Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Ibrahim Erol[a]; Ozkan Sen[a]; Cemal Cifci[a]; Zeki Gurler[b]
[a] Department of Chemistry, Faculty of Science and Arts, University of Afyon Kocatepe, Afyonkarahisar, Turkey [b] Department of Food Hygiene and Technology, Faculty of Veterinary, University of Afyon Kocatepe, Afyonkarahisar, Turkey

Online publication date: 30 August 2010

To cite this Article Erol, Ibrahim , Sen, Ozkan , Cifci, Cemal and Gurler, Zeki(2010) 'New Methacrylate Copolymers Based on the Benzofurane Ring: Synthesis, Characterization, Monomer Reactivity Ratios and Biological Activity', Journal of Macromolecular Science, Part A, 47: 10, 1032 — 1041
To link to this Article: DOI: 10.1080/10601325.2010.508015
URL: http://dx.doi.org/10.1080/10601325.2010.508015

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2010) **47**, 1032–1041

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2010.508015

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New Methacrylate Copolymers Based on the Benzofurane Ring: Synthesis, Characterization, Monomer Reactivity Ratios and Biological Activity

IBRAHIM EROL[1,*], OZKAN SEN[1], CEMAL CIFCI[1] and ZEKI GURLER[2]

[1]*Department of Chemistry, Faculty of Science and Arts, University of Afyon Kocatepe, Afyonkarahisar, Turkey*
[2]*Department of Food Hygiene and Technology, Faculty of Veterinary, University of Afyon Kocatepe, Afyonkarahisar, Turkey*

Received February 2010, Accepted May 2010

The free radical copolymerization of (5-bromo-1-Benzofuran-2-yl)(phenyl)-O-methacrylketoxime (BPMKO) with 2-(4-acetyl-phenoxy)-2-oxoethyl-2-methylacrylate(AOEMA) has been carried out in 1, 4-dioxane at 65°C ± 1 and was analyzed by Fourier transform infrared, ^{1}H-NMR, ^{13}C-NMR and gel permeation chromatography. Elemental analysis was used to determine the molar fractions of BPMKO and AOEMA in the copolymers. The monomer–reactivity ratios were calculated according to the general copolymerization equation using Kelen-Tüdõs and Finemann-Ross linearization methods. The reactivity ratios indicated a tendency toward random copolymerization. The polydispersity indices of the polymers were determined by gel permeation chromatography and 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 BPMKO content in the copolymers. All the products showed moderate activity against different strains of bacteria and fungi.

Keywords: Antimicrobial activity, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), benzofurane, methacrylate, monomer reactivity ratios, radical polymerization

1 Introduction

Polymethacrylates with keto side chains have attracted increasing interest (1, 2). Polymers with carbonyl functional groups have been particularly interesting because they being used as photoresists to make large-scale integrated circuits, printing plates, photocurable coatings (3, 4), photoconductors (5), energy-exchange materials (6), enzyme fixing materials (7), protecting groups in organic syntheses (8), and photosensitizers (9) of organic syntheses (10).

Acrylate and methacrylate polymers have figured prominently in the development of soft-tissuecompatible materials (11) and orthopedic (12) and dental cements (13). Acrylate- and methacrylate-activated vinyl esters are readily polymerized by free-radical polymerization to form linear, branched, and network polymers (14). The hydrophilic/hydrophobic balance, charge type, and concentration in the polymer may be adjusted by the simple copolymerization of acrylate or methacrylate monomers bearing different substituents (15).

The benzofuran ring system itself is a common structural element that appears in a large number of medicinally important compounds (16). Benzofuran neolignans and nor-neolignans, which are contained in most plants, have attracted much attention in medicinal chemistry for their wide range of various biological activities including insecticidal, fungicidal, antimicrobial and antioxidant properties (17). Melatonin is a derivative of benzofuran and appears to play an important role in the regulation of mammalian circadian rhythms and reproduction functions then it has been implicated in a number of pathological states suggesting its therapeutic application in several disorders (18–21).The benzofuran type ring structures occur extensively among natural products, e.g. furocoumarins and furanoquinoline alkaloids (22). Benzofuran derivatives are useful intermediates for the synthesis of drugs; it is also an intermediate for the synthesis of 4-hydroxyindole, which is a key intermediate for the synthesis of an arrhytmic agent, Pindalol (23).

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

*Address correspondence to: Ibrahim Erol, Department of Chemistry, Faculty of Science and Arts, University of Afyon Kocatepe, Afyonkarahisar, Turkey. Tel: +90-272-2281339/216; Fax: +90-272-2281235; E-mail: ierol@aku.edu.tr, iberol@hotmail.com

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 determined parameters to be determined (24, 25). 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 (26,27), 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.

BPMKO and AOEMA are functional methacrylate monomers. BPMKO is new methacrylate monomers bearing benzofuarane ring and oxime ester groups. AOEMA is a new methacrylate monomers having pendant ketone group and synthesized as in the literature (28).

In this work, the results of the radical copolymerization of BPMKO with AOEMA, the determination of the monomer reactivity ratios with elemental analysis, the effects of the copolymer composition/thermal behavior relationships, and an investigation of the biological activity properties are presented and discussed.

2 Experimental

2.1 Materials

Methacryloyl chloride (Merck) were used as received. Ethanol, acetone, chloroform, n-hexane and benzene were freshly distilled over Molecular Sieves prior to use.

1,4-dioxane, acetonitrile and potassium carbonate (Merck) were used as received. (5-Bromo-1-benzofuran-2-yl)(phenyl)methanone and (5-bromo-1-benzofuran-2-yl)(phenyl)methanone oxime were prepared as reported (29). 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.

2.2 Measurements

Infrared spectra were obtained with a Perkin-Elmer 460 Fourier transform infrared (FTIR) spectrometer with KBr pellets in the 4000–400 cm^{-1} range, and 10 scans were taken at a 4-cm^{-1} resolution. ^{1}H-NMR and ^{13}C-NMR spectra in DMSO solutions were recorded on a Bruker GmbH DPX-400 400 MHz FT-NMR spectrometer with tetramethylsilane as an internal reference. The molecular weights [weightaverage molecular weight (Mw) and numberaverage 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 an N_2 atmosphere. Elemental analyses were carried out with a Elementar CHNS microanalyzer.

2.3 Synthesis of the BPMKO Monomer

Synthesis of (5-bromo-1-Benzofuran-2-yl)(phenyl)-O-methacrylketoxime (BPMKO) was as follows: (5-bromo-1-benzofuran-2-yl)(phenyl)methanone oxime (1 mol) and K_2CO_3 (1 mol)were dissolved in 20 ml of CH_2Cl_2 at 0°C, and then methacryloyl chloride (1.1 mol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 24 h. The organic layer was washed several times with diethyl ether and dried over $MgSO_4$. After removing diethyl ether, (5-bromo-1-benzofuran-2-yl)(phenyl)-O-methacrylketoxime (BPMKO) was crystallized from ethanol. The yield was about 85%.

IR (neat), cm^{-1}: 1761 (C=O for oxime ester), 1674 (C=N), 3061 (Aromatic C-H), 1635 (C=C).

^{1}H-NMR (δ, ppm from TMS in DMSO): 6.9–7.8 (aromatic protons, 9H); 5.6 (CH_2 =, 1H); 5.8 (CH_2 =, 1H); 1.8 (CH_3−, in olefinic carbon, 3H).

^{13}C-NMR (δ, ppm from TMS in DMSO): 174.2 (C=O of oxime ester); 138.0 (=C); 124.1 (CH_2 =); 155.4, 17.7 (CH_3), 110–135 (Aromatic carbons).

2.4 Polymerization of the BPMKO Monomer

Polymerization of (BPMKO) was 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 cycles and then immersed in an oil bath at 60°C for a given reaction time. The polymers were separated by precipitation in ethanol and reprecipitated from 1,4-dioxane solution. The polymers were finally dried under vacuum to a constant weight at room temperature and kept in a desiccator under vacuum until use.

2.5 Copolymerization

Copolymerizations of BPMKO with AOEMA, with six different feed compositions were carried out in 1, 4-dioxane at 60°C with AIBN (1%, based on the total weight of the monomers) as an initiator. Appropriate amounts of BPMKO with AOEMA in 1,4-dioxane was mixed in a polymerization tube, purged with N_2 for 20 min, and kept at 60°C in a thermostat. The reaction time 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

Table 1. Monomer compositions in feed and in the copolymer

	Feed composition (mol fraction)				*Copolymer composition (mol fraction)*	
Sample	*BPMKO (M_1)*	*AOEMA (M_2)*	*Conv. (%)*	*Elemental nitrogen(%)*	*BPMKO(m_1)*	*AOEMA(m_2)*
1	0,90	0,10	7.50	0,29	0,059	0,941
2	0,75	0,25	8.50	0,75	0,150	0,850
3	0,60	0,40	7.50	1,35	0,286	0,714
4	0,50	0,50	9.50	1,76	0,390	0,610
5	0,30	0,70	9.00	2,49	0,597	0,403
6	0,15	0,85	7.50	2,81	0,694	0,306

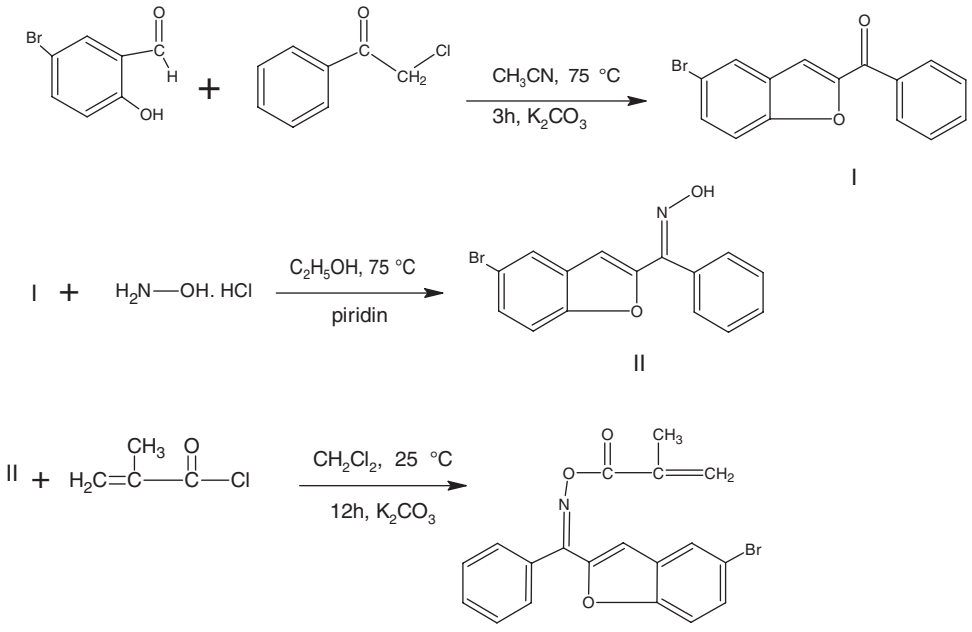
method. After the desired time, the copolymerization was stopped. These copolymers were poured into excess ethanol to precipitate, then filtered and purified by repeated reprecipitation from a solution of each polymer in 1,4-dioxane by ethanol at last dried in a vacuum oven at 60°C to a constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis (N content for BPMKO units). The results are presented in Table 1.

3 Results and Discussion

As shown in Scheme 1, we propose a new route for the new methacrylate having pendant benzofurane and oxime ester moieties monomer which was synthesized from (5-bromo-1-benzofuran-2-yl)(phenyl)methanone with methacryloyl chloride, according to the usual method (30). The yields of the reactions in Scheme 1 are of medium quantity (80%). The structure of BPMKO was identified by elemental analysis, IR and NMR spectroscopy and the results were in good agreement with the structure of the compounds.

3.1 Structural Characterization of the poly(BPMKO)

The FTIR spectrum of the poly(BPMKO) showed some characteristic absorption peaks at 1774 cm^{-1} (oxime ester carbonyl stretching) and 1660 cm^{-1} (C=N stretching). During the polymerization of the monomers, the IR band at 1630 cm^{-1} (C=C) disappearance and oxime ester carbonyl stretching for polymers shifted to about 1760 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 ^1H and ^{13}C-NMR spectrum of the BPMKO is presented in Figure 1 and they are in good agreement with the structure. From ^1H-NMR spectroscopy, the



Sch. 1. Synthesis of the BPMKO monomer.

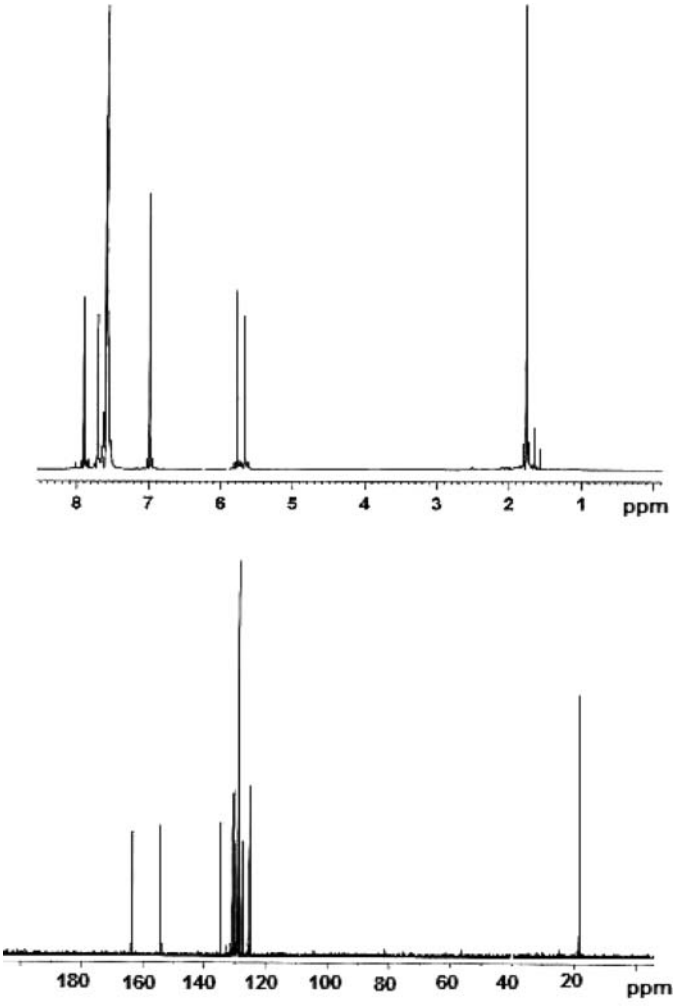


Fig. 1. FTIR spectrum of BPMKO monomer.

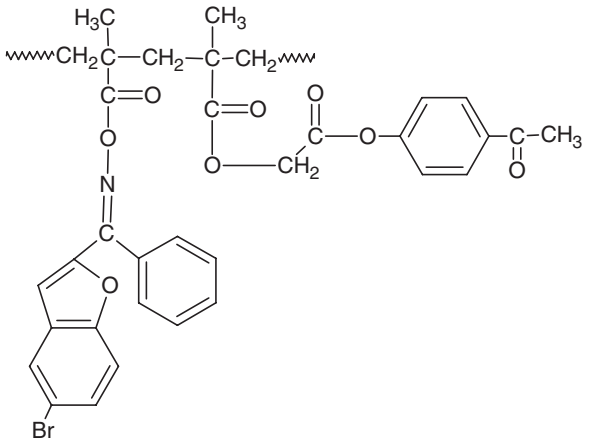
formation of the polymer is also clearly evident from the vanishing of two singlet at 5.6 and 5.8 ppm of the vinyl protons and the appearance of the broad signal at 1.5 and 2.2 ppm assigned to an aliphatic $-CH_2-$ group. In the proton decoupled ^{13}C-NMR spectrum of poly(BPMKO), chemical shift assignments were made from the off-resonance decoupled spectra of the polymer. Resonance signals at 170 ppm correspond to the oxime ester group present in the polymer. The aromatic carbons are observed at 125–135 ppm. The α-methyl group of polymer shows resonance signals at 18 ppm.

3.2 Characterization of the Copolymers

The constituent monomeric units of the copolymer are shown in Scheme 2.

3.2.1. *Solubility*

The solubility of the homopolymers and copolymers was tested via the mixing of 12 mg of each polymer with



Sch. 2. The formula of the copolymers.

4 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 dimethylacetamide, dimethylformamide, dimethyl sulfoxide (DMSO), dichloromethane, but they were insoluble in n-hexane, n-heptane, ethanol, and methanol solvents.

3.2.2. *Spectroscopic Characterization*

The FT-IR spectra of the BPMKO-AOEMA copolymers show characteristic bands at 1742 and 1745 cm^{-1} (esters carbonyl of AOEMA), 1652 cm^{-1} (C=O of AOEMA), 1780 cm^{-1} (oxime esters carbonyl of BPMKO), 1573 cm^{-1}(−C=N), 3100–3000 cm^{-1} and 1610 cm^{-1} (aromatic). The ^{1}H-NMR spectrum of poly(BPMKO-co-AOEMA) (Fig. 2) is consistent with is chemical structure. Multiplet resonance absorptions at 7.2–8.0 ppm are due to the aromatic protons of BPMKO and AOEMA units. The signals at 4.8 ppm are due to $-OCH_2$ protons. The backbone methylene protons of the two comonomer units are observed between 1.0–2.2 ppm. ^{13}C-NMR spectrum of BPMKO-AOEMA copolymer the resonance signals at 167, 168 and 169 ppm are due to the oxime ester and methacrylic esters carbonyl carbons, respectively. The ketone carbonyl of AOEMA units observed at 160 ppm. The group of signals at 127–135 ppm arises from aromatic carbons in the two monomeric units. The signals at 67 ppm are due to the $-OCH_2$ carbons of AOEMA unit. The backbone methylene carbons of two comonomer units are observed at 47 ppm. The signal at 18 ppm corresponds to the α-methyl carbons of both monomeric unit.

3.2.3. *Molecular Weights of the Polymers*

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard solvent, respectively. The *M*w and *M*n values and polydispersity indices (*M*w/*M*n) of the polymer samples are presented in Table 2. The polydispersity index of the polymers ranges from 1.61 to 1.78. The theoretical values

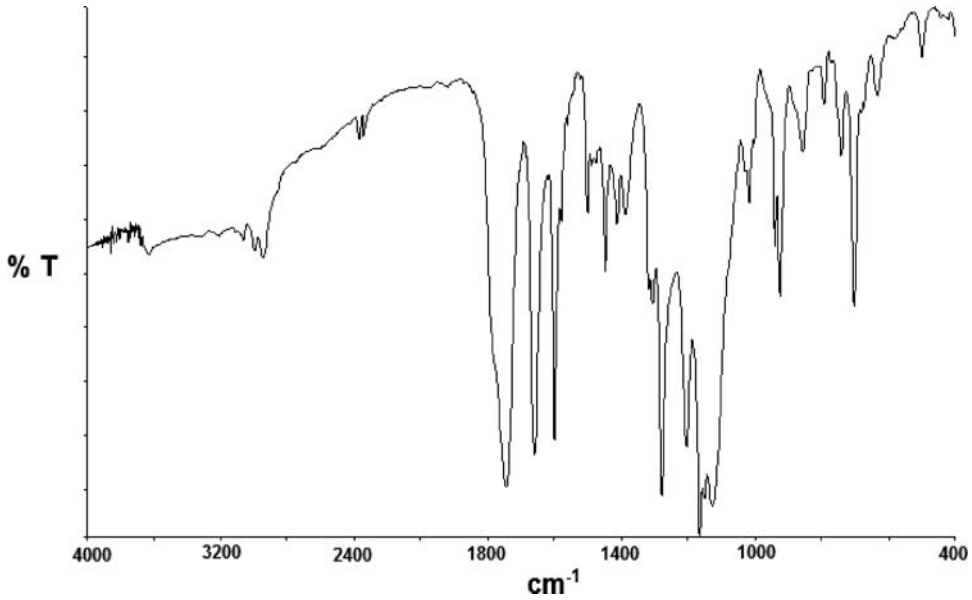


Fig. 2. ^{1}H-NMR spectrum of poly (BPMKO co-AOEMA); m_1:m_2: [15:85].

of Mw/Mn for the polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (31). The values of *M*w/ *M*n in copolymerization are also known to depend on chain termination in the same way as in homopolymerization (32).

3.3 Determination of the Monomer Reactivity Ratios

Copolymerization of BPMKO with AOEMA in 1,4-dioxane solution was studied for a molar fraction of BPMKO from approximately 0.85 to 0.10 in the feed. The amounts of monomeric units in the copolymers were determined by elemental analysis. The monomer reactivity ratios for the copolymerization of BPMKO with AOEMA 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 3. According to the FR method, the monomer reactivity ratios can be obtained as follows:

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

Where r_1 and r_2 correspond to the BPMKO and AOEMA 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

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

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.

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

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

Table 2. Molecular weights, polydispersity index and Tg values of polymers

Sample	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	$\bar{M}_w/\bar{M}_n$	*Tg*
Poly(BPMKO)	8.12	4.80	1.69	136
Poly(AOEMA)	11.13	6.75	1.65	90
Poly(BPMKO-co-AOEMA)				
6/94	6.45	3.87	1.66	94
15/85	7.88	4.90	1.61	100
29/71	8.50	5.21	1.63	109
39/61	6.45	3.80	1.69	118
60/40	7.50	4.20	1.78	125
69/31	7.20	4.20	1.71	132

Table 3. F-R and K-T parameters for poly(BPMKO-co-AOEMA) systems

Sample no.	$F=M_1/M_2$	$f=m_1/m_2$	$G=F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\varepsilon=H/(\alpha+H)$
1	0,111	0,063	–1,662	0,197	–0,890	0,106
2	0,33	0,176	–1,559	0,630	–0,678	0,274
3	0,666	0,400	–1,000	1,112	–0,359	0,399
4	1,000	0,640	–0,563	1,563	–0,174	0,483
5	2,333	1,481	0,758	3,675	0,142	0,688
6	5,666	2,268	3,168	14,156	0,200	0,894

$\alpha = (H_{max}.H_{min})^{1/2} = 1.670$.

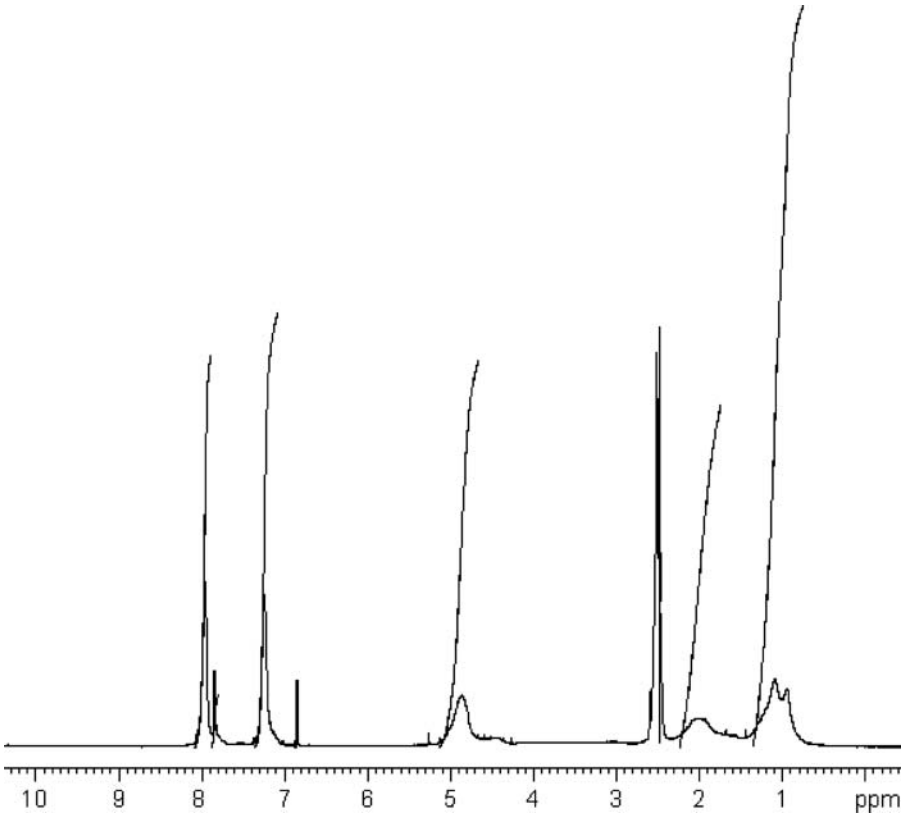


Fig. 3. ^{1}H-NMR spectrum of poly (BPMKO co-AOEMA); m_1:m_2: [60:40].

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

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

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:

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

The graphical plots concerning the methods previously reported are given in Figure 3(a,b), whereas the reactivity ratios are summarized in Table 4. 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.

Table 4. Copolymerization parameters for the free-radical copolymerization of BPMKO with AOEMA[a]

Methods	r_1	r_2	r_1r_2	$1/r_1$	$1/r_2$
F-R	0.33 ± 0.012	1.32 ± 0.011	0.44	3.03	0.76
K-T	0.49 ± 0.010	1.67 ± 0.015	0.81	2.04	0.60
Average	0.41 ± 0.011	1.50 ± 0.013	0.62	2.44	0.67

[a]r_1 and r_2 are the monomer reactivity ratios for BPMKO and AOEMA, respectively.

The difference in the reactivity ratio values obtained by the FT and KT methods is negligible. The reactivity of growing radicals with BPMKO unit, as measured by $1/r_2$ seems to be higher toward AOEMA monomer than its own monomer. The higher r_2 value of AOEMA confirms the higher reactivity of AOEMA compared with that of BPMKO. Although the reactivities of growing radicals with the AOEMA ends are higher toward BPMKO than AOEMA, the reactivity of growing radicals with the BPMKO end is higher toward AOEMA than BPMKO. The reactivity ratio values ($r_1$and r_2) of copoly(-BPMKO-co-AOEMA) are less than one. The product $r_1 . r_2$ indicates that the two systems copolymerize randomly in the polymer chain although there is a possible tendency for alternation. For both systems, r_1 and r_2 values strongly suggest that the copolymer chain contains a greater number of AOEMA units and less BPMKO units than in the feed.

3.4 Glass Transition Temperatures

The Tg values of poly(BPMKO) and poly(AOEMA) obtained under the same conditions with the copolymers were found as 136°C and 90°C, respectively. The glass transition temperature of poly(BPMKO) is considerably higher than the other polymers. The Tg value of poly(BPMKO)

is higher than the other methacrylate polymers. Apparently the bulky benzofurane and C=N side group decreases the flexibility of the chain and the free volume, thereby increasing Tg. Tg values for both copolymer systems ranged between the values of the two homopolymers. The Tg values of the copolymers increase with an increase in the BPMKO 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 BPMKO content in the polymer chain. The observed Tg values increase with increasing BPMKO 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 BPMKO and AOEMA units. The DSC thermograms of the polymers indicatedendothermic degradation. Representative DSC thermograms of the polymers are given in Figure 5. The Tg values of the copolymers are indicated in the Table 2.

3.5 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 4, the TGA thermograms of the polymers are shown. 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 ester)s.

It is clear that two degradation stages are observed for poly (BPMKO). The initial decomposition temperatures of poly (BPMKO) are around 260°C, 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 (BPMKO) occurred in three stages. The first stage was observed 260–300°C. The second stage decomposition commenced at 320–380°C and the last stage was observed 390–450°C. The degradation of poly(AOEMA) occurred in three stages. The first stage was observed 290–355°C. The second stage decomposition commenced at 360–410°C, and the last stage was observed 415–490°C. The thermal stabilities of two copolymers are between those of the corresponding homopolymers. The copolymers samples showed also two decomposition steps. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymer. The initial decomposition temperature and thermal stability of the BPMKO-AOEMA copolymers increases with an increase in the AOEMA monomers concentration. The thermal stability of the BPMKO-AOEMA copolymer systems

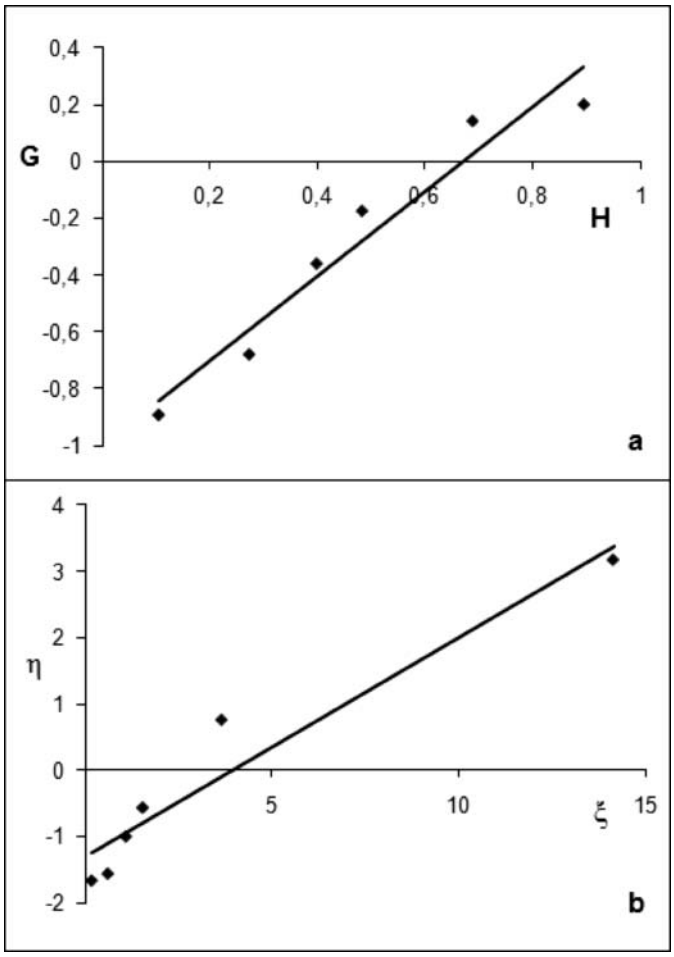


Fig. 4. K-T and F-R plot for poly (BPMKO co-AOEMA) system.

increases with an increase in the AOEMA units in the copolymers.

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 (33). 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 (ΔEd) for the thermal degradation of the polymers were calculated 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 5, the TGA thermograms of poly (BPMKO-co-AOEMA) (0.50:0.50) are shown. Samples (5–8 mg) held in alumina open crucibles were used, and their weights were measured as a function of the temperature

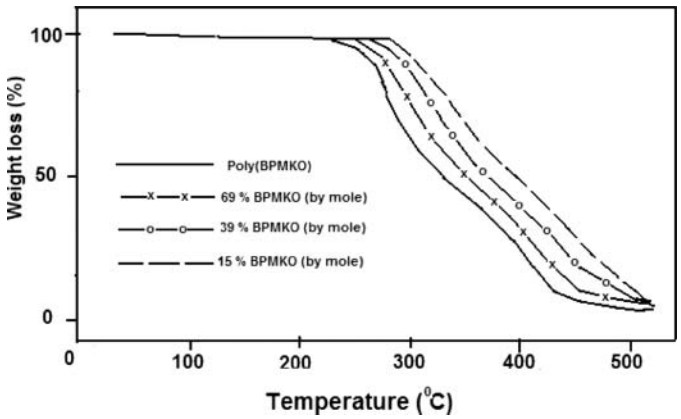


Fig. 5. TGA curves for poly(BPMKO co-AOEMA) and some copolymers.

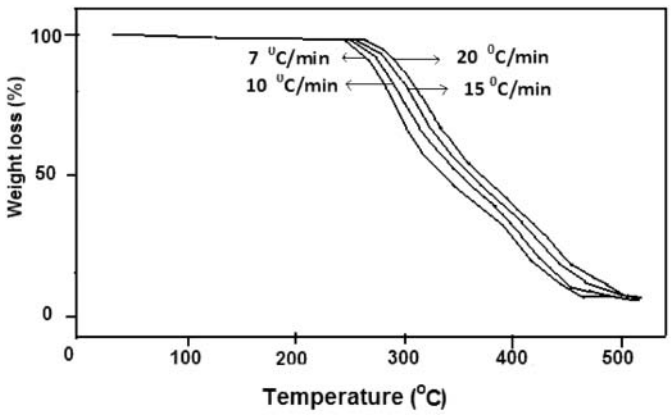


Fig. 6. The thermal degradation curves of poly (BPMKO co-AOEMA) at different heating rates. m_1:m_2: [39:61].

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 (34), the apparent thermal decomposition activation energy (Ed) can be determined from the TGA thermograms at various heating rates, such as those in Figure 6, and with the following equation:

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

Where R is the gas constant; b is a constant (0.4567); and β is 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 the reciprocal of the temperature, as shown in Figure 6; the ΔEd values for the polymers are given in Table 5. ΔEd 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 (35). Therefore; ΔEd calculated from the Ozawa method is superior to the former methods for complex degradation (Fig. 7).

3.6 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 concentrations was 100 μg. All microorganism strains were obtained from the Culture Collection of Microbiology Laboratory of Afyon Kocatepe University (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 (36). 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.

The antibiotic sensitivity of the polymers was tested with the antibiotic disk assay as described (37). Nutrient Agar

Table 5. The apparent activation energies of investigated copolymers under thermal degradation in N_2

Sample	*10*	*20*	*30*	*40*	*50*	*60*	*70*	*80*
Poly(BPMKO)	70.5	74.8	78.1	81.2	83.8	85.0	87.2	91.0
Poly(AOEMA)	96.7	108.4	123.4	117.3	117.2	108.1	122.3	143.9
Poly(BPMKO 6%-co-AOEMA)	95.4	103.7	119.2	100.0	113.3	105.8	118.0	141.1
Poly(BPMKO 15%-co-AOEMA)	93.4	99.6	116.1	102.9	110.5	102.2	115.8	135.0
Poly(BPMKO 29%-co-AOEMA)	88.6	93.0	111.2	118.4	105.9	104.8	110.7	129.6
Poly(BPMKO 39%-co-AOEMA)	85.5	89.2	101.8	113.2	101.6	105.0	101.1	127.2
Poly(BPMKO 60%-co-AOEMA)	81.9	85.2	96.8	115.1	97.8	101.4	95.8	119.8
Poly(BPMKO 69%-co-AOEMA)	75.4	79.1	87.3	127.6	93.6	101.9	90.0	111.9

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*
BPMKO	15	16	17	16	15	18	17
AOEMA	11	12	10	9	—	14	—
Poly(BPMKO)	13	13	12	11	12	14	14
Poly(AOEMA)	13	12	12	11	—	14	—
Poly(BPMKO-co-AOEMA)							
6/94	14	15	16	14	13	16	16
15/85	12	14	15	—	—	—	—
29/71	—	12	13	—	10	13	15
39/61	11	—	13	10	9	11	14
60/40	11	11	11	9	8	—	—
69/31	9	11	10	—	8	10	11
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).

(NA) was purchased from Merck. About 1.5 ml of each prepared different cell culture was 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 (50 and 100 μg) were placed on the surface of the agar medium (38). 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.

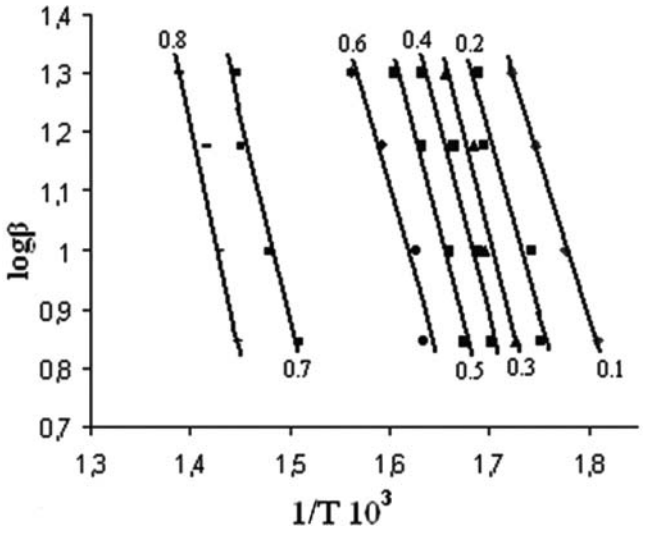


Fig. 7. Ozawa's plots of logarithm of heating rate (β) versus reciprocal temperature (1/T) at different conversions for poly(BPMKO co-AOEMA); m_1:m_2 [69:31].

Generally, monomers have higher activity than their polymers. However, poly(AOEMA) is more active against some microorganisms than AOEMA monomer in this study. This can be observed for some polymer molecules, because the ester and amide content of the poly(AOEMA) 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 antimicrobial activity.

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 are the average data of three experiments. The results show that the investigated polymers have good biological activity comparable to 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 *Staphylococcus aureus* microorganisms in comparison with standard drugs.

4 Conclusions

The synthesis of new methacrylamide monomers (BPMKO) having pendant benzofurane and oxime esters moieties have been reported for the first time. The structure of monomer and its polymer was characterized by spectroscopic methods. Copolymers of BPMKO with AOEMA 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 r_2 values were higher than the corresponding r_1 values in all

cases, and this means that a kinetic preference exists for the incorporation of AOEMA in the copolymer structure. The values strongly suggest that the growing radicals of both monomeric ends preferentially add to the AOEMA monomer, thus leading to the formation of a copolymer with a higher amount of AOEMA. 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 BPMKO 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 to that of standard drugs such as penicilin, g. and teicoplanin.

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