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Copolymers of 2-[(5-Methylisoxazol-3-yl)amino]-2-oxo-ethyl Methacrylate with Ethyl Methacrylate: Monomer Reactivity Ratios, Thermal Properties and Antimicrobial Activity

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We report the monomer reactivity ratios for copolymers of ethyl methacrylate (EMA) and a reactive monomer, 2-[(5-methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate (IAOEMA), using the Fineman-Ross, Kelen-Tüdös, and a nonlinear error invariable model method using a computer program RREVM. Copolymers were obtained by radical polymerization initiated by α,α'-azobisisobutyronitrile in 1,4-dioxane solution and were analyzed by FTIR, ^{1}H-NMR, and gel permeation chromatography. Elemental analysis was used to determine the molar fractions of EMA and IAOEMA in the copolymers. The reactivity ratios indicated a tendency toward ideal copolymerization. The polydispersity indices of the polymers determined using gel permeation chromatography suggest a strong tendency for chain termination by disproportionation. Thermal behaviors of copolymers with various compositions were investigated by differential scanning calorimetry and thermogravimetric analysis. It was observed that glass transition temperature of copolymers increased with increasing of IAOEMA content in copolymers. Also, the apparent thermal decomposition activation energies (ΔE_d) were calculated by Ozawa method using the SETARAM Labsys TGA thermobalance. The homo- and copolymers were tested for their antimicrobial properties against selected microorganisms. All the products show moderate activity against different strains of bacteria, fungi and yeast.

Keywords 2-[(5-methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate, monomer reactivity ratios, gel permeation chromatography, activation energy, antimicrobial activity

Introduction

Contamination by microorganisms is of great concern in several areas, such as medical devices, healthcare products, water purification systems, hospital and dental office equipment, food packaging, food storage, etc. Consequently, biocidal polymers have received much attention in recent years (1). One possible way to avoid microbial contamination is to develop materials with antimicrobial activities (2). New materials prepared by

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copolymerization with reactive or functional monomers are of increasing interest. These materials are important because of the potentially wide range of applications for functionalized polymeric materials. A polymer with the desired pendant functional group can be synthesized in two ways: (1) by the incorporation of the functional group as a pendant unit of the monomer itself and polymerizing the same by any one of the chain-growth mechanisms; (2) by the chemical modification of the nonfunctionalized polymer (3). With respect to vinyl polymers, both routes are used on a regular basis. With polymeric resins, the issue of whether to modify a polymer chemically or to carry out a polymerization using an appropriately functionalized comonomer is usually settled by the relative difficulty of the two methods of synthesis. The synthesis and studies on acrylate polymers have attracted the attention of various groups in recent times (4). The extensive applications of both homo- and copolymers of this class of macromolecules have been reported (5). Acrylate homopolymers along with their copolymers are used in various fields such as thin films, fibers, filament coatings, lithography, lacquers, adhesives, printing inks, and binders (6). The activated acrylate polymers find applications in pharmacological drugs as polymer supports, which are easily degradable, and in the binding of drugs into existing natural and synthetic polymers (7). Various compounds starting from ısoxazole derivatives exhibit a wide range of biological activities (8). Isoxazolines can be effectively used as antibacterial (9), antitubercular, antiviral, antifungal, herbicidal and insecticidal agents (10). 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 required physical, chemical properties and in evaluating the specific end application of copolymers. The main aim in commercial copolymerization is to obtain a product having uniform composition. In the past few decades, ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of tacticity and sequence distribution, as well as for the estimation of copolymer composition because of its simplicity, rapidity and sensitivity (11). The monomer reactive ratios were determined by a number of linearization methods (12, 13). As the monomer reactive ratios determined by these methods are only approximate, a number of non-linear methods have been proposed to obtain correct values of monomer reactivity ratios (14–16). Notable among them is the non-linear-error-in-variables-model (EVM) method using a recent computer program, RREVM (16), which gives more reliable results.

Thermogravimetric analysis (TGA) has been widely used to investigate the decomposition characteristics of many materials. Some methods have already been established to evaluate the kinetic parameters from thermogravimetric data (17). In a previous study (18), we described the synthesis and characterization of 2-[(5-methylisoxazol-3-yl)amino]-2-oxo-ethyl methacrylate (IAOEMA) monomer and its homopolymer. In the present work, the results of radical copolymerization of IAOEMA with ethyl methacrylate (EMA), determination of monomer reactivity ratios and the effects of copolymer composition on thermal behavior relationships are presented and discussed. The average compositions of the copolymer samples were determined from the elementel analysis and ^{1}H-NMR method (for two polymers). Homo- and copolymers have been characterized in their antimicrobial activity against microorganism such as bacteria (*Stabhylococcus aureus, Bacillus subtilis, Escherichia coli*), fungi (*Aspergillus niger, Trichoderma lignorum, Trichoderma viridis*) and yeast (*Candiada albicans, Saccharomyces cerevisiae, Candiada utilis*).

Experimental

Materials

IAOEMA monomer was prepared as reported (18). Ethyl methacrylate (EMA) monomer (Aldrich) was freed from the inhibitor by washing with 5% NaOH solution followed by distillation under vacuum before use: b.p. 78°C/13 mmHg. 1,4-Dioxane, chloroform, methanol, and ethanol (Merck), anhydrous magnesium sulphate (Aldrich) were analytical grade commercial products and used as received. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform-methanol.

Characterization Techniques

Infra red spectra were obtained with a Jasco 460 Plus FTIR spectrometer using KBr pellets in 4000–400 cm^{-1} range, where 10 scans were taken at 4 cm^{-1} resolution. ^1H-NMR spectra in $CDCl_3$ solution were recorded on a Varian Gemini 200 MHz spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weight; ($\bar{M}_w$ and $\bar{M}_n$) of the polymer was determined using Waters 410 gel permeation chromatography equipped with a RI detector and calibrated with polystyrene standards. Thermal data were obtained by using a Setaram DSC-131 instrument at a heating rate of 20°C min^{-1} and Labsys TGA thermobalance at a heating rate of 10°C min^{-1} in N_2 atmosphere. Elemental analyses were carried out by a LECO-932 microanalyzer.

Copolymerization

Copolymerizations of IAOEMA with EMA, having six different feed compositions were carried out in 1,4-dioxane at 60 ± 0.1°C using AIBN (1%, based on the total weight of monomers) as an initiator. Appropriate amounts of IAOEMA with EMA, and 1,4-Dioxane was mixed in a polymerization tube, purged with N_2 for 20 min, and kept at 60 ± 0.1°C in a thermostat. The copolymerization reactions were carried out with different mole ratios of IAOEMA and EMA (0.00 : 1.00 through 1.00 : 0.00). The reaction time ($\approx$1 h), was selected to give conversions less than 10% to satisfy the differential copolymerization equation (19). After the desired time, the copolymers were separated by precipitation in ethanol and reprecipitated from CH_2Cl_2 solution.The polymers were finally dried under vacuum at 40°C to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis (N content for IAOEMA units) and peak integrations of ^1H-NMR signals were also used for some copolymer composition determination. The results are presented in Table 1. The data of elemental analyses reported in Table 1 are the average data of two experiments.

Results and Discussion

The constituent monomeric units of the copolymer are shown in Scheme 1.

Solubility

The solubility of the homopolymers and the copolymers was tested by mixing 20 mg of the polymer with 2 ml of various solvents in test tubes. After setting aside the closed tubes for one day, the solubility was recorded. The homo-and copolymers were soluble in water,

Table 1
Monomer compositions in feed and in copolymer

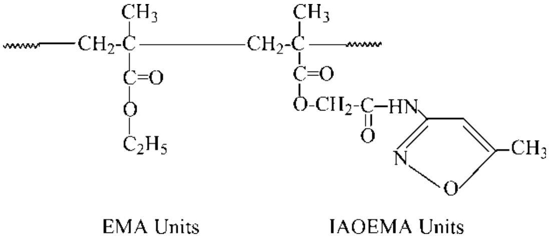
Sample code no	Feed composition in mole fraction		Conversion (%)	Elementel (%) N	Copolymer composition in mole fraction	
	IAOEMA(M_1)	EMA(M_2)			IAOEMA(m_1)	EMA(m_2)
M-1	—	1.00	—	—	—	1.00
M-2	0.10	0.90	9.0	1.76	0.08	0.92
M-3	0.20	0.80	8.4	3.48	0.16	0.84
M-4	0.35	0.65	7.9	4.86	0.25; 0.24[a]	0.75; 0.76[a]
M-5	0.50	0.50	8.8	6.82	0.38	0.62
M-6	0.60	0.40	10.2	7.90	0.47; 0.46[a]	0.53; 0.54[a]
M-7	0.80	0.20	8.5	9.84	0.65	0.35
M-8	1.00	—	—	—	1.00	—

[a] Determined by ^{1}H-NMR spectra.

dichloromethane, 1,4-dioxane, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, but insoluble in benzene, toluene, xylene n-hexane, n-heptane and hydroxy-group containing solvents such as methoxyethanol and ethanol.

Spectroscopic Characterization

The FTIR spectra of the polymers are shown in Figure 1. The FTIR spectra confirmed the structure of polymers in all aspects. In the FTIR spectra of (c) and (d) the band at 3230 cm^{-1} (–NH in the IAOEMA unit) is the most characteristic for the copolymer. 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 1985, 2940 and 2865 cm^{-1}. The peak at 1740 cm^{-1} are attributed to the ester carbonyl stretching of both IAOEMA and EMA units. The absorption at 1662 cm^{-1} could be assigned for a complex stretching vibrations of C=O and C–N, while the strong absorption at 1300 cm^{-1} could be attributed to predominantly C–O stretching. The broad band at 1440 cm^{-1} could be due to the C–N scissoring vibration of the –N–C=O group. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1505 and 1470 cm^{-1}. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1455 and 1380 cm^{-1}. The C–O stretching is



Scheme 1. The structure monomeric units of the copolymer.

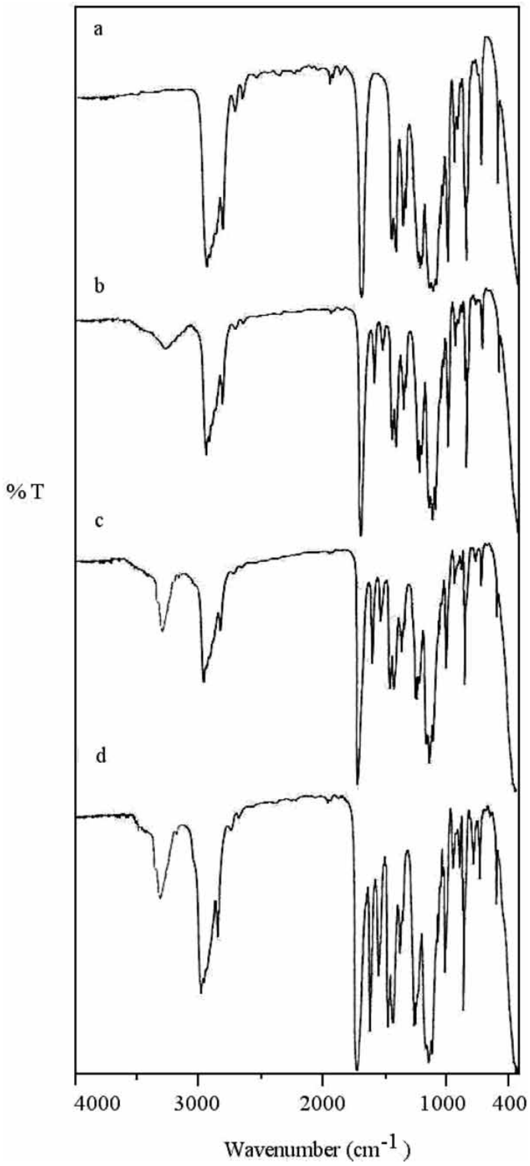


Figure 1. FTIR spectrum of (a) poly(EMA), (b) poly(IAOEMA-co-EMA) (0.16 : 0.84), (c) poly (IAOEMA-co-EMA) (0.47 : 0.53) and (d) poly(IAOEMA).

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.

The ^{1}H-NMR spectrum of poly(IAOEMA-co-EMA) [0.25 : 0.75 (a) and 0.47 : 053 (b)] (Figure 2) is consistent with its chemical structure. The resonance signals at 9.7 ppm correspond to the NH protons of the IAOEMA unit. The resonance absorptions at 6.6–6.9 ppm are due to the isoxazol ring protons of IAOEMA. The signals at 4.3 ppm is due to the –OCH$_2$ protons. The ethoxy proton resonance of the EMA unit appears at 3.8 ppm. The backbone methylene protons of the two comonomer units are observed between

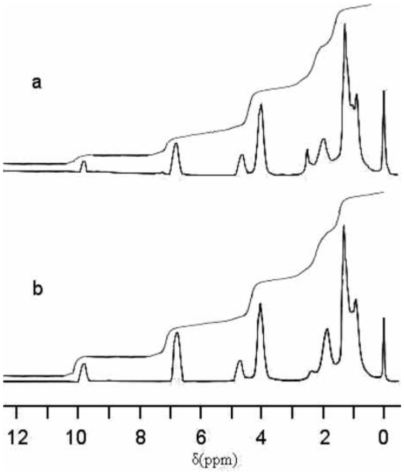


Figure 2. ^{1}H-NMR specrum of poly(IAOEMA-co-EMA) (a) (0.25 : 0.75), (b) (0.47 : 0.53).

1.4–2.4 ppm. The α-methyl protons of both types of monomer units are observed at 1.0–1.3 ppm. The methyl proton resonance of the isoxazol ring appears at 0.7–0.9 ppm.

Molecular Weights of the Polymers

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard and solvent, respectively. The weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights and the polydispersity indexes ($\bar{M}_w/\bar{M}_n$) of polymer samples are presented Table 2. The polydispersity index of the polymers ranges between 1.55 to 2.01. The theoretical values of $\bar{M}_w/\bar{M}_n$ for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (20).

Copolymer Composition and Monomer Reactivity Ratios

The monomer reactivity ratios for the copolymerization of IAOEMA with EMA were determined from the monomer feed ratios and the copolymer composition.

Table 2
Differantiel scanning calorimetry, molecular weight data of polymers

Sample	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Tg (°C)	ΔH_o^d (J/g)	ΔCp (J/g · K)
M-1	4.36	2.82	1.55	85	1.2420 (Endo)	−0.4120
M-2	3.96	2.28	1.74	87	1.1818 (Endo)	−0.3120
M-3	3.82	2.38	1.60	90	1.3140 (Endo)	−0.5510
M-4	2.39	1.18	2.01	95	1.6220 (Endo)	−0.6880
M-5	3.33	1.73	1.92	104	1.8080 (Endo)	−0.8100
M-6	4.40	2.72	1.62	114	2.3450 (Endo)	−0.1322
M-7	3.66	2.20	1.66	122	2.8095 (Endo)	−0.1790
M-8	4.60	2.80	1.64	128	2.8276 (Endo)	−0.1950

The classical approach for acquiring copolymer data was to isolate the copolymers from each of 6 feed compositions at early conversions and analyze the copolymer compositions by elemental analyses. The plot of the mole fraction of IAOEMA in the feed vs. that in the copolymer (Figure 3) 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 IAOEMA in the feed (M_1) vs. the mole fraction of IAOEMA in the copolymer (m_1) (Figure 3) does not intersect the ideal line. Figure 3 details the behavior of the system via a plot of the copolymer composition vs. feed composition. It is evident from the plot that the system shows azeotropic bahavior at low feed fractions of IAOEMA.

The Fineman-Ross (FR) (12), and Kelen-Tüdös (KT) (13) methods were used to determine the monomer reactivity ratios. According to the FR method the monomer reactivity ratios can be obtained by the equation:

$$G = Hr_1 - r_2 \tag{1}$$

Where the reactivity ratios, r_1 and r_2 correspond to the IAOEMA with EMA monomers respectively. The parameters G and H are defined as follows:

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

With

$$F = M_1/M_2 \text{ and } f = m_1/m_2 \tag{3}$$

M_1 and M_2 are the monomer molar compositions in feed and m_1 and m_2 the copolymer molar compositions.

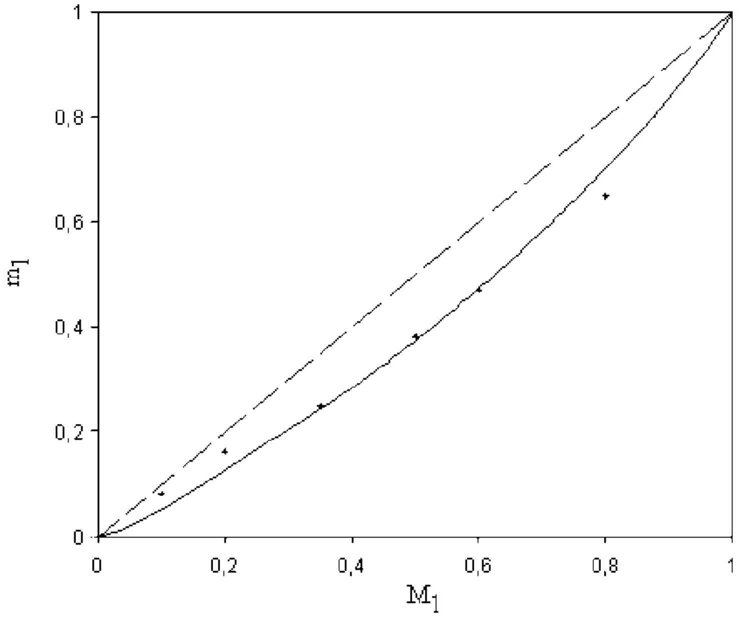


Figure 3. Copolymer composition diagram for poly(IAOEMA-co-EMA) system. (M_1: Feed composition in mole fraction for IAOEMA; m_1: Copolymer composition in mole fraction for IAOEMA).

Alternatively, the reactivity ratios can be obtained using the KT method which is based on the equation:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{4}$$

where η and ξ are functions of the parameters G and H:

$$\eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H) \tag{5}$$

and α a constant which is equal to $(H_{max}.H_{min})^{1/2}$, H_{max}, H_{min} being the maximum and the minimum H values, respectively from the series of measurements. From the linear plot of η as a function of ξ, the values of η for $\xi = 0$ and $\eta = 1$ is used to calculate the reactivity ratios according to the equations:

$$\xi = 0 => \eta = -r_2/\alpha \text{ and } \xi = 1 => \eta = r_1 \tag{6}$$

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.

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 (16). 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 (14) produced 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 (16) 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 4. The r_1 and r_2 values from methods such as F-R, K-T and RREVM are presented in Table 3.

The value of r_1 is <1 and that of r_2 is >1, which indicates the presence of a higher amount of EMA units in the copolymer than that in the feed. However, the value of the product $r_1 r_2 < 1$, which indicates that the system deviates from one of the ideal copolymerizations.

Differential Scanning Calorimetry Experiments

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 ($5\ l \cdot h^{-1}$) were used for the measurements. From DSC measurements, T_g was taken as the midpoint of the transition region. All the copolymers show

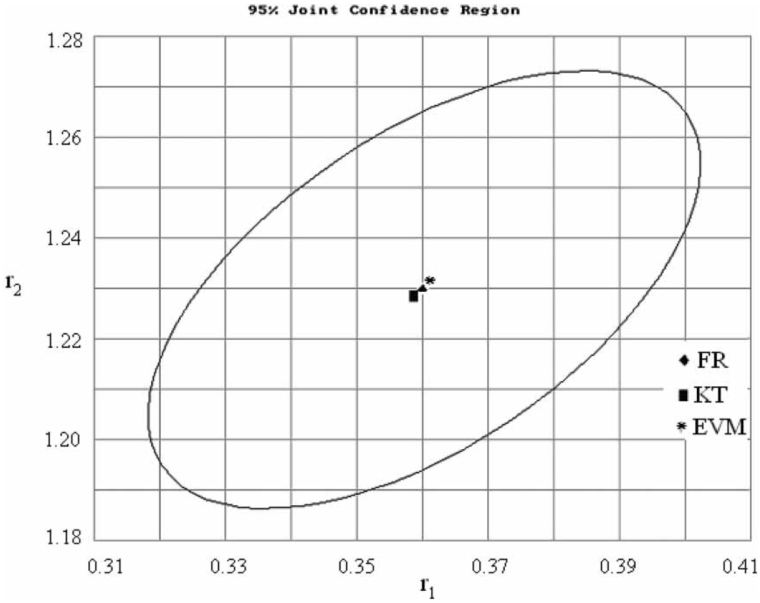


Figure 4. 95% joint confidence region of r_1 and r_2 values by RREVM for IAOEMA-EMA copolymer system.

a single T_g, showing the absence of a mixture of homopolymers or the formation of a block copolymer. The T_g of poly(IAOEMA) is 128°C and that of poly(EMA) is at 85°C. The gradual increase in the T_g of the copolymer was observed with an increase in the mol percent of IAOEMA in the copolymer (Table 2) indicating that the presence of sterically bulky isoxazol group in the copolymer increases the T_g of the copolymer.

Representative DSC thermograms of polymers are given in Figure 5. Data analysis was carried out with the Setaram software package. The enthalpy changes (ΔH_o^d) and heat capacity (ΔCp) during thermal degradation obtained from the DSC thermograms of polymers are given in Table 2. The gradual increase of (ΔH_o^d) and (ΔCp) of the polymers [except (M-2)] were observed with an increase in the mol percent of IAOEMA unit in the copolymer (Figure 7). (ΔH_o^d) and (ΔCp) were significantly increased with IAOEMA content depending on the endothermic peak area and mass of sample.

Table 3
Copolymerization parameters for the free radical copolymerization of IAOEMA with EMA

Method	r_1[a]	r_2[a]	r_1r_2
Fineman-Ross	0.3595	1.2275	0.4413
Kelen-Tüdös	0.3579	1.2279	0.4395
RREVM	0.3646	1.2357	0.4505

[a] r_1 and r_2 are the monomer reactivity ratios of IAOEMA and EMA, respectively.

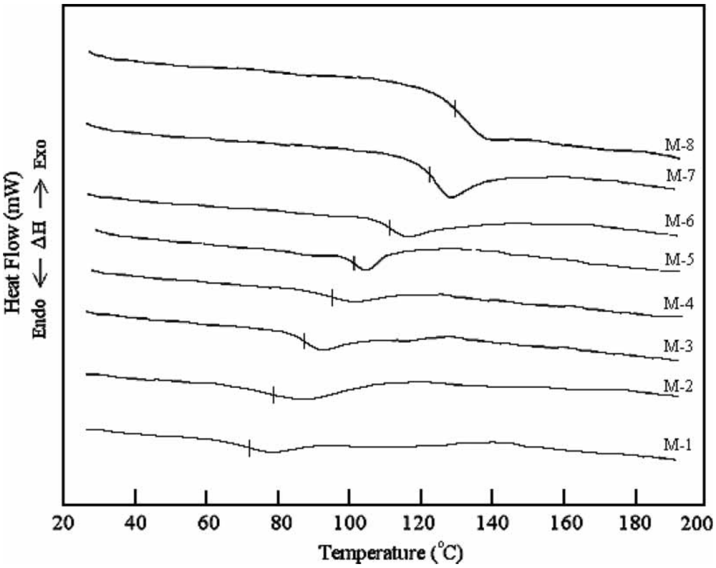


Figure 5. DSC thermograms of investigated homo-and copolymers.

Decomposition Kinetics

The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TGA) in a nitrogen stream at a heating rate of 10°C $\min^{-1}$. In Figure 6, the TGA thermograms of polymers are shown. It is clear that two degradation stages for poly(IAOEMA),

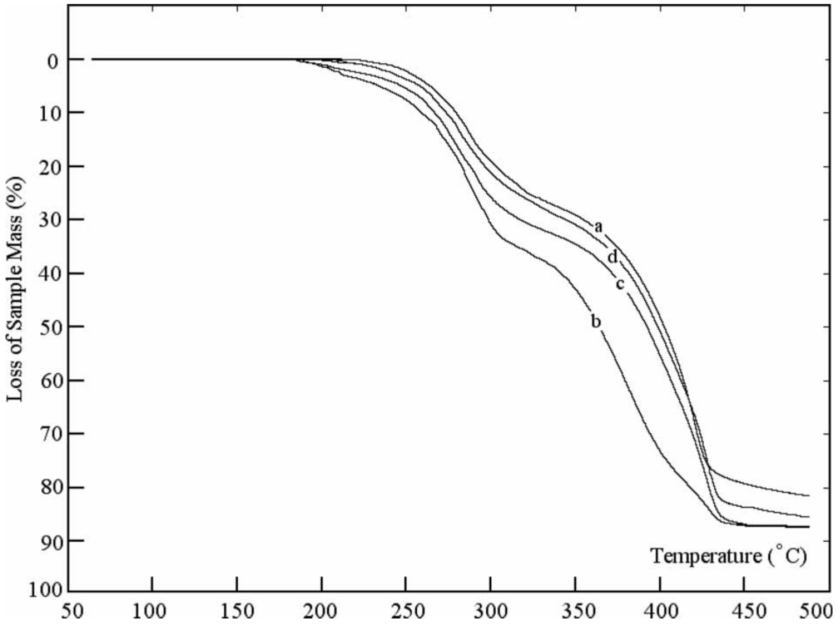


Figure 6. TGA curves of (a) poly(IAOEMA) (b) poly(EMA), (c) and (d) IAOEMA-EMA copolymers with different compositions (mol% of IAOEMA unit); (c) 0.25, and (d) 0.65.

poly(IAOEMA-co-EMA) and poly(EMA) are observed. The thermal degradation of poly-n-alkyl methacrylates typically produces the monomer as a result of depolymerization. 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.

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 (21). ITG is superior to obtain an 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 ($20\,\text{ml} \cdot \text{min}^{-1}$), at various heating rates (β: 7.0, 12.5, 15.0, and $20.0^{\circ}\text{C} \cdot \text{min}^{-1}$). 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 immediately 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 (17), the apparent thermal decomposition activation energy, E_d, can be determined from the TGA thermograms under various heating rates, and the following equation:

$$Ed = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right] \tag{7}$$

where R is the gas constant; b, a constant (0.4567); and β, the heating rate (°C/min). According to Equation (7), 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 7; the ΔE_d values for polymers are given in Table 4. As can be seen from Table 4, the

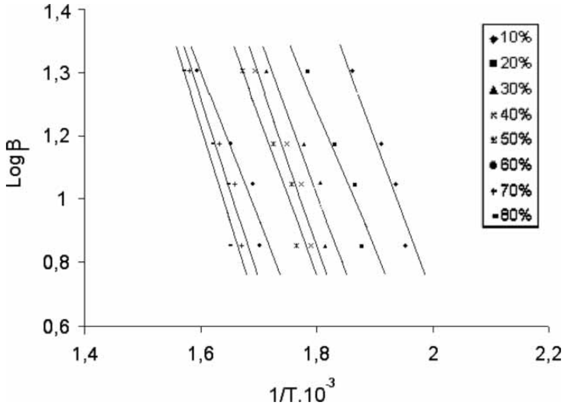


Figure 7. Ozawa's plots of logarithm of heating rate (β) versus reciprocal temperature (1/T) at different conversions for a poly(IAOEMA-co-EMA): (0.38 : 0.62).

Table 4

The apparent activation energies of investigated polymers under thermal degradation in N_2

	Activation energy ΔE_d (kJ/mol) Conversion (%)								
Sample	10	20	30	40	50	60	70	80	Average
M-1	92.4	90.6	88.0	86.4	90.2	95.4	101.1	94.0	92.3
M-2	96.2	94.0	90.6	94.3	92.8	96.1	97.0	101.1	95.3
M-3	98.0	95.6	100.6	98.8	94.0	95.2	104.4	103.0	98.7
M-4	102.2	114.0	110.8	107.4	108.0	112.4	116.2	110.2	110.2
M-5	110.6	112.2	110.3	115.0	116.2	120.6	120.2	118.4	115.4
M-6	116.4	119.2	108.3	118.2	116.0	121.2	120.4	122.8	117.8
M-7	114.2	120.0	118.0	130.0	128.2	134.4	122.1	124.8	124.0
M-8	116.4	122.1	115.2	138.0	139.3	144.4	130.1	134.2	130.0

data from the slowest heating rate appear to deviate from linearity in all the cases. ΔE_d was significantly changed with IAOEMA content depending on the heating rates and degradation stages.

ΔE_d 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 (22). Therefore, ΔE_d calculated from the Ozawa method was superior to the former methods for complex degradation.

Antimicrobial Screening

The biological activities of polymers were tested against different microorganisms using DMSO as the solvent (23, 24). The sample concentrations was 100 μg. In this study, *Stabhylococcus aureus, Bacillus subtilis, and Escherichia coli* have been used as bacteria, *Aspergillus nigar, Trichoderma lignorum, and Trichoderma viridis* as fungi, with *Candiada albicans, Saccharomyces cerevisiae, and candiada utilis* as yeast.

Figures 8, 9, and 10 are the average data of three experiments. The results show that the investigated polymers have good biological activity comparable with control drugs such as Kanamycin and Amphicillin. In the case of bacteria, poly(IAOEMA), has only about 50% efficiency in comparison with control drugs. It is said that poly(IAOEMA) allowed least growth (50%) and and that the copolymers exhibited 18–38% growth. Fungi and yeast in the presence of poly(IAOEMA) showed 50% growth, while 20–35% growth was observed with copolymers. However, inhibition zone was significantly increased with IAOEMA content.

Conclusions

Copolymers of IAOEMA with EMA have been prepared by free radical polymerization in 1,4-dioxane at 60°C. The reactivity ratios of the copolymers were estimated using linear

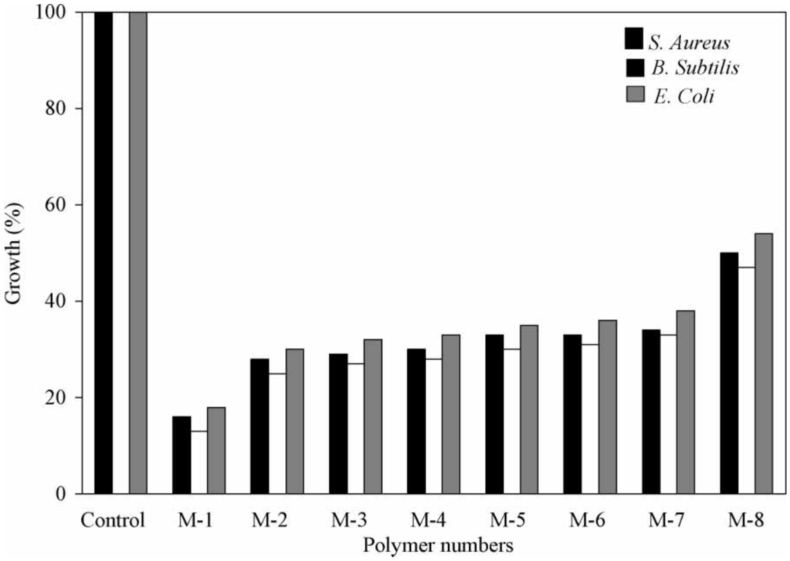


Figure 8. Effect of homo- and copolymers on percentage growth of bacteria.

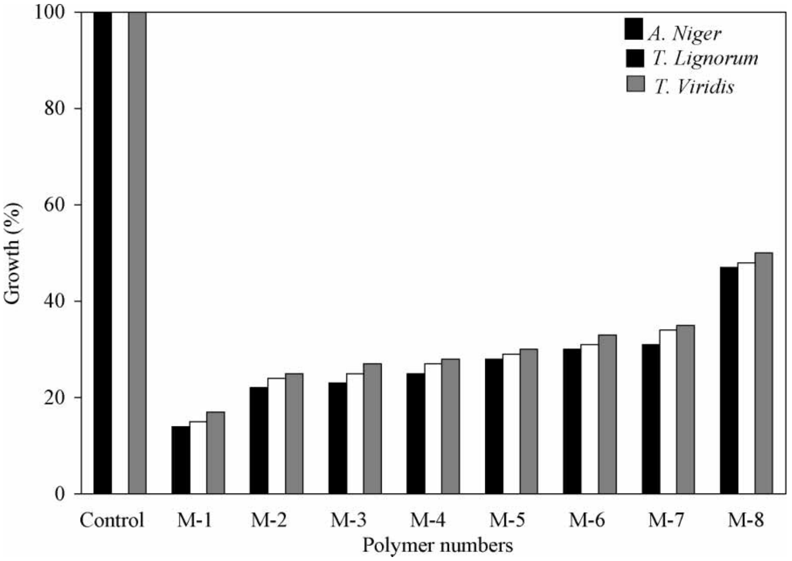


Figure 9. Effect of homo- and copolymers on percentage growth of fungi.

graphical and non-linear methods. The r_2 values were higher than the corresponding r_1 values in all cases, meaning that a kinetic preference exists for the incorporation of ethyl methacrylate in the copolymer structure. The values strongly suggest that the growing radicals of both monomeric ends preferentially add to the EMA monomer, thus leading to the formation of a copolymer with a higher amount of EMA. It was observed

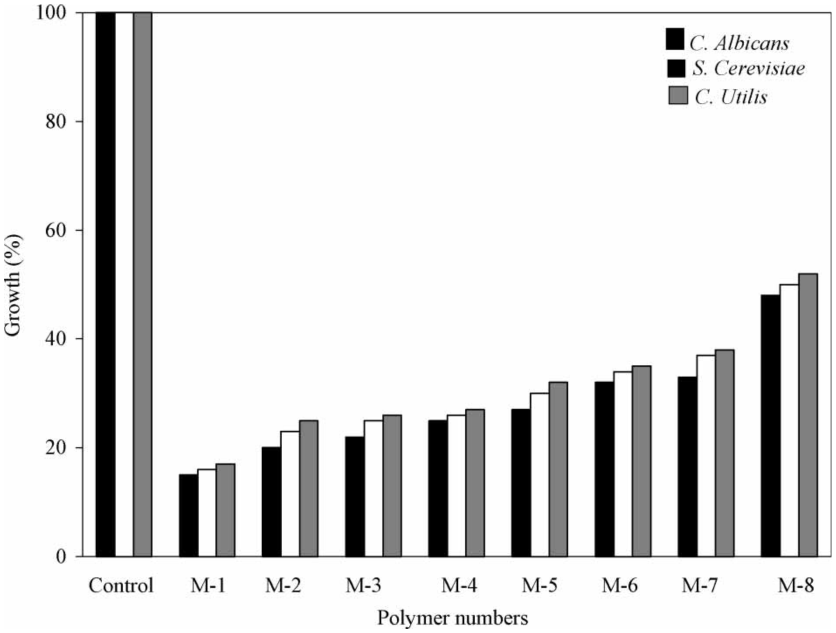


Figure 10. Effect of homo- and copolymers on percentage growth of yeast.

that glass transition temperature of copolymers increased with increasing of IAOEMA content in copolymers. The poly(IAOEMA) was found to be excellent in inhibiting the growth of microorganisms. This must be traced to the high isoxazol content of this homopolymer. As the percentage of IAOEMA in the copolymers increases, the effectiveness of the copolymers to inhibit the growth of the microorganisms increases.

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