Novel Copolymers of 4-Chloronaphthyl Methacrylate with Acrylonitrile: Determination of Monomer Reactivity Ratios and Antimicrobial Activity

Cengiz Soykan[a]; Ali Delibas[a]; Ramazan Coskun[a]

[a] Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat, Turkey

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CENGIZ SOYKAN*, ALI DELIBAS and RAMAZAN COSKUN

Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat, Turkey

Methacrylate based monomer, 4-chloronaphthyl methacrylate (4-CNMA) was synthesized by reacting 4-chloro naphthol with methacryloyl chloride in the presence of triethylamine (NR_3) at 0–5°C. The free-radical initiated copolymerization of (4-CNMA), with acrylonitrile (AN) was carried out in 1,4-dioxane-dimethyl sulfoxide mixture (8:2) solution at 70 ± 1°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The monomer 4-CNMA, poly(4-CNMA) and copolymers were characterized by FT-IR and ^{1}H-and ^{13}C-NMR spectral studies. The copolymer composition obtained by elemental analysis led to the determination of reactivity ratios employing Fineman-Ross (F-R), Kelen-Tüdös (KT) and Extended Kelen-Tüdös (EKT) linearization methods. These parameters were also estimated using a non-linear computational fitting procedure, known as reactivity ratios error in variable model (RREVM). The solubility of the polymers was tested in various polar and non-polar solvents. Gel permeation chromatography was employed to determine the molecular weights (M_w and M_n) and polydispersity index of polymers. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with increase in the mole fraction of 4-CNMA in the copolymers. The prepared homo and copolymers were tested for their antimicrobial activity against bacteria, fungi and yeast.

Keywords: 4-chloronaphthyl methacrylate, copolymerization, monomer reactivity ratio, thermal properties, antimicrobial activity

1 Introduction

Several studies have been done in our laboratories on the synthesis of new methacrylate monomers (1–3) and their radical copolymerization with commercial monomers. These studies clearly show that the nature, as well as position, of the substituent had a large effect on monomer reactivity ratios, glass transition temperatures and antimicrobial properties. Copolymers with reactive or functional monomers are steadily gaining importance. Many polymers with reactive functional groups are now being synthesized, tested and used not only for their macromolecular properties, but also for the properties of functional groups (4). These functional groups provide an approach to a subsequent modification of the polymer for specific end applications (5). Nowadays, a strong demand prevails for "functional polymer" with very specific properties. Functional groups give a polymer structure a special character

substantially different from the inherent properties of the basic polymer chain (6). The antimicrobial property of the polymers plays an important role for many of its applications. Contamination by microorganisms is of great concern in several areas such as medical devices, health care products, water purification systems, hospital and dental equipments, etc. One possible way to avoid the microbial contamination is to develop materials possessing antimicrobial activities. Consequently, biocidal polymers have received much attention in recent years (7). Chlorine containing phenyl methacrylate and its polymer have been used as biocides in various applications (8, 9). Many other chlorine containing polymers possessing antimicrobial property have been reported (10, 11). The use of polymeric systems based on acrylic derivatives as biomaterials for clinical application has increased during last two decades because of their excellent biocompatibility and long term stability (12). Potin and coworkers (13) synthesized acrylate esters, useful in antifungal paints, by reacting pentachloro phenol/o-phenylphenol/p-chloro-m-cresol with acryloyl chloride. Copolymers of 5-chloro-8-quinolinyl acrylate with acrylamide/acrylicacid/methacrylic acid have been found to possess antimicrobial property (14). The technological importance of polyacrylonitrile (PAN) is known to suffer

*Address correspondence to: Cengiz Soykan, Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat, Turkey. E-mail: soykan@erciyes.edu.tr or E-mail:cengiz.soykan@bozok.edu.tr

from several disadvantages: weak modability, color instability, and weak dyeability. Besides other efforts to abolish these difficulties, several monomers have been used as co-monomers for the production of acrylonitrile (AN) copolymers (15) with improved thermal stability.

The study of the structure-property relationship exhibited by vinyl monomers in their radical copolymerization is very important (16). Functional polymers are produced either by chemical modification of preformed nonfunctional polymers or by direct copolymerization of the functional monomers with desired physico mechanical properties.

The chemical composition of the copolymers depends on the degree of incorporation of the comonomers and also on the relative reactivity between them. Monomer reactivity ratios are very important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor made copolymers with the required physical, chemical properties, and in evaluating the specific end application of copolymers. Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments. Therefore, properties such as the glass transition temperature, melt point, solubility, crystallinity, permeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits (17). Most existing procedures for calculating reactivity ratios can be classified as linear least-squares (LLS), and non-linear least-squares (NLLS) methods. It is accepted that LLS methods such as those proposed by Finemann and Ross (18), and by Kelen and Tüdös (19), can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation. The only LLS method, as an exception, is an extended Kelen-Tüdös method (20), which involves a rather more complex calculation.

We report here the synthesis and characterization of monomer 4-CNMA, as well as homo and copolymers of 4-CNMA using different feed ratios. The copolymer composition was determined by elemental analysis. The effect of 4-CNMA content on the thermal properties of resulting copolymers has been investigated. Homo- and copolymers were also tested in their antimicrobial activity against microorganisms such as *bacteria* (*Staphylococcus aureus, Bacillus megaterium, Escherichia coli*), *fungi* (*Aspergillus niger, Trichoderma Lignorum, Trichoderma viridis*) *and yeast* (*Candida tropicalis, Saccharomyces cerevisiae, Candida albicans*).

2 Experimental

2.1 Materials

4-chloro naphthol (Merck), methacryloyl chloride (Alfa Easer) was used as received. Acrylonitrile (AN) (Aldrich,
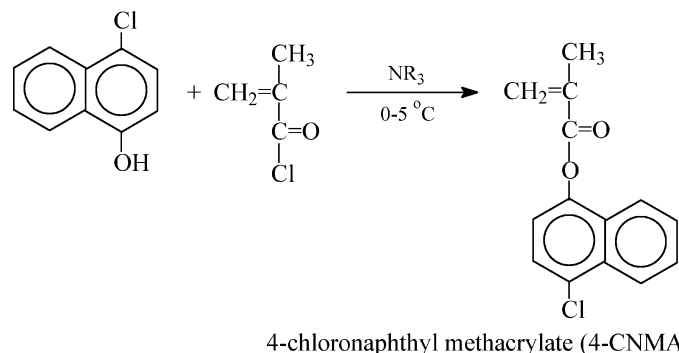
Fig. 1. Reaction scheme of 4-chloronaphthyl methacrylate (4-CNMA) monomer.

99%) was purified by alkali washing followed by distillation. 2,2′-Azobisisobutyronitrile (AIBN) was purified by successive crystallizations from chloroform- methanol mixture. Triethylamine, 1,4-dioxane, dimethyl sulfoxide, acetone, methanol (Merck), were analytical grade commercial products and used as received.

2.2 Synthesis of 4-Chloronaphthyl Methacrylate (4-CNMA) Monomer

To a well-stirred solution of 0.028 mole 4-chloro naphthol and 0.084 mole of triethylamine (NR₃) in 30 ml dichloromethane, 0.030 mole of methacryloylchloride was added dropwise under cooling in an ice bath (0–5°C), (Figure 1). After the complete addition of methacryloyl chloride, the reaction mixture was stirred for 12 h at room temperature, then filtered and evaporated with a rotavapour. A yellow product was obtained and recrystallized from ethanol as a yellow powder (yield 70%). The reaction scheme of the copolymer is shown in Figure 1.

2.3 Homopolymerization

The preparation of homopolymer of monomer 4-CNMA and AN were synthesized by free radical polymerization in 1,4-dioxane-dimethyl sulfoxide (8:2) solvent using AIBN as a free radical initiator. The polymers were purified by repeated reprecipitation from 1,4-dioxane-dimethyl sulfoxide [(8:2) as solvent]/acetone-methanol [(1:1) as non-solvent) and then filtered and dried until a constant weight was attained.

2.4 Copolymerization

Copolymerization reactions were conducted with AIBN as the initiator and 1,4-dioxane-dimethyl sulfoxide (8:2) as the solvent at 70 ± 0.1°C in Pyrex-glass ampoules sealed under a high vacuum. For each feed composition, the calculated amount of the monomers and initiator were weighed and added to the required volume of 1,4-dioxane-dimethyl

sulfoxide. We isolated the resulting copolymers by pouring the contents of the glass ampoules into acetone/methanol (1:1) mixture. The precipitated materials were purified by reprecipitation from 1,4-dioxane-dimethyl sulfoxide [(8:2) as solvent]/acetone-methanol [(1:1) as non-solvent) and then filtered and dried until a constant weight was attained.

2.5 Characterization Techniques

Infra-red spectra were measured on a Jasco 460 Plus FT-IR spectrometer. ^{1}H-and ^{13}C-NMR spectra of the polymers were recorded in CDCl$_3$ with tetramethylsilane as the internal standard using a Gemini Varian 300 MHz NMR spectrometer. Thermal data were obtained by using a Setaram 131 DSC and Labsys TG-DSC/DTA thermobalance in

N$_2$ atmosphere. The glass transition (T$_g$) temperatures were determined by a Setaram 131 DSC. Samples of about 5–8 mg held in sealed aluminum crucibles and the heating rate of 20°C/min under a dynamic nitrogen flow (5 l.h^{-1}) were used for the measurements. The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TGA) in a nitrogen stream at a heating rate of 10°C.min^{-1}. Elemental analyses were carried out by a LECO CHNSO-932 automicroanalyzer. The molecular weights and distributions of the copolymers were measured on a Waters GPC system equipped with a Waters 410 controller, a Waters 717 autosampler, and a Waters 2410 refractive index detector, a μ-styragel 500 columns eluted with tetrahydrofuran (THF) at a flow rate of 1 mL/min at the ambient temperature of about 20°C. The column was calibrated with five polystyrene standards, with molecular weights ranging
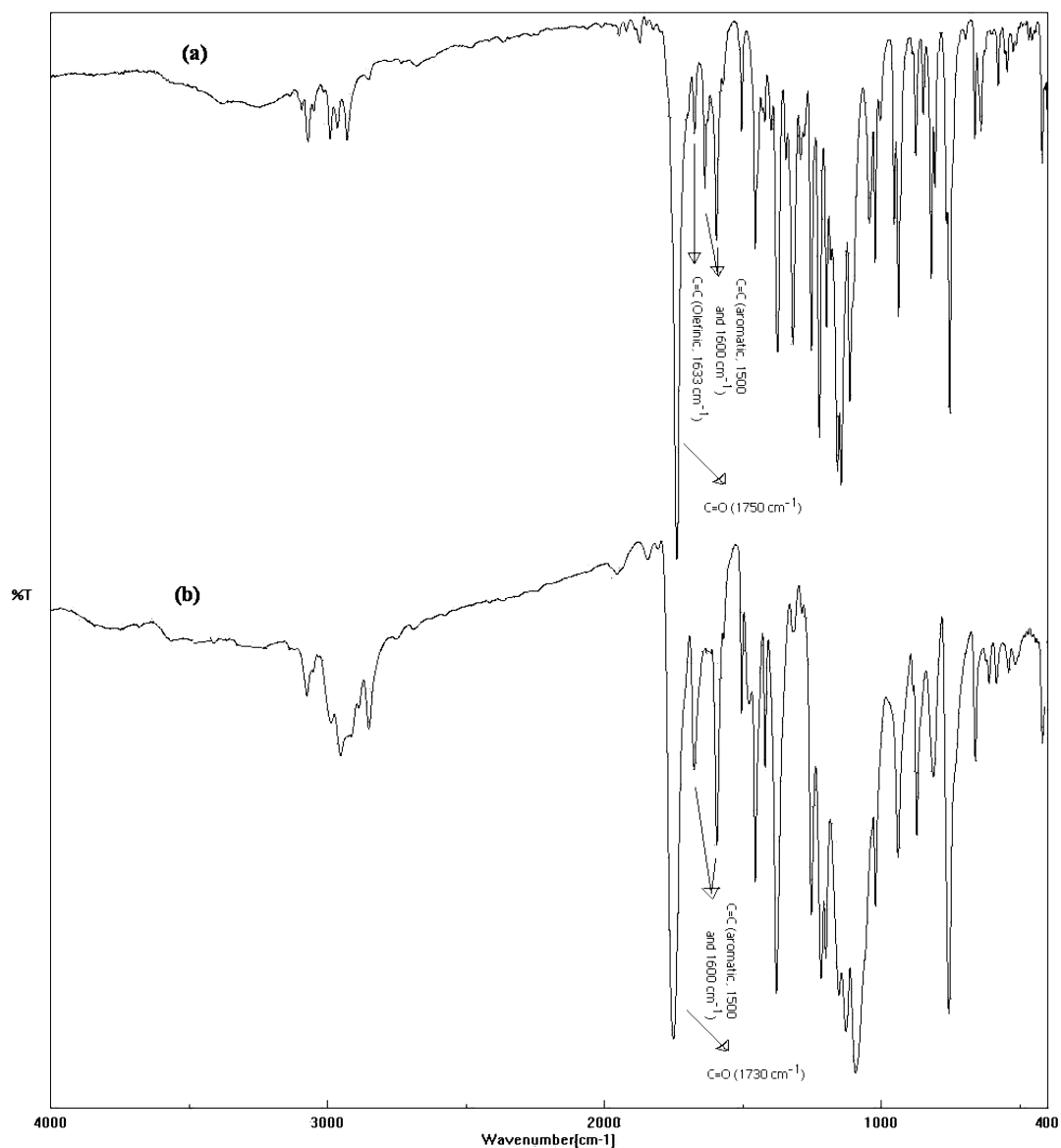
Fig. 2. FTIR spectra of 4-CNMA (a) and poly(4-CNMA) (b).

from 5000 to 200,000 g/mol, obtained from American Polymer Standards Corp.

2.6 Antimicrobial Activity Studies

Three bacteria, three fungi and three yeasts were used as test organisms. Those are: Staphylococcus aureus, Bacillus megaterium, Escherichia as bacteria, Aspergillus niger, Trichoderma Lignorum, Trichoderma viridis as fungi and Candida tropicalis, Saccharomyces cerevisiae, Candida albicans as yeast. The compounds and standart antibiotic (Kanamycin) were dissolved in dimethyl sulfoxide (DMSO) at a sample concentration of 100 μg ml^{-1} (21–23).
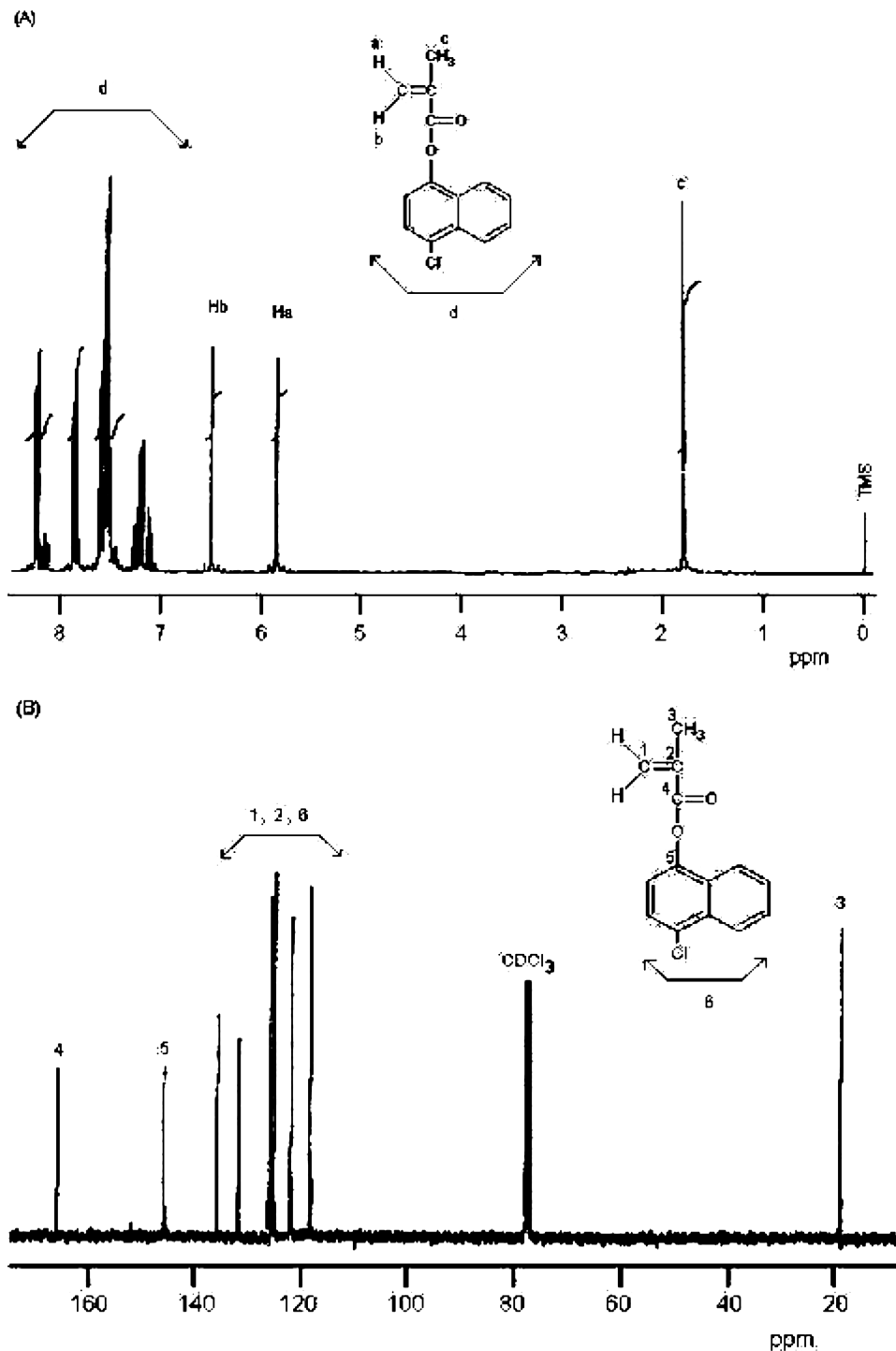

Fig. 3. ^{1}H-NMR spectra of 4-CNMA (A) and ^{13}C-NMR spectra of 4-CNMA (B)

3 Results and Discussion

3.1 Characterization of Homopolymer

The FTIR spectra of the monomer 4-CNMA and its homopolymer is shown in Figure 2. The FTIR spectrum of the poly(4-CNMA) showed few characteristic absorption peaks at 1750 cm^{-1} (carbonyl stretching), 1500 and 1600 cm^{-1} ($v_{C=C}$ in aromatic ring). During the polymerization of the monomers, the FTIR band at 1633 cm^{-1} ($v_{C=C}$ olefinic) disappears and the C=O stretching vibration at around 1750 cm^{-1} shows a significant blue shift comparing to that of the monomer 4-CNMA (at 1730 cm^{-1}). The main evidence for the polymer formation is certainly the disappearance of some characteristic signals of the double bond in the FTIR spectra. Thus two bands, one at 950 cm^{-1} due to out of plane C-H bending of geminal =CH$_2$ and the other due to stretching vibration band of C=C at 1633 cm^{-1}, disappeared in FTIR spectrum.

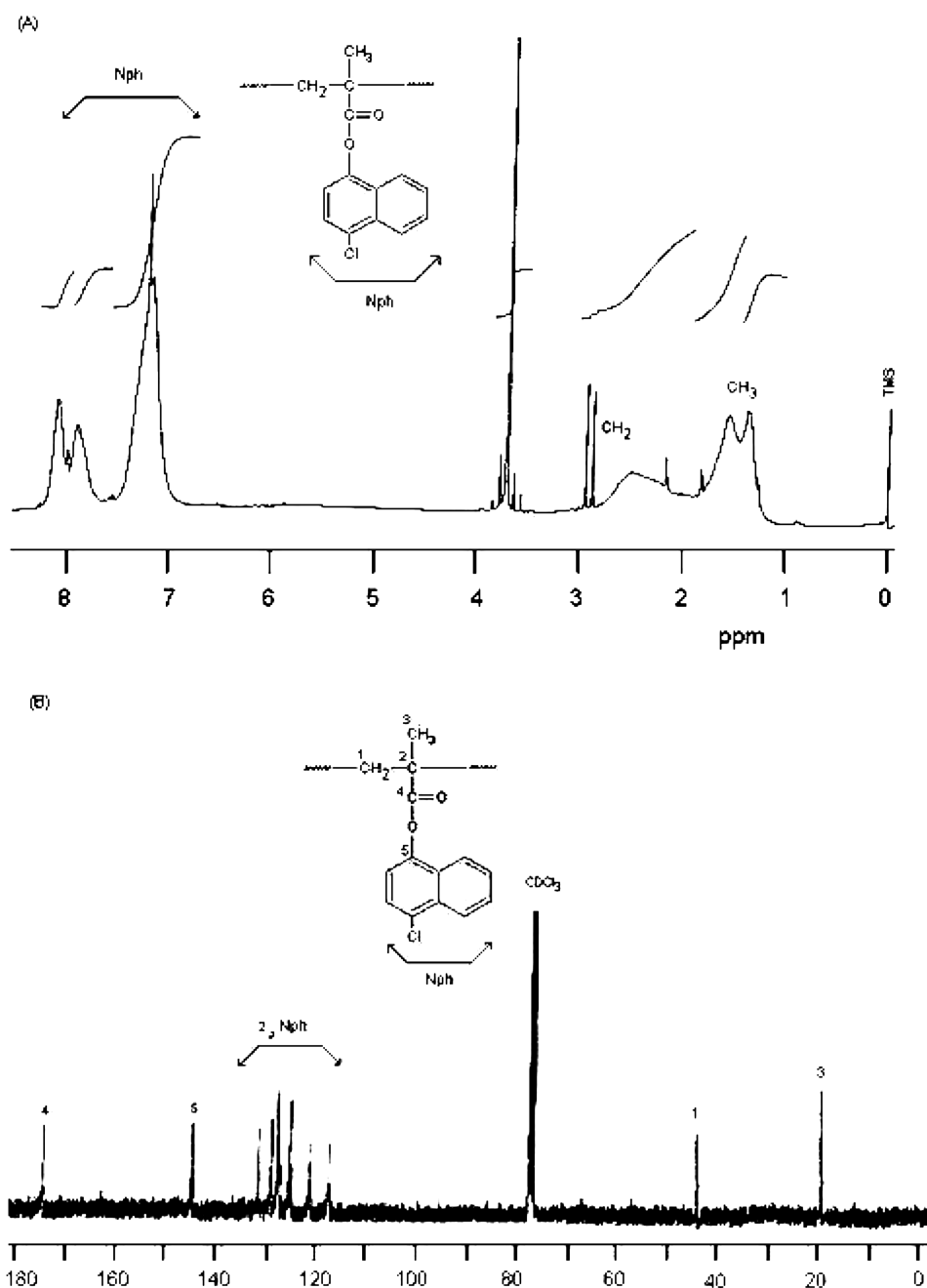The ^{1}H- and ^{13}C-NMR spectra of 4-CNMA and its attributions are shown in Figure 3A and B, respectively. The

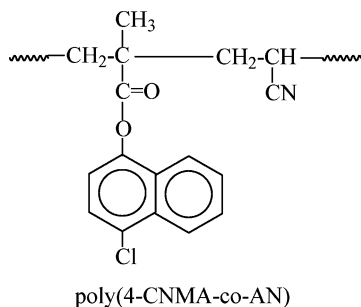**Fig. 4.** ^{1}H-NMR spectra of poly(4-CNMA) (A) and ^{13}C-NMR spectra of poly(4-CNMA) (B)

poly(4-CNMA-co-AN)

Fig. 5. Reaction scheme of copolymer.

structure of 4-CNMA is confirmed by ^{1}H- and ^{13}C-NMR spectral data.

The ^{1}H- and ^{13}C-NMR spectra of poly(4-CNMA) is shown in Figure 4A and B, respectively. The NMR spectra of the polymer have the characteristic peaks of the polymeric units.

3.2 Characterization of Copolymers

The copolymeric units of 4-CNMA with AN can be represented according to Figure 5.

3.3 FTIR Spectrum

The FTIR spectrum of the copolymers are shown in Figure 6. The peak at 3050 cm^{-1} corresponds to the C-H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2983, 2938 and 2863 cm^{-1}. The peak at 2340 cm^{-1} corresponds to the CN stretching of the AN units. The shoulder at 1740 is attributed to the ester carbonyl stretching of 4-CNMA. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1504 and 1470 cm^{-1}. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1460 and 1385 cm^{-1}. The C-O stretching is observed at 1165 and 1200 cm^{-1}. The C-H and C=C out of plane bending vibrations of the aromatic nuclei are observed at 790 and 565 cm^{-1}, respectively.

3.4 ^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the copolymer poly(4-CNMA-co-AN) (0.59:0.41) is shown in Figure 7(A). The chemical shift assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The naphthalene ring protons show signals between 8.32 and 6.93 ppm. The backbone methylene and methyne groups show signals at 1.84–3.11 ppm. The signals obtained at 1.80 and 1.23 ppm are due to the α-methyl protons of 4-CNMA units.

3.5 ^{13}C-NMR Spectrum

The proton decoupled ^{13}C-NMR spectrum of the copolymer poly(4-CNMA-co-AN) (0.59:0.41) is shown in Figure 7(B). The ester carbonyl of 4-CNMA appeared at 176.6 ppm. The aromatic carbons of 4-CNMA unit in copolymer appeared at 142.2, 136.3, 127.4 and 124.0 ppm, respectively. The CN carbon atoms of AN units give a resonance signal at 68.1 ppm. The methine carbons of the AN show signals at around 30.1 ppm. The signals due to the backbone methylene carbon atoms are observed at 46.0 ppm. The α-methyl carbon atoms of 4-CNMA units give a series of resonance signal at 18.2 ppm.

3.6 Solubility Studies

The copolymers were found to be soluble in chloroform, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, benzen, but insoluble in n-hexane, n-heptane, hydroxyl group containing solvent such as methanol, ethanol and n- butylalcohol.

3.7 Molecular Weights

The gel permeation chromatography (GPC) curves of the copolymers poly(4-CNMA-co-AN) (0.83:0.17) and (0.59:0.41) are shown in Figures 8 and 9. The GPC system calibrated with polystyrene in tetrahydrofuran (THF) showed that the weight-average molecular mass of the 4-CNMA-co-AN (83% 4-CNMA) was 48226 (Polydispersity index, PDI:1.76). The weight-average molecular mass of the 4-CNMA-co-AN (59% 4-CNMA) was 52279 (Polydispersity index, PDI:1.85). The theoretical values of PDI for polymers produced via radical recombination and disproportionation are 1.5–2.0, respectively (24). The values of PDI of the copolymers are 1.76 and 1.85, which suggests that the chain termination takes place predominantly by disproportionation than coupling.

3.8 Copolymer Composition and Monomer Reactivity Ratios

The monomer reactivity ratios for the copolymerization of 4-CNMA with AN were determined from the monomer feed ratios and the copolymer composition. The classical approach for acquiring copolymer data was to isolate the copolymers from each of nine feed compositions at early conversions and analyze the copolymer compositions by elemental analyses. The analytical data for copolymerization of 4-CNMA with AN as an example are illustrated in Table 1.

The plot of the mole fraction of 4-CNMA in the feed vs. that in the copolymer (Figure 10) indicates the way in which the composition in the feed differs from that of the copolymer. The copolymer composition curve, obtained by plotting the mole fraction of 4-CNMA in the feed (M_1)
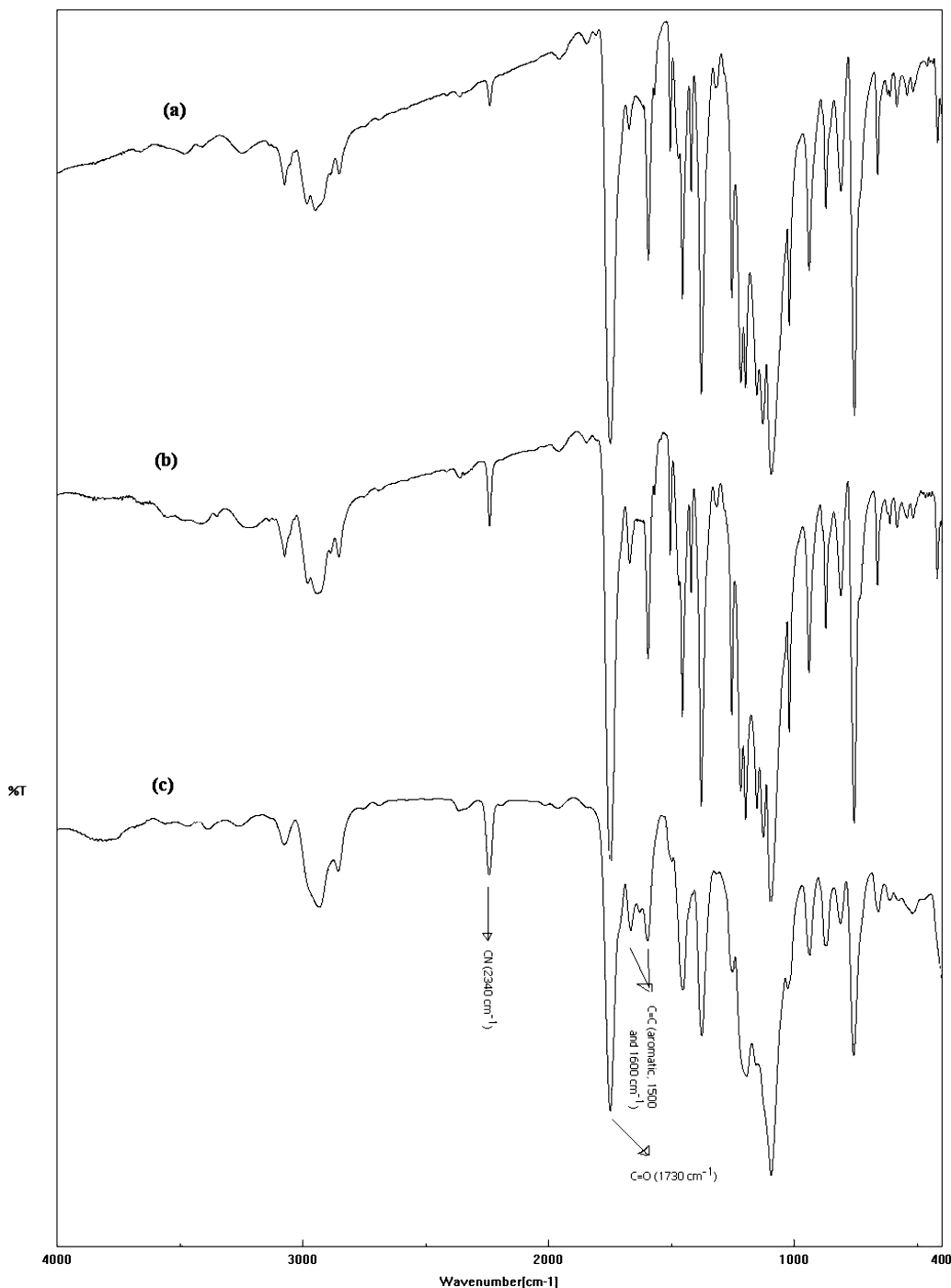
Fig. 6. FTIR spectra of investigated copoly(4-CNMA-co-AN): (a-c): [0.76:0.24], [0.51:0.49], [0.29:0.71].

versus the mole fraction of 4-CNMA in the copolymer (m_1) (Figure 9) does not intersect the ideal line. It clearly indicates that the feed composition and copolymer composition do not become equal during the polymerization process and the azeotropic copolymer composition has not been achieved in this case. It indicates that the composition of 4-CNMA in the copolymer is always bigger than that in the feed. The Fineman-Ross (FR) (18) , and Kelen-Tüdös (KT) (19) methods were used to determine the monomer reactivity ratios.

Fineman-Ross utilized a graphical method for evaluating the reactivity ratios r_1 and r_2 of a given pair of monomers.

(A)

(B)
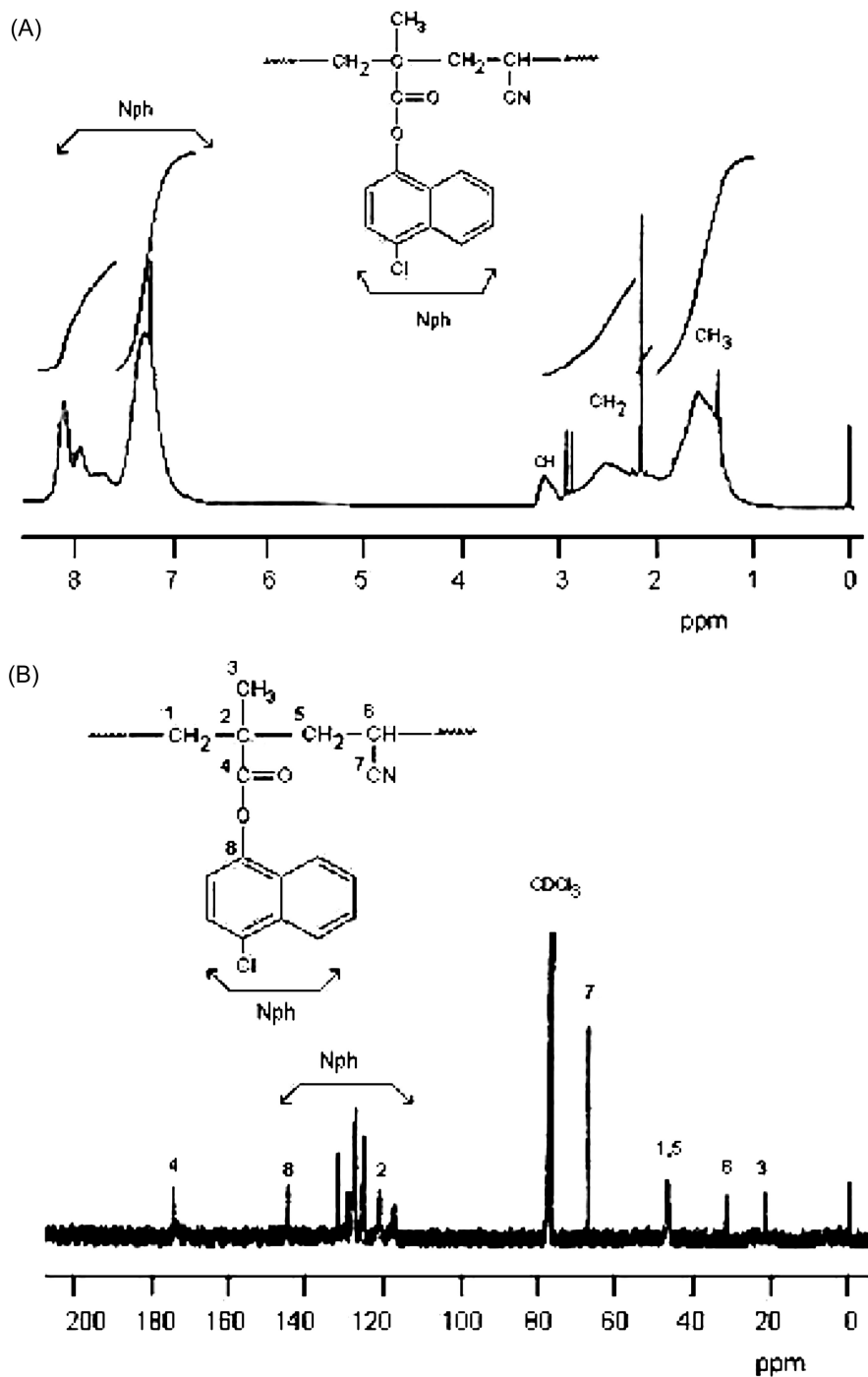
Fig. 7. ^{1}H-NMR spectra of copoly(4-CNMA-AN) (A) and ^{13}C-NMR spectra of copoly(4-CNMA-AN), (B) [0.51:0.49].

A plot of G vs H is a straight line whose slope gives r_1 and the intercept gives $-r_2$. Here,

$$G = F(f-1)/f \quad \text{and} \quad H = F^2/f \tag{1}$$

Where F and f are given by:

$$F = M_1/M_2 \quad \text{and} \quad f = m_1/m_2 \tag{2}$$

M_1 and M_2 = mole fraction of monomers 1 and 2 in feed
m_1 and m_2 = mole fraction of monomers 1 and 2 in copolymer.

The Fineman-Ross method described above does not give equal weight to the experimental points and do not allow for a non-linear dependence of the error on the composition.

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Table 1. Copolymer compositions data of copolymers of 4-CNMA and AN.

Sample Code No	Monomer feed composition in mole fraction		Amounts of each monomer		Amounts of catalyst	Amounts of solvents				Composition of 4-CNMA in copolymers
	M_{4-CNMA} (%)	M_{AN} (%)	4-CNMA (g)	AN (g)	AIBN (g)	1,4-Dioxane:DMSO (8:2 ratio) (ml)	$N(\%)^a$	Conv. $(\%)^b$	Amounts of polymer product$(g)^b$	m_{4-CNMA}
M-1	1.00	–	2.000	–	0.033	16:4	–	96.00	1.92	–
M-2	0.90	0.10	4.440	0.105	0.033	16:4	0.69	8.60	0.39	0.89
M-3	0.80	0.20	3.947	0.211	0.033	16:4	1.14	9.52	0.40	0.83
M-4	0.70	0.30	3.454	0.316	0.033	16:4	1.72	10.22	0.38	0.76
M-5	0.60	0.40	2.960	0.421	0.033	16:4	2.51	9.00	0.30	0.67
M-6	0.50	0.50	2.467	0.527	0.033	16:4	3.49	8.81	0.26	0.59
M-7	0.40	0.60	1.974	0.632	0.033	16:4	4.55	9.83	0.26	0.51
M-8	0.30	0.70	1.480	0.737	0.033	16:4	5.66	9.52	0.21	0.44
M-9	0.20	0.80	0.987	0.842	0.033	16:4	9.23	9.02	0.17	0.29
M-10	0.10	0.90	0.493	0.948	0.033	16:4	16.12	9.14	0.13	0.12
M-11	–	1.00	–	2.000	0.033	16:4	–	92.00	1.84	–

Reaction conditions: Solvent:1,4-dioxane:DMSO (8:2 ratio); Conversion < 10% (less than 25 min.); Temperature: 70 ± °C.
[a]Obtained from elementel analysis.
[b]Obtained gravimetrically

Fig. 8. The GPC curve of poly(4-CNMA-co-AN) [0.83:0.17].

Fig. 10. Copolymer composition diagram for poly(4-CNMA-co-AN) system. (M_1: Feed composition in mole fraction for 4-CNMA; m_1: Copolymer composition in mole fraction for 4-CNMA).
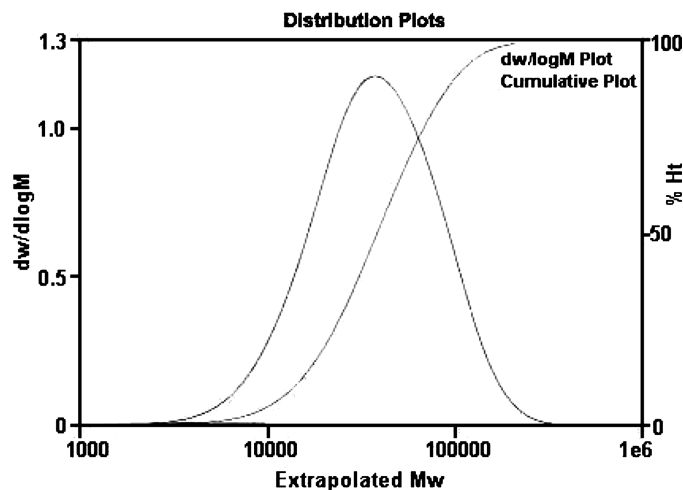
Consequently it gives erroneous results. In order to overcome this drawback, the following linear equation was proposed by Kelen-Tüdös:

$$G/(\alpha + H) = (r_1 + r_2/\alpha)\ (F/(\alpha + F) - r_2/\alpha \quad (3)$$

Where $\alpha = (F_{min}.F_{max})^{1/2}$ is obtained from the experimental data and:

$$G = F(f - 1)/f \quad and \quad H = F^2/f$$

By introducing $\eta = G/(\alpha + H)\ and\ \xi = H/(\alpha + H)$, the above equation changes to,

$$\eta = r_1\xi - r_2/\alpha(1 - \xi) \quad (4)$$

A plot of η vs ξ gives a straight line having the value of r_1 at the intercept when $\xi = 1$ and the value of $-r_2/\alpha$ as the intercept at $\xi = 0$.

We calculated the reactivity ratios using the extended Kelen-Tüdös (EKT) method when the effect of conversion is considered (20).
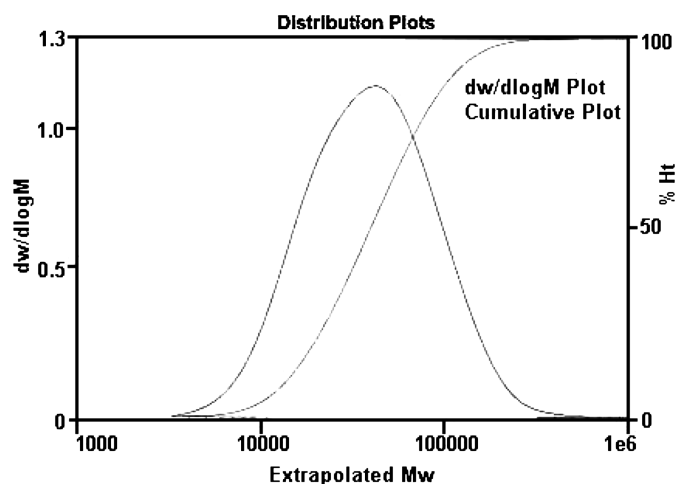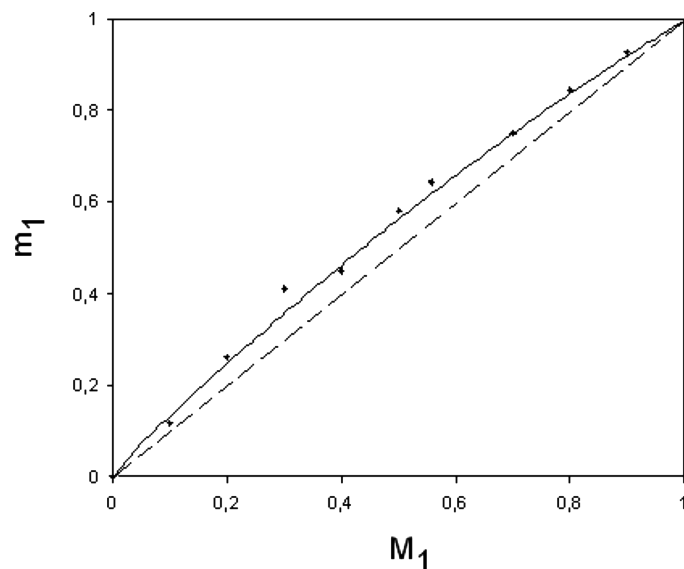

Fig. 9. The GPC curve of poly(4-CNMA-co-AN) [0.59:0.41].

In the extended Kelen-Tüdös method, instead of $F = M_1/M_2$, an average value of F is used. Walling and Briggs have used a constant z given by:

$$z = \log(1 - \zeta_1)/\log(1 - \zeta_2) \quad (5)$$

where ζ_1 and ζ_2 are partial molar conversion given by:

$$\zeta_2 = w(\mu + F)/(\mu + f)/100 \quad (6)$$

$$\zeta_1 = \zeta_2.f/F \quad (7)$$

where w is the weight conversion of polymerization, and $\mu = Mw_2/Mw_1$ of the monomers, respectively.

$$F = f/z \quad (8)$$

But, $H = F^2/f$ and $G = F(f - 1)/f$; by substituting z for F, we get,

$$H = f/z^2 \quad and \quad G = (f - 1)/z \quad (9)$$

The rest of the calculation is similar to Kelen-Tüdös method, i.e.,

$$\eta = G/(\alpha + H) \quad and \quad \xi = H/(\alpha + H) \quad (10)$$

where $\alpha = (H_{min}.H_{max})^{1/2}$

The graphical plots concerning the methods previously reported are given in Figures 11, 12, and 13.

In all cases, and for all graphical methods, the plots were linear indicating that these copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit. The monomer reactivity ratios determined by conventional linear methods are only approximate and are usually employed as good starting values for non-linear parameter estimation schemes. Linearization of
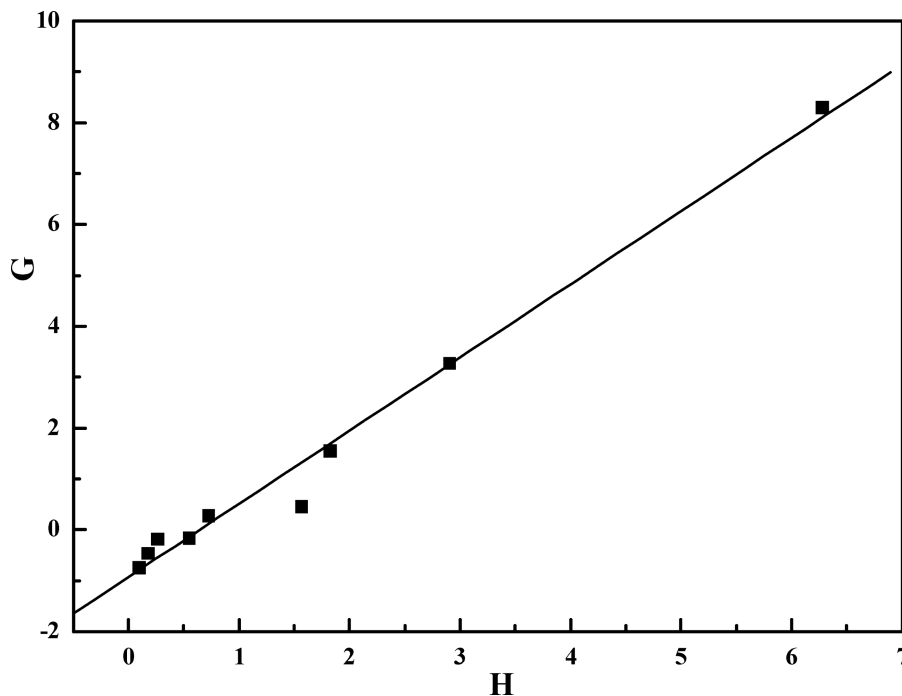
Fig. 11. Finemann-Ross (F-R) plot for poly(4-CNMA-co-AN) system.

the copolymer composition equation will distort the error distributions associated with the data. However, these approaches, aside from requiring that the instantaneous copolymer composition equation be valid, are statistically unsound, because the "independent variables" contain errors and the "dependent variable" does not have constant variance. Both of the latter assumptions are necessary for linear least squares to be a statistically valid estimation method. It has been found that they often lead to very poor estimates with misleading confidence intervals. On
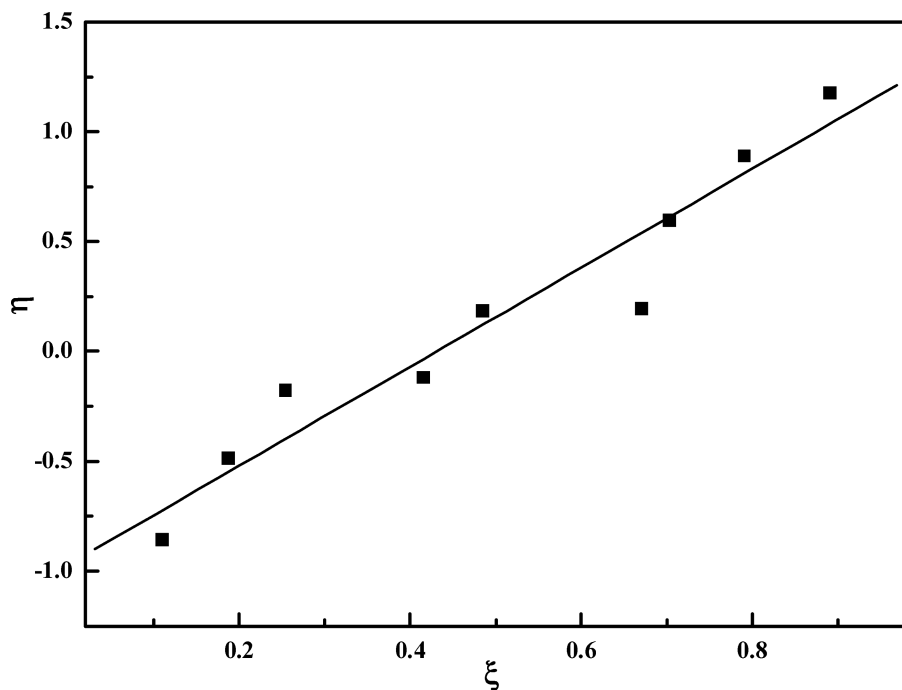
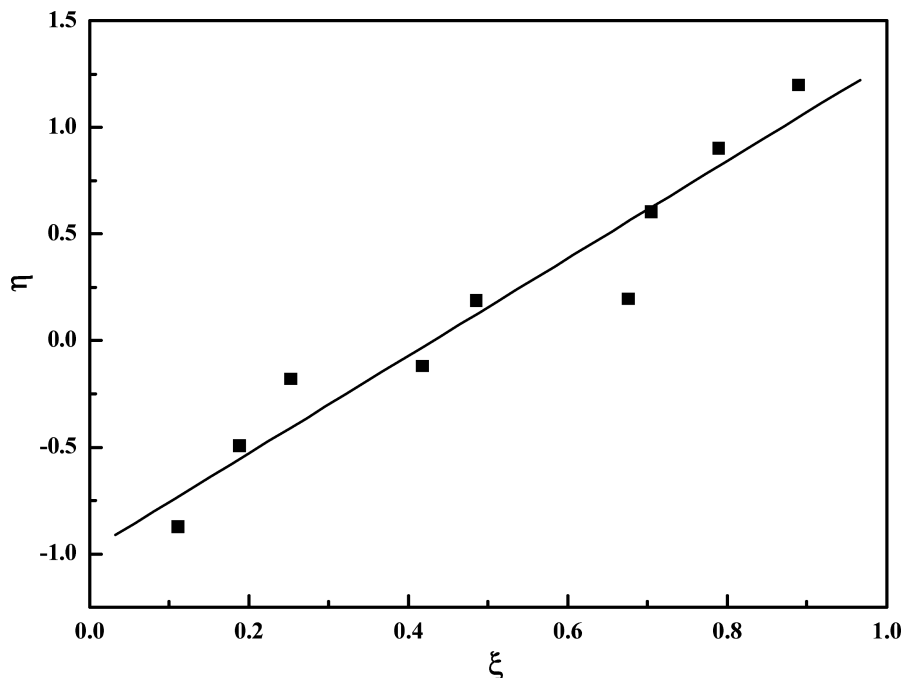**Fig. 12.** Kelen-Tüdos (K-T) plot for poly(4-CNMA-co-AN) system.

Fig. 13. Extended Kelen-Tüdös (EKT) plot for poly(4-CNMA-co-AN) system.

the other hand, non-linear least-squares (NLLS) data analysis is a valid statistical evaluation method for the determination of monomer reactivity ratios, but these methods are iterative, time-consuming, need a suitable initial guess of the parameters under estimation and offer convergence to a local solution which may have multiple minima. The approach which is taken here to find more reliable and statistically sound monomer reactivity ratios is different.

To determine more reliable values of monomer reactivity ratios, a non-linear error-in-variables model (EVM) method is used utilizing the computer program, RREVM (25). Various statistical treatments of the feed and copolymer compositions can be used to determine monomer reactivity ratios. The nonlinear methodology used selected values of r_1 and r_2, where the sum of the squares of the differences between the observed and the computed polymer compositions was minimized. With this criterion for the nonlinear least-squares method of analysis, the values for the monomer reactivity ratios were unique for a given set of data. The program produces monomer reactivity ratios for the monomers in the system with a 95% joint confidence limit determination. The joint confidence limit is a quantitative estimation of the validity of the results of the experiments and the calculations performed. This method of data analysis consists of obtaining initial estimates of the monomer reactivity ratios for the system and experimental data of comonomer charge amounts and comonomer amounts that have been incorporated into the copolymer, both in molar fractions. Tidwell and Mortimer (26) pro-

duced a nonlinear least-squares method that allowed rigorous applications of statistical analysis for reactivity ratios r_1 and r_2. This method is a modification or extension of the curve-fitting model and allows the calculations to be quantitatively analyzed. Extensive calculations are needed, but a computer program by A. Penlidis (25) permits rapid data analysis of the nonlinear calculations. The 95% joint confidence region for the determined r_1 and r_2 values using RREVM is shown in Figure 14. The r_1 and r_2 values from methods such as F-R, K-T, EKT and RREVM are presented in Table 2.

The higher r_1 value of 4-CNMA confirms the higher reactivity of 4-CNMA than of AN. The copolymer sequence will be of a random nature with more 4-CNMA units. Depending on the composition of the copolymer, some tendency to give small blocks is observed. In fact, based on the higher feed composition of 4-CNMA in the copolymer, with the help of reactivity ratios, small block formation

Table 2. Copolymerization parameters for the free radical copolymerization of 4-CNMA with AN.

Method	r_1^a	r_2^a	$r_1 r_2$	$1/r_1$	$1/r_2$
Fineman-Ross	1.32	0.83	1.09	0.76	1.20
Kelen-Tüdös	1.28	0.75	0.96	0.78	1.33
Ext.Kelen-Tüdös	1.30	0.74	0.96	0.77	1.35
RREVM	1.27	0.76	0.97	0.79	1.32

[a] r_1 and
[a] r_2 are the monomer reactivity ratios of 4-CNMA and AN, respectively.
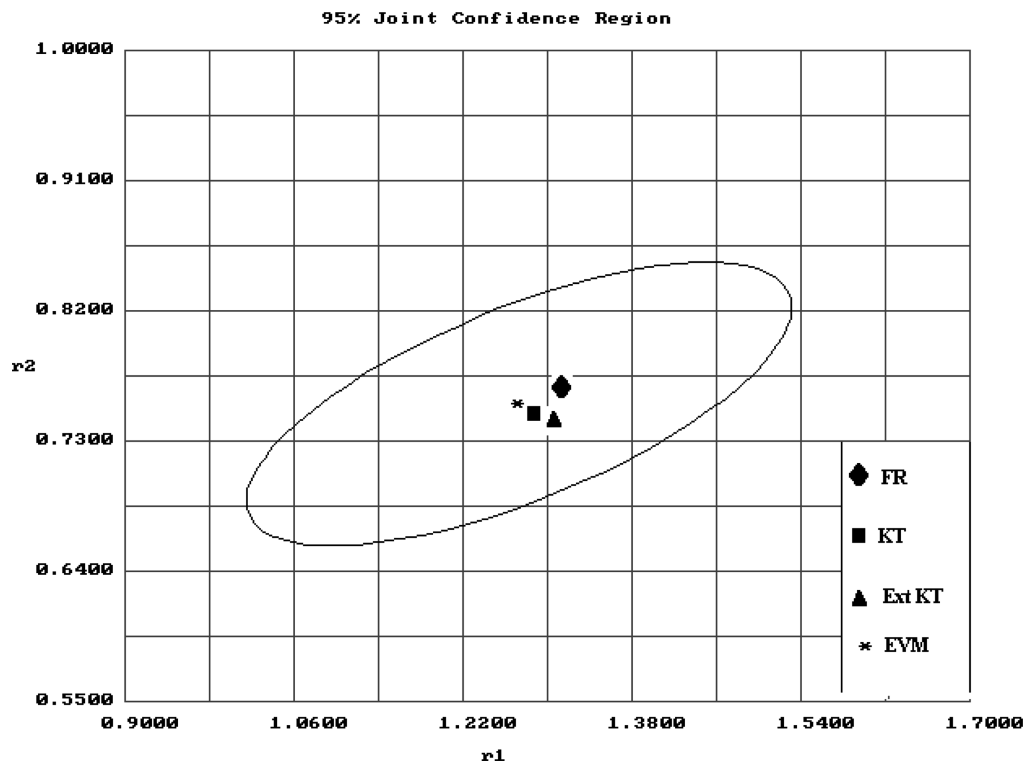
Fig. 14. 95% joint confidence region of r_1 and r_2 values by RREVM for 4-CNMA-AN copolymer system.

tendency is observed. This may be because the 4-CNMA monomer is more reactive towards the growing chain regardless of whether the radical was derived from 4-CNMA or AN.

The microstructure of a polymeric material plays an important role in the behavior of the material toward a variety of biological systems and can be especially important in copolymerizations with monomers of different reactivities (27). This implies that the type of copolymer prepared (i.e., random, alternating, or block) may affect the response elicited by the material in a biological environment. Monomer reactivity ratios provide a tool for estimating the average compositions of copolymers and the relative placement of reactive or functional monomers along the polymer chain (27). The reactivity ratio values are also valuable because the final composition of a copolymer is not simply dependent on the amounts of the two monomers present; this is especially true for monomers displaying substantial differences in the copolymerization rates. The final composition of a copolymer also depends on the method of monomer introduction, that is, whether the monomers are added all at once or incrementally over the course of the copolymerization. Both the composition and placement of monomers are dependent on the relative reactivity of each monomer in the system toward the growing polymer radicals, and vice versa.

The reactivity ratios of vinylic monomer is affected by the distance of the substituent to the vinyl double bond,

the size of the substituent, and the number of unshared electron pairs in the substituent (28, 29). Though 4-CNMA has a large substituent, 4-CNMA is more reactive than AN. It is likely that the presence of the electron-with-drawing effect of ester groups and conjugate effect (29, 30) contribute to the high reactivity of 4-CNMA. From Table 2, the r_1r_2 products for our systems are greater than unity. It is generally believed that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. The value of $r_1r_2 \geq 1$ may be plausible for polarity and bulky groups of 4-CNMA. In the literature, including free radical copolymerizations, that contradict the belief that $r_1r_2 = 1$ represents the upper limit for proper copolymerization (31, 32). Therefore, the copolymer chain contains a greater number of 4-CNMA units than in the feeds and probably has some 4-CNMA blocks along the copolymer chain.

3.9 Glass Transition Temperature

From DSC measurements T_g was taken as the midpoint of the transition region. For comparison, homopolymers of 4-CNMA and AN were also synthesized under the same conditions. The T_g of poly (AN) is 104°C and that of poly(4-CNMA) is at 144°C. Polymer glass transition temperature, which represents the molecular mobility of polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer (33). The gradual increase in the T_g of the copolymer was
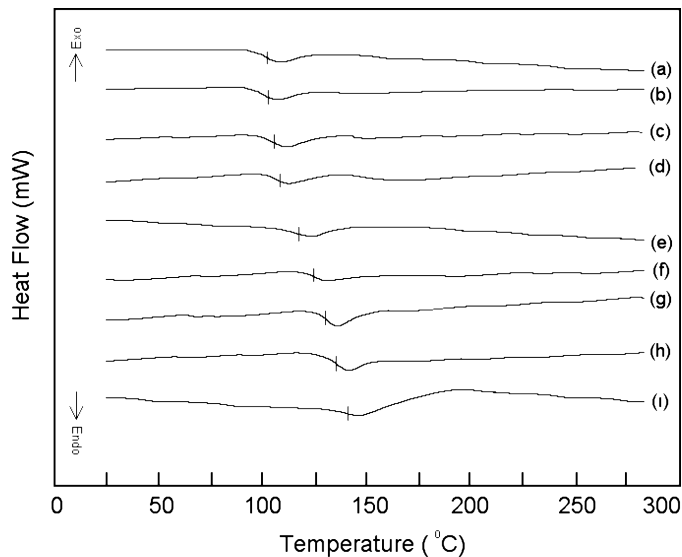
Fig. 15. DSC thermograms of investigated copolymers; (a) poly(AN), (b-h) poly(4-CNMA-co-AN):[0.83:0.17],[0.76:0.24], [0.67:0.33], [0.59:0.41],[0.51:0.49],[0.44:0.56],[0.29:0.71], (i) poly(4-CNMA).

observed with an increase in the mol percent of 4-CNMA in the copolymer (Figure 15) indicating that the presence of sterically bulky 4-chloronaphthyl group in the copolymer increases the T_g of the copolymer. High T_g of the copolymers in comparison with that of polystyrene (T_g =95 °C) indicates substantial decrease of chain mobility of the

copolymer due to high dipolar character of the structural unit.

3.10 Decomposition Kinetics

In Figure 16, the TGA thermograms of copolymer, poly(4-CNMA-co-AN) (0.59:0.41) are shown. It is clear that three degradation stages for poly(4-CNMA-co-AN) (0.59:0.41) are observed. The thermal degradation of poly-n-alkyl methacrylates typically produces the monomer as a result of depolymerization (34,35). The thermal behavior of any polymer should be affected appreciably by the introduction of a comonomer in the polymer chain. It was thus important to investigate the thermal behavior of the prepared copolymers. The TGA curves of 4-CNMA-AN copolymers in N_2 atmosphere (Figure 16) shows the existence of three transitions, probably reflecting more than one process during the thermal degradation reaction. Also, the TG curves show many processes probably including scission, cyclization, crosslinking, and decomposition at the higher-temperature exotherm. The first stage of decomposition could be attributed to scission of the C-N bond in a manner similar to that occurring in the suggested degradation of homopolymers, followed by cyclization and crosslinking. The TGA peaks of the copolymers were shifted to lower temperatures relative to that of polyacrylonitrile (PAN), indicating an initiating effect of the 4-CNMA comonomers by a cyclization process. The thermal characteristic of PAN were previously studied in detail by Grassie and Azab (36,37). In the present investigation, the thermal analysis of PAN
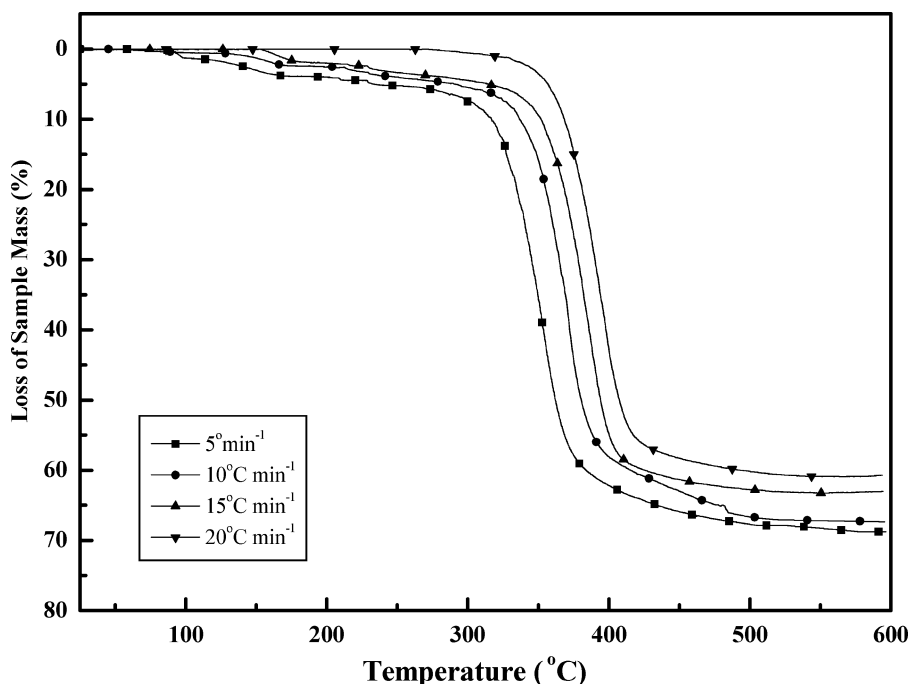
Fig. 16. The thermal degradation curves of poly(4-CNMA-co-AN) (0.59:0.41) at different heating rates
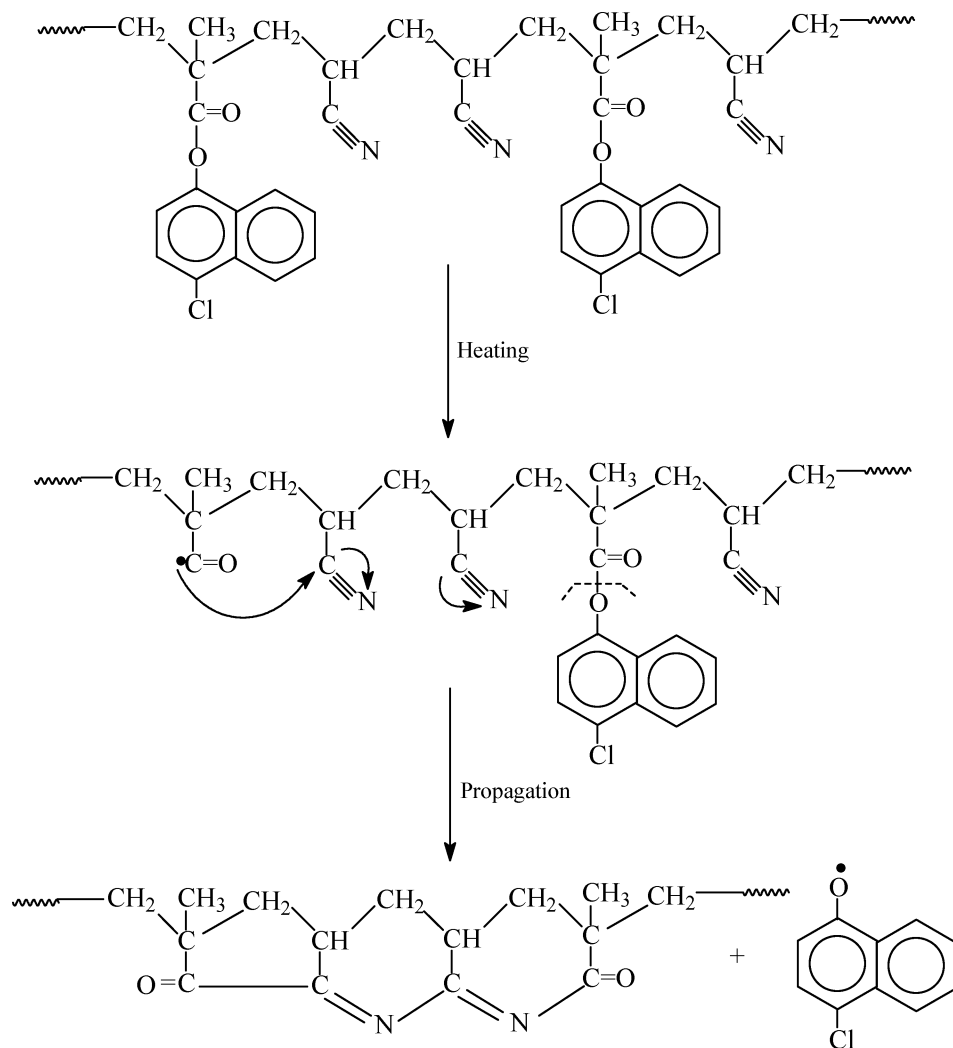
Fig. 17. Thermal degradation scheme of 4-CNMA-AN copolymer

is given as a reference; that is, the 4-CNMA-AN copolymers will illustrate the effect of these comonomers on the thermal behavior of the products. The formation of cyclic anhydride type structures by intramolecular cyclisation is another main process in degradation of these polymers. The latter produces some low molecular weight products, depending on the chemical structures of the side chain of poly-methacrylic esters. The increasing thermal stability at higher temperatures may probably be because of the presence of 4-chloronaphthyl group in the side chain, which form cross-links. Based on the above-mentioned thermal data, the mechanisms in Figure 17 are suggested for the thermal degradation of copolymers. Although the AN content of the copolymers appears to be most important to impart thermal properties, it is possible that the conformation of the copolymers acquired under experimental conditions may also be a factor for their thermal properties. This study however is beyond the scope of the present investigation.

For the study on the kinetics of thermal degradation of polymers, we can select the isothermal thermogravimetry (ITG) or the thermogravimetry (TG) at various heating rates (38). ITG is superior to obtain accurate activation energy for thermal degradation, although it is time-consuming. In the case of thermal degradation of polymers, in which depolymerization is competing with cyclization or crosslinking due to the side groups, the TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in the present work, TG curves at various heating rates were obtained and the activation energies (ΔE_d) for thermal degradation of polymers were calculated by Ozawa's plot, which is a widely used method. Degradations were performed in the scanning mode, from 35 up to 500°C, under nitrogen flow (20 ml.min^{-1}), at various heating rates (β: 5.0, 10.0, 15.0, and 20.0°C.min^{-1}). In Figure 16, the TGA thermograms of poly(4-CNMA-co-AN) [0.59:0.41]
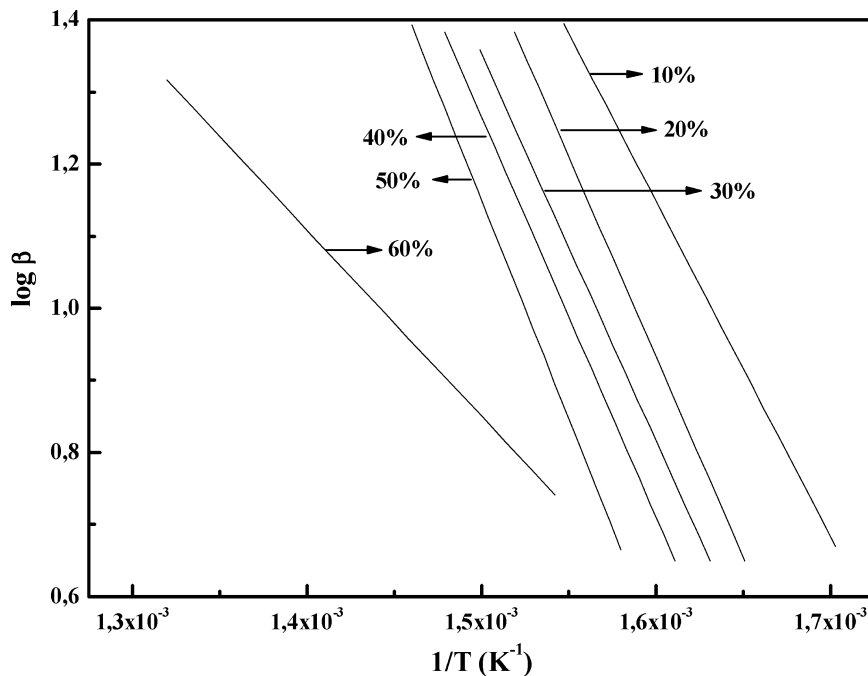
Fig. 18. Ozawa's plots of logarithm of heating rate (β) versus reciprocal temperature (1/T) at different conversions for poly(4-CNMA-co-AN) (0.59:0.41)

are shown. Samples of 5–8 mg held in alumina open crucibles, were used and their weights were measured as a function of temperature and stored in the list of data of the appropriate built-in program of the processor. The TGA curves were printed at the end of each experiment and the

weights of the sample were then transferred to a PC at various temperatures.

According to the method of Ozawa (39), the apparent thermal decomposition activation energy, E_d, can be determined from the TGA thermograms under various heating
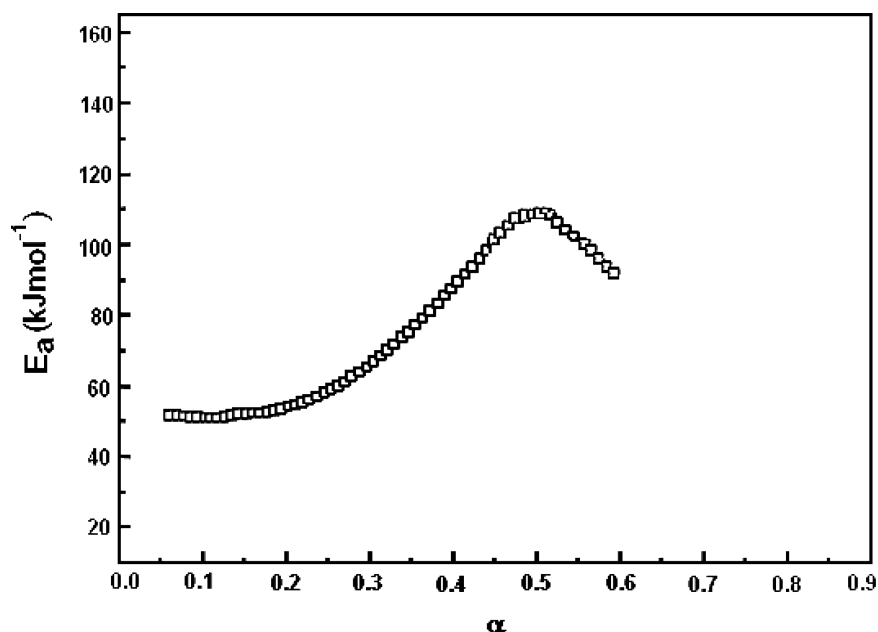
Fig. 19. The E_a dependencies obtained for the thermal degradation of poly(4-CNMA-co-AN)s studied in TGA experiments under nitrogen.
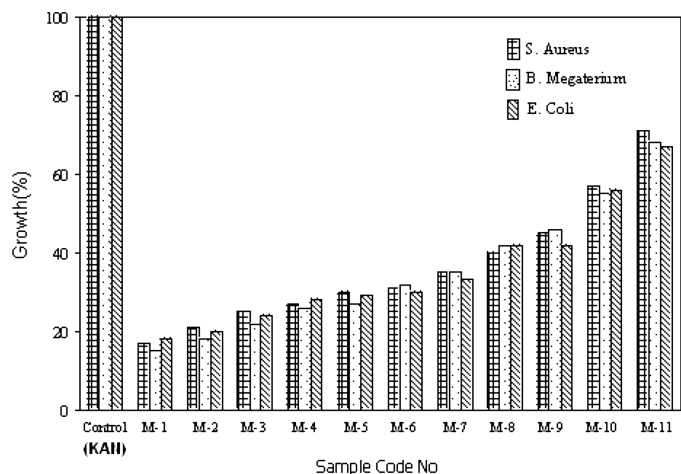
Fig. 20. Effect of homo- and copolymers on percentage growth of bacteria.
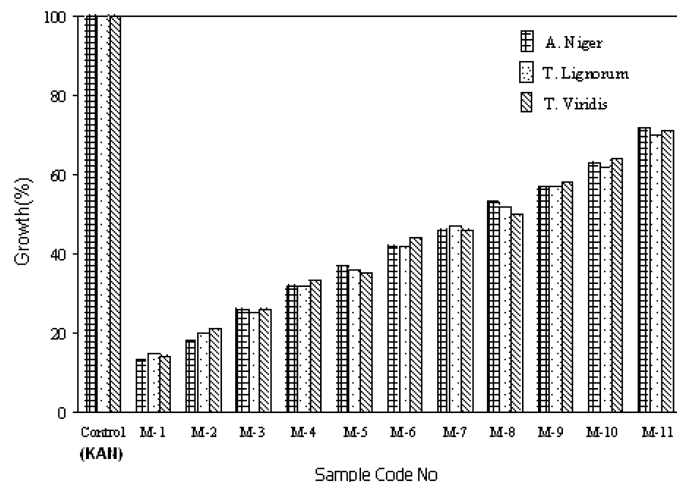
Fig. 21. Effect of homo- and copolymers on percentage growth of fungi.

rates, such as in Figure 16, and the following equation:

$$Ed = -\frac{R}{b}\left[\frac{d\log\beta}{d\,(1/T))}\right] \qquad (11)$$

Where R is the gas constant; b, a constant(0.4567); and β, the heating rate (°C/min). According to Equation 11, the activation energy of degradation can be determined from the slope of the linear relationship between log β and 1/T, as shown in Figure 18. The E_a dependencies extent of conversion (α) are shown in Figure 19. Analysis of the E_a-dependences proves generally to be very helpful in exploring an effect of the structure or a composition of a polymer material on its degradation kinetics. The E_a-dependencies obtained for the thermal degradation of these samples exhibit significant difference for the early degradation stages associated with initiation, whereas the later stages ($\alpha >$ 0.3) demonstrate almost identical E_a values of around 60 kJ.mol^{-1}.Comparison of the E_a -dependencies related to individual degradation products with the E_a -dependence derived from the mass loss data allowed for mechanistic insights into the origin of the latter dependence. E_a calculated from the Ozawa method is superior to other methods for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy (40).Therefore, E_a calculated from the Ozawa method was superior to the former methods for complex degradation.

3.11 Antimicrobial Screening

The microbial screening on the homo and copolymer of 4-CNMA and AN was carried out.

The antibiotic sensitivity of the polymers was tested by using the antibiotic disk assay as described (23). Muller-Hinton Agar 1.0% (w/v) beef extract, 2.0% (w/v) bactopeptone, 1.0% (w/v) glucose, 2.0% (w/v) agar was purchased from Difco. 1.5 ml of each prepared different cell

culture was transferred into 20 ml of Muller-Hinton Agar (MHA) and mixed gently. The mixture was inoculated into the plate. The plates were rotated firmly and allowed to dry at room temperature for 10 min. Prepared antibiotic disks (100 μg) were placed on the surface of the agar medium. The plates were kept at 5°C for 30 min then incubated at 35°C for 2 days. If a toxic compound leached out from the disc the microbial growth was inhibited around the sample. The width of this area expressed the antibacterial or antifungal activities by diffusion. The zones of inhibition of the microorganisms growth of the standard samples, investigated polymers were measured with a millimeter ruler at the end of incubation period. Figures 20, 21, and 22 are the average data of three experiments. The results show that the investigated polymers have moderate biological activity comparable with control drug such as Kanamycin (KAN). Poly(4-CNMA) allows 18% growth for
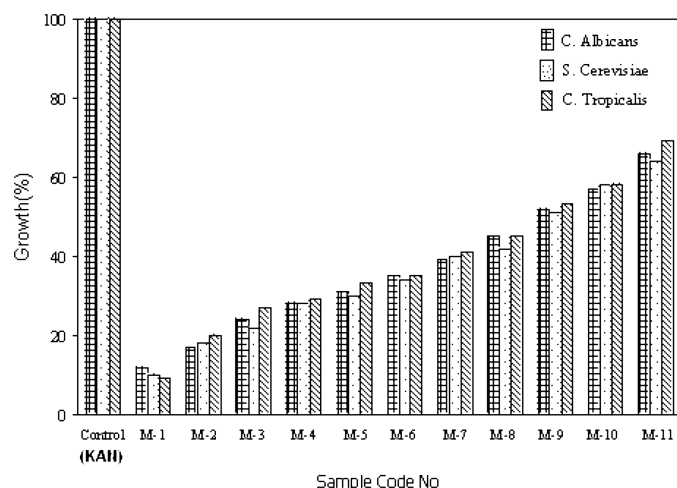
Fig. 22. Effect of homo- and copolymers on percentage growth of yeast.

bacteria, where as its copolymers favour 22–60% growth. Fungi in the presence of poly(4-CNMA) register around 17% growth, while 22–58% growth for fungi is observed in the copolymers. Yeast shows almost the same results as fungi. The poly(4-CNMA) is found to be most effective in inhibiting the growth of microorganisms, these may be traced to high chlorine content of this homopolymer. As the percentage of AN in the copolymer increases the effectiveness of the copolymers to inhibit the growth of microorganisms decreases. As expected, compared to poly(4-CNMA), poly(AN) is less effective to inhibit the growth of microorganisms. Although the chlorine content of the polymers appears to be most important to impart antimicrobial properties.

4 Conclusions

The structure of the 4-CNMA and its copolymer with AN was confirmed by FTIR and ^{1}H-and ^{13}C-NMR spectroscopic techniques. The copolymer compositions were obtained by elementel analysis technique. The reactivity ratio of 4-CNMA (r_1) is bigger than that of AN (r_2) and the product of reactivity ratios was less than one. This shows that the monomers were distributed in a random fashion in the copolymer chain. The DSC analysis indicated that the Tg of the copolymers increases with increase in 4-CNMA content. Chlorine content is important to impart antimicrobial property in the polymers. The fact that amongst the polymers investigated., the homopolymers of 4-CNMA is most effective antimicrobial agent lends support to this view.

Acknowledgements

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