

SYNTHESIS AND CHARACTERIZATION OF A METHACRYLATE POLYMER WITH SIDE CHAIN KETONE AND ITS DERIVATIVES

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Abstract A new type of methacrylate monomer, 2-(4-benzoylphenoxy)-2-oxoethyl methacrylate (BOEMA) was synthesized. The radical homopolymerization of BOEMA was performed at 65°C in a 1,4-dioxane solution with benzoyl peroxide as an initiator. The oxime and thiosemicarbazone derivatives of poly[2-(4-benzoylphenoxy)-2-oxoethyl methacrylate] poly(BOEMA) were prepared with hydroxylamine hydrochloride, and thiosemicarbazone hydrochloride, respectively. The monomer and its homopolymer were characterized with Fourier transform infrared and NMR techniques. The thermal stabilities of poly(BOEMA) and its derivatives were investigated with thermogravimetric analysis and differential scanning calorimetry. The ultraviolet stability of the polymers was compared. The antibacterial and antifungal effects of the monomer and the polymer and its derivatives were also investigated on various bacteria and fungi. The activation energies of the thermal degradation of the polymers were calculated with the Ozawa and Kissinger methods.

Keywords: Acetyl group; Ethylene dimethacrylate; Oxime; Thermal stability; Biological activity; Activation energies.

INTRODUCTION

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

Acrylate and methacrylate polymers have figured prominently in the development of soft-tissuecompatible materials^[10] and orthopedic^[11] and dental cements^[12]. Acrylate- and methacrylate-activated vinyl esters are readily polymerized by free-radical polymerization to form linear, branched or network polymers^[13]. 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^[14]. Thiosemicarbazones have attracted considerable interest because of their chemistry and potentially beneficial biological activities, including antitumor, antibacterial, antiviral and antimalarial effects^[15, 16]. The potential biological activity of compounds containing sulfur and nitrogen may be responsible for this increased interest. Kinetics of thermal degradation of solids has been investigated from thermogravimetric (TG) thermograms at linear rates of temperature rise in a number of studies. Thermogravimetry is widely used as a method to investigate the thermal degradation of polymers and to determine the kinetic parameters. The thermal stability and degradation depend on the composition^[17, 18]. The methods may be best known through their most popular representatives, the methods of Kissinger^[19] and Ozawa^[20]. The isoconversional methods require performing a series of experiments at different temperature programs and yield the values of effective activation energy as a function of conversion. More often than not, the activation energy is found to vary with the extent of conversion. The full potential of

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Received December 30, 2009; Revised February 8, 2010; Accepted March 1, 2010

doi: 10.1007/s10118-010-1005-7

the isoconversional methods has been appreciated as Vyazovkin^[21] brought analysis of the Ea-dependences to the forefront and demonstrated that they can be used for exploring the mechanisms of processes and for predicting kinetics. In a previous study^[2], the synthesis and characterization of a methacrylate monomer with side chain acetyl and amide groups and its derivatives were described. We report here the preparation of a new methacrylate with ketone on the benzoyl group and ester moieties and its oxime and thiosemicarbazone derivatives. Because one aim of this article is to demonstrate the synthetic procedure and the wide variety of functional groups that can be attached to the monomer backbone, some representative experimental procedures are included for future studies.

EXPERIMENTAL

Materials

4-Hydroxy benzophenone, chloroacetyl chloride, hydroxylamine hydrochloride and thiosemicarbazide hydrochloride (Merck) were used as received. Ethanol, acetonitrile, chloroform, benzene, *n*-hexane and dichloromethane were freshly distilled over molecular sieves before use. Pyridine, dimethyl sulfoxide (DMSO), diethyl ether, 1,4-dioxane and sodium methacrylate (Aldrich) were used as received. Benzoyl peroxide (BPO) was recrystallized from ethanol. All the other chemicals were analytical grade commercial products. They were used without any further purification.

Characterization Techniques

Infra-red spectra were measured on a Perkin Elmer Spectrum BX II FTIR spectrometer. ¹H-NMR spectra were recorded in CDCl₃ with tetramethylsilane as the internal standard using a Bruker GmbH DPX-400 400 MHz spectrometer. Elemental analyses were carried out by an Elementar CHNS auto microanalyser. Thermal analysis of polymer was conducted with a Shimadzu TGA/DSC 60H at a heating rate of 20 K/min under nitrogen (99.99% purity) with aluminum pans at temperatures from ambient (25°C) to 500°C. The powdered sample, about 5–8 mg in weight was packeted into the aluminum pan, and the gas flow rate was kept at 5 L h⁻¹.

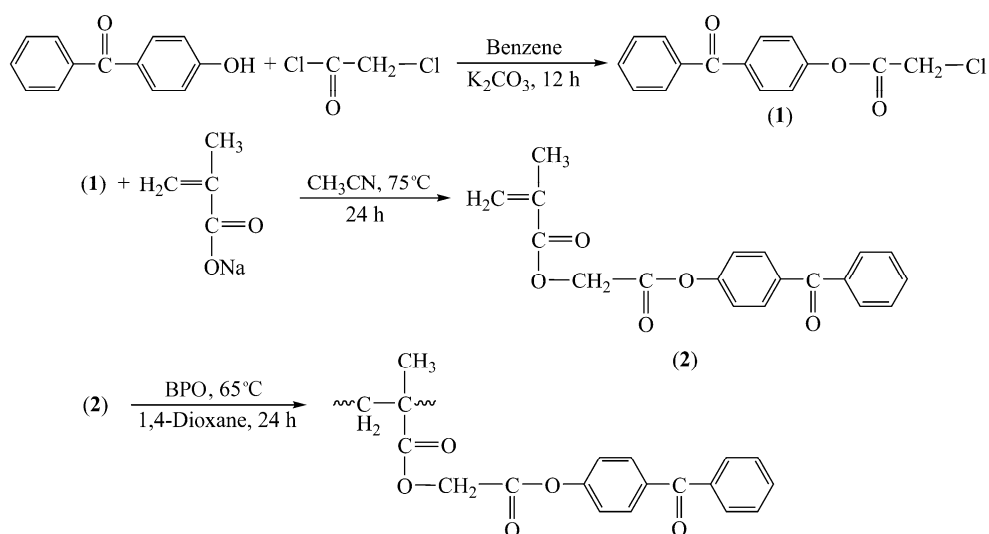
Synthesis of Monomer

The first monomer, 4-benzoylphenyl chloroacetate, was prepared through the reaction of 4-hydroxy benzophenone with chloroacetyl chloride with potassium carbonate. Chloroacetyl chloride (2.5 mmol) was added dropwise to a mixture of *p*-hydroxy benzophenone (2.5 mmol) and K₂CO₃ (2.5 mmol) in 100 mL of dried benzene at 0°C, and the reaction was stirred at room temperature for 12 h. The precipitate was filtered off, washed with water and dissolved in diethyl ether. After the benzene was evaporated, the residue was added to the ether solution, and it was dried over anhydrous MgSO₄. After the ether was evaporated, the solid products were crystallized from methanol. The yield was 88%. The second monomer was synthesized from 1 mol of 4-benzoyl phenyl chloroacetate, 1.1 mol of sodium methacrylate and 100 mL of acetonitrile in a 250 mL beaker. Hydroquinone (100 × 10⁻⁶) was added to this mixture to inhibit the polymerization of the 2-(4-benzoylphenoxy)-2-oxoethyl methacrylate (BOEMA) monomer. The mixture was stirred at 75°C for 24 h. BOEMA was extracted with diethyl ether and was dried over magnesium sulfate. Ether was evaporated, and BOEMA was recrystallized from methanol. The reactions are shown in Scheme 1. The yield was about 85%.

Elemental analysis (%): C = 70.85 (found), 70.36 (calcd), H = 4.67 (found), 4.97 (calcd).

IR (neat), cm⁻¹: 1781, 1728 (ester and methacrylic carbonyl), 1655 (acetyl carbonyl), 1634 (CH₂=C—), 1611 (C=C), 1253 (C—O—C).

¹H-NMR (δ, from TMS in CDCl₃): 1.9 (s, 3H, CH₃ on the methacrylate), 7.3–7.7 (m, 9H, aromatic protons), 5.6 (CH₂=, 1H); 6.3 (CH₂=, 1H), 4.8 (s, 2H, OCH₂).



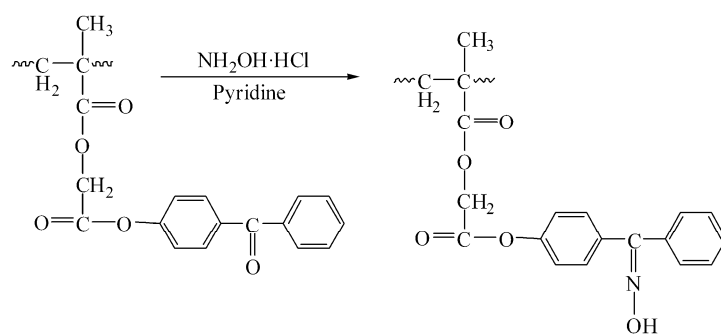
Scheme 1 Synthesis of BOEMA monomer and its homopolymer

Polymerization of the Monomer

Polymerization of BOEMA was carried out in glass ampoules under N₂ atmosphere in 1,4-dioxane solution with BPO (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 polymer was separated by precipitation in ethanol and reprecipitated from dichloromethane solution. The polymer was finally dried under vacuum to constant weight at room temperature and kept in desiccators under vacuum until use.

Preparation of the Oxime Derivative of Poly(BOEMA) (Oxime Polymer)

Poly(BOEMA) (1 g) was dissolved in 50 mL of 1,4-dioxane, 0.5 g of hydroxylamine hydrochloride and 6 mL of pyridine were added with stirring. The mixture was refluxed for 8 h and then was cooled and poured slowly into excess water. The oxime polymer was filtered off, purified by reprecipitation in ethanol from an acetone solution, and dried *in vacuo*. The reaction is shown in Scheme 2.

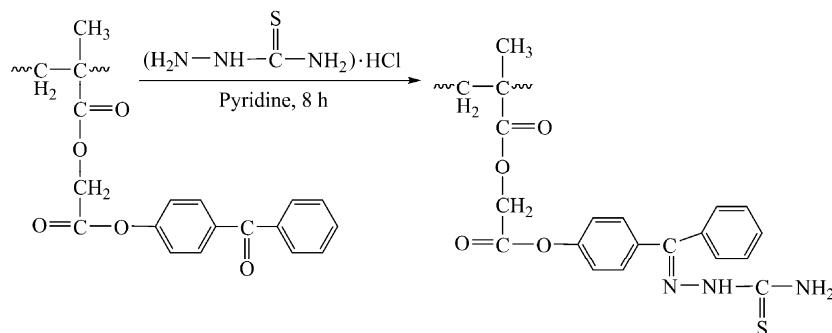


Scheme 2 Synthesis of the oxime polymer

Preparation of the Thiosemicarbazone Derivative of Poly(BOEMA) (Tsc Polymer)

A dioxane (50 mL) solution of poly(BOEMA) (0.75 g) was added drop wise to a solution of thiosemicarbazide hydrochloride (0.5 g) and pyridine in ethanol at room temperature, and the mixture was refluxed for 12 h at 70°C and then was cooled and poured slowly into excess water. The thiosemicarbazone polymer was filtered off, purified by reprecipitation in ethanol from a DMSO solution, and dried *in vacuo* at 50°C for 18 h. The

reaction is shown in Scheme 3.



Scheme 3 Synthesis of the thiosemicarbazone polymer

RESULTS AND DISCUSSION

Structural Characterization of the Monomer and Its Homopolymer

The FTIR spectrum of the BOEMA monomer is shown in Fig. 1. The IR spectrum of the polymer showed some characteristic absorption peaks at 1781 and 1728 cm^{-1} (ester and methacryl carbonyl stretching) and 1655 cm^{-1} (C=O for benzoyl). During polymerization of the monomer, the IR band at 1634 cm^{-1} (C=C) disappeared and ester carbonyl stretching for polymer 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 921 cm^{-1} assigned to the C—H bending of geminal $=\text{CH}_2$ and the stretching vibration band of C=C at 1605 cm^{-1} . The ^1H -NMR spectrum of the BOEMA monomer is in good agreement with the structure. The ^1H -NMR spectrum of the monomer has the characteristic peaks of the monomeric units. The ^1H -NMR spectrum of the monomer is shown in Fig. 2. From ^1H -NMR spectroscopy the formation of the polymer is also clearly evident from the vanishing of two singlets at $\delta = 5.6$ and 6.2 of the vinyl protons and the appearance of the broad signal at $\delta = 2.2$ assigned to an aliphatic $-\text{CH}_2-$ group.

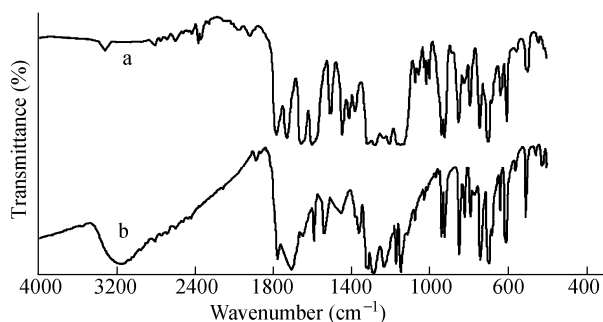


Fig. 1 FTIR spectrum of BOEMA (a) and oxime polymer (b)

Characterization of the Derivatives

Oxime and thiosemicarbazone polymers were characterized by using IR spectra. The IR spectrum of the oxime polymer is shown in Fig. 1. During the derivatization of poly(BOEMA) with hydroxylamino hydrochloride and thiosemicarbazide hydrochloride, the ketone carbonyl band at 1655 cm^{-1} disappeared, and new bands appeared at 3550–3200 (O—H, broad), 1650 (C=N) and 950 cm^{-1} (=N—O) in the oxime derivative, and at 3335 (—N—H, stretching band), 1628 (C=N) and 1154 cm^{-1} (C=S) in the thiosemicarbazone derivative.

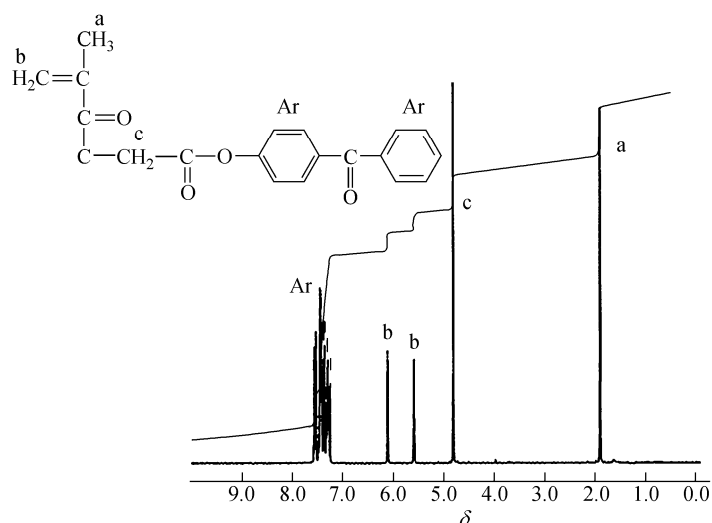


Fig. 2 ^1H -NMR spectrum of BOEMA

Glass Transition Temperatures

The glass-transition temperatures (T_g 's) of the polymers were determined by differential scanning calorimetry (DSC), which was performed at a heating rate of 20 K/min under a nitrogen atmosphere. From the DSC measurements, T_g was taken as the midpoint of the transition region. The observed T_g values were 95°C for poly(BOEMA), 117°C for the oxime polymer and 132°C for the thiosemicarbazone polymer. The T_g values of the polymers with hydrazone and thiosemicarbazone groups on the side chains were higher than those of poly(BOEMA) polymer. This effect might be attributable to bulky substituent groups; polymers bearing bulky side groups generally have a raised T_g because the moving segment for such a chain is necessarily large. However, a polymer that has high attraction forces between the chains will expand less readily than noninteracting polymers; therefore, such an interacting polymer must be heated to a higher temperature before the free volume becomes as large as required at T_g . T_g 's of the derivatives were obtained because of intermolecular and/or intramolecular hydrogen bonding. The oxime and thiosemicarbazone groups are incapable of making hydrogen-bonding interactions because of the $-\text{N}-\text{H}-$ unit. Structures having such properties reduce the flexibility of the chain and the free volume and, therefore, increase T_g . The DSC curves of poly(BOEMA) and its derivatives are shown in Fig. 3.

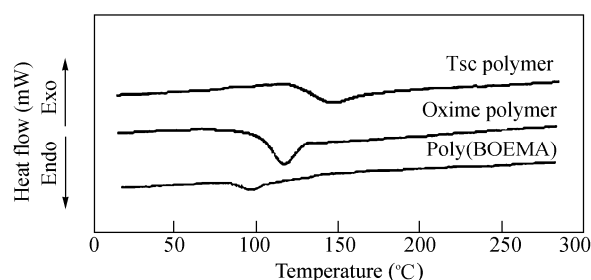


Fig. 3 DSC thermograms of polymers

Thermal Stability

The thermogravimetric (TG) curves (Fig. 4) of poly(BOEMA) and its derivatives were obtained at a heating rate of 20 K/min under nitrogen flow. The initial decomposition temperatures of poly(BOEMA) and its derivatives are around 220°C and 310°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(BOEMA) occurred in three stages. The first stage was observed at 220–350°C. The second stage decomposition commenced at 355–390°C, and the last stage was observed at 395–440°C. The derivatives polymers had initial decomposition temperatures similar to those of poly(BOEMA). The oxime and thiosemicarbazone polymers are more stable than poly(BOEMA). The derivatives have strong intermolecular and/or intramolecular hydrogen bonding between N–H and carbonyl groups. Some of the degradation characteristics are summarized in Table 1. The thermal degradation of poly-*n*-alkyl methacrylates typically produces the monomer as a result of depolymerization. The formation of cyclic anhydride type structures by intramolecular cyclization is another main process in degradation of these polymers. The latter produces some low molecular weight products, depending on the chemical structures of the side chains of methacrylate.

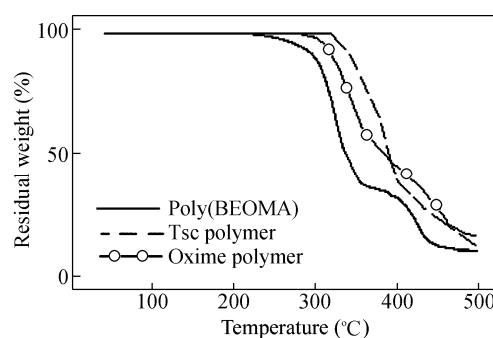


Fig. 4 TGA curves for polymers

Table 1. Some TGA results of the poly(BOEMA) and its derivatives

Polymer	IDT (°C) ^a	The temperature (°C) for a weight loss (%) of			The residue (%) at 450°C
		20	50	70	
Poly(BOEMA)	220	310	345	397	14
Tsc-polymer	317	325	388	425	19
Oxime-polymer	280	328	370	400	22

^a IDT: initial decomposition temperature

Thermal Degradation Kinetics

The degradation parameters of poly(BOEMA) and its derivatives are estimated by two methods. TGA was used to investigate the activation energies. The thermal degradation 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^[22]. The different analysis methods are described. These methods require several TGA curves at different heating rates. Hence, the dynamic thermogravimetric analysis in nitrogen of the polymers has been performed at various heating rates 7, 10, 15 and 20 K/min. Figure 5 shows the TG and DTG curves at the different heating rates of poly(BOEMA).

Kissinger method

Kissinger method has been used in the literature to determine the activation energy of solid state reactions from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The activation energy can be determined by Kissinger method without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln \frac{\beta}{T^2} = -\frac{E_a}{RT} + A \quad (1)$$

where β is the heating rate, R is the gas constant, T is the temperature and A is a constant. From a plot of $\ln(\beta/T^2)$ versus $1/T$ and fitting to a straight line, the activation energy E_a can be calculated from the slope. Using Kissinger's method the activation energy of the decomposition of poly(BOEMA) and its derivatives was calculated from a straight line fit of a plot of $\ln(\beta/T^2)$ versus $1000/T$. Figure 6 shows the Kissinger plot for

oxime-polymer. The value obtained from Fig. 6 for the activation energy for oxime-polymer was 224 kJ/mol. The E_a value of poly(BOEMA) and tsc-polymer are 195 and 238 kJ/mol respectively. From this information we can conclude that tsc-polymer and oxime polymer have a higher activation energy than that of poly(BOEMA). Thus, the derivative polymers have higher thermal resistance. The derivative polymers have side groups as oxime and thiosemicarbazone larger than those of poly(BOEMA). The tsc and oxime polymers have the OH and NH groups. There is strong hydrogen bonding between these groups in the polymer chain. For this reason the thermal stability of the derivative polymers are higher than that of the poly(BOEMA).

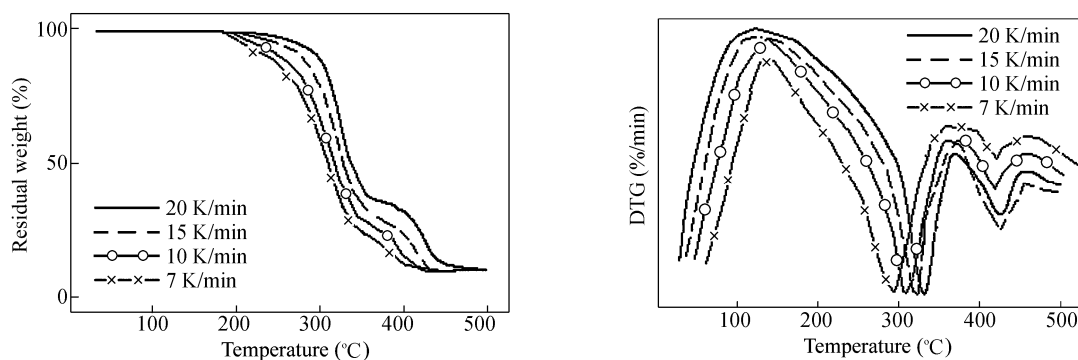


Fig. 5 Thermal degradation curves of poly(BOEMA) at different heating rates

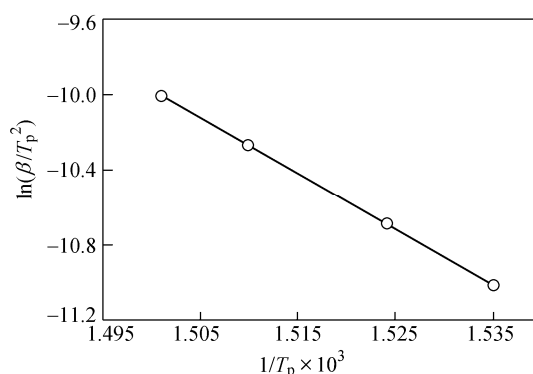


Fig. 6 Kissinger plot of oxime polymer in nitrogen atmosphere

Ozawa method

According to the method of Ozawa the apparent thermal decomposition activation energy, E_d , can be determined from the TGA thermograms under various heating rates and the following equation:

$$E_d = -\frac{R}{b} \left[\frac{d \lg \beta}{d(1/T)} \right] \quad (2)$$

where R is the gas constant; b , a constant (0.4567); and β , the heating rate (K/min). According to Eq. (2), the activation energy of degradation can be determined from the slope of the linear relationship between $\lg \beta$ and $1/T$. The results of the Ozawa analysis are given in Fig. 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 2. E_d calculated from the Ozawa method is superior to other methods for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy. Therefore, E_d calculated from the Ozawa method was superior to the former methods for complex degradation.

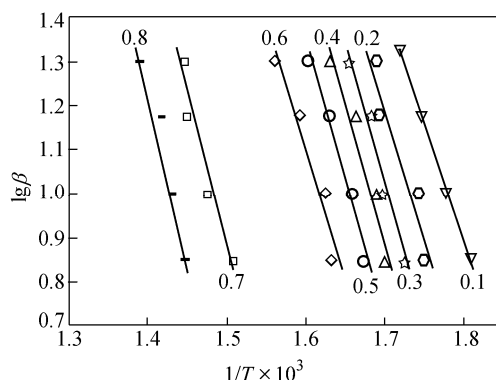


Fig. 7 Ozawa plots of the logarithm of the heating rate ($\lg\beta$) versus the reciprocal of the temperature ($1/T$) at different conversions for poly(BOEMA)

Table 2. The apparent activation energies of polymers under thermal degradation in N_2

Sample	Activation energy E_d (kJ/mol)							
	Conversion (%)							
	10	20	30	40	50	60	70	80
Poly(BOEMA)	98.73	111.79	119.36	121.21	117.25	108.19	126.18	135.45
Oxime polymer	119.23	137.24	151.83	138.55	134.26	113.78	135.13	149.39
Tsc-polymer	223.41	234.33	249.14	238.26	224.77	193.17	158.38	230.92

Ultraviolet (UV) Spectra of the Polymers

A solution of polymers in CH_2Cl_2 was cast onto a quartz glass plate with a spin coater and then was annealed for 30 min at $40^\circ C$. The thin film ($0.8\text{--}1\ \mu m$) was irradiated with a fixed energy of light from a Shimadzu 1700 spectrometer with a 450 W xenon lamp. Figure 8 compares the absorption spectra of the polymers. The maximum absorption at 240 nm showed a $\pi\text{--}\pi^*$ transition of $C=C$ of the pendant aryl group chromophore present in the polymer unit. Thus, this specific absorption spectrum of an oxime polymer suggests that the energy states of a chromophore substituted by an oxime group differ somewhat from those of other chromophores. To achieve a highly integrated chromophore system, an arrangement of the chromophores in a first-order structure of a polymer is not enough; one should resort to a higher order structure formed by the polymer^[23]. In this context, a number of studies have focused on amphiphilic polyelectrolytes carrying aromatic chromophores as pendant groups^[24]. The amphiphilic polyelectrolyte loadings are high enough that the hydrophobic chromophores are forced to be densely packed in an aqueous solution^[25].

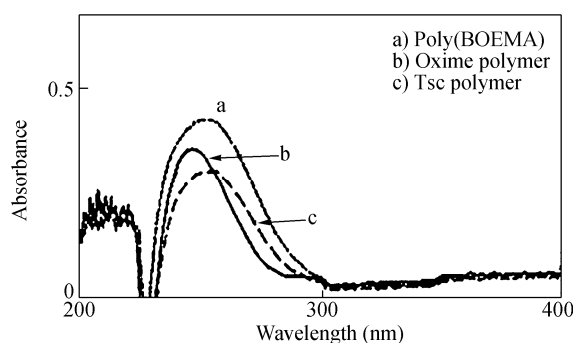


Fig. 8 The absorption spectra of the polymers

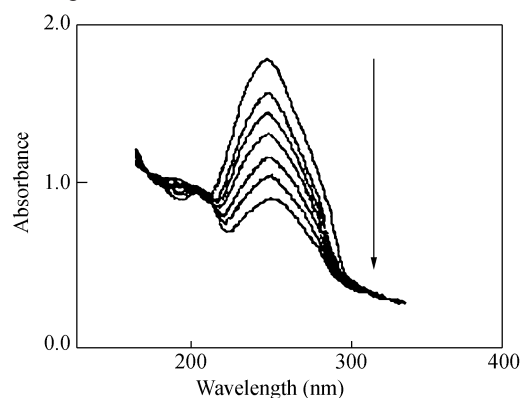


Fig. 9 UV spectral changes due to the photoreaction time of poly(BOEMA) in the film state (0, 10, 20, 40, 80, 140, and ∞ s, as direction of arrow)

To obtain more information about the UV stability of the polymers, we have investigated the structural changes of the carbonyl chromophore in polymer. For the poly(BOEMA) solution, the absorption maxima are centered at about 275 nm. Figure 9 presents a typical example for the change of UV absorption curve during photodecomposition. The carbonyl chromophore absorption band at 275 nm decreases with irradiation time. All the experimental data indicated that photodegradation in the carbonyl region occurred and crosslinking followed. Some polymers with ketone side chains displayed photodegradation^[26]. In addition, dichloromethane solutions of the polymers were cast separately onto salt plates and dried. The polymer films were irradiated with a 500 W, high-pressure mercury lamp at 254 nm. After irradiation for 12, 24, 36 and 72 h, the FTIR spectra of the polymers showed changes. A new band appearing as a shoulder at 1705 cm^{-1} was observed in the spectra of the polymers, and the absorbance of the shoulder at 1705 cm^{-1} increased relatively as that of the band at 1730 cm^{-1} decreased from 12 h to 72 h. In addition, although all of the polymers were soluble in CH_2Cl_2 , CHCl_3 , dimethylformamide, DMSO, 1,4-dioxane, and so forth before irradiation, no one of the polymers was soluble in any solvent. Although a practical evaluation from spectral data is rather dubious because the sensitivity of photocrosslinkable polymers is a function of the T_g , molecular weight, polymer solubility, and so forth, the discrimination of photoresponsibilities of the chromophores themselves is possible to a certain extent.

Biological Activity of the Polymers

Disc diffusion method was used for antimicrobial activity. In this study, *Staphylococcus aureus* ATCC 29213, *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 27853 were used as bacteria. *Candida albicans* CCM 31 was a fungus. Mueller-Hinton agar (Difco, Detroit, USA) for all bacterial strains were used. The media were melted at 100°C and after being cooled to 50°C were poured into plates of 9 cm diameter in quantities of 20 mL, and left on a flat surface to solidify and the surface of media was dried at 37°C. Then, the inoculum was prepared using a 4–6 h Mueller-Hinton broth adjusted to a turbidity equivalent to a 0.5 McFarland standard (10^8 cfu mL^{-1}). A sterile cotton swab was dipped in the inoculum and the surfaces of the Mueller-Hinton agar were inoculated by streaking the swab over the surface. The surface of the media was allowed to dry 3–5 min at room temperature. The 100 μg (in DMSO, E. Merck) compound impregnated disks were applied to the surface of inoculated plates. The Mueller-Hinton agar plates were incubated at 35°C for 18–24 h. The plates were examined and the diameter of the inhibition zone was measured^[27]. The data reported in Table 3 represent the average of three experiments. The benzene, oxime and thiosemicarbazone moiety will have electron rich as well as electron deficient centres. As the number of coumarin moiety increases, these centers also increase. The microorganism depending on its nature will attack the electron rich or electron deficient centres. In order to investigate the relationships between antimicrobial activity and structure, we have designed and synthesized a novel polymer and its derivatives with side chain ketone. It has been suggested that the poly(BOEMA) and its derivatives with N and O donor system and carboxyl and azomethine ($\text{C}=\text{N}$) groups might have inhibition on the enzyme production, which would require a free hydroxy group for their activity appear to be especially susceptible to deactivation by the donor atoms of the polymers. The results were compared with the standard drugs as penicillin G and teicoplanin. These results suggest that the thiosemicarbazone polymers have good biological activity in comparison with standard drugs such as teicoplanin and penicillin G.

Table 3. Antimicrobial effects of the compounds (mm of zones)

Compounds	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>	<i>Candida albicans</i>	<i>Staphylococcus aureus</i>
Poly(BOEMA)	14	13	—	13
Tsc polymer	21	19	17	18
Oxime polymer	15	14	—	16
Penicillin G	—	6	—	35
Teicoplanin	—	6	12	15
DMSO	—	—	—	—

Compound concentration: 100 $\mu\text{g}/\text{disc}$; the symbol (—) reveals that the compounds have no activity against the microorganisms; DMSO: dimethylsulfoxide (control)

CONCLUSIONS

The synthesis of a new methacrylate with pendant amide and acetyl groups has been reported. The structures of the monomer and polymer were characterized with spectroscopic methods. The oxime, and thiosemicarbazone derivatives of poly(BOEMA) were synthesized. The thermal stability and biological activity of the polymers were investigated. The thermal behavior of the derivatives polymers was similar to that of poly(BOEMA). The decomposition activation energies were calculated with the Ozawa and Kissinger methods. The tsc and oxime polymers have thermal stability higher than that of the poly(BOEMA). Finally, the photocrosslinking behavior of the polymers as thin films was tested in the presence of UV light. The increasing utility of photosensitive polymers in many applications, such as microelectronics, printing and UV-curable lacquers, and inks, has provided us with an incentive to obtain novel polymers. The microbial activity of the new polymer and its derivatives are investigated by disc diffusion method.

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