

Kinetic Studies on the Dilatometric-Free Radical Copolymerization of New Modified Laser Dye Monomer with Methyl Methacrylate and Characterization of the Obtained Copolymer

S. M. Sayyah,¹ M. Reahn,² A. H. M. Elwahy,³ M. T. H. Abou-Kana⁴

¹Chemistry Department, Faculty of Science, Beni Suef University, Beni-Suef, Egypt

²Deutsche Kunststoff-Institute (DKI), TU-Darmstadt, Darmstadt, Germany

³Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

⁴Laser Systems Department, National Institute of Laser Enhanced Science (NILES), Cairo University, Giza, Egypt

Received 12 May 2008; accepted 23 October 2008

DOI 10.1002/app.29475

Published online 18 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of the new modified laser dye from fluorescein ester (II) and acryloyl chloride was performed. The structure of the new monomer 2-(6-acryloyloxy-3-oxo-3H-xanthene-9-yl)-benzoic acid ethyl ester [AOXBE] was confirmed by ¹HNMR, IR, ¹³CNMR, mass spectroscopy, and elemental analysis. Free radical copolymerization of AOXBE with methyl methacrylate (MMA) was discussed using dilatometric technique. The effect of different solvents on the rate of copolymeriza-

tion reaction was carried out. The rate equation was found to be $R_p = [\text{Initiator}]^{0.5473} [\text{Monomer}]^{1.5}$. It was also noticed that the increase of AOXBE concentration in the monomer feed has an inhibition effect on the rate of copolymerization. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2462–2471, 2009

Key words: copolymerization; monomers; photochemistry; radical polymerization

INTRODUCTION

Free radical polymerization is an extensively used polymerization technique because, besides the easy manipulation, it is applicable to a great variety of monomers.^{1,2} Additionally, with random copolymerization, the range of accessible structures and properties is much broader, covering an unlimited field of possible applications. The types of available structures have recently been extended with the advent of controlled radical polymerization,^{3,4} allowing the simple synthesis of block copolymers and of polymers with more complex structures.^{5–7} Besides the exciting possibility of creating new polymers, free radical polymerization also offers the chance to better control the structural characteristics of macromolecules that have been known and applied for a long time. This has been the case for most homopolymers (styrene and derivatives, acrylates, methacrylates, . . . etc).

The large majority of the end functional oligomers described in the literature has a homopolymer type main chain. Only, few articles deal with the preparation of terminally reactive oligomers with a random

or alternating copolymer-type backbone by chain polymerization, all of them employing free radical copolymerization in the presence of a chain transfer agent.^{8–18}

Different trials of preparing laser dye monomers and their copolymerization with other vinyl monomers to produce a new type of copolymers containing the laser dyes covalently bonded in the copolymeric chains have been investigated.^{19,20} To the best of our knowledge, no one in literature has introduced fluorescein dye which is covalently bonded in a structure of macromonomer. Moreover, the kinetic studies of its copolymerization with methyl methacrylate using dilatometric free radical technique have not been reported.

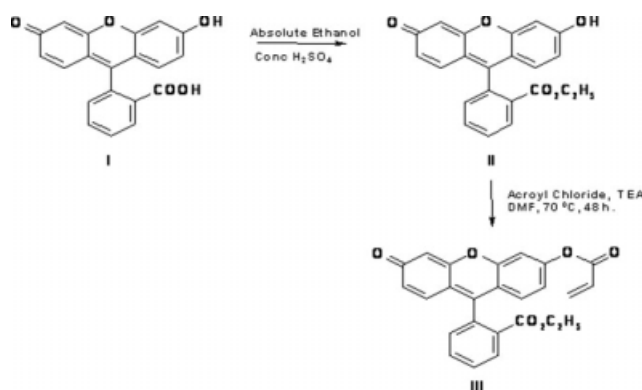
The aim of this work is to investigate the preparation of new vinyl monomer containing fluorescein moiety covalently bonded with the vinyl group and its copolymerization with methyl methacrylate. Also, characterization of the copolymer obtained should be discussed.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer was a product of Merck-Schuchardt, yield 99%, stabilized with

Correspondence to: M. T. H. Abou-Kana (mabou202@hotmail.com).



Scheme 1 Synthesis of AOXBE.

100 ppm hydroquinone, specific gravity 0.942 g/cm^3 at 20°C . It was purified as described in a previous article.²¹ Fluorescein (I) was a product of BDH, Germany. Absolute ethanol was a product of El-Nasr pharmaceutical chemical company, Egypt. It was refluxed over CaO and then doubly distilled before use. Acryloyl Chloride (AC) (Aldrich chemical Co., Milwaukee WI) was degassed and twice distilled on a vacuum line, dried over anhydrous sodium sulfate, and kept below -18°C in a tightly stoppered flask. 2,2 azobisisobutyronitrile (AIBN) (Eastman Kodak, UK) was used as an initiator for all copolymerization reactions. It was purified by dissolving it in chloroform, then filtering the solution, and finally, left to dry in a dessicator at laboratory temperature. Dimethylformamide (DMF) was a product of El-Nasr pharmaceutical chemical company (Analytical pure grade division). It was also doubly distilled before use.

Preparation of the modified laser dye monomer

We planned to construct acryloyl-substituted fluorescein [2-(6-acryloyloxy-3-oxo-3H-xanthene-9-yl)-benzoic acid ethyl ester] [AOXBE], which can be then utilized as promising monomer for the synthesis of polymer supported fluorescein. The fluorescein ester (II) was chosen as key intermediate. It was obtained by esterification of fluorescein according to the method described by Feuerstein and Dutoit.²² The synthetic procedure was as follows: solution of fluorescein ester II; (1 mmol) in dimethyl-formamide (DMF) (10 mL) containing triethyl amine (TEA) (2 mL); acryloyl chloride (1.3 mmol) was added. The reaction mixture was heated at 70°C for 48 h with continuous stirring (Scheme 1). The solid obtained upon cooling and dilution with water was collected and purified by chromatography on alumina using CH_2Cl_2 : methanol (15 : 1) as an eluent to yield orange crystals, m.p. $157\text{--}159^\circ\text{C}$.

General copolymerization process

The required amounts of the two comonomers in different molar ratios (Table I), together with the required amount of initiator (AIBN), and solvent were charged into glass vials. The vials were then closed with rubber septum through which passed two needles, one for bubbling purified nitrogen to eliminate dissolved oxygen and the second to equilibrate the pressure. The copolymerization was performed at 60°C ($\pm 0.1^\circ\text{C}$) in a water thermostat with periodical shaking for a definite time in such a way to keep always the conversion below 10%. At that time, the copolymerization reaction brought to a stop by cooling the vials in an ice-water-salt mixture followed by pouring the content into a large amount of cold methanol; the copolymers were then purified by repeated precipitation from tetrahydrofuran (THF) by methyl alcohol and then allowed to dry under high-vacuum at room temperature.

Determination of the rate of copolymerization

The rate of the copolymerization was measured dilatometrically using Pyrex glass dilatometers with calibrated and graduated capillary tubes with bulb capacity of 1–2 mL and fitted with ground joint. The monomers with the required amount of initiator were dissolved in the appropriate solvent and adjusted to 5 mL (using 5 mL measuring flask). The concentration of the monomers was determined in mol/L. The reaction mixture was transferred to the dilatometer to fill the bulb and part of the capillary tube to a constant mark. The dilatometer was then placed in a water thermostat adjusted to the required temperature ($\pm 0.1^\circ\text{C}$). The meniscus of the liquid inside the capillary tube was recorded every 2.5 min and plotted directly as volume contraction (ΔV) versus time of polymerization. At the end of polymerization time, the dilatometer was removed from the water thermostat and quickly immersed in an ice-water salt mixture to stop the radical polymerization reaction. The polymeric solution was withdrawn using a vacuum line and precipitated in cold methanol, filtered, washed several times with

TABLE I
Monomer Feed Composition of
AOXBE-MMA Copolymerization

Ex.	Monomer composition	
	AOXBE (wt %)	AIBN (mol/L)
1	2.08	0.02
2	4.18	0.02
3	6.30	0.02
4	8.45	0.02
5	10.62	0.02

methanol, and finally, dried in an air oven at 60°C until constant weight. The degree of conversion was then calculated gravimetrically, since in all cases the decrease in volume was a linear function of polymerization time. The rate curves were then converted into mol L⁻¹ s⁻¹.

Instrumental analysis

Microanalysis

The carbon, hydrogen contents of the prepared samples were recorded by Perkin-Elmer CHN 240 B. Column chromatography: Basic alumina [activity B II-III (Brock-mann) ICN Biomedical. in the micro analytical laboratory, Cairo University, Egypt.

Ultraviolet, infrared, ¹HNMR, and ¹³CNMR

The UV-vis spectra were measured using a Perkin-Elmer Lambda 40 double beam spectrophotometer in the range 300–1100 nm. Infrared measurements were carried out using Pye-Unicam SP 2000 spectrophotometer. ¹HNMR and ¹³CNMR spectra were recorded with a Bruker NMR spectrometer WM 300 in CDCl₃ with tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

Structure of the modified laser dye monomer

Infrared spectroscopic analysis

The strong absorption band in the IR spectra of fluorescein and AOXBE monomer appearing at 754 cm⁻¹ and 759 cm⁻¹, respectively. This slight shift could be attributed to CH deformation of 1,2-disubstituted benzene ring. The strong absorption bands appearing in the region 783–864 cm⁻¹ in case of fluorescein appears also in case of the prepared monomer with slight shift which could be attributed to the CH deformation of fused benzene ring in the fluorescein structure indicating that fluorescein moiety is incorporating in the monomer structure. The medium band appearing at 1375 cm⁻¹ in case of monomer disappears in case of fluorescein which could be attributed to CH-stretching vibrations of CH₃ present in ester group indicating that esterification of the fluorescein compound is occurred. Also, a strong absorption band appears at 1444 cm⁻¹ in case of monomer disappears in case of fluorescein compound indicating the introduction of CH₂ of acroyl moiety in the monomer structure. The three absorption bands appearing in the region 1470–1600 cm⁻¹ in case of fluorescein appears also in case of monomer with slight shift which are due to the stretching vibration of C=C in quinoide structure indicating that fluorescein moiety is introduced in the mono-

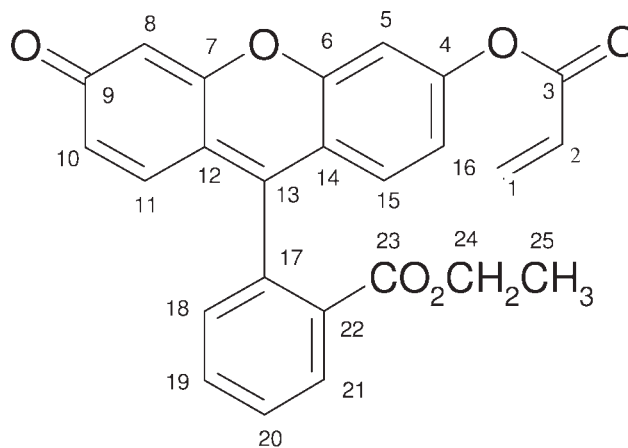
meric structure. The broad absorption band appearing at 3200–2310 cm⁻¹ in case of fluorescein which could be attributed to the stretching vibration of OH in carboxylic group moiety disappears in case of monomer indicating a full esterification of fluorescein before the introduce of fluorescein (II) in the monomeric structure.

¹HNMR spectroscopic analysis

The ¹HNMR spectrum of the prepared monomer (AOXBE) (Fig. 1) was measured in DMSO using tetramethylsilane as internal standard. The ¹HNMR signals and their assignments are summarized as follows: δ = 0.93 (t, 3H, CH₃CH₂O), 3.98 (q, 2H, CH₃CH₂O), 6.2–6.4 (m, 2H, CH=CH), 6.8–8.2 (m, 10H, ArH) ppm.

¹³CNMR spectroscopic analysis

The ¹³CNMR measurement of the prepared monomer (Fig. 2) was performed in CDCl₃ as solvent. The ¹³CNMR signals of the prepared monomer and their assignments are summarized as follows: δ = 12.5 (CH₃CH₂), 60.48 (CH₃CH₂), 105.02, 109.17, 114.60, 117.37, 118.01, 118.53, 127.74, 128.92, 129.33, 129.50, 130.16, 131.72, 132.82, 132.98, 148.93, 151.76, 153.15, 156.5, 157.82, 162.52, 164.14, 174.26, 185.05 ArC's, CH=CH) ppm.



Structure of AOXBE

Elemental analysis

The elemental analysis of the prepared monomer was carried out in the microanalytical laboratory at Cairo University. The data are given in Table II and they are found to be in good agreement with the suggested structure.

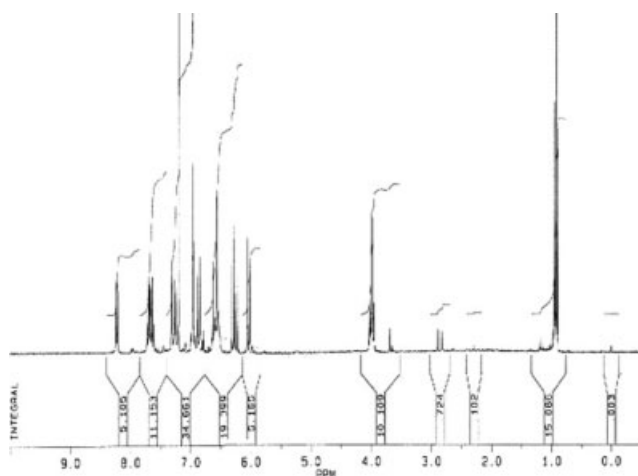


Figure 1 ^1H NMR spectrum of AOXBE.

Free radical copolymerization of AOXBE with MMA

Attempts to homopolymerize the new monomer AOXBE by heating a solution of AOXBE (0.5M, 1.035 g) in DMF (5 mL) in the presence of AIBN using different concentrations at 60°C for 24 h were unsuccessful. This may be attributed to the bulkiness of the new monomer AOXBE.

The negative results of the above homopolymerization prompted us to study the copolymerization of AOXBE with MMA.

Effect of reaction medium on the rate of copolymerization

Here in this work, the effect of different solvents on the rate of copolymerization of the new monomer

AOXBE was investigated at constant monomer composition (1.98M of MMA : 0.02M of AOXBE), temperature = 60°C, and [AIBN] = 0.02M, and the data are graphically represented in Figure 3 from which it can be seen that the rate of copolymerization is higher in THF and DMF than in the other solvents used. This improved rate could be due to better solubility or the high polarity of DMF. The low boiling point of THF may restrict its use at high temperature. Therefore, it has been decided to choose DMF as the working solvent in the subsequent measurements.

Effect of initiator concentrations on the rate of the copolymerization reaction

To study the effect of the initiator concentrations on the rate of copolymerization reaction, the copolymerization process was carried out by copolymerizing AOXBE with MMA at constant temperature and monomer compositions [as mentioned under point "General copolymerization process"].

The influence of the initiator on the rate of copolymerization process was carried out dilatometrically. By plotting the meniscus of the volume of the liquid monomer (ΔV) versus the time of polymerization, a straight line is obtained with a slope equal to the rate of polymerization (R_i) as in Figure 4. Figure 4 shows the conversion–time curves for the copolymerization of AOXBE with MMA in DMF at 60°C for different initiator concentrations [AIBN] at constant monomer concentration $[M] = 2 \text{ mol/L}$. By plotting the logarithm of the slopes of the lines in Figure 4 versus the logarithm of initiator concentrations, we get the straight line in Figure 5, which

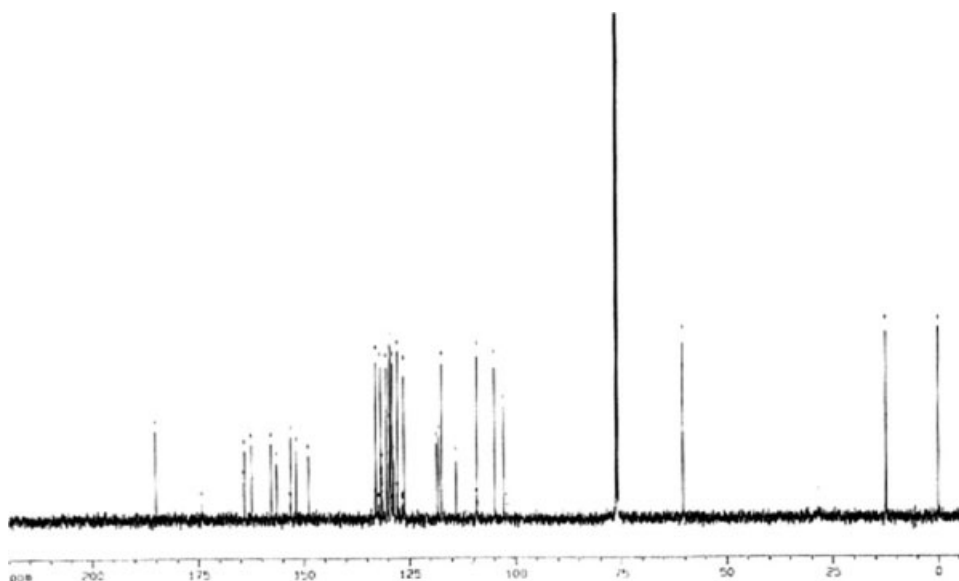


Figure 2 ^{13}C NMR spectrum of AOXBE.

TABLE II
Elemental Analysis of AOXBE

Monomer name	Element (%)			
	C		H	
	Cal.	Found	Cal.	Found
AOXBE	72.46	72.60	4.38	4.60

corresponds to the initiator exponent. The value obtained is equal to 0.5473, indicating that the initiator plays a double role, i.e., as initiator and chain transfer agent. Therefore, termination occurs mainly bimolecular.²³

Also, the polymer composition was calculated by using Beer's law and summarized in Table III.

Effect of monomer concentrations on the rate of the copolymerization reaction

To study the effect of the monomer concentrations on the rate of copolymerization reaction, the copolymerization process was carried out by copolymerizing AOXBE with MMA at constant temperature and initiator concentration.

The influence of the monomer concentration on the rate of copolymerization process was carried out dilatometrically. By plotting the meniscus of the volume of the liquid monomer (ΔV) versus the time of polymerization, a straight line is obtained with a slope equal to the rate of polymerization (R_i) as in Figure 6, which shows the conversion-time curves for the copolymerization of AOXBE with MMA in DMF at 60°C for different monomer concentrations $[M]$ at constant initiator concentration $[AIBN] = 0.02M$.

By plotting the logarithm of the slopes of the lines in Figure 6 versus the logarithm of monomer concentrations, we get the straight line in Figure 7,

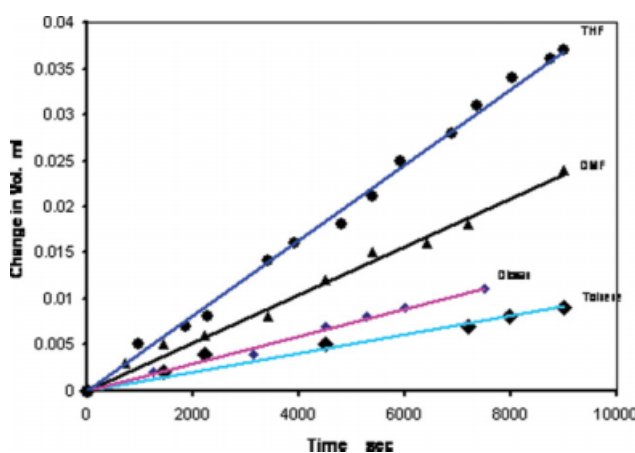


Figure 3 Effect of different solvents on the rate of copolymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

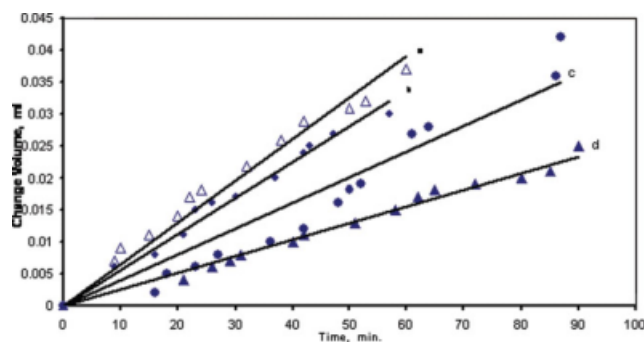


Figure 4 Change in volume (Δv)-time curves for the copolymerization of AOXBE with MMA at different initiator concentrations. $[AIBN]$ in a = 0.04M, b = 0.03M, c = 0.014M, and d = 0.0086M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which corresponds to the order of polymerization reaction with respect to monomer concentration. The obtained value is equal to 1.3425.

Also, the polymer composition was calculated by using Beer's law and summarized in Table IV.

Effect of monomer feed composition on the rate of copolymerization reaction

Monomer concentrations and their reactivity ratios are very important factors for free radical copolymerization reaction. They control the overall composition of the copolymer formed at that instant and also the sequence distribution of the different units in the copolymeric chains. Therefore, the effect of monomer feed composition and their reactivity ratios should be studied.

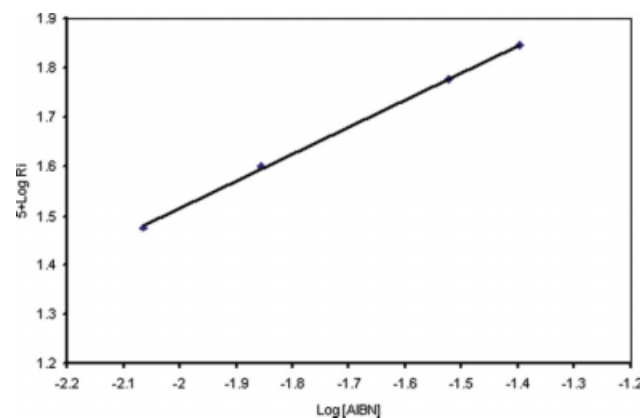


Figure 5 Double logarithmic plot of the initial rate of polymerization and initiator concentrations in case of copolymerization of AOXBE with MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
The Effect of Initiator Concentration on the Rate of Copolymerization of MMA with AOXBE

Ex.	Monomer composition		Time of reaction (min)	Conversion (%)	Polymer composition
	AOXBE M ₁ (wt %)	AIBN (mol/L)			AOXBE m ₁ (wt %)
1	4.18	0.0086	90	7.38	0.071
2	4.19	0.014	90	8.96	0.093
3	4.19	0.03	60	11.36	0.144
4	4.17	0.04	60	14.30	0.249

To study the effect of the monomer composition on the rate of copolymerization reaction, the copolymerization process was carried out by copolymerization of AOXBE with MMA at constant initiator concentration and reaction temperature. The influence of the monomer composition on the rate of copolymerization process was carried out dilatometrically. By plotting the change of the volume of the reaction medium (DMF+monomers) (ΔV) versus the time of polymerization, a straight line is obtained with a slope equal to the rate of polymerization (R_i) as in Figure 8.

As mentioned above, the volume of the copolymerization medium decreases with time and its decrease is proportional to the extent of polymerization. Figure 8 shows the conversion–time curves for the copolymerization of AOXBE with MMA in DMF at constant temperatures 60°C and constant initiator (AIBN = 0.02M), from which it is noticed that as the concentration of AOXBE increases in the reaction medium, the copolymerization reaction rate decreases.

The effect of the new monomer concentrations AOXBE on the rate of copolymerization reaction was

summarized by plotting R_i versus the concentration of AOXBE as shown in Figure 9.

Also, the polymer compositions were calculated by using Beer's law and summarized in Table V.

It is clear that from Table V, the type of copolymer is Block-type copolymer.

Effect of the reaction temperature on the rate of copolymerization reaction

The effect of the reaction temperature on the rate of copolymerization reaction was carried out at constant initiator concentration, monomer compositions, and monomer concentrations by dilatometric method. By plotting the change of the volume of the liquid (ΔV) versus the time of polymerization, a straight line is obtained with a slope equal to the rate of polymerization (R_i) as in Figure 10.

As mentioned above, the volume of the copolymerization medium decreases with time and this decrease is proportional to the extent of polymerization. Figure 10 shows the conversion–time curves for the copolymerization of AOXBE with MMA in DMF at different temperatures at constant initiator

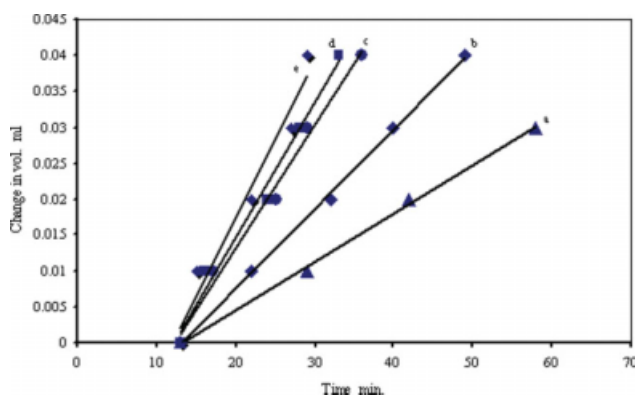


Figure 6 Change in volume (Δv)-time curves for the copolymerization of AOXBE with MMA at different [M] concentrations. [M] in a = 0.5M, b = 0.75M, c = 1.0M, d = 1.25M, and e = 1.5M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

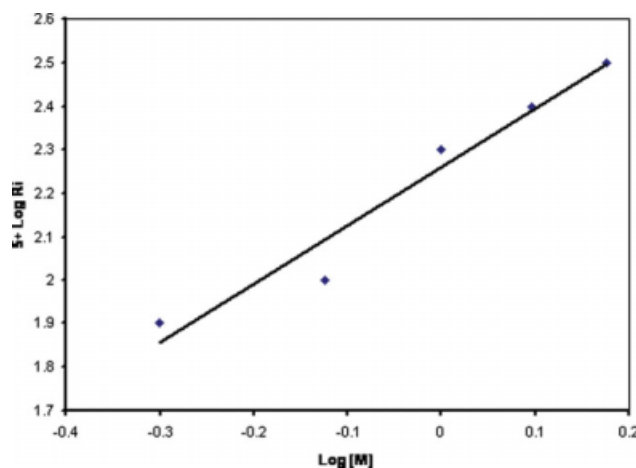


Figure 7 Double logarithmic plot of the initial rate of polymerization and monomer concentrations in case of copolymerization of AOXBE with MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Effect of Monomer Concentration on the Rate of Copolymerization of MMA with AOXBE

Ex.	Monomer concentration		Time of reaction (min)	Conversion (%)	Polymer composition
	Σ AOXBE-MMA (M)	AIBN (M)			AOXBE m_1 (wt %)
A	0.5	0.02	60	6.28	0.051
B	0.75	0.02	60	7.16	0.073
C	1.0	0.02	60	7.92	0.094
D	1.25	0.02	60	8.30	0.124
E	1.5	0.02	60	9.00	0.203

concentration (AIBN = 0.02M) and monomer concentration $[M] = 2$ mol/L.

By plotting the logarithm of the slope of the line in Figure 10 versus the reciprocal of absolute temperature, the activation energy of AOXBE-MMA copolymerization can be determined from the slope of the line shown in Figure 11 and applying in Arrhenius equation and it was found to be 99.08 kJ/mol.

The enthalpy and entropy of activation for the copolymerization reaction can be calculated by calculation of k_2 from the following equation

$$R_i = k_2[\text{monomer}]^a[\text{initiator}]^b$$

where, a and b are the exponents with respect to monomer and initiator concentrations, respectively.

The enthalpy (ΔH^*) and entropy (ΔS^*) of activation associated with k_2 were calculated using Eyring equation,

$$k_2 = \frac{kT}{h} e^{\Delta S^*/k} e^{-\Delta H^*/RT}$$

where, k is the Boltzmann constant.

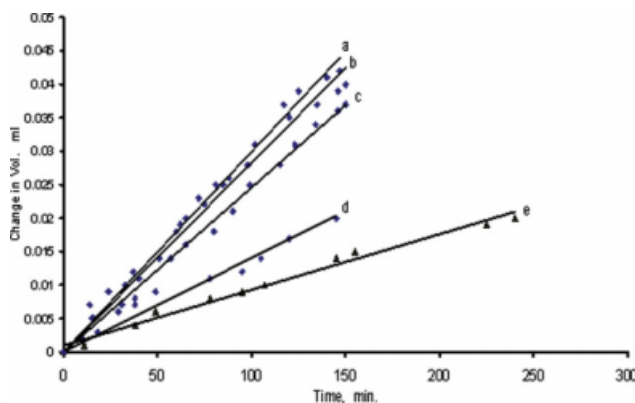


Figure 8 Change in volume (Δv)-time curves for the copolymerization of AOXBE with MMA at different monomer feed compositions. [AOXBE] in a = 0.01M, b = 0.02M, c = 0.03M, d = 0.03M, and e = 0.05M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

h is plank's constant.

By dividing the above equation by T and taking its natural logarithm, one obtains the following equation:

$$\ln \frac{k_2}{T} = \frac{\ln k/h}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

By plotting $\log k_2/T$ versus $1/T$, we obtained a linear relationship (Fig. 12) with slope $-\Delta H^*/R$ and intercept $(\log \frac{k}{h} + \frac{\Delta S^*}{R})$.

From the slopes and intercepts, the values of ΔH^* and ΔS^* were obtained.

The value of ΔH^* was found to be 95.218 kJ mol⁻¹ and ΔS^* was found to be -17.087 J/k mol.

The polymer composition was calculated by using Beer's law and summarized in Tables VI.

Infrared spectroscopic studies of the prepared AOXBE-MMA copolymer

The infrared spectra of the prepared pure PMMA homopolymer and AOXBE-MMA copolymer were summarized in Table VII and show the following:

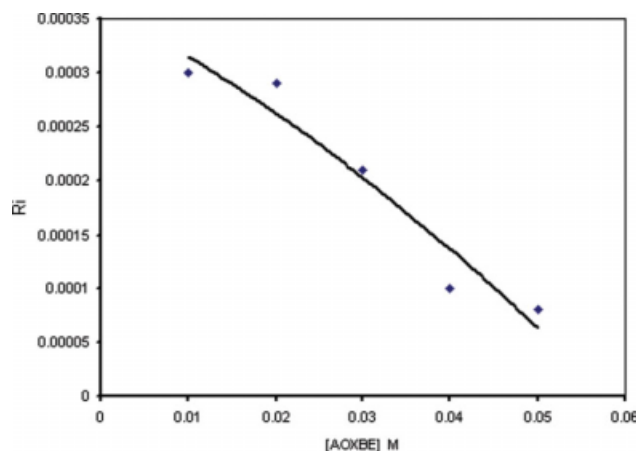


Figure 9 Effect of AOXBE concentrations on the rate of copolymerization with MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
The Effect of Monomer Composition on the Rate of Copolymerization of AOXBE with MMA

Ex	Monomer composition		Conversion (%) after 72h	Intensity of absorbance at 429 nm	Polymer composition
	AOXBE M ₁ (wt %)	AIBN (mol/L)			AOXBE m ₁ (wt %)
a	2.08	0.02	86	0.3893	0.180
b	4.18	0.02	70.7	0.9179	0.336
c	6.30	0.02	64.9	0.8810	0.467
d	8.45	0.02	61.0	0.6583	0.512
e	10.62	0.02	49.0	0.6877	0.567

The strong absorption band appearing at 1065 cm^{-1} which could be attributed to skeletal vibration of C—C backbone of polymeric chain in case of PMMA appears also in case of AOXBE-MMA copolymer as medium absorption band at 1064 cm^{-1} .

The strong absorption band appearing at 1388 cm^{-1} which could be attributed to symmetric stretching vibrations of methyl group in case of PMMA appears also as medium absorption band at 1388 cm^{-1} in case of AOXBE-MMA copolymer.

The weak absorption band appearing at 2850 cm^{-1} which could be attributed to symmetric stretching for CH in CH₂ group in case of PMMA appears as medium absorption band at 2846 cm^{-1} in case of AOXBE-MMA copolymer.

The two strong absorption bands appearing at 2950 and 2990 cm^{-1} which could be attributed to the symmetric stretching vibrations of CH in CH₃ group in case of PMMA appear also in case of AOXBE-MMA copolymer with slight shift at 2950 and 2997 cm^{-1} .

The two medium absorption bands appearing at 1590 and 1604 cm^{-1} which could be attributed to

the stretching vibration of C=C in quinoide structure and in benzene ring, respectively, in case of AOXBE-MMA copolymer disappear in case of PMMA.

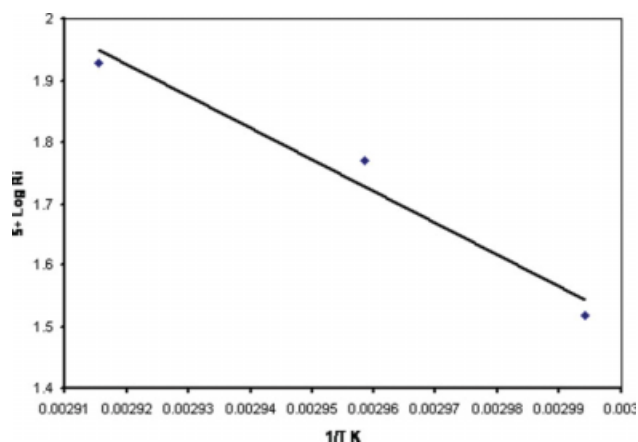


Figure 11 Log R_i versus $1/T$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

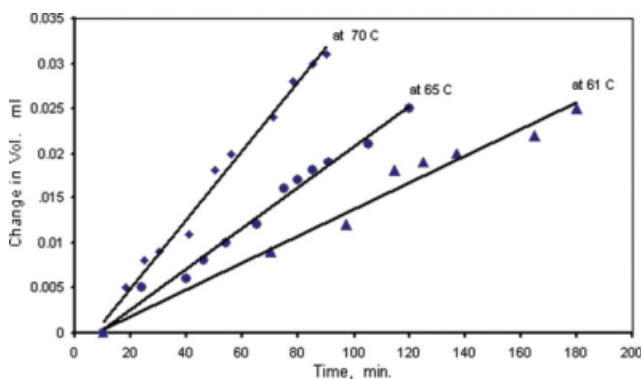


Figure 10 Plot of the change in volume (Δv) versus time at different temperatures in case of the copolymerization of AOXBE with MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

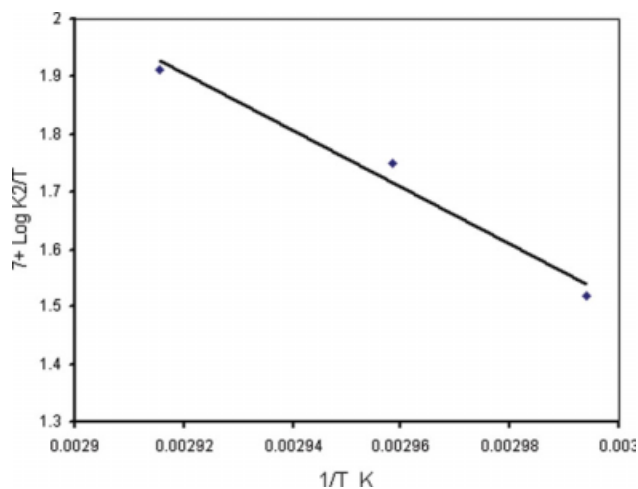


Figure 12 Log k_2/T versus $1/T$ in case of the copolymerization reaction between MMA and AOXBE at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Effect of Temperature on the Rate of Copolymerization of MMA with AXOBE

Ex.	Monomer composition		Time of reaction (min)	Reaction temperature (°C)	Conversion (%)	Copolymer composition
	AXOBE M ₁ (wt %)	AIBN (mol/L)				AXOBE m ₁ (wt %)
1	4.18	0.02	180	61	20.02	0.132
2	4.17	0.02	120	65	21.10	0.192
3	4.18	0.02	90	70	23.63	0.219

The medium absorption band appearing at 3050 cm⁻¹, which could be attributed to symmetric stretching vibration of CH in benzene ring, in case of AOXBE-MMA copolymer disappears in case of PMMA homopolymer.

From the aforementioned characteristic absorption bands and their assignments, it is clear that the fused aromatic structure of fluorescein and methyl methacrylate moieties are present in the copolymer chain.

UV and visible spectra of the prepared monomer (AOXBE) and AOXBE-MMA copolymer

The UV-visible spectra of AOXBE monomer shows a maximum absorption bands at 335, 429, and 449 nm which are due to the π - π^* transition of the conjugated single-double bonds in the macromonomer laser dye (AOXBE). But in case of the prepared AOXBE-MMA copolymer in THF as a solvent, the following maximum absorption bands appear at 335, 435, 455, and a shoulder at 465 nm which are due to the π - π^* transition. In case of the copolymer film

TABLE VII
Infrared Spectroscopic Absorption Bands and Their Assignments for PMMA and AOXBE-MMA Copolymer

Wavenumber (cm ⁻¹)		Assignments
PMMA	AOXBE-MMA	
-	418 ^s	Stretching for carbon skelton or rocking deformation for CH ₂ group.
685 ^s	-	
-	710 ^w	
750 ^s	754 ^s	CH deformation of 1,2-disubstituted benzene ring or CH ₂ rocking deformation
800 ^s	-	CH ₃ rocking deformation or CH deformation of fused benzene ring or stretching for OCH ₃ group.
-	830 ^s	
840 ^s	844 ^s	
903 ^m	-	Deformation of methyl group or C—O stretching vibration.
-	914 ^m	
950 ^s	-	
984 ^s	987 ^s	Δ_a (C—O—C) combined with CH ₃ O
1065 ^s	1064 ^m	C—C skeleton
1145 ^s	1149 ^s	C—O stretching vibration.
1193 ^s	1210 ^m	
1242 ^s	1245 ^s	C—C—O combined with CH deformation.
1274 ^s	1260 ^{sh}	
1365 ^{sh}	-	Symmetric stretching vibrations of methyl group.
1388 ^s	1388 ^m	
1450 ^{s,sp}	1442 ^s	CH stretching for CH ₃ group or stretching vibration of C=C in quinoid structure.
1488 ^{s,sp}	1471 ^m	
-	1520 ^w	
-	1590 ^w	
-	1604 ^m	Stretching vibration of C=C in benzene ring.
1717 ^s	1700 ^s	Stretching vibration of C=O in ester group.
	1732 ^s	
2850 ^w	2846 ^m	Symmetric stretching for CH in CH ₂ group.
2935 ^{sh}	-	Symmetric stretching for CH in CH ₃ group.
2950 ^s	2950 ^m	
2990 ^s	2997 ^s	

s = strong, m = medium, w = weak, sh = shulder, s, sp = sharp and splitted.

(500 μm thickness), the maximum absorption bands appear at 340, 395, 430, and 450 nm for π - π^* transition of the conjugated system in the prepared copolymer.

References

1. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon/Elsevier: Oxford, 1995.
2. Chernikova, E.; Terpugova, P.; Chuong, B.; Charleux, B. *Polymer* 2003, 44, 4101.
3. Wang, Y.; Huang, J. *Macromolecules* 1998, 31, 4037.
4. Fischer, A.; Bremilla, A.; Lochon, P. *Eur Polym J* 2001, 37, 33.
5. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem Rev* 2001, 102, 3661 and references there in.
6. Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921 and references there in.
7. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
8. Niwa, M.; Higashi, N.; Noma, K. *Sci Eng Rev Doshisha Univ* 1981, 22, 78.
9. Niwa, M.; Higashi, N.; Noma, K. *Chem Abstr* 1981, 95, 187763c.
10. Patel, K.; Snyder, W. H. *Am Chem Soc Polym Progr* 1981, 22, 217.
11. Patel, K.; Snyder, W. H. *Chem Abstr* 1982, 97, 216775g.
12. Niwa, M.; Higashi, N.; Noma, K. *Sci Eng Rev Doshisha Univ* 1983, 24, 129.
13. Niwa, M.; Higashi, N.; Noma, K. *Chem Abstr* 1984, 100, 86184f.
14. Chen, G. F.; Jones, F. N. *Macromolecules* 1991, 24, 2151.
15. Teodorescu, M.; Dimonic, M.; Cerchez, I. *Eur Polym J* 1999, 35, 247.
16. Busfield, W. K.; Zayas-Holdsworth, C. I.; Thang, S. H. *Polymer* 1999, 40, 389.
17. Busfield, W. K.; Zayas-Holdsworth, C. I.; Thang, S. H. *Polymer* 2000, 41, 4409.
18. Busfield, W. K.; Zayas-Holdsworth, C. I.; Thang, S. H. *J Polym Sci Part A: Polym Chem* 2001, 39, 2911.
19. Ferrer, M. L.; Acuna, A. U.; Amat-Gurri, F.; Costela, A.; Figuera, J. M.; Florido, F.; Sastre, R. *Appl Opt* 1994, 33, 2266.
20. Costela, A.; Amat-Gurri, F.; Santa Maria, M. D. *J Appl Phys* 1996, 80, 3167.
21. Sayyah, S. M.; El-shafiey, Z. A.; Barsoum, B. N.; Khaliel, A. B. *J Appl Polym Sci* 1937, 91, 2004.
22. Feuerstein, W.; Dutoit, M. *Chem Ber* 1901, 34, 2637.
23. Jiang, X.; Yan, D.; Zhu, X.; Lin, J.; Xia, P. *J Appl Polym Sci* 1999, 74, 1417.