BINARY COPOLYMERIZATION REACTIONS OF N-ANTIPYRYL ACRYLAMIDE WITH METHYLMETHACRYLATE, BUTYLMETHACRYLATE, ACRYLONITRILE, VINYL ACETATE, AND N-TRIBUTYLTIN ACRYLATE

تفاعل البلمرة المشاركة الثنائية للانتى بيرايل أكريلاميت العادئ
مع بعض المونيمرات

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الخلاصــــة :

تم تحضير مونومر الأنتيبريل أكـرالاميد العادى (ن أأ) (٢ـ٣ داى ميثيل ـ ١ ـ
قينيــــــل ـ ٥ ـ أوكسو ٣ـ بيرالزولين ـ ٤ ـ اكـريلويل أمين) بتفاعل ٤ ـ أمينـو
أنتيبيرين مع أكـريلويل كلوريد تحت ظروف تفاعل معينة . وقد تمت دراسة تركيـــب
المونومر المحضر بواسطة الاشعة تحت الحمراء والرنين النووى المغناطيسى كما تــــم
استخدام هذا المونومر الجديد فى عمل بلمرة مشاركة ثنائية مع كلا من قينبيل ميثاكريلات
(م م أ) ، بيوتيل ميثاكريلات (ب م أ) ، الاكريلونتيريل (أن أ) ، قينيل الاستيان ا فأ أ
والتراى بيوتيل تين اكربلات (ت ب ت أ) فى وجود الداى ميثيل فورما ـ آميد مــع
أستخدام جزئى واحد فى المائة من الازوبيس أيزوبيوتيرونــنيتريل كبادى للتفاعل عنـــد
درجة ٦٥ْ م .

ولقد استخدم الرنين النووى المغناطيسى لتقدير نسبة البولمر المشارك فى كــل
عينة وكما استخدمت كلا من طريقة (فينمان وروس) و (كيلين وتديوس) لحـــــاب
معاملات التفاعل للمونومرات فى البلمرة المشاركة .

ولقد وجد أن معاملات تفاعل المونومرات فى البلمرة المشاركة لكلا من تفاعـــل
(ن أ أ ـ م م أ) ، (ن أ أ ـ ب م أ) ، (ن أ أ ـ أن أ) ، (ن أ أ ـ فأ أ) ،(ن أ أ ـ
ت ب ت أ) هى (ر١ = ٩٨ر٠ ، ر٢= ٥٢٩ر١) ، (ر١ = ٥٨ر٠ ، ر٢ = ٦٦ر١) ، ر١= ٨٠ر٠
، ر٢ = ١٤٢ر١) ، (ر١ = ٩ر٠ ، ر٢= ١٩٣ر٠) ، (ر١ = ٩٧ر٠ ، ر٢ = ١٩٧ر١).

SYNOPSIS

N-Antipyryl acrylamide monomer (NAA), (2,3 Dimethyl-1-phenyl-5-oxo-3 pyrazolin-4-Yl acryloylamine) was prepared by the reaction of 4-amino anti-pyrine with acrylcyl chloride under specific reaction conditions. The structure of the prepared monomer was investigated by IR and ^{1}H NMR spectroscopy. Binary copolymerization reactions of this new monomer with each of methyl-methacrylate (MMA), butylmethacrylate (BuMA), Acrylonitrile (AN), Vinyl acetqte (VA) and n-tributyltin acrylate (TBTA) was carried out in dimethyl-formadine, using 1 mole % azobisisobutyronitrile (ABIN) as a free radical

initiator at 65°C. ^{1}H NMR spestroscopy was used for determining the copolymer composition of each sample and the copolymerization parameters for each system were calculated by both Fineman & Ross and Kelen & Tüdos methods. The monomer reactivity ratios for the copolymer systems NAA-MMA, NAA-BuMA, NAA-AN, NAA-VA and NAA-TBTA have bee found to be $r_1^1 = 0.98$, $r_2^2 = 1.529$; $r_1^1 = 0.58$. $r_2^2 = 1.266$; $r_1^1 = 0.80$, $r_2^2 = 1.142$; $r_1^1 = 1.09$, $r_2^2 = 0.193$; and $r_1 = 1.097$, $r_2 = 1.197$ also gthe Q and e values for NAA were found to be 0.51 and -0.43.

INTRODUCTION

Interest on multifunctional synthetic polymers or copolymers is steadily increasing either as macromolecular catalysts (1-4) or as macromolecular drugs (antiheparin) (5-8) or antimetastatic agents (9). 4-Amino antipyrine and its derivatives were used in many drugs as endotoxin induced fever (10) and for the influence of phenobarbitone pretreatment on deposition of amino-pyrine and its metabolites in animals (11).

Free radical copolymerization is a method of modifying the properties of polymers. The incorporation of higher properties of a functional monomer and its better distribution within the polymer chain can be achieved through fundamental studies on copolymerization parameters under specified reaction conditions. ^{1}H NMR spectroscopy offers simple and rapid evaluation of copolymer composition (12-14), compared to the other tehniques. The aim of the present work was to prepare N-antipyryl acrylamide (NAA) and to study its copolymerization reactions with each of MMA, BuMA, AN, VA and TBTA.

EXPERIMENTAL

4-Amino antipyrine was provided by Fluka Chemical Company. Tributyltin oxide (TBTO) was supplied by M & T Chemicals Inc. Rahway, New Jersy, and acryloyl chloride from Aldrich Chemical Company. Butylmethacrylate from Aldrich, Methylmethacrylate from Merck (Darmstadt Products), vinyl acetate and acrylonitrile from BDH, all these monomers were purified by distillation under reduced pressure and the middle fractions retained for use. Azobisiso-butyronitrile, supplied by Merck, was recrystallized from ethanol.

N-Antipyryl acrylamide [2,3 Dimethyl-1-phenyl-5-oxo-3 pyrazolin-4-Yl acryloylamine] monomer was prepared as follows: To a well stirred cold solution of 4-amino antipyrine (1 mole) 20.3 gm. in dry methylene chloride (50 c.c.), acryloyl chloride (1 mole) (9.05 gm.) was added dropwise and the reaction mixture was then allowed to stand at room temperature for 2 hours, the precipitated monomer was collected by filteration and recrystallized from ethanol as a white powder m.p 216°C yield 65%.

n-Tributyltin acrylate (TBTA) monomer was prepared according to the method of Cummins and Dunn (15), by he reaction of tributyltin oxide with acrylic acid, and recystallized from petroleum ehter (60:80) as colourless crystals, yield 90% m.p. 72°C.

N-Antipyryl acrylamide (NAA) homopolymer and its copolymers with each of MMA, BuMA, AN, VA ad TBTA were obtained by solution polymeriza-tion in DMF (2 mole/L) under nitrogen atmosphere at 65°C in the presence of 1 mole % ABIN, based on total monomer concentration (0.235 mole/L). Thge overall conversions were limited to less than 10% in every case, and

the obtained copolymers were soluble in the reaction medium and were re-covered by precipitation in methanol. They were dissolved again, repricipitated, washed with methanol, dried and weighed.

Infrared spectrum was measured as KBr disc using a Perkin - Elmer 598 (4000-200 cm^{-1}) spectrophotometer. The ^{1}H NMR spectra in CDCl$_3$ and deuterated DMSO as a solvent and using TMS as an internal reference were recorded on a Varian EM-390 spectrometer operating at 90 MHz.

RESULTS AND DISCUSSION

N-Antipyryl acrylamide (NAA) monomer has been prepared by the reaction of 4-amino antipyrine with acryloyl chloride in methylene chloride according to the following scheme:
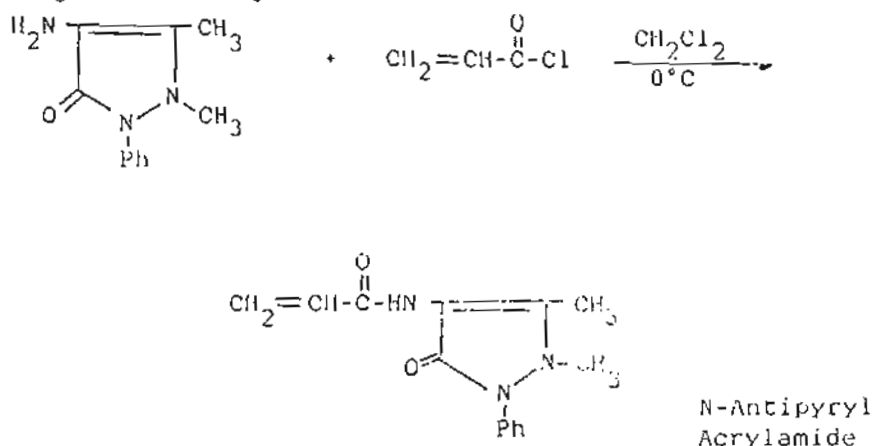

The prepared monomer was found to polymerize in presence of ABIN in DMF at 65°C. The yield of homopolymer was 65% after 6 hours. The structure of the monomer was investigated by IR and ^{1}H NMR spectroscopy.

The infrared spectrum of NAA monomer Figure (1) shows bands at 3200, 3040-2920, 1685, 1645, 1620 and 1580 cm-1 due to v NH, v C-H, v C=O of pyrazolin ring (16), v C=O of the acryloyl carbonyl (amide I), N-H bending vibrations (amide II) and v C-C of acrylaes., respectively

The ^{1}H NMR spectra of NAA monomer and its homopolymer show characteristic bands represented in table (1). Figure (2) shows the ^{1}H NMR spectra of both N-antipyryl acrylamide monomer and homopolymer, from Figure (2) it is shown that the band ranged at 5.4-6.6 ppm. corresponding protons of CH$_2$ = CH group of the monomer Fig. (2a), disappeared in spectrum (2b) of homopolymer.

In the present investigation, the copolymerization reactions for NAA monomer with each of MMA, BuMA, AN, VA and TBTA were studied and the reactions can be represented as:

NAA
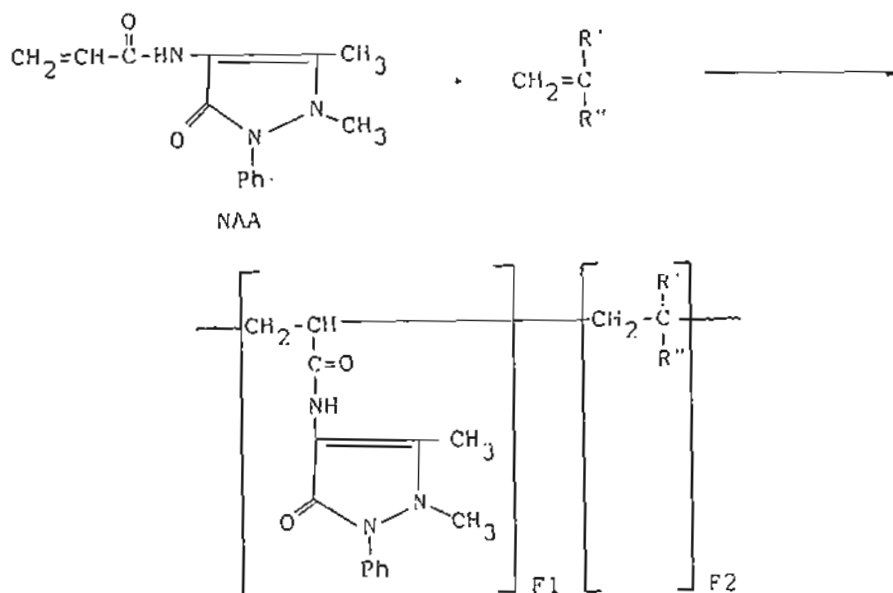
	R'	R"
MMA	CH_3	$COOCH_3$
BuMA	CH_3	$COOC_4H_9$
AN	H	$C = N$
VA	H	$O-C-CH_3$ O
TBTA	H	$C-O-Sn(C_4H_9)_3$ O

Copolymer samples of NAA-MMA, NAA-BuMA and NAA-VA systems were obtained as white powder, soluble in most organic solvents, while copolymer samples of NAA-TBTA system were colourless rubbery materials, soluble in most organic solvents, and copolymer samples of NAA-AN were yellowish solids, soluble in acetone, DMF and DMSO.

The copolymer composition for each sample of te prepared copolymers was estimated by ^{1}H NMR spectroscopy, using the approach of Grassie et al. (17) and the characteristic signals used for the quantitative determination of the copolymer composition for 0.5: 0.5 mole fraction of monomer feed for each system are illustrated in Table (2). The following expressions are derived for the estimation of the copolymer composition for each sample of NAA-MMA system as an example.

$$I_{C_6H_5} \; \alpha \; 5[\text{No of NAA units in copolymer chain}]$$

$$I_{O-CH_3} \; \alpha \; 3[\text{No of MMA units in copolymer chain}]$$

in which $I_{C_6H_5}$ and I_{O-CH_3} are the integral peak areas of $-C_6H_5$ and $O-CH_3$ protons respectively. If b = molar ratio of NAA/MMA in the copolymer, then

$$I_{C_6H_5} / I_{O-CH_3} \equiv \frac{5}{3} b$$

The ^{1}H NMR spectra of NAA-MMA copolymer samples and its analytical data are ilustrated in Figure (3) and Table (3), as an example.

The monomer reactivity ratios r_1 and r_2 for the five systems studied were deduced from the feed composition - copolymer - comonomer respectively, using Fineman & Ross and Kelen & Tüdos methods (18-19). The results are represented in Table (4), which shows that there is a good agreement between the values of the reactivity ratios calculated by the two methods. Figure (4) shows the Kelen & Tüdos plots for the five systems studied. The copolymerization parameters and $r_1 \cdot r_2$ values illustrated in Table (4) as well as the composition curves Figure (5), indicate that the copolymers of NAA monomer with each of MMA, BuMA, AN and TBTA show lower content of NAA monomer rather than the monomer mixture and should have random distribution of monomer units with tendency towards ideal behaviour. However, in case of NAA-VA system the NAA monomer is overproportionally incorporated into the copolymer which should be composed of large segments of NAA interrupted with few units of VA. The results also show that all systems studied gave no azeotropic composition.

On the basis of Alfrey & Price (20) equations, the reactivity of the double bond Q and the polarity e of NAA monomer have been evaluated using the Alfrey & Price equations

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{1/2}$$

$$Q_1 \equiv \frac{Q_2}{r_2} \exp \{-e_2 (e_2 - e_1)]$$

Thus, by using the literature value of Q_2 and e_2 for the monomers MMA, BuMA, AN, VA and TBTA, the r_1 and r_2 values determined in the present study and setting the product $r_1 \cdot r_2 = 1$ whenever it is greater than 1, the Q_1 and e_1 values for NAA monomer could be calculated. The average Q_1 and e_1 values for NAA monomer were found to be $Q_1 = 0.51$ and $e_1 = -0.43$ which are in good agreement with the values reported in literature for acrylamide derivatives (21).

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Table 1

Chemical Shift of N-Antipyryl Acrylamide (NAA) and its homopolymer.

Resonance Signal p p m	N-Antipyryl Acrylamide			Homopolymer		
	Proton	Integral Peak Area	Assignment	Proton	Integral Peak Area	Assignment
9.2-9.0	1	6	NH	1	5.3	NH
7.3	5	29	C_6H_5	5	26	C_6H_5
6.6-5.4	3	19	ABX system of $CH_2=CH$	---	----	----
3.0	3	18	$N-CH_3$	6	31	$N-CH_3$, CH_2-CH
2.1	3	18	$=C-CH_3$	3	16	$=C-CH_3$

Table (2)

Characteristic ^1H NMR Signals for NAA copolymers with MMA, BuMA, AN, VA and TBTA (5·1)*.

M1-M2	Resonance Signal ppm	Integral Peak Area	Assignment	b*
NAA-MMA	7.3	44	$-C_6H_5$	0.799
	3.5	33	$-O-CH_3$	
NAA-BuMA	7.3	19	$-C_6H_5$	0.608
	3.8	11	$-O-CH_2$	
NAA-AN	7.3	56	$-C_6H_5$	0.8362
	3.3-1.3	140	$2 \times -CH_2-CH-$ $-N-CH_3$ & $=C-CH_3$	
NAA- VA	7.3	80	$-C_6H_5$	1.72
	3.3-1	104	$2 \times -CH_2-CH-$ & $-\overset{\text{O}}{C}-CH_3$	
NAA-TBTA	7.3	20	$-C_6H_5$	0.99
	3.3-0.4	170	$2 \times -CH_2-CH-$ $N-CH_3$ & $=C-CH_3$	

* a and b are the molar ratios of M1/M2 in the monomer feed copolymer, respectively.

Table (3)
Analytical Data for the copolymerization
of NAA with MMA.

a*	Integral Peak Area		b*
	$-C_6H_5$ (5H)	$-O-CH_3$ (3H)	
0.111	3.5	28	0.075
0.25	12	42	0.171
0.333	18	47	0.23
0.4286	22	43	0.306
0.5385	26	41	0.3802
0.6667	31	37	0.502
1	44	33	0.799

* a and b are the molar ratios M1/M2 of the monomer feed
and copolymer, respectively.

Table (4)
Monomer Reactivity Ratios for
N-Antipyryl Acrylamide (NAA) monomer with
MMA, BuMA, AN, VA and TBTA.

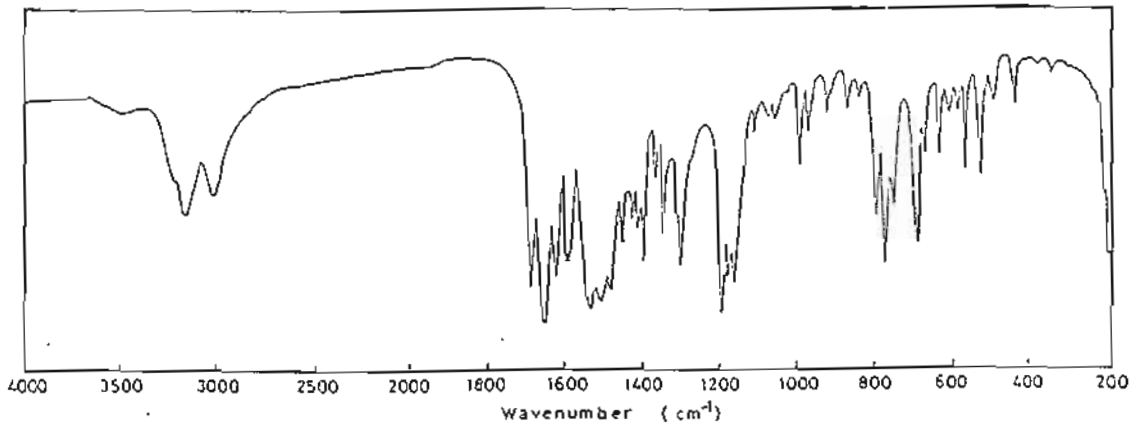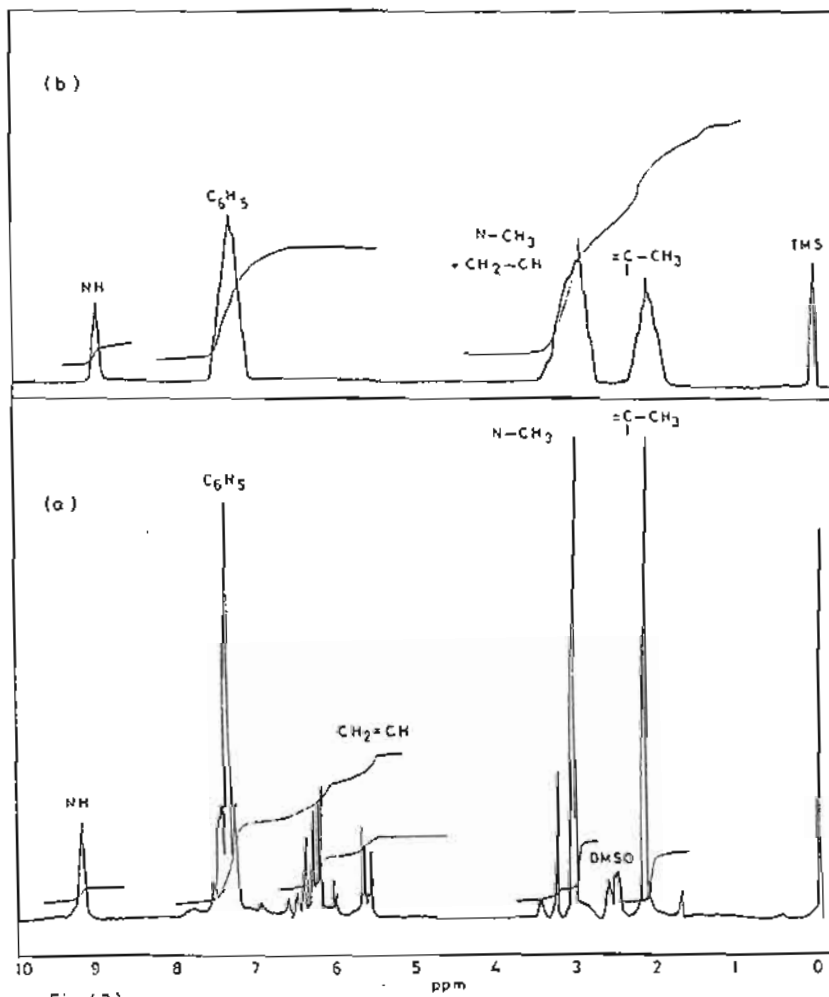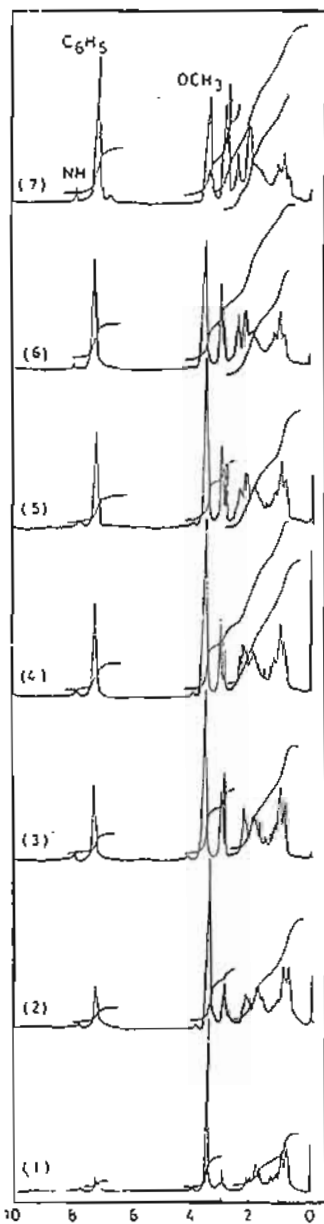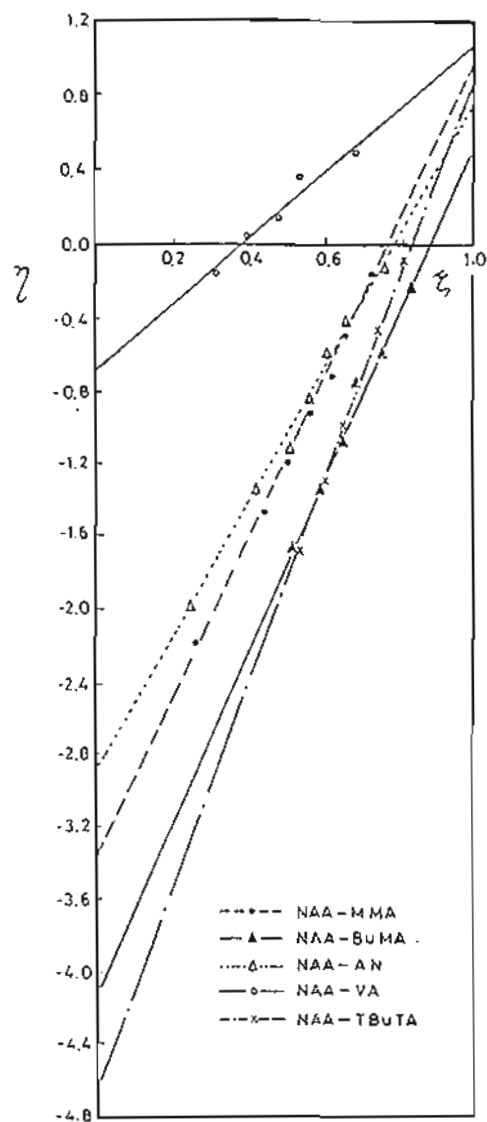| Copolymer System	Fineman & Ross		Kelen & Tüdös		Kelen & Tüdös $r_1 \cdot r_2$	α
	r_1	r_2	r_1	r_2		
NAA-MMA	1.02	1.57	0.98	1.529	1.498	0.4343
NAA-BuMA	0.552	1.27	0.58	1.266	0.734	0.3729
NAA-AN	0.85	1.14	0.8	1.142	0.9136	0.2983
NAA-VA	1.27	0.215	1.09	0.1933	0.21	0.2147
NAA-TBTA	1.06	1.24	1.097	1.197	1.313	0.4457

Fig.(1).

Fig.(2).

Fig.(3).

Fig.(4).

$$\xi = \frac{a^2}{\propto b + a^2} \quad \text{and} \quad \zeta = \frac{a(b-1)}{\propto b + a^2}$$

where a and b are the molar ratios (M1/M2) of the comonomer in the feed and copolymer, respectively,

and $\propto = \dfrac{a_{min} \times a_{max}}{(b_{min} \times b_{max})^{1/2}}$.

Legend in Fig.(4):
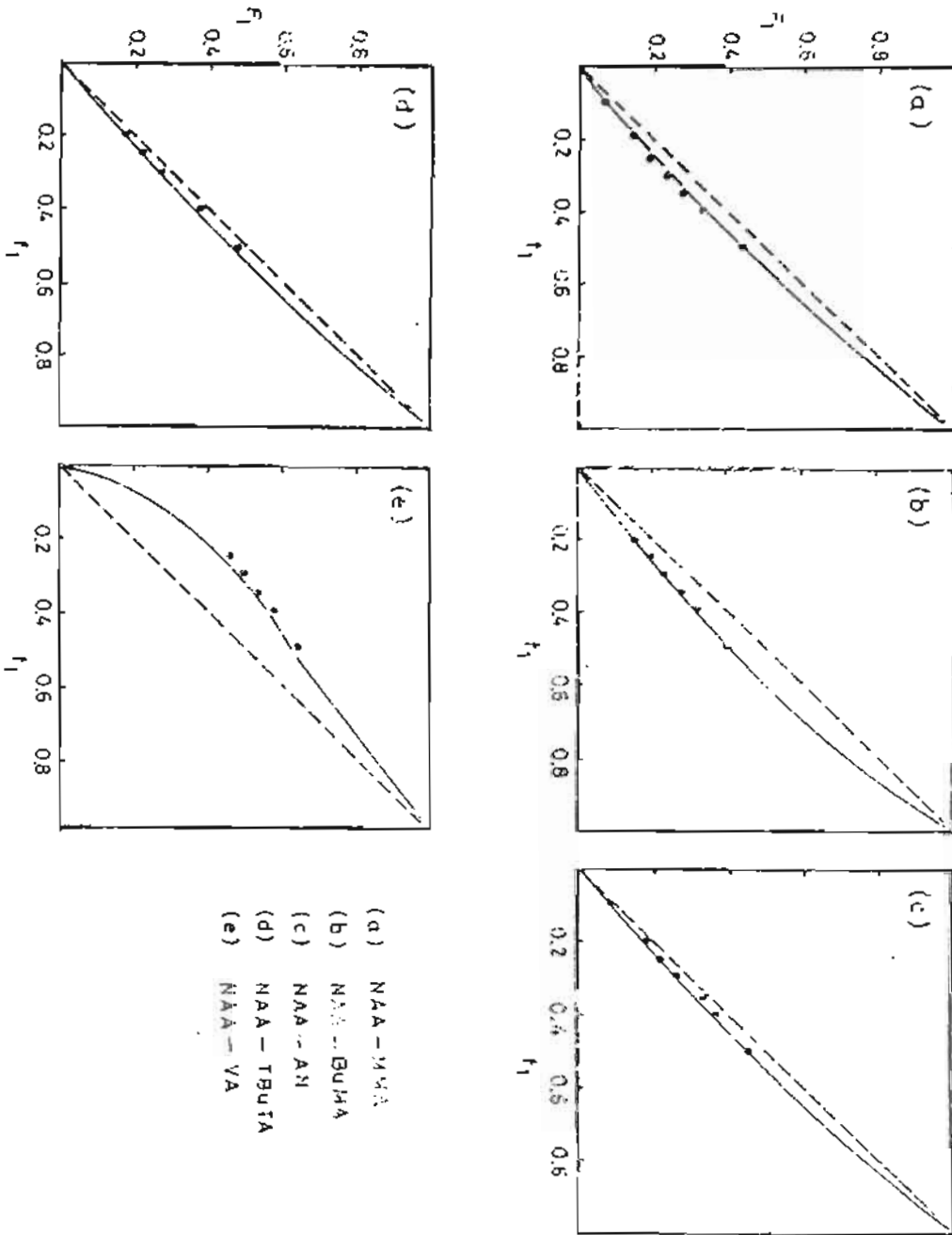- NAA–MMA
- NAA–BuMA
- NAA–AN
- NAA–VA
- NAA–TBuTA

Fig.(5).

(a) NAA — MMA
(b) NAA — BuMA
(c) NAA — AN
(d) NAA — TBuTA
(e) NAA — VA