Synthesis and Characterization of Novel Methacrylate Copolymers based on Sulfonamide and Coumarine: Monomer Reactivity Ratios, Biological Activity, Thermal Stability, and Optical Properties

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ABSTRACT: The free radical copolymerization of 2-oxo-2-[(4-sulfamoylphenyl)amino]ethyl-2-methylpropenoate (SAEMA) with 4-methyl-2-oxo-2*H*-chromen-7-yl-2-methylpropenoate (MCMA) has been carried out in 1, 4-dioxane at 65 °C ± 1 °C and the copolymers were analyzed by Fourier-transform infrared, ^{1}H-NMR, ^{13}C-NMR and gel permeation chromatography. ^{1}H-NMR and elemental analysis was used to determine the molar fractions of SAEMA and MCMA in the copolymers. The monomer-reactivity ratios were calculated according to the general copolymerization equation using Kelen-Tüdõs and Fineman-Ross linearization methods. The reactivity ratios indicated a tendency toward random copolymerization. The polydispersity indices of the polymers, determined with gel permeation chromatography, suggested a strong tendency for chain termination by disproportionation. The thermal behaviors of copolymers with various compositions were investigated by differential scanning calorimetry and thermogravimetric analysis. The glass-transition temperature of the copolymers increased with increasing MCMA content in the copolymers. Also, the apparent thermal decomposition activation energies were calculated by the Ozawa method with a Shimadzu TGA 60 thermogravimetric analysis thermobalance. All the products showed moderate activity against different strains of bacteria and fungi. The photochemical properties of the polymers were investigated by UV spectra. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4323–4334, 2010

KEYWORDS: activation energy; biological activity; biomaterials; coumarin methacrylate; differential scanning calorimetry (DSC); functionalization of polymers; monomer reactivity ratios; radical polymerization; suflonamide methacrylate

INTRODUCTION Functional groups give a polymer structure a special character substantially different from the inherent properties of the basic polymer chain.[1] In recent years, some comprehensive work has been published on functional monomers and their polymers.[2–5] Sulfonamide is a generic name for derivatives of *para*-aminobenzene sulfonamide. The importance of sulfonamide nucleus is well established in the pharmaceutical chemistry and drug design. A considerable number of sulfonamides are well known as antibacterial,[6] anticancerous,[7] carbonic anhydrase inhibitors,[8] and also as anti-inflammatory agents.[9] Just how good a drug the sulfonamide is depends on the nature of the group attached to the amido nitrogen. Although many thousands of derivatives have been synthesized only a few had the proper combination of high antibacterial activity and low toxicity to human beings that is necessary for an effective drug.[10] The antibacterial activity of sulfonamides set in motion for other chemicals, related to sulfonamides that have even better chemotherapeutic effects. Literally thousands of chemical variations were played on the sulfanilamide theme; the structure of sulfanilamide was varied in almost every imaginable way. In previous reports, a new class of pH-sensitive polymers containing a sulfonamide group was shown to demonstrate a sharp transition in solubility and swelling around pH 7.4[11–19] and its reversibility.[20]

Coumarin-containing polymers have been well studied and widely applied in many fields, such as biochemicals, electro-optical materials, organic-inorganic hybrid materials, liquid crystalline materials, and light harvesting/energy transferring materials.[21–25] However, most reported coumarin-containing polymers were linear polymers. And the coumarin functional group was introduced as a pendent group or terminal group of the polymer chain.[26–29] A recent review article highlighted the photochemistry of 7-hydroxycoumarin and various derivatives that are known to undergo photodimerization ($2\pi + 2\pi$ cycloaddition) reactions when irradiated with ultraviolet-A (UVA) sources (320–400 nm).[30] Some photodimerized coumarins have reversible cleavage potential at wavelengths below 290 nm, shifting the equilibrium toward the monomeric coumarin species.

Knowledge of the copolymer composition is an important step in the evaluation of its utility. The copolymer composition and its distribution depend on monomer reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the

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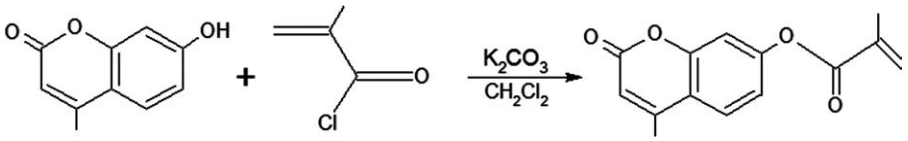


SCHEME 1 Synthesis of the MCMA monomer.

composition of copolymers and the composition of the monomer feed in which the monomer-reactivity ratios are the parameters to be determined.[31,32] The calculation of the monomer-reactivity ratios requires the mathematical treatment of experimental data on the composition of copolymers and monomer in feed mixtures. The most fundamental quantity characterizing a copolymer is its composition on a molar basis, which eventually is used for the determination of the relevant monomer reactivity ratios. Spectroscopic methods, preferably ^{1}H-NMR spectroscopy,[33,34] and elemental analysis are probably the most widely used methods for the analysis of copolymers and the determination of reactivity ratios r_1 and r_2.

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.[35,36] In previous study,[16] Han Bae et al. described the synthesis and characterization of the methacrylamide monomer based on the sulfonamide and its homopolymer.

In this work, we have synthesized two new methacrylate monomers. One of them has sulfonamide group in side chain. Almost all the polymers bearing sulfonamide published in the literature are as methacrylamide. We have synthesized and characterized a new monomer and its polymer as methacrylate having pendant sulfonamide. The other monomer that we have synthesized is methacylate containing coumarine ring. As far as we know, in the literature, an acrylate monomer bearing coumarine has been synthesized[37] but a methacrylate has not. It is thought that methacrylate polymers bearing two important groups such as coumarine and sulfonamide and their copolymerization acts will be interesting for polymer chemistry. In addition, the effects of the copolymer composition/thermal behavior relationships, and an investigation of the biological activity and optical properties are presented and discussed.

EXPERIMENTAL

Materials

Methacryloyl chloride, sodium methacrylate, 4-methyl-7-hydroxy coumarin, sulfonamide (Aldrich) were used as received. Ethanol, methanol, chloroform, *n*-hexane, and benzene were freshly distilled over molecular sieves before use. Then 1,4-dioxane, acetonitrile, and potassium carbonate (Merck) were used as received. Azobisizobutyronitrile (AIBN) was recrystallized from a chloroform-methanol mixture. All the other chemicals were analytical grade and commercial products, and they were used without any further purification.

Instrument and Measurements

Infrared spectra were obtained with a Perkin–Elmer 460 Fourier-transform infrared (FT-IR) spectrometer with KBr pellets in the 4000 to 400 cm^{-1} range, and 10 scans were taken at a 4 cm^{-1} resolution. ^{1}H-NMR and ^{13}C-NMR spectra in DMSO and CD_2Cl_2 solutions were recorded on a Bruker GmbH DPX-400 400 MHz FT-NMR spectrometer with tetramethylsilane as an internal reference. The molecular weights [weight average molecular weight (*Mw*) and number average molecular weight (*Mn*)] of the polymer were determined with a Waters 410 gel permeation chromatograph equipped with a refractive index detector and calibrated with polystyrene standards. Thermal data were obtained with a Shimadzu DSC-60H instrument at a heating rate of 10 °C min^{-1} and with a Labsys TGA thermobalance at a heating rate of 10 °C min^{-1} in a N_2 atmosphere. Elemental analyses were carried out with an Elementar CHNS microanalyzer. UV-vis absorption spectra were measured using a Shimadzu UV-1700 Pharma spectrophotometer. The photoluminescence were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer.

Syntheses

*Synthesis of 4-Methyl-2-oxo-2*H*-chromen-7-yl-2-methylpropenoate Monomer (MCMA)*

The synthesis of 4-methyl-2-oxo-2*H*-chromen-7-yl-2-methylpropenoate (MCMA) monomer was carried out according to the usual method.[38] Scheme 1 shows the reaction leading to the formation of monomer. The melting point of MCMA was 110 °C, and yield was about 82%.

IR (neat), cm^{-1}: 1734 (broad, C=O of methacrylate and of coumarin group), 3082 (—CH stretching vibration of the aromatic ring), 2990 (—CH_3 on coumarin and methacrylate), 1634 (C=C), 1240 (asymmetric C—O—C), 1142 (symmetric C—O—C), 890 (—CH bending mode of vinyl group).

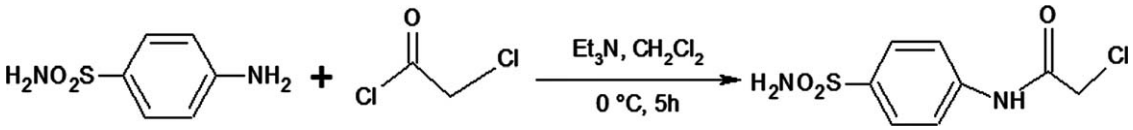
^{1}H-NMR (δ, ppm from TMS in $CDCl_3$): 6.4–7.8 (aromatic protons, 4H); 5.6 (CH_2=, 1H); 6.2 (CH_2=, 1H); 2.5 (CH_3—, on coumarin, 3H); 1.9 (CH_3—, on methacrylate, 3H).

^{13}C-NMR (δ, ppm from TMS in $CDCl_3$): 165.5 and 160.6 (*C*=O of methacrylate and coumarine moiety respectively); 135.7 (=*C*); 128.0 (*C*H_2=); 156-119 (Aromatic carbons); 19 (*C*H_3 in olefinic and on coumarine carbon).

*Synthesis of 2-Chloro-*N*-(4-sulfamoylphenyl)acetamide (ClSPA)*

Synthesis of the 2-chloro-*N*-(4-sulfamoylphenyl)acetamide was carried out according to the usual method.[38] The synthesis route is shown in the Scheme 2.

IR (neat), cm^{-1}: 1684 (C=O for amide), 1160–1300 (SO_2), 3187 (—NH—), 680 (C-Cl).



SCHEME 2 Synthesis of the 2-chloro-*N*-(4-sulfamoylphenyl)acetamide.

Synthesis of 2-Oxo-2-[(4-sulfamoylphenyl)amino]ethyl-2-methylpropenoate (SAEMA) Monomer

The synthesis of monomer is shown in Scheme 3. Synthesis of 2-oxo-2-[(4-sulfamoylphenyl)amino]ethyl-2-methylpropenoate(SAEMA) was as follows: 2-chloro-*N*-(4-sulfamoylphenyl)acetamide (ClSPA) (1 mol) and sodium methacrylate (1.1 mol) were stirred in 75 mL acetonitrile at 75 °C in a reflux condenser for 24 h in the presence of 100 ppm hydroquinone as inhibitor. Then the solution was cooled to room temperature and neutralized with a 5% KOH solution. The organic layer was washed several times with water and the water layer was washed with diethyl ether a few times. The acetonitrile layer and diethyl ether layer were collected and dried over anhydrous $MgSO_4$ overnight. Acetonitrile and diethyl ether were evaporated. The organic layers were collected and the residue was crystallized from methanol. Yield: 80%. The reactions path is shown in Scheme 3.

IR (neat), cm^{-1}: 1724 (C=O for ester), 1684 (C=O, for amide), 1160–1300 (SO_2), 3187 (NH—), 3082 (CH—, of the aromatic ring), 2980 (C—H—, aliphatic stretching vibration), 1630 (C=C), 895 (C—H bending mode of vinyl group).

^{1}H-NMR (δ, ppm from TMS in $CDCl_3$): 7.3–7.8 (aromatic protons, 4H); 5.6 (CH_2=, 1H); 6.2 (CH_2=, 1H); 10.8 (—NH—, 1H); 1.9 (CH_3—, in olefinic carbon, 3H); 7.4 (SO_2NH_2), 4.8 (OCH_2—, 2H).

^{13}C-NMR (δ, ppm from TMS in $CDCl_3$): 167.0 and 165.4 (*C*=O of amide and ester); 129.6 (=*C*); 125.1 (CH_2=); 110–150 (aromatic carbons); 65 (OCH_2); 18 (CH_3 in olefinic carbon).

Polymerization of the Monomers

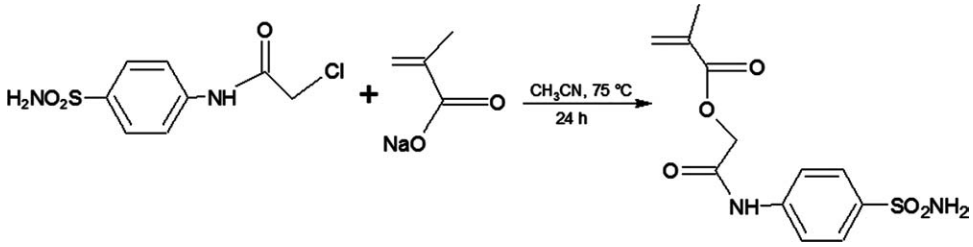
Polymerization of SAEMA and MCMA were carried out in glass ampoules under N_2 atmosphere in DMSO solution with AIBN (1% based on the total weight of monomers) as an initiator. The reacting components were degassed by threefold freeze-thawing cycles and then immersed in oil bath at 65 °C for a given reaction time. The polymers were separated by precipitation in ethanol and reprecipitated from DMF solution. The polymers were finally dried under vacuum to constant weight at room temperature and kept in desiccators under vacuum until use.

Copolymerization

Copolymerizations of SAEMA with MCMA, with five different feed compositions, were carried out in DMSO at 65 °C with AIBN (1%, based on the total weight of the monomers) as an initiator. Appropriate amounts of SAEMA with MCMA and DMSO was mixed in a polymerization tube, purged with N_2 for 20 min, and kept at 65 °C in a thermostat. The reaction time (≈3.5 h) was selected to give conversions less than 10 wt % to satisfy the differential copolymerization equation. The conversion of the monomer to the polymer was determined by a gravimetric method. After the desired time, the copolymerization was stopped. These copolymers were poured into excess ethanol to precipitate, were filtered, were purified by repeated reprecipitation from a solution of each polymer in DMF by ethanol, and were dried in a vacuum oven at 60 °C to a constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis (N and S content of SAEMA units) and ^{1}H-NMR analysis.

Antimicrobial Screening

The biological activities of the monomers and their homopolymers and copolymers were tested against different microorganisms with DMSO as the solvent. The sample concentration was 100 μg. In this study, *Staphylococcus aureus* ATCC 29,213, *Escherichia coli* 0157:H7, *Pseudomonas aeruginasa* ATCC 27,853, *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.[39] 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), was 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.



SCHEME 3 Synthesis of the SAEMA monomer.

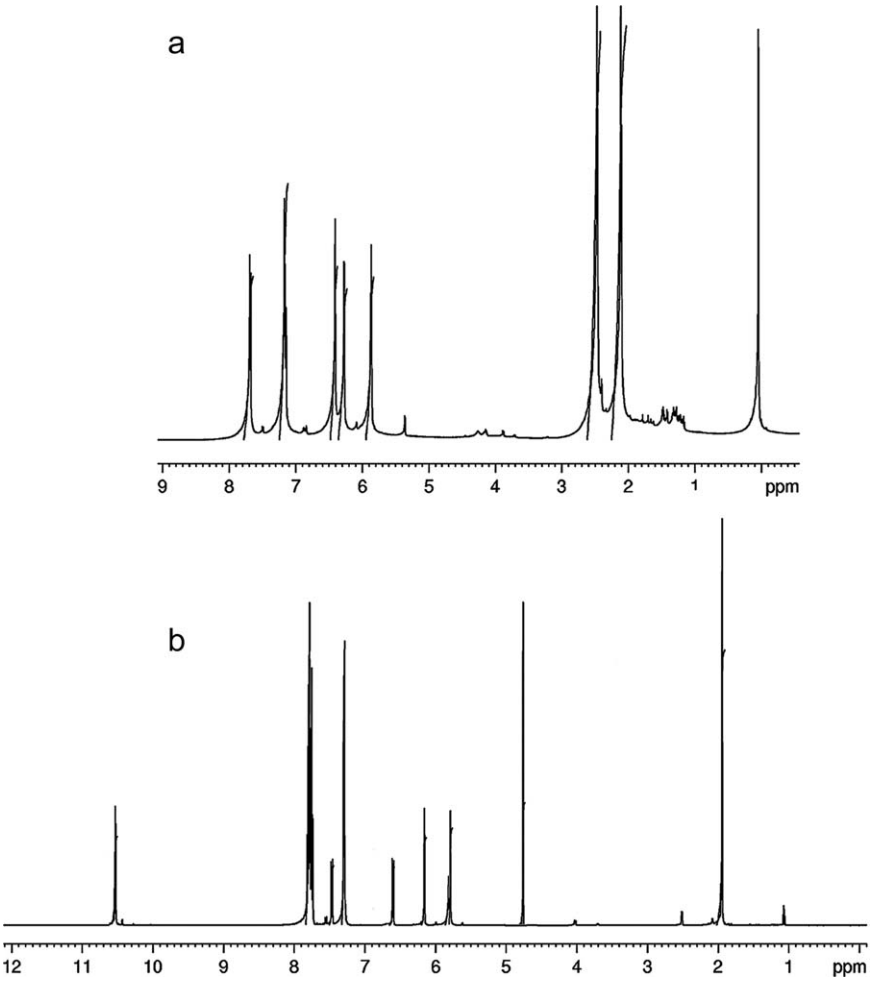


FIGURE 1 ^{1}H-NMR spectra of (a) poly(MCTMA) and (b) poly(SAEMA).

The antibiotic sensitivity of the polymers was tested with the antibiotic disk assay as described.[40] 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. Prepared antibiotic discs (100 μg) were placed on the surface of the agar medium.[41] The plates were kept at 5 °C for 30 min and then incubated at 35 °C for 2 days. If a toxic compound 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 monomers, homopolymers and copolymers, were measured with a millimeter ruler at the end of the incubation period.

RESULTS AND DISCUSSION

Structural Characterization of the Monomers and their Polymers

During the polymerization of the both monomers, the IR band at 1630 cm^{-1} (C=C) disappearance and ester carbonyl stretching for polymers shifted to about 1740 cm^{-1}. The main evidence of the polymer is certainly the disappearance of some characteristic signals of the double bond in the spectra and this fact was effectively observed in our case. Thus, two bands vanished in the IR spectrum: the absorption band at 923 cm^{-1} assigned to the C-H bending of geminal $=CH_2$ and the stretching vibration band of C=C at 1600 cm^{-1}. The ^{1}H-NMR spectrum of the monomers are presented in Figure 1 and are good agreement with the structure. From ^{1}H-NMR spectroscopy the formation of the polymers are also clearly evident from the vanishing of two singlet at 5.6 and 6.2 ppm of the vinyl protons and the appearance of the broad signal at 1.5 and 2.2 ppm assigned to an aliphatic $-CH_2-$ group. In the proton decoupled ^{13}C-NMR spectrum of poly(SAEMA) (Fig. 2), chemical shift assignments were made from the off-resonance decoupled spectra of the polymer. Resonance signals at 168 and 165 ppm correspond to ester and amide group present in polymer. The signal due to carbon of the aromatic ring attached to the NH group shifts toward downfield and is observed at 142 ppm. The other aromatic carbons are observed at 125 to 135 ppm. The α-methyl group of polymer shows resonance signals at 18 ppm.

Characterization of the Copolymers

The copolymeric units of SAEMA with MCMA can be represented according to Scheme 4.

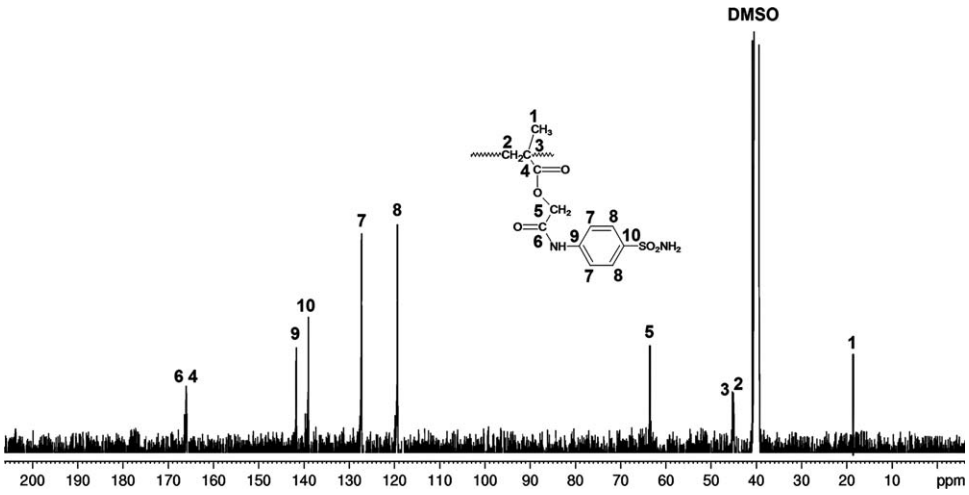


FIGURE 2 ^{13}C-NMR spectra of poly(SAEMA).

Solubility

The solubility of the homopolymers and copolymers was tested via the mixing of 10 mg of each polymer with 3 mL of various solvents in test tubes. After the closed tubes were set aside for 1 day, the solubility was observed. The homopolymers and copolymers were soluble in 1,4-dioxane, dimethylacetamide, dimethylformamide, dimethyl sulfoxide (DMSO), tetrahydrofuran, but were insoluble in *n*-hexane, *n*-heptane, ethanol, and methanol solvents.

Spectroscopic Characterization

FT-IR Spectrum

The FT-IR spectrum of the copolymer, poly-(SAEMA-*co*-MCMA) (0.48:0.52), is shown in Figure 3. The peak at 3340 cm^{-1} which is attributed to *N*-H stretching of the amide group. 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 is observed at 2983, 2938, and 2863 cm^{-1}. The shoulder at 1740 and a peak at 1680 cm^{-1} are attributed to the ester and amide carbonyl stretching of SAEMA and ester and lactone carbonyl stretching of MCMA. 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.

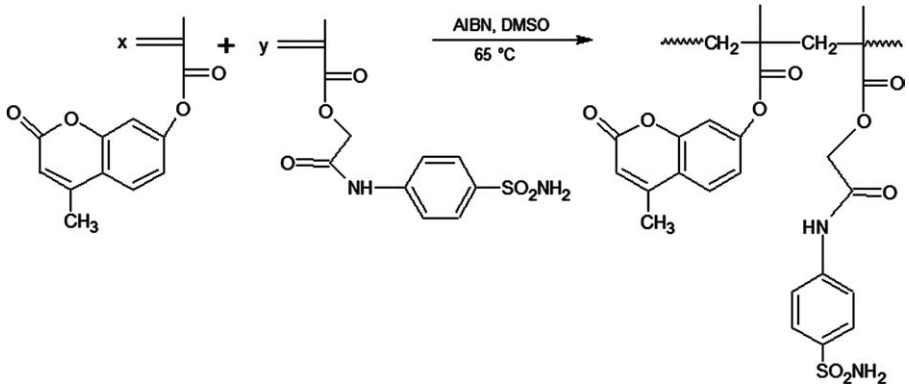
^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of the copolymer poly(SAEMA-*co*-MCMA) (0.70:0.30) is shown in Figure 4(a). The chemical shift assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The resonance signals at 10.50 ppm correspond to the NH protons of the SAEMA unit. The aromatic protons show signals between 7.82 and 7.35 ppm.

The spectrum shows a signal at 4.8 ppm, which are due to —OCH_2— group at SAEMA units. The methyl protons on MCMA show signal at 2.6 pmm. The backbone methylene groups show signals at 2.24 to 2.60 ppm. The signals obtained at 1.10 and 1.42 ppm are due to the α-methyl protons of both the monomer units.

^{13}C-NMR Spectrum

The proton decoupled ^{13}C-NMR spectrum of the copolymer poly(SAEMA-*co*-MCMA) (0.70:0.30) is shown in Figure 4(b). The amide and ester carbonyl of SAEMA appeared at 168.1 and 166 ppm, respectively, while the ketone and ester carbonyl of MCMA appeared at 165.6 and 163.1 ppm. The aromatic carbons in copolymer appeared at 115 to 150 ppm.



SCHEME 4 The structure monomeric units of the copolymer.

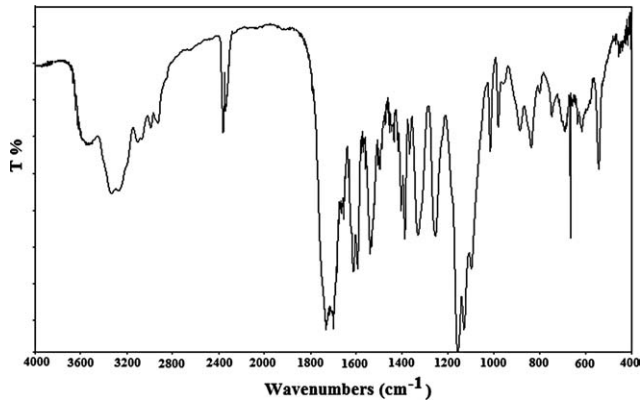


FIGURE 3 FT-IR spectrum of poly(SAEMA-*co*-MCMA) (0.70:0.30).

The methylenoxy group in SAEMA unit show signal at 66.3 ppm. The signals due to the backbone methylene carbon atoms are observed at 43.2 and 45.0 ppm, while that of the tertiary carbons is observed at 45.1 and 48.3 ppm. The methyl carbons on the coumarin appeared at 25.6 ppm. The α-methyl carbon atoms of both monomeric units give a series of resonance signal at 18.2 ppm.

Copolymer Compositions

The copolymerization of MCTMA with IAOEMA in a 1,4-dioxane solution was studied for SAEMA molar fractions of approximately 0.90 to 0.10 in the feed. The number of monomeric units in the copolymers was determined by ^{1}H-NMR spectroscopy and by elemental analysis. Thus, the mole fraction of SAEMA in the copolymer was determined from the ratio of the integrated values of the intensities of the aromatic protons (7.3–7.8) and the methylenoxy (4.8) of SAEMA and aromatic protons (6.4–7.8 ppm) of MCMA units.

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

$$\frac{\text{Integrated intensities of aromatic protons and } NH_2 \text{ protons}}{\text{Integrated intensities of methylenoxy protons}} = \frac{4m_1 + 2m_1 + 4m_2}{2m_1} = C \quad (1)$$

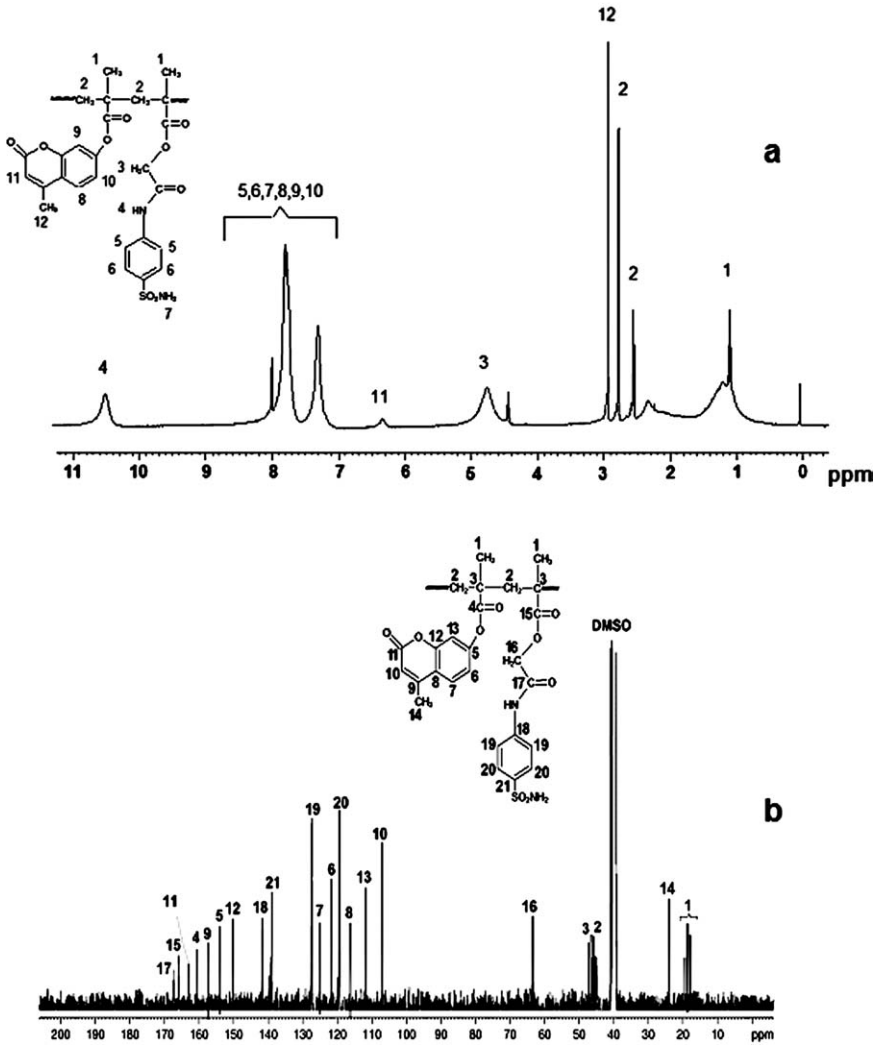


FIGURE 4 (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of poly(SAEMA-*co*-MCMA) (0.70:0.30).

TABLE 1 Monomer Compositions in Feed and in the Copolymer

Sample	Feed Composition (mol Fraction) SAEMA (M_1)	Feed Composition (mol Fraction) MCMA (M_2)	Conv. (%)	Intensty of Methylenoxy Protons	Copolymer Composition (mol Fraction) SAEMA (m_1)	Copolymer Composition (mol Fraction) MCMA (m_2)
1	0.10	0.90	9.50	0.55	0.20	0.80, 0.81[a]
2	0.25	0.75	7.50	1.25	0.36	0.64, 0.65[a]
3	0.50	0.50	8.90	2.05	0.48	0.52
4	0.70	0.30	8.40	3.12	0.60	0.40, 0.39[a]
5	0.85	0.15	9.20	4,34	0.70	0.30

[a] Determined by elemental analysis (*N* content).

On simplification

$$m_1 = \frac{4}{2C - 2} \tag{2}$$

where m_1 and m_2 are the copolymer molar compositions. With eq 2, the molar fractions of SAEMA in the copolymers were determined by the measurement of the integrated peak heights of the total aromatic, methylenoxy, and NH_2 protons signals of SAEMA units. The results are presented in Table 1.

Molecular Weights

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard solvent, respectively. The *Mw* and *Mn* values and polydispersity indices (*Mw*/*Mn*) of the polymer samples are presented in Table 2. The polydispersity index of the polymers ranges from 1.61 to 1.82. The theoretical values of *Mw*/*Mn* for the polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively.[42] In the homopolymerization of SAEMA, the growing chains terminate by disproportionation. The polydispersity indices of poly (SAEMA) and poly(MCMA) suggest that in both cases chain termination by disproportionation outweighs coupling, and the tendency for termination by disproportionation is greater for MCMA than for SAEMA. The values of *Mw*/*Mn* in copolymerization are also known to depend on chain termination in the same way as in homopolymerization.[43]

TABLE 2 Molecular Weights, Polydispersity Index, and *Tg* Values of Polymers

Sample	$\overline{M}_w \times 10^4$	$\overline{M}_n \times 10^4$	$\overline{M}_w/\overline{M}_n$	*Tg*
Poly(SAEMA)	8.12	4.69	1.73	170
Poly(MCMA)	9.50	5.22	1.82	198
Poly(SAEMA-*co*-MCMA)				
20/80	5.48	3.10	1.77	190
36/64	7.88	4.60	1.71	186
48/52	7.84	4.67	1.68	183
60/44	7.40	4.48	1.65	180
70/30	6.80	4.22	1.61	177

Determination of the Monomer Reactivity Ratios

The monomer reactivity ratios for the copolymerization of SAEMA with MCMA were determined from the monomer feed ratios and the copolymer composition. The plot of the mole fraction of SAEMA in feed (M_1) versus that of SAEMA in copolymer (m_1) is shown in Figure 5. The Fineman-Ross (FR)[44] and Kelen-Tudos (KT)[45] methods were used to determine the monomer reactivity ratios. According to the FR method, the monomer reactivity ratios can be obtained as follows:

$$G = Hr_1 - r_2 \tag{3}$$

where r_1 and r_2 correspond to the SAEMA and MCMA monomers, respectively. The parameters G and H are defined as follows:

$$G = F/(f-1)/f \quad \text{and} \quad H = F^2/f \tag{4}$$

with

$$F = M_1/M_2 \quad \text{and} \quad f = m_1/m_2 \tag{5}$$

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.

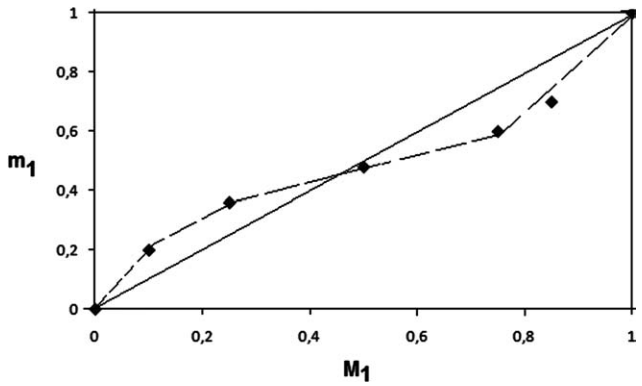


FIGURE 5 Copolymer composition diagram for poly(SAEMA-*co*-MCMA) system. M_1, feed composition in mole fraction for SAEMA; m_1: Copolymer composition in mole fraction for SAEMA.

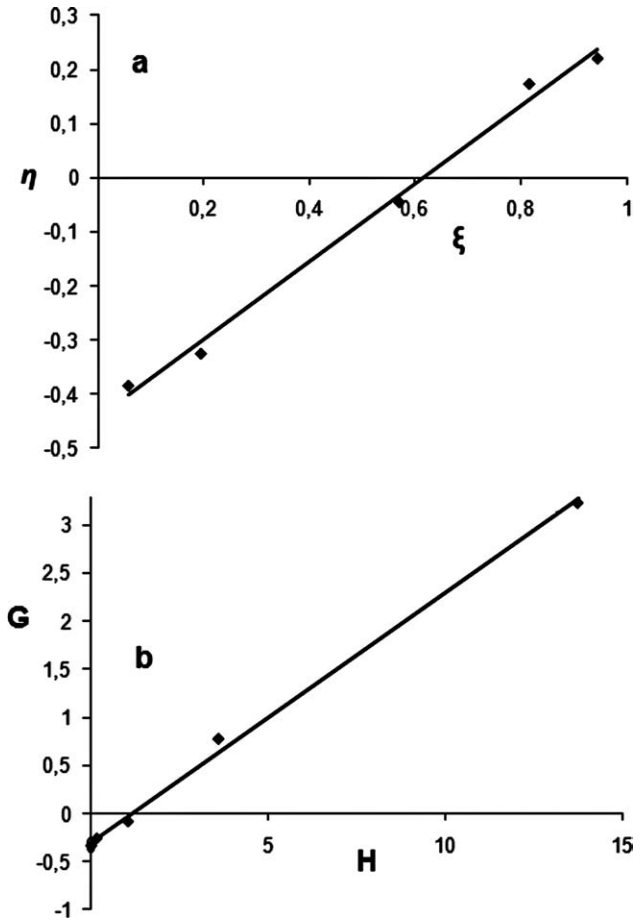


FIGURE 6 (a) FR plots and (b) KT plots for determining the monomer reactivity ratios in the copolymerization of SAEMA (M_1) and MCMA (M_2).

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

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{6}$$

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

$$\eta = G/(\alpha + H) \quad \text{and} \quad \xi = H/(\alpha + H) \tag{7}$$

and α is a constant equal to $(H_{max} \cdot H_{min})^{1/2}$, 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:

$$\xi = 0 \longrightarrow \eta = -r_2/\alpha \quad \text{and} \quad \xi = 1 \longrightarrow \eta = r_1 \tag{8}$$

The graphical plots concerning the methods previously reported are given in Figure 6(a,b), whereas the reactivity ratios are summarized in Table 3. In all cases and for all graphical methods, the plots are linear, and this indicates that these copolymerizations follow conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

The values of r_1 and r_2 is less than 1, which indicates that the system copolymerizes statistically. The reactivity of growing radicals with SAEMA unit, as measured by $1/r_2$ seems to be higher toward MCMA monomer than its own monomer. The r_1 and r_2 values strongly suggest that the copolymer chain contains a greater number of MCMA units and less SAEMA units than in the feed. Taking into account the microstructures of these copolymer systems, we know that the intermolecular hydrogen bonding between the carbonyl group of MCMA and the amide group of SAEMA has a larger probability of occurring than the self-association through hydrogen bonding of pure MCMA.[46,47] The microstructure of a polymeric material plays an important role in the behavior of the material toward a variety of biological systems and could be especially important in copolymerizations with monomers of different reactivities.[48]

Glass Transition Temperatures

The glass transition temperatures (*Tg*'s) were determined with a Shimadzu DSC-60 instrument.

Samples (about 5–8 mg) held in sealed aluminum crucibles at a heating rate of 20 °C/min under a dynamic nitrogen flow (5 L h^{-1}) were used for the measurements. From DSC measurements, *Tg* was taken as the midpoint of the transition region. *Tg* of is poly(MCMA) 198 °C, and that of poly (SAEMA) is 170 °C. The *Tg* values of the copolymers increase with an increase in the MCMA content in the copolymers. The results clearly indicate that the *Tg* values of the copolymers depend on the compositions of the comonomers and increase with increasing MCMA content in the polymer chain. The observed *Tg* values increase with increasing MCMA and present a striking positive deviation with respect to linearity, which can be associated with lower free volume, mobility, and flexibility than those of a mixture of MCMA and SAEMA units. The *Tg* values of the copolymers are indicated in the Table 2.

Decomposition Kinetics

The thermal stabilities of the polymers were investigated by TGA in a nitrogen stream at a heating rate of 20 °C min^{-1}. In Figure 7, the TGA thermograms of the polymers are shown. It is clear that one degradation stages are observed for poly(SAEMA) and poly(MCMA). The initial decomposition temperatures of poly(SAEMA) are around 318 °C, and

TABLE 3 Copolymerization Parameters for the Free-Radical Copolymerization of SAEMA with MCMA[a]

Methods	r_1	r_2	$r_1 r_2$	$1/r_1$	$1/r_2$
F-R	0.26 ± 0.015	0.30 ± 0.014	0.078	3.85	3.33
K-T	0.28 ± 0.08	0.36 ± 0.011	0.100	3.75	2.78
Average	0.27 ± 0.095	0.33 ± 0.013	0.090	3.70	3.03

[a] r_1 and r_2 are the monomer reactivity ratios for SAEMA and MCMA, respectively.

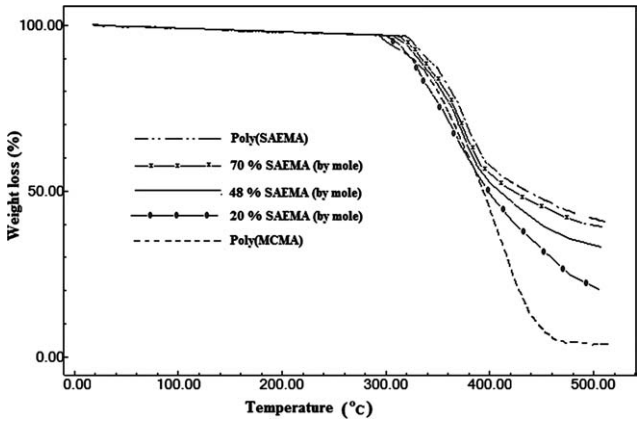


FIGURE 7 TGA curves for homoplymers and some copolymers.

independent of the side-chain structures. The initial decomposition temperatures for poly(MCMA) are observed at around 300 °C. One degradation stages for all copolymer are observed. Some degradation characteristics of the copolymers are given in Table 4 by comparison with those of the homopolymers. The thermal degradation of poly(*n*-alkyl methacrylate)s typically produces the monomer as a result of depolymerization. The formation of cyclic anhydride-type structures by intramolecular cyclization is another main process in the 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 of the kinetics of the thermal degradation of polymers, we can select isothermal thermogravimetry (ITG) or thermogravimetry (TG) at various heating rates.[49] ITG is superior for obtaining an accurate activation energy for thermal degradation, although it is time-consuming. For the thermal degradation of polymers, in which depolymerization is competing with cyclization or crosslinking due to the side groups, TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in this work, TG curves at various heating rates were obtained, and the activation energies (ΔE_d) for the thermal degradation of the polymers were calculated

TABLE 4 Some TGA Result of the Copolymers

	The Temperature (%) for a Weight Loss of the Residue (%)				
Polymer	IDT (%)[a]	20 °C	50 °C	70 °C	At 450 °C
Poly(SAEMA)	317	331	440	–	48
Poly(MCMA)	301	349	392	416	8
Poly(SAEMA-*co*-MCMA)					
(20/80)	305	347	373	404	20
(48/52)	308	317	377	497	34
(70/30)	311	323	435	–	42

[a] Initial decomposition temperature.

with Ozawa plots, which are widely used. Degradations were performed in the scanning mode, from 35 to 500 °C, under a nitrogen flow (20 mL min^{-1}), at various heating rates (7.0, 10.0, 15.0, and 20.0 °C min^{-1}). In Figure 8, the TGA thermograms of poly (SAEMA-*co*-MCMA) (0.70:0.30) are shown. Samples (5–8 mg) held in alumina open crucibles were used, and their weights were measured as a function of the temperature and stored in a 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 personal computer at various temperatures.

According to the method of Ozawa,[50] the apparent thermal decomposition activation energy (E_d) can be determined from the TGA thermograms at various heating rates, such as those in Figure 9, and with the following equation:

$$E_d = -\frac{R}{b}\left[\frac{d\log\beta}{d(1/T)}\right] \tag{9}$$

where R is the gas constant; b is a constant (0.4567); and β is the heating rate (°C/min). According to eq 9, the activation energy of degradation can be determined from the slope of the linear relationship between log β and the reciprocal of the temperature, as shown in Figure 8; the ΔE_d values for the polymers are given in Table 5. ΔE_d calculated from the

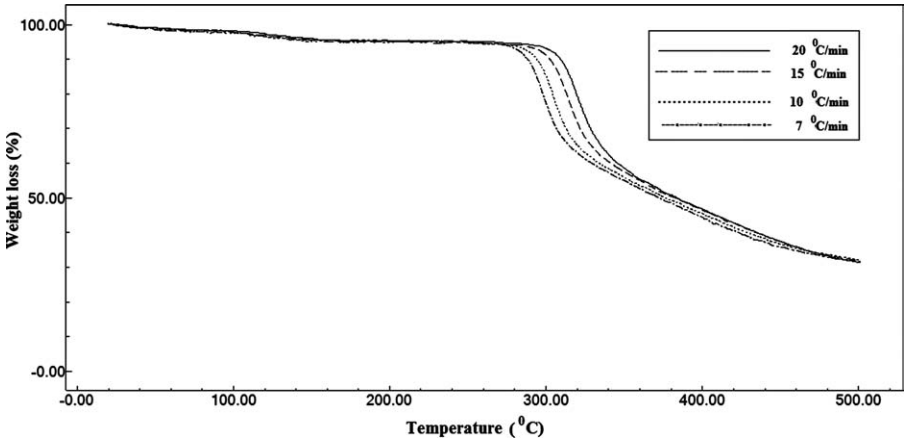


FIGURE 8 Thermal degradation curves of poly(SAEMA-*co*-MCMA) (0.48:0.52) at different heating rates.

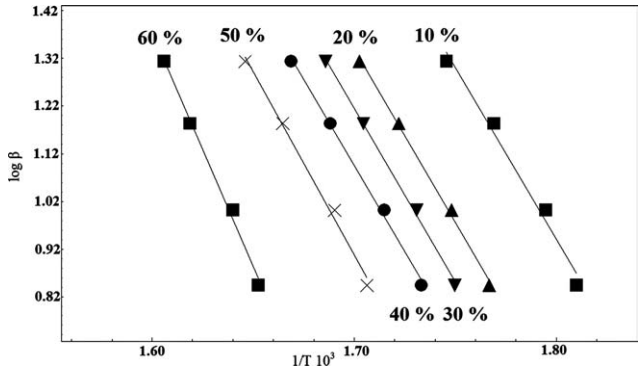


FIGURE 9 Ozawa plots of the logarithm of the heating rate (log β) versus the reciprocal of the temperature (1/T) at different conversions for poly(SAEMA-*co*-MCMA) (0.48:0.52).

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.[51] Therefore; ΔE_d calculated from the Ozawa method is superior to the former methods for complex degradation.

Antimicrobial Activity of the Polymers

The homopolymers and copolymers thus obtained, were tested against different microorganisms that are commonly employed in biodegradability examinations. The results were standardized against penicilin G and teicoplanin under the same conditions. All the compounds exhibited moderate activity comparable to that of the standard drugs. The data reported in Table 6 and are the average data of three experiments. The results show that the investigated polymers have good biological activity comparable with that of standard drugs such as penicilin G and teicoplanin. The results suggest that the monomers, polymers, and the some copolymers have good biological activity on the *E. coli* microorganisms in comparison with standard drugs. Consequently, the peculiar chemical structure of these copolymers with sulfonamides with mutual lipophilic and hydrophilic groups may have the proper combination of surface activity and bacterial effect. Although the lipophilic portion of the surfactant is important to biological function in general, the polar group contributes to biocidal activity. Thus, the activity of these compounds may allow to design surfactant and antimicrobial systems specifically effective against certain microorganisms and for

TABLE 5 The Apparent Activation Energies of Investigated Copolymers under Thermal Degradation in N_2

	Activation Energy (kJ/mol) Conversion (%)								
Sample	10	20	30	40	50	60	70	80	90
Poly(SAEMA)	162.8	163.4	166.7	160.8	156.7	–	–	–	–
Poly(MCMA)	116.4	92.0	78.4	86.6	90.8	98.4	100.2	84.0	87.3
Poly(SAEMA 20%-*co*-MCMA)	121.4	96.7	112.2	98.0	125.8	105.8	119.0	–	–
Poly(SAEMA 36%-*co*-MCMA)	129.4	114.6	121.1	117.2	133.5	119.2	–	–	–
Poly(SAEMA 48%-*co*-MCMA)	132.6	137.0	139.2	133.6	139.1	149.8	–	–	–
Poly(SAEMA 60%-*co*-MCMA)	139.5	136.2	138.8	134.2	141.6	–	–	–	–
Poly(SAEMA 70%-*co*-MCMA)	154.7	153.5	158.2	163.3	147.9	–	–	–	–

TABLE 6 Antimicrobial Effects of the Compounds (mm of Zones)

Compounds	*Pseudomonas aeruginasa*	*Escherichia coli*	*Proteus vulgaris*	*Salmonella enteridis*	*Klebsiella pneumoniae*	*Staphylococcus aureus*	*Candida albicans*
SAEMA	27	35	25	19	28	29	28
Poly(SAEMA)	23	34	23	17	26	24	25
Poly(SAEMA-*co*-MCMA)							
20/80	23	24	17	–	19	21	–
36/64	25	28	–	14	–	22	23
48/52	27	31	19	16	22	24	–
60/70	–	33	20	–	24	–	24
70/30	28	34	22	17	25	26	–
Penicillin G	16	12	9	16	18	17	35
Teicoplanin	18	18	11	22	25	12	15
DMSO	–	–	–	–	–	–	–

Compound concentration: 100 μg/disc; the symbol (–) reveals that the compounds have any activity against the microorganisms. DMSO, dimethylsulfoxide (control).

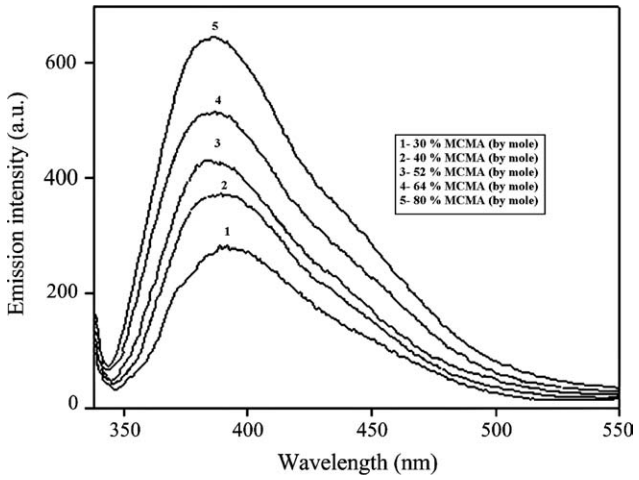


FIGURE 10 Emission spectra of polymers in DMF, $\lambda_{ex} = 320$ nm.

probably certain health care, food services, and other practical applications.

Photophysical Properties

UV-vis absorption spectra of the copolymers were recorded in DMF solutions. In these measurements 7×10^{-5} M solutions of each polymer was used. Obviously the spectrum of these structures two intense absorption bands at 272 and 313 nm. Of these absorption bands $\lambda_{max} = 272$ nm corresponds to the sulfonamide structure and $\lambda_{max} = 313$ nm corresponds to the coumarin chromophore. As expected an increase in the quantity of the coumarin leads an increased coumarin absorption and decreased sulfonamide absorption. Fluorescence emission spectra for 7×10^{-5} M solutions of polymers are shown in Figure 10. Excitation of the polymer series at $\lambda_{ex} = 320$ nm (maximum absorption wavelength for coumarin) showed a strong fluorescence peak at about 385 to 386 nm, which was the charactesistic fluorescence peak of the coumarine chromophore.[52] Furthermore, it showed that there was an apperent increase in the fluorescence intensity from the 30% coumarine to the 80% coumarine containing polymers.

CONCLUSIONS

The synthesis of new methacrylate monomers (SAEMA) having pendant sulfonamide and MCMA pendant coumarine ring moieties have been reported for the first time. The structure of monomers and their polymers were characterized by spectroscopic methods. Copolymers of SAEMA with MCMA were prepared by free-radical polymerization in 1,4-dioxane at 65 °C. The reactivity ratios of the copolymers were estimated with linear graphical methods. The reactivity values r_1 and r_2 are smaller than 1, and this indicates that the system copolymerizes statistically. GPC data imply that the polydispersity index of the copolymers is nearly equal to 2, and this implies a strong tendency for chain termination by disproportionation. *Tg* of the copolymers increased with increasing MCTMA content in the copolymers. The activation energy of the decomposition of the investigated polymers was calculated by the Ozawa method with the TGA data. The polymers have good biological activity comparable with that of standard drugs such as penicilin G and teicoplanin.

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