

Synthesis, Spectral, and Thermal Characterization of Photosensitive Poly(ether-ester)s Containing α,β -Unsaturated Ketone Moieties in the Main Chain Derived from 2,6-Bis[4-(3-hydroxypropyloxy)-3-methoxybenzylidene]cyclohexanone

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ABSTRACT: A series of photosensitive poly(ether-ester)s containing α,β -unsaturated ketone moieties in the main chain were synthesized from 2,6-bis[4-(3-hydroxypropyloxy)-3-methoxybenzylidene]cyclohexanone (BHPMBCH) and aliphatic and aromatic diacid chlorides. The diol precursor, BHPMBCH, was synthesized from 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone and 3-bromo-1-propanol. The solubility of the polymers was tested in various solvents. The intrinsic viscosity of the synthesized polymers, determined by an Oswald viscometer, was found to be 0.06–0.80 g/dL. The molecular structures of the monomer and polymers were confirmed by Fourier transform infrared, ultraviolet-visible, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectral analyses. The thermal properties were studied with thermogravimetric analysis and differential scanning calorimetry.

The thermogravimetric analysis data revealed that the polymers were stable up to 220°C and started degrading thereafter. The thermal stability initially increased with increasing spacer length and then decreased due to negative effects of the spacer. The self-extinguishing properties of the synthesized polymers were studied by the determination of the limiting oxygen index values with Van Krevelen's equation. In addition, the photocrosslinking properties of the polymer chain were studied with UV spectroscopy, and we observed that the rate of photocrosslinking increased significantly with increasing methylene carbon chain length of the acid spacer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3141–3150, 2011

Key words: differential scanning calorimetry (DSC); polyesters; polymer synthesis and characterization

INTRODUCTION

There has been much research on the synthesis of thermotropic polyesters^{1–3} and on a wide variety of systems, each with unique thermal and physical properties. Thermotropic polyesters with photosensitive groups find wide applications in photoresists to make integrated circuits, printing plates, photocurable coatings, photorecorders photoconductors, energy-exchange materials, photosensitizers for organic synthesis, and liquid-crystal displays.⁴ Photosensitivity, solubility, and thermal stability are the prime requirements for the use of these polymers in this field.⁵ Among them, some aliphatic and wholly aromatic thermotropic polyesters generally have high crystal-to-isotropic transitions [melting temperatures (T_m 's)]

and are insoluble in most organic solvents. To obtain polymers with considerably low T_m 's and increased solubility, several chemical modifications can be made: (1) the introduction of bulky or nonsymmetrical substituents; (2) the introduction of long, flexible spacers into the mesogen backbones; (3) the use of nonlinear or bent monomers; and (4) the copolymerization of different monomers.⁶ Most studies have paid attention to semiflexible polymers, in which the hard mesogenic groups are connected by flexible spacer groups. To this point, an enormous number of semiflexible-type thermotropic polymers have been synthesized. Typical examples are polyesters, poly(ether-ester)s, poly(ester-amide)s, and polyethers.⁷ Recently, various thermotropic poly(ether-ester)s with flexible spacers have also been synthesized.⁸ Poly(ether-ester)s with a regular sequence of flexible spacers and aromatic groups showed a great difference in polarity between the aliphatic spacer and ester linkages; these properties increase the solubility and decreased the transition temperature because of the impact of the spacer. Liquid-crystalline poly(ether-ester)s have captured the excitement and imagination of contemporary polymer scientists and

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engineers. These materials exhibit many unique properties, which present not only challenges for basic research but also numerous technological opportunities. Liquid-crystalline poly(ether-ester)s have provided a number of potential applications in photonic and optoelectronic-based technologies, such as speed data storage devices and optical fiber communications.⁹ The general drawbacks of this kind of polyester are its poor thermal resistance and fire behavior.¹⁰ This can be minimized by the addition of flame retardants.¹¹

A series of articles were published on the synthesis and characterization of arylidene polyethers and polyesters containing rigid cycloalkanone moieties. The incorporation of a methylene spacer played a significant role in determining the relationship between the thermomechanical history and structural and morphological organization of the polymers.¹² Such polymers were reported to possess interesting semiconducting and mechanical properties, an attractive morphology, and liquid-crystalline behavior.

In this study, we dealt with the synthesis of photo-reactive bisbenzylidene aromatic diols with α,β -unsaturated ketone moieties in the main chain and the incorporation of an aliphatic methylene spacer possessing free hydroxyl groups at both terminals. The synthesized diol monomer was polymerized with various aliphatic and aromatic acid chlorides by a solution polycondensation technique. Spectral, thermal, and photosensitive studies were also carried out in this investigation.

EXPERIMENTAL

Materials

Vanillin (S. D. Fine Chemicals, Mumbai, India), dimethyl formamide (DMF; S. D. Fine Chemicals), potassium carbonate (S. D. Fine Chemicals), adipic acid (S. D. Fine Chemicals), sebacic acid (S. D. Fine Chemicals), terephthalic acid (S. D. Fine Chemicals), isophthalic acid (S. D. Fine Chemicals), cyclohexanone (Merck, Mumbai, India), dioxane (Merck), *n*-hexane (Merck), thionyl chloride (Ranbaxy, New Delhi, India), methanol (Loba Chemie, Mumbai, India), and other solvents were purified by procedures reported in the literature.^{13,14} Boron trifluoride diethyletherate (Fluka, Steinheim, Germany), subaric acid (Fluka), 3-bromo-1-propanol (Aldrich, Steinheim, Germany), and azelaic acid (Aldrich) were used as received.

Characterization

The solubility of the polymers was examined with 0.3–0.5 mg of polymer in 5 mL of solvent at room temperature. The intrinsic viscosity of the synthesized

polymers was measured in dimethyl sulfoxide (DMSO) at 30°C with an Oswald viscometer (S. D. Fine Chemicals, Mumbai, India). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) values of the polymers were estimated with gel permeation chromatography (GPC) in tetrahydrofuran (THF) with a Shimadzu LC-20AD GPC (Merck, Mumbai, India). Polystyrene standards of known molecular weight were used for calibration. The infrared spectra were recorded on a Shimadzu Fourier transform spectrophotometer with KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded on a 400-MHz Bruker AV-III 400 NMR spectrometer in CDCl₃ with tetra methyl silane (TMS) as an internal standard (Fisher, Fair Lawn, New Jersey). The differential scanning calorimetry (DSC) analysis was carried out on a PerkinElmer Pyris 6 differential scanning calorimeter for all polymers with an empty aluminum pan as a reference and at a heating rate of 10°C/min in a nitrogen atmosphere. The temperature and heat-flow scale of the instrument were calibrated with precrimped In and Zn as standard references. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TG/DTA in a nitrogen atmosphere at a heating rate of 10°C/min. The photocrosslinking studies of the synthesized polymers were performed in the solution state with a UV spectrophotometer. The polymer was dissolved in DMSO in a quartz cuvette and irradiated in a UV curing reactor with a medium-pressure Hg lamp (Heber Scientific Photo-reactor, 300–420 nm) exposed at a distance of 10 cm from the sample (Heber Scientific, Chennai, India). Subsequently, the irradiated solution was subjected to UV spectral analysis on a Systronics 119 UV spectrophotometer (New Delhi, India).

Synthesis of the precursor 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone (BHMBCH)

A mixture of cyclohexanone (25 mmol) and 4-hydroxy-3-methoxybenzaldehyde (50 mmol) was dissolved in 25 mL of absolute ethanol with three drops of boron trifluoride diethyl etherate. The solution was stirred for 4 h at 80°C and cooled to room temperature. The solid product formed was filtered off, washed with cold ethanol, and dried in a vacuum oven. Recrystallization from hot ethanol gave a fine yellow product with more than 75% yield of the title compound (mp = 181°C; the literature value was 179°C).^{15,16}

IR (KBr, cm⁻¹): 1637 ($\gamma_{C=O}$), 1579 ($\gamma_{C=C}$ exocyclic), 1513 ($\gamma_{C=C}$ aromatic), 1254 ($\gamma_{C_{Ar}-O-C_{Me}}$ asym), 3367 (γ_{OH}). ¹H-NMR (CDCl₃, TMS, ppm): 9.50 (s, 2H, —OH), 6.80–7.20 (m, 6H, aromatic protons), 7.67 (s, 2H, —CH=), 3.82 (s, 6H, —OCH₃), 2.92 (s, 4H, β CH₂ of cyclohexanone), 1.75 (s, 2H, γ CH₂ of cyclohexanone). ¹³C-NMR (CDCl₃, ppm): 188.55 (C=O,

ketonic), 133.6 (=CH—), 130.0 (α carbon of cyclohexanone), 115–125 (aromatic carbons), 55.77 (—OCH₃), 22.59 (β carbon of cyclohexanone), 27.94 (γ carbon of cyclohexanone).

Synthesis of the monomer 2,6-bis[4-(3-hydroxypropyloxy)-3-methoxybenzylidene]cyclohexanone (BHPMBCH)

BHPMBCH (5 mmol) was dissolved in dimethyl formamide (10 mL) in a 100-mL round-bottom flask and stirred with a magnetic stirrer. Anhydrous potassium carbonate (12.5 mmol) was added to it. Immediately, a change in color from yellow to red was observed as an indication of the formation of anion.¹⁷ The mixture was heated to 80°C with constant stirring; to this reaction, a mixture of 3-bromo-1-propanol (10 mmol) was added dropwise, and then, the reaction was allowed to continue for 4 h. The reaction mixture was cooled to room temperature, poured into cold water (ca. 250 mL), and allowed to stand overnight in a refrigerator. The yellow precipitate was filtered off, washed with water, dried *in vacuo* for 1 day, and recrystallized with chloroform (yield = 72%, mp = 110°C).

Fourier transform infrared (FTIR) spectroscopy (KBr, cm⁻¹): 1659 ($\gamma_{C=O}$), 1593 ($\gamma_{C=C}$ exocyclic), 1514 ($\gamma_{C=C}$ aromatic), 1252 ($\gamma_{C_{Ar}-O-C_{Me}}$ asym), 766–854 (γ_{C-H} aromatic bending), 3392 (γ_{OH}), 2935 (γ_{C-H} of the methylene spacer). ¹H-NMR (CDCl₃, TMS, ppm): 7.25 (s, 2H, —OH), 6.80–7.10 (m, 6H, aromatic protons), 7.7 (s, 2H, —CH=), 2.10 (p, 4H, —CH₂ spacer), 3.85–3.95 (t, 4H, —OCH₂ spacer), 4.20–4.25 (t, 4H, —CH₂O spacer), 3.90 (s, 6H, —OCH₃), 2.90 (s, 4H, β CH₂ of cyclohexanone), 1.80 (s, 2H, γ CH₂ of cyclohexanone). ¹³C-NMR (CDCl₃, ppm): 190.0 (C=O, ketonic), 137.0 (=CH—), 130.0 (α carbon of cyclohexanone), 115.0–125.0 (aromatic carbons), 56.0 (—OCH₃), 28.5 (β carbon of cyclohexanone), 23.0 (γ carbon of cyclohexanone), 68.0 (—OCH₂ spacer), 61.5 (—CH₂, spacer), 31.5–32.0 (—CH₂O, spacer).

Preparation of the acid chlorides

Recrystallized adipic acid (100 mmol) and distilled thionyl chloride (240 mmol) were placed in a 250-mL round-bottom flask and refluxed in an oil bath for 4 h. After refluxing, excess thionyl chloride was removed under reduced pressure. Sebacyl chloride, subaryl chloride, and azeloyl chloride were also prepared by the adoption of procedures similar to that used for the preparation of adipoyl chloride.¹⁸ Terephthaloyl chloride and isophthaloyl chloride were prepared by the refluxing of the respective diacids with thionyl chloride with the addition of two drops of pyridine as a catalyst for 12 h. The solid product obtained was recrystallized from *n*-hexane.¹⁹

Synthesis of the polymers

Poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] esters

All of the polymers were synthesized by the solution polycondensation technique with pyridine as a catalyst.²⁰

Poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] adipate (**P1**)

BHPMBCH (4 mmol) was dissolved in 15 mL of dioxane placed in a 100-mL round-bottom flask. To this solution, dry pyridine (10 mmol) was added and stirred with the temperature kept at 70°C. Then, adipoyl chloride (4 mmol) was added dropwise, and stirring was continued for 4 h at 90°C. The reaction mixture was cooled to room temperature, and the content was poured into *n*-hexane (100 mL) to precipitate the polymer. The precipitated polymer was washed with methanol four or five times and dried *in vacuo* (yield = 80%).

FTIR (KBr, cm⁻¹): 1650 ($\gamma_{C=O}$ keto), 1593 ($\gamma_{C=C}$ exocyclic), 1514 ($\gamma_{C=C}$ aromatic), 1728 ($\gamma_{C=O}$ ester), 1250 ($\gamma_{C_{Ar}-O-C_{Me}}$ asym), 2920 (γ_{C-H} of the methylene spacer). ¹H-NMR (CDCl₃, TMS, ppm): 6.85–7.10 (m, aromatic protons), 7.75 (s, =CH—), 2.20 (p, —CH₂ spacer), 3.90–3.95 (t, —OCH₂ spacer), 4.25–4.30 (t, —CH₂O, spacer), 3.85–3.90 (s, —OCH₃), 2.9–3.0 (s, β CH₂ of cyclohexanone), 1.85 (s, γ CH₂ of cyclohexanone), 1.65–2.40 (m, methylene protons of the aliphatic acid spacer). ¹³C-NMR (CDCl₃, ppm): 190.0 (C=O, ketonic carbon), 174.0 (ester carbonyl carbon), 137.0 (=CH—), 130.0 (α carbon of cyclohexanone), 115–125 (aromatic carbons), 56.0 (—OCH₃), 28–29 (β carbon of cyclohexanone), 23.0 (γ carbon of cyclohexanone), 65.0 (—OCH₂, spacer), 62.0 (—CH₂, spacer), 34.0 (—CH₂O, spacer), 24.5–34.5 (methylenic acid spacer carbons).

The other polymers, namely, poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] subarate (**P2**), poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] azelate (**P3**), poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] sebocate (**P4**), poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] terephthalate (**P5**), poly[2,6-bis[4-(3-hydroxypropyloxy)-(3-methoxybenzylidene)cyclohexanone]] isophthalate (**P6**), were synthesized in a similar manner.

P2

Yield = 80%. FTIR (KBr, cm⁻¹): 1660 ($\gamma_{C=O}$ keto), 1595 ($\gamma_{C=C}$ exocyclic), 1520 ($\gamma_{C=C}$ aromatic), 1732 ($\gamma_{C=O}$ ester), 1251 ($\gamma_{C_{Ar}-O-C_{Me}}$ asym), 2933 (γ_{C-H} of the methylene spacer). ¹H-NMR (CDCl₃, TMS, ppm):

6.8–7.3 (m, aromatic protons), 7.75 (s, $-\text{CH}=\text{}$), 2.30 (p, $-\text{CH}_2$ spacer), 3.70 (t, $-\text{OCH}_2$ spacer), 3.85–3.95 (t, $-\text{CH}_2\text{O}$, spacer), 3.90 (s, $-\text{OCH}_3$), 2.90 (s, βCH_2 of cyclohexanone), 1.80 (s, γCH_2 of cyclohexanone), 1.4–2.3 (m, methylene protons of the aliphatic acid spacer). ^{13}C -NMR (CDCl_3 , ppm): 190.0 (C=O, ketonic carbon), 174.0 (ester carbonyl carbon), 137.0 ($=\text{CH}-$), 130.0 (α carbon of cyclohexanone), 115–125 (aromatic carbons), 56.0 ($-\text{OCH}_3$), 28–29 (β carbon of cyclohexanone), 23.0 (γ carbon of cyclohexanone), 66.0 ($-\text{OCH}_2$, spacer), 61 ($-\text{CH}_2$, spacer), 36.0 ($-\text{CH}_2\text{O}$, spacer), 23–34.5 (methylenic acid spacer carbons).

P3

Yield = 73%. FTIR (KBr, cm^{-1}): 1650 ($\gamma_{\text{C}=\text{O}}$ keto), 1600 ($\gamma_{\text{C}=\text{C}}$ exocyclic), 1520 ($\gamma_{\text{C}=\text{C}}$ aromatic), 1735 ($\gamma_{\text{C}=\text{O}}$ ester), 1251 ($\gamma_{\text{C}_{\text{Ar}}-\text{O}-\text{C}_{\text{Me}} \text{ asym}}$), 2940 ($\gamma_{\text{C}-\text{H}}$ of the methylene spacer). ^1H -NMR (CDCl_3 , TMS, ppm): 6.9–7.1 (m, aromatic protons), 7.75 (s, $-\text{CH}=\text{}$), 2.3–2.4 (p, $-\text{CH}_2$ spacer), 3.85–3.90 (t, $-\text{OCH}_2$ spacer), 4.25–4.3 (t, $-\text{CH}_2\text{O}$, spacer), 3.85–3.90 (s, $-\text{OCH}_3$), 2.95 (s, βCH_2 of cyclohexanone), 1.8 (s, γCH_2 of cyclohexanone), 1.3–2.4 (m, methylene protons of the aliphatic acid spacer). ^{13}C -NMR (CDCl_3 , ppm): 190.0 (C=O, ketonic carbon), 173.5 (ester carbonyl carbon), 134.0 ($=\text{CH}-$), 129.0 (α carbon of cyclohexanone), 112–124 (aromatic carbons), 55.8 ($-\text{OCH}_3$), 28.0 (β carbon of cyclohexanone), 22.8 (γ carbon of cyclohexanone), 65.5 ($-\text{OCH}_2$, spacer), 60.9 ($-\text{CH}_2$, spacer), 34 ($-\text{CH}_2\text{O}$, spacer), 25–37 (methylenic acid spacer carbons).

P4

Yield = 60%. FTIR (KBr, cm^{-1}): 1660 ($\gamma_{\text{C}=\text{O}}$ keto), 1593 ($\gamma_{\text{C}=\text{C}}$ exocyclic), 1512 ($\gamma_{\text{C}=\text{C}}$ aromatic), 1732 ($\gamma_{\text{C}=\text{O}}$ ester), 1251 ($\gamma_{\text{C}_{\text{Ar}}-\text{O}-\text{C}_{\text{Me}} \text{ asym}}$), 2926 ($\gamma_{\text{C}-\text{H}}$ of the methylene spacer). ^1H -NMR (CDCl_3 , TMS, ppm): 6.9–7.2 (m, aromatic protons), 7.70 (s, $-\text{CH}=\text{}$), 2.4 (p, $-\text{CH}_2$ spacer), 3.8–3.95 (t, $-\text{OCH}_2$ spacer), 4.0–4.35 (t, $-\text{CH}_2\text{O}$, spacer), 3.85–3.90 (s, $-\text{OCH}_3$), 2.95 (s, βCH_2 of cyclohexanone), 1.80 (s, γCH_2 of cyclohexanone), 1.3–2.4 (m, methylene protons of the aliphatic acid spacer). ^{13}C -NMR (CDCl_3 , ppm): 191.0 (C=O, ketonic carbon), 173.5 (ester carbonyl carbon), 134.0 ($=\text{CH}-$), 130.0 (α carbon of cyclohexanone), 112–124 (aromatic carbons), 55.8 ($-\text{OCH}_3$), 28.0 (β carbon of cyclohexanone), 22.8 (γ carbon of cyclohexanone), 65.5 ($-\text{OCH}_2$, spacer), 60.5 ($-\text{CH}_2$, spacer), 33 ($-\text{CH}_2\text{O}$, spacer), 25–35 (methylenic acid spacer carbons).

P5

Yield = 85%. FTIR (KBr, cm^{-1}): 1689 ($\gamma_{\text{C}=\text{O}}$ keto), 1595 ($\gamma_{\text{C}=\text{C}}$ exocyclic), 1510 ($\gamma_{\text{C}=\text{C}}$ aromatic), 1716

($\gamma_{\text{C}=\text{O}}$ ester), 1249 ($\gamma_{\text{C}_{\text{Ar}}-\text{O}-\text{C}_{\text{Me}} \text{ asym}}$), 2935 ($\gamma_{\text{C}-\text{H}}$ of the methylene spacer). ^1H -NMR (CDCl_3 , TMS, ppm): 6.9–7.1 (m, aromatic protons), 7.75 (s, $-\text{CH}=\text{}$), 2.1 (p, $-\text{CH}_2$ spacer), 3.90–3.95 (t, $-\text{OCH}_2$ spacer), 4.25 (t, $-\text{CH}_2\text{O}$, spacer), 3.85 (s, $-\text{OCH}_3$), 2.95 (s, βCH_2 of cyclohexanone), 1.85 (s, γCH_2 of cyclohexanone). ^{13}C -NMR (CDCl_3 , ppm): 192.0 (C=O, ketonic carbon), 165.5 (ester carbonyl carbon), 134.0 ($=\text{CH}-$), 131 (α carbon of cyclohexanone), 112–135 (aromatic carbons), 56.0 ($-\text{OCH}_3$), 28.5 (β carbon of cyclohexanone), 23 (γ carbon of cyclohexanone), 65.8 ($-\text{OCH}_2$, spacer), 62.3 ($-\text{CH}_2$, spacer), 31.7 ($-\text{CH}_2\text{O}$, spacer).

P6

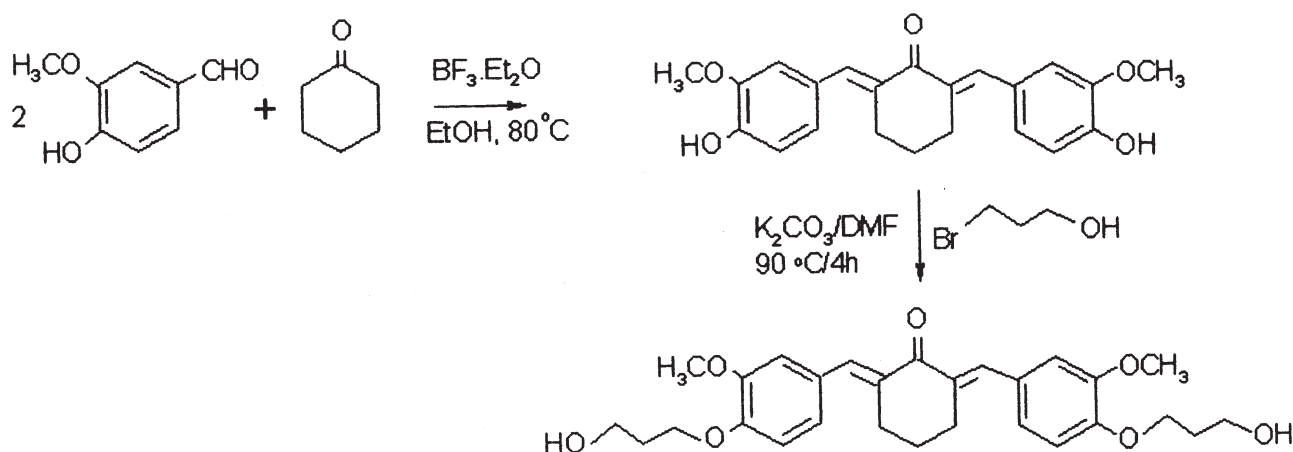
Yield = 80%. FTIR (KBr, cm^{-1}): 1650 ($\gamma_{\text{C}=\text{O}}$ keto), 1593 ($\gamma_{\text{C}=\text{C}}$ exocyclic), 1512 ($\gamma_{\text{C}=\text{C}}$ aromatic), 1722 ($\gamma_{\text{C}=\text{O}}$ ester), 1249 ($\gamma_{\text{C}_{\text{Ar}}-\text{O}-\text{C}_{\text{Me}} \text{ asym}}$), 2935 ($\gamma_{\text{C}-\text{H}}$ of the methylene spacer). ^1H -NMR (CDCl_3 , TMS, ppm): 6.8–7.1 (m, aromatic protons), 7.75 (s, $-\text{CH}=\text{}$), 2.1 (p, $-\text{CH}_2$ spacer), 3.85–3.95 (t, $-\text{OCH}_2$ spacer), 4.25 (t, $-\text{CH}_2\text{O}$, spacer), 3.85 (s, $-\text{OCH}_3$), 2.95 (s, βCH_2 of cyclohexanone), 1.80 (s, γCH_2 of cyclohexanone), 2.1–2.4 (m, methylene protons of the aliphatic acid spacer). ^{13}C -NMR (CDCl_3 , ppm): 190.0 (C=O, ketonic carbon), 167.0 (ester carbonyl carbon), 134.0 ($=\text{CH}-$), 131.0 (α carbon of cyclohexanone), 112–135 (aromatic carbons), 56.0 ($-\text{OCH}_3$), 28.5 (β carbon of cyclohexanone), 23 (γ carbon of cyclohexanone), 64 ($-\text{OCH}_2$, spacer), 61.5 ($-\text{CH}_2$, spacer), 32 ($-\text{CH}_2\text{O}$, spacer).

RESULTS AND DISCUSSION

Synthesis

We prepared the monomer, BHPMBCH, by the alkylation of BHMBCH under a Williamson aryl alkyl ether synthesis¹⁷ using 3-bromo-1-propanol and following a nucleophilic substitution reaction mechanism in dimethyl formamide (Scheme 1). It was then polymerized with various aliphatic and aromatic acid chlorides. All of the polymers were prepared by a solution polycondensation technique, and the synthetic route for the preparation is depicted in Scheme 2.

All of the polymers were obtained fairly in good yield. All of the aliphatic and aromatic polymers were brown and yellow in color, respectively. All of the polymers were soluble in polar solvents, such as DMSO, DMF, and CHCl_3 , at room temperature and were insoluble in nonpolar solvents, such as ethanol, methanol, toluene, and *n*-hexane. The solubility increased in polar aprotic solvents with increasing polarity index. This may have been due to the intermolecular interactions of polar solvents with ester linkages of the polymer molecules.¹⁹ The yield and



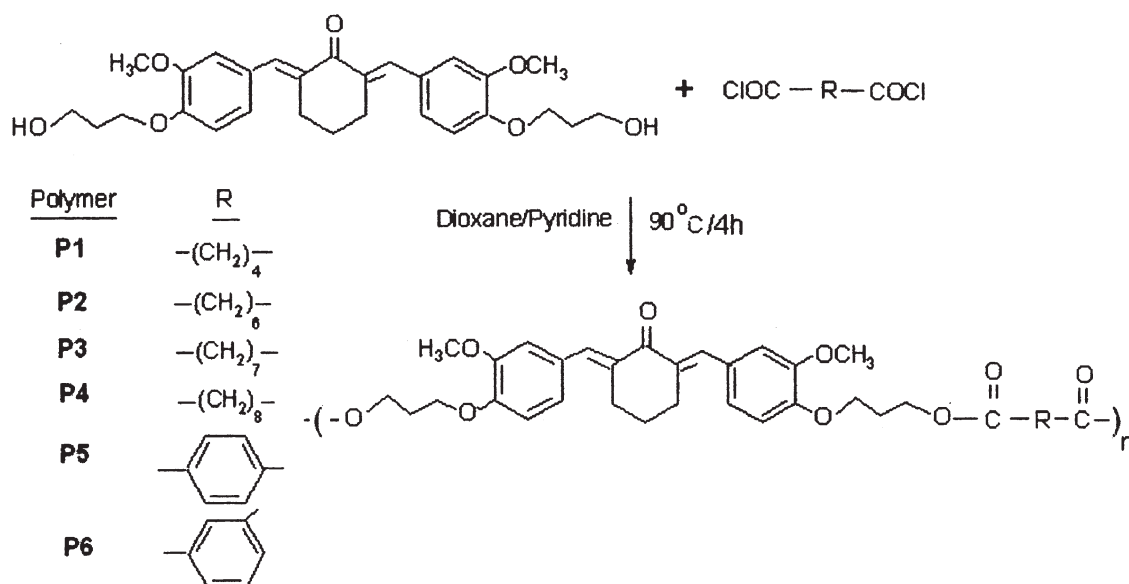
Scheme 1 Synthesis of the monomer BHPMBCH.

solubility data of the poly(ether-ester)s are given in Table I. The molecular weights of the resulting polymers were determined by GPC. The M_n values of polymers were in the range 1527–2003 with PDIs of 1.19–1.57. The intrinsic viscosities of the polymers were found to be in the range 0.06–0.80 g/dL (Table II).

The structure of the polymers was studied by ultraviolet-visible (UV-vis), FTIR, and NMR spectroscopic techniques. The representative FTIR spectrum of polyester **P2** is shown in Figure 1. The characteristic absorptions at 1660 and 1520 cm^{-1} corresponded to carbonyl (C=O) and exocyclic olefinic double bond (C=C) groups, respectively. All of the polymers showed a strong absorption band at 1716–1735 cm^{-1} , which was attributed to the presence of ester carbonyl linkages.²¹ The peak appearing between

2933 and 2920 cm^{-1} confirmed the presence of methylene groups in the backbone of the polymer. Asymmetric aryl alkyl ether stretching appeared at 1249–1252 cm^{-1} . These results support the formation of the polyesters.

The $^1\text{H-NMR}$ spectrum of polyester **P3** is shown in Figure 2. The olefinic protons appeared as a singlet around 7.75 ppm in all of the polymers as in the monomer; this indicated the existence of an E configuration.^{22,23} The methylene protons ($-\text{CH}_2-$) flanked between two $-\text{OCH}_2-$ groups appeared as a pentet at 2.3–2.4 ppm. The multiplet at 6.9–7.1 ppm was attributed to aromatic protons. The methoxy protons attached to the phenyl ring appeared as a singlet at 3.85–3.90 ppm. The singlet peaks appearing at 2.95 and 1.8 ppm corresponded to β and γ methylene protons of cyclohexanone, respectively.²⁴ A multiplet



Scheme 2 Synthesis of the polyesters.

TABLE I
Yield and Solubility Data of the Poly(ether-ester)s

Polymer code	Yield (%)	Solubility										
		Hexane	CCl ₄	Toluene	Benzene	THF	CHCl ₃	Acetone	MeOH	EtOH	DMF	DMSO
P1	80	--	--	--	+-	++	++	++	+-	--	++	++
P2	80	--	--	--	+-	++	++	++	+-	--	++	++
P3	73	--	--	--	+-	++	++	++	+-	--	++	++
P4	60	--	--	--	+-	++	++	++	+-	--	++	++
P5	85	--	--	--	+-	++	++	+-	+-	--	++	++
P6	80	--	--	--	+-	++	++	+-	+-	--	++	++

++: soluble at room temperature; +-: partially soluble at room temperature; --: insoluble even on heating.

of strongly shielded proton peaks arising around 1.3–2.4 ppm confirmed the presence of the aliphatic acid spacer protons in polymers P1–P4.

The proton-decoupled ¹³C-NMR spectrum of polyester P4 is shown in Figure 3. The peaks appearing at 130, 28, and 22.8 ppm corresponded to the α, β, and γ carbons of cyclohexanone, respectively. The resonance peaks appearing around 112–124 ppm were attributed to the aromatic carbons present in the polymer. The peaks corresponding to 191 and 173.5 ppm in all of the polymers signified the presence of ketonic and ester carbons, respectively.²⁵ The methoxy carbon attached to the phenyl ring resonated around 55–57 ppm in all of the polymers.

The UV-Vis spectra of the BHPMBCH monomer and all of the poly(ether-ester)s were determined in DMF solvent at ambient temperature. The absor-

bances of the monomer and all of the poly(ether-ester)s are given in Table II. Both the monomer and polymers showed an absorption peak around 371–388 nm in DMF; this peak corresponded to the π→π* transition of the C=C chromophoric group present in the compounds.²⁴ This confirmed the presence of the olefinic moiety in both the monomer and polymers.

Thermal properties

The TGA traces of all of the polyesters are shown in Figure 4. The temperatures corresponding to 10, 20, 30, 40, and 50% weight losses were determined from thermograms and are summarized in Table III. The results reveal that the polymers were stable up to 220°C and that 10% weight loss occurred around

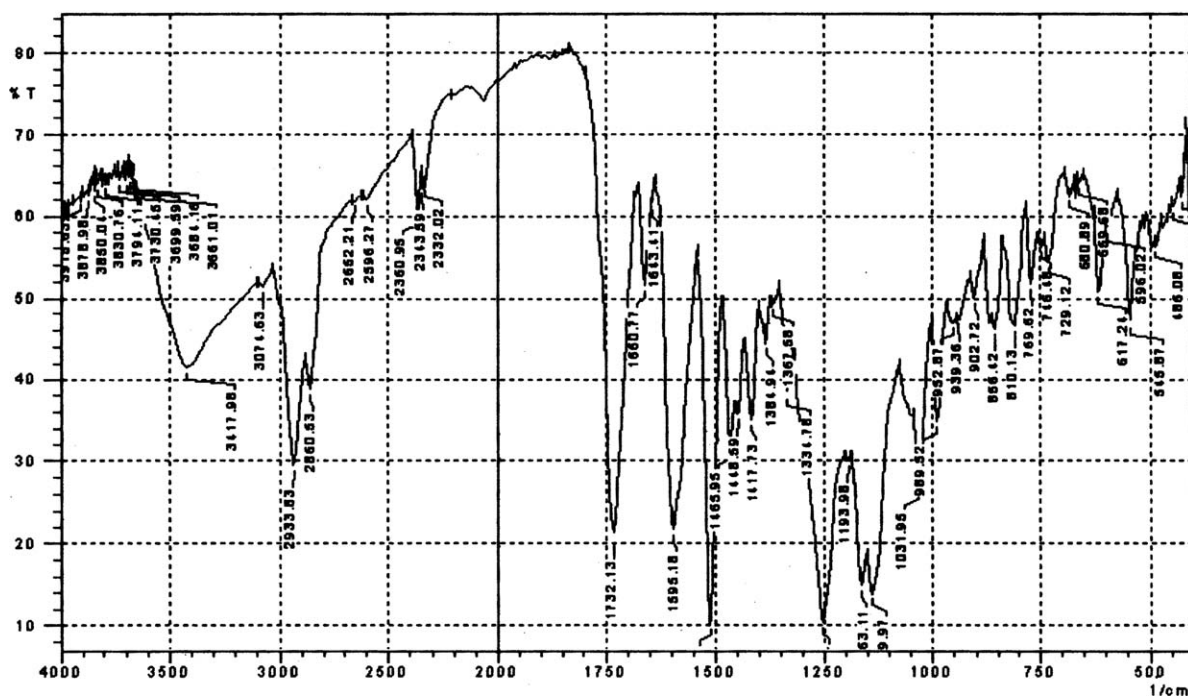


Figure 1 FTIR spectrum of polyester P2.

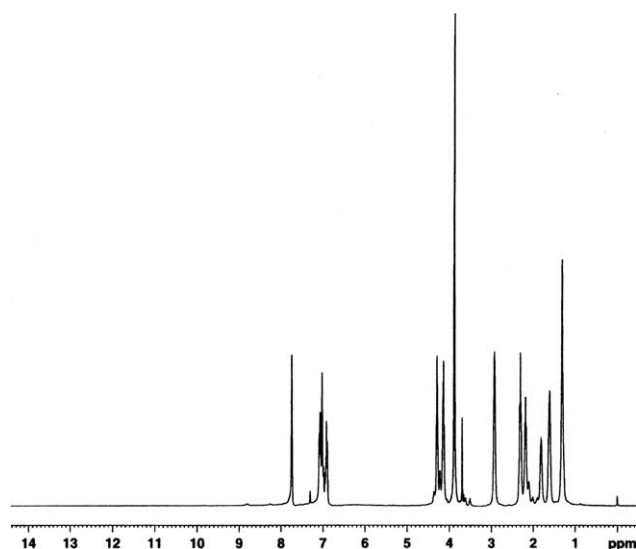


Figure 2 ^1H -NMR spectrum of polyester P3.

250°C. The 50% weight loss was observed around 400–445°C for all of the polymers; this may have been due to the decomposition of the rigid cyclohexanone segment.²⁶ All of the synthesized polyesters, except P1 and P6, showed a higher char yield at 700°C. Among the synthesized polyesters, polymer P3, derived from azelaic acid, had a higher thermal stability. Close inspection of the TGA thermograms revealed that the thermal stability initially increased with increasing spacer length, but further increases in the spacer length led to decreases in the thermal stability. This may have been due to the opposing effects of the decoupling function of the spacer and the flexibility of the spacer on the thermal stability. This type of observation was also reported by

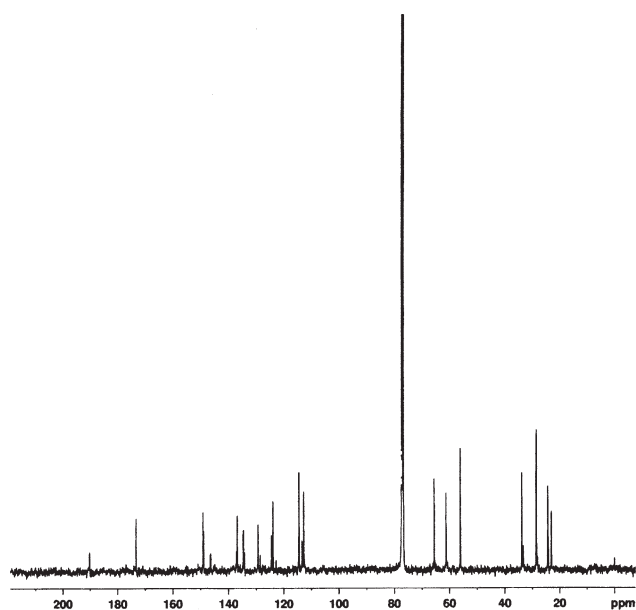


Figure 3 ^{13}C -NMR spectrum of polyester P4.

TABLE II
UV-Vis Spectral, Intrinsic Viscosity, and Molecular Weight Data of the Poly(ether-ester)s

Monomer/ polymer code	$\lambda_{\text{max}}^{\text{a}}$	Intrinsic viscosity (g/dL) ^b	GPC ^c		
			M_n	M_w	PDI
BHPMBCH	378	—	—	—	—
P1	376	0.06	1796	2643	1.47
P2	376	0.23	1627	2188	1.34
P3	377	0.20	2003	3080	1.54
P4	378	0.10	1699	2664	1.57
P5	377	0.80	1701	2026	1.19
P6	376	0.35	1527	1897	1.24

λ_{max} : wavelength at which maximum absorbance in the spectrum.

^a Measured in solutions of DMF.

^b Measured in solutions of 0.5 g/dL in DMSO at 30°C.

^c THF as an eluent against polystyrene standards.

Li et al.²⁷ Among the aromatic polyesters, the polymer containing terephthaloyl units showed a higher stability and char yield compared to the polyester containing isophthaloyl units. This may have been due to the higher crystallinity inside the hard domain of the polyester derived from terephthalic acid compared to that of the polyester derived from isophthalic acid.

The limiting oxygen index (LOI) for all of the polymers was determined with the Van Krevelen equation²⁸ and were in the range 21–30. According to Van Krevelen, polymers having an LOI above a threshold value of 26 possess self-extinguishing properties.²⁹ The LOI data indicated that all of the polyesters, except P1 and P7, had self-extinguishing properties. Polymer P1, derived from adipic acid, exhibited an LOI below the threshold value because of a lower number of methylene units in its chain compared to the other aliphatic polyesters. Similarly, the isophthaloyl polymer P7 also showed an LOI value below the threshold value because of a lack of symmetry compared to terephthaloyl polyester.

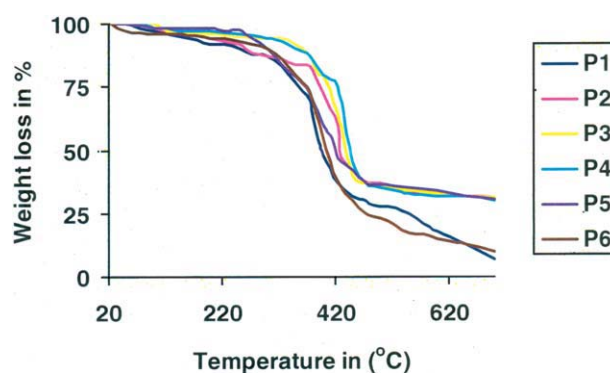


Figure 4 TGA traces of the polyesters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
DSC and TGA Data of the Poly(ether-ester)s

Polymer code	T_g (°C) ^a	T_m (°C) ^a	Temperature ^b (°C) corresponding to					Char residue (%) at 700°C ^b	LOI ^c
			10% weight loss	20% weight loss	30% weight loss	40% weight loss	50% weight loss		
P1	52.3	Multiple meltings	250	345	375	385	400	7	20.3
P2	–	118.9, 131.48	260	380	405	420	430	31	29.9
P3	–	148.4	370	405	415	435	445	32	30.3
P4	–	Multiple meltings	340	405	420	430	445	30	29.5
P5	–	–	300	330	380	400	415	31	29.9
P6	–	–	290	350	375	390	410	10	21.5

^a Measured by DSC at a heating rate of 10°C/min in nitrogen atmosphere.

^b The values were determined by TGA at a heating rate of 10°C/min in nitrogen atmosphere.

^c Determined with Van Krevelen's equation.

The DSC data of the synthesized poly(ether-ester)s is given in Table III. Figure 5 shows the DSC traces of all of the polyesters (P1–P7). Polymer P2 showed significant melting peaks at 118.9 and 131.4°C. Polymer P1, which had a lower number of methylene spacers, showed a low glass-transition temperature (T_g) of 52.3°C, along with multiple melting peaks. Polymers, P2–P4, with greater numbers of methylene units, showed no T_g 's. This may have been due to the negative effect of the spacer.²⁷ The absence of significant melting peaks in polyester P4 may have been due to an increased number of methylene units (CH₂)₈ in the polymer chain, which increased the flexibility, and also to the presence of methoxy groups at the phenyl ring, which reduced the aspect ratio of the polymer chain.³⁰ The multiple meltings in all of the aliphatic polyesters may have been due to the melting of microcrystalline units inside the hard macromolecules.³¹ It was observed that aromatic polyesters containing terephthaloyl and isophthaloyl units showed neither T_g nor melting. This may have been due to increased rigidity inside the hard domains.^{32,33}

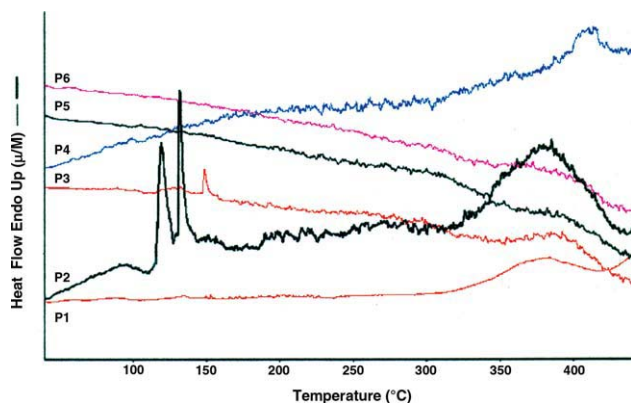


Figure 5 DSC traces of the polyesters. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

Photocrosslinking studies

Polymers having olefinic groups are sensitive to UV irradiation. The peculiar property of these type of polymers is the tendency to proceed to rapid photocrosslinking without the addition of any photoinitiators.³⁴ The scope of this investigation was to study the photoreactivity of the polymers in the solution state by UV spectrophotometry. Figures 6 and 7 show the changes in the UV spectral patterns during the photolyses of polyesters P1 and P3, respectively, at various intervals of time. The peak observed around 371–388 nm for all of the polymers corresponded to the $\pi \rightarrow \pi^*$ transition of the exocyclic double bond. During successive irradiations, a decrease in the intensity of absorbance was observed. This may have been due to the photocrosslinking of the polymer chains, which involved the $2\pi + 2\pi$ cycloaddition of the exocyclic double bond and led to the formation of cyclobutane ring.³⁵ For complete saturation of the exocyclic double bond, these polymers took more time. This may have been due to the rigid ring size of the cyclohexanone unit, which gave a

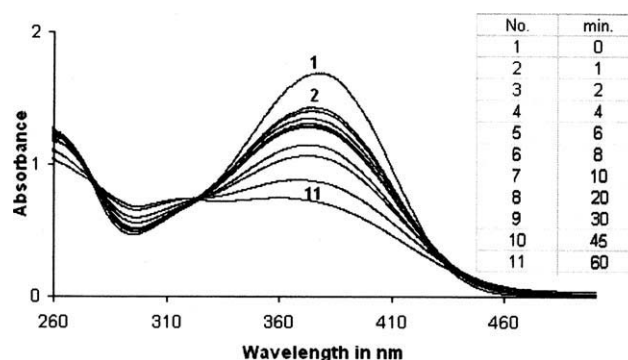


Figure 6 Change in the UV-vis spectral characteristics of polyester P1 in DMSO at various intervals of time, top to bottom, time $t = 0, 1, 2, 4, 6, 8, 10, 20, 30, 45,$ and 60 min.

slightly unfavorable geometry for $2\pi + 2\pi$ cycloaddition.^{34,36} The relative reactivity $[(A_0 - A_t)/A_0]$, where A_0 is the absorbance before irradiation and A_t is the absorbance after irradiation time t] was plotted against the time of irradiation. As shown in Figure 8, the rate of photocrosslinking increased significantly with increasing methylene carbon chain length of the acid spacer. The time required for 50% crosslinking of polymers **P1**, **P2**, and **P3** were 47, 37, and 20 min, respectively. Polymer **P3** had a higher molecular weight than **P2** and **P1**, as indicated in the GPC results. The higher molecular weight of **P3** may have restricted the chain mobility of the polymer and may have facilitated the photocrosslinking of the polymer chain. This may have been the reason for the higher crosslinking rate of polymer **P3** over those of **P1** and **P2**.

CONCLUSIONS

Photosensitive poly(ether-ester)s were synthesized from BHPMBCH and aliphatic and aromatic acid chlorides by solution polycondensation. Both the aliphatic and aromatic polymers were soluble in polar solvents and insoluble in nonpolar solvents. The formation of the poly(ether-ester)s was confirmed by UV-Vis, FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectral techniques. The TGA results clearly indicate that these polymers were stable up to 220°C and that the thermal stability of polymers **P1-P4** initially increased with increasing spacer length; however, further increases in the spacer length led to a decrease in the thermal stability. DSC analysis showed that the polyesters with an increased number of methylenic acid spacer carbons imparted a higher crystallinity with multiple meltings because of the negative effect of the spacer. This system could be suitably exploited for the LC studies. The UV spectral studies revealed that the polymer underwent photocrosslinking under the influence of UV radiation and

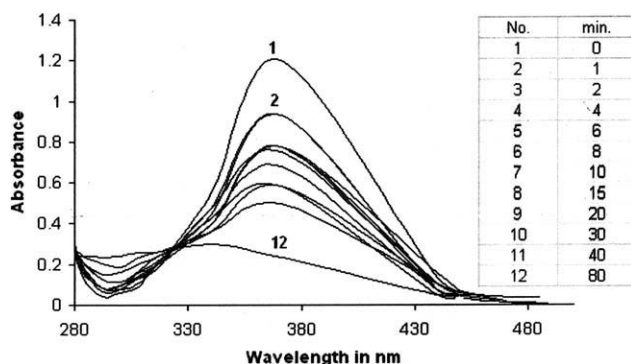


Figure 7 Change in the UV-vis spectral characteristics of polyester **P3** in DMSO at various intervals of time, top to bottom, time $t = 0, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40,$ and 80 min.

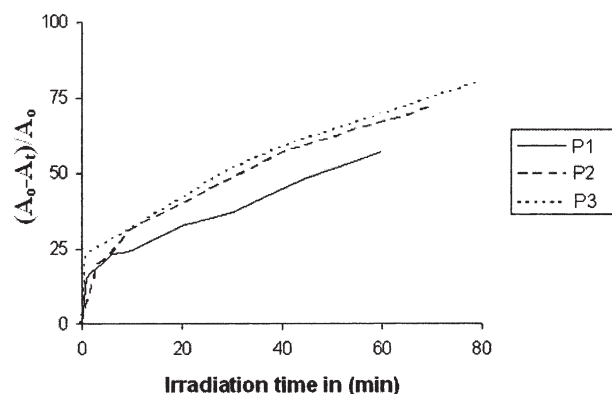


Figure 8 Relative rate of the crosslinking of the polyesters (**P1-P3**).

showed that with increasing methylene carbon content, the rate of photocrosslinking also increased because of the proper orientation of the polymer molecule.

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