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Poly[4-pyridinyl-4´-(2-methacryloyloxyethoxy)styryl ketone-co-2-hydroxypropyl methacrylate]: Synthesis, Characterization, Thermal and Electrical properties, and Photocrosslinking behavior

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Abstract: Synthesis of a chalcone bearing pyridine ring, 4-pyridinyl-4´-(2-hydroxyethoxy)styryl ketone, was carried out from the reaction of 4-acetyl pyridine and 4-(2-hydroxyetoxy)benzaldehyde in an aqueous solution of NaOH. 4-Pyridinyl-4´-(2-methacryloyloxyethoxy)styryl ketone which is the methacrylate monomer bearing chalcone structure in side chain, was obtained from acylation of 4-pyridinyl-4´-(2-hydroxyethoxy)styryl ketone with methacryloyl chloride in the cold. The copolymer of 4-pyridinyl-4´-(2-methacryloyloxyethoxy)styryl ketone and 2-hydroxypropyl methacrylate was prepared by free radical polymerization in presence of AIBN at 70 ^{o}C. FTIR, ^{1}H-NMR and ^{13}C-APT spectroscopic techniques were used for structural characterization of the Chalcone, the monomer and the copolymer. Thermal characterization of the copolymer was carried out using DSC and TGA techniques. DSC curve shows that this copolymer has a glass transition temperature of 78 ^{o}C. The TGA curve shows that decomposition given volatile product started at 230 °C and a residue of 21% left at 500 °C. Dielectric constant (ε´) of the copolymer decreased rapidly from 8.8 to 4.2 with increasing frequency in the range of 100-1000 Hz, and after this frequency ε´ quantity remained constant at a value such as 4.2. ε´ Value of the copolymer increased only from 4.2 to 4.9 with increasing from 290 K to 385 K. The AC conductivity of the copolymer increases from 5.01×10^{-10} S/cm to 126.0×10^{-10} S/cm as the frequency increase from 100 Hz to 5000 Hz. The AC conductivity increases slightly with increasing temperature, 2.52×10^{-9} S/cm at 300 K, and 2.89×10^{-9} S/cm at 385 K. After a solution of the copolymer was irradiated using UV light at 365 nm at room temperature, the absorption band at 356 nm disappeared and a new band was seen at 284 nm.

Key words : chalcone, photocrosslink, thermal properties, conductivity, dielectric constant

Poli[4-piridinil-4´-(2-metakriloiloksietoksi)stiril keton-ko-2-hidroksipropil metakrilat]: Sentezi, Karakterizasyonu, Termal ve Elektriksel Özellikleri ve Fotoçaprazbağlanma Davranışı

Özet : Piridin halkası taşıyan kalkonun sentezi, 4-piridinil-4´-(2-hidroksietoksi)stiril keton, 4-asetil piridin ve 4-(2-hidroksietoksi)benzaldehitin NaOH in sulu çözeltisinde reaksiyonundan gerçekleştirildi. Yan zincirinde kalkon yapısı taşıyan bir metakrilat monomeri olan 4-piridinil-4´-(2-metakriloiloksietoksi)stiril keton, 4-piridinil-4´-(2-hidroksietoksi)stiril ketonun metakriloil klorürle soğukta açillenmesinden elde edildi. 4-piridinil-4´-(2-metakriloiloksietoksi)stiril keton ve 2-hidroksipropil metakrilatın kopolimeri, AİBN yanında 70 ^{o}C de serbest radikal polimerizasyonuyla elde edildi. Kalkon, monomer ve kopolimerin yapısal karakterizasyonunda FTIR, ^{1}H-NMR ve ^{13}C-APT spektroskopik teknikleri kullanıldı. Kopolimerin termal karakterizasyonu DSC ve TGA teknikleriyle gerçekleştirildi. DSC eğrisi kopolimerin camsı geçiş sıcaklığının 78 ^{o}C olduğunu gösterdi. TGA eğrisi uçucu madde veren temel parçalanmanın 230 ^{o}C de başladığını ve 500 ^{o}C de %21 artık bıraktığını gösterdi. Kopolimerin dielektrik sabiti (ε´) 100-1000 Hz aralığında artan frekansla 8.8 den 4.2 ye hızla düştü ve bu frekanstan sonra ε´ niceliği 4.2 gibi bir değerde

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sabit kaldı. Kopolimerin ε´ değeri, sıcaklık 290 K den 385 K e artarken sadece 4.2 den 4.9´a yükseldi. Kopolimerin AC iletkenliği, frekansın 100 Hz´den 5000 Hz´e çıkmasıyla 5.01×10^{-10} S/cm´den 126.0×10^{-10} S/cm´ye arttı. AC iletkenliği artan sıcaklıkla çok az yükseldi, 300 K´de 2.52×10^{-9} S/cm ve 385 K´de 2.89×10^{-9} S/cm. Kopolimerin bir çözeltisi 365 nm dalga boylu UV ışığa maruz bırakıldığında 356 nm´deki band kayboldu ve 284 nm´de yeni bir band oluştu.

Anahtar kelimeler: Kalkon, fotoçapraz bağlanma, termal özellikler, iletkenlik, dielektrik sabiti

1. Introduction

Chalcones have been identified as interesting compounds that are associated with several biological activities and photochemical behaviors. In chalcones, two aromatic rings are linked by an aliphatic three carbon chain. Chalcones are α,β-unsaturated ketones (-CH=CH-CO-) containing of two aromatic rings which are interconnected by a highly electrophonic three carbon that assumes linear or nearly planar structure [1]. Chalcones can be natural or synthetic. Synthetic chalcones are commonly synthesized with the reaction of aromatic ring bonded to acetyl group and benzaldehyde derivatives via the Claisen-Schmidt condensation in presence of bases or acids catalyst [2-7]. One of the important characteristics of the chalcones is that they have the ability to photocrosslinking under ultraviolet light [8-13]. Photochemical reactions may provoke many changes in physicochemical properties such as solubility, dielectric constant, electrical conductivity, optical transparency and refractive index [14,15]. Photoresponsive polymers containing chalcone or any photoreactive group have also acquired potential importance in various industrial application, such in microlithography [16], printing materials [17], medical fields [18], and fluorescent probes for sensing of DNA [19] or metal ions [20,21].

The conductivity and dielectric properties of photosensitive polymers have not been studied adequately. K. Demirelli et al. have investigated their thermal properties as well as their dielectric properties of a coumarin polymer [22]. Panday et al. also examined the optical properties of a polymer bearing chalcone group, as well as their dielectric properties [23].

In this work, synthesis of a chalcone bearing pyridine ring, [4-pyridinyl-4´-(2-hydroxyethoxy)styryl ketone], PHSK, and its transformation to a methacrylate monomer, and its copolymerization with 2-hydroxypropyl methacrylate, HPMA, were studied. Besides the structural characterization via FT-IR and NMR, the thermal and electrical properties, and UV irradiation behavior of poly(PHSK-*co*-HPMA) were also investigated.

2. Experimental

2.1. Materials

4-acetyl pyridine, 4-(2-hydroxyetoxy)benzaldehyde, methacryloyl chloride, methanol, tetrahydrofuran (THF), 1,4-dioxane and sodium hydroxide were obtained from Sigma-Aldrich and used as purchased. AIBN was received from Fluka and recrystallized from methanol before use.

2.2. Synthesis of 4-pyridinyl-4´-(2-hydroxyethoxy)styryl ketone (PHSK)

In a reaction flask an aqueous solution of 0.1 M 15 mL NaOH was added to 4-acetyl pyridine (1.33 g, 10.97 mmol) in 5 mL of methanol. The reaction content was cooled to 5-8 ^{o}C and then a solution of 4-(2-hydroxyetoxy)benzaldehyde (1.83 g, 11 mmol) in 5 mL methanol was added dropwise while the temperature was allowed below 5 ^{o}C. After the reaction mixture was stirred at room temperature for 24 h, the product was precipitated by pouring to 100 mL cold water and filtered off and dried under vacuum at 60 ^{o}C for 24 h. Yield : 2.22 g (75 %); m.p. 139-140 ^{o}C.

FT-IR (KBr, cm^{-1}) : 3283 (O-H stretching), 3040 (aromatic and olefinic =C-H stretching), 1663 (C=O stretching of the chalcone), 1583 (aromatic C=C stretching) and 823 (out of plane bending vibration of =C-H in p-disubstituted aromatic structure).

^{1}H-NMR (Chloroform-d) (ppm) 3.65 (2H, in aromatic-O-C-CH_2-O- group), 4.7 (2H, in aromatic-O-CH_2-C-O- group), 5.3 (1H, -OH), 6.7 (aromatic protons in ortho position according to oxygen in p-disubstituted benzene ring), 8.5-9.0 ppm (aromatic protons in 2,6 position of pyridine ring), 7.0-8.0 (other aromatic ring protons).

^{13}C-APT (chloroform-d, ppm): Negative signals: 190 (C=O carbon in chalcone), 161 (aromatic quaternary carbon bonded oxygen), 144 (quaternary carbon in pyridine ring), 127 (quaternary carbon in para position according to oxygen), 70 (methylene carbon in aromatic-O-CH_2- group) and 61 (methylene carbon in aromatic-O-C-CH_2-OH group). Positive signals:151 (aromatic carbons in 2,6-position of pyridine ring), 146 ppm (olefinic β-C according to carbonyl), 131 ppm (aromatic carbons in metha according to oxygen), 121 ppm (carbons in 3-number of pyridine ring), 119 ppm (olefinic -C according to carbonyl), 115 ppm (ortho carbons according to oxygen),

2.3. Synthesis of 4-pyridinyl-4´-(2-methacryloyloxyethoxy)styryl ketone (PMSK)

In a 50 mL reaction flask, PHSK (1,345 g, 5 mmol) and 4-(N,N-dimethylamino)pyridine (0.702 g, 5.75 mmol) were dissolved in 10 mL of THF and cooled to 0 ^{o}C. Methacryloyl chloride (0.572 g, 5.5 mmol) in 3 mL of THF was then added dropwise with stirring, keeping the temperature in the range 0 to 5 ^{o}C. After the reaction mixture was stirred for 3 hours below 5 °C, the temperature of the reaction mixture was allowed to rise to room temperature and stirring was continued for 24 hours. The quaternary ammonium salt formed was filtered off.

After some part of THF was evaporated in a rotary evaporator, the product was precipitated in excess cold n-hexane, filtered off and dried under vacuum at 40 ^{o}C for 24 h. Yield : 1.20 g (71 %); m.p. 118-121 ^{o}C

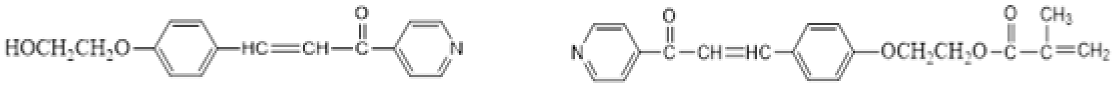
FT-IR (KBr, cm^{-1}): 3070 (aromatic and olefinic =C-H stretching), 1730 (ester C=O stretching), 1649 (C=O stretching in chalcone and carbon to carbon double bond streching in C=CH_2), 1216 (C-O-C asymmetric stretching in ester), 1038 (C-O-C asymmetric stretching in ester) and 823 cm^{-1} (out of plane bending vibration of =C-H in p-disubstituted aromatic structure).

^{1}H-NMR (chloroform-d, ppm): 7.0-8.5 (aromatic ring protons), 6.0-6.5 ppm (olefinic protons), 4.0-4.5 ppm (protons in –OCH_2 group) and 1.4 ppm (-CH_3 protons).

^{13}C-APT (chloroform-d, ppm): Negative signals: 192 (C=O carbon in chalcone), 170 (C=O in ester), 162 (aromatic quaternary carbon bonded oxygen), 73 (methylene carbon in aromatic-O-CH_2-group) and 65 (methylene carbon in aromatic-O-C-CH_2-OC(=O) group). Positive signals:151 (aromatic carbons in 2,6-position of pyridine ring), 146 ppm (olefinic β-C according to carbonyl), 131 ppm (aromatic carbons in metha according to oxygen), 121 ppm (carbons in 3-number of pyridine ring), 119 ppm (olefinic -C according to carbonyl), 115 ppm (ortho carbons according to oxygen). Positive signals: 115-160 (aromatic =C-H carbons) and 17 (-CH_3 carbons).

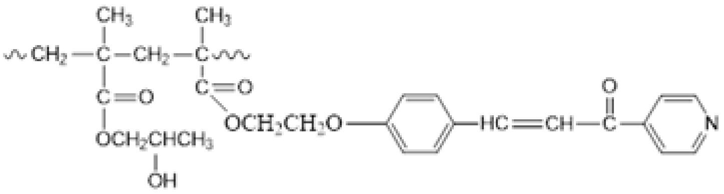
2.4. Copolymerization of 2-hydroxypropyl methacrylate (HPMA) and PMSK

A solution in a mixture of 1 mL 1,4-dioxane and 0.5 mL THF of PMSK (1,216 g, 3.62 mmol), 2-hydroxypropyl methacrylate (HPMA, 2.100 g, 14.56 mmol) and AIBN (as a free radical initiator) in an amount of 1% of the monomer mixture were added into a polymerization tube. After the mixture was flushed with argon gas for 10 min, the polymerization tube was tightly closed and copolymerization was carried out at 70 °C for 6 h. After this time, the copolymer solution was diluted by adding some 1,4-dioxane into the polymerization tube and then the copolymer was precipitated in cold n-hexane, filtered off, and purified by reprecipitation with the same precipitor. The copolymer was dried in a vacuum oven at 40 °C for 24 h.



4-pyridinyl-4´-(2-hydroxyethoxy)styryl ketone (PHSK)

4-pyridinyl-4´-(2-methacryloyloxyethoxy)styryl ketone (PMSK)



poly(HPMA-*co*-PMSK)

Figure 1. Chemical structure of the chalcone, the monomer with chalcone side chain and the copolymer

2.5. Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer using KBr pellets. NMR spectra were obtained with a Bruker 400 MHz, FT-NMR spectrometer with TMS as an internal standard reference in $CDCl_3$ or DMSO-d_6 solutions. Calorimetric measurements were carried out on a Shimadzu DSC-50 thermal analyzer under N_2 flow a using a heating rate of 20 °C/min. Thermal stability studies were carried out on a Shimadzu TGA-50 thermobalance under N_2 flow with a heating rate of 10 °C/min. For capacitance measurements according to the previous work [24], the copolymer was ground with an agate mortar and pestle, and the final fine powder was pressed at four tons of pressure into disk-shaped sample with a thickness of 0.95 mm and a diameter of 12 mm for the disk. The entire surface of the disk was coated with silver cake, which acts as a good contact for capacitance measurements. The measurements were carried out with a QuadTech 7600 precision LRC meter impedance analyzer over the frequency range 0.1 - 5 kHz. The dielectric features against the frequency and temperature were examined, and AC conductivity of the copolymer against the temperature were also examined at 1 kHz constant frequency. For UV irradiation, a medium pressure mercury vapor lamp given 365 nm UV light was used as a UV source. The copolymer solutions were irradiated with UV lamp at distance of 10 cm from light source for different intervals of time at room temperature. UV-vis spectroscopic measurements were carried out using a Secomam S-500 UV-vis spectrophotometer at room temperature.

3. Results and Discussion

3.1. Synthesis and characterization

4-Pyridinyl-4´-(2-hydroxyethoxy)styryl ketone (PHSK, the chalcone) was prepared by reacting of 4-(2-hydroxyetoxy)benzaldehyde with 4-acetylpyridine in methanol in presence of NaOH as base according to the method adopted from the literature [25]. The photosensitive methacrylate monomer (PHSKM) having pendant chalcone group was prepared from the reaction of the chalcone (PHSK) and methacryloyl chloride. The copolymerization of PHSKM and 2-hydroxypropyl methacrylate

(HPMA) (feed ratio : 1:4 by mol) were carried out in presence of AIBN as free radical initiator at 70 °C for 6 h.

FT-IR spectrum (Figure 2) of poly(PHSKM-*co*-NPMA) showed the characteristic bands at 3437 cm^{-1} (OH stretching), 3050 cm^{-1} (aromatic =C-H stretching), 2850-2980 cm^{-1} (aliphatic C-H stretching), 1731 cm^{-1} (ester C=O stretching), 1591 cm^{-1} (aromatic C=C stretching), 1180 cm^{-1} (ester (C=O)-O-C asymmetric stretching), 1070 cm^{-1} (ester (C=O)-O-C symmetric stretching). In the ^{1}H-NMR spectrum (Figure 3) of the copolymer signals at 8.7 ppm and 6.9 ppm corresponds to nitrogen-adjacent protons in the pyridine ring and aromatic ortho protons according to oxygen (and -CH proton according to carbonyl in chalcone), respectively. The signals at 7.2-8.0 ppm were attributed other aromatic protons and β-CH olefinic proton according to carbonyl in chalcone. The signals at 3.0-4.7 pmm showed the protons in (O=C)O-CH_2-CH(O)- in side group of HPMA units and (O=C)O-CH_2CH_2O- in chalcone units. The signals at 0.8-2.0 ppm were attributed the protons at polymer backbone and methyl group.

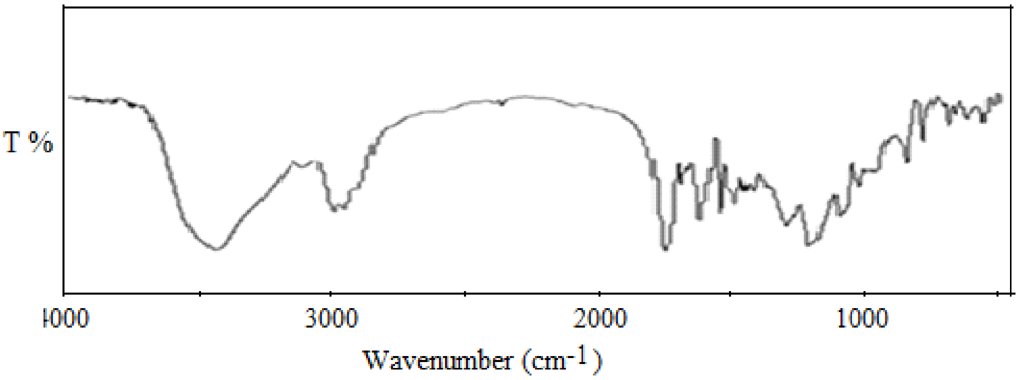


Figure 2. FT-IR spectrum of poly(PHSKM-*co*-HPMA)

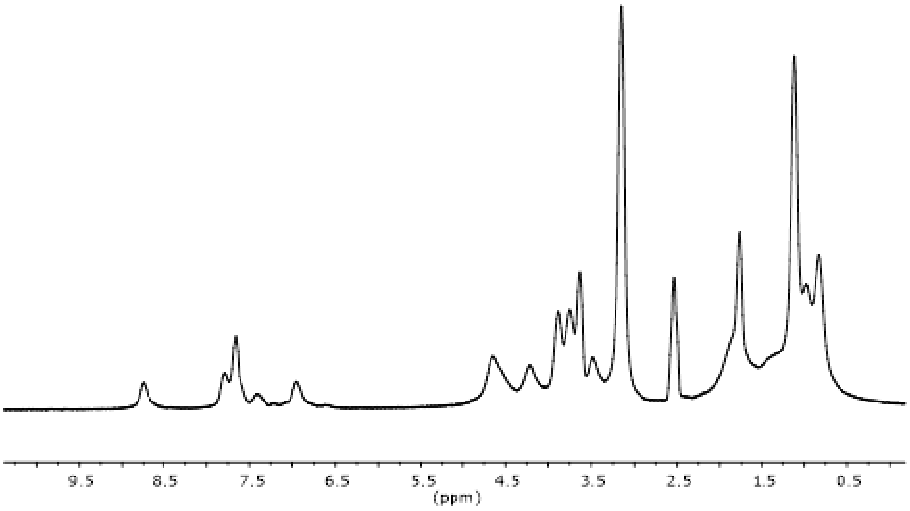


Figure 3. ^{1}H-NMR spectrum of poly(PHSKM-*co*-HPMA)

3.2. Thermal investigation

Thermal investigation was carried out by TGA (Figure 4a) and DSC (Figure 4b) technique. After a volatilization starting at about 120 °C given a weight loss of 4 % which is probably solvent and/or precipitator, it was understood from the TGA curve that the rapid breakdown of the poly (4-

HEPPKM-*co*-2-HPMA) copolymer initiated at 230 °C and a residue of 50% at 350 °C and 21% at 500 °C left. The DSC curve showed that this copolymer has a glass transition temperature at around 78 °C. Considering that the 2-HPMA units in the copolymer are of very high values, it is understood that this Tg value more reflects that of poly (2-HPMA). Indeed in the literature, values such as 72 °C [26], 76 °C [27] for Tg of poly (2-HPMA) are given.

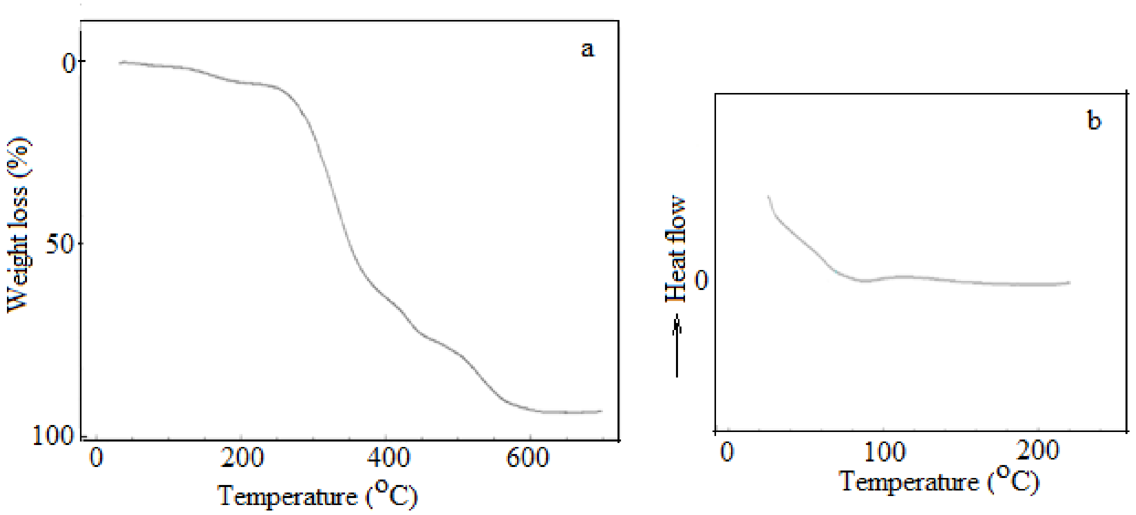


Figure 4. TGA (a) and DSC (b) curves of poly(PHSKM-co-HPMA)

3.3. Electrical investigation

Dielectric constant, a characteristic of an electric insulator, is defined as the ratio of the capacitance of a capacitor filled with a given material to the capacitance of a similar capacitor in a vacuum without dielectric material. A material with a high dielectric constant is placed in an electrical field, the magnitude of the field will be reduced within the volume of the dielectric. Dielectric constant (ε′) is evaluated from the capacitance measurement using the following equation:

$$\varepsilon' = \frac{C.d}{A\varepsilon_o} \qquad (1)$$

where ε_o is permittivity in free space, which is equal to ε_o = 8.856x10^{-14} F/cm, C is parallel capacitance, d and A are thickness and area of the sample, respectively.

The dependence of the dielectric constant on frequency and temperature has been investigated (Figure 5). The dielectric constant decreased rapidly (Figure 5a) from 8.8 to 4.2 with increasing frequency in the range of 100-1000 Hz, and after this frequency ε′ quantity remained constant at a value such as 4.2. This may be due to very low orientation and oscillation of permanent dipoles in the applied field, that is this phenomenon is related to the effect of polarization [28,29]. The variation of dielectric constant with temperature at 1 kHz fixed frequency for the copolymer is seen in Fig 5b. The Figure shows that dielectric constant of the copolymer increases only from 4.2 to 4.9 with increasing from 290 K to 385 K of temperature due to an increase of total polarization arising from dipoles and trapped charge carriers [28]. At around 365 K (93 °C), a value slightly above the T_g temperature, ε′ quantity increased more rapid with increasing temperature because of formation of free volume enough to freedom of movement of dipole molecular chain of the copolymer [30].

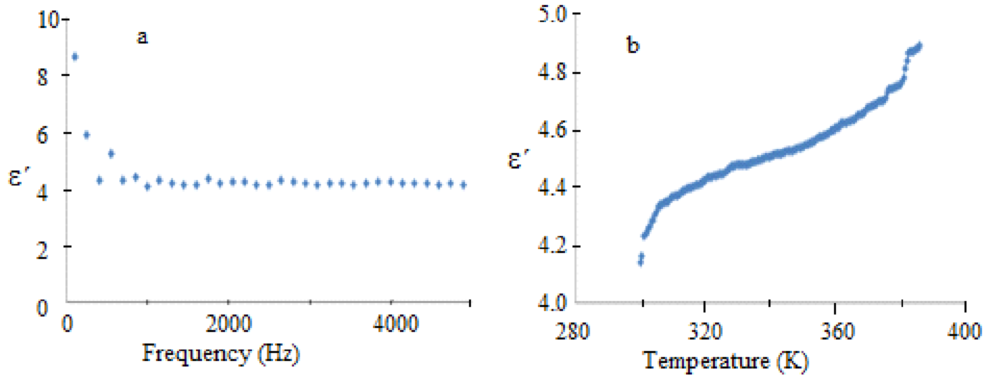


Figure 5. Frequency (a) and temperature (b) dependence of dielectric constant of poly(PHSKM-co-HPMA)

The variation of AC conductivity with frequency at room temperature in range of 100-5000 Hz for the copolymer is seen in Figure 6a. The figure shows that the AC conductivity of the copolymer increases with frequency from 5.01x10^{-10} S/cm to 126.0x10^{-10} S/cm as the frequency increase from 100 Hz to 5000 Hz. The conductivity increases more rapid with frequency up to about 1500 Hz, and increase in range of 1500-5000 Hz is slower. The temperature dependence of the AC conductivity is studied in range of 300-385 K at 1 kHz. It was observed that the AC conductivity increases with increasing temperature (Figure 6b). As the conductivity at 300 K was 2.52x10-9 S/cm, it increased only to 2.89x10^{-9} S/cm at 385 K. In other words, the increase in conductivity was only about 0.37x10^{-9} S/cm for a temperature increase of 85 degrees. It can be said that there is generally no linearity in the increase in conductivity, but two linear regions with relatively different slopes in the range of 310-350 K and 350-378 K. The temperature of the 350 K (77 ^{o}C) which is the intersection point of approximate lines corresponds to the glass transition temperature of the copolymer.

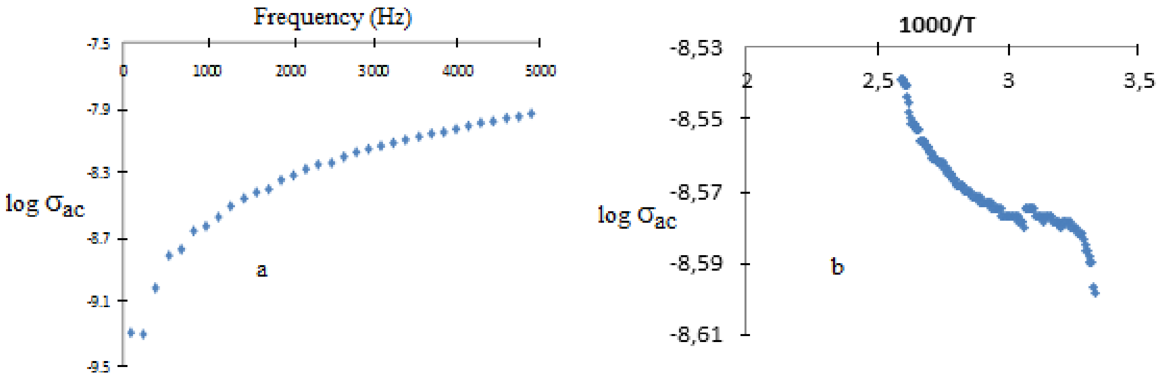


Figure 6. The plots of AC conductivity (log σ_{ac}) vs frequency (a) and log σ_{ac} vs 1/T of of poly(PHSKM-*co*-HPMA)

3.4. UV-vis absorption spectroscopic study after UV—irradiation

The photocrosslinking properties of poly (4-HEPPKM-co-2-HPMA) sample having a photosensitive chalcone moiety have been examined in DMSO solution with concentration 15 mg/25 mL in absence of photosensitizer. The copolymer solution was irradiated using a medium pressure Hg lamp with UV light at 365 nm at room temperature. The UV-vis absorption spectra of the copolymer before and after each irradiation were recorded (Figure 7). The copolymer showed maximum absorption at 356 nm (λ_{max} = 356 nm), due to the π-π* transitions of C=C in side chain chalcone moiety of the copolymer [31], before irradiation. Absorbance value of this band decreased rapidly with irradiation time from 0 to 315 min, and a new band at 284 nm, which is attributed to a new structure, arised. It is well known that the chalcone double bonds transform to cyclobutane ring with UV irradiation [11,14,31-33]. The formation of cyclobutane ring by $2\pi + 2\pi$ addition of pendant chalcone units of the copolymer causes a decrease in the intensity of the band at 356 nm and formation of a new absorption band at 284 nm. The shift from 356 nm to 284 nm of maximum absorption band can be attributed to the decrease in the conjugated double bond system together with the cycloaddition reaction. An isosbestic point is at 307 nm due to the cis–trans isomerization of the double bond in chalcone moiety [14,32]. The UV absorption band at 356 nm is almost completely disappeared within 315 min of irradiation. The rate of disappearance of the double bond in the photosensitive groups was followed by using the expression [14]:

$$Percent\ of\ decay = \frac{A_o - A_t}{A_o} x100 \qquad (2)$$

where A_o and A_t are absorption intensities at λ_{max} 356 nm, due to double bond of the photosensitive groups after irradiation times t = 0 and t = t, respectively. Plot of decay percent verses irradiation time (t) is shown in Figure 8. The rate of decay in the C=C bond of the chalcone on exposure to UV irradiation is fast in the first 60 min (about 63%) followed by a slow rate (about 82% in 185 min) and then very slow at between 185-315 min (about 90% in 315 min). The gradual decrease of the decay rate with the time of irradiation has also been observed for many other chalcones [13,14,32-34]

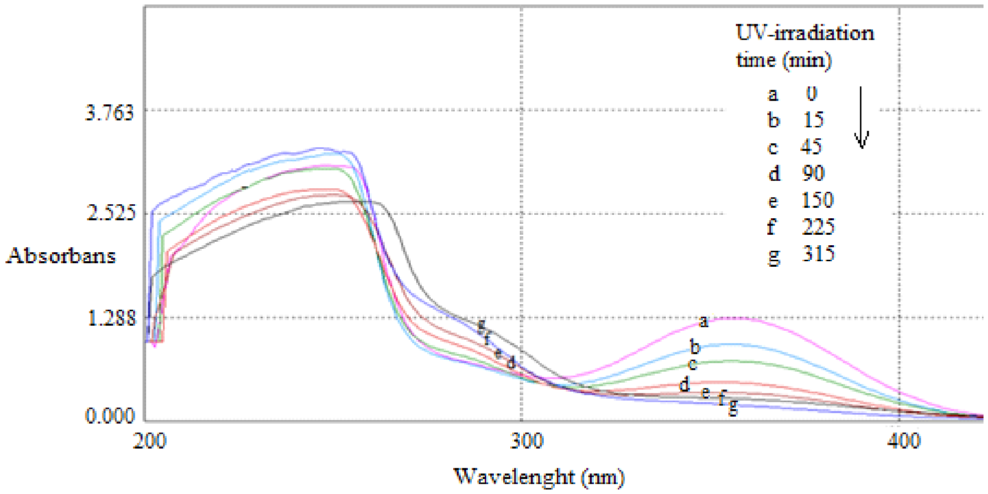


Figure 7. Changes in the UV spectral pattern of poly(PHSKM-*co*-HPMA) in DMSO solution upon irradiation.

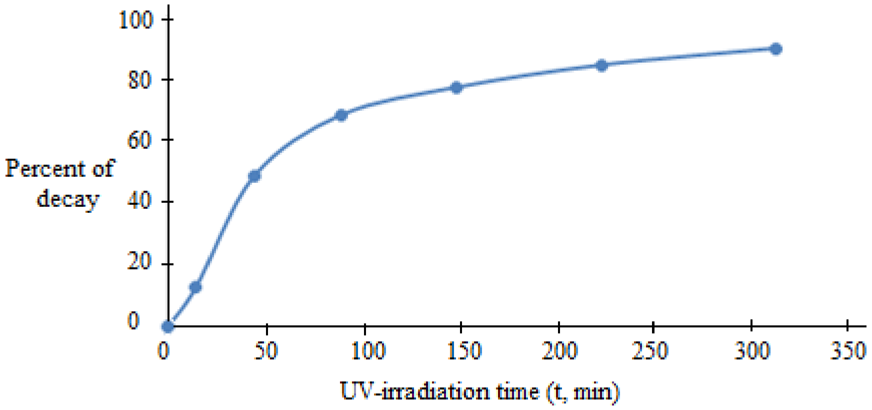


Figure 8. Plot of decay percent vs UV-irradiation time (t, min)

4.Conclusions

A new methacrylate copolymer bearing photo-crosslinkable chalcone group was synthesized by free radical polymerization in solution using AIBN as initiator. The structure of the chalcone, monomer and the copolymer were characterized using FTIR, ^{1}H-NMR and ^{13}C-APT spectroscopic techniques. The thermal characterization showed that glass transition temperature of the copolymer is 78 ° C, that the basic decomposition giving volatile products was started at 230 ° C, and that left a residual of 21 % at 500 ° C.

The electrical investigation indicated that the dielectric constant and the AC conductivity of the copolymer dependent slightly on temperature. However, it has been observed that these quantities are significantly dependent on the frequency, especially at low frequencies. It was seen that the dielectric constant rapidly decreased with frequency up to 1000 Hz and the conductivity increased faster with frequency up to 1000 Hz. The UV absorbance at λ_{max} = 356 nm characterized the chalcone structure was disappeared at the end of the exposure of the solution in DMSO of poly (PHSKM-co-HPMA) and a new UV band at λ_{max} = 284 nm was rised. These results show that the conjugated double bond system has been reduced to a new structure.

Acknowledgments

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