Synthesis and Characterization of Novel Fluorine-Containing Methacrylate Copolymers: Reactivity Ratios, Thermal Properties, and Antimicrobial Activity

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ABSTRACT: The free-radical-initiated copolymerization of 2-(4-acetylphenoxy)-2-oxoethyl-2-methylacrylate (AOEMA) and 2-(4-benzoylphenoxy)-2-oxoethyl-2-methylacrylate (BOEMA) with 2-[(4-fluorophenyoxy]-2-oxoethyl-2-methylacrylate (FPEMA) were carried out in 1,4-dioxane solution at 65°C using 2,2′-azobisisobutyronitrile as an initiator with different monomer-to-monomer ratios in the feed. The monomers and copolymers were characterized by FTIR and ^{1}H- and ^{13}C-NMR spectral studies. ^{1}H-NMR analysis was used to determine the molar fractions of AOEMA, BOEMA, and FPEMA in the copolymers. The reactivity ratios of the monomers were determined by the application of Fineman-Ross and Kelen-Tudos methods. The analysis of reactivity ratios revealed that BOEMA and AOEMA are less reactive than FPEMA, and copolymers formed are statistically in nature. The molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and polydispersity index of the polymers were determined using gel permeation chromatography. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with an increase in the mole fraction of FPEMA in the copolymers. Glass transition temperatures of the copolymers were found to decrease with an increase in the mole fraction of FPEMA in the copolymers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3351–3359, 2009

Key words: fluorine; methacrylate; monomer reactivity ratios; thermal stability; biological activity

INTRODUCTION

It is well known that the fluorine-containing polymers are widely used in material science because of their extremely low surface energy. Fluorine-containing polymers are particularly attractive and useful compounds because of their unique properties including high thermal, chemical, aging, and weather resistance; low dielectric constants, refractive index, surface energy, and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalies, and moisture adsorption as well as interesting oil and water repellency due to the low polarizability and the strong electronegativity of the fluorine atom.[1–4] Up to now, the investigations on fluorine-containing polymers emulsion, especially on fluorine-containing methacrylate emulsion have attracted many researchers. There are various approaches for preparing fluorine-containing acrylate emulsion, such as producing block, graft or random fluorine-containing acrylate copolymers,[5–8] blending fluorine-containing acrylate polymers, and fluorine-free acrylate polymers[9–11] and synthesizing core–shell fluorine-containing polyacrylate emulsion with fluorine-free acrylate and fluorine-containing acrylate monomers.[12–14] Reactivity ratios are among the most important parameters for composition equation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimate the copolymer composition. Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and its distribution are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed, in which the monomer reactivity ratios are the parameters to be determined. The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures. Monomer reactivity ratios are generally determined at low conversion. In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only. Among several methods available to determine monomer reactivity ratio values, the Finemann-Ross and Kelen-Tudos methods are appropriate for the determination of

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monomer reactivity ratios at low conversions. 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.[15,16]

In this study, 2-(4-acetylphenoxy)-2-oxoethyl-2-methylacrylate (AOEMA), 2-(4-benzoylphenoxy)-2-oxoethyl-2-methylacrylate (BOEMA), and 2-[(4-fluorophenyoxy]-2-oxoethyl-2-methylacrylate (FPEMA) were synthesized. AOEMA and BOEMA are new methacrylate monomers having pendant ketone side chain. FPEMA is also a new methacrylate monomer having pendant ester and fluorine group. In previous studies, the synthesis, characterization, and copolymerization behavior of similar monomers and their polymers have been described.[17,18] This article investigates the synthesis, structural, and thermal characterization of copolymers of FPEMA with AOEMA and BOEMA as well as the determination of reactivity ratios in the copolymerization. The biological activities and activation energies of the copolymers were also obtained. For this purpose, reactivity ratios r_1 for the classical copolymerization model were determined using the linearization methods of Finemann-Ross (FR method) and Kelen-Tüdös (KT method).[19,20]

EXPERIMENTAL

Materials

Acetophenone, benzophenone, chloracetylchloride, and sodium hydroxide (Merck, Germany), and sodium methacrylate, 1,4-dioxane, potassium carbonate, acetonitrile, and anhydrous magnesium sulfate (Aldrich, Germany) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform–methanol. Bactopeptone and glucose were obtained from Difco. All other chemicals were of analytical grade and used without any further purification. AOEMA, BOEMA, and FPEMA were prepared according to the methods used in the preparation of similar monomers in the literature.[17,18]

Characterization techniques

FTIR spectra were measured on a Perkin-Elmer Spectrum BX FTIR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded in CDCl$_3$ with tetramethylsilane as the internal standard using Bruker GmbH DPX-400 400 MHz spectrometer. The glass transition (T_g) temperatures were determined by a Shimadzu DSC60H. Samples of about 4–7 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. From DSC measurements, T_g was taken as the midpoint of the transition region. The

thermal stabilities of the polymers were investigated by TGA in a nitrogen stream at a heating rate of 20°C min^{-1}. The thermal stability of the polymers was determined by Shimadzu TG60H. Molecular weight ($\overline{M}_w$ and $\overline{M}_n$) of the polymers were determined by e waters 410 gel permeation chromatography equipped with a differential refractive index detector and calibrated with polystyrene standards.

Copolymerization

Copolymerizations of FPEMA with BOEMA and AOEMA using different proportions of FPEMA were carried out in glass ampoules under N$_2$ atmosphere in 1,4-dioxane solution, with AIBN (1%, based on the total weight of monomers) as an initiator. The reacting components were degassed by threefold freeze–thawing cycle and then immersed in an oil bath at 65°C ± 0.1°C for a given reaction time. The reaction time was selected to give conversions less than 10% to satisfy the differential copolymerization equation. After the desired time, the copolymers were separated by precipitation in ethanol and reprecipitated from CH$_2$Cl$_2$ solution. The polymers, purified by reprecipitation, avoid the formation of homopolymers. The polymers were finally dried over vacuum at 45°C to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis. The results are presented in Table I.

Determination of the monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of AOEMA and BOEMA with FPEMA were determined from the monomer feed ratios and the copolymer composition. The Fineman-Ross (FR) and Kelen-Tüdös (KT) methods were used to determine the monomer reactivity ratios. The significance of parameters of FR and KT equations are presented in Table II.

According to the FR method, the monomer reactivity ratios can be obtained as follows:

$$G = Hr_1 - r_2 \qquad (1)$$

where r_1 and r_2 correspond to the AOEMA or BOEMA and FPEMA monomers, respectively. The parameters G and H are defined as follows:

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

With

$$F = M_1/M_2 \quad \text{and} \quad f = m_1/m_2, \qquad (3)$$

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

TABLE I
Copolymer Composition Data and Molecular Weight

System	M_2^a	C^b	m_2^c	$M_w \times 10^4$	$M_n \times 10^4$	M_w/M_n	T_g
Poly(AOEMA-co-FPEMA)	0.8	0.42	0.78	3.02	2.12	1.42	108
	0.7	0.53	0.74	3.45	2.19	1.57	106
	0.6	0.78	0.66	4.13	2.42	1.71	103
	0.5	0.95	0.61	5.39	2.88	1.87	99
	0.4	1.23	0.55	4.96	2.14	2.31	97
	0.3	2.21	0.40	5.75	2.45	2.34	95
	0.2	3.01	0.33	5.46	2.16	2.52	93
Poly(BOEMA-co-FPEMA)	0.8	2.45	0.82	6.33	2.35	2.69	
	0.7	2.65	0.74	3.91	2.45	1.60	108
	0.6	2.85	0.67	4.12	2.37	1.74	107
	0.5	3.01	0.60	5.82	2.78	2.09	105
	0.4	3.25	0.50	5.47	2.31	2.37	103
	0.3	3.52	0.39	5.88	2.26	2.60	101
	0.2	3.74	0.30	6.21	2.33	2.67	99
Poly(AOEMA)				5.53	3.08	1.73	92
Poly(BOEMA)				5.65	3.34	1.69	98
Poly(FPEMA)				6.62	2.71	2.44	109

Solvent: 1,4 dioxane; temperature: 65°C ± 1°C; initiator: AIBN (1 wt % of monomer); nonsolvent: ethanol.
[a] The mol fraction FPEMA in the feed.
[b] Determined by ^{1}H-NMR spectral data.
[c] The mol fraction of FPEMA in the copolymer.

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

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha, \qquad (4)$$

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

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

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

reactivity ratios according to the following equations:

$$\xi = 0 \rightarrow \eta = -r_2/\alpha \text{ and } \xi = 1 \rightarrow \eta = r_1 \qquad (6)$$

Copolymer compositions

The copolymerization of AOEMA with FPEMA in a 1,4-dioxane solution was studied for FPEMA molar fractions of approximately 0.80–0.20 in the feed. The copolymer compositions for this system were determined by ^{1}H-NMR spectroscopy analysis. Thus, the mole fraction of FPEMA in the copolymer was determined from the ratio of the integrated values of the

TABLE II
FR and KT Parameters for Poly(AOEMA-co-FPEMA) and Poly(BOEMA-co-FPEMA) System

System	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\mu = G/\alpha + H$	$\zeta = H/\alpha + H$
Poly(AOEMA-co-FPEMA)	0.250	0.282	−0.636	0.221	−0.412	0.143
	0.429	0.351	−0.791	0.521	−0.429	0.283
	0.667	0.515	−0.627	0.861	−0.287	0.394
	1.000	0.639	−0.564	1.564	−0.195	0.542
	1.500	0.818	−0.333	2.750	−0.081	0.675
	2.333	1.500	0.777	3.628	0.157	0.733
	4.000	2.030	2.029	7.881	0.220	0.856
Poly(BOEMA-co-FPEMA)	0.250	0.219	−0.891	0.285	−0.529	0.169
	0.429	0.351	−0.791	0.521	−0.412	0.271
	0.667	0.429	−0.687	0.901	−0.298	0.391
	1.000	0.666	−0.501	1.501	−0.172	0.517
	1.500	1.000	0.000	2.250	0.000	0.616
	2.333	1.564	0.841	3.480	0.172	0.713
	4.000	2.333	2.285	6.858	0.276	0.830

$\alpha = 1.319$ for the poly(AOEMA-co-FPEMA) system and $\alpha = 1.398$ for the poly(BOEMA-co-FPEMA) system.

intensities of the methyl protons on the acetophenone group of AOEMA (3.2 ppm) and the methylenoxy (4.9 ppm) of FPEMA units.

Let m_1 be the mole fraction of AOEMA and $m_1 = (1 - m_2)$ that of the FPEMA unit.

$$\frac{\text{Integrated intensities of methyl protons}}{\text{Integrated intensities of methylenoxy protons}}$$
$$= \frac{3m_1}{2m_2} = C. \quad (7)$$

On simplification,

$$m_1 = \frac{2C}{3 + 2C}, \quad (8)$$

where m_1 and m_2 are the copolymer molar compositions. With eq. (8), the molar fractions of AOEMA in the copolymers were determined by the measurement of the integrated peak heights of the methyl proton signals and the methylenoxy proton signals of FPEMA units. The results are presented in Table I.

The copolymer compositions for the poly-(BOEMA-co-FPEMA) system were determined by ^{1}H-NMR spectroscopy analysis. Thus, the mole fraction of FPEMA in the copolymer was determined from the ratio of the integrated values of the intensities of the aromatic protons of BOEMA and FPEMA units and the methylenoxy protons for both monomeric units.

Let m_1 be the mole fraction of BOEMA and $m_1 = (1 - m_2)$ that of the FPEMA unit.

$$\frac{\text{Integrated intensities of aromatic protons}}{\text{Integrated intensities of methylenoxy protons}}$$
$$= \frac{9m_1 + 4m_2}{2m_1 + 2m_2} = C. \quad (9)$$

On simplification,

$$m_1 = \frac{2C - 4}{5}, \quad (10)$$

where m_1 and m_2 are the copolymer molar compositions. With eq. (10), the molar fractions of BOEMA and FPEMA in the copolymers were determined by the measurement of the integrated peak heights of the aromatic proton signals and the methylenoxy proton signals. The results are presented in Table I.

Biological activity of the polymers

The biological activities of the homopolymers and copolymers were tested against different microorganisms with DMSO as the solvent. The sample concentrations were 50 and 100 μg. All microorganism strains were obtained from the Culture Collection of Microbiology Laboratory of Afyon Kocatepe Univer-
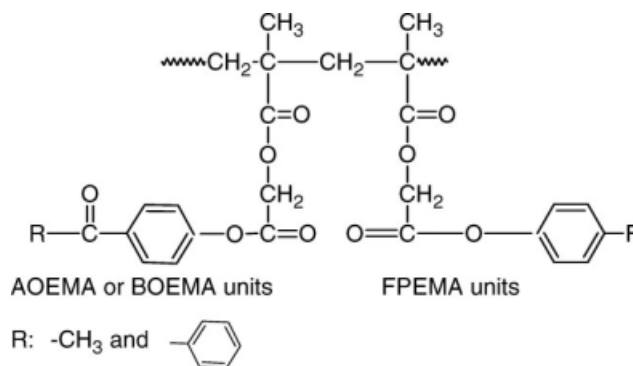
Scheme 1 The constitution of the copolymers.

sity (Afyon, Turkey). In this study, *Staphylococcus aureus* (ATCC 29213), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginasa* (ATCC 27853), *Proteus vulgaris*, *Salmonella enteridis*, and *Klebsiella pneumoniae* were used as bacteria. *Candida albicans* (CCM 31) was a fungus. YEPD medium cell culture was prepared as described by Connerton.[21] Ten milliliters of YEPD medium were inoculated with each cell from plate cultures. Yeast extract 1% (w/v), bactopeptone 2% (w/v), and glucose 2% (w/v) were obtained from Difco. Microorganisms were incubated at 35°C for 24 h. About 1.5 mL of these overnight stationary phase cultures were inoculated onto 250 mL of YEPD and incubated at 35°C until OD_{600} reached 0.5. The antibiotic sensitivity of the polymers was tested with the antibiotic disk assay as described.[22] Nutrient agar (NA) was purchased from Merck. About 1.5 mL of each prepared different cell culture were transferred into 20 mL of NA 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. The prepared antibiotic discs (100 μg) were placed on the surface of the agar medium.[23] The plates were kept at 5°C for 30 min and then incubated at 35°C for 2 days. If a toxic compound is leached out from the disc, it means that the microbial growth is inhibited around the sample. The width of this area expressed the antibacterial or antifungal activity by diffusion. The zones of inhibition of microorganism growth of the standard samples polymers were measured with a millimeter ruler at the end of the incubation period.

RESULTS AND DISCUSSION

Structural characterization of the copolymers

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

The FTIR spectrum of poly(AOEMA-co-FPEMA) is shown in Figure 1. The absorption peak at 3083 cm^{-1} is due to aromatic C—H stretching. The peaks at 2943 and 2955 cm^{-1} are due to C—H
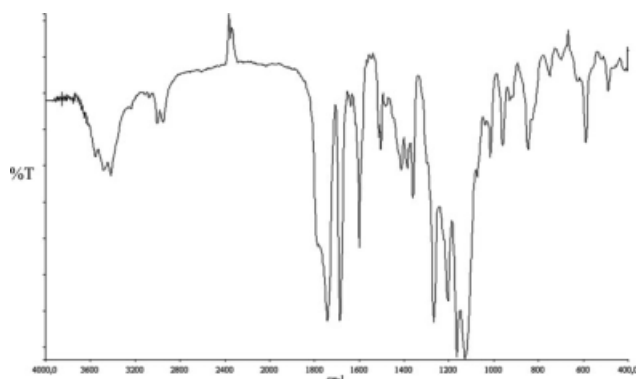
Figure 1 FTIR spectrum of poly(AOEMA-*co*-FPEMA); m_1 : m_2: [45 : 55].

stretching of methyl and methylene groups. The strong absorptions at 1795 cm^{-1} and 1750 cm^{-1} in the FTIR spectra of poly(AOEMA-*co*-FPEMA)s are due to the carbonyl stretching of oxycarbonyl and methacryl carbonyl for both monomeric units, respectively. The peak at 1700 cm^{-1} is due to the ketone peak of AOEMA. The aromatic C=C stretching appears at about 1582 and 1465 cm^{-1}. Peaks at 753–778 cm^{-1} may be assigned to the aromatic C—H out-of-plane bending, and those at 1452 cm^{-1} may be assigned to CH_3 bending vibrations. The ^{1}H-NMR and ^{13}C-NMR spectrums of poly(AOEMA-*co*-FPEMA) are shown in Figure 2(a,b). The ^{1}H-NMR spectrum of poly(AOEMA-*co*-FPEMA) is consistent with its chemical structure. Multiplet resonance absorptions at 7.1–7.9 ppm are due to the aromatic protons of AOEMA and FPEMA. The signals at 4.6–4.8 ppm are due to —OCH_2 protons of two mono-meric units. The methoxy protons of AOEMA reso-
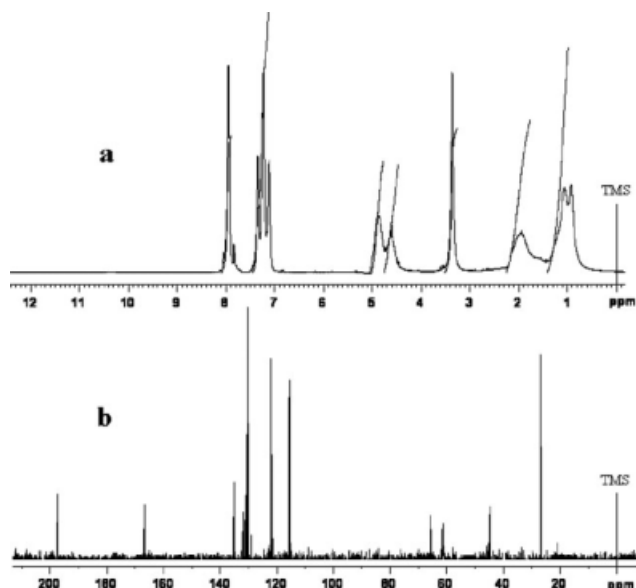
nance appears at 3.3 ppm. The backbone methylene protons of the two comonomer units are observed at 1.8 ppm. The α-methyl protons of monomer units are observed between 0.9 and 1.1 ppm. The chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers. In the proton-decoupled ^{13}C-NMR spectrum of copoly(AOEMA-*co*-FPEMA), the resonance signals at 168 ppm are due to the aryloxy carbonyl carbon for both monomers. The methacryl carbonyl carbons of both the monomeric units appear at 196 ppm. The group of signals at 115–135 ppm arises from aromatic carbons in the AOEMA and FPEMA units. The signals at 61 and 64 ppm are due to the OCH_2 carbons of AOEMA and FPEMA units, respectively. The methyl carbon on the acetyl group signal is observed at 45 ppm.

Although the IR spectra of the poly(BOEMA-*co*-FPEMA) copolymers show characteristic bands at 1740 cm^{-1} (C=O of ester of the both polymer) and 1760 cm^{-1} (C=O of aryloxycarbonyl) for both poly-mers, the peak at 1680 cm^{-1} is due to the ketone peak of BOEMA. The ^{1}H-NMR spectrum of poly-(BOEMA-*co*-FPEMA) are shown in Figure 3. The ^{1}H-NMR spectrum of poly(BOEMA-*co*-FPEMA) is con-sistent with its chemical structure. There are broad peaks at 7.0–7.9 ppm (phenyl protons of two mono-meric unit), 4.5–5.1 ppm (—OCH_2 protons for both polymer), 1.7–1.9 ppm (methylene protons of two monomeric units), 0.9–1.1 ppm (other aliphatic pro-tons including those in the backbone). ^{13}C-NMR peak assigments of this copolymer are 48.0 ppm (—OCH_2— carbons), 115–142 ppm (aromatic ring car-bons), and 165 and 167 ppm (—C=O for aryloxycar-bonyl carbons). The ester carbonyl carbon of both the monomeric units appear at 195 ppm.
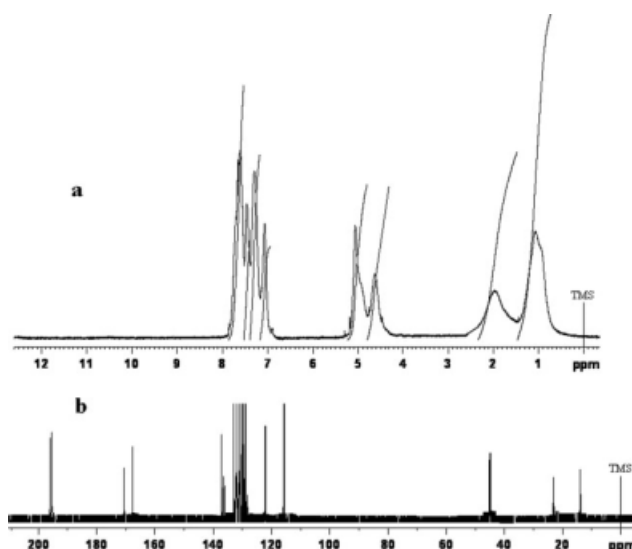

Figure 2 ^{1}H-NMR (a) and ^{13}C-NMR (b) spectrum of poly-(AOEMA-*co*-FPEMA); m_1 : m_2: [45 : 55].

Figure 3 ^{1}H-NMR (a) and ^{13}C-NMR (b) spectrum of poly-(BOEMA-*co*-FPEMA); m_1 : m_2: [18 : 82].
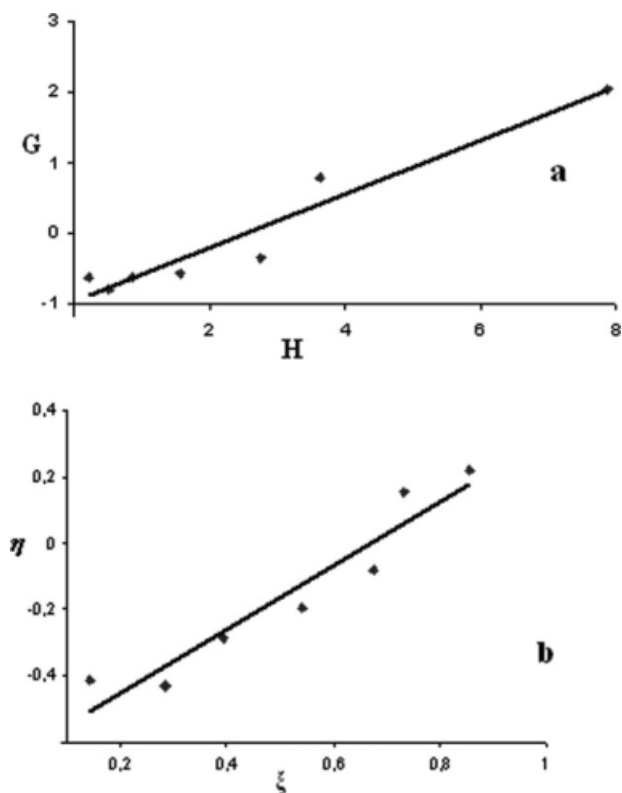
Figure 4 KT (a) and FR (b) plot for poly(AOEMA-co-FPEMA) system.

Molecular weights of the polymers

The weight average ($\overline{M}_w$) and number average ($\overline{M}_n$) molecular weights and the polydispersity indexes ($\overline{M}_w/\overline{M}_n$) of polymer samples are presented in Table I. The number-average and weight-average molecular weights ($\overline{M}_n$, $\overline{M}_w$) and the polydispersity index of homopolymers as well as copolymer samples were obtained from gel permeation chromatography. The values of $\overline{M}_n$ and $\overline{M}_w$ of poly(AOEMA-co-FPEMA) range from 21,200 to 28,800 and 30,200 to 63,300, respectively. The values of $\overline{M}_n$ and $\overline{M}_w$ of poly-(BOEMA-co-FPEMA) range from 22,600 to 33,400 and 39,100 to 62,100, respectively. The polydispersity index of homo and copolymers varied in the range of 1.42–2.44. These data clearly indicate that as FPEMA content in the copolymer increases, the molecular weight and polydispersity also increases.

Monomer reactivity ratios

The graphical plots concerning the methods previously reported are given for poly(AOEMA-co-FPEMA) in Figure 4, whereas the reactivity ratios are summarized in Table III. 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.

For AOEMA and FPEMA systems, the r_2 values are higher than the r_1 values. The higher r_2 value of FPEMA confirms the higher reactivity of FPEMA when compared with that of AOEMA. For BOEMA and FPEMA systems, the r_2 values are higher than the r_1 values. The higher r_2 value of FPEMA confirms the higher reactivity of FPEMA when compared with that of BOEMA. The reactivity ratio values (r_1 and r_2) of copoly(AOEMA-FPEMA) and copoly(BOEMA-FPEMA) are less than 1. Taking into account the microstructures of these copolymer systems, we know that the intermolecular hydrogen bonding between the carbonyl group of AOEMA or BOEMA and the amide group of FPEMA has a larger probability of occurring than the self-association through hydrogen bonding of pure FPEMA.[24,25] The product $r_1 \times r_2$ indicates that the two system copolymerizes randomly in the polymer chain; however, there is a possible tendency for alternation.

T_gs of the polymers

The T_g values of poly(AOEMA), poly(BOEMA), and poly(FPEMA) obtained under the same conditions with the copolymers were found to be 92, 98, and 109°C, respectively. In comparison with that of poly-(AOEMA) or poly(BOEMA), the shift to higher temperature is also noted for all the copolymers studied, and its magnitude is dependent on the increasing molar fraction of FPEMA in the copolymer chain. An increase in T_g of copolymers may be due to the introduction of comonomer into AOEMA or BOEMA, and FPEMA, which increases the intermolecular polar interactions between the molecular chains due to structure stretching. These results clearly indicate that T_g values of copolymers depend

TABLE III
Comparison of Reactivity Ratios by Various Methods

System	Methods	r_1	r_2	r_1r_2	$1/r_1$	$1/r_2$
Poly(AOEMA-co-FPEMA)	FR	0.38	0.94	0.36	2.63	1.06
	KT	0.32	0.84	0..30	3.13	1.19
	Average	0.35	0.89	0.31	2.86	1.12
Poly(BOEMA-co-FPEMA)	FR	0.49	1.09	0.53	2.05	0.92
	KT	0.49	1.07	0.52	2.05	0.93
	Average	0.49	1.08	0.53	2.05	0.93
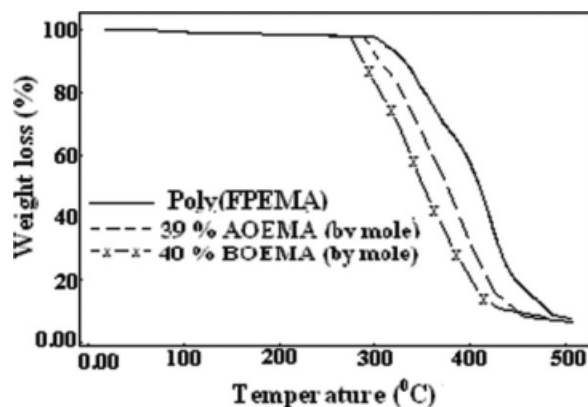
Figure 5 TGA curves for poly(FPEMA) and some copolymers.

Figure 6 The thermal degradation curves of poly-(FPEMA) at different heating rates.

on the composition of comonomers and increase with increasing FPEMA contents in the polymer chain. These values are indicated in Table I. It can be seen that the observed T_g increases with increasing FPEMA and presents a striking positive deviation with respect to linearity, which can be associated with a lower free volume, mobility, and flexibility than a mixture of AOEMA or BOEMA and FPEMA units. In addition, the incorporation of polar flour atoms in the copolymer backbone resulted in an increase of T_g due to chain stiffening and marked inhibition or rotation about C—C bonds. The presence of strong C—F dipoles in the backbone increases the interaction between the chains.

Thermal analysis

The initial decomposition temperatures of poly-(AOEMA) and poly(BOEMA) are around 298°C and 260°C, respectively, and independent of the side-chain structures. This result shows that main-chain scission is an important reaction in the degradation of polymers, at least in the beginning. The degradation of poly(FPEMA) occurred in three stages. The first stage was observed at 315–395°C. The second stage of decomposition commenced at 400–425°C, and the last stage was observed at 440–500°C. The residue at 450°C for the three polymers is about 10%. The thermal stability of the copolymers was improved by the incorporation of FPEMA. The initial decomposition temperatures of the copolymers were between those of the homopolymers.

Thermal degradation kinetics

Thermogravimetric curves of the poly(FPEMA) and some copolymers are shown in Figure 5. In this section, the degradation parameters of polymers are estimated by two methods. TGA was used to investigate the activation energies. The thermal degrada-
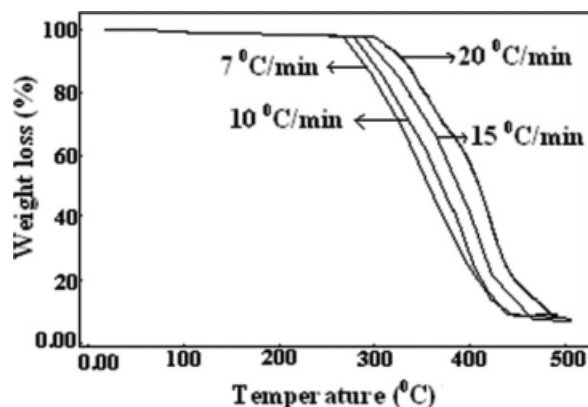
tion expression results differ based on the different assumptions and derivatives, for example, bulk or powder, carrier gas, flow rate, would directly affect the results of parameters.[26] The different analysis methods are described. These methods require several TGA curves at different heating rates. Hence, the dynamic TGA in nitrogen of the polymers has been performed at various heating rates 7, 10, 15, and 20°C/min. Figure 6 shows the TG curves at the different heating rates of poly(FPEMA).

Ozawa method

According to the method of Ozawa,[27] the apparent thermal decomposition activation energy, E_a, can be determined from the TGA thermograms under various heating rates by the following equation:

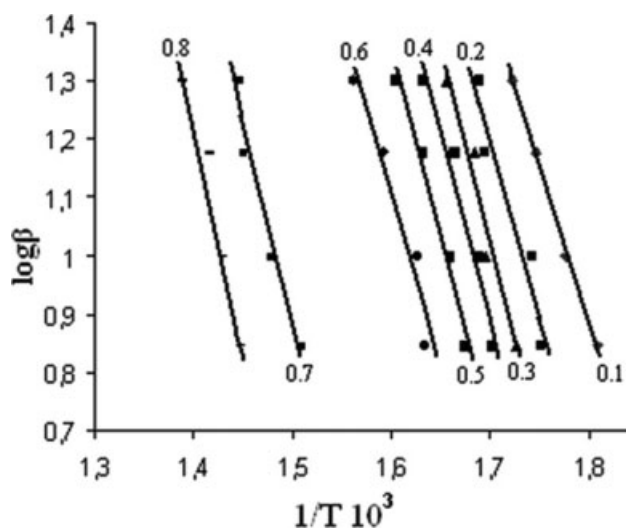$$E_a = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right] \quad (11)$$

Figure 7 Ozawa's plots of logarithm of heating rate (β) versus reciprocal temperature $(1/T)$ at different conversions for poly(AOEMA-co-FPEMA); $m_1 : m_2$ [67 : 33].

TABLE IV
The Apparent Activation Energies of Investigated Polymers Under Thermal Degradation in N_2

Sample	10	20	30	40	50	60	70	80
Poly(FPEMA)	142.8	151.5	161.1	160.9	163.2	165.2	164.1	159.3
Poly(AOEMA)	96.73	108.39	123.36	117.32	117.25	108.11	122.28	143.85
Poly(BOEMA)	98.73	111.79	119.36	121.21	117.25	108.19	126.18	135.45
Poly(AOEMA-*co*-FPEMA)								
29/71	178.2	173.1	176.1	181.1	180.5	181.2	180.4	182.1
48/52	167.3	172.1	164.5	169.3	167.4	171.5	176.5	166.8
71/29	151.5	156.1	170.9	171.7	168.9	166.7	171.6	167.4
Poly(BOEMA-*co*-FPEMA)								
28/72	220.2	224.5	228.5	230.6	231.5	233.5	231.1	230.4
45/55	215.2	217.4	213.6	214.5	220.2	221.4	223.5	220.1
69/31	210.2	211.3	212.5	209.3	213.2	208.1	213.2	217.2

where R is the gas constant; b, a constant (0.4567); and β, the heating rate (°C/min). According to eq. (11), the activation energy of degradation can be determined from the slope of the linear relationship between log β and $1/T$. The results of the Ozawa analysis for poly (BOEMA-*co*-FPEMA) are given in Figure 7, which shows that the best-fitting straight lines are nearly parallel, indicating a constant activation energy range of conversions analyzed and confirming the validity of the approach used. Activation energies corresponding to the different conversions are listed in Table IV. E_a calculated from the Ozawa method is superior to other methods for complex degradation because it does not use the reaction order in the calculation of the decomposition activation energy. Therefore, E_a calculated from the Ozawa method was superior to the former methods for complex degradation.

Antimicrobial effects of the monomers and polymers

The poly(FPEMA) is found to be the most effective in inhibiting the growth of microorganisms. These may be traced to high fluorine content of this homopolymer. As the percentage of AOEMA or BOEMA in the copolymer increases, the effectiveness of the copolymers to inhibit the growth of microorganisms decreases. As expected, when compared with poly-(FPEMA), poly(AOEMA) or poly(BOEMA) is less effective to inhibit the growth of microorganisms. Although the fluorine content of the polymers appears to be most important to impart antimicrobial properties, it is possible that the conformation of the polymers acquired under experimental conditions may also be a factor for their antigrowth activity. However, this study is beyond the scope of the present investigation. The use of fluorine to increase the biological half-life by impeding oxidative metabolism[28] and to increase bioabsorption by lipophilic effects are examples of directed strategies of fluorine substitution. As more data are collected in the literature, it becomes clearer what may be the biological squeal of a given substitution pattern. The data are listed in Table V, which is the average data of two experiments.

TABLE V
Antimicrobial Effects of the Compounds (mm of Zones)

Compounds	*Pseudomonas aeruginasa*	*Escherichia coli*	*Proteus vulgaris*	*Salmonella enteridis*	*Klebsiella pneumoniae*	*Staphylococcus aureus*	*Candida albicans*
Poly(FPEMA)	15	15	14	14	15	15	14
Poly(AOEMA)	13	12	–	–	–	14	–
Poly(BOEMA)	14	13	12	10	–	13	–
Poly(AOEMA-*co*-FPEMA)							
29/71	17	17	13	15	17	12	16
48/52	16	15	–	13	13	11	–
71/29	15	14	12	–	11	9	15
Poly(BOEMA-*co*-FPEMA)							
28/72	16	16	16	16	15	15	14
45/55	14	15	14	–	12	13	11
69/31	12	13	13	12	–	11	–
Penicillin G	18	15	9	19	21	19	35
Teicoplanin	19	19	21	23	27	14	19
DMSO	–	–	–	–	–	–	–

Compound concentration: 100 μg/disc; the symbol (–) reveals that the compounds have no activity against the microorganisms; DMSO: dimethylsulfoxide (control).

CONCLUSIONS

In this study, the copolymers of AOEMA and BOEMA with FPEMA have been prepared by free-radical polymerization in 1,4-dioxane at 65°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The r_2 values were higher than the corresponding r_1 values in all cases, which means that a kinetic preference exists for the incorporation of FPEMA in the copolymer structure. The glass transition temperatures of the AOEMA and BOEMA with FPEMA copolymers were obtained and compared. The TGA studies concluded that the thermal stability of the copolymers increases with an increase of FPEMA in the copolymer chain. The biological activity and thermal stability of the polymers were investigated. The decomposition activation energies of the polymers were calculated with the Ozawa method. The biological activity of the polymers increases with an increase in the mole fraction of FPEMA in the copolymers.

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