



**Copolymerization parameters of
N-Methacryloyloxytetrabromophthalimide with different vinyl
monomers**

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Abstract:

N-Methacryloyloxytetrabromophthalimide (NMTP) was synthesized by the reaction of N-hydroxytetrabromophthalimide with either methacryloyl chloride or methacrylic acid in the presence of triethylamine or N, N-dicyclohexylcarbodiimide. Binary copolymerization reactions of the prepared monomer with ethyl acrylate (EA), *n*-butyl methacrylate (*n*.BMA), tertiary butylacrylate (*t*.BA) and vinyl acetate (VA) were performed in methylene chloride at 65 °C using 1 mol % azobisisobutyronitrile (AIBN) as initiator. The structure of the prepared monomer was investigated by IR and ¹H NMR spectroscopy. The copolymer compositions were determined from bromine analysis. Copolymerization parameters for each system were calculated by the Fineman-Ross and Kelen-Tüdös methods. The monomer reactivity ratios for the systems NMTP-EA, NMTP-*n*.BMA, NMTP-*t*.BA and NMTP-VA were found to be $r_1 = 0.180$, $r_2 = 0.893$, $r_1 = 0.025$, $r_2 = 0.680$, $r_1 = 0.014$, $r_2 = 0.956$ and $r_1 = 1.002$, $r_2 = 1.004$ respectively.

Keywords: Copolymerization, reactivity ratios, acrylate polymers, N-Methacryloyloxy-tetrabromophthalimide polymers.

Introduction

The last years have been the rise in the popularity of attaching chemically reactive species to insoluble supports. A wide variety of vinyl-derivative molecules can be obtained and polymerized or copolymerized to produce functionalized supports among the active groups that have been introduced into polymer chains which are act as stabilizers, complexing agents, pharmaceutical and catalysts^(1,2). Several activated esters and amides of acrylic and methacrylic acid and their polymers have been described. Free radical copolymerization is a method of modifying the properties of polymers. The incorporation of higher proportions of activated monomers and its better distribution within the polymer chain can be achieved through fundamental studies on copolymerization parameters under specified reaction conditions⁽³⁻¹⁰⁾. In



the present study, the estimation of copolymer composition and the determination of the monomer reactivity ratios for copolymerization of N-Methacryloyloxy-tetrabromophthalimide (NMTP) with ethyl acrylate (EA), *n*.butyl methacrylate (*n*.BMA), tertiary butylacrylate (*t*.BA) and vinyl acetate (VA) are investigated.

Experimental Procedures

Materials

Ethyl acrylate (EA), *n*.Butyl methacrylate (*n*.BMA), tertiary butylacrylate (*t*.BA) and vinyl acetate (VA) (E. Merck, Darmstadt, Germany) were freed from inhibitors by distillation under reduced pressure and the middle cuts retained for use. Azobisisobutyronitrile (AIBN) and N, N-dicyclohexyl carbodiimide (DCCI) from Eastman Kodak Co. Azobisisobutyronitrile (AIBN) was recrystallized from absolute ethanol, m.p. 102 °C. All solvents used were of reagent grade and were purified by usual method before use.

Synthesis and copolymerization reactions⁽¹¹⁾

N-Methacryloyloxytetrabromophthalimide (NMTP) was prepared by either the reaction of N-hydroxytetrabromophthalimide (NHTP) with the corresponding acid chloride or through the reactions of N-hydroxytetrabromophthalimide with corresponding acid in the presence of N,N'-dicyclohexylcarbodiimide as follows:

Acid chloride method

To a well-stirred solution (0-5 °C) of N-hydroxytetrabromo-phthalimide (0.2 mole) in 250 mL of methylene chloride, methacryloylchloride (0.2 mole) was added dropwisely. The reactions mixture was then allowed to stand at room temperature for 2 hours and poured in excess petroleum ether 40-60 to precipitate the triethylamine hydrochloride. After filtration, the filtrate was extracted with water to remove any residual triethylamine hydrochloride, and evaporated to dryness in vacuum. The residue obtained was recrystallized from benzene / petroleum ether mixture (20-80) yield 85%, m.p. 184-186 °C.

N, N-Dicyclohexylcarbodiimide (DCCI) method



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N-Methacryloyloxytetrabromophthalimide was prepared by the reaction of methacrylic acid with N-hydroxytetrabromophthal-imide (NHTP) in the presence of N, N-dicyclohexylcarbodiimide (DCCI). To a cooled solution (0-5 °C) of 14.37g (0.03 mol) NHTP and 2.58g (0.03 mol) methacrylic acid in methylene chloride (60 mL) was added 6.18 g (0.03 mol) of DCCI with stirring. After 20 hrs. stirring at room temperature, the precipitated dicyclohexyl urea was removed by filtration and the filtrate was evaporated to dryness in vacuum. The residue was recrystallized from benzene to give NMTP as a yellowish solid m.p. 186 °C, yield 22.78 g (98.5%).

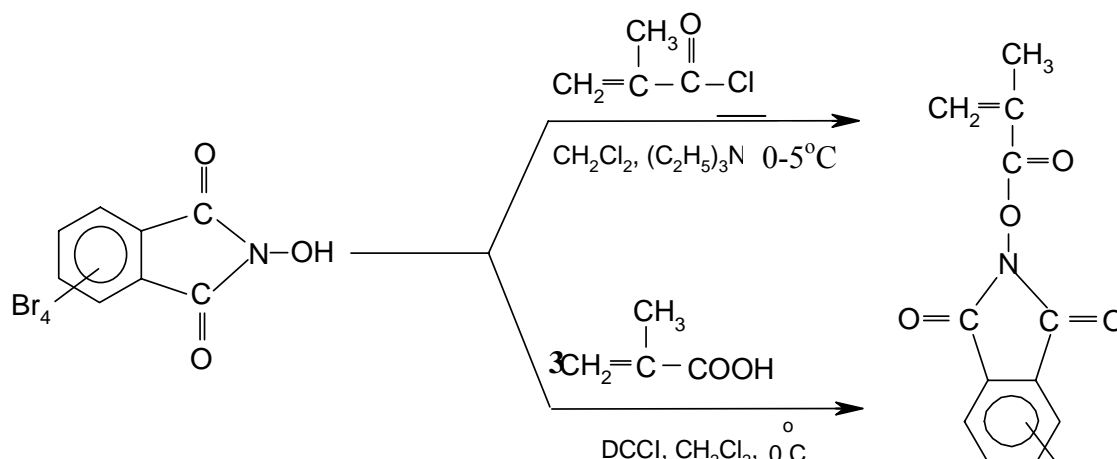
Copolymerization reactions

The copolymers were obtained by solution polymerization, the predetermined amounts of the comonomers were placed in glass tubes and diluted with methylene chloride so that the total monomer concentration was about (4 mol/L). The copolymerization was commenced by adding AIBN of 1 mol /100 mol of monomers to each tube. The tubes were flushed with oxygen-free nitrogen for 10 min., capped and thermostated at 65 °C for 5 hrs. depending on the comonomer pairs and composition. The copolymers were reprecipitated by pouring the polymerization mixtures into methanol, washed several times, dried and weighed. The conversion was kept below 10% in all the preparations.

The composition of the copolymers was determined by elemental analysis of bromine. Infrared spectra was measured using KBr discs and a Perkin-Elmer 598 (4000-200 cm⁻¹) spectrometer. ¹H NMR spectra was measured on a 90 MHz Varian EM-390 spectrometer in DMSO with tetramethylsilane as the internal standard. Bromine analysis was carried out at the Microanalytical Center, Cairo University.

Results and Discussion

N-Methacryloyloxytetrabromophthalimide (NMTP) was prepared according to the following scheme:



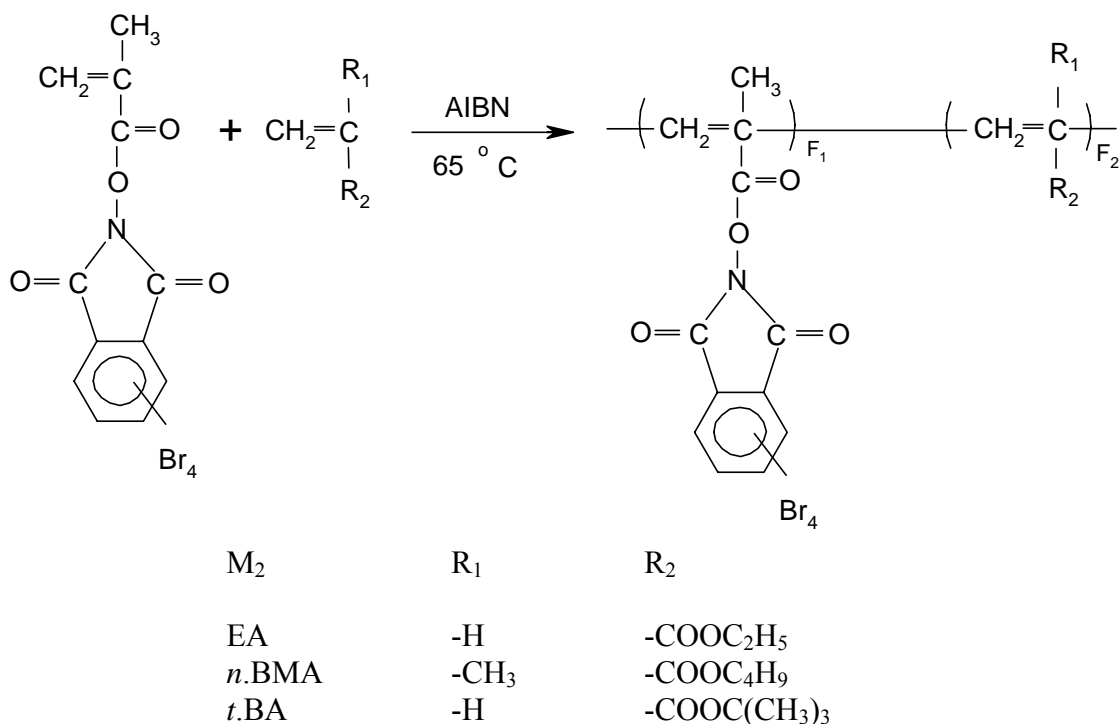


0-5°C

The structure of NMTP monomer was confirmed by IR and ¹H NMR spectroscopy. The IR spectrum of NMTP shows signals at 2950 cm⁻¹ due to the C-H stretching vibrations, at 2875 cm⁻¹ due to C-Br stretching vibration, a strong band at 1790 cm⁻¹ characteristic of C=O stretching vibrations of the phthalimide group, a strong band at 1735 cm⁻¹ due to the C=O stretching vibrations of the carboxylic group, a strong band at 1640 cm⁻¹ due to C=C of vinylidene group and a strong band at 660 cm⁻¹ characteristic of C-Br bending vibrations of bromine compounds.

The ¹H NMR spectrum of NMTP show signals at δ 6.3 ppm and 5.8 ppm due to the two protons of the CH₂=C group and a signal at δ 2.0 ppm corresponding to the three protons of the CH₃ group.

The copolymerization of NMTP with EA, *n*.BMA, *t*.BA and VA can be represented by:





VA

-H

-OCOCH₃

The copolymers were yellowish soluble in most organic solvents. Table (1) shows analytical data for copolymerization of NMTP-VA as an example. The monomer reactivity ratios (r_1 and r_2) for each system were calculated using the Fineman Ross⁽¹²⁾ and Kelen-Tüdös⁽¹³⁾ methods and the standard deviations of the results were calculated by regression analysis as given in Table (2). Figure (1) shows the Kelen-Tüdös plots for the four systems studied. The values of r_1 and r_2 from the Kelen-Tüdös method are almost identical to those obtained by the Fineman-Ross method. Figure (2) shows the experimental results and the composition curves calculated on the bases of the determined monomer reactivity ratios.

The sequence distribution of the monomer units along the copolymer chains were calculated from the monomer reactivity ratios on the basis of terminal copolymerization model⁽¹³⁾. The variation in the sequence distribution of the triad fractions (f_{111} , f_{212} , and f_{112}) with feed composition are represented in Figure (3). It is clear that triad fractions f_{111} increase with increasing f_1 while triad fractions f_{212} decrease with increasing f_1 . Triad fractions f_{112} have maximum values for f_1 equal to 0.49, 0.42, 0.38 and 0.50 for NMTP-EA, NMTP-*n*.BMA, NMTP-*t*.BA and NMTP-VA respectively.

Table (2) indicates that the reactivity ratios (r_1 and r_2) for NMTP-EA, NMTP-*n*.BMA and NMTP-*t*.BA systems are both less than unity and these systems should have an azeotropic composition. The composition curve (Fig.2) for the copolymerization of NMTP-EA, NMTP-*n*.BMA and NMTP-*t*.BA seems to cross-line representing $F_1 = f_1$ at about 0.116, 0.247, and 0.043 mole fraction as predicted from the values of r_1 and r_2 respectively. These points of intersection correspond to the azeotropic composition yielding homogenous copolymers regardless of conversion.

The Q and e values were calculated from the monomer reactivity ratios by using the Alfrey-Price equations⁽¹⁴⁾.

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{1/2}$$
$$Q_1 = (Q_2/r_2) \exp [-e_2 (e_2 - e_1)]$$

The Q and e values which represent the extent of resonance stabilization and polarity of the double bond, respectively in monomer and its radical were extensively



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tabulated by Young⁽¹⁵⁾ for various monomers from earlier copolymerization data. Thus the average Q and e values for NMTP are obtained by using the monomer reactivity ratios of the present work and the Q and e values for the vinyl monomers. The Q and e values for NMTP for NMTP-EA (as an example) have been found to be Q = 0.615 and e = 0.465, which are comparable with the Q and e values reported in the literature⁽¹⁵⁾ for the esters of NMTP.

Conclusion:

Copolymers from N-Methacryloyloxytetrabromophthalimide (NMTP) with ethyl acrylate (EA), n-butyl methacrylate (n. BMA), tertiary butylacrylate (t.BA) and vinyl acetate (VA) were easily prepared by free radical copolymerization. The monomer reactivity ratios for the four systems studied, NMTP-EA, NMTP-n.BMA, NMTP-t.BA and NMTP-VA were found to be $r_1 = 0.180$, $r_2 = 0.893$; $r_1 = 0.025$, $r_2 = 0.680$; $r_1 = 0.014$, $r_2 = 0.956$ and $r_1 = 1.003$, $r_2 = 1.004$, respectively. The reactivity ratios of NMTP for some of the copolymerizations studied are small compared to those of vinyl monomers (EA, n. BMA, t. BA) which indicates that the growing radical ending with a NMTP unit prefers M_2 monomer to M_1 monomer during the propagation stage.

References

- 1- Maradiya, H. and Patel, V.S., J. Serb. Chem. Soc., 60 (2001) 87.
- 2- Stieber, F., Grether, M.; Mazitschek, R., Soris, N. Giannis, A. and Waldman, H., Chem. Eur. J., 9, (2003) 3282.
- 3- Ferruti, P.; Fere, A.; Cottica, G.; J. Polym. Sci., 12 (1974) 553.
- 4- Ferruti, P. and Cotico, G., J. Polym. Sci., 12 (1974) 2453.
- 5- Shaaban, A.F.; Arief, M.M. H.; Khalil, A.A.; and Messiha, N.N.; Acta polymerica 39 (1988) 154.
- 6- Mahmoud, A.A.; Shaaban, A.F.; Khalil, A.A.; and Messiha, N.N.; Die Angew. Makromol. Chem. 198 (1992) 31.
- 7- Shaaban, A.F., Salem, M.A., Azab, M.M. and Messiha, N.N., Acta Polymerica, 39, (1988) 11.
- 8- Shaaban, A.F., Azab, M.M. and Messiha, N.N., Die Angewandte Macromolekulare Chemie, 59, (1989) 169.
- 9- Mahmoud, A.A., Azab, M.M. and Messiha, N.N., Eur. Polym. Journal. 29 (1993) 1125.
- 10- Azab, M.M., J. Applied Polymer Science, 91 (2004) 296.
- 11- Mahmoud, A.A., Shaaban, A.F., Azab, M.M. and Messiha, N.N. Eur. Polym. Journal, 28, (1992) 555.
- 12- Finemen, M. and Ross, S.P., J. Poly. Sci., 5, (1950) 259.
- 13- Kelen, T. and Tüdöds, F., J. Macromol. Sci. Chem. 9 (1) (1971) 1.
- 14- Alfrey, T., Jr and Price, C., J. Polym. Sci. A1 (1963) 1137.
- 15- Young, L.J., In Polymer Handbook (Brandrup, J. and Immergut, E.H.) 2nd Edn., Wiley-Interscience, New York 1975, pp. II. 105-II. 404.

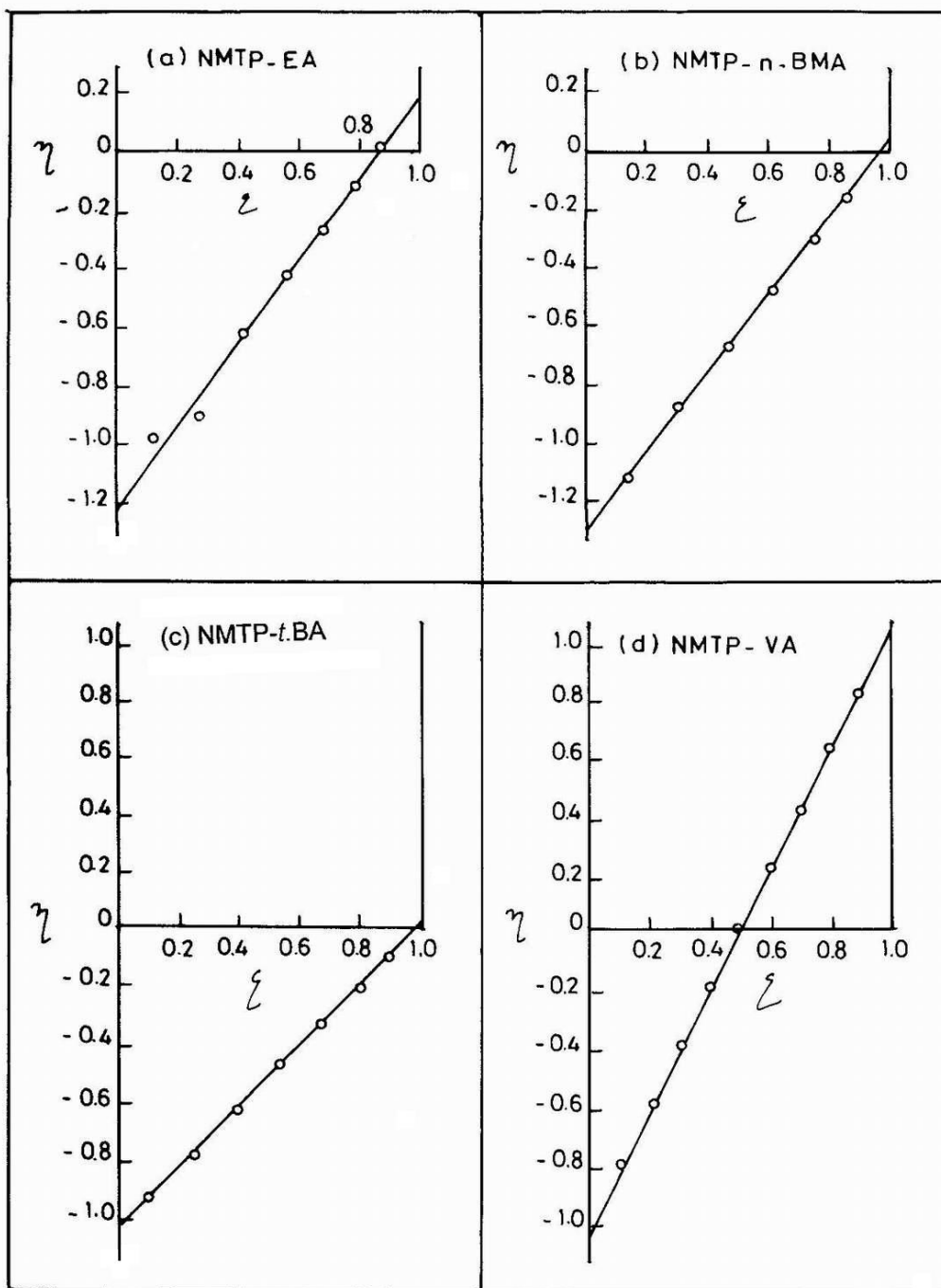


Figure (1): Kelen-Tüdös plots for copolymerizations of (a) NMTP-EA, (b) NMTP-n.BMA, (c) NMTP-t.BA and (d) NMTP-VA, $\eta = \frac{a(b-1)}{ab+a^2}$ and $\zeta = \frac{a^2}{\alpha b + a^2}$ where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and $\alpha = (a_{\min} \times a_{\max}) / (b_{\min} \times b_{\max})^{1/2}$

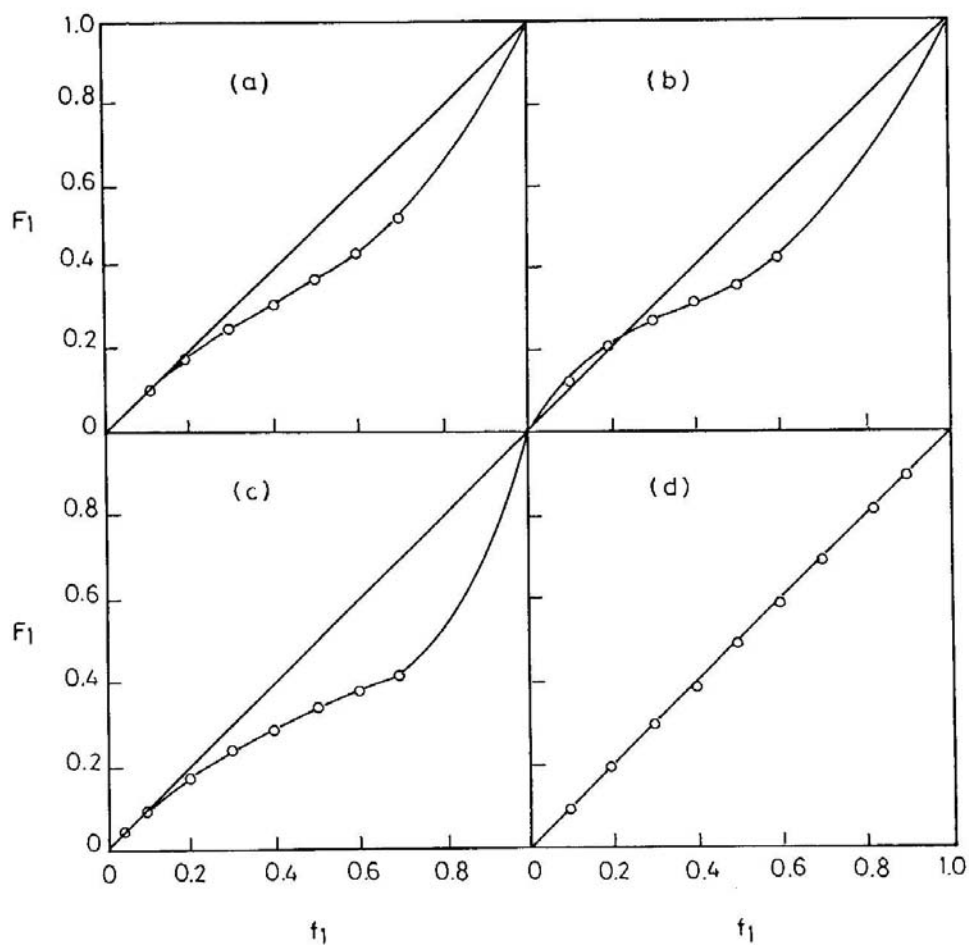


Figure (2): Composition curve for copolymerization of (a) NMTP-FA, (b) NMTP-n.BMA, (c) NMTP-t.BA and (d) NMTP-VA. The Line represents calculated values and the (o) represent experimental values, f_1 is the mole fraction of M_1 in feed and F_1 is the mole fraction of M_1 in copolymer.

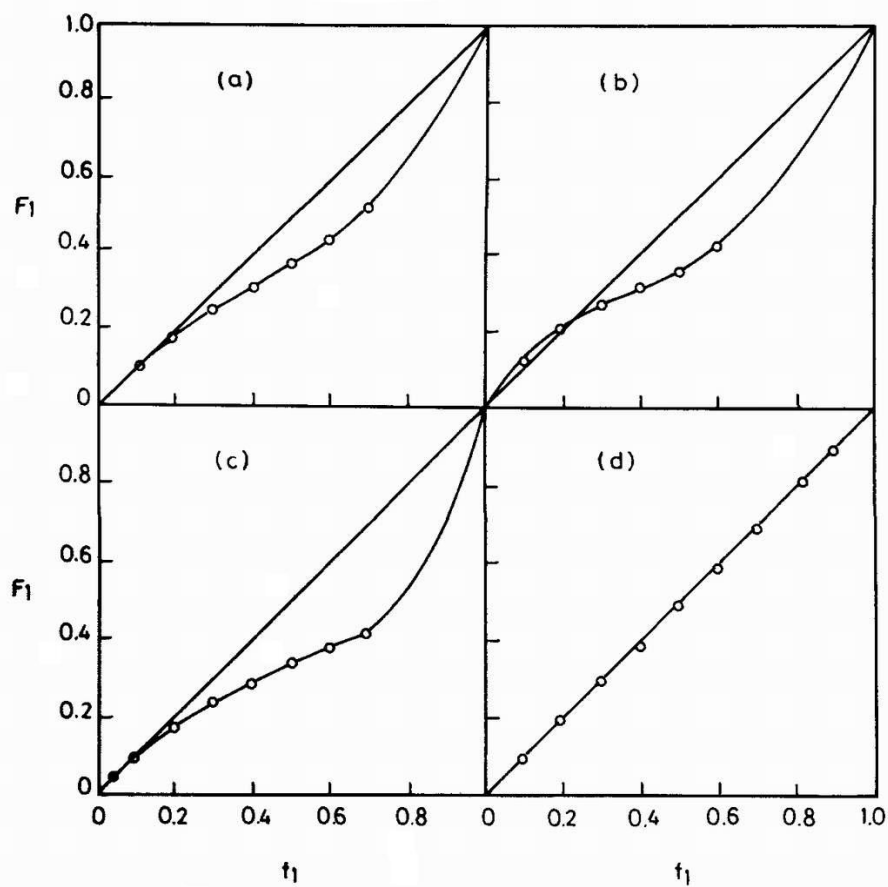


Figure (2): Composition curve for copolymerization of (a) NMTP-EA, (b) NMTP-n.BMA, (c) NMTP-*t*.BA and NMTP-VA. Lines represent calculated values and (●) represent experimental values f_1 = mole fraction of M_1 in feed and F_1 = mole fraction of M_1 in copolymer.



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Table (1): Analytical data for copolymerization of NMTP-VA.

| Monomer composition | | Conversion weight (%) | Br (%) | Copolymer composition | |
|---------------------|----------------|-----------------------|--------|-----------------------|----------------|
| a | f ₁ | | | b | F ₁ |
| 0.1111 | 0.9000 | 8.3 | 24.20 | 0.1110 | 0.9009 |
| 0.2500 | 0.8212 | 7.3 | 35.90 | 0.2500 | 0.8291 |
| 0.4285 | 0.6985 | 8.6 | 42.80 | 0.4261 | 0.6997 |
| 0.6666 | 0.5978 | 9.0 | 47.30 | 0.6647 | 0.5993 |
| 1.0000 | 0.5000 | 8.2 | 50.60 | 1.0081 | 0.5020 |
| 1.5000 | 0.4003 | 7.9 | 52.90 | 1.4956 | 0.3992 |
| 2.3333 | 0.3007 | 8.3 | 54.80 | 2.3310 | 0.3002 |
| 4.0000 | 0.1987 | 6.8 | 56.28 | 3.9899 | 0.2000 |
| 9.0000 | 0.0990 | 9.1 | 57.50 | 9.0497 | 0.0999 |

a = M₁/M₂ in the feed composition.

f₁ = mole fraction of M₁ in the feed composition

b = m₁/m₂ in the copolymer composition.

F₁ = mole fraction of M₁ in the copolymer composition.

Table (2): Monomer reactivity ratios for copolymerization of NMTP with EA, *n*.BMA, *t*.BA and VA.

| M ₁ -M ₂ | Fineman-Ross | | Kelen-Tüdös | | | r ₁ r ₂ |
|--------------------------------|----------------|----------------|----------------|----------------|--------|-------------------------------|
| | r ₁ | r ₂ | r ₁ | r ₂ | α | |
| NMTP-EA | 0.205 ± 0.014 | 0.923 ± 0.033 | 0.180 ± 0.009 | 0.893 ± 0.030 | 0.7259 | 0.1607 |
| NMTP- <i>n</i> .BMA | 0.032 ± 0.004 | 0.686 ± 0.006 | 0.025 ± 0.003 | 0.680 ± 0.005 | 0.5235 | 0.0170 |
| NMTP- <i>t</i> .BA | 0.001 ± 0.004 | 0.937 ± 0.012 | 0.014 ± 0.002 | 0.956 ± 0.007 | 0.9264 | 0.0134 |
| NMTP-VA | 1.005 ± 0.002 | 1.006 ± 0.006 | 1.002 ± 0.003 | 1.004 ± 0.003 | 0.9975 | 1.0060 |

$$\alpha = [(a_{\min.} \times a_{\max.}) / (b_{\min.} \times b_{\max.})^{1/2}]$$