Journal of Basic and Environmental Sciences 4 (2017) 268-276

ISSN

Online: 2356-6388

Print: 2536-9202

Research Article Open Access

Copolymerization reactions of N-acryloyl-morpholine with some vinyl monomers.

A.A.Khalil[1], M.El-Hefnawy[2], M.S.Behalo[1], M.H.M.Ahmed[1] and H.A.Elkhawaga

[1]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[2]Basic Science Department, Faculty Engeneering, Benha University (Shoubra- Branch), Benha, Egypt

Abstract

N-Acryloylmorpholine was prepared by the reaction of acrylic acid with morpholine in the presence of N,N'-dicyclohexylcarbodiimide. The monomer reactivity ratios for copolymerization reactions of N-acryloylmorpholine with methyl acrylate, methyl methacrylate, styrene and vinyl acetate, respectively, in solution with azobisisobutyronitrile (AIBN) as initiator were estimated by nitrogen analysis. The structure of the copolymers was investigated by IR and ^{1}HNMR spectroscopy. The Q and e values for N-acryloylmorpholine were calculated.

Received; 15 May. 2017

Revised form; 17 Jun. 2017, Accepted; 17 Jun. 2017, Available online 1 July, 2017

1- Introduction

The last years have seen the rise in the popularity of attaching chemically reactive species to insoluble supports. A wide variety of vinyl derivated molecules can be obtained and polymerized or copolymerized to produce functionalized supports. Among the active groups that have been introduced into polymer chains are groups which are known to act as stabilizers, complexing agents, pharmaceuticals and catalysts. Several activated esters and amides of acrylic and methacrylic acid and their polymers have been described[1-7]. N-acryloylmorpholine was used for many years to synthesize cross-linked networks for gel-phase synthesis of peptides[8-10], semipermeable membrane for plasma separation,[11-13] polymeric supports for gel chromatography[14] and capillary electrophoresis. [15]. Linear poly (N-acryloylmorpholine) was also used for drug-delivery applications, protecting liposomes from blood clearance[16] , or increasing the lifetime of enzymes both in vitro and in vivo[17]. N-acryloylmorpholine was homopolymerized in the presence of a chain transfer agent to give end-functionalized low molecular weight oligomers, [18-20] and copolymerized forming a linear copolymer[19]. This paper reports on a kinetic study of the free radical solution copolymerization with methyl acrylate(MA), methyl methacrylate (MMA), styrene (ST) and vinyl acetate (VA).To characterize such a binary systems, the determination of the reactivity ratios and composition curves are necessary.

2- Experimental

2.1- Material

Acryloyl chloride and morpholine from Aldrich Chemical Co. Triethylamine from Fluka Company. Methylacrylate, methyl methacrylate, styrene and vinyl acetate from Aldrich Company. Azobis-isobutyronitril (AIBN), were from E.Merck, Darmstadt was recrystallized from absolute ethanol, m.p102^{0}C**.**

2,2 –Synthesis of N-acryloylmorpholine NAM [21]

Morpholine (0.125mol, 11ml) and triethylamine (0.175mol, 20ml) were dissolved in 150ml of dry tetrahydrofuran (THF) in a 250 ml two-necked round bottled flask. The flask was cooled in an ice-water bath (4˚C) and maintained under flowing nitrogen. THF solution (30ml) containing acryloyl chloride (0.13mol,10.5ml) was added dropwise over a period of 60 min with constant stirring. The reaction mixture was then allowed to equilibrate to room temperature and continuously stirred overnight. Triethylamine hydrochloride was removed by filtration and washed repeatedly with warm THF solution .The filtrate was concentrated using a rotary evaporator. N-acryloylmorpholine in a form of brown liquid was obtained by distillation at 98-100˚C under a reduced pressure of 5mmHg. Hydroquinone (0.5 wt%) was added prior to distillation to inhibit any spurious polymerization of monomer.

2.3 – Copolymerization [22,23]

The copolymers were obtained by solution polymerization. Predetermined amounts of the comonomers were placed in glass tubes, and diluted with dimethylformamide so that the total monomer composition was about (1mol/1). Polymerization was commenced by adding AIBN (1 mol%). The tubes were flushed with oxygen-free nitrogen for 10 min., capped , and thermostated at 70˚C for 3-5h depending on the comonomer pairs and composition. The copolymers were

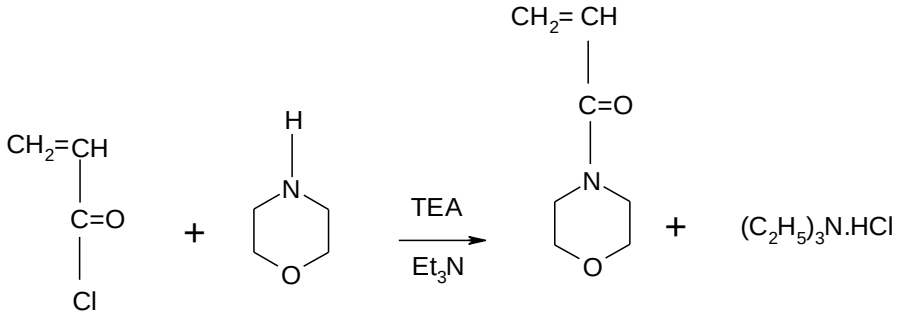
precipitated by pouring the polymerization mixtures into methanol, washed several times, dried and weighed. The conversion were kept below 10% in all preparations. The composition of copolymers was determined by nitrogen analysis.

2.4 - Chracterization

IR spectra were recorded (KBr) on a pye-Unicam SP-883 Perkin Elemer spectrophotometer.[1]HNMR spectra were recorded on a Varian Gemini 200 MHz spectrophotometer, Cairo University. The chemical shift (δ) are given downfield relative to tetraethylsillan (TMS) as the internal standard . The elemental analysis were also carried out in Microanalytical Center, Cairo University.

3-Results and discussion

N-Acryloylmorpholine was prepared according to the following scheme:

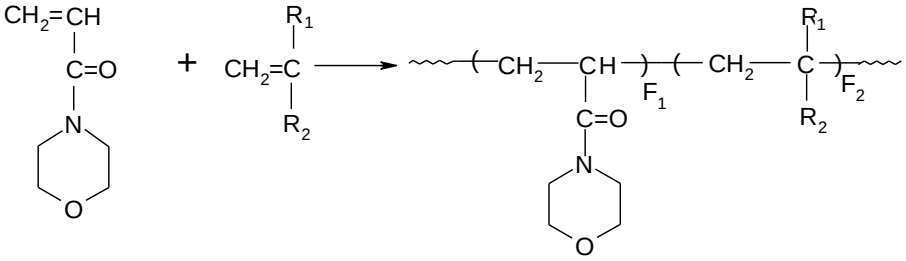


The structure of NAM monomer was confirmed by IR and [1]HNMR spectroscopy.

The IR spectrum of NAM shows a band at 2907 cm^{-1} due to the υ CH stretching vibrations, a strong band at 2857 cm^{-1} due to υ -O-CH_2, a strong band at 1645cm^{-1} due to υ N-C=O, a strong band at 1444cm^{-1} due to υ –CH_2-, a band at 1366 cm^{-1} due to υ C-N and a strong band at 1240 cm^{-1} due to υ C-O.

The [1]HNMR spectrum of NAM shows signal at δ2.45 corresponding to the proton of -OCH_2 group, signals at δ3.4, δ3.6 corresponding for the proton of $OCN(CH_2)_2$, a doublet at δ5.68 and δ5.72 due the proton in CH=C-CON group (trans), a doublet at δ6.17 and δ6.19 due to the proton in CH=C-CON group (cis), a multiplied at δ6.76-6.82 due to the proton in =CH-CON group.

In the present investigation, the copolymerization parameters for NAM-MA, NAM-MMA, NAM-ST, NAM-VA systems were studied. The reaction can be written as :



M_1 - M_2	R_1	R_2
NAM-MA	H	$COOCH_3$
NAM-MMA	CH_3	$COOCH_3$
NAM-ST	H	C_6H_5
NAM-VA	H	$OCOCH_3$

The copolymerizations were allowed to proceed to low conversions and the composition of each copolymer was calculated from its nitrogen content. The structure of the copolymers was investigated by IR spectroscopy. The structure of the copolymers was investigated by IR spectroscopy. The IR spectrum of NAM-MA shows a band at 2922 cm^{-1} due to the υ CH stretching vibrations, strong band at 1731 cm^{-1} due to υ C=O stretching vibrations of ester group, a strong band at 1638 cm^{-1} due to υ N-C=O, a strong band at 1455 cm^{-1} due to υ C-N, and strong band at 1238.08cm^{-1} due to υ C-O. Tables(1-4) illustrate the analytical data for copolymerization reactions of NAM with MA, MMA, ST and VA from the values of feed and copolymer composition, the monomer reactivity ratios (r_1 and r_2) for each system were evaluated using the Fineman-Ross[23] and Kelen-Tudos[24] methods and the standard deviations of the results were calculated by regression analysis as given in Table (5). Figer (1-4)

shows the Kelen-Tudos plots for four systems studied. The values of r_1 and r_2 from the Kelen–Tudos method are almost identical to those obtained by the Fineman-Ross method. Typical values obtained by the two methods are Tabulated in Table (5). The r_1r_2 values for NAM-MA, NAM-MMA, NAM-ST and NAM-VA systems (0.2889, 0.1106, 0.0908 and 0.0151, respectively) indicate that the copolymers in each case should have a random distribution of the monomer units with a tendency toward alternation. Figure (5-8) shows the experimental results and the composition curves calculated on the bases of the determined monomer reactivity ratios and it is found that NAM-MA and NAM-MMA systems have azeotropic composition.

The composition curves (Figure 5,6) for the copolymerization of NAM-MA and NAM-MMA seem to cross line representing $F_1=f_1$ at about 0.44, 0.33, respectively, as predicated from the values of r_1 and r_2.This point of intersection corresponds to azeotropic composition yielding homogenous copolymers regardless of conversion .The NAM-ST, NAM-VA, systems have no azeotropic composition.

Table 1: Analytical data for copolymerization of NAM-MA

Feed composition M1/M2 (a)	Conversion (%)	N (%)	Copolymer composition M1/M2 (b)
0.11	6.9	2.22	0.18
0.25	8.4	3.28	0.3
0.43	7.5	4.37	0.48
0.67	9.2	5.13	0.65
1	5.6	6.22	1.02
1.5	7.9	6.49	1.15
2.3	8.2	6.99	1.45
4	5,9	8.32	3.13

Table 2: Analytical data for copolymerization of NAM-MMA

Feed composition M1/M2 (a)	Conversion (%)	N (%)	Copolymer composition M1/M2 (b)
0.25	7.3	3.14	0.33
0.43	9.5	3.82	0.44
0.67	5.7	4.23	0.53
1	8.6	4.84	0.68
1.5	7.3	5.93	1.05

Table 3: Analytical data for copolymerization of NAM-ST

Feed composition M1/M2 (a)	Conversion (%)	N (%)	Copolymer composition M1/M2 (b)
0.11	7.9	1.22	0.103
0.25	5.8	1.79	0.16
0.43	6.5	2.91	0.31
0.67	9.1	3.83	0.46
1	8.5	4.57	0.63

Table 4: Analytical data for copolymerization of NAM-VA

Feed composition M1/M2 (a)	Conversion (%)	N (%)	Copolymer composition M1/M2
0.25	6.8	6.81	1.33
0.43	9.6	8.86	5.05
0.67	8.4	8.62	4.016
1	5..4	8.88	5.15
1.5	6.5	9.38	10.42

Table 5: Monomer reactivity ratios for copolymerization of NAM with MA,MMA,ST and VA.

M1-M2	Fineman Ross method		Kelen-Tudos method			
	r1	r2	r1	r2	r1 r2	α
NAM-MA	0.56868 ±0.7616	0.70391 ±0.0325	0.47927 ±0.0471	0.6028 ±0.0537	0.2889	0.59
NAM- MMA	0.2794 ±0.1136	0.6933 ±0.10903	0.18295 ±0.0469	0.6044 ±0.0949	0.1106	1.081
NAM-ST	0.3661 ±0.1642	1.1912 ±0.1471	0.0909 ±0.0240	0.9987 ±0.1603	0.0908	0.43
NAM-VA	5.5309 ±1.3722	0.0541 ±0.19404	5.043 ±2.9862	0.0029896 ±0.1573	0.0151	0.101

The Q and e values were calculated by using the Alfrey-Price equations [25]

$$e1=e2 \pm (-\ln r1r2)^{1/2} \quad (1)$$

$$Q1=(Q2/r2)\exp[-e2(e2-e1)] \quad (2)$$

The Q and e values represending the extent of resonance stabilization and polarity of double bond ,respectively, in a monomer and its radical are extensively tabulated by Young [26] from earlier copolymerization data .Thus , the Q and e values for NAM were obtained by using the monomer reactivity ratios determined for the copolymer systems NAM-MA,NAM-MMA,NAM-ST and NAM-VA(Table5) and using the Q and e values for the MA , MMA, ST and VA.The average Q and e values for NAM monomer were calculated and were found to be Q=1.3164 and e= 0.7569, respectively, and are in agreement with those reported in the literature [27] for the esters of methacrylic acid.

Referances

1- P. Ferruti,A. Fere, G.J. Cottica, "Poly-1-acryloylbenzotriazole as polyester and polyacrylamide precursor" Pollym. Sci., polym. Chem. Ed. 12 (1974) 553.

2- P. Ferruti, F.J. Vaccaroni, " Polymeric acrylic and methacrylic esters and amides by reaction of poly(acrylic acid) and poly(methacrylic acid) with N,N′-carbonyl-diimidazole and alcohols or amines" Polym. Sci., Polym. Chem. Ed. 13 (1975) 2859.

3- P. Ferruti, G.J. Cottica, " poly-1-acryloylbenzotriazole as polyester and polyacrylamide precursor." J.Polym. Sci., Polym. Chem. Ed. 12 (1974) 2453.

4- P. Ferruti, F. Vaccaroni, M.C.J. Tanzi, "Synthesis and exchange reactions of some polymeric benzotriazolides" polym. Sci., Polym. Chem. Ed. 16 (1978) 1435.

5- P. Ferruti, Reactions on Polymers (Ed. J. A. Moore), PP. 73-101. Dordrecht; D. Redial & Co. 1973.
6- A.F. Shaaban, M.M.H. Arief, A.A. Khalil,N.N. Messiha, "Poly-N-acryloyloxy- and -N-methacryloyloxyphthalimides as activated drug-binding matrices" Acta Polymerica. 39 (1988) 145-148.
7- A.A. Mahmoud, A.F. Shaaban, A.A. Khalil, N.N. Messiha,"Synthesis and exchange reactions of polymers containing reactive phthalimide groups"Die.AagewMakromol. Chem. 198 (1992) 31-38.8- K.N.Chander,K. Brunfeldt, E. Kjeld," Oligonucleotide synthesis on a crosslinked polyacrylmorpholide support" Tetrahedron Lett. 21 (1977) 1819.
9- R. Epton, G. Marr,J.V. Mclaren,G.J. Morgan, "Phenolic poly (acryloyl morpholine)-based bead matrix for solid (gel) phase peptide synthesis" Polymer 20 (1979) 1444.
10- R. Epton, S.J. Hocart, G. Marr, "A poly (acryloylmorpholine)-based bead matrix of improved versatility for solid (gel) phase peptide synthesis" Polymer 21 (1980) 481.
11- P. Apte, R. Fries, J. Neel, "High molecular weight hydrophilic functional copolymers by free-radical copolymerization of acrylamide and of N-acryloylmorpholine with N-acryloxysuccinimide: Application to the synthesis of graft copolymer"MembrPermeabilite Sel. Colloq(1967)119.
12- Ger. Offen 2, 414, 795, 27 (1973), Daicel Ltd., invs.: K. Ishii, Z. Honda; Chem. Abstr. 1973, 82, 58534.
13- PCT Int. Appl. Wo 8900, 878 (1989) Terumo Corp., invs.: M. Onishi, T. Fujii; Chem. Abstr. 1990, 110, 194367 h.
14- R. Epton, S.R. Holding, J.V. Mclaren, "Synthesis and evaluation of cross-linked poly (acryloylmorpholine) supports for thin-layer gel permeation chromatography" J. Chromatogr. 110 (1975) 327.
15- C. Gelfi,P. de Besi, A. Alloni,P.G. Righetti, "Investigation of the properties of novel acrylamido monomers by capillary zone electrophoresis" J. Cromatogr. 608 (1992) 333.
16-V. P.Torchilin, V. S. Trubetskoy, K. R. Whiteman, P. Caliceti, P.Ferruti, F.M. Veronese, "New synthetic amphiphilic polymers for steric protection of liposomes in vivo." J. Pharm. Sci. 84 (1995) 1049.
17- F.M. Veronese, O. Schiavon, P. Calceti, L. Sartore, E. Ranucci, P. Ferruti, , U. S. 5, 629, 384 (1994), invs.
18- E. Ranucci, G. Spagnoli, P. Ferruti, "Synthesis and molecular weight characterization of low molecular weight end-functionalized poly (4-acryloylmorpholine)"Macromol. Chem. Phys. 195 (1994) 3469.
19- E. Ranucci, F. Bignotti, P. Ferruti, "Synthesis of low molecular weight poly (*N*-acryloylmorpholine) end-functionalized with primary amino groups, and its use as macromonomer for the preparation of poly(amidoamines)"Macromol. Chem. Phys. 196 (1995) 2927.
20- M.M. Temüz, M. COŞKUN, "Graft copolymerization of poly(styrene-co-p-choloromethylstyrene) with methyl methacrylate and acryloylmorpholine by atom transfer radical polymerization: Graft copolymer characterization and monomer reactivity ratios"Polym. Sci. Polym. Chem. 43 (2005) 3771-3777.
21- F.M. Veronese, R. Largajolli, C. Visco, P. Ferruti, A. Miucci, " Surface modification of proteins by covalent binding of acrylic polymers" Appl. Biochem. Biotechnol. 11 (1985) 269.
22- J.Z. Yi, S.H. Goh, "Interactions in miscible blends and complexes of poly (N-acryloylmorpholine) with poly (p-vinylphenol)" Polymer 43 (2002) 4515-4522.
23- A.A. Khalil, "Monomer reactivity ratios for copolymerizations of N-methacryloyloxytetrabromophthalimide (NMTP) with methyl acrylate (MA), methyl methacrylate (MMA), styrene (St) and acrylonitrile (AN)" Delta J. Sci. 19 (2) (1995) 127-141.
24- M. Fineman, S.D. Ross, "Liner method for determining monomer reactivity ratios in copolymerization"J MACROMOL SCI CHEM. 5(2) (1950) 259-261.
25- T. Kelen, F. Tüdös, "Analysis of the linear methods for determining copolymerization reactivity ratios.I. A new improved linear graphic method"J MACROMOL SCI CHEM. 9(1)(1975) 1-27.
26- L.J. Young, Polymer Handbook, 2nd ed., J. Brandrup, and E. H. Immergut, Eds., New York, Wiley-Interscience, PP. II. 105-II. 404 (1975)
27- T. Alfrey, C.C. Price, "Relative reactivities in vinyl copolymerization" J POLYM SCI POL CHEM. 2 (1947) 101

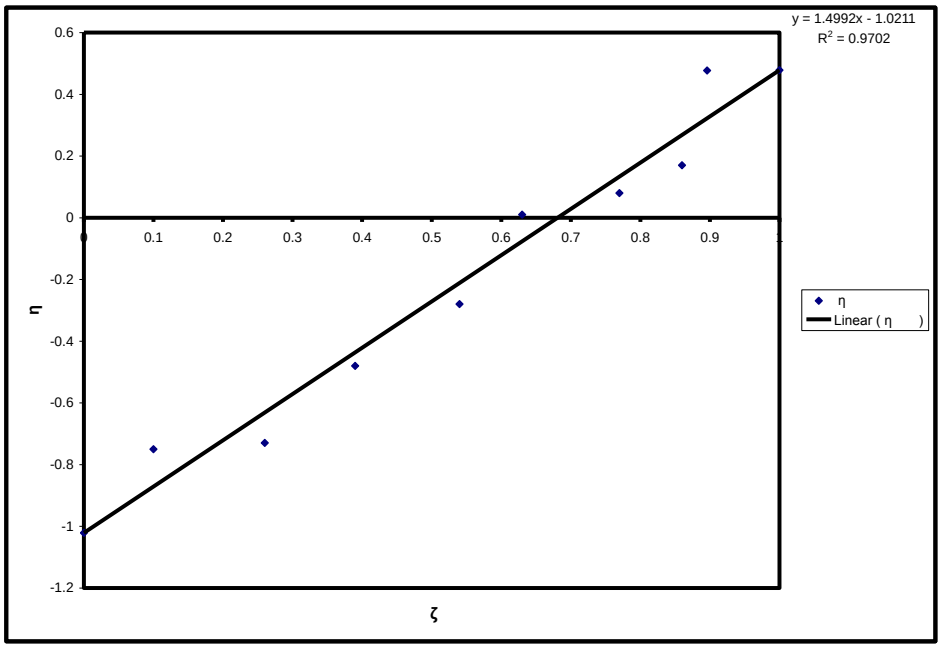


Fig. (1) : Kelen-Tüdös plots for the copolymerization of NAM with MA

Where:

$$\eta = \frac{a(b-1)}{\alpha b + a^2} \qquad , \qquad \zeta = \frac{a^2}{\alpha b + a^2}$$

and:

$$\alpha = \frac{a_{min} \cdot X\ a_{max}}{\sqrt{b_{min} \cdot X\ b_{max}}}$$

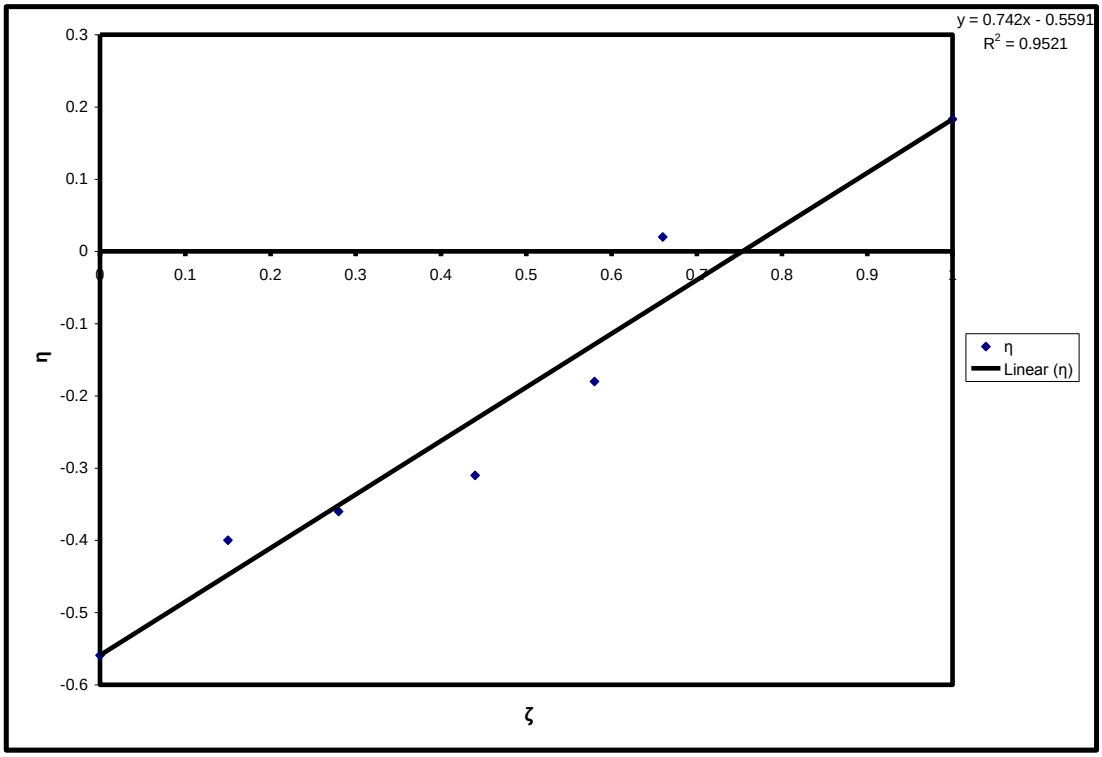


Fig. (2) : Kelen-Tüdös plots for the copolymerization of NAM with MMA

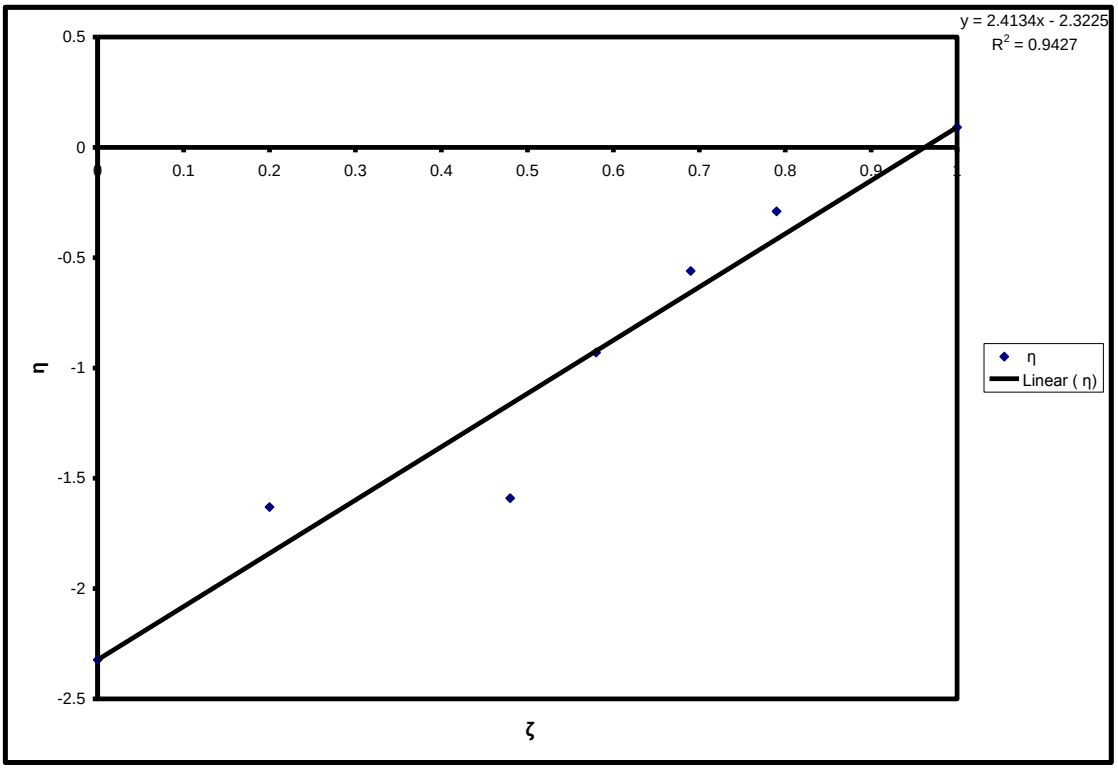


Fig. (3) : Kelen-Tüdös plots for the copolymerization of NAM with ST

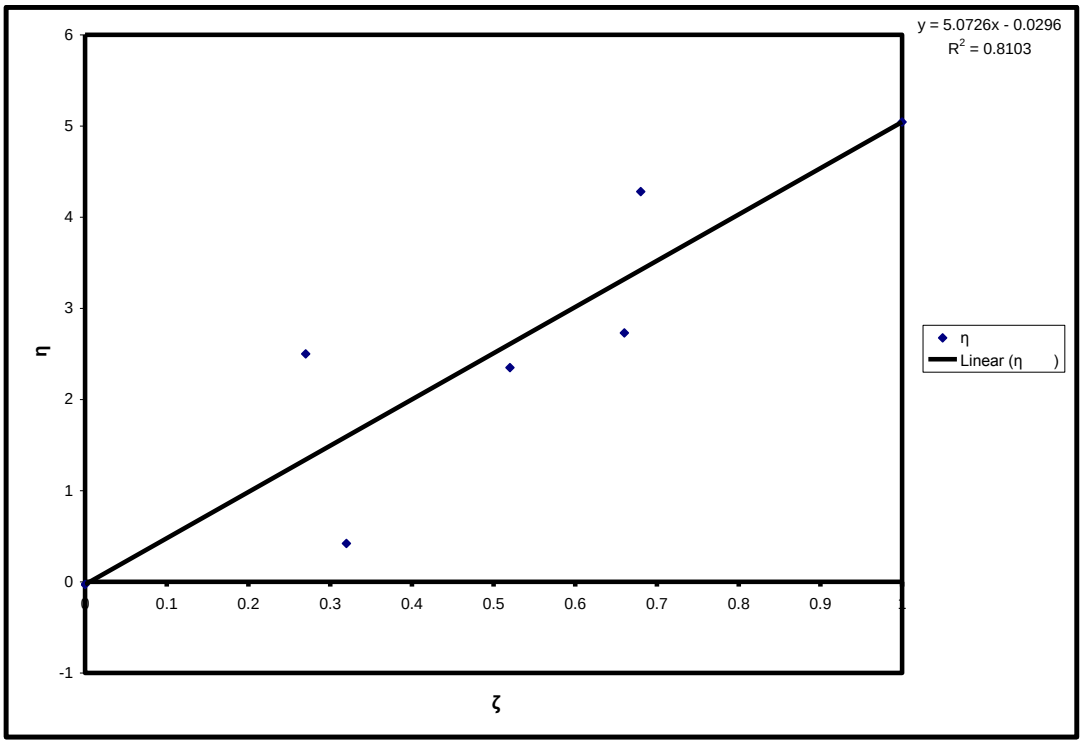


Fig. (4) : Kelen-Tüdös plots for the copolymerization of NAM with VA

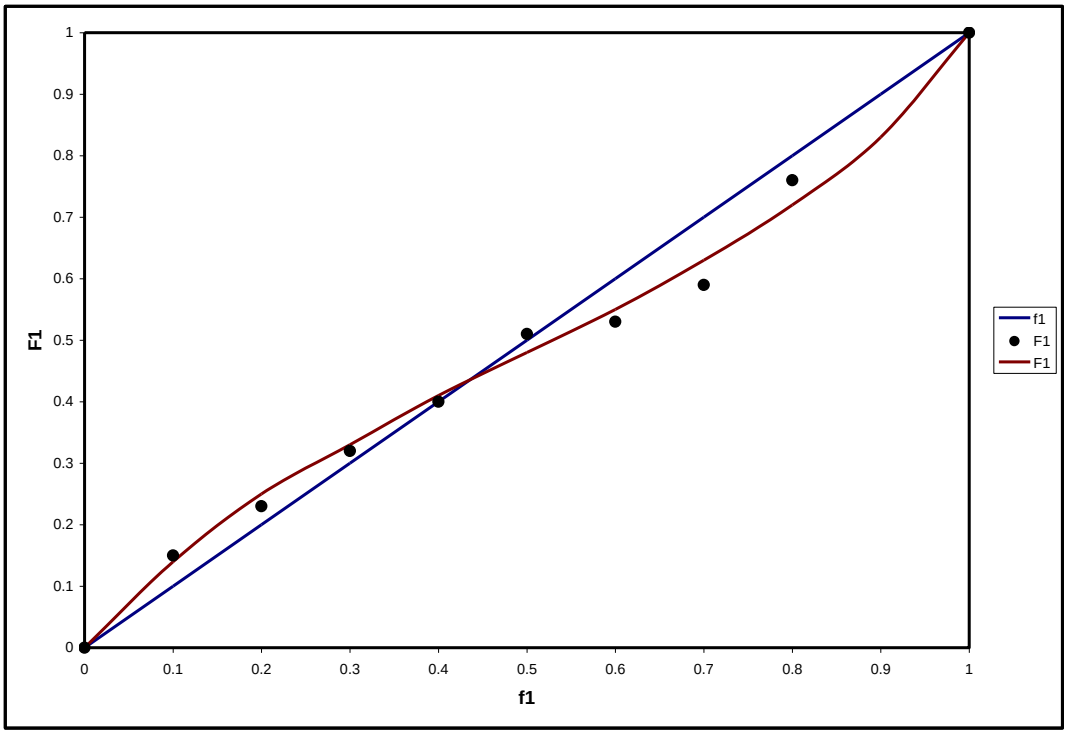


Fig. (5) Composition curves for copolymerizations of NAM with MA. Line represents calculated values and (●) represent experimental values. f_1=molar fraction of M_1 in feed and F_1=molar fraction of M_1 in copolymer.

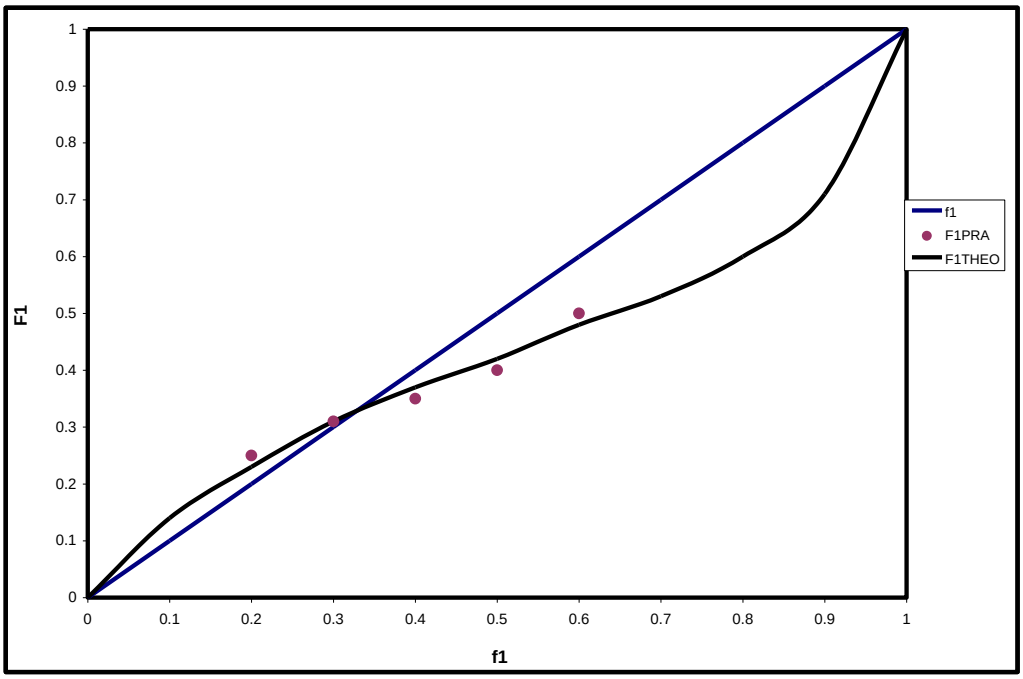


Fig. (6): Composition curve for copolymerization of NAM with MMA

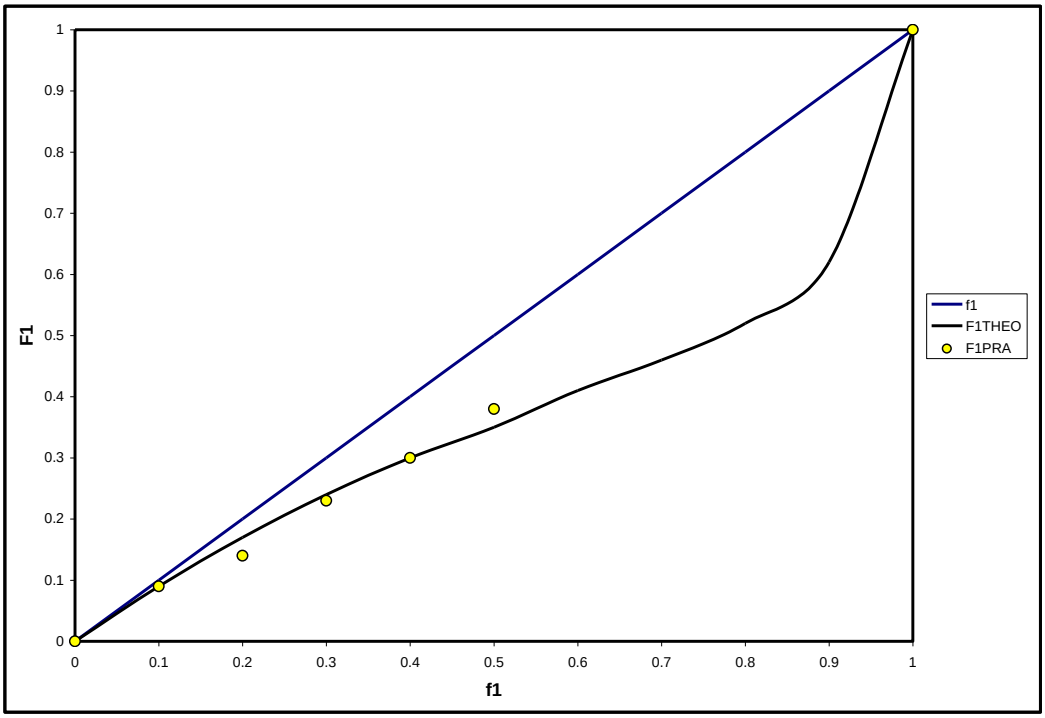


Fig. (7): Composition curve for copolymerization of NAM with ST

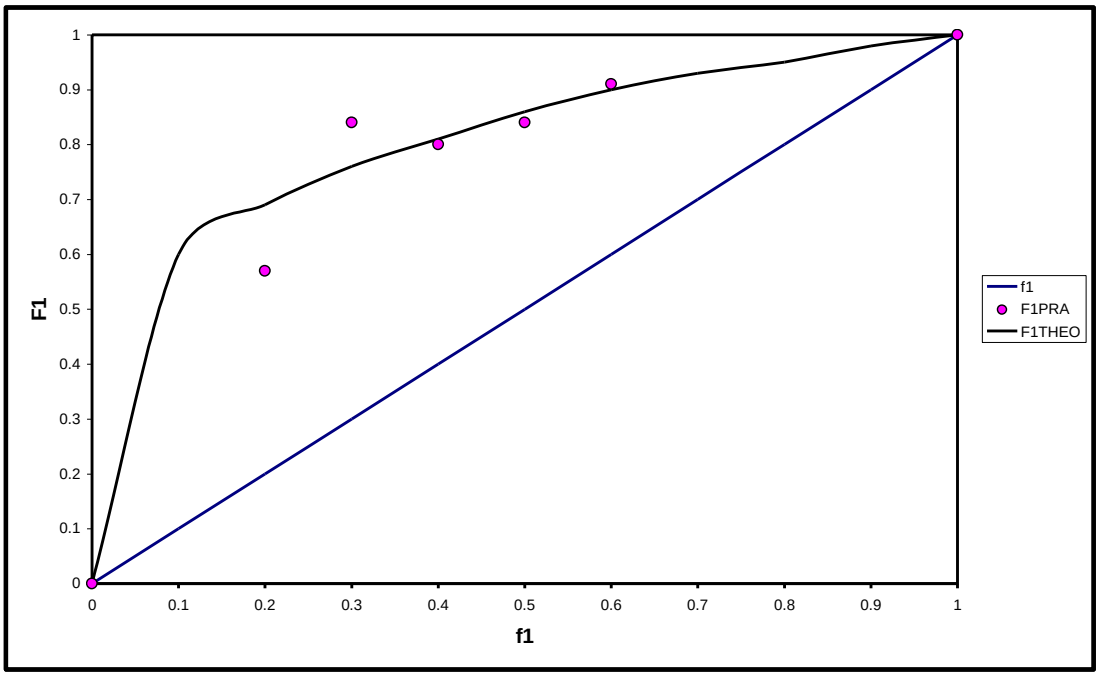


Fig. (8): Composition curve for copolymerization of NAM with VA