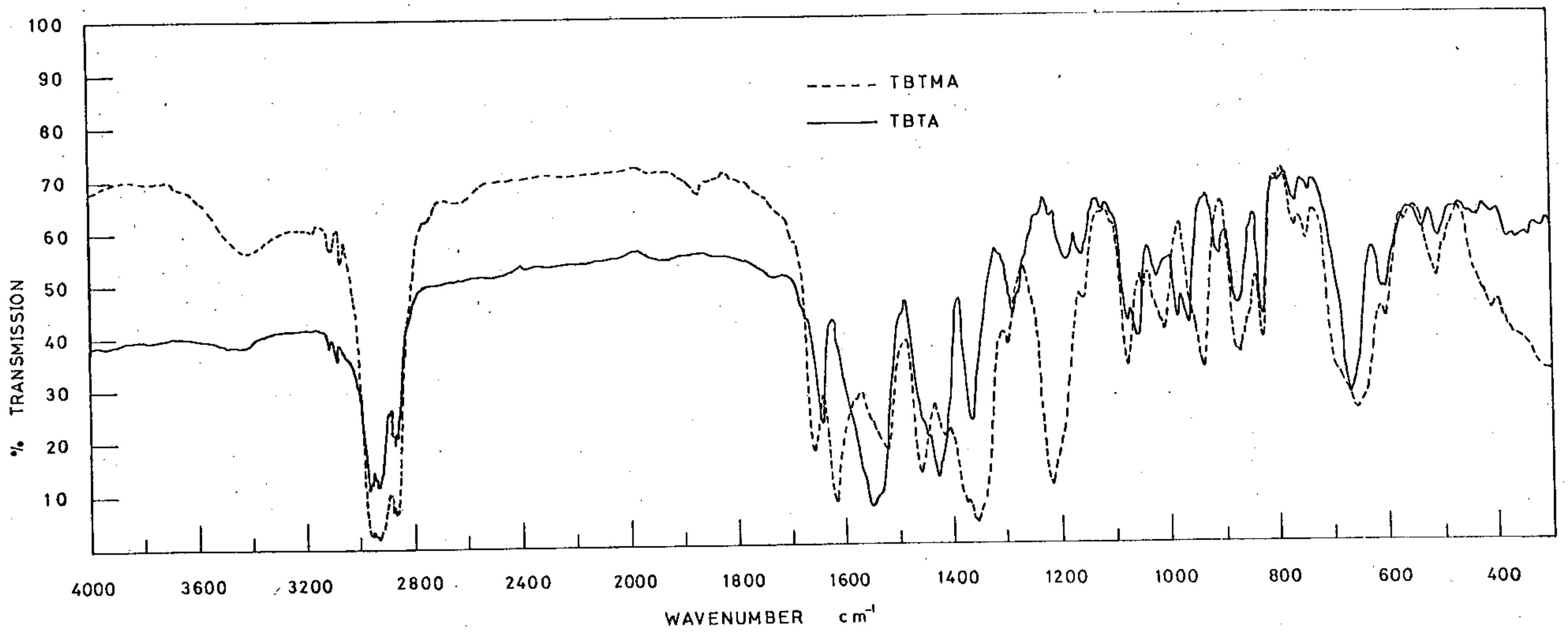


Fig. (1). The infrared spectra of TBTMA, and TBTA .

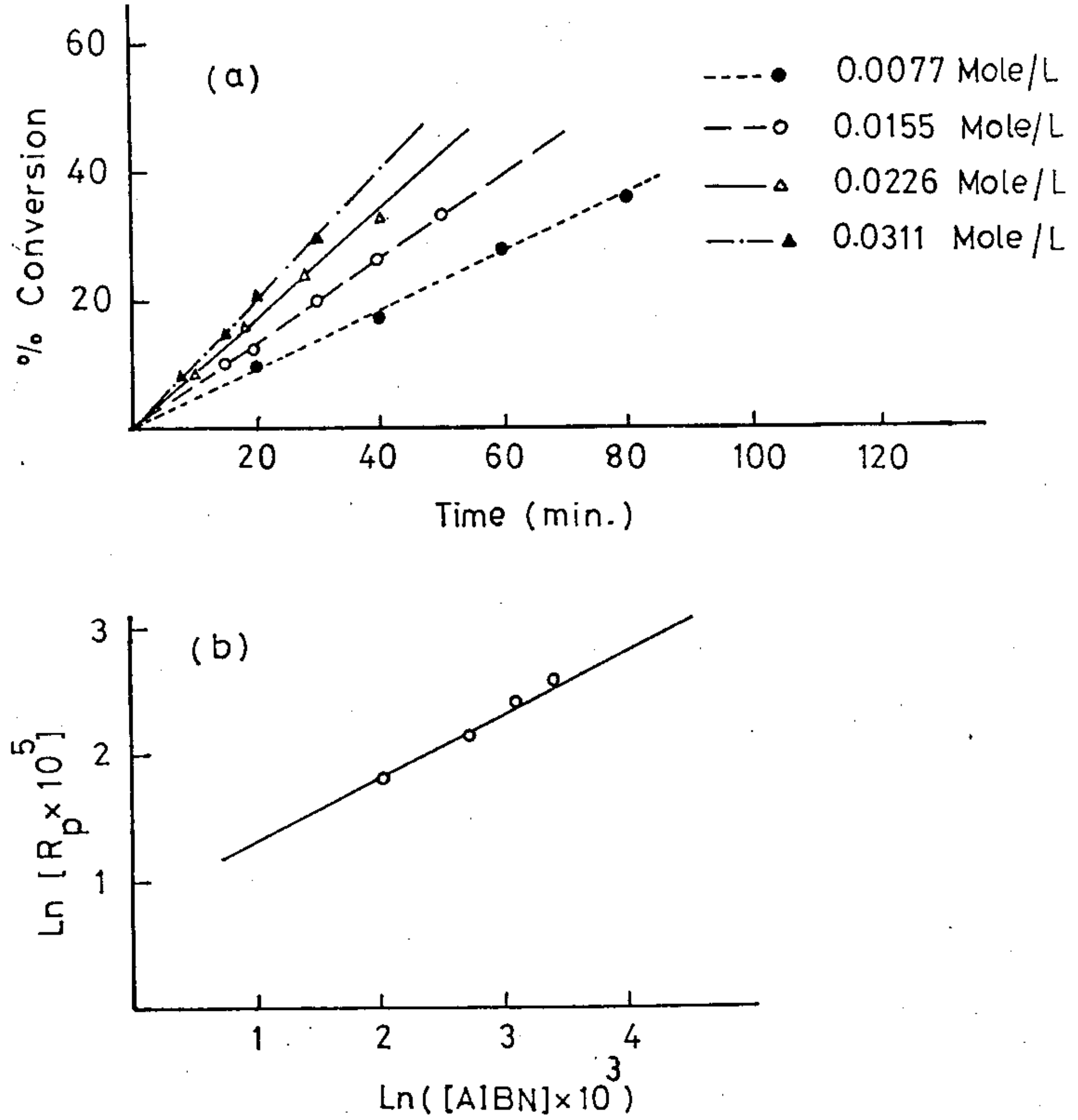


Fig. (2). Effect of AIBN concentration on the R_p of TBTA.

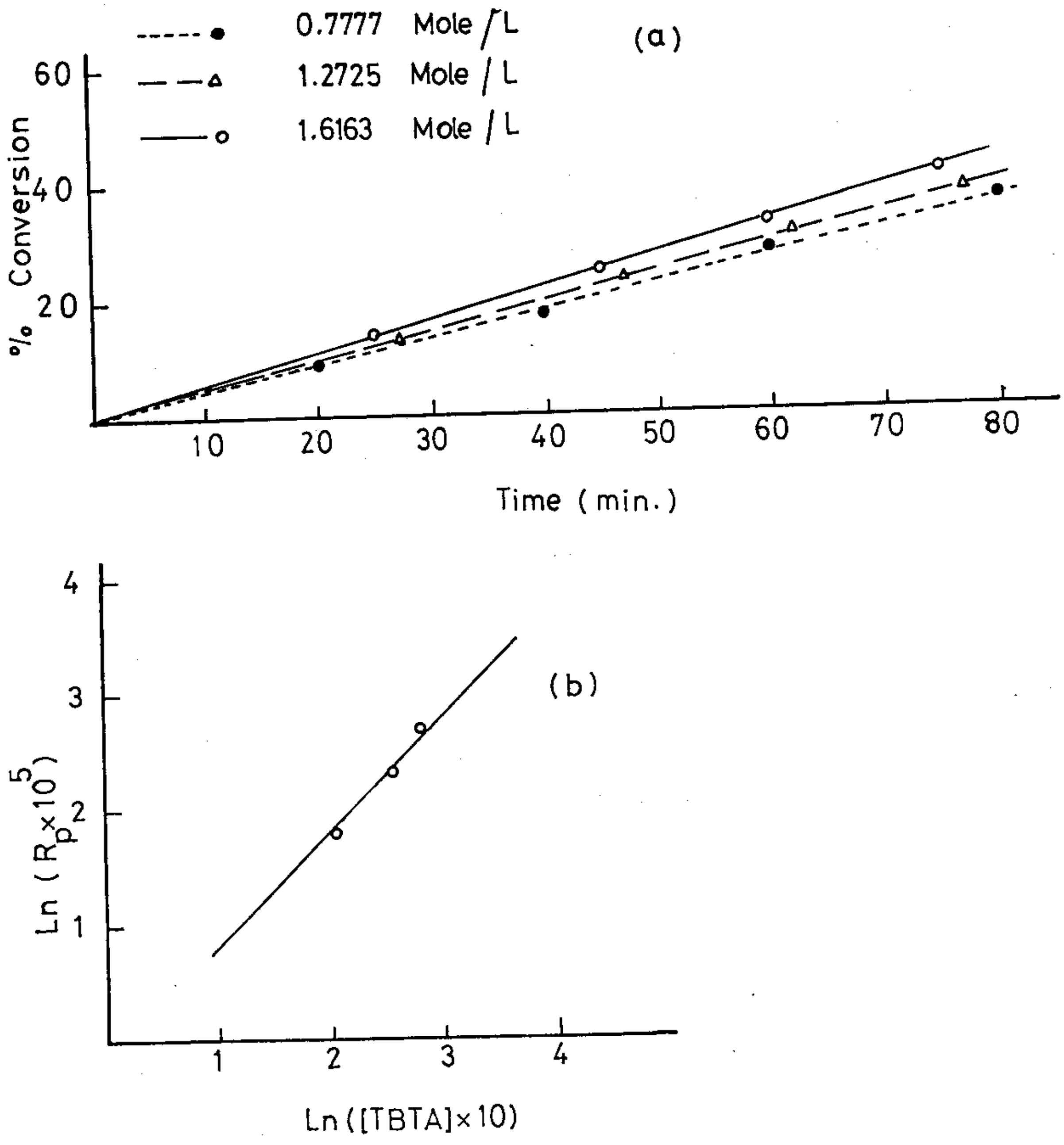


Fig. (3). Effect of TBTA concentration on its rate of polymerization.

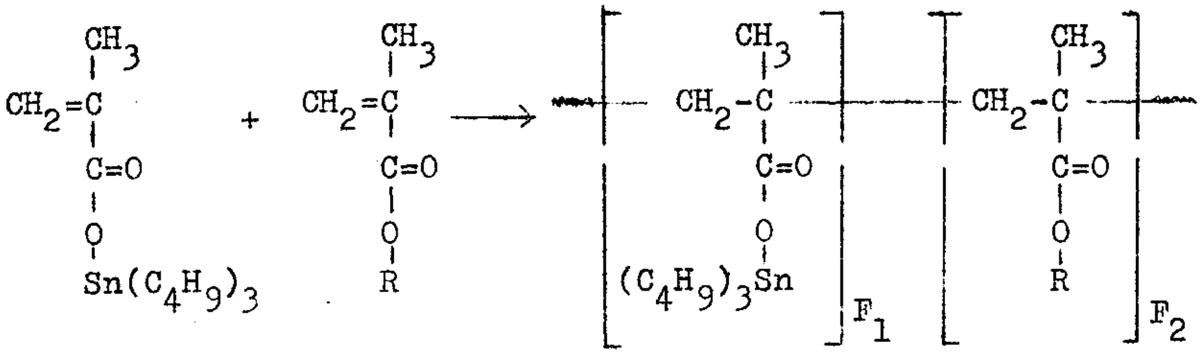
CHAPTER IV

Copolymerization Reactions

The copolymerization reactions of tri-n-butyltin methacrylate or acrylate with methacrylate esters, acrylate esters, styrene or acrylonitrile, were carried out by solution polymerization in toluene at 70°C in presence of 1 mole % AIBN as described earlier (page 45). The copolymers were prepared at low conversions and the copolymer composition of each sample was calculated from its tin content. The monomer reactivity ratios (r_1 and r_2) of each system were calculated according to Fineman and Ross[14] (page 20) and also by the method recently developed by Kelen and Tüdős[18] (page 22).

Monomer reactivity ratios for copolymerizations of tri-n-butyltin methacrylate (TBTMA) with methyl methacrylate (MMA), n-propyl methacrylate (PrMA), n-butyl methacrylate (BMA) and allyl methacrylate (AMA).

The copolymerization reactions of TBTMA with MMA, PrMA, BMA and AMA were studied and the reactions can be represented as:



where R = $-CH_3$, $n-C_3H_7$, $n-C_4H_9$ or $-CH_2-CH=CH_2$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (3-6).

Fig. (4) shows the Fineman-Ross plots of a-a/b as a function of a^2/b for the copolymerizations of TBTMA with MMA, PrMA, BMA, and AMA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$. Also, Fig. (5) illustrates the Kelen-Tüdös plots of the four systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in Tables (3-6) and figures (4 and 5) for the copolymerization of the four systems studied, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdös methods are summarized in Table (7). The data illustrated in Table (7) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods. Also, the range of experimental error in r_1 and r_2 is quite small and can be considered as within the experimental error.

From the reactivity ratios of the four systems studied and tabulated in Table (7), it is clear that the copolymer should have random distribution of the monomer units in the copolymer molecules. The copolymerization of TBTMA with MMA shows almost

Table (3)

Copolymerization of TBTMA (M_1) with MMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.9102$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ε
5.6445	0.8495	7.93	29.99	4.5944	0.8213	4.4160	6.9346	0.5629	0.8839
4.1867	0.8072	5.56	29.46	3.4601	0.7757	2.9768	5.0588	0.4981	0.8477
2.3467	0.7012	6.54	28.08	2.0138	0.6682	1.1814	2.5070	0.3241	0.5503
1.5165	0.6026	4.87	26.30	1.3091	0.5669	0.3581	1.7566	0.1343	0.6587
0.9882	0.4970	8.52	24.40	0.8908	0.4711	-0.1210	1.0961	-0.0604	0.5464
0.6893	0.4080	10.53	22.00	0.6085	0.3775	-0.4433	0.7807	-0.2623	0.4617
0.4303	0.3000	9.85	18.80	0.3897	0.2804	-0.6739	0.4753	-0.4864	0.3430
0.2527	0.2010	7.54	15.01	0.2393	0.1931	-0.8030	0.2668	-0.6824	0.2268
0.1834	0.1550	8.81	12.64	0.1767	0.1502	-0.8545	0.1903	-0.7766	0.1728
0.1139	0.1023	9.50	9.18	0.1086	0.0980	-0.9349	0.1194	-0.9079	0.1159

(*) Molar ratio (○) Mole fraction

Table (4)

Copolymerization of TBTMA (M_1) with PrMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1989$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ε
5.6461	0.8494	7.22	29.11	3.7921	0.7913	4.1571	8.4065	0.4328	0.8752
3.9826	0.7995	9.63	28.08	2.6264	0.7245	2.4662	6.0389	0.3407	0.8344
2.9849	0.7490	11.72	27.29	2.0976	0.6779	1.5619	4.2477	0.2868	0.7799
2.3201	0.6989	10.35	26.53	1.7421	0.6353	0.9884	3.0899	0.2304	0.7205
1.4888	0.5980	4.86	24.24	1.1024	0.5243	0.1383	2.0106	0.0431	0.6265
0.9902	0.4977	3.99	22.22	0.7972	0.4435	-0.2518	1.2300	-0.1037	0.5064
0.6603	0.3977	7.17	19.72	0.5604	0.3591	-0.5179	0.7780	-0.2620	0.3935
0.4117	0.2916	7.46	17.13	0.4011	0.2861	-0.6145	0.4224	-0.3791	0.2606
0.2406	0.1939	8.19	13.41	0.2497	0.1998	-0.7226	0.2317	-0.5053	0.1621
0.1764	0.1510	3.04	11.03	0.1820	0.1540	-0.7931	0.1711	-0.5788	0.1247

(*) **Molar ratio** (∘) **Mole fraction**

Table (5)

Copolymerization of TBTMA (M_1) with BMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.8024$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
4.8110	0.8279	7.84	28.64	3.5045	0.7780	3.4382	6.6045	0.4642	0.8917
3.3813	0.7717	5.62	27.63	2.5340	0.7170	2.0470	4.5118	0.3852	0.8490
2.8280	0.7387	6.76	27.21	2.3030	0.6973	1.6001	3.4720	0.3743	0.8123
2.2385	0.6912	8.53	26.71	2.0054	0.6672	1.1223	2.4980	0.3399	0.7569
1.8110	0.6443	7.54	25.57	1.5705	0.6109	0.6575	2.0880	0.2266	0.7224
1.1260	0.5296	4.51	23.55	1.0893	0.5213	0.0924	1.1638	0.0469	0.5919
0.8068	0.4460	9.07	21.40	0.7830	0.4391	-0.2235	0.8312	-0.1369	0.5038
0.5157	0.3402	7.04	19.07	0.5705	0.3630	-0.3890	0.4664	-0.3061	0.3674
0.2815	0.2196	6.56	15.75	0.3731	0.2717	-0.4729	0.2122	-0.4661	0.2092
0.1245	0.1107	7.52	9.44	0.1590	0.1373	-0.6585	0.0974	-0.7318	0.1083

(*) Molar ratio (∘) Mole fraction

Table (6)

Copolymerization of TBTMA (M_1) with AMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6255$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
3.9129	0.7964	9.37	30.47	8.3333	0.8904	3.3434	1.8373	1.3981	0.7460
2.9068	0.7440	8.25	29.94	5.6529	0.8489	2.3926	1.4947	1.1285	0.7050
2.3723	0.7035	7.38	29.40	4.2391	0.8091	1.8127	1.3276	0.9281	0.6797
1.4763	0.5962	9.82	28.34	2.7724	0.7375	0.9438	0.7861	0.6686	0.5569
0.9727	0.4931	8.34	26.68	1.7835	0.6402	0.4273	0.5305	0.3697	0.4589
0.6585	0.3971	9.14	23.39	0.9423	0.4852	-0.0403	0.4602	-0.0371	0.4238
0.4256	0.2986	7.31	19.95	0.5690	0.3629	-0.3223	0.3183	-0.3416	0.3372
0.2528	0.2018	9.87	14.97	0.3001	0.2308	-0.5896	0.2129	-0.7032	0.2540

(*) Molar ratio (○) Mole fraction

Table (7)

Monomer reactivity ratios in copolymerization of TBTMA with MMA, PrMA, BMA and AMA

M_1 - M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA-MMA	0.789±0.012	1.004±0.034	0.792	0.790±0.010	1.023±0.009	0.808
TBTMA-PrMA	0.580±0.012	0.900±0.046	0.522	0.571±0.014	0.893±0.024	0.510
TBTMA-BMA	0.623±0.016	0.646±0.048	0.402	0.642±0.022	0.678±0.028	0.435
TBTMA-AMA	2.306±0.100	1.013±0.104	2.336	2.380±0.145	1.058±0.078	2.518

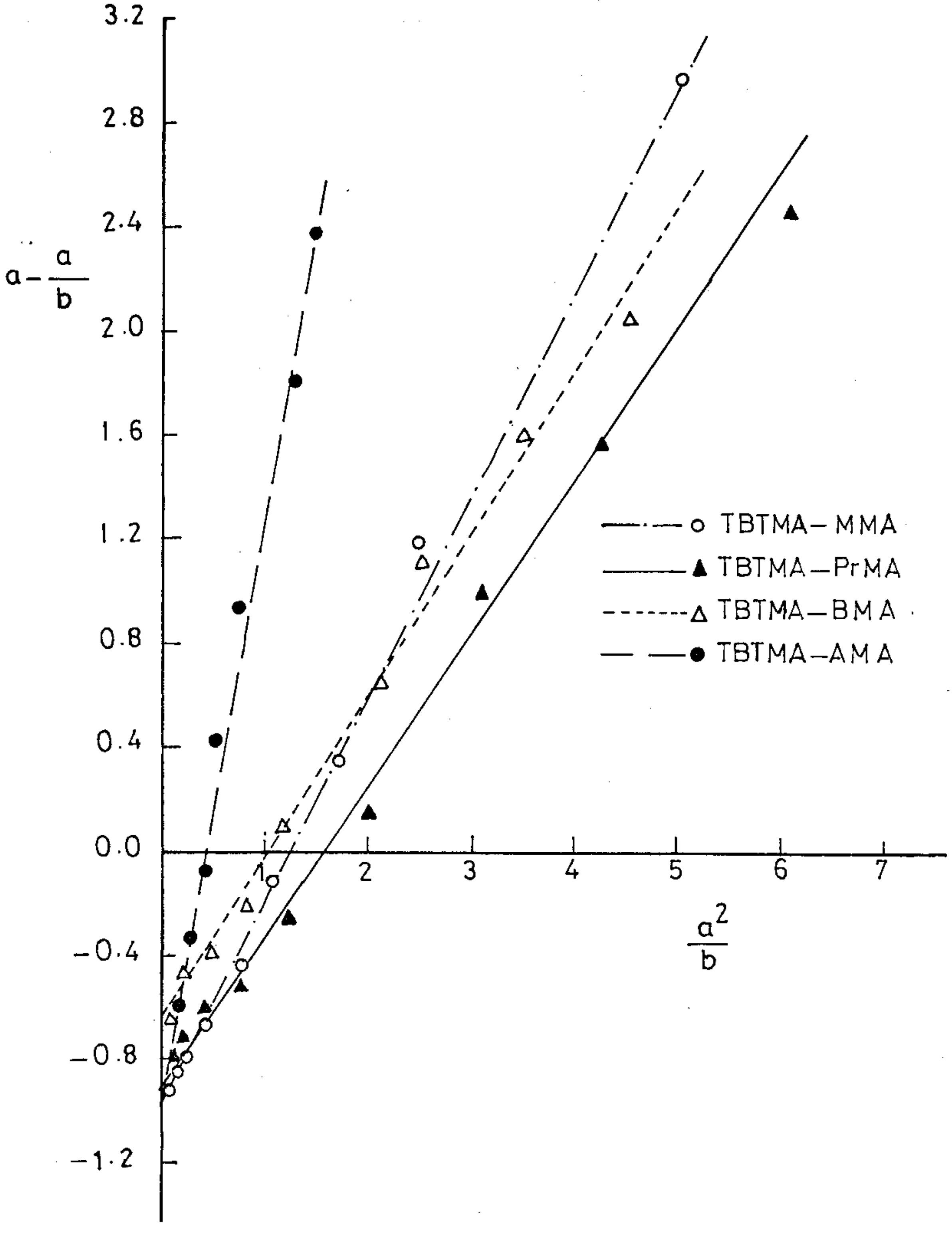


Fig. (4). Fineman–Ross plots for the copolymerization of: TBTMA–MMA, TBTMA–PrMA, TBTMA–BMA, and TBTMA–AMA.

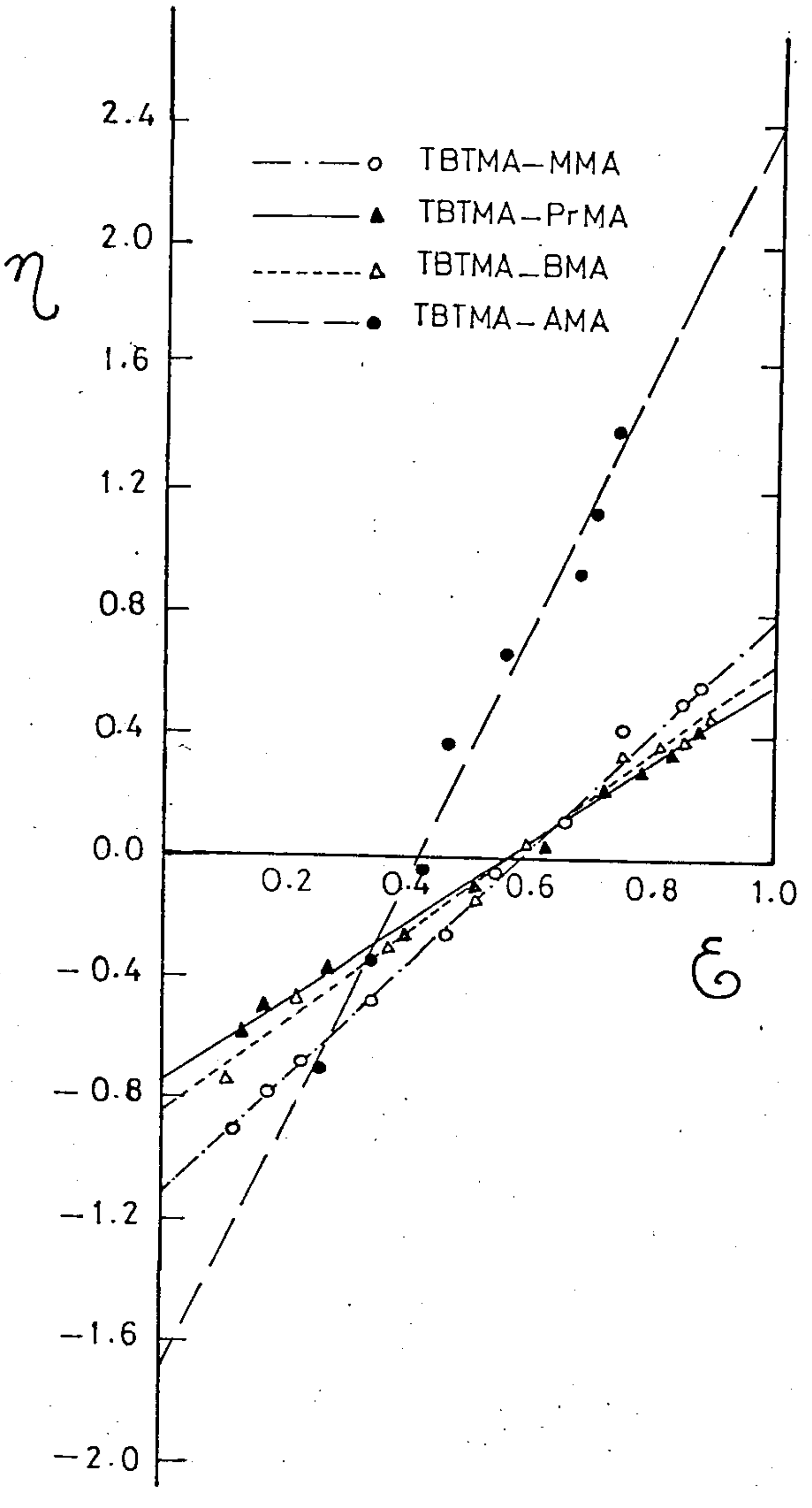


Fig. (5). Kelen–Tüdős plots for the copolymerization of: TBTMA–MMA, TBTMA–PrMA, TBTMA–BMA and TBTMA–AMA.

ideal behaviour (r_1r_2 = 0.792, while copolymerization of TBTMA with AMA shows almost block copolymerization behaviour ($r_1 > 1$, $r_2 > 1$ and $r_1r_2 = 2.336$). Table (7) also shows that the monomer reactivity ratios determined for the copolymerization of TBTMA with PrMA and BMA are less than unity and should have azeotropic copolymerization behaviour. The azeotropic composition of TBTMA-PrMA system was calculated from the monomer reactivity ratios and was found to be at 19.23 : 80.77 mole ratio. Similarly the azeotropic composition of TBTMA-BMA system was found to be 48.43 : 51.57 mole ratio. These data are in agreement with the composition curves shown in Fig. (6) illustrating the relation between F_1 (mole fraction of TBTMA in copolymer) versus f_1 (mole fraction of TBTMA in comonomer feed). From figures 6b and 6c it is clear that the curves cross the line representing $F_1 = f_1$ at 0.19 and at 0.48 mole fractions for copolymerizations of TBTMA with PrMA and BMA, respectively. These points of intersection correspond to the azeotropic compositions yielding homogeneous copolymers regardless of conversion.

The azeotrppic comonomer composition of TBTMA-PrMA and TBTMA-BMA systems were polymerized; by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C to several conversions covering a wide range. Tables 8 and 9 illustrate the experimental conditions and the results for both systems.

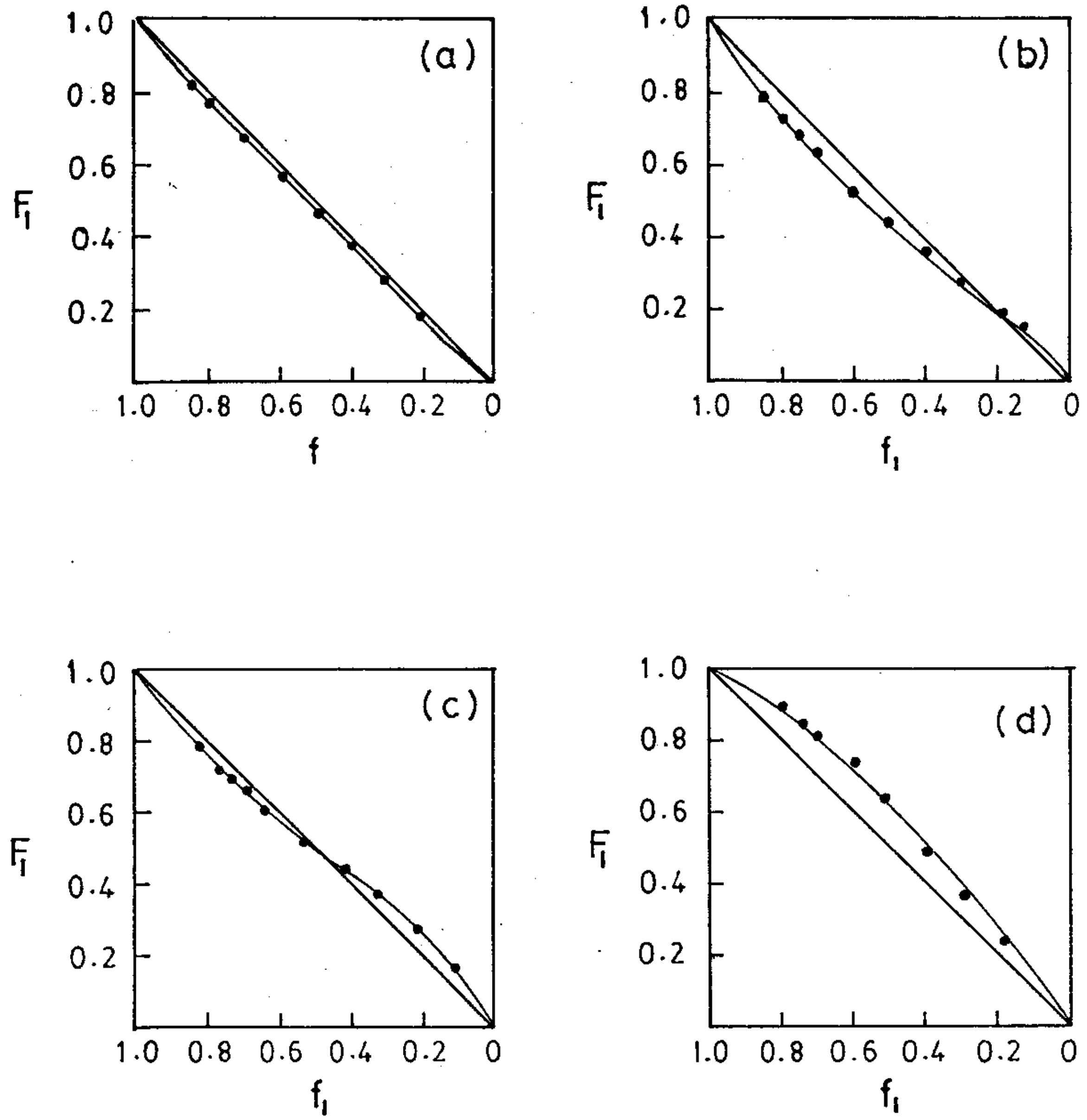


Fig. (6). Composition curves for the co-polymerization of: (a) TBTMA–MMA, (b) TBTMA–PrMA, (c) TBTMA–BMA, and (d) TBTMA–AMA.
f_1 = mole fraction of M_1 in feed and
F_1 = mole fraction of M_1 in copolymer.

Fig. (7) shows the change of the conversion with time for both azeotropic copolymerizations. Fig. (8) shows F_1 (mole fraction of TBTMA in copolymer) against the conversion and that the experimental points - calculated from the tin content of each sample - are in good agreement with the points of inflection on the lines representing the azeotropic composition in both systems.

From Tables (8) and (9), and Fig. (8), it is clear that the azeotropic copolymer composition of TBTMA-PrMA and TBTMA-BMA systems remain constant up to 90 % conversion, and the tin content of the copolymers gave a mean value of 13.0 percent against a calculated value of 12.9 percent for the azeotropic composition of TBTMA-PrMA system, while for the azeotropic copolymerization of TBTMA with BMA gave a mean value of 22.62 % tin against a colculated value of 22.6 %.

Izu and O'Driscoll[61] proposed a normograph for calculating the sequence distribution of the monomers in the copolymer chain based on the feed composition and the monomer reactivity ratios. Thus, the triad fractions of TBTMA (M_1) for the azeotropic compositions of TBTMA-PrMA and TBTMA-BMA systems were calculated and found to be as follows :

Table (8)

Azeotropic copolymerization of TBTMA (M_1) with PrMA (M_2)

	mole fraction	gram
TBTMA :	0.192	10.8
PrMA :	0.808	15.51
AIBN :	(1 mole %)	0.246

Solution polymerization in toluene (3 moles/l, total volume 50 ml), at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
40	14.75	13.02	0.1919
50	18.23	13.78	0.2076
60	27.01	13.62	0.2043
90	48.06	12.73	0.1861
120	61.82	12.77	0.1869
180	90.03	12.89	0.1893

Table (9)

Azeotropic copolymerization of TBTMA (M_1) with BMA (M_2)

	Mole fraction	Gram
TBTMA :	0.4843	27.24
BMA :	0.5157	10.984
AIBN :	(1 mole %)	0.246

Solution polymerization in toluene (3 moles/l, total volume 50 ml) at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
90	4.37	22.42	0.4770
120	19.7	22.67	0.4865
150	26.83	22.39	0.4758
180	37.27	22.73	0.4889
200	42.24	22.84	0.4931
230	50.25	22.58	0.4831
290	75.13	22.86	0.4939
360	90.27	22.45	0.4781

	F_{111}	f_{112}	f_{121}	f_{212}
TBTMA - PrMA	0.0022	0.0179	0.0356	0.1502
TBTMA - BMA	0.0622	0.1105	0.1717	0.1928

which indicates that the alternating behaviour of TBTMA-BMA system is greater than that of TBTMA-PrMA system.

The structure of the prepared copolymers of tributyltin methacrylate with the alkyl esters of methacrylic acid as well as allyl methacrylate was investigated by infrared spectroscopy and were found to be quite similar in the region between 400 cm^{-1} to 1400 cm^{-1}. Also, the I.R. spectra of these copolymers are characterized by the presence of two strong bands at 1640 cm^{-1} and at 1730 cm^{-1} due to the stretching frequencies of the $\rangle C=O$ groups of tributyltin carboxylates and the methacrylic esters, respectively. The bands at 2850-3000 cm^{-1} are due to the symmetrical and assymetrical stretching frequencies of the C-H bond due to $-CH_2$ and $-CH_3$ groups. Fig. (9) illustrates the I.R. spectrum of the TBTMA-AMA copolymer as an example of the studied copolymerizations of TBTMA with methacrylic acid esters.

Copolymers prepared from the reaction of TBTMA with alkyl methacrylates are clear, transparent and soluble in most organic solvents even at higher conversions, except methanol, while the copolymer of TBTMA with AMA gave an insoluble gel product at higher conversions. Also, copolymers produced from TBTMA with MMA were clear solids suitable for film formation while those from TPTMA with both PrMA and BMA were rubbery products and gave tacky films.

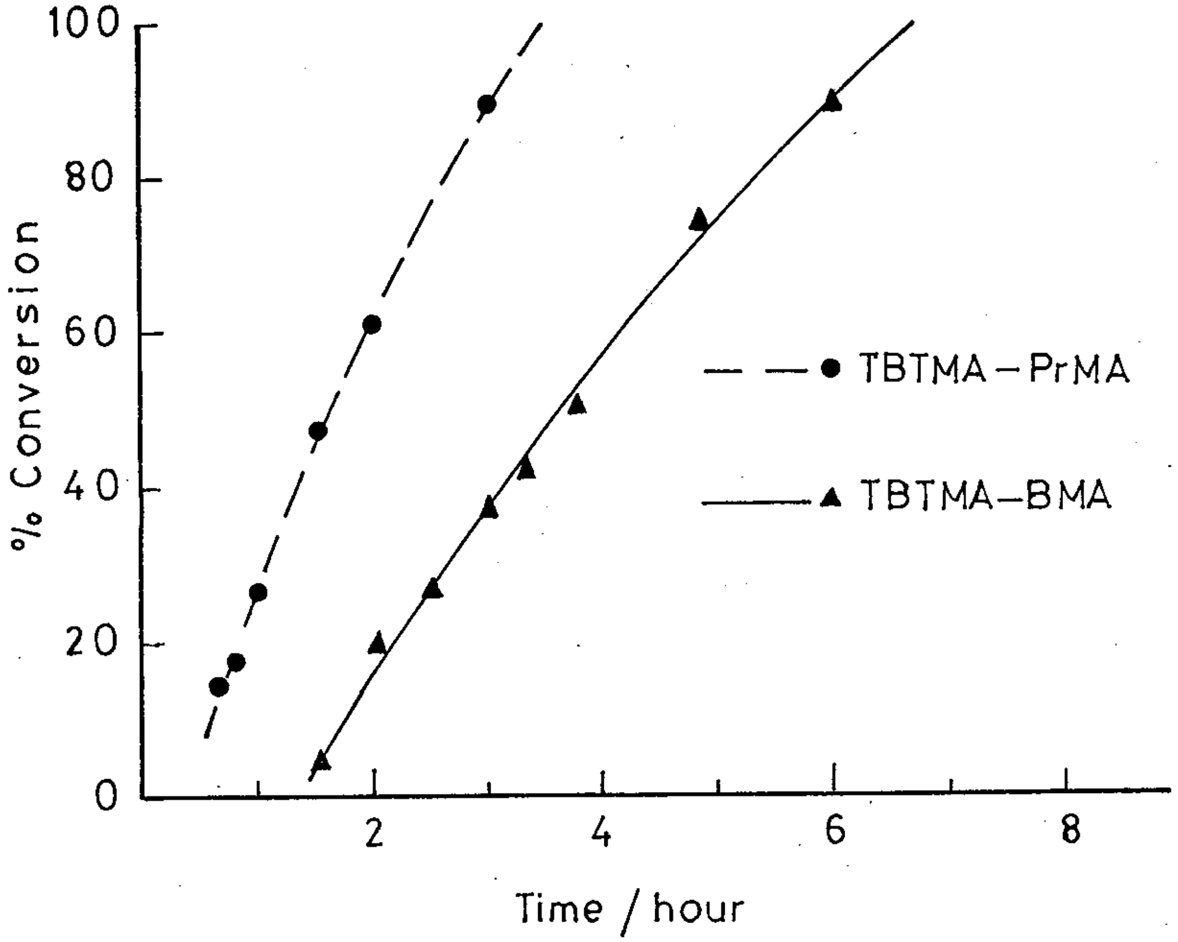


Fig. (7). Variation in percent azeotropic copolymers produced with time for: TBTMA–BMA and TBTMA–PrMA.

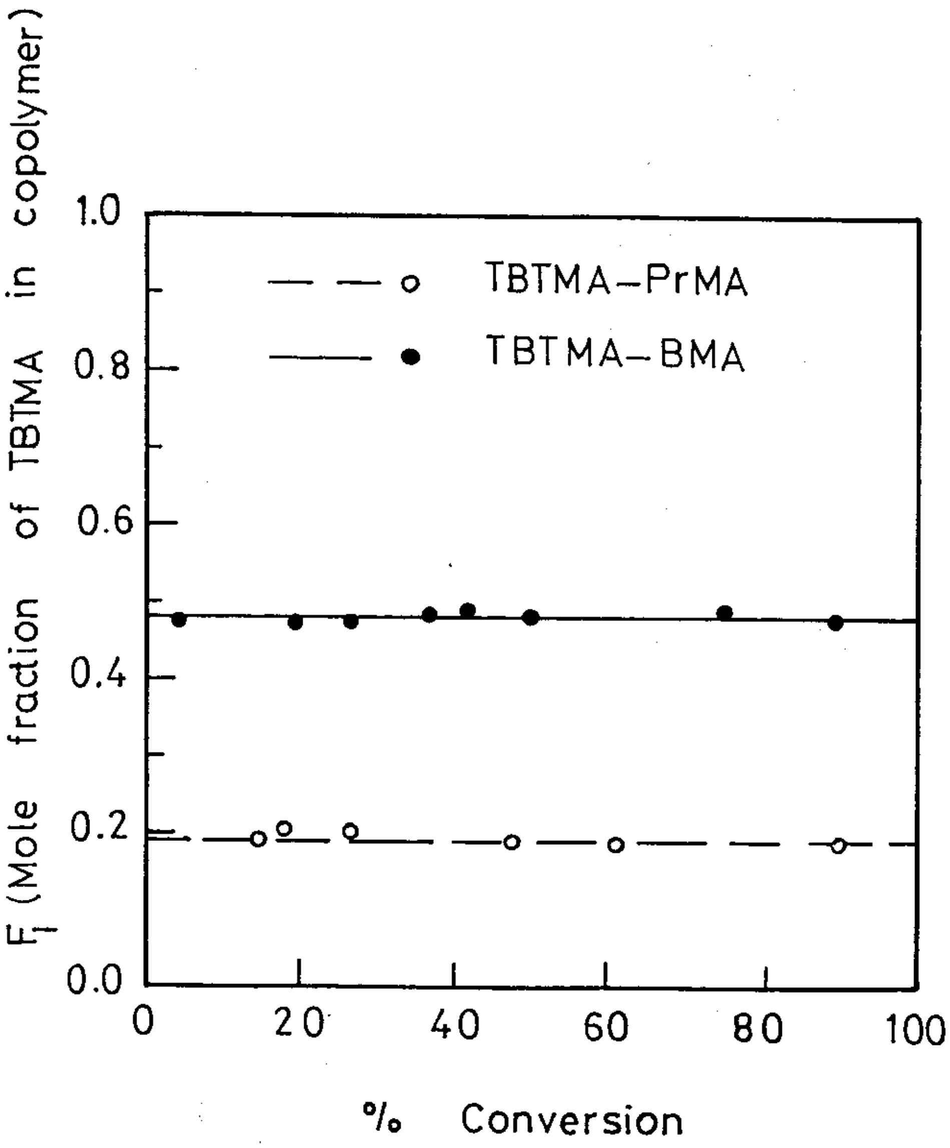


Fig. (8). F_1 as a function of conversion for azeotropic copolymerizations of : TBTMA–PrMA and TBTMA–BMA.

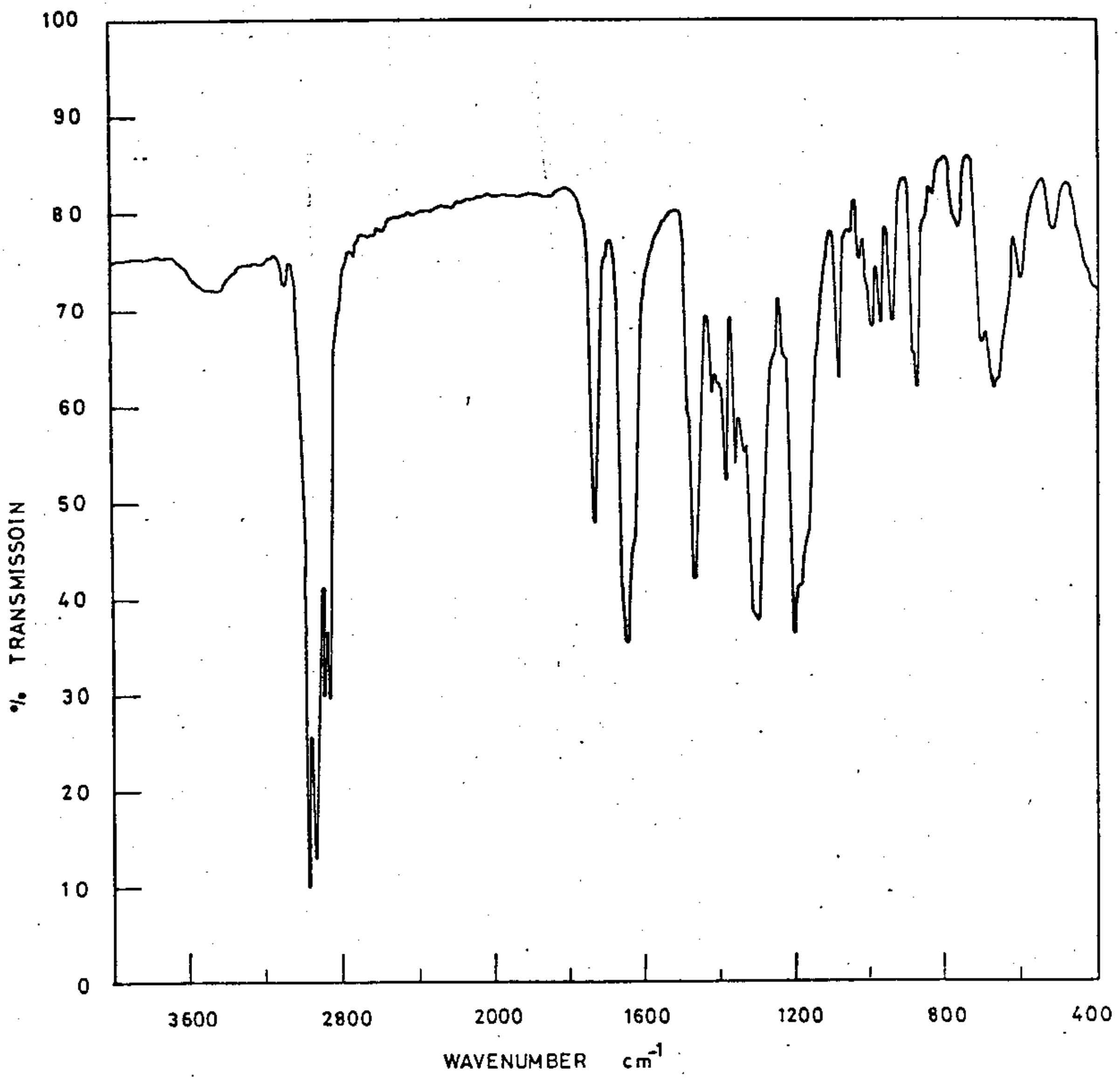
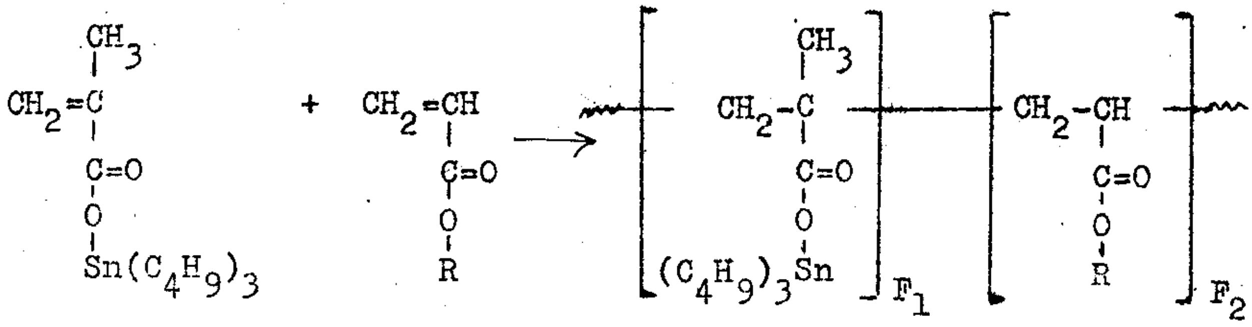


Fig. (9). I.R Spectrum for TBTMA – AMA copolymer.

CHAPTER V

Monomer reactivity ratios for copolymerizations of tri-n-butyltin methacrylate (TBTMA) with methyl acrylate (MA), ethyl acrylate (EA) and n-butyl acrylate (BA)

The copolymerization reactions of TBTMA with alkyl esters of acrylic acid can be represented as :



where R = $-CH_3$, $-C_2H_5$ or $n-C_4H_9$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables 10-12.

Fig. (10) shows the Fineman-Ross plots of $a-a/b$ as a function of a^2/b for the copolymerization of TBTMA with MA, EA and BA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$.

Also, Fig. (11) illustrates the Kelen-Tüdős plots of the three systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in tables 10-12 and figures 10, 11 for the copolymerization of TBTMA with MA, EA and BA, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdös methods are summarized in table (13). It is clear that there is a good agreement between the monomer reactivity ratios calculated by the two methods, and the experimental errors in r_1 and r_2 are quite small.

From the reactivity ratios of the three systems for the copolymerization of TBTMA with the alkyl esters of acrylic acid given in Table (13), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules, and the tendency towards alternation increases with increasing the alkyl chain length of acrylic acid esters. Table (13) also shows that the monomer reactivity ratios determined for the copolymerization of TBTMA with BA is less than unity and should have azeotropic copolymerization behaviour while the copolymerization of TBTMA with MA and EA gave no azeotropic copolymers. The azeotropic composition of TBTMA-BA system was calculated from the monomer reactivity ratios and was found to be at 73.53:26.47 mole ratio. These data are in agreement with the composition curves (Fig. 12) which shows the relation between F_1 (mole fraction of TBTMA in copolymer) versus f_1 (mole fraction of TBTMA in comonomer feed). From Fig. 12c, it is clear that the curve crossed the line representing $F_1 = f_1$ at 0.74 mole fraction for copolymerization of TBTMA with BA.

Table (10)

Copolymerization of TBTMA (M_1) with MA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6997$	
$a^{(*)}$	$f_1^{(o)}$			$b^{(*)}$	$F_1^{(o)}$	$a-a/b$	a^2/b	η	ε
5.4861	0.8456	7.00	30.99	9.5151	0.9049	4.9096	3.1630	1.2709	0.8189
4.0141	0.8006	6.61	30.69	6.7358	0.8707	3.4182	2.3920	1.1055	0.7737
2.9435	0.7464	10.83	30.39	5.1456	0.8535	2.3715	1.6838	0.9949	0.7064
2.3383	0.7005	11.94	29.96	3.8865	0.7953	1.7367	1.4068	0.8244	0.6678
1.5006	0.6001	9.52	29.15	2.5893	0.7214	0.9211	0.8696	0.5869	0.5541
0.9981	0.4994	3.53	27.65	1.5537	0.6084	0.3557	0.6411	0.2653	0.4782
0.6605	0.3978	10.04	26.27	1.0984	0.5235	0.0592	0.3971	0.0539	0.3621
0.4316	0.3015	9.24	23.71	0.6782	0.4041	-0.2047	0.2747	-0.2102	0.2819
0.2531	0.2019	10.48	20.42	0.4139	0.2927	-0.3584	0.1548	-0.4194	0.1812

(*) Molar ratio (o) Mole fraction

Table (11)

Copolymerization of TBTMA (M_1) with EA (M_2)

Initial monomer composition		Coversion	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6737$	
$a^{(*)}$	$f_1^{(\circ)}$	%		$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ε
5.4681	0.8454	10.03	30.59	7.0590	0.8759	4.6936	4.2350	0.9560	0.8628
3.7541	0.7896	7.64	30.10	4.9000	0.8305	2.9880	2.8760	0.8417	0.8102
2.9048	0.7442	9.31	29.73	3.9513	0.7980	2.1696	2.1354	0.7723	0.7602
2.2913	0.6917	9.80	29.21	3.0790	0.7548	1.5472	1.7049	0.6504	0.7168
1.5000	0.6000	8.10	28.17	2.1159	0.6793	0.7911	1.0630	0.5003	0.6122
0.9636	0.4908	7.03	26.58	1.3724	0.5785	0.2615	0.6765	0.1936	0.5011
0.6424	0.3912	10.40	24.24	0.8621	0.4633	-0.1027	0.4786	-0.0892	0.4154
0.4141	0.2928	9.09	21.90	0.5936	0.3725	-0.2835	0.2888	-0.2945	0.3001
0.1742	0.1483	9.20	16.35	0.2832	0.2207	-0.4409	0.1071	-0.5648	0.1370

(*) Molar ratio (°) Mole fraction

Table (12)

Copolymerization of TBTMA (M_1) with BA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.0261$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
5.6498	0.8498	11.02	29.79	5.2374	0.8397	4.5710	6.0946	0.6419	0.8559
4.0098	0.8003	10.34	29.15	3.8574	0.7941	2.9701	4.1675	0.5718	0.8025
3.0156	0.7509	8.28	28.48	2.9730	0.7483	2.0013	3.0588	0.4899	0.7488
2.2950	0.6965	7.32	27.75	2.3758	0.7038	1.3290	2.2169	0.4098	0.6836
1;4986	0.5997	4.53	26.40	1.6878	0.6297	0.6107	1.3300	0.2591	0.5646
0.9943	0.4984	10.55	24.40	1.1358	0.5318	0.1188	0.8688	0.0627	0.4585
0.6649	0.3994	9.71	22.57	0.8408	0.4568	-0.1250	0.5257	-0.0811	0.3388
0.4301	0.3000	3.63	19.91	0.5749	0.3650	-0.3180	0.3217	-0.2359	0.2387
0.2528	0.2018	8.82	16.53	0.3699	0.2700	-0.4306	0.1727	-0.3592	0.1441

(*) Molar ratio (°) Mole fraction

Table (13)

Monomer reactivity ratios in copolymerization of

TBTMA with MA, EA and BA

M_1 - M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA - MA	1.747±0.028	0.644±0.004	1.160	1.730±0.025	0.649±0.024	1.120
TBTMA - EA	1.259±0.016	0.606±0.032	0.763	1.262±0.014	0.613±0.024	0.773
TBTMA - BA	0.846±0.005	0.572±0.015	0.484	0.855±0.008	0.578±0.008	0.494

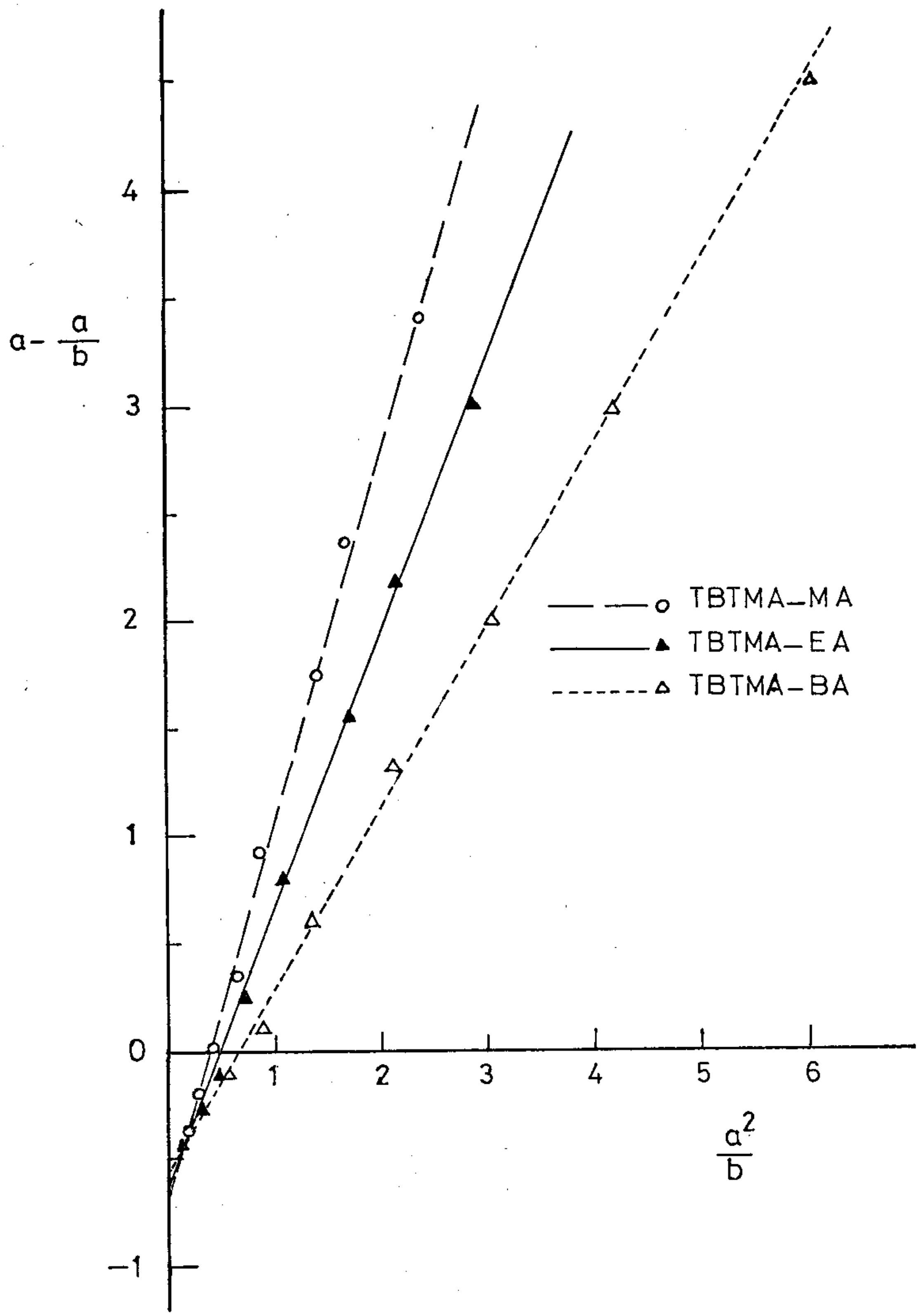


Fig. (10). Fineman–Ross plots for the copolymerization of: TBTMA–MA, TBTMA–EA, and TBTMA–BA.

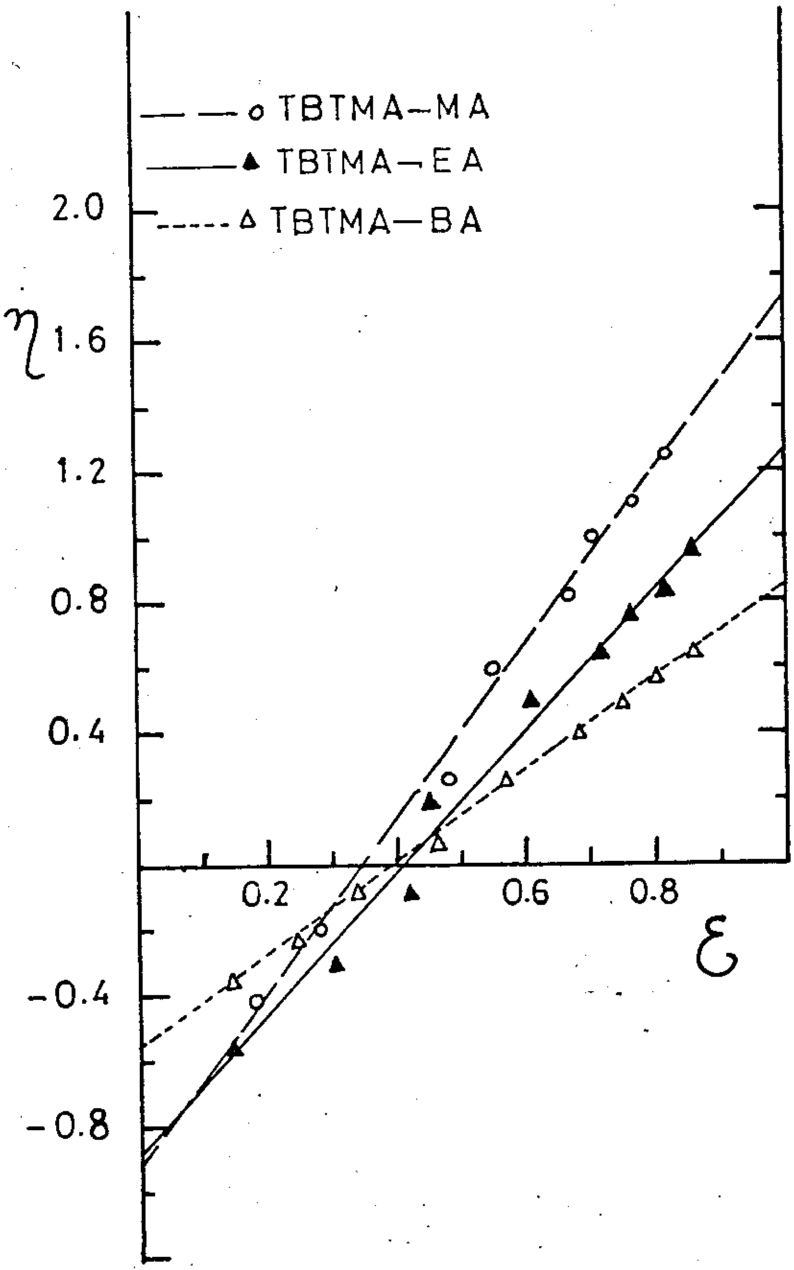


Fig. (11). kelen—Tüdős plots for the copolymerization of: TBTMA—MA , TBTMA—EA , and TBTMA—BA.

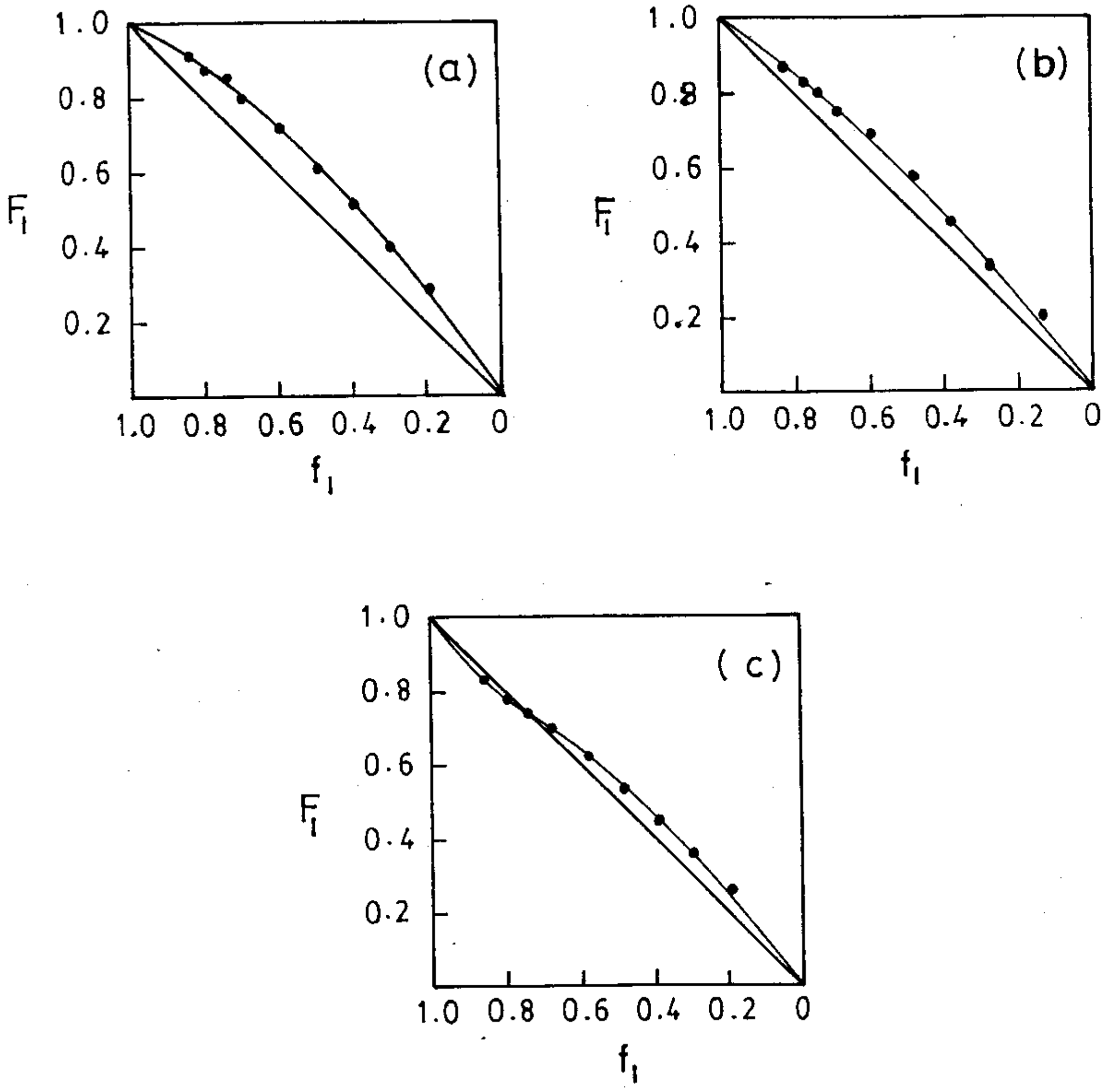


Fig. (12). Composition curves for the copolymerization of (a) TBTMA–MA, (b) TBTMA–EA, and (c) TBTMA–BA. f_1 = mole fraction of M_1 in feed and F_1 = mole fraction of M_1 in copolymer.

This point of intersection corresponds to the azeotropic composition yielding homogeneous copolymer regardless of conversion.

The azeotropic comonomer composition of TBTMA-BA system was polymerized; by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C to several conversions covering a wide range. Table (14) illustrates the experimental conditions and the results for azeotropic copolymerization of TBTMA with BA. (Fig. (13) shows the relation between percent conversion versus time for the azeotropic mixture of TBTMA and BA. Fig. (14) shows F_1 (mole fraction of TBTMA in copolmyer) against % conversion and indicates that the experimental points, calculated from the tin content of each sample, are in good agreement with the line representing the azeotropic composition. From Table (14), and Fig. (14), it is clear that the azeotropic copolymer composition of TBTMA-BA remains constant up to 90 % conversion, and the tin content of the copolymer gave a mean value of 28.28 % against a calculated value of 28.26 % for the azeotropic composition.

The sequence distribution of the monomers at the azeotropic composition of the TBTMA-BA system was calculated from the normograph of Izu and O'Driscol[61]. Thus, the triad fractions for the azeotropic copolymer of TBTMA-BA was found to be as follows:

f_{111}	f_{112}	f_{121}	f_{212}
0.3818	0.1522	0.1794	0.0606

Table (14)

Azeotropic copolymerization of TBTMA (M_1) with BA (M_2)

		Mole fraction	gram
TBTMA	=	0.7353	27.5738
BA	=	0.2647	3.3882
AIBN	=	(1 mole %)	0.1640

Solution polymerization in toluene (3 Moles/L, total volume 33.33 ml).

Time (minutes)	Conversion %	Sn %	F_1
5	15.02	28.17	0.7398
10	37.04	28.02	0.7205
20	65.83	28.39	0.7437
40	77.98	28.49	0.7501
60	89.96	28.31	0.7386

The structure of the prepared copolymers of tri-n-butyltin methacrylate with the alkyl esters of acrylic acid was investigated by infrared spectroscopy and was found to be quite similar in the region between 400 cm^{-1} to 1400 cm^{-1}. Also, the IR spectra of these copolymers are characterized by the presence of two strong bands at 1645 cm^{-1} and at 1738 cm^{-1} due to the stretching frequencies of the $>C=O$ groups of the tri-n-butyltin carboxylates and the acrylic esters, respectively. The bands at 2860-2970 cm^{-1} are due to the symmetrical and assymetrical stretching frequencies of the C-H bonds due to $-CH_2$ and $-CH_3$ groups. Fig. (15) illustrates the IR spectrum of TBTMA-BA azeotropic copolymer as an example of the studied copolymerizations of TBTMA with alkyl acrylates.

Copolymers prepared from the reaction of TBTMA with alkyl acrylates are clear, transparent and soluble in most organic solvents even at high conversions except the alcohols methanol and ethanol. Films prepared from the copolymers of TBTMA-MA, TBTMA-EA and TBTMA-BA exerted some tackiness which might limit their use as binders for antifouling coatings. To improve the film properties, the copolymers were prepared at various lower initiator concentrations ranging from 0.25 to 0.05 mole/100 moles monomers, but the tackiness of the films was only a little improved. The viscosity measurements of the azeotropic copolymer are illustrated in Table (15) which shows that the reduced viscosity of the azeotropic copolymer (TBTMA-BA), 1 % solution in toluene at 30°C, increases with decreasing the initiator concentration. The tackiness of the copolymer and the relatively low reduced viscosity values may be due to a chain transfer effect with the solvent (toluene).[62]

Table (15)

Initiator concentration	$\eta_{sp/c}$
1 mole %	0.1989
0.25 mole %	0.2159
0.10 "	0.2381
0.05 "	0.3115

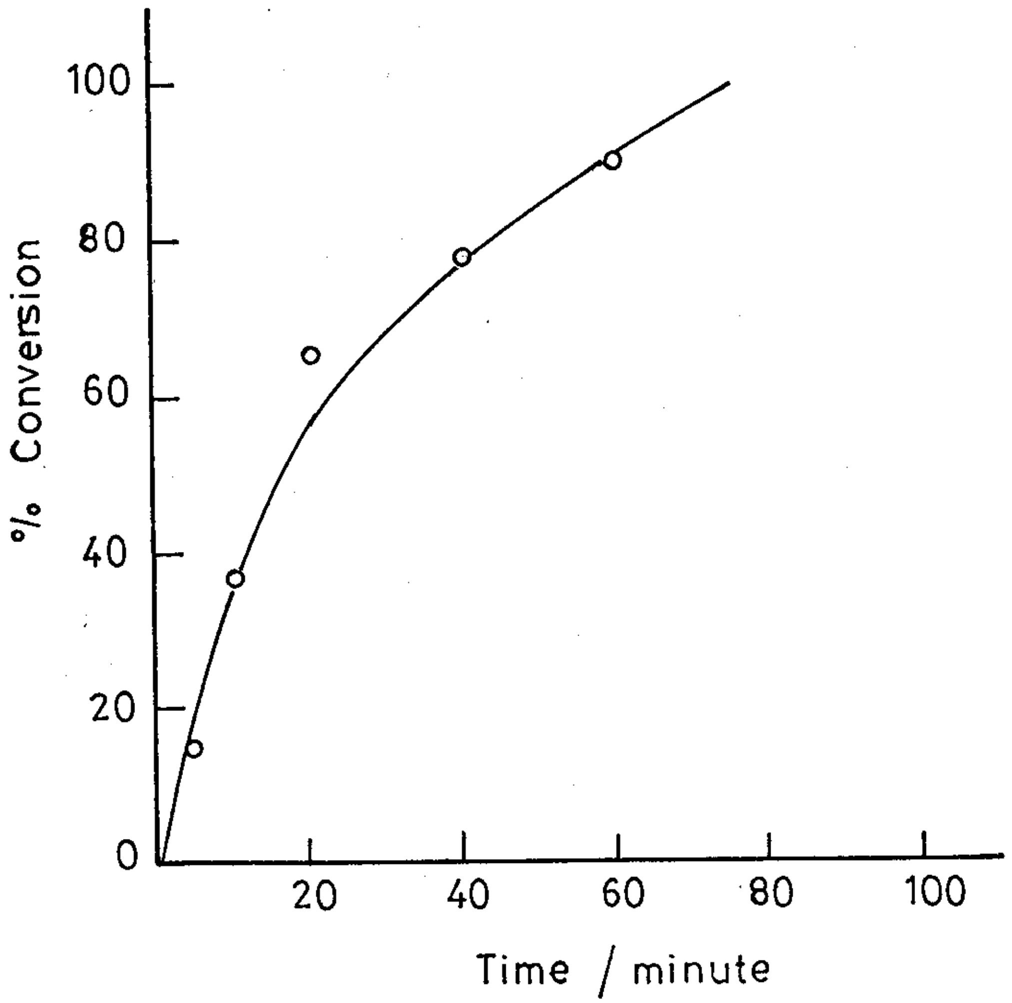


Fig. (13). Variation in percent azeotropic copolymer produced with time for azeotropic copolymerization of TBTMA—BA.

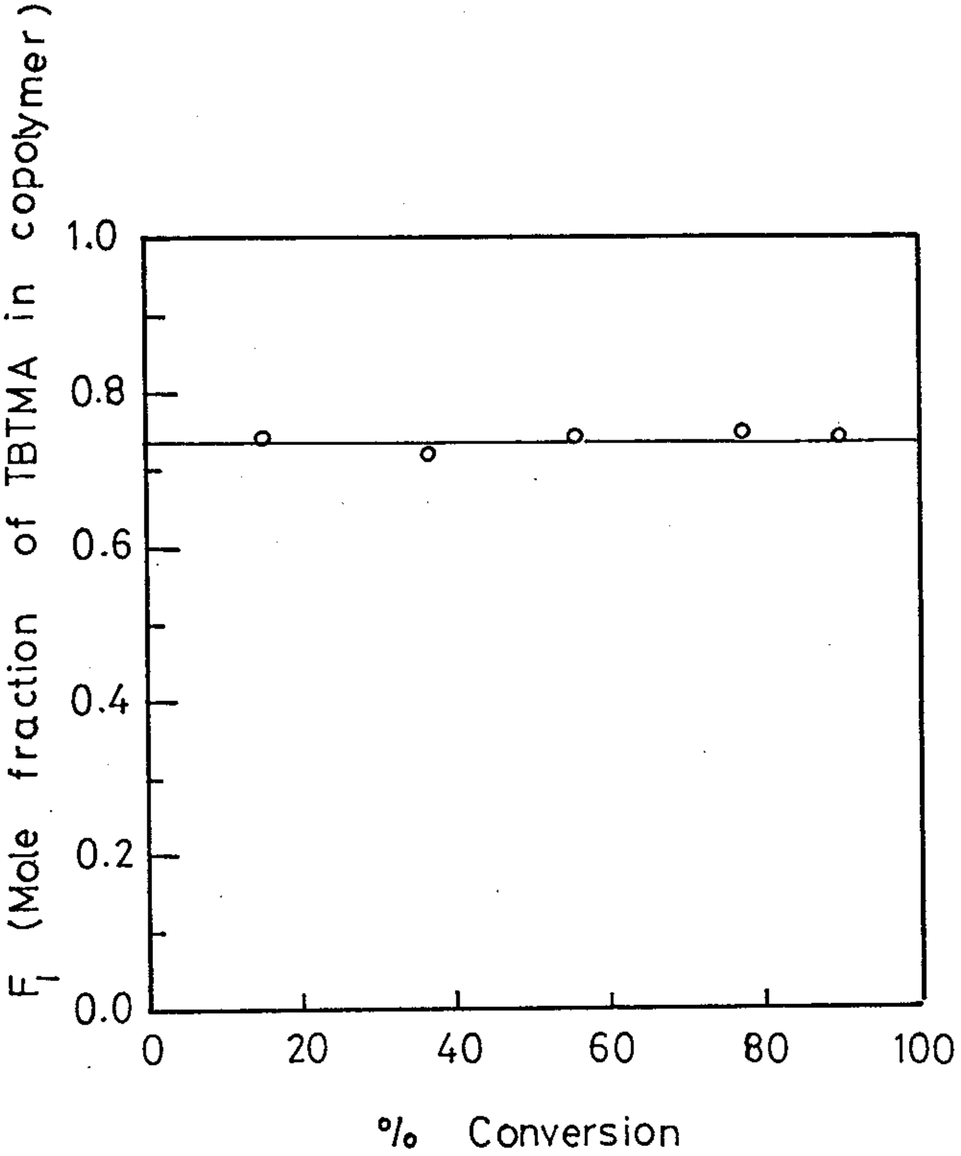


Fig. (14). F_1 as a function of conversion for azeotropic copolymerization of TBTMA– BA

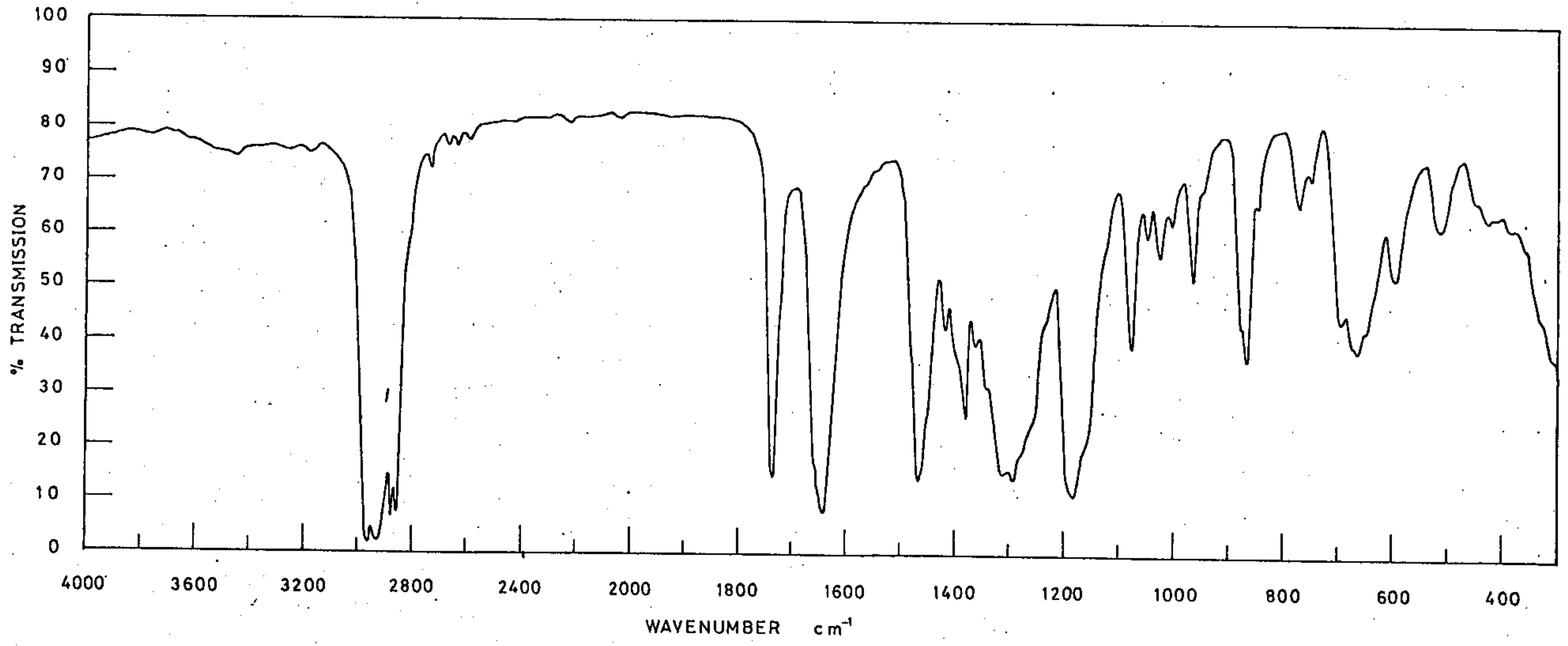
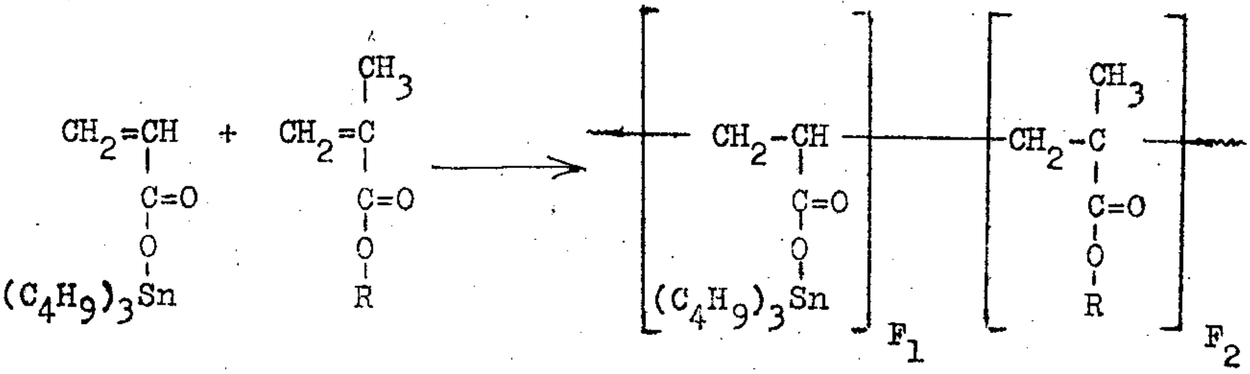


Fig. (15). I.R Spectrum for TBTMA-BA copolymer.

CHAPTER VI

Monomer reactivity ratios for copolymerizations of tri-n-butyltin acrylate (TBTA) with methyl methacrylate (MMA), n-propyl methacrylate (PrMA), n-butyl methacrylate (BMA) and allyl methacrylate (AMA)

The copolymerization reactions of TBTA with the alkyl esters of methacrylic acid and allyl methacrylate can be represented as :



$$CH_2{=}CH(COOSn(C_4H_9)_3) + CH_2{=}C(CH_3)(COOR) \longrightarrow \left[CH_2{-}CH(COOSn(C_4H_9)_3) \right]_{F_1} \left[CH_2{-}C(CH_3)(COOR) \right]_{F_2}$$

where R = $-CH_3$, $n-C_3H_7$, $n-C_5H_9$ and $-CH_2-CH{=}CH_2$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (16-19).

Fig. (16) shows the Fineman-Ross plots of $a-a/b$ as a function of a^2/b for the copolymerizations of TBTA with MMA, PrMA, BMA and AMA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$. Also, Fig. (17) illustrates the Kelen-Tüdos plots of the four systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in Tables (16-19) and Figs. 16 and 17) for the copolymerization of TBTA with MMA, PrMA, BMA and AMA, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdos methods are summarized in Table (20). The data illustrated in Table (20) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods, and the experimental errors in r_1 and r_2 are in a small range within the experimental error.

From the reactivity ratios of the four systems for the copolymerization of TBTA with the alkyl esters of methacrylic acid and allyl methacrylate tabulated in Table (20), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules, and the tendency towards alternation increases with increasing the alkyl chain length of methacrylic acid esters. This behaviour is in agreement with the data obtained on copolymerization of TBTMA with alkyl methacrylates and alkyl acrylates, and with the work of Zabotin and Malysheva[45] on emulsion copolymerization of TBTA with alkyl acrylates using $K_2S_2O_8$ as initiator. Table (20) also shows that the copolymerization of TBTA with MMA, PrMA, BMA and AMA gave no azeotropic copolymers (r_2 values are always greater than unity). Also, the composition curves illustrated in Fig. (18) show that the four systems gave no azeotropic copolymers.

Table (16)

Copolymerization of TBTA (M_1) with MMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 3.4621$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	γ	ε
8.3634	0.8932	11.91	30.22	3.0553	0.7534	5.6261	22.8935	0.2135	0.8686
4.2636	0.8100	8.52	28.51	1.7746	0.6396	1.8610	10.2436	0.1358	0.7474
2.8922	0.7431	6.23	26.96	1.2447	0.5545	0.5686	6.7203	0.0558	0.6599
2.2893	0.6959	5.64	25.76	0.9911	0.4978	-0.0206	5.2879	-0.0023	0.6043
1;5169	0.6027	9.43	23.23	0.6613	0.3981	-0.7769	3.4795	-0.1119	0.5013
0.9854	0.4963	7.64	19.64	0.4085	0.2900	-1.4268	2.3769	-0.2444	0.4071
0.6727	0.4022	8.13	16.92	0.2922	0.2261	-1.6295	1.5486	-0.3252	0.3091
0.4251	0.2983	7.98	13.34	0.1883	0.1585	-1.8395	0.9596	-0.4144	0.2170
0.2494	0.1996	8.26	9.89	0.1188	0.1062	-1.8499	0.5236	-0.4641	0.1398

(*) Molar ratio (∘) Mole fraction

Table (17)

Copolymerization of TBTA (M_1) with PrMA (M_2)

Initial monomer composition		Conversion	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 3.2234$	
a(*)	f_1 (o)	%		b(*)	F_1 (o)	a-a/b	a^2/b	η	ξ
5.9176	0.8554	9.85	28.06	2.0305	0.6700	3.0032	17.2464	0.1467	0.8425
4.0439	0.8017	9.13	27.14	1.6534	0.6231	1.5981	9.8906	0.1219	0.7542
2.9799	0.7487	8.25	25.51	1.2141	0.5484	0.5255	7.3139	0.0499	0.6941
2.2936	0.6964	10.32	24.26	0.9887	0.4972	-0.0262	5.3207	-0.0031	0.6227
1.5172	0.6027	7.92	21.80	0.6917	0.4089	-0.6762	3.3279	-0.1032	0.5080
0.9952	0.4988	8.87	19.08	0.4874	0.3277	-1.0466	2.0320	-0.1992	0.3867
0.6631	0.3987	9.79	15.88	0.3297	0.2479	-1.3480	1.3333	-0.2958	0.2926
0.4291	0.3003	8.63	13.21	0.2372	0.1917	-1.3799	0.7761	-0.3450	0.1941
0.3334	0.2500	10.03	11.29	0.1845	0.1557	-1.4736	0.6024	-0.3852	0.1575

(*) Molar ratio (o) Mole fraction

Table (18)

Copolymerization of TBTA (M_1) with BMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method α = 2.9145	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
4.2388	0.8091	6.02	25.31	1.3014	0.5655	0.9817	13.8062	0.0587	0.8257
2.9759	0.7485	5.41	23.86	1.0314	0.5077	0.0906	8.5864	0.0079	0.7466
2.2279	0.6902	5.57	22.45	0.8402	0.4566	-0.4237	5.9075	-0.0480	0.6696
1.4664	0.5945	5.94	19.81	0.5926	0.3721	-1.0081	3.6286	-0.1541	0.5546
0.9937	0.4984	6.35	17.43	0.4415	0.3063	-1.2570	2.2365	-0.2440	0.4342
0.6370	0.3891	5.48	14.67	0.3155	0.2398	-1.3820	1.2862	-0.3290	0.3062
0.5353	0.3487	6.55	13.06	0.2582	0.2052	-1.5379	1.1096	-0.3822	0.2757
0.4245	0.2980	3.89	12.04	0.2264	0.1846	-1.4505	0.7959	-0.3909	0.2145
0.3300	0.2481	4.97	10.23	0.1770	0.1504	-1.5344	0.6153	-0.4347	0.1743

(*) Molar ratio (∘) Mole fraction

Table (19)

Copolymerization of TBTA (M_1) with AMA (M_2)

Initial monomer composition		Conversion	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 5.1901$	
$a^{(*)}$	$f_1^{(\circ)}$	%		$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
5.5767	0.8479	8.23	26.43	1.4127	0.5855	1.6292	22.0143	0.0600	0.8088
3.9315	0.7972	7.57	24.83	1.0659	0.5159	0.2433	14.4999	0.0124	0.7364
2.8842	0.7425	9.64	23.38	0.8518	0.4599	-0.5018	9.7659	-0.0336	0.6529
2.3649	0.7028	9.28	22.08	0.7103	0.4153	-0.9645	7.8739	-0.0738	0.6027
1.4782	0.5965	8.18	18.81	0.4639	0.3169	-1.7078	4.7096	-0.1725	0.4757
0.9948	0.4987	8.37	16.13	0.3345	0.2507	-1.9792	2.9584	-0.2429	0.3631
0.6478	0.3931	9.05	12.91	0.2247	0.1835	-2.2351	1.8674	-0.3167	0.2646
0.4267	0.2991	8.53	9.85	0.1488	0.1295	-2.4409	1.2238	-0.3806	0.1908

(*) Molar ratio (∘) Mole fraction

Table (20)

Monomer reactivity ratios in copolymerization of TBTA with MMA, PrMA, BMA and AMA

M_1-M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTA-MMA	0.401±0.012	2.199+0.060	0.882	0.395±0.013	2.180±0.058	0.861
TBTA-PrMA	0.323±0.010	1.713±0.048	0.553	0.314±0.008	1.684±0.033	0.529
TBTA-BMA	0.196±0.005	1.661±0.032	0.326	0.197±0.005	1.668±0.028	0.329
TBTA-AMA	0.195±0.005	2.575±0.054	0.502	0.201±0.004	2.619±0.041	0.526

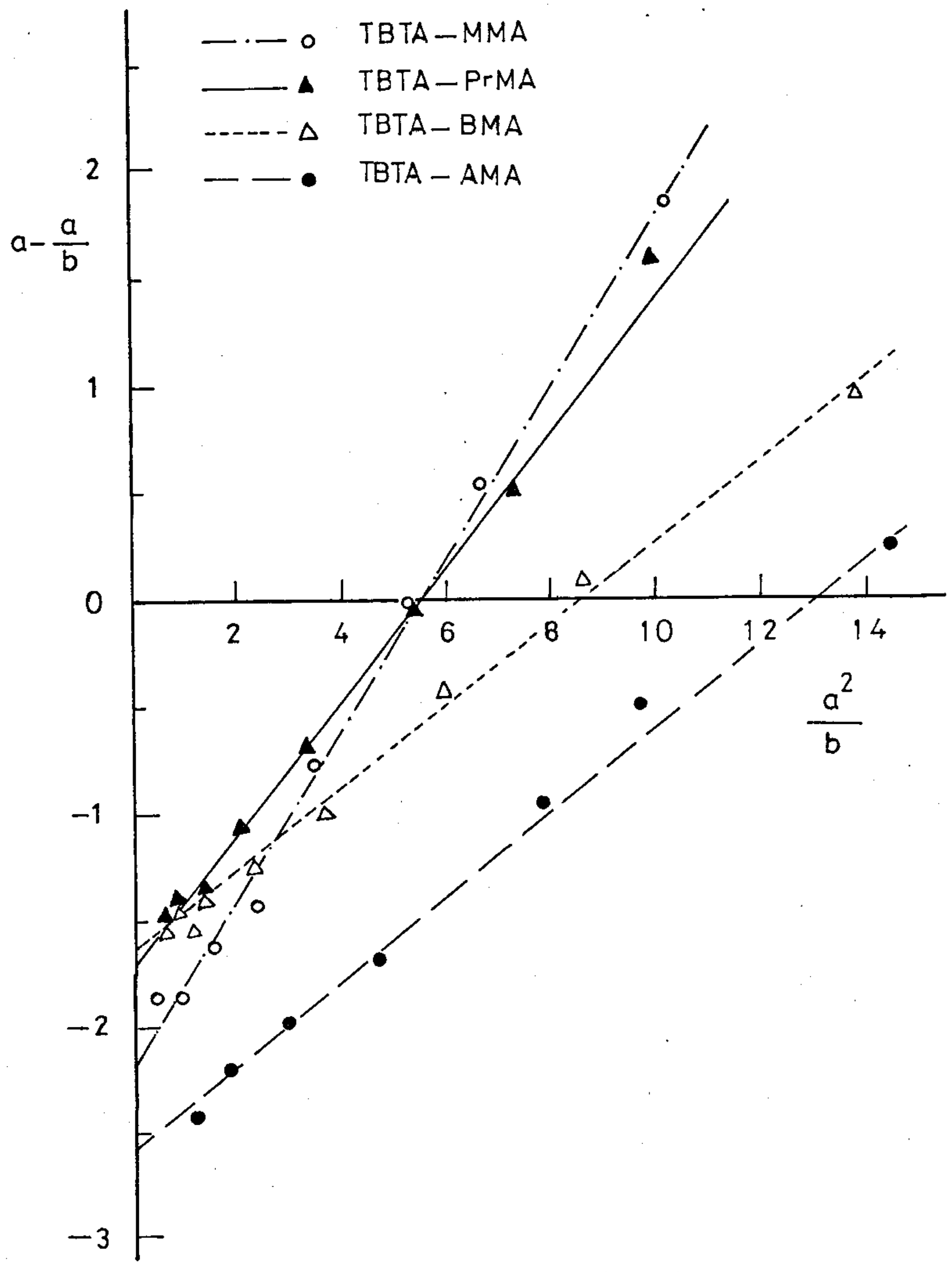


Fig. (16). Fineman—Ross plots for the copolymerization of: TBTA-MMA, TBTA-PrMA, TBTA-BMA, and TBTA-AMA.

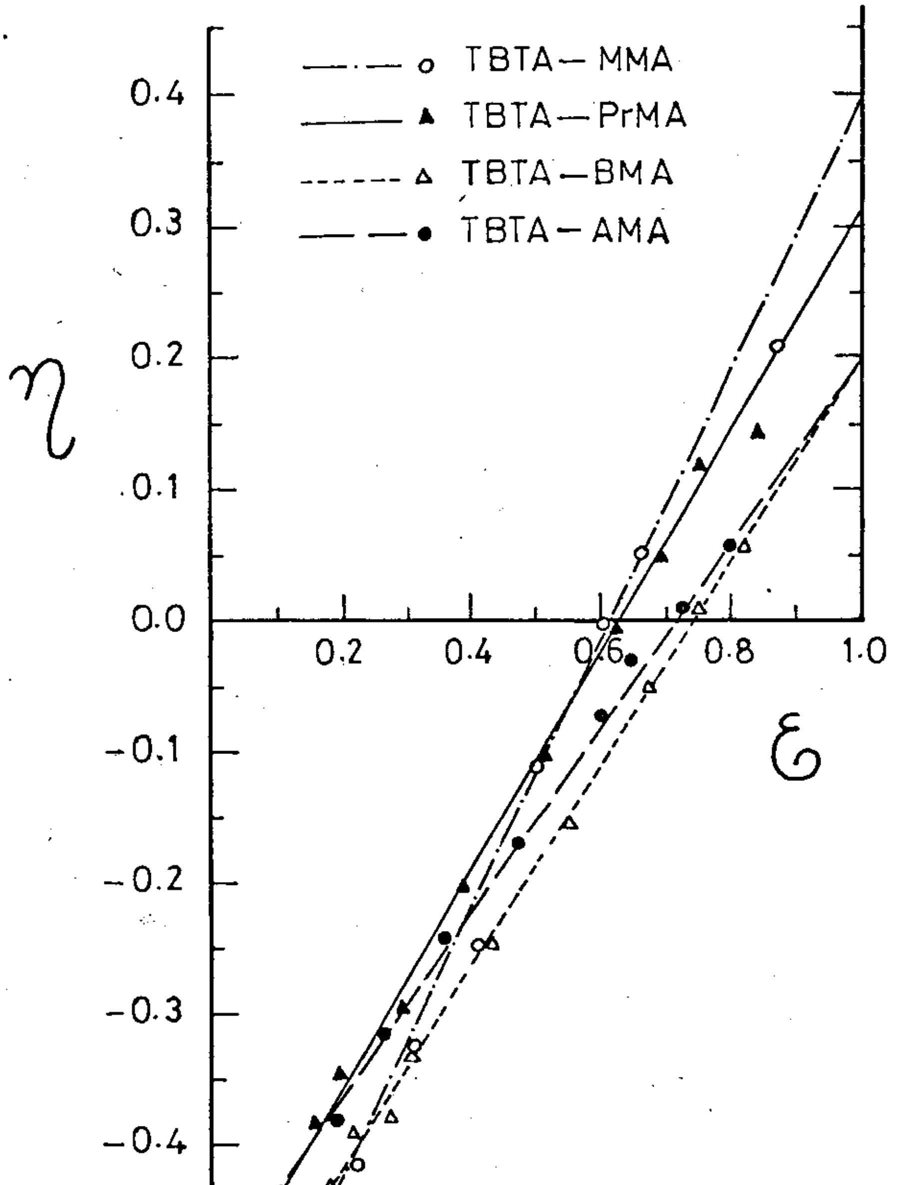


Fig. (17). Kelen–Tüdös plots for the copolymerization of: TBTA–MMA, TBTA–PrMA, TBTA–BMA, and TBTA–AMA.

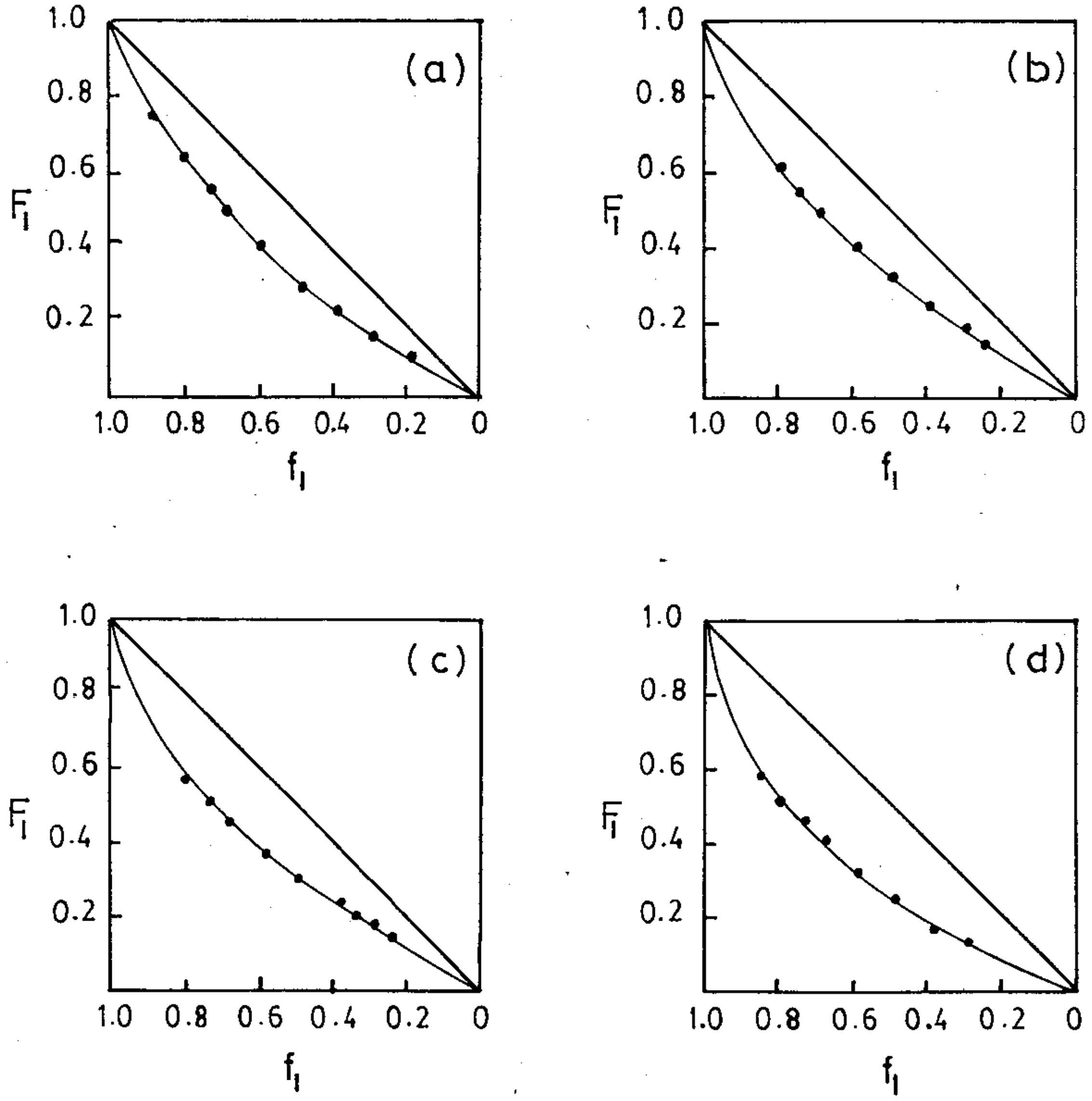


Fig. (18). Composition curves for the copolymerization of: (a) TBTA–MMA, (b) TBTA–PrMA, (c) TBTA–BMA, and (d) TBTA–AMA.

f_1 = mole fraction of M_1 in feed and

F_1 = mole fraction of M_1 in copolymer.

The correctness of the determined reactivity ratios was checked by studying the variation of copolymer composition with conversion. Thus, a feed composition of 30:70 mole % for TBTA-MMA and TBTA-BMA systems was polymerized over a wide range of conversion. Each sample at each level of conversion was analyzed for its tin content, from which the copolymer composition was calculated. Tables (21) and (22) illustrate the experimental conditions and results of both systems and Fig. (19) shows the conversion as a function of time for both systems. From the feed composition (30:70) and the determined reactivity ratios of these systems (Table 20), the variation of average copolymer composition with conversion was calculated by integration of the copolymer composition equation (page 17) according to the method described by Skeist[12], assuming that the copolymer composition within 10 % interval is constant. Fig. (20) shows good agreement between the calculated curves and the experimental points over a wide range of conversion indicating the correctness of the determined reactivity ratios of both systems.

The structure of the prepared copolymers of tri-n-butyltin acrylate with the alkyl esters of methacrylic acid as well as allyl methacrylate was investigated by infrared spectroscopy and the diagrams were found to be quite similar in the region

Table (21)

Variation of average copolymer composition for copolymerization of TBTA with BMA.

	Mole percent	gram
TBTA :	30	10.8300
BMA :	70	9.9400
AIBN :	(1 mole %)	0.1640

Solution polymerization in toluene (3 mole/l, total volume 33.33 ml).

Time (hour)	Conversion %	Sn %	Copolymer composition mole % TBTA	Copolymer composition mole % BMA
0.5	22.20	12.30	18.96	81.04
1.0	43.22	12.80	19.97	80.03
2.0	65.96	13.81	22.09	77.91
3.0	74.92	13.97	22.40	77.60
4.0	85.32	14.24	23.01	76.99
5.0	92.40	15.11	24.90	75.10

Table (22)

Variation of average copolymer composition for copolymerization of TBTA with MMA

	Mole percent	gram
TBTA :	30	10.8300
MMA :	70	7.0000
AIBN :	(1 mole %)	0.1640

Solution polymerization in toluene (3 mole/l, total volume 33.33 ml).

Time (hour)	Conversion %	Sn %	Copolymer composition mole %	
			TBTA	MMA
0.5	18.90	13.90	16.79	83.21
1.0	36.70	14.56	17.96	82.04
2.0	62.50	15.24	19.23	80.77
3.0	75.40	16.38	21.47	78.53
4.0	81.90	17.20	23.20	76.80
5.0	95.5	17.70	24.30	75.70

between 400 cm^{-1} to 1400 cm^{-1}. Fig. (21) illustrates the IR spectrum of TBTA-PrMA copolymer as an example of this group and shows that these copolymers are characterized by the presence of two strong bands at 1650 cm^{-1} and at 1730 cm^{-1} due to the stretching frequencies of the $\rangle C=O$ groups of the tributyltin carboxylates and the methacrylic esters, respectively. The bands at 2880-2970 cm^{-1} are due to the symmetrical and assymmetrical stretching frequencies of the C-H bonds due to the CH_2 and $-CH_3$ groups.

Copolymers prepared from the reaction of TBTA with alkyl methacrylates are clear, transparent, and soluble in most organic solvents even at higher conversions, while the copolymer of TBTA with AMA gave an insoluble gel product at higher conversions. Also, copolymers produced from TBTA with MMA were clear solids suitable for film formation while those from TBTA with both PrMA and BMA were rubbery and tacky products.

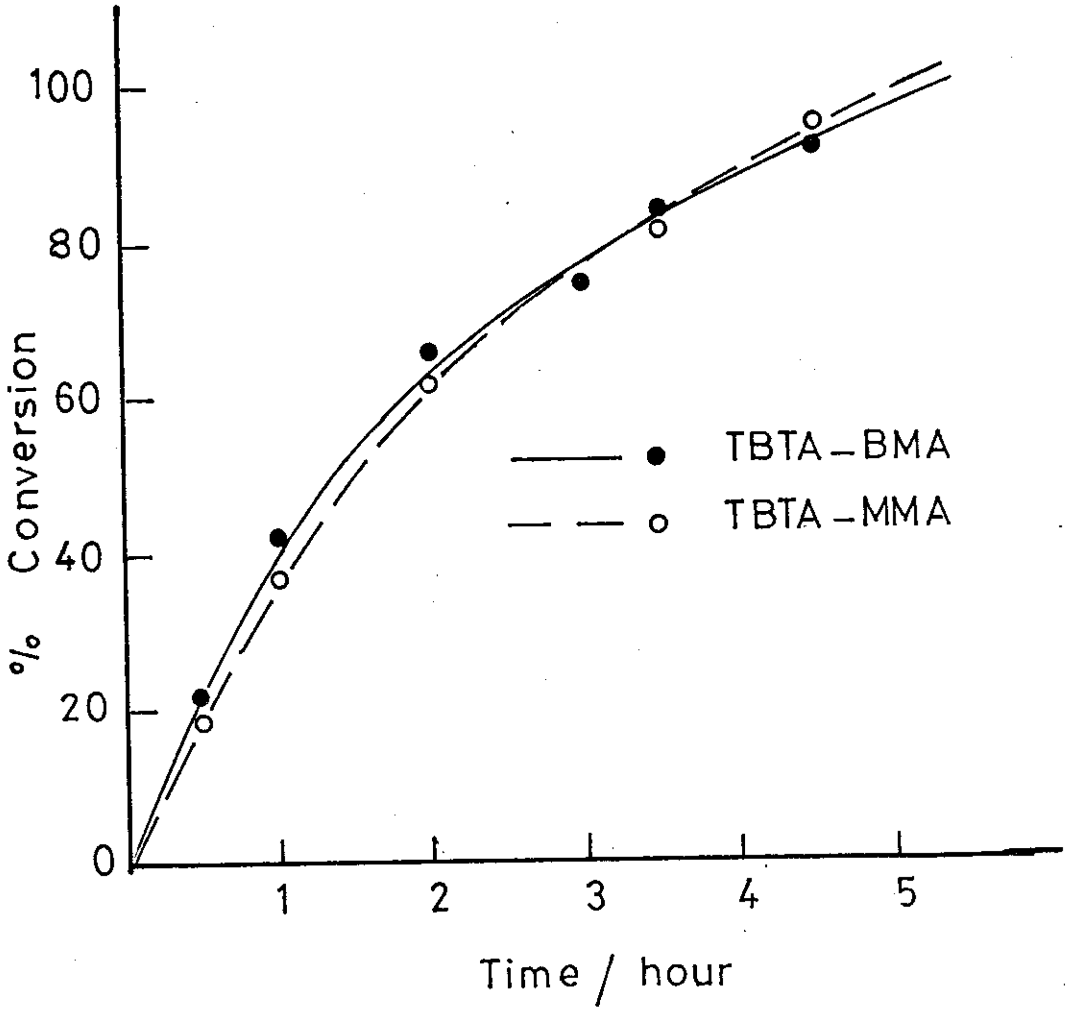


Fig. (19). Variation in percent copolymers produced with time for : TBTA–MMA and TBTA–BMA .

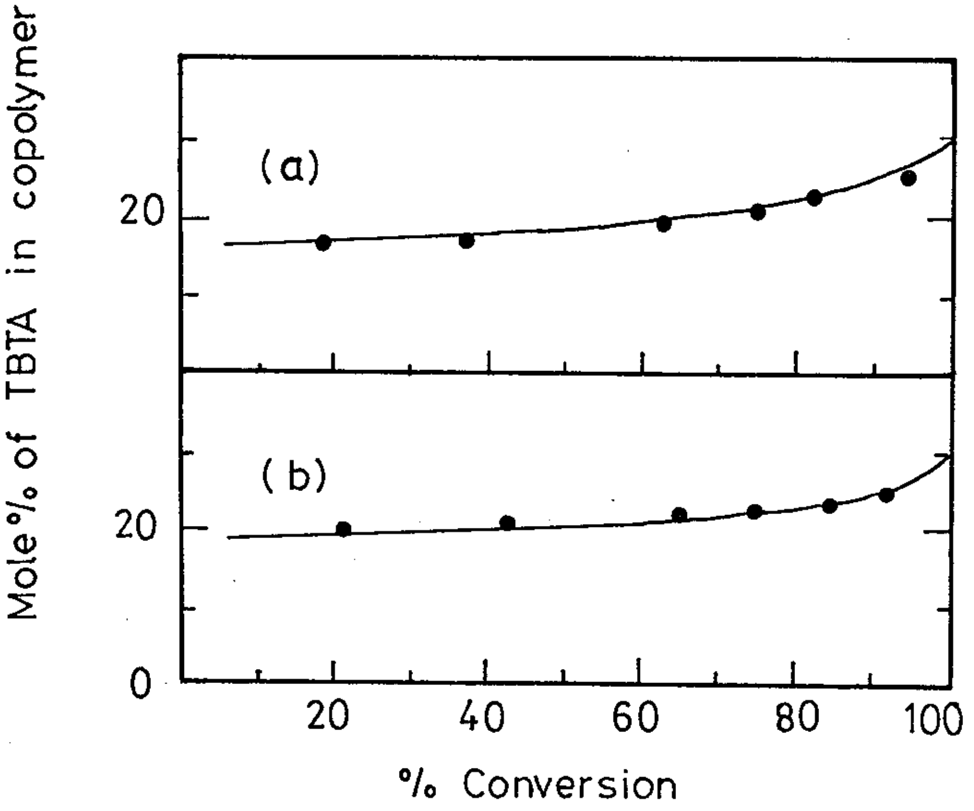


Fig. (20). Average copolymer composition with conversion for: (a) TBTA-MMA and (b) TBTA-BMA, lines represent calculated copolymer composition and (●) from tin analysis.

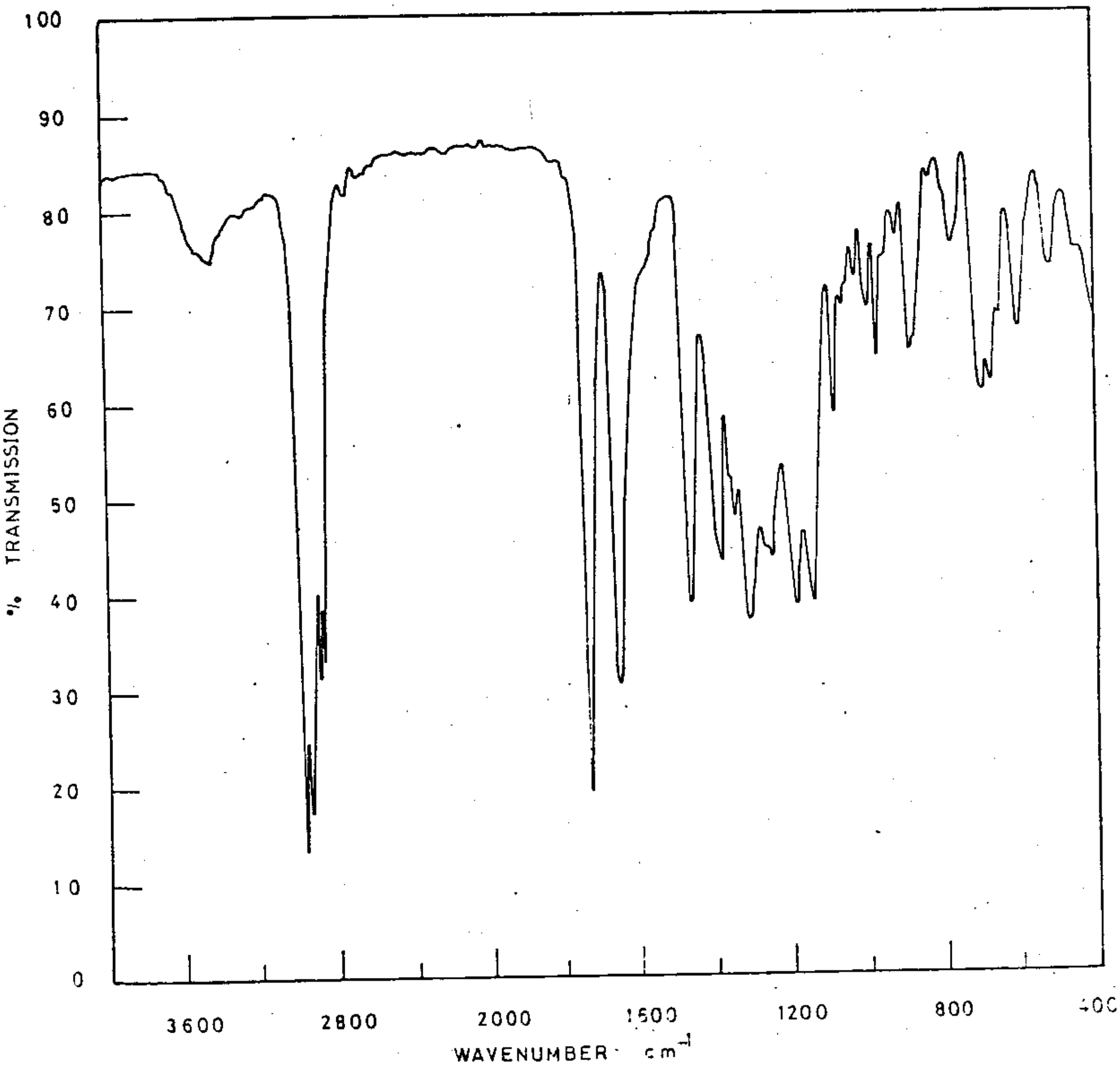
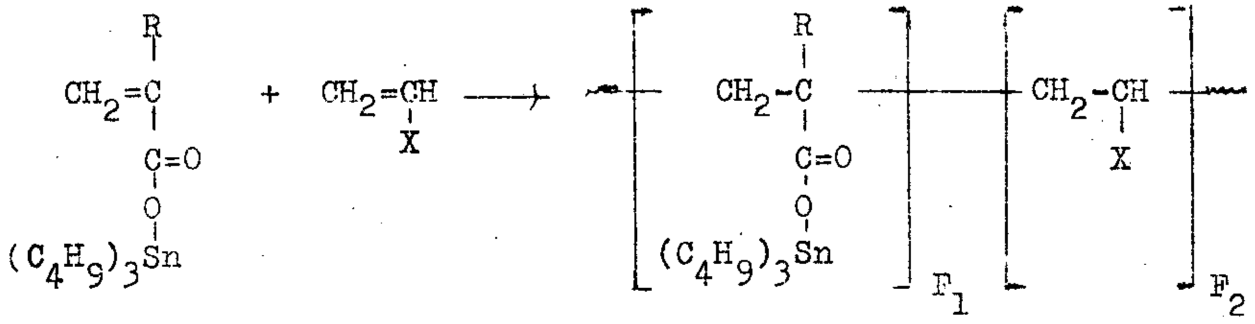


Fig. (21). I.R Spectrum for TBTA–PrMA copolymer.

CHAPTER VII

Monomer reactivity ratios for copolymerizations of tri-n-butyltin acrylate and methacrylate with acrylonitrile (AN) and styrene (St).

The copolymerization reactions of both TBTMA and TBTA with St and AN can be represented as :



$$CH_2{=}C(R){-}C({=}O){-}O{-}Sn(C_4H_9)_3 + CH_2{=}CH{-}X \longrightarrow \sim\!\left[CH_2{-}C(R)(C({=}O){-}O{-}Sn(C_4H_9)_3)\right]_{F_1}\!\!-\!\left[CH_2{-}CH(X)\right]_{F_2}\!\sim$$

where R = H or $-CH_3$, and X = $-C_6H_5$ or $-C{\equiv}N$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (23-26).

Fig. (22) shows the Fineman-Ross plots for the copolymerizations of TBTMA and TBTA with AN and St. Also Fig. (23) illustrates the Kelen-Tüdos plots of the four systems.

From the experimental data tabulated in Tables (23-26) and figures (22 & 23) for the copolymerization of TBTMA and TBTA with AN and St, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdos methods are summarized in Table (27).

Table (23)

Copolymerization of TBTMA (M_1) with AN (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.7046$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
2.3150	0.6330	8.23	29.34	1.7258	0.6982	0.9735	3.1060	0.2555	0.8151
1.8474	0.5953	7.94	28.96	1.4721	0.6487	0.5925	2.3184	0.1959	0.7669
1.4854	0.5642	9.95	28.61	1.2946	0.5976	0.3381	1.7042	0.1403	0.7075
1.2245	0.5353	8.74	28.27	1.1519	0.5504	0.1615	1.3018	0.0805	0.6488
1.0034	0.5055	6.27	27.88	1.0225	0.5009	0.0221	0.9847	0.0131	0.5829
0.8272	0.4669	5.69	27.33	0.8761	0.4527	-0.1169	0.7809	-0.0787	0.5257
0.6617	0.4314	8.78	26.75	0.7586	0.3981	-0.2106	0.5771	-0.1643	0.4503
0.5455	0.4018	7.89	26.22	0.6720	0.3530	-0.2662	0.4428	-0.2320	0.3859
0.4329	0.3624	9.35	25.42	0.5685	0.3021	-0.3286	0.3296	-0.3177	0.3188
0.2491	0.2795	7.48	23.27	0.3881	0.1994	-0.3927	0.1599	-0.4542	0.1851

(*) Molar ratio (∘) Mole fraction

Table (24)

Copolymerization of TBTMA (M_1) with St (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1491$	
a(*)	f_1(∘)			b(*)	F_1(∘)	a-a/b	a^2/b	η	ξ
4.000	0.8000	8.12	26.98	1.5910	0.6140	1.4859	10.0566	0.1326	0.8975
2.3300	0.6999	10.16	25.21	1.0726	0.5175	0.1577	5.0614	0.0254	0.8150
1.5000	0.60000	6.00	23.56	0.7970	0.4435	-0.3799	2.8199	-0.0957	0.7105
1.0000	0.5000	8.92	21.83	0.6134	0.3802	-0.6303	1.6303	-0.2268	0.5866
0.6667	0.4000	8.24	19.39	0.4354	0.3033	-0.8645	1.0209	-0.3984	0.4705
0.4286	0.3000	8.83	16.79	0.3120	0.2378	-0.9451	0.5888	-0.5438	0.3388
0.2500	0.2000	9.81	13.07	0.1946	0.1628	-1.0347	0.3212	-0.7033	0.2185
0.1111	0.0999	9.62	8.00	0.0937	0.0856	-1.0746	0.1313	-0.8393	0.1025

(*) Molar ratio (∘) Mole fraction

Table (25)

Copolymerization of TBTA (M_1) with AN (M_2)

Initial monomer composition		Conversion	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 2.8824$	
a(*)	f_1(°)			b(*)	F_1(°)	a-a/b	a^2/b	γ	ε
9.0000	0.9000	6.35	31.36	2.8672	0.7414	5.8611	28.2500	0.1883	0.9074
3.9973	0.7998	7.53	30.14	1.5691	0.6108	1.4498	10.1830	0.1109	0.7794
2.9255	0.7453	9/31	29.54	1.2723	0.5599	0.6263	6.7314	0.0652	0.7002
2.3220	0.6989	8.07	28.98	1.0691	0.5166	0.1501	5.0432	0.0189	0.6363
1.3728	0.6519	8.49	28.56	0.9529	0.4879	-0.0926	3.6809	-0.0441	0.5608
1.5062	0.6009	9.14	27.94	0.8171	0.4497	-0.3371	2.7765	-0.0596	0.4906
P/9858	0.4964	9.93	26.63	0.6165	0.3814	-0.6132	1.5762	-0.1375	0.3535
0.6638	0.3989	8.45	25.03	0.4634	0.3166	-0.7689	0.9508	-0.2005	0.2480
0.4244	0.2979	10.01	22.84	0.3344	0.2489	-0.8563	0.5434	-0.2499	0.1586
0.2492	0.1995	8.27	19.45	0.2112	0.1745	-0.9297	0.2937	-0.2931	0.0926

(*) Molar ratio (°) Mole fraction

Table (26)

Copolymerization of TBTA (M_1) with St (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1559$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
4.0000	0.8000	10.24	26.79	1.2562	0.5567	0.8158	12.7568	0.0587	0.9168
2.3300	0.6997	10.42	24.48	0.8298	0.4534	0.4779	6.5424	-0.0621	0.8499
1.5000	0.6000	7.51	21.93	0.5741	0.3647	-1.1128	3.9192	-0.2193	0.7722
1.0000	0.5000	6.62	19.48	0.4166	0.2940	-1.4004	2.4004	-0.3938	0.6749
0.6667	0.4000	10.25	16.66	0.2946	0.2275	-1.5960	1.5088	-0.5989	0.5662
0.4286	0.3000	10.01	13.56	0.2009	0.1666	-1.7048	0.9144	-0.8235	0.4417
0.2500	0.2000	10.02	9.89	0.1240	0.1103	-1.7661	0.5040	-1.1304	0.3036
0.1111	0.1000	11.34	5.39	0.0559	0.0529	-1.8763	0.2200	-1.3637	0.1599
0.0526	0.0500	9.51	2.79	0.0267	0.0260	-1.9174	0.1049	-1.5208	0.0832

(*) Molar ratio (∘) Mole fraction

Table (27)

Monomer reactivity ratios in copolymerization of

TBTMA and TBTA with AN and St.

M_1-M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA-AN	0.465±0.006	0.467±0.009	0.217	0.471±0.007	0.474±0.008	0.223
TBTMA-St	0.256±0.003	1.104±0.039	0.283	0.259±0.004	1.108±0.009	0.287
TBTA-AN	0.243±0.001	1.008±0.011	0.245	0.240±0.001	0.997±0.007	0.239
TBTA-St	0.213±0.010	1.910±0.049	0.407	0.219±0.013	1.939±0.038	0.425

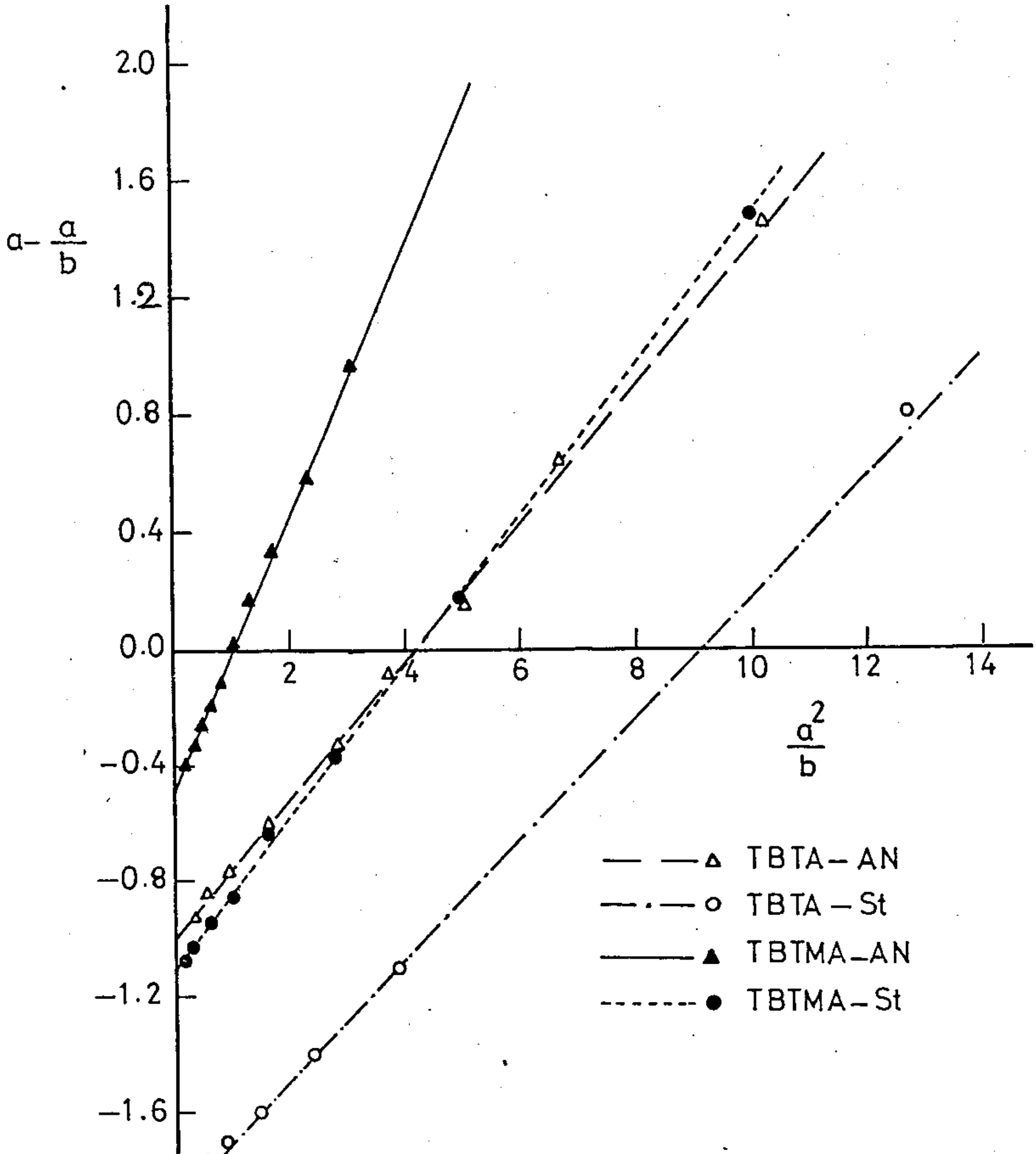


Fig. (22). Fineman−Ross plots for the copolymerization of TBTA-AN , TBTA-St , TBTMA-AN , and TBTMA-St .

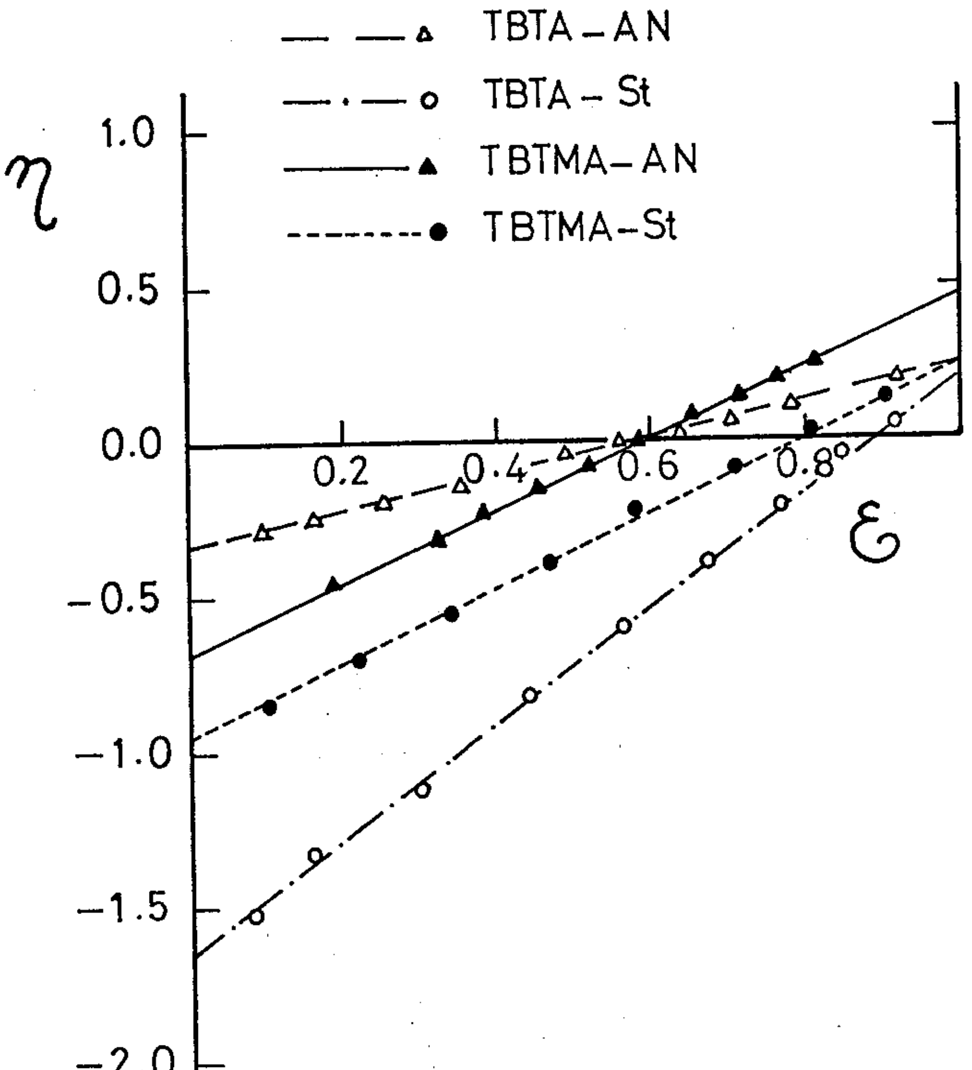


Fig. (23). Kelen–Tüdős plots for the copolymerization of: TBTA-AN, TBTA-St, TBTMA-AN, and TBTMA-St.

The data illustrated in Table (27) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods.

From the reactivity ratios of the four systems for the copolymerization of TBTMA and TBTA with AN and St given in Table (27), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules. Table (27) also shows that r_1 and r_2 determined for the copolymerization of TBTMA with AN is less than unity and should have azeotropic copolymerization behaviour. The azeotropic composition of TBTMA-AN system was calculated from the monomer reactivity ratios and was found to be at 49.91:50.02 mole ratio. This data is in agreement with the composition curves (Fig. 24) which shows the relation between F_1 (mole fraction of TBTMA or TBTA in copolymer) versus f_1 (mole fraction of TBTMA or TBTA in comonomer feed). From Fig. (24a), it is clear that the curve crosses the line representing $F_1 = f_1$ at 0.50 mole fraction for copolymerization of TBTMA with AN. This point of intersection corresponds to the azeotropic composition yielding homogeneous copolymer regardless of conversion.

The azeotropic comonomer mixture of TBTMA and AN was polymerized, by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C, to several conversions covering a

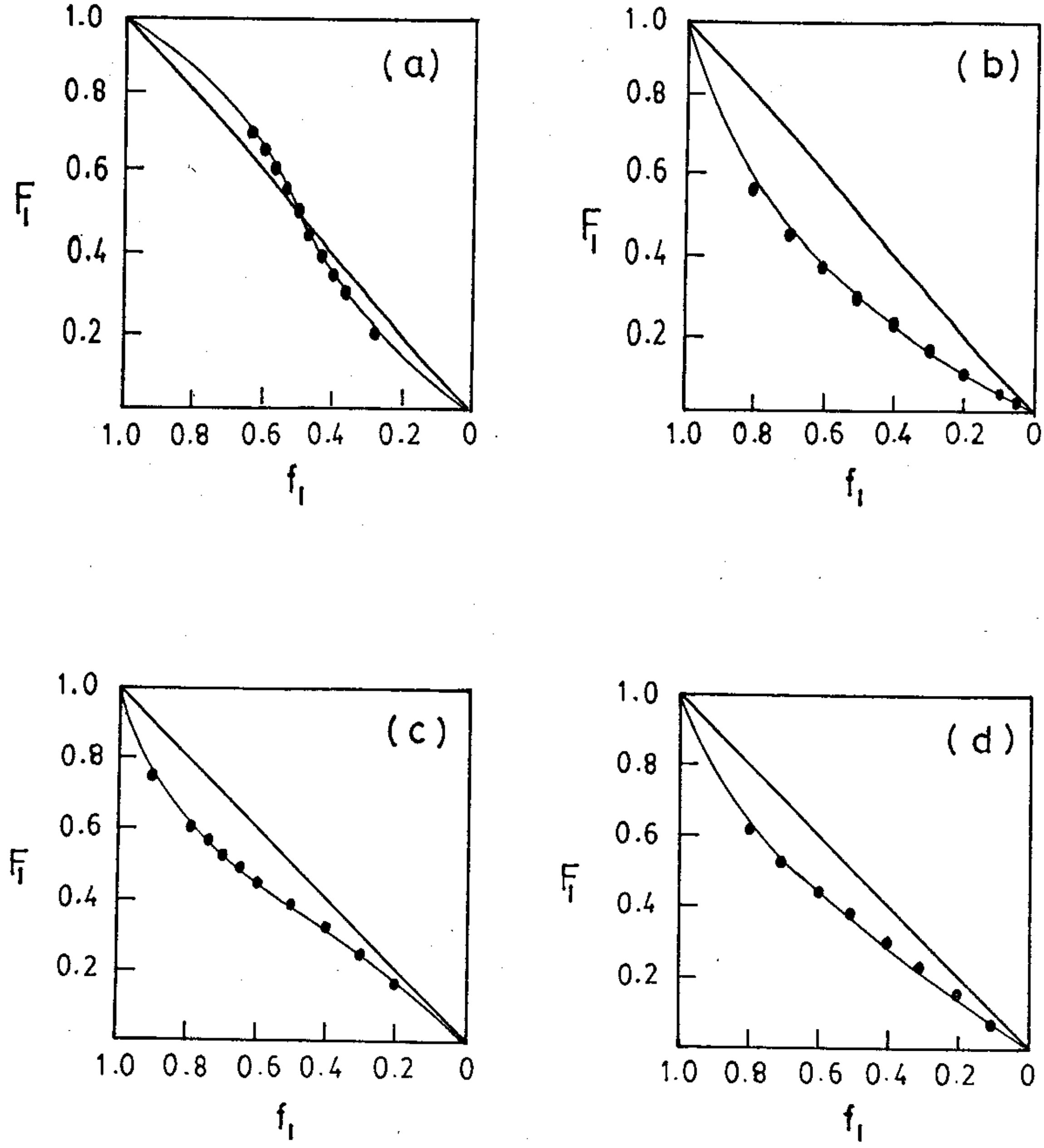


Fig. (24). Composition curves for the copolymerization of : (a) TBTMA-AN , (b) TBTA —St , (c) TBTA-AN , and (d) TBTMA-St where f_1 = mole fraction of M_1 in feed and F_1 = mole fraction of M_1 in copolymer.

wide range. Table (28) illustrates the experimental conditions and the results for the azeotropic copolymerization of TBTMA with AN. Fig. (25) shows the relation between percent conversion versus time for the azeotropic copolymerization of TBTMA-AN. Fig. (26) shows F_1 (mole fraction of TBTMA in copolymer) against % conversion and indicates that the experimental points, calculated from the tin content of each sample, are in good agreement with the line representing the azeotropic composition of TBTMA-AN system. From Table (28) and Fig. (26), it is clear that the azeotropic copolymer composition of TBTMA-AN remains constant up to 90 % conversion, and the tin content of the copolymers gave a mean value of 27.52 % against a calculated value of 27.80 % for the azeotropic composition of TBTMA-AN system.

The sequence distribution of the monomer units at the azeotropic composition of the TBTMA-AN system was calculated from the normograph of Izu and O'Driscoll[61]. Thus, the triad fractions for the azeotropic copolymer of TBTMA-AN was found to be as :

f_{111}	f_{112}	f_{121}	f_{212}
0.0480	0.1069	0.2380	0.2380

Table (28)

Azeotropic copolymerization of TBTMA (M_1) with AN (M_2)

	Mole fraction	gram
TBTMA	0.4998	18.7425
AN	0.5002	2.6511
AIBN	(1 mole %)	0.1640

Solution polymerization in toluene (3 moles/l, total volume 33.33 ml) at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
30	13.87	26.69	0.4281
50	21.55	27.64	0.4885
70	29.50	27.91	0.5080
100	36.89	27.75	0.4963
120	45.46	26.51	0.4178
150	53.79	27.88	0.5058
180	62.06	27.79	0.4992
240	78.39	27.77	0.4978
290	90.23	27.75	0.4963

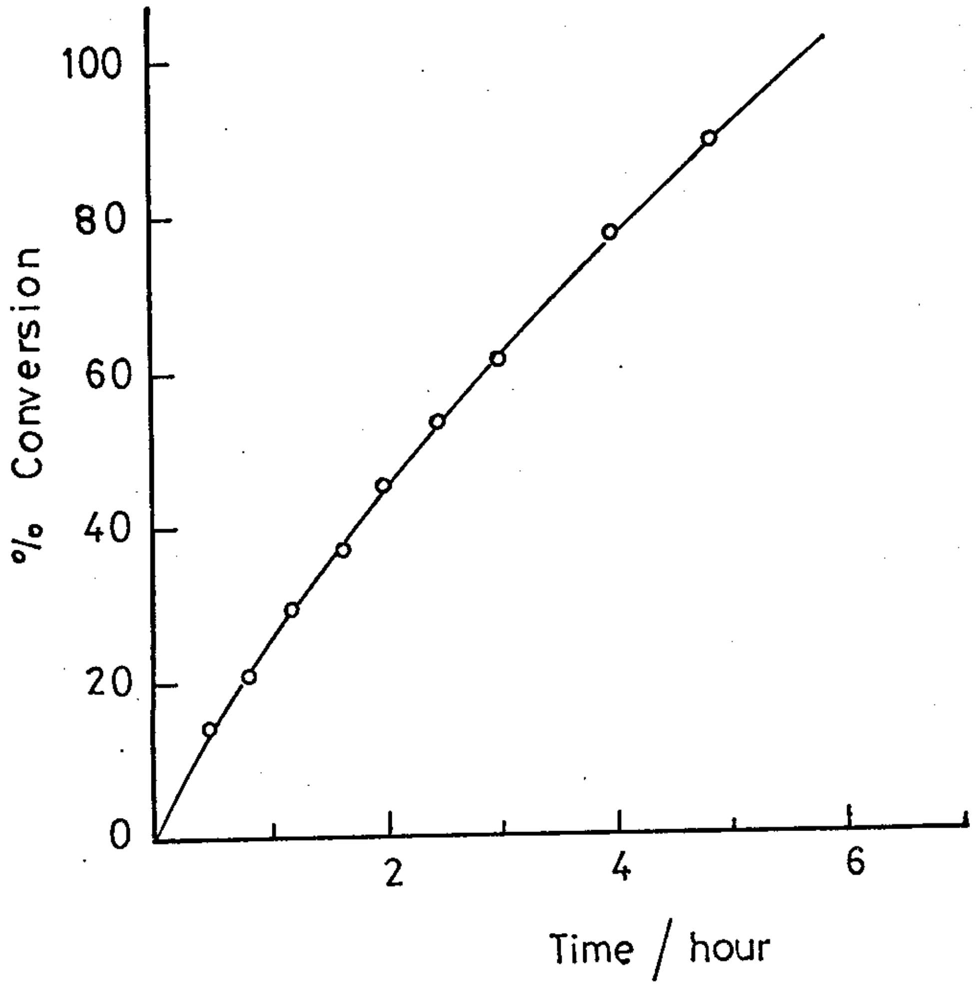


Fig. (25). Variation in percent azeotropic copolymer produced with time for azeotropic copolymerization of TBTMA – AN.

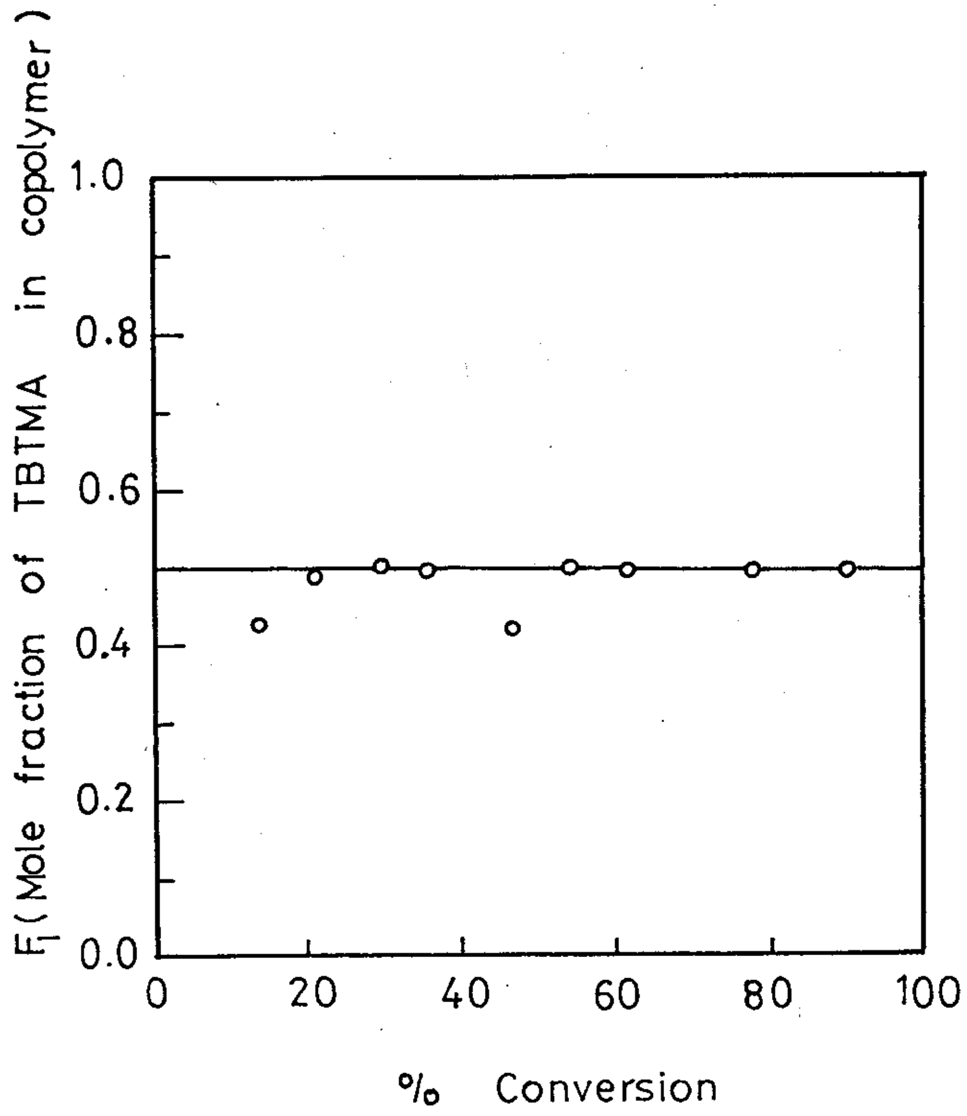


Fig. (26). F_1 as a function of conversion for azeotropic copolymerization of TBTMA – AN.

The structure of the prepared copolymers of TBTMA and TBTA with AN and St was investigated by infrared spectroscopy. The infrared spectra of TBTMA-AN and TBTA-AN copolymers are found to be quite similar and are characterized by the presence of one carboxyl carbonyl band at 1640 cm^{-1} due to the tributyltin carboxylates and a band at 2240 cm^{-1} due to the $-C{\equiv}N$ group, as shown in Fig. (27) which illustrates the IR spectrum of TBTMA-AN copolymer. Also the IR spectra of TBTMA-St and TBTA-St copolymers are quite similar and were characterized by the presence of two strong bands at 700 cm^{-1} and 750 cm^{-1} due to the mono-substituted benzene ring of styrene and a strong band at 1640 cm^{-1} due to the tributyltin carboxylates and also show bands at 3050-3100 cm^{-1} due to the stretching frequencies of the =C-H bonds. Fig. (28) illustrates the IR spectrum of TBTMA-St copolymer.

Copolymers prepared from the reactions of TBTMA-and TBTA with AN and St are clear, transparent and soluble in several organic solvents even at higher conversions. Films prepared from the azeotropic copolymer of TBTMA-AN exerted some tackiness which might limit its use as binders for antifouling coatings. To improve its film properties, the azeotropic copolymer was prepared at various lower initiator concentrations ranging from 0.25 to 0.05 mole/100 moles monomers, but the

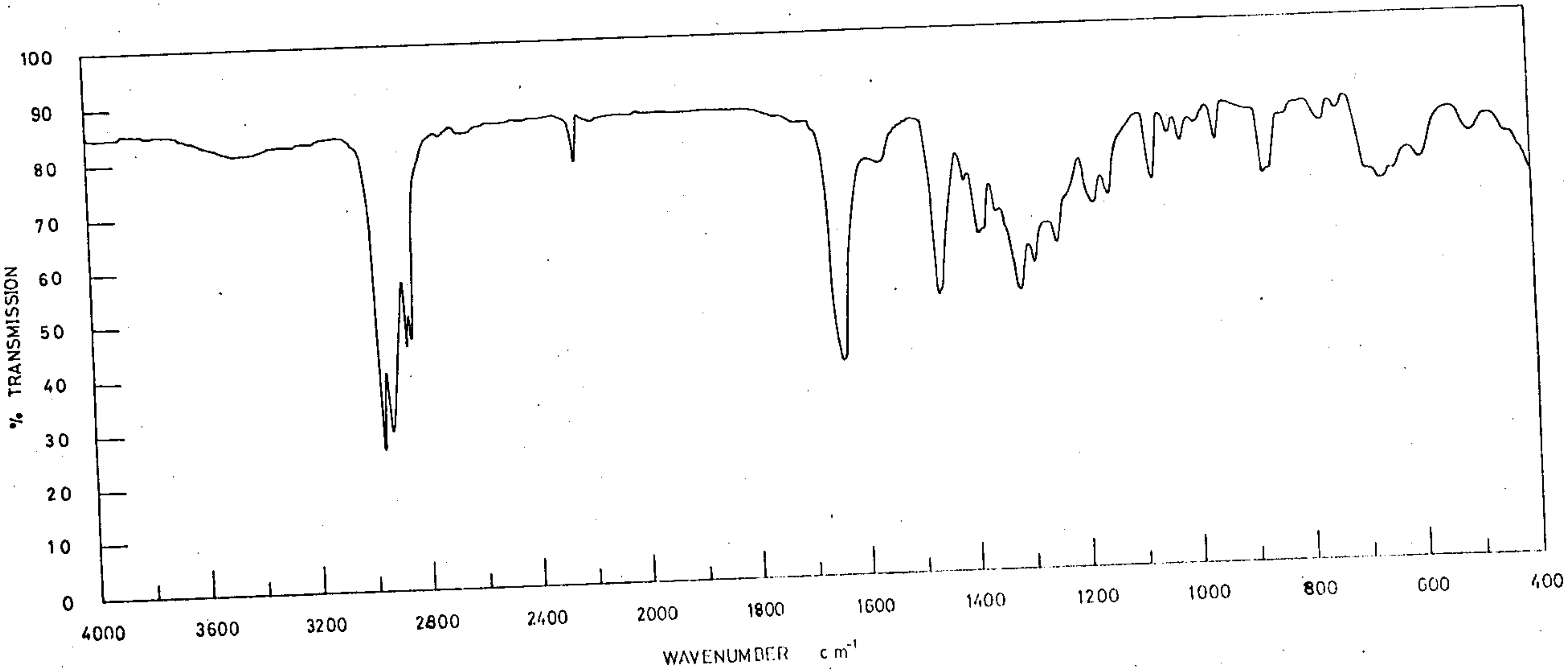


Fig. (27). I.R Spectrum for TBTMA – AN copolymer.

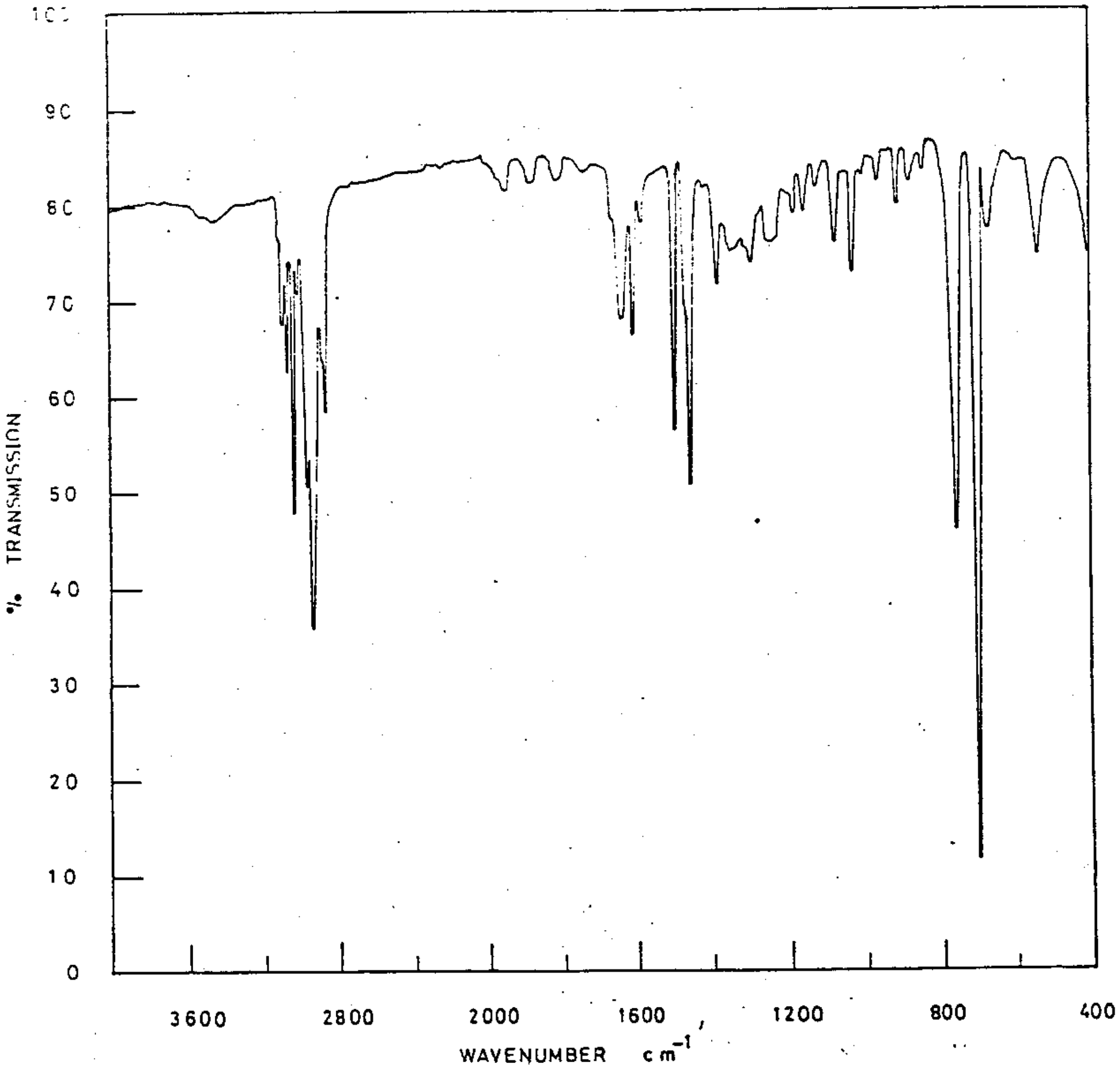


Fig. (28). I.R Spectrum for TBTMA—St copolymer.

tackiness of the films was only a little improved. The viscosity measurements of the azeotropic copolymer (TBTMA-AN) are illustrated in Table (29) which shows that the reduced viscosity of the azeotropic copolymer, 1 % solution in toluene at 30°C, increases with decreasing the initiator concentration. The tackiness of the azeotropic copolymers and the relatively low reduced viscosity values may be due to a chain transfer effect with the solvent (toluene).[62]

Table (29)

Reduced viscosity for the azeotropic copolymerization of TBTMA-AN

Initiator concentration	$\eta_{sp/c}$
1.00 mole %	0.1296
0.25 "	0.1593
0.10 "	0.2113
0.05 "	0.2740

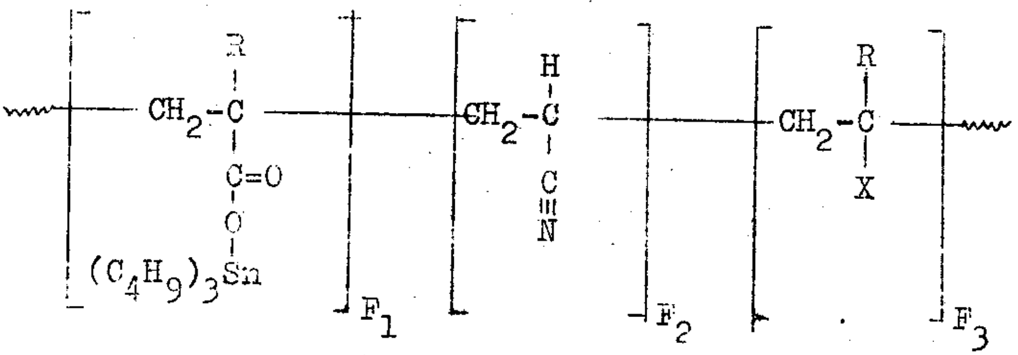
Copolymers prepared from the reaction of styrene with TBTMA and TBTA were clear, transparent solids suitable for film formation.

CHAPTER VIII

Terpolymerization Reactions

Ternary copolymerization reaction of the system involving tri-n-butyltin acrylate or methacrylate and acrylonitrile with the alkyl esters of acrylic or methacrylic acids as well as styrene were prepared by solution polymerization in toluene (3 mole/L) in presence of 1 mole % AIBN initiator at 70°C in the way described before (page 45). Four terpolymer systems involving TBTMA and AN with EA, BA, MMA, or BMA, and also three terpolymer systems involving TBTA and AN with MMA, BMA or St were prepared.

The terpolymers prepared in the present study can be represented by the following general formula as :



$$\left[CH_2-\overset{R}{\underset{\underset{\underset{(C_4H_9)_3Sn}{O}}{C=O}}{C}} \right]_{F_1} \left[CH_2-\overset{H}{\underset{C\equiv N}{C}} \right]_{F_2} \left[CH_2-\overset{R}{\underset{X}{C}} \right]_{F_3}$$

where R = -H or $-CH_3$ and

X = $-COOCH_3$, $-COOC_2H_5$, $-COOC_4H_9$ or $-C_6H_5$.

To study the instantaneous terpolymer composition of each system, the terpolymers were polymerized to low conversions (less than 10 %) and the terpolymers produced were analyzed for tin and nitrogen. From the tin content and the nitrogen content of each sample, the terpolymer composition could be calculated. The initially formed terpolymer composition of each system could be calculated by using the terpolymer composition equation in the form proposed by Khan and Horowitz[27] (page 27). The prediction of the terpolymer composition requires the monomer ~~reactivity~~ ratios of the individual two-component systems. Thus, the reactivity ratios used for calculated the terpolymer composition of each system, determined previously from the binary copolymerization reactions of organotin monomers, as well as the literature values for EA-AN, BA-AN, MMA-AN, BMA-AN and St-AN systems, are illustrated in Table (30).

To check the correctness of the reactivity ratios tabulated in Table (30), two feed compositions for each system were selected, polymerized at low conversions, and analyzed for tin and nitrogen. Table (31) illustrates the feed composition and the results of the analysis of the prepared fourteen terpolymer compositions. Also, Table (31) shows good agreement between the found terpolymer composition (based on tin and nitrogen analysis), and the calculated terpolymer composition for each feed, which indicates the correctness of monomer reactivity ratios.

Table (30)

Reactivity ratios in terpolymer systems

M_1-M_2-M_3	Reactivity ratios determined in this work				Reactivity ratios cited from literature		
	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	Refs.
TBTMA-AN-EA	0.465	0.467	1.259	0.606	1.12	0.93	63
TBTMA-AN-BA	0.465	0.467	0.846	0.572	1.003	1.005	64
TBTMA-AN-MMA	0.465	0.467	0.789	1.004	0.15	1.20	65
TBTMA-AN-BMA	0.465	0.567	0.623	0.646	0.31	1.08	66
TBTA-AN-MMA	0.243	1.008	0.401	2.199	0.15	1.20	65
TBTA-AN-BMA	0.243	1.008	0.196	1.661	0.31	1.08	66
TBTA-AN-St	0.243	1.008	0.213	1.91	0.03	0.52	67

Table (31)

Terpolymer compositions using tin and nitrogen analyses

Exp. No.	M_1 M_2 M_3	Feed Composition (Mole %)	Sn %	N %	Terpolymer composition (Mole %)	
					Found	Calculated
	TBTMA	19.97			27.98	27.87
Ia	AN	50.07	21.65	4.48	49.23	50.92
	EA	29.96			22.80	21.21
	TBTMA	52.11			54.51	53.63
Ib	AN	28.67	27.83	2.15	35.78	34.59
	EA	19.22			9.71	11.78
	TBTMA	19.95			27.86	27.37
IIa	AN	40.03	19.70	3.16	37.99	39.78
	BA	40.02			34.14	32.95
	TBTMA	39.17			45.64	43.34
IIb	AN	41.53	25.87	2.74	41.08	42.34
	BA	19.30			13.27	14.32
	TBTMA	19.95			17.99	17.32
IIIa	AN	50.02	16.19	3.88	36.63	38.06
	MMA	30.03			45.37	44.72
	TBTMA	29.93			26.89	25.18
IIIb	AN	40.10	20.23	2.97	33.54	33.36
	MMA	29.97			39.55	41.46

Table (31), continued.

Exp. No.	M_1 M_2 M_3	Feed composition (mole %)	Sn %	N %	Terpolymer composition (mole %) Found	calculated
	TBTMA	20.00			24.36	23.24
IVa	AN	60.35	18.71	4.45	49.23	48.96
	BMA	19.65			26.39	27.80
	TBTMA	30.03			29.77	30.88
IVb	AN	39.94	19.69	2.75	35.32	34.31
	BMA	30.03			34.90	34.81
	TBTA	19.64			10.24	8.87
Va	AN	39.90	10.8	3.71	29.86	32.65
	MMA	40.46			59.89	58.48
	TBTA	61.90			36.69	36.56
Vb	AN	23.48	24.10	2.40	31.06	32.11
	MMA	14.62			32.25	31.33
	TBTA	29.99			16.77	15.54
VIa	AN	40.50	13.30	3.00	32.15	32.74
	BMA	29.51			51.07	51.72
	TBTA	55.21			26.50	27.09
VIb	AN	24.90	17.51	1.74	22.45	23.37
	BMA	19.89			51.05	49.54
	TBTA	20.13			6.67	7.10
VIIa	AN	20.34	8.26	3.25	27.68	25.85
	St	59.53			66.64	67.06
	TBTA	39.22			12.68	11.91
VIIb	AN	40.36	12.91	4.60	38.44	40.11
	St	20.42			48.86	47.98

It is well known that molecular heterogenity has a direct effect on the physical properties of polymers, and the co- or terpolymer composition varies with conversion except for the systems having azeotropic behaviour. On the basis of the determined reactivity ratios determined from the binary copolymerization reactions of TBTMA and TBTA (Tables 7, 13, 20 and 27) and the literature values, it was found that any terpolymer system involving organotin moiety with azeotropic composition could be prepared. Thus, terpolymer systems illustrated in Table (31) with feed compositions Ia-VIIa, were polymerized to different extents of conversion as shown in Figs. (29 and 30) which illustrate the percent conversion as a function of time for each system. Then, each sample at each extent of conversion was analyzed for its tin and nitrogen contents, from which the terpolymer composition of each sample was calculated.

Tables (32-38), illustrate the experimental conditions and results of the terpolymerization reactions.

Prediction of both the instantaneous and average terpolymer composition at each extent of conversion was calculated for each terpolymer system on the basis of the feed composition and the monomer reactivity ratios of each system tabulated in Table (30) by integration of the terpolymer composition

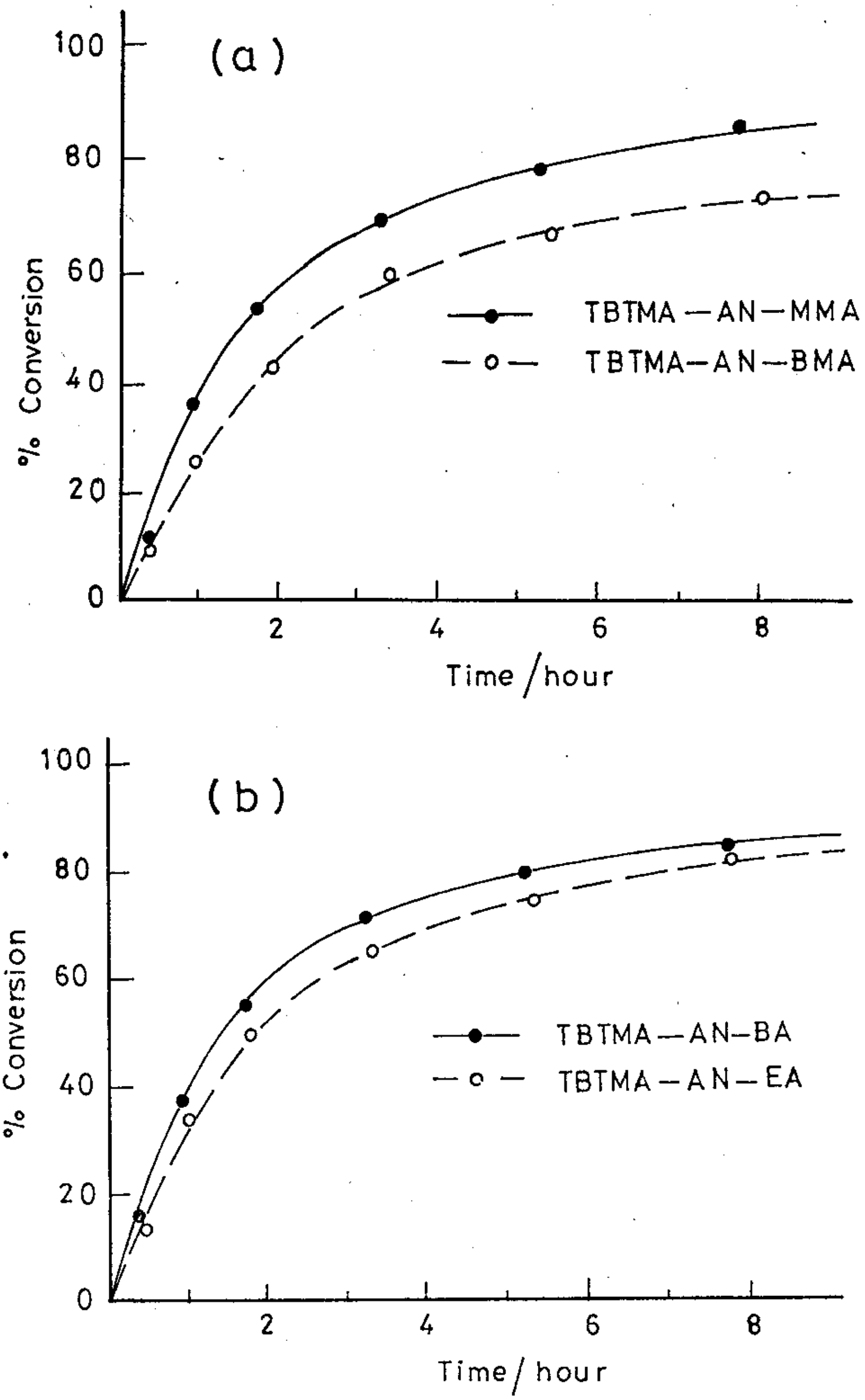


Fig. (29). Variation in percent terpolymers produced with time for: (a) TBTMA–AN–MMA and TBTMA–AN–BMA; and (b) TBTMA–AN–EA and TBTMA–AN–BA.

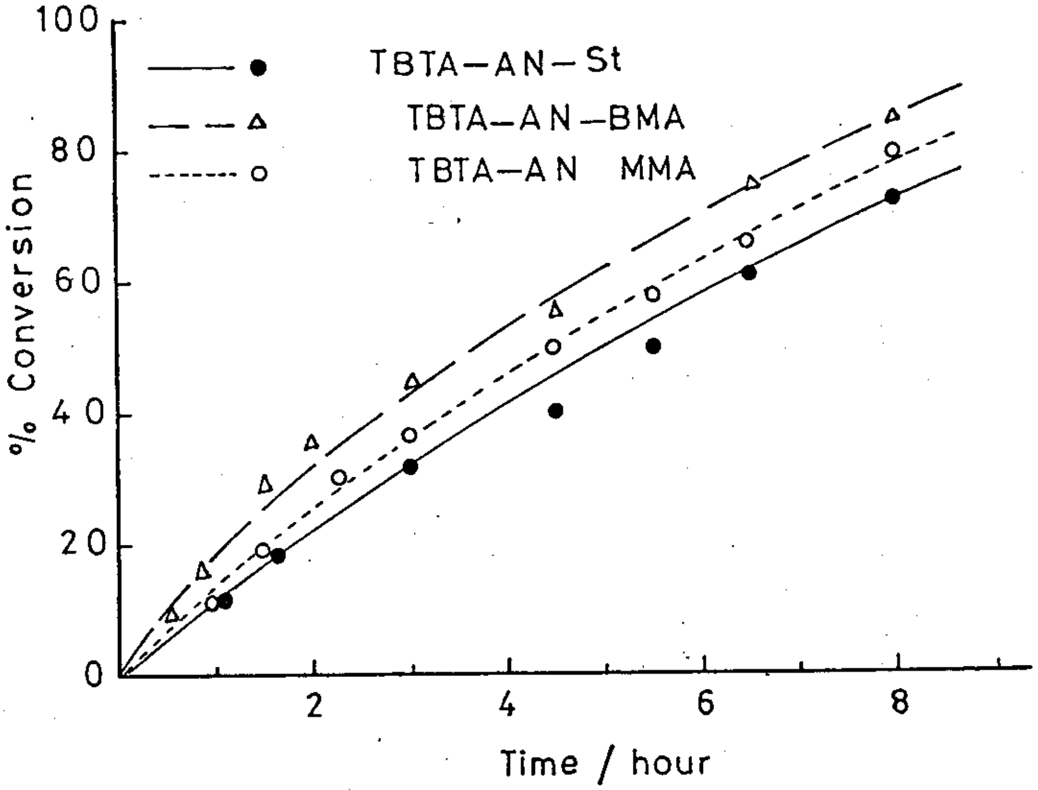


Fig. (30). Variation in percent terpolymers produced with time for : TBTA-AN-St, TBTA-AN-BMA and TBTA-AN-MMA.

equation proposed by Khan and Horowitz[27] (page 27), assuming that the terpolymer composition is constant within 10 % intervals. The variations of the calculated instantaneous terpolymer composition (Mole %) and average terpolymer composition (wt. %) as a function of conversion for the seven terpolymer systems studied are illustrated in Figs. (31-37).

From the conversion-composition curves of TBTMA-AN-EA and TBTMA-AN-BA systems (Figs. 31 and 32), it is clear that TBTMA is completely consumed at 95 % conversion in the both systems, after which a copolymers of AN-EA and AN-BA are formed, and that AN content of the two terpolymers remain almost constant up to 90 % conversion.

From Figs. (33 and 34) which illustrate the conversion-composition curves for TBTMA-AN-MMA and TBTMA-AN-BMA systems, it is clear that both MMA and BMA decrease continuously with conversion and were completely consumed at 86 % and 90 % conversions, respectively. Also, TBTMA in the both systems was completely disappeared at 95 % conversion, while acrylonitrile content increase continuously with conversion for both systems.

Figs. (35 and 36) illustrate the conversion-composition curves for TBTA-AN-MMA and TBTA-AN-BMA systems, which show that MMA and BMA contents were decreased continuously with conversion and were completely disappeared at 85 % and at 77 % conversions, respectively. Also AN was consumed at 97 % and 96 % conversions, respectively, while TBTA content for both systems increase continuously up to 100 % conversion.

From Fig. (37), which illustrates the conversion-composition curve for TBTA-AN-St system, it is clear that both AN and St decrease continuously with conversion and were consumed at 93 % and at 95 % conversions, after which a homopolymer of TBTA was only formed.

Tables (32-38) indicate that the results obtained from the analysis of the seven terpolymer systems studied at different levels of conversions, calculated as average terpolymer composition (wt. %) are in good agreement with the predicted curves as illustrated in Figs. (31-37). Also, from Figs. (31-37), it is clear that terpolymerization of the systems studied give a wide spectrum of polymer compositions with conversion and obviously when uniformity of polymer composition is desired, proper amounts of the more reactive monomers must be continuously added.

Terpolymers obtained from the seven systems studied were pale yellowish rubbery products, except terpolymers containing MMA or St which were solids, and soluble in organic solvents even at higher conversions.

The structure of the prepared terpolymers was investigated by IR spectroscopy and were found to show as expected two strong bands at 1640 cm^{-1} and at 1720 cm^{-1} due to the carboxylate carbonyl groups and the carbonyl groups of the alkyl acrylates or methacrylates, respectively, and also the bands due to the $-C\equiv N$ of acrylonitrile appeared at 2240 cm^{-1}. Fig. (38) illustrates the IR spectra for the TBTMA-AN-BMA and TBTA-AN-St systems, as examples for the prepared terpolymers.

Table (32)

Average terpolymer composition for terpolymerization of TBTMA, AN and EA

	Mole percent	gram
EA :	29.96	5.992
TBTMA :	19.97	14.9775
AN :	50.07	5.3074
AIBN :	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt.%		
				TBTMA	AN	EA
0.41	12.7	21.65	4.48	68.22	16.96	14.82
0.916	34.1	21.48	4.68	67.68	17.71	14.61
1.75	49.4	21.12	4.80	66.55	18.17	15.28
3.25	65.4	20.38	4.83	64.22	18.28	17.50
5.25	73.9	20.31	4.94	64.00	18.7	17.30
7.55	82.1	19.16	4.89	60.37	18.51	21.12

Table (33)

Average terpolymer composition for terpolymerization of TBTMA, AN and BA

		Mole percent	gram
BA	:	40.02	10.2451
TBTMA	:	19.95	14.9625
AN	:	40.03	4.2432
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt %.		
				TBTMA	AN	BA
0.41	15.80	20.70	3.16	65.23	11.96	22.81
0.916	37.80	20.02	3.14	63.08	11.88	25.04
1.75	54.80	18.92	3.33	59.62	12.60	27.78
3.25	71.00	18.22	3.28	57.41	12.41	30.18
5.25	79.30	17.76	3.53	55.96	13.36	30.68
7.75	84.00	17.38	3.65	54.76	13.81	31.43

Table (34)

Average terpolymer composition for terpolymerization of TBTMA, AN and MMA

	Mole percent	gram
MMA :	30.03	6.0060
TBTMA :	19.95	14.9625
AN :	50.02	5.3021
AIBN :	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTMA	AN	MMA
0.41	12.18	16.90	3.88	51.02	14.68	34.29
0.916	37.40	16.32	3.95	51.42	14.95	33.62
1.75	54.10	16.43	4.33	51.77	16.39	31.83
3.25	70.50	16.82	4.48	53.00	16.96	30.04
5.25	78.40	17.80	4.58	56.09	17.33	26.57
7?75	85.40	18.00	4.58	56.72	17.33	25.94

Table (35)

Average terpolymer composition for terpolymerization of TBTMA, AN and BMA

		Mole percent	gram
BMA	:	19.65	5.5806
TBTMA	:	20.00	15.0000
AN	:	60.35	6.3971
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTMA	AN	BMA
0.41	9.76	18.71	4.45	58.96	16.84	24.20
0.91	25.80	18.83	4.45	59.33	16.84	23.83
1.91	43.50	18.71	4.23	58.96	16.01	25.03
3.41	59.90	18.23	4.38	57.40	16.58	26.02
5.41	66.60	18.38	4.88	57.92	18.47	23.61
8.00	73.30	18.40	4.96	57.98	18.72	23.30

Table (36)

Average terpolymer composition for terpolymerization of TBTA, AN and MMA

		Mole percent	gram
MMA	:	40.46	8.0920
TBTA	:	19.64	14.1801
AN	:	39.90	4.2294
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	MMA
1.0	10.9	10.82	3.71	32.81	14.04	53.15
1.5	18.9	10.85	4.03	32.91	15.25	51.84
2.25	30.7	10.85	3.90	32.91	14.70	52.39
3.0	36.8	11.28	4.11	34.21	15.50	50.29
4.5	49.5	11.28	4.11	34.21	15.50	50.29
5.5	57.5	11.89	3.93	36.07	14.80	49.13
6.5	65.5	12.50	3.90	37.90	14.70	47.40
8.0	79.5	13.50	4.00	40.90	15.14	43.96

Table (37)

Average terpolymer composition for terpolymerization of TBTA, AN and BMA

		Mole percent	gram
BMA	:	29.51	8.3808
TBTA	:	29.99	21.6528
AN	:	40.50	4.293
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	BMA
0.5	9.50	13.30	3.00	40.34	11.35	48.31
0.83	16.00	13.30	3.00	40.34	11.35	48.31
1.5	29.50	13.80	3.10	41.86	11.73	46.41
2.0	36.80	14.30	3.19	43.38	12.07	44.55
3.0	44.50	14.80	3.15	44.80	11.92	43.28
4.5	55.00	15.09	3.26	45.77	12.34	41.89
6.5	74.00	16.47	3.28	49.90	12.41	37.69
8.0	85.00	17.20	3.30	52.17	12.49	35.34

Table (38)

Average terpolymer composition for terpolymerization of TBTA, AN and St

		Mole percent	gram
St	:	59.53	12.3822
TBTA	:	20.13	14.5339
AN	:	20.34	2.1560
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	St
1.08	11.17	8.26	3.25	25.05	12.30	62.65
1.66	18.31	8.30	3.20	25.17	12.11	62.72
3.00	31.60	9.04	3.19	27.42	12.07	60.51
4.50	39.90	8.73	3.15	26.48	11.92	61.60
5.50	49.30	9.60	3.00	29.12	11.35	59.53
6.50	60.90	10.09	3.00	30.60	11.35	58.05
8.00	72.50	10.90	2.90	33.06	10.97	55.97
9.00	85.00	11.98	2.85	36.34	10.78	52.88

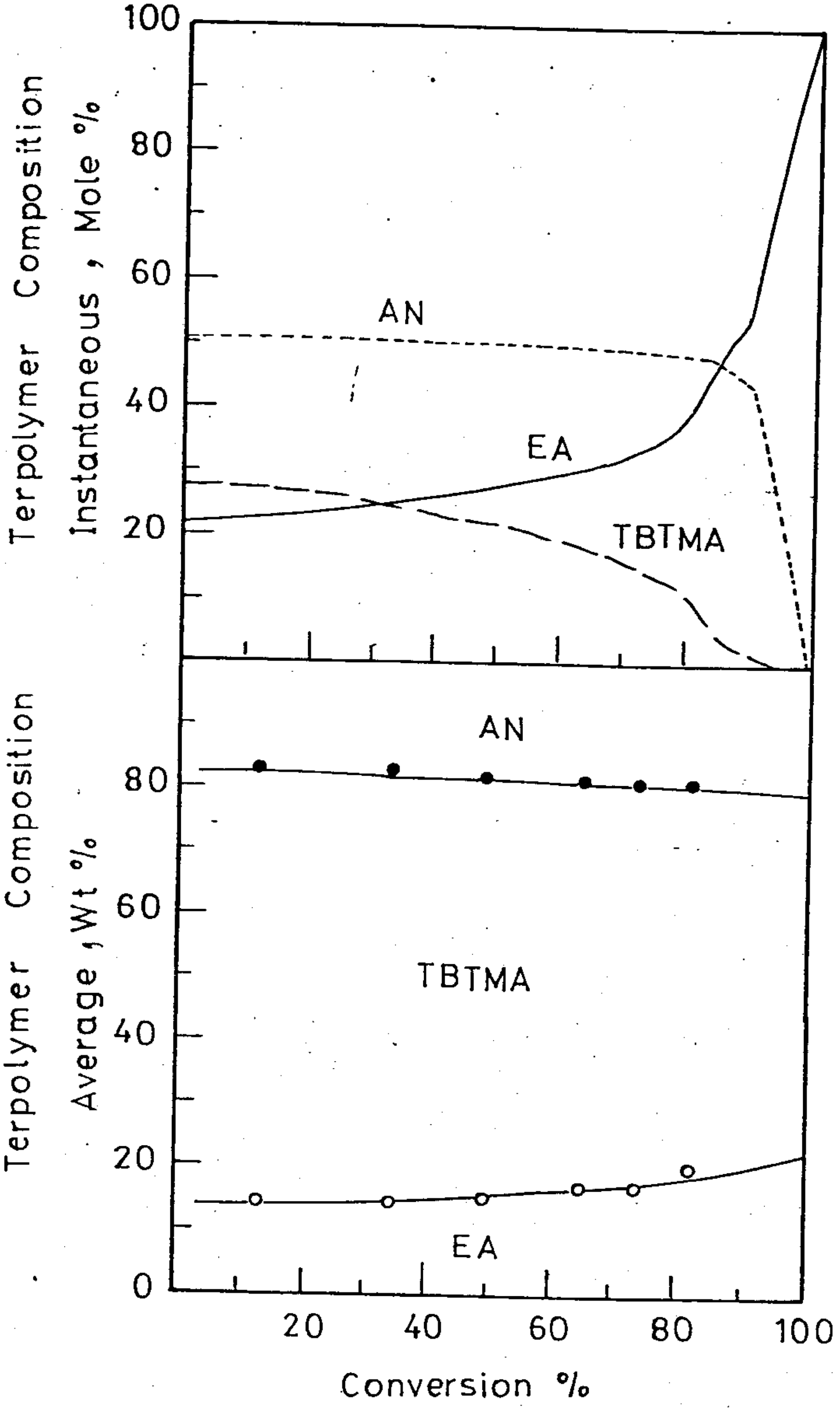


Fig. (31). Variation of instantaneos and average terpolymer composition with conversion for TBTMA-AN-EA, feed charge Ia, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

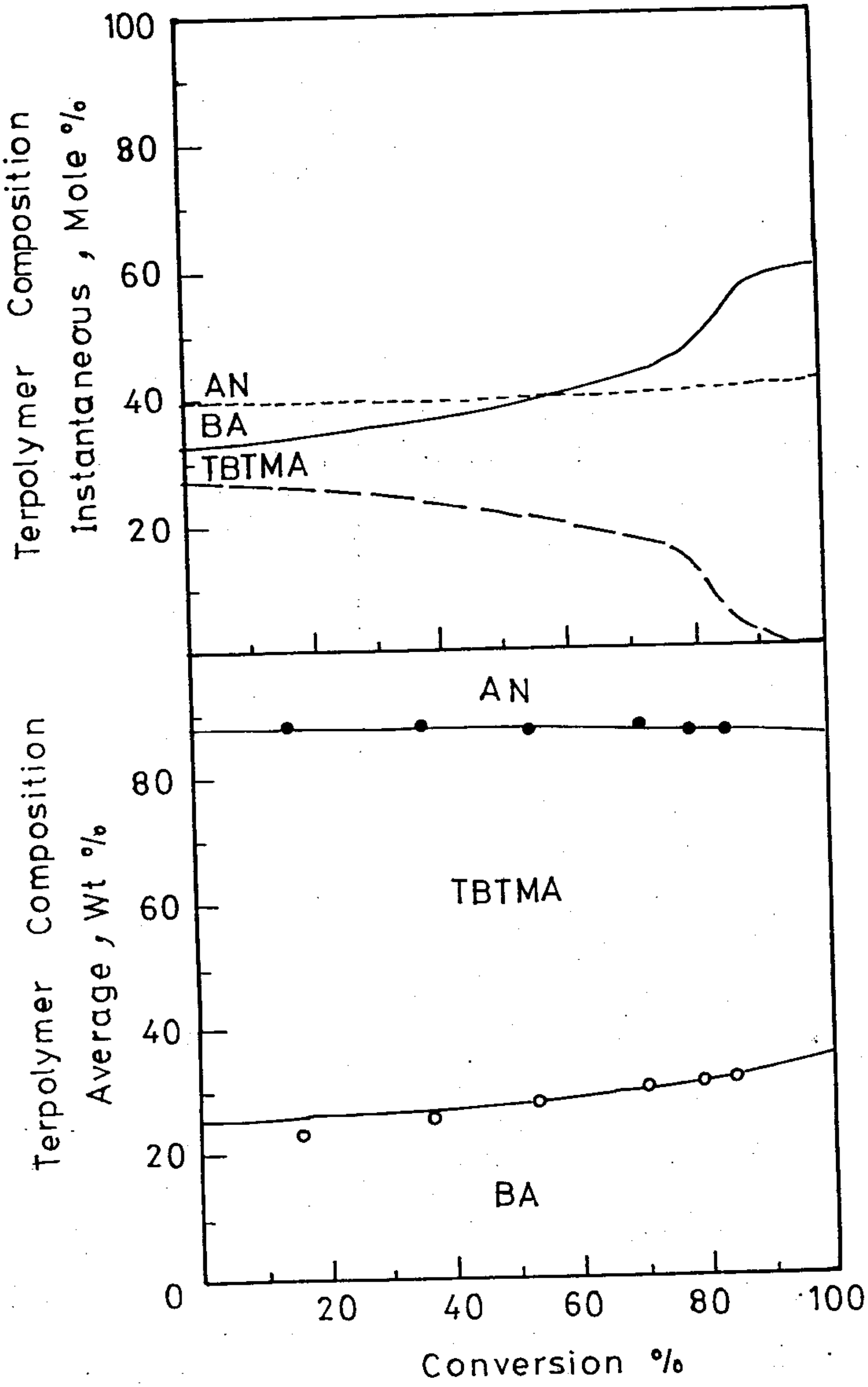


Fig. (32). Variation of instantaneous and average terpolymer composition with conversion for TBTMA-AN-BA, feed charge IIa, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

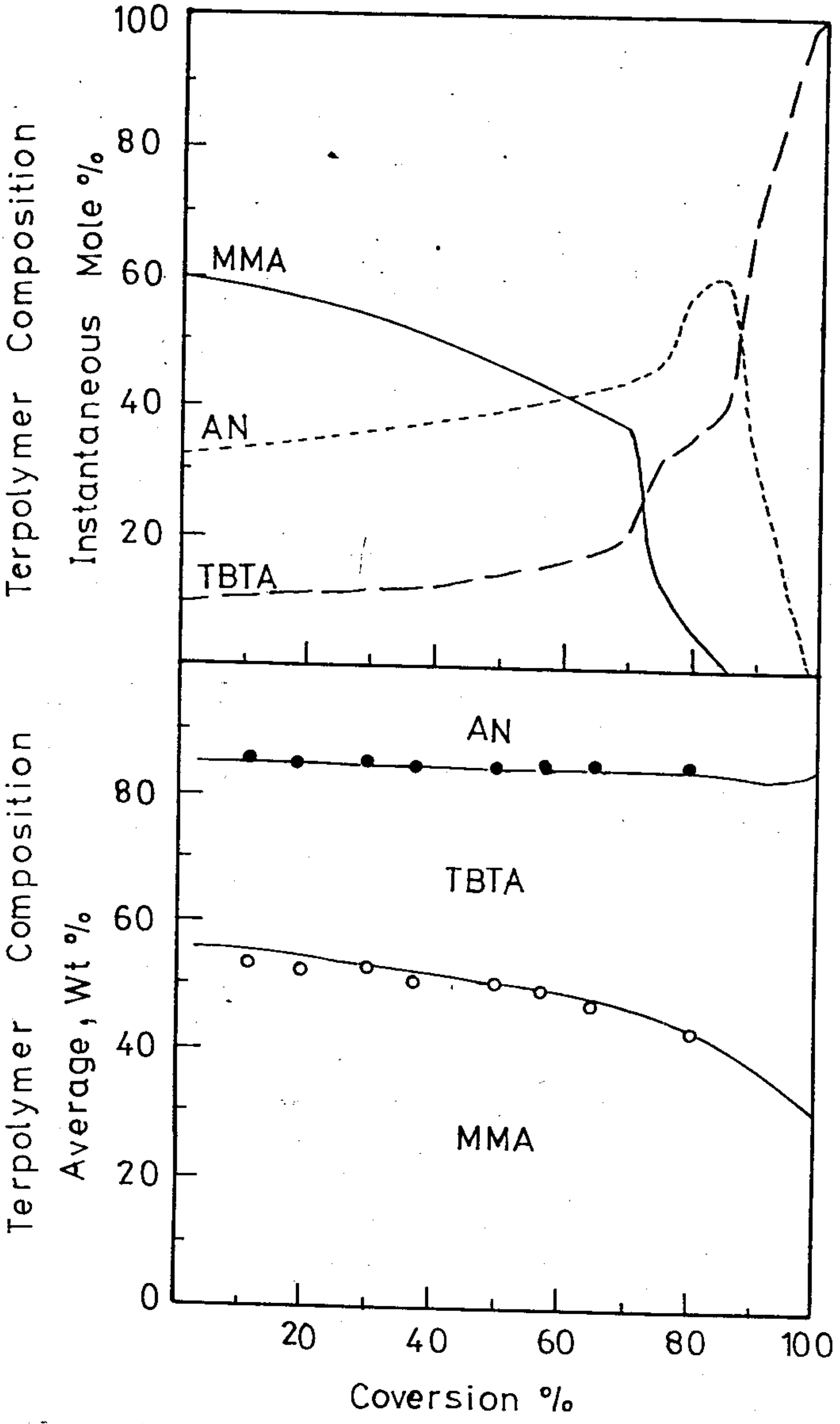


Fig. (35). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-MMA, feed charge Va, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

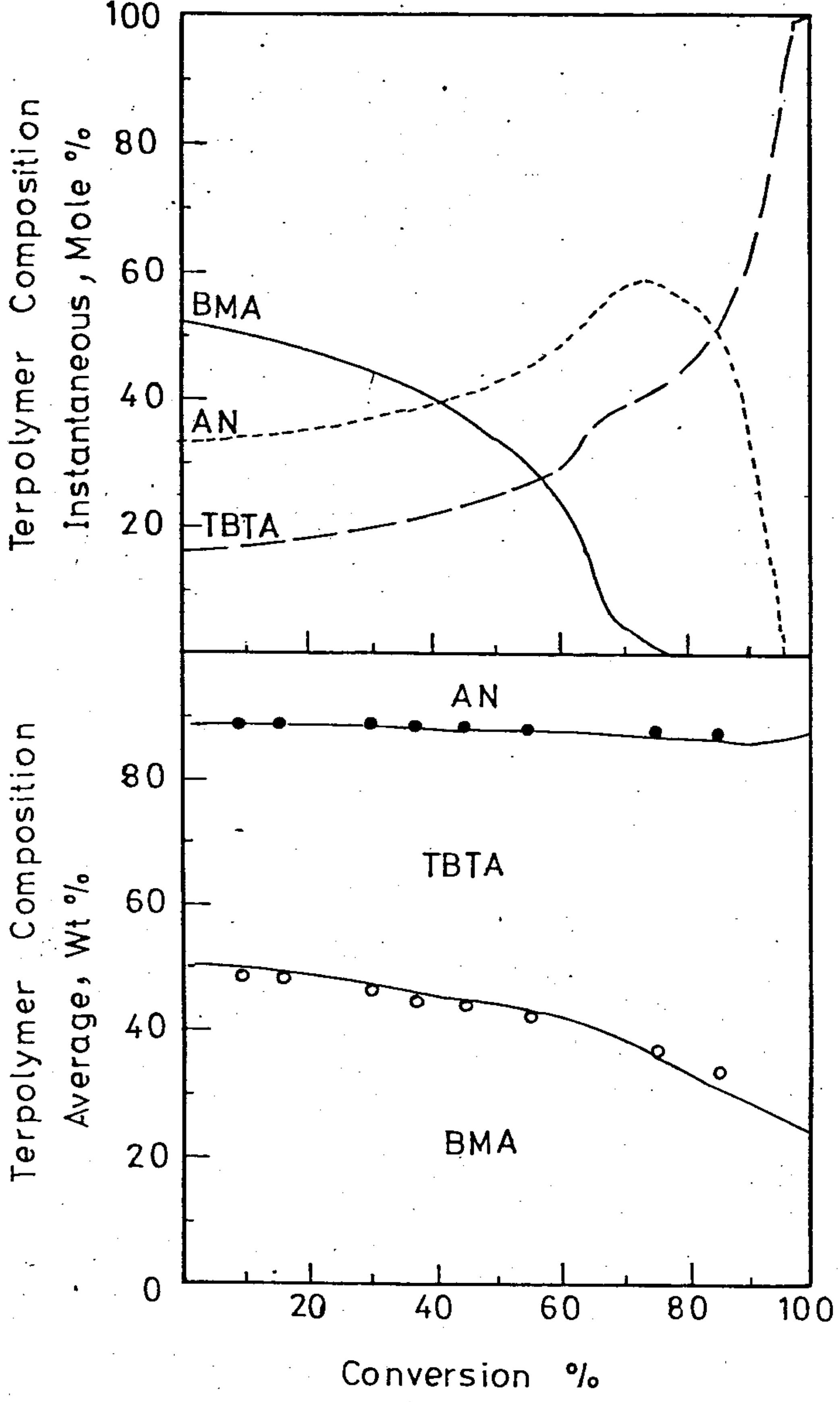


Fig. (36). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-BMA, feed charge VIa, lines represent calculated values and (o&●) from nitrogen and tin analyses.

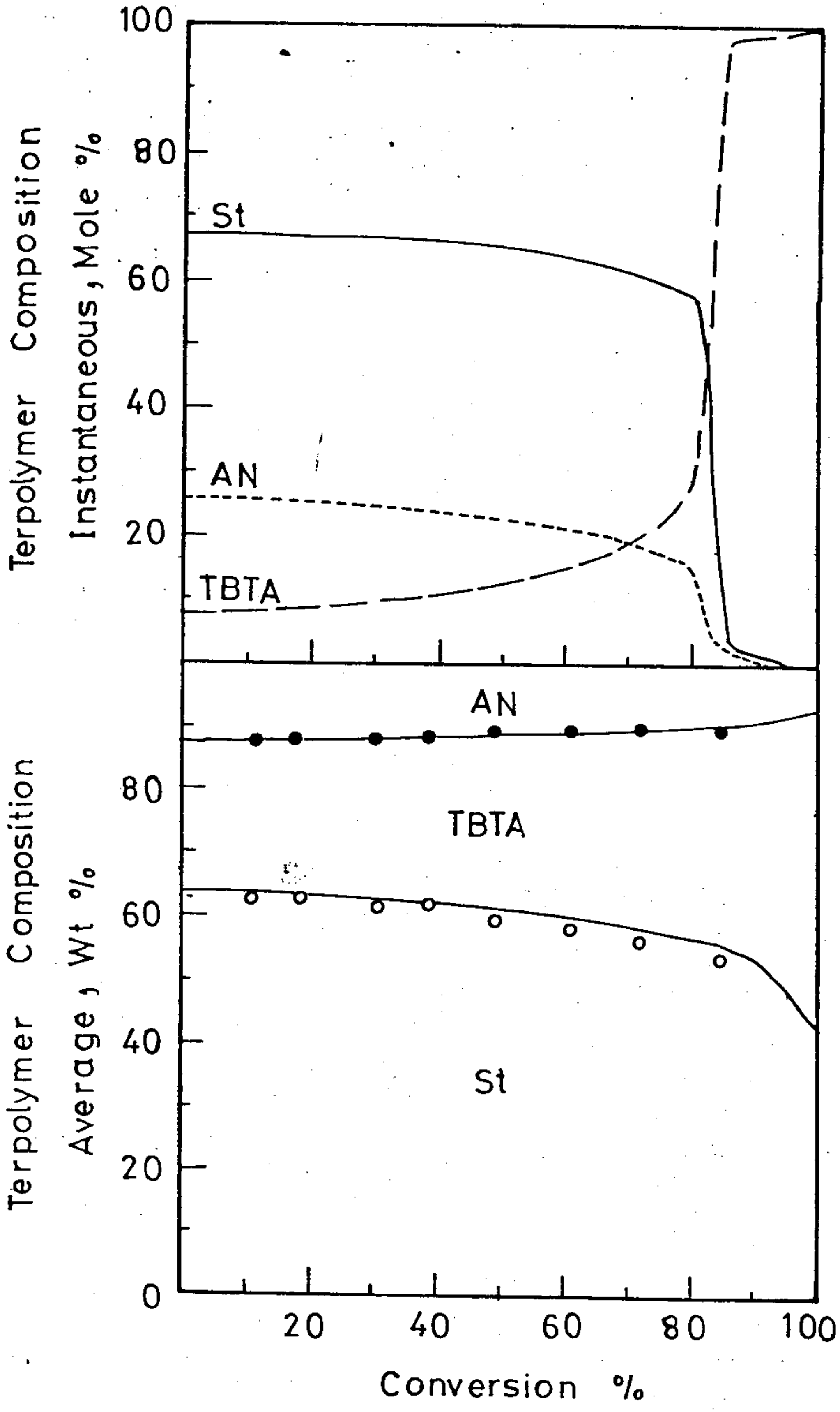


Fig. (37). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-St, feed charge VIIa, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

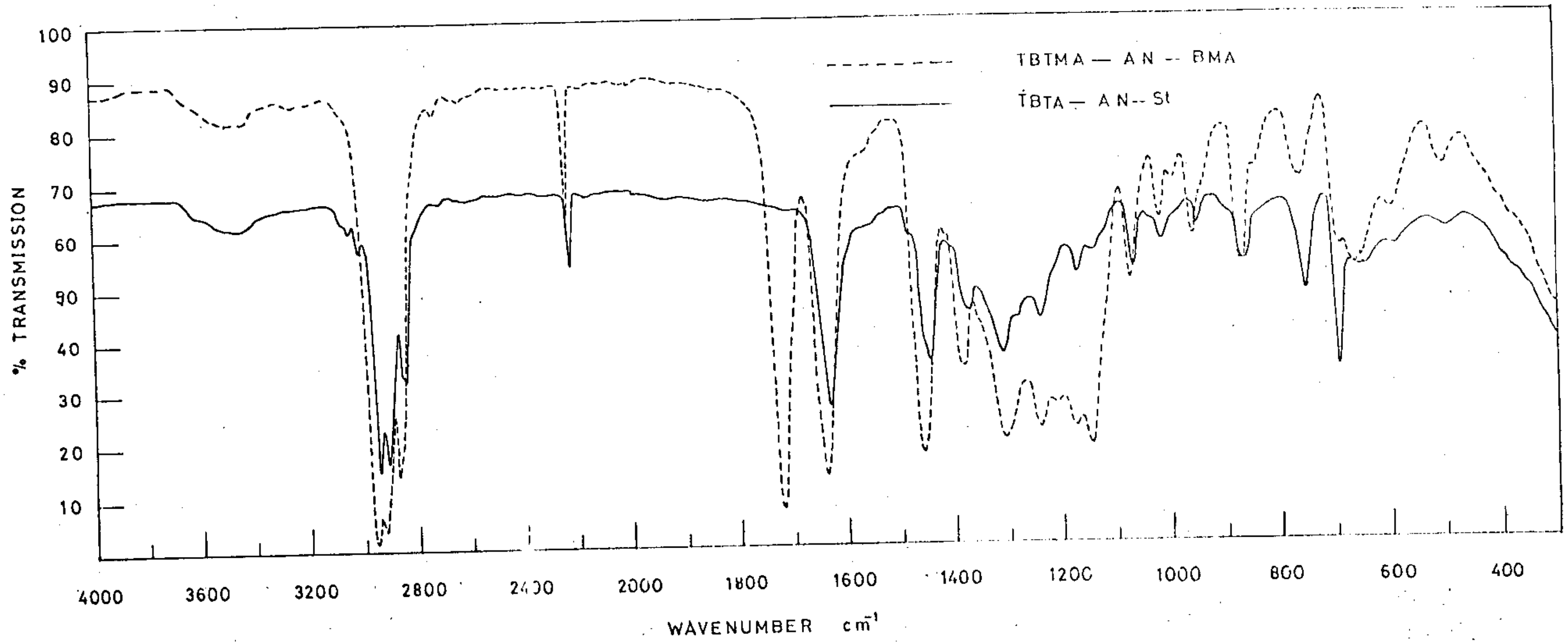


Fig. (38). I.R Spectra for TBTMA-AN-BMA and TBTA-AN-St terpolymers.

CHAPTER IX

Preparation and Properties of Some Film-Forming Organotin Polymers

A set of co- and terpolymer compositions were selected, according to the behaviour of different monomers in co- and terpolymerization reactions which were described in chapters IV-VIII. The aim was to prepare co- and terpolymers having suitable film properties. Three copolymer and eight terpolymers were prepared according to the method described in page (45) at high conversions of about 90 %.

The films were prepared by pouring the solution of co- and terpolymers on glass, tin, and PVC plates to obtain suitable films for testing and evaluation. Film hardness, cold and hot water resistance, synthetic sea water resistance, impact strength and elasticity were performed according to the specifications detailed in Chapter II. The experimental conditions and results are summarized in Tables (39-49).

Table (39)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate copolymer

TBTMA : MMA = 30:70 mole %

Reaction time = 5 hours

Conversion = 88 %

Tin content = 18.72%(calc. 19.56 %, at 100 % conversion).

Film properties of TBTMA-MMA copolymer

Test	Result
Thickness	100 µm
Hardness (pendulum)	101.3 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (40)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-n-butyl methacrylate terpolymer

TBTMA:MMA:BMA = 30:50:20 mole %
Reaction time = 5 hours
Conversion = 97 %
Tin content = 18.59%(calc. 18.70% at 100 conversion).

Film properties of TBTMA-MMA-BMA terpolymer

Test	Result
Thickness	95 µm
Hardness (pendulum)	81.67 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (41)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-acrylonitrile terpolymer

TBTMA:MMA:AN = 30:50:20 mole %

Reaction time = 5 hours

Conversion = 82 %

Tin content = 19.98%(20.62% calc.,at 100 % conversion)

Film properties of TBTMA-MMA-AN terpolymer

Test	Result
Thickness	85 μm
Hardness (pendulum)	95.67 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	damaged
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (42)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-tri-n-butyltin acrylate terpolymer

TBTMA:MMA:TBTA = 20:70:10 mole %

Reaction time = 5 hours

Conversion ≃ 96 %

Tin content = 18.94%(calc. 19.71%,at 100 % conversion).

Film properties of TBTMA-MMA-TBTA terpolymer

Test	Result
Thickness	120 µm
Hardness (pendulum)	97.9 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (43)

Preparation of tri-n-butyltin acrylate-methyl methacrylate copolymer

TBTA:MMA = 30:70 mole %

Reaction time = 6 hours

Conversion = 96 %

Tin content = 19.14%(Calc. 20.02%, at 100 % conversion)

Film properties of TBTA-MMA copolymer

Test	Result
Thickness	140 µm
Hardness (pendulum)	31.7 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (44)

Preparation of tri-n-butyltin acrylate-methyl methacrylate-acrylonitrile terpolymer

TBTA:MMA:AN = 30:50:20 mole %

Reaction time= 6 hours

Conversion = 90 %

Tin content = 19.92%(Calc. 21.14%, at 100 % conversion)

Film properties of TBTA-MMA-AN terpolymer

Test	Result
Thickness	105 µm
Hardness (pendulum)	29.5 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	damaged
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.3 foot

Table (45)

Preparation of tri-n-butyltin acrylate-methyl methacrylate-n-butyl methacrylate terpolymer

TBTA:MMA:BMA = 30:50:20 mole %

Reaction time = 6 hours

Conversion = 97 %

Tin content = 19.04%(Calc. 19.12%,at 100 % conversion)

Film properties of TBTA-MMA-BMA terpolymer

Test	Result
Thickness	95 µm
Hardness (pendulum)	17 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.25 foot

Table (46)

Preparation of tri-n-butyltin methacrylate-styrene copolymer

TBTMA:St = 40:60 mole %

Reaction time = 10 hours

Conversion = 70 %

Tin content = 20.85 % (Calc. 22.41%, at 100 % conversion)

Film properties of TBTMA-St copolymer

Test	Result
Thickness	90 µm
Hardness (pendulum)	1.73 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.25 foot

Table (47)

Preparation of tri-n-butyltin methacrylate-styrene-n-butyl methacrylate terpolymer

TBTMA:St:BMA = 40:40:20 mole %

Reaction time= 10 hours

Conversion = 82 %

Tin content = 20.54% (Calc. 21.64%, at 100 % conversion)

Film properties of TBTMA-St-BMA terpolymer

Test	Result
Thickness	100 µm
Hardness (pendulum)	2 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.5 foot

Table (48)

Preparation of tri-n-butyltin methacrylate-styrene-tri-n-butyltin acrylate terpolymer

TBTMA:St:TBTA = 20:60:20 mole %

Reaction time = 10 hours

Conversion = 75 %

Tin content = 21.70 % (Calc. 22.70%, at 100% conversion)

Film properties of TBTMA-St-TBTA terpolymer

Test	Result
Thickness	90 µm
Hardness (pendulum)	1.8 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.3 foot

Table (49)

Preparation of tri-n-butyltin methacrylate-styrene-acrylonitrile terpolymer

TBTMA:St:AN = 40:40:20 mole %

Reaction time = 10 hours

Conversion = 90 %

Tin content = 22.38 % (Calc. 23.54 %, at 100 % conversion).

Film properties of TBTMA-St-AN terpolymer

Test	Result
Thickness	100 µm
Hardness (pendulum)	20 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1 foot

From Tables (39-49), it is clear that all films prepared from copolymers and terpolymers involving methyl methacrylate with either tri-n-butyltin acrylate or tri-n-butyltin methacrylate possess good film properties as adhesion, hardness and resistance towards dilute acid and alkaline solutions.

However, organotin copolymers and terpolymers involving styrene (Tables 46-49) showed good adhesion and elastic properties with slight tackiness which may be due to its high organotin moieties (40 mole %).

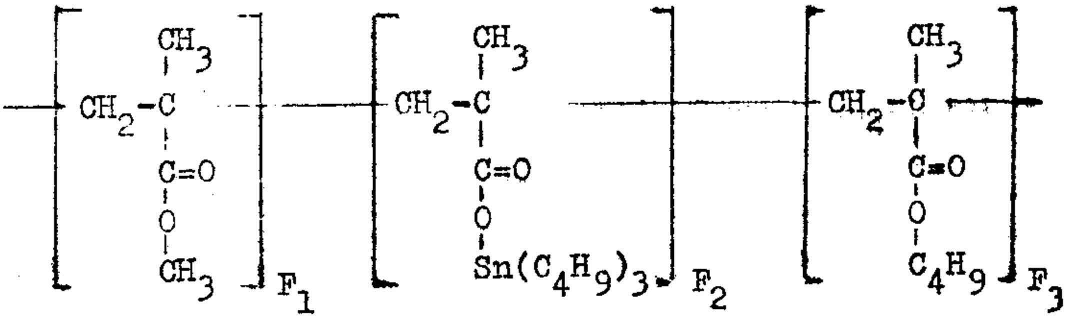
All films showed sensitivity towards dilute sodium hydroxide solution while they were not affected by dilute sodium carbonate solutions. Also the films showed good resistance towards cold water, hot water and synthetic sea water and remained unaffected for prolonged periods of time.

The purpose of this study was to select copolymers and terpolymers suitable for practical, and eventually, industrial applications.

CHAPTER X

Terpolymers with Pendent Organotin Moieties as Antifouling Coatings

Three new organotin polymers with built-in-organotin moieties were prepared from solution polymerization (page 45) of methyl methacrylate, tri-n-butyltin methacrylate and butyl methacrylate, in various molar ratios to produce terpolymers with tin content of 15, 19 and 24 %, which can be represented by the following general structure:



$$\left[CH_2-\overset{CH_3}{\underset{\substack{C=O\\O\\CH_3}}{C}} \right]_{F_1} \left[CH_2-\overset{CH_3}{\underset{\substack{C=O\\O\\Sn(C_4H_9)_3}}{C}} \right]_{F_2} \left[CH_2-\overset{CH_3}{\underset{\substack{C=O\\O\\C_4H_9}}{C}} \right]_{F_3}$$

Table (50), illustrates the terpolymer composition, the results of tin analysis and the intrinsic viscosity data for the prepared three terpolymers.

Table (50)

Terpolymer	Terpolymer composition	Tin content		$[\eta_{sp/c}]_{C=0}$
	MMA:TBTMA:BMA	Found	Calc.	
I	0.250 :0.250:0.500	15.97	15.7	0.150
II	0.333 :0.333:0.333	19.14	19.3	0.145
III	0.250 :0.500:0.250	23.95	24.04	0.115

The prepared terpolymers were soluble, colourless ranging from transparent solids to hard rubbery materials and were suitable for film formation. Terpolymer solutions with applicable viscosity were obtained from 50 % solutions in xylene. Unpigmented films were prepared from such terpolymer solutions, on glass and metal plates, and were left to complete drying for several days at room temperature. The films were found to have good elasticity and adhesion properties. Films prepared from terpolymers I and II (Table 50), 15 and 19 % tin content, respectively) were hard enough and tack-free, while films from terpolymer III (24 % tin content) were slightly tacky and did not reach complete dryness even after prolonged periods of time. These results are in agreement with the intrinsic viscosity measurements illustrated in Table (50), which indicate that the terpolymer intrinsic viscosity decreases as the tributyltin moiety in the terpolymer backbone increases. Unpigmented films from such terpolymers, when immersed in slightly alkaline salt solution (pH 8.2), did not develop turbidity or milkiness in the depth of the films, and remained unaffected after 3 weeks of immersion.

Raft Testing:

Test panels were cut to 200x150x3 mm from impact PVC sheets, then the surfaces and edges were roughened by sandpaper. The panels were connected to the testing stand with PVC threads through holes in the panels. After washing and cleaning with methanol, the panels were coated by two successive coats with the unpigmented and pigmented terpolymer formulations. The average film thickness was between 60-90 μ. The testing stand was left at room temperature for one week to ensure complete drying of the films; then submerged in the floating raft launched in the eastern harbour of Alexandria, at a depth of 150 cm from the water surface. Periodic visual and biological examination and photographic recording of the panels were performed. The film conditions like adhesion, cracks, blisters, erosion, ... etc, were also recorded.

Panel immersion in sea water is still an important method for evaluating new antifouling coating devices. In the present work, the prepared organotin polymers (I, II, III, Table 50) were used in seven formulations as unpigmented and pigmented coatings as shown in Table (51) which illustrates the dry film composition of the seven formulations:

Table (51)

Dry Film(x) Composition in Weight percent

Formulation No.	Group A		Group B		Group C		
Consituents	1	2	3	4	5	6	7
Terpolymer I	100	60	---	---	---	---	---
Terpolymer II	---	---	100	60	---	---	---
Terpolymer III	---	---	---	---	100	60	60
Titanium Dioxide(xx)	---	33	---	40	---	40	33
TPTF	---	7	---	---	---	---	7
Total pigment	---	40	---	40	---	40	40
Total binder	100	60	100	60	100	60	60
Pigment/binder	---	2/3	---	2/3	---	2/3	2/3

(x) Solvent xylene
(xx) Rutile type

It is well known that pigmentation may improve the film properties and may have a role in increasing the permeability of the film, which permits continuous contact between sea water and the toxin centres in the polymer chains leading to simultaneous release of the hydrolyzed toxic groups. Thus, the prepared terpolymers were pigmented essentially with titanium dioxide and in some formulations triphenyltin fluoride (TPTF) was added as an external toxin along with the prepared organotin polymers (Table 51). TPTF is considered to be a strong antifouling agent and less soluble in sea water than tributyltin oxide or fluoride.

In the present investigation, fourteen PVC panels were coated on both sides with the seven formulations (Table 51) in duplicates and were arranged on the testing stand as shown in Fig. (39), i.e. each formulation is represented by four surfaces.

1	2	6	7	6	2	1
3	4	5	7	5	4	3

Fig. (39). Diagram of the testing stand showing the positions of the seven tested formulations.

The advantage of using plastic panels is to eliminate corrosion and rust problems and to avoid the probable problems of incomplete compatibility between the anticorrosive and the top coat. The testing stand was submerged in the sea, in Alexandria eastern harbour; on August 17, 1978. This region is known for its high fertility for most serious fouling organisms all the year round. The physico-chemical and biological conditions near the testing raft were previously reported[68].

Testing Results:

The seven unpigmented and pigmented formulations are classified into three groups, A, B and C; according to the terpolymer composition used in each formulation as illustrated in Table (51). The following results were derived from the periodical inspections throughout 15 months of immersion in sea water:

1. All the fourteen test panels were covered with a heavy slime film. Slime usually occurs to any painted surface submerged in the sea soon after a few days of immersion. It is usually composed of bacteria, diatoms and considerable amounts of organic and inorganic detritus materials. Brown and green algae were the primary foulers detected after 3 weeks of immersion. The rate of algal growth increased rapidly and some panels were covered completely after two months, as shown from Fig. (40b). The rate of slime and algal growth on the panels can be arranged as follows: group $A > B > C$, i.e. the rate is indirectly proportional to the tin content of the organotin polymer. This result agrees with the conclusions previously reported by Ghanem & Abd El-Malek[69], that antifouling compositions prepared

with organotin compounds could not prevent plant fouling.

2. Attachment of animal foulers started by a few number of branacles on some panels during the first month of immersion (Fig. 40a). The attachment began at the edges and spread gradually to the inside of the panels as follows:

a- For group A formulations (1 and 2, Table 51) signs of failure appeared on the fourth month by slight to moderate attachment of some branacles, after heavy accumulation of algae. In the period between the fifth and seventh month, the panels areas were almost completely covered by heavy fouling of branacles, bryozoans and ascidians (Fig. 40d) and only 30 % of the panels areas of group A were left free of fouling. It was observed that the unpigmented terpolymer I (formulation 1) is more efficient than the pigmented one.

b- The antifouling efficiency of group B (formulations (3, 4, Table 51) extended only one month longer than group A. At the end of the 8th month, 40 % of the panels areas of the unpigmented terpolymer II (formulation 3) was still clean, while those of the pigmented ones were completely fouled.

c- Group C formulations (5,6 and 7, Table 51) possessed good antifouling properties against animal fouling for eleven months and all the panels were clean except for a little attack of the edges of the panels (Fig. 40e). After thirteen months, the pigmented formulations 6 and 7 began to fail and about 50 % of the panels areas were heavily fouled. At the end of fifteen months only panels coated with unpigmented terpolymer III (formulation 5) were relatively more successful with about 70 % fouling-free areas, while the pigmented formulations 6 and 7 were almost completely covered with heavy fouling and only small areas were still clean.

3. It seems that all tested organotin polymer formulations possessed better antifouling resistance against tube worms than branacles, which was clearly demonstrated by the early attack of the panels by some branacles which continued through the first six months of immersion, although the ribs of the testing stand (taken as a blank), were heavily fouled with intensive quantities of tube worms reaching 10-12 cm thickness, along with few amounts of branacles as shown in Fig. (40c). The only attack of tube worms on the panels was found at the edges accumulating over an older layer of branacles.

4. All pigmentations showed different degrees of chalking (self polishing) during the inspection period. On passing a finger on the films, some of the pigment with part of the binder was rubbed off. This behaviour was clearly demonstrated for formulations 6 and 7, which may be due to the type of the nature of terpolymer III being softer than terpolymer I and II.

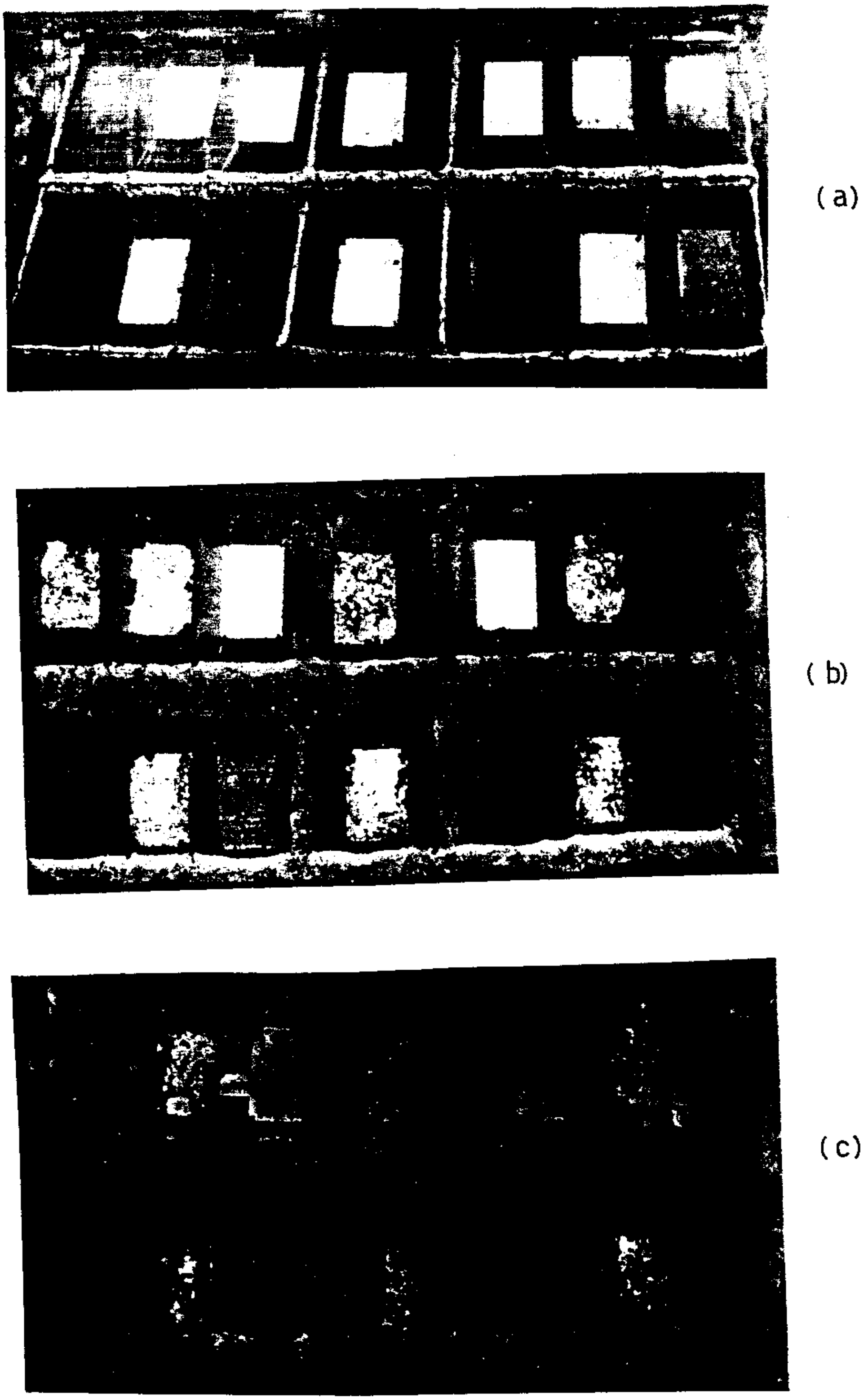


Figure (40). Photographic recording of the testing stand submerged in the eastern harbour of Alexandria for: (a) 21 days, (b) 2 months, (c) 4 months,