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Photoactive poly(hydroxyl-amino ether)s based on 4-methyl-cyclohexanone and 4-*tert*-butylcyclohexanone moieties in the main chain: synthetic methodology and characterization

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Abstract

A new class of photoactive poly(hydroxyl-amino ether)s **P1a-d** & **P2a-d** based on diarylidene-epoxy moieties were synthesized by ring opening polymerizations of diarylidene epoxy monomers **2a-d** during the reaction with 4,4'-diamino diphenyl methane (DDM) or 4,4'-diamino diphenyl ether (DDE). Diarylidene-epoxy monomers **2a-d** were synthesized by the reaction of diarylidene cycloalkanones derivatives **1a-d** with excess of epichlorohydrin in presence of NaOH and TBAI as a catalyst. The molar masses of the resulting polymers were determined by gel permeation chromatography (GPC), all polymers have moderate molar masses. Moreover, the photo-responsive properties of selected examples of polymers were tested in THF by studying the photolysis of their solutions in THF under UV lamp (450 nm) at different time intervals. This study revealed the occurrence of photocrosslinking behavior in the system under these conditions. The thermal properties of these polymers were evaluated by thermogravimetric analysis (TGA). In addition, the morphological properties of selected examples of polymers were tested using scanning electron microscope (SEM).

Keywords: New series of photoactive polymers, Diarylidene-cycloalkanones, Poly(hydroxyl-amino ether)s, Synthesis.

1. Introduction

In recent years, much emphasis has been given to the synthesis of epoxy resins. They have attracted properties such as stiffness, higher thermal stability, chemical resistance, higher resistance to moisture absorption or corrosive liquids and good electrical insulation in addition to many other properties [1-5]. Owing to their important properties, epoxy resins are involved in many industrial fields as surface coatings, electronic packaging, optoelectronics, advanced composites and electronic/electrical industries [6-10]. The reaction of epoxides with diamines described as poly(hydroxyl-amino ether)s are mostly interesting, because it leads to the formation of β-amino alcohols by ring-opening reactions which are the basic intermediates to many organic compounds, including new glassy, moulding polymers [11, 12], crystalline thermoplastics [13, 14], liquid crystalline polymers [15] and elastomeric material [16]. Poly(amino-ether)s (PAE) resins exhibited a powerful combination of properties such as excellent adhesion to different substrates, high optical quality, excellent resistance to penetration by atmospheric gases, optical clarity, low color, high solubility and good mechanical behavior [17-21]. PAE have important industrial applications as they used in thermoplastics and packing industries [22-28]. The incorporation of bis arylidene-cyclolkanone molecules into the polymeric architectures may lead to enhancement in their properties by cooperative mechanisms. The bis arylidene-cycloalkanone molecules facilitate photochemical reactions of the polymer chains under the influence of UV irradiation [29–32].

The photosensitivity of these materials is mainly attributed to the π-electron density of the photoactive chromophore in the polymer backbone [33]. Photoirradiation reactions occur changes in the physical and chemical properties of the polymers [34, 35]. The photocrosslinkability of the polymers is due to the presence of photocrosslinkable moieties like arylidene ketones, arylidene esters [36]. Over the last two decades, photocrosslinkable polymers have potentially interesting applications, such as photocurable materials, surface coatings, printing inks, printing plates in photo recorders [37] and digital computers [38-43].

As a continuation of our study on the synthesis and properties of different polymers based on diarylidene-cycloalkanones moieties in the main chain [44-54], two new series of polymers possessing photoresponsive properties were prepared. These series are poly(hydroxyl-amino ether)s containing 4-methylcyclo-hexanone and 4-tert-butylcyclohexanone moieties. They were synthesized by ring-opening polymerization of four new diarylidene-cycloalkanone epoxy monomers during the reaction with 4,4'-diamino diphenyl methane (DDM) or 4,4'-diamino diphenyl ether (DDE). The characterizations of these new polymers were studied with elemental and spectral analyses in addition to TGA and SEM. Moreover, these polymers undergo of dimerization through [2π + 2π] cycloaddition under UV-Vis irradiation at wavelengths 450 nm at different time intervals. These polymers displayed high thermal stability with good char yield which makes polymers can act as flame retardants.

2. Experimental

2.1. Materials

All polymers are new; details of the synthesis and characterization of these polymers are given in the experimental part. 4-Methylcyclohexanone (Sigma–Aldrich, 99%), 4-tert-butylcyclohexanone (Merck, 99%), *p*-hydroxybenzaldehyde (Sigma-Aldrich, 98%), 4-hydroxy-3-methoxybenzaldehyde (vanillin) (EL-Nassr Chemical Company, Egypt), ± epichlorohydrin (Sigma–Aldrich, ≥ 99%), tetra-n-butylammonium iodide (TBAI) (Sigma–Aldrich, ≥ 98%),), 4,4'-diamino diphenyl methane (DDM) (Sigma–Aldrich, ≥ 97%) and 4,4'-diamino diphenyl ether (DDE) (Sigma–Aldrich, 97%), All reactions were monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminum plates 60F $_{254}$ (Merck). Other reagents and solvents were purchased and used as received unless otherwise listed. All reactions were achieved under nitrogen atmosphere.

2.2. Instrumentation

Fourier transform infrared spectro-photometer (FT-IR) spectra were recorded on Nicolet 6700 Thermo Fisher Scientific, using the KBr pellet technique (Assiut University, Egypt). ^{1}H NMR spectra were recorded on GNM-lA 400-MHz spectrometer (400MHz in Cairo University, Egypt). The chemical shifts are reported relative to internal Me_4Si. Mass spectra were performed on a Jeol JMS-600 mass spectrometer (National research centre, Cairo) and Shimad Zu QP- 2010 Plus mass spectrometer (Micro analytical center, Cairo University, Egypt). Elemental analyses were carried out using an elemental analyses system

GmbH VAR IDEL V2.3 July 1998 (C, H, N, S) Mode. The samples were dried rigorously under vacuum prior for analysis to remove strongly adhering solvent molecules. Thermogravimetric analysis (TGA) was carried out under nitrogen with TA 2000 thermal analyzer at a heating rate of 10 °C/min (Assiut University, Egypt). The morphologies of selected polymers were examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument (Assiut University, Egypt). SEM sample was prepared on a copper holder by placing a smooth part of the polymer powder then covered with gold–palladium alloy. SEM images were taken using a Penta Z Z-50P Camera with Ilford film at an accelerating voltage of 15 kV using a low-dose technique. The molecular weights of selected polymers were determined using gel permeation chromatography (GPC) (National research centre, Cairo, Egypt) which carried out on a Waters 1515 Isocratic HPLC Pump and waters 2720 Auto-Sampler instrument with 3 column set (Styragel HR3 + HR4 + HR5) equipped with refractive index detector (Waters 2414), and THF as eluent at 30^0C. The calibration was performed with polystyrene standards in the range of Mp =1270-2 700 000 (SHOWA DENKO K.K.). This was a G-1362A with 100-104-105 Å Altrastyragel coulmns connected in series. THF was used as eluent with a flow rate 1mL/min, under these conditions: flow rate = 2.000 mL/min, injection volume 100.000 μL and sample concentration = 1.000 g/L. Electronic spectra were recorded in THF in the range 200-700 nm with Shimadzu 2110 PC scanning

spectrophotometer (Assiut University, Egypt). The solubility of polymers was examined using 0.02 g of the polymer in 3-5 mL of solvent at room temperature.

2.3. Monomers Syntheses

Monomers syntheses general procedure A for synthesis of diarylidene monomers

A mixture of cycloalkanone derivatives (4-methylcyclohexanone or 4-*tert*-butylcyclohexanone) (10 mmol) and (20 mmol) of (*p*-hydroxybenzaldehyde or vanillin) in methanol (50 mL) in presence of hydrochloric acid (37% w/v, 0.5 g) was stirred at room temperature for 16–22 h. A solid product separated out during stirring, which was filtered off and dried. Purification was achieved by recrystallization.

Monomers syntheses general procedure B for synthesis of diarylidene-epoxide monomers

In a three-necked flask equipped with stirrer, condenser, dry nitrogen inlet, and dropper, a mixture of diarylidene cycloalkanone derivative (8 mmol), epichlorohydrin (240 mmol) and TBAI (0.24 mmol). The reaction mixture was refluxed under nitrogen until a yellow solution was obtained. A solution of 15% sodium hydroxide was added drop wise over a period of 20 min to the reaction mixture. After completing the addition, the reflux kept for 30 min, and then stirring was continued for 90 min. The by-product of salt was filtered out; the excess of epichlorohydrin was removed at 60 °C under reduced pressure. A solid product was precipitated after poured into the reaction mixture a large amount of distilled water with stirring overnight. The product was filtered, washed with distilled water,

dried at 70 °C under vacuum for 24h and purified by using column chromatography on silica gel.

2.3.1 2,6-Bis(4-hydroxybenzylidene)-4-methylcyclohexanone (*1a*)

According to general procedure A: 4-methylcyclohexanone (1.12 g, 10 mmol) with *p*-hydroxybenzaldehyde (2.44 g, 20 mmol), methanol at room temperature for 16 h. Purified by recrystallization from chloroform/methanol (9:1) as green plates; yield = 80%; m.p.: 208–210 °C. Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.66; H, 6.20. FT-IR (KBr): 3511 cm^{-1} (OH), 2957 cm^{-1} (CH aliphatic), 1648 cm^{-1} (C=O of 4-methylcyclohexanone), 1592 cm^{-1} (C=C). ^{1}H NMR (Acetone): δ = 8.86 (s, 2H, OH), 7.64 (s, 2H, CH=C), 7.45 (d, 4H, Ar-H), 6.94 (d, 4H, Ar-H), 3.08 (dd, 2H, CH$_2$ of cyclohexanone), 2.56 (t, 2H, CH$_2$ of cyclohexanone), 1.87 (m, 1H, CH middle in cyclohexanone), 1.12 (d, 3H, CH$_3$). MS: m/z (%) [M-1]$^+$ = 319.03 (100 %).

2.3.2. 2,6-Bis(4-hydroxy-3-methoxy-benzylidene)-4-methylcyclohexanone (*1b*)

According to general procedure A: 4-methylcyclohexanone (1.12 g, 10 mmol) with 4-hydroxy-3-methoxybenzaldehyde (3.04 g, 20 mmol), methanol at room temperature for 20 h. Purified by recrystallization from chloroform/methanol (1:9) as yellow crystal; yield = 75%; m.p.: 162–164 °C. Anal. Calcd. for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.54.; H, 6.25. FT-IR (KBr): 3488 cm^{-1} (OH), 2940 cm^{-1} (CH aliphatic), 1643 cm^{-1} (C=O of 4-methylcyclohexanone), 1582 cm^{-1} (C=C). ^{1}H NMR (CDCl$_3$): δ = 7.76 (s, 2H, CH=C), 7.12 – 6.95 (m, 6H, Ar-H), 5.86 (s, 2H, OH), 3.95 (s, 6H, OCH$_3$), 3.09 (dd, 2H, CH$_2$ of cyclohexanone),

2.53 (t, 2H, CH$_2$ of cyclohexanone), 1.93 (m, 1H, CH middle in cyclohexanone), 1.12 (d, 3H, CH$_3$). MS: m/z (%) [M$^+$] = 380.20 (100 %).

2.3.3. 4-tert-Butyl-2,6-bis*(4-hydroxy-benzylidene)cyclohexanone (1c)*

According to general procedure A: 4-*tert*-butylcyclohexanone (1.54 g, 10 mmol) with *p*-hydroxybenzaldehyde (2.44 g, 20 mmol), methanol at room temperature for 18 h. Purified by recrystallization from chloroform/methanol (1:1) as green crystal; yield = 75%; m.p.: 270–272 °C. Anal. Calcd. for C$_{24}$H$_{26}$O$_3$: C, 79.53; H, 7.23. Found: C, 78.77; H, 7.15. FT-IR (KBr): 3332 cm^{-1} (OH), 2958 cm^{-1} (CH aliphatic), 1648 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1590 cm^{-1} (C=C). ^{1}H NMR (Acetone): δ = 8.82 (s, 2H, OH), 7.64 (s, 2H, CH=C), 7.49 (d, 4H, Ar-H), 6.95 (d, 4H, Ar-H), 3.20 (dd, 2H, CH$_2$ of cyclohexanone), 2.54 (t, 2H, CH$_2$ of cyclohexanone), 1.45 (m, 1H, CH middle in cyclohexanone), 1.01 (s, 9H, C(CH$_3$)$_3$). MS: m/z (%) [M+1]$^+$ = 363.08 (100 %).

2.3.4. 4-tert-Butyl-2,6-bis*(4-hydroxy-3-methoxybenzylidene)cyclohexanone (1d)*

According to general procedure A*:* 4-*tert*-butylcyclohexanone (1.54 g, 10 mmol) with 4-hydroxy-3-methoxy-benzaldehyde (3.04 g, 20 mmol), methanol at room temperature for 22 h. Purification by recrystallization from chloroform/methanol (1:9) yellow crystal; yield = 75%; m.p.: 180–182 °C. Anal. Calcd. for C$_{26}$H$_{30}$O$_5$: C, 73.91; H, 7.16. Found: C, 73.80; H, 7.10. FT-IR KBr): 3390 cm^{-1} (OH), 2958 cm^{-1} (CH aliphatic), 1651 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1588 cm^{-1} (C=C).

(^{1}H NMR (CDCl$_3$): δ = 7.74 (s, 2H, CH=C), 7.04 – 6.99 (m, 6H, Ar-H), 5.98 (s, 2H, OH), 3.94 (s, 6H, OCH$_3$), 3.20 (dd, 2H, CH$_2$ of cyclohexanone), 2.45 (t, 2H, CH$_2$ of cyclohexanone), 1.51 (m, 1H, CH middle in cyclohexanone), 1.00 (s, 9H, C(CH$_3$)$_3$). MS: m/z (%) [M$^+$] = 422.22 (100 %).

2.3.5. 2,6-Bis*(4-epoxypropoxy-benzylidene)-4-methylcyclohexanone (2a)*

According to general procedure B: Compound **1a** (2.60 g, 8mmol) with epichlorohydrin (22.20 g, 240 mmol) and TBAI (0.09 g, 0.24 mmol) in presence of NaOH. Column chromatography on silica gel (CH$_2$Cl$_2$: MeOH = 98:2) as yellow crystals; yield = 65%; m.p.: 138–140 °C. Anal. Calcd. for C$_{27}$H$_{28}$O$_5$: C, 74.98; H, 6.53. Found: C, 74.92; H, 6.48. FT-IR (KBr): 2922 cm^{-1} (CH aliphatic), 1660 cm^{-1} (C=O of 4-methylcyclohexanone), 1598 cm^{-1} (C=C), 1258 cm^{-1} (C-O-C), 914 cm^{-1} (epoxy). ^{1}H NMR (CDCl$_3$): δ = 7.77 (s, 2H, CH=C), 7.46 (d, 4H, Ar-H), 6.98 (d, 4H, Ar-H), 4.30 – 4.01 (dd, 4H, -O-CH$_2$), 3.39 (m, 2H, CH epoxy), 3.05 (dd, 2H, CH$_2$ of cyclohexanone), 2.94 – 2.79 (dd, 4H, CH$_2$ epoxy), 2.51 (t, 2H, CH$_2$ of cyclohexanone), 1.90 (m, 1H, CH middle in cyclohexanone), 1.11 (d, 3H, CH$_3$). MS: m/z (%) [M-1]$^+$ = 431.00 (100 %)

2.3.6. 2,6-Bis*(3-methoxy-4-epoxy-propxybenzyliden)-4-methyl-cyclo-hexanone (2b)*

According to general procedure B: Compound **1b** (3.00 g, 8 mmol) with epichlorohydrin (22.20 g, 240 mmol) and TBAI (0.09 g, 0.24 mmol) in presence of NaOH. Column chromatography on silica gel (CH$_2$Cl$_2$: MeOH = 98:2) as yellow crystals; Yield = 70%; m.p.: 134–136 °C.

FT-IR (KBr): 2940 cm^{-1} (CH aliphatic), 1658 cm^{-1} (C=O of 4-methylcyclohexanone), 1596 cm^{-1} (C=C), 1244 cm^{-1} (C-O-C), 911 cm^{-1} (epoxy). ^{1}H NMR (CDCl$_3$): δ = 7.76 (s, 2H, CH=C), 7.12 – 6.93 (m, 6H, Ar-H), 4.34 – 4.10 (dd, 4H, -O-CH$_2$), 3.92 (s, 6H, OCH$_3$), 3.43 (m, 2H, CH epoxy), 3.09 (dd, 2H, CH$_2$ of cyclohexanone), 2.94 – 2.79 (dd, 4H, CH$_2$ epoxy), 2.53 (t, 2H, CH$_2$ of cyclohexanone), 1.92 (m, 1H, CH middle in cyclohexanone), 1.12 (d, 3H, CH$_3$); Anal. Calcd. for C$_{29}$H$_{32}$O$_7$: C, 70.71; H, 6.55. Found: C, 70.63; H, 6.35. MS: m/z (%) [M$^+$] = 492.37 (84.88 %).

2.3.7. *4-tert-Butyl-2,6-bis(4-epoxy-propoxybenzylidene)cyclohexanone (2c)*

According to general procedure B: Compound 1c (2.90 g, 8 mmol) with epichlorohydrin, (22.20 g, 240 mmol) and TBAI (0.09 g, 0.24 mmol) in presence of NaOH. Column chromatography on silica gel (CH$_2$Cl$_2$: MeOH = 98:2) as yellow crystals; Yield = 75%; m.p.:140–142 oC. Anal. Calcd. for C$_{30}$H$_{34}$O$_5$: C, 75.92; H, 7.22. Found: C, 75.80; H, 7.17. FT-IR (KBr): 2957 cm^{-1} (CH aliphatic), 1659 cm^{-1} (C=O of 4-tert-butylcyclohexanone), 1597 cm^{-1} (C=C), 1256 cm^{-1} (C-O-C), 914 cm^{-1} (epoxy). ^{1}H NMR (CDCl$_3$): δ = 7.74 (s, 2H, CH=C), 7.47 (d, 4H, Ar-H), 6.99 (d, 4H, Ar-H), 4.30 – 4.02 (dd, 4H, -O-CH$_2$), 3.40 (m, 2H, CH epoxy), 3.15 (dd, 2H, CH$_2$ of cyclohexanone), 2.95 – 2.80 (dd, 4H, CH2 epoxy), 2.43 (t, 2H, CH$_2$ of cyclohexanone), 1.50 (m, 1H, CH middle in cyclohexanone), 0.99 (s, 9H, C(CH$_3$)$_3$). MS: m/z (%) [M+] = 474.32 (62.57 %).

2.3.8. *4-tert-Butyl-2,6-Bis(3-methoxy-4-epoxypropoxybenzylidene)cyclohexanone (2d)*

According to general procedure B: Compound 1d (3.40 g, 8 mmol) with epichlorohydrin (22.20 g, 240 mmol) and TBAI (0.09 g, 0.24 mmol) in presence of NaOH. Column chromatography on silica gel (CH$_2$Cl$_2$: MeOH = 98:2) as yellow crystals; yield = 65%; m.p.:122–124 oC. Anal. Calcd. for C32H38O7: C, 71.89; H, 7.16. Found: C, 71.75; H, 7.09. FT-IR (KBr): 2957 cm^{-1} (CH aliphatic), 1655 cm^{-1} (C=O of 4-tert-butylcyclohexanone), 1592 cm^{-1} (C=C), 1245 cm^{-1} (C-O-C), 918 cm^{-1} (epoxy). ^{1}H NMR (CDCl$_3$): δ = 7.72 (s, 2H, CH=C), 7.12 – 6.95 (m, 6H, Ar-H), 4.33 – 4.09 (dd, 4H, -O-CH$_2$), 3.92 (s, 6H, OCH$_3$), 3.42 (m, 2H, CH epoxy), 3.19 (dd, 2H, CH$_2$ of cyclohexanone), 2.93 – 2.78 (dd, 4H, CH$_2$ epoxy), 2.45 (t, , 2H, CH$_2$ of cyclohexanone), 1.50 (m, 1H, CH middle in cyclohexanone), 0.99 (s, 9H, C(CH$_3$)$_3$). MS: m/z (%) [M+] = 534.37 (29.22 %).

2.4. *Polymers syntheses*

Polymers syntheses general procedure C for synthesis of poly(hydroxyl-amino ether)s

Fusing a mixture of diarylidene-epoxide (2 mmol) and 4,4'-diamino diphenyl methane or 4,4'-diamino diphenyl ether (2 mmol) until the mixture became homogeneous. The mixture was stirred in (30 mL) of DMF at 80 ^{o}C for 8 h. The resulting polymer was precipitated in 200 mL of crushed ice. The polymer product was filtered, washed several time by distilled water and dried at 70 ^{o}C in vacuum oven for 24 h.

2.4.1. Synthesis of poly(hydroxyl-amino ether)s **P1a**

According to general procedure C: Compound **2a** (0.648 g, 1.5 mmol) with 4,4'-diamino diphenyl methane (0.356 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as yellow powder; yield = 55%. FT-IR (KBr): 3361 cm^{-1} (NH and OH), 2867 cm^{-1} (CH aliphatic), 1657 cm^{-1} (C=O of 4-methycyclohexanone), 1597 cm^{-1} (C=C), 1248 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.56 (s, 2H, CH=C),7.43 (m, 4H, Ar-H), 6.97 (d, 4H, Ar-H), 6.85 (dd, 4H, Ar-H), 6.50 (dd, 4H, Ar-H), 5.34 (s, 1H, NH), 5.23 (s, br, 1H, OH), 4.09 (dd, 8H, -CH_2-O- and -CH_2-NH-), 3.59 (d, 2H, CH_2), 3.18 (m, 2H, -CH(OH)-), 3.01 (d, 4H, CH_2 of cyclohexanone), 1.78 (m, 1H, CH middle in cyclohexanone), 1.03 (d, 3H, CH_3).

2.4.2. Synthesis of poly(hydroxyl-amino ether)s **P1b**

According to general procedure C: Compound **2b** (0.738 g, 1.5 mmol) with 4,4'-diamino diphenyl methane (0.356 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as yellow powder; yield = 47%. FT-IR (KBr): 3362 cm^{-1} (NH and OH), 2923 cm^{-1} (CH aliphatic), 1656 cm^{-1} (C=O of 4-methycyclohexanone), 1595 cm^{-1} (C=C), 1243 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.61 (s, 2H, CH=C), 7.05 (m, 6H, Ar-H), 6.85 (d, 4H, Ar-H), 6.53 (dd, 4H, Ar-H), 5.38 (s, 1H, NH), 5.20 (s, br, 1H, OH), 4.23–3.87 (m, 8H, -CH_2-O- and -CH_2-NH-), 3.81 (s, 6H, OCH$_3$), 3.59 (d, 2H, CH_2), 3.24–3.15 (m, 2H, -CH(OH)-), 3.03 (d, 4H, CH_2 of cyclohexanone), 1.81 (m, 1H, CH middle in cyclohexanone), 1.03 (d, 3H, CH_3).

2.4.3. Synthesis of poly(hydroxyl-amino ether)s **P1c**

According to general procedure C: Compound **2c** (0.711 g, 1.5 mmol) with 4,4'-diamino diphenyl methane (0.356 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as brown powder; yield = 58%. FT-IR (KBr): 3368 cm^{-1} (NH and OH), 2959 cm^{-1} (CH aliphatic), 1659 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1598 cm^{-1} (C=C), 1250 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.29 (s, 2H, CH=C),7.24 (d, 4H, Ar-H), 6.77 (m, 4H, Ar-H), 6.59 (d, 4H, Ar-H), 6.25 (dd, 4H, Ar-H), 5.04 (s, 1H, NH),), 4.98 (s, br, 1H, OH), 3.69 (dd, 8H, - CH_2-O- and -CH_2-NH-), 3.42 (s, 2H, CH_2), 2.94 (m, 2H, $_2$-CH(OH)-), 2.79 (d, 4H, CH_2 of cyclohexanone), 1.08 (m, 1H, CH middle in cyclohexanone), 0.65 (s, 9H, C(CH_3)$_3$).

2.4.4. Synthesis of poly(hydroxyl-amino ether)s **P1d**

According to general procedure C: Compound **2d** (0.801 g, 1.5 mmol) with 4,4'-diamino diphenyl methane (0.356 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as brown powder; yield = 36%. FT-IR (KBr): 3372 cm^{-1} (NH and OH), 2955 cm^{-1} (CH aliphatic), 1650 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1596 cm^{-1} (C=C), 1243 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.60 (s, H, CH=C), 7.11 (d, 6H, Ar-H), 6.85 (dd, 4H, Ar-H), 6.51 (dd, 4H, Ar-H), 5.18 (s, 2H, NH), 4.81 (s, br, 2H, OH), 3.95 (m, 8H, -CH_2-O- and -CH_2-NH-), 3.82 (s, 6H, OCH$_3$), 3.60 (d, 2H, CH_2), 3.19 (d, 2H, -CH(OH)-), 3.08 (d, 4H, CH_2 of cyclohexanone), 1.39 (m, 1H, CH middle in cyclohexanone), 0.94 (s, 9H, C(CH_3)$_3$).

2.4.5. Synthesis of poly(hydroxyl-amino ether)s **P2a**

According to general procedure C: Compound **2a** (0.648 g, 1.5 mmol) with 4,4'-diamino diphenyl ether (0.360 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as brown powder; yield = 69%. FT-IR (KBr): 3366 cm^{-1} (NH and OH), 2924 cm^{-1} (CH aliphatic), 1654 cm^{-1} (C=O of 4-methycyclohexanone), 1597 cm^{-1} (C=C), 1250 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.56 (s, 2H, CH=C), 7.13 (m, 8H, Ar-H), 6.84–6.55 (m, 8H, Ar-H), 5.33 (s, 1H, NH), 5.27 (s, br, 1H, OH), 3.92 (m, 4H, -CH_2-O- and -CH_2-NH-), 3.25–3.15 (m, 2H, -CH(OH)-), 3.13–2.85 (d, 4H, CH_2 of cyclohexanone), 1.77 (m, 1H, CH middle in cyclohexanone), 1.05 (d, 3H, CH_3).

2.4.6. Synthesis of poly(hydroxyl-amino ether)s **P2b**

According to general procedure C: Compound **2b** (0.738 g, 1.5 mmol) with 4,4'-diamino diphenyl ether (0.360 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as brown powder; yield = 56%. FT-IR (KBr): 3365 cm^{-1} (NH and OH), 2925 cm^{-1} (CH aliphatic), 1655 cm^{-1} (C=O of 4-methylcyclohexanone), 1596 cm^{-1} (C=C), 1227 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.59 (s, 2H, CH=C), 7.12 (m, 6H, Ar-H), 6.65 (dd, 8H, Ar-H), 5.30 (s, 1H, NH), 5.10 (s, br, 1H, OH), 3.94 (m, 4H, -CH_2-O- and -CH_2-NH-), 3.82 (s, 6H, OCH$_3$), 3.11 (m, 2H, -CH(OH)-), 2.98 (d, 4H, CH_2 of cyclohexanone), 1.82 (m, 1H, CH middle in cyclohexanone), 1.03 (d, 3H, CH$_3$).

2.4.7. Synthesis of poly(hydroxyl-amino ether)s **P2c**

According to general procedure C: Compound **2c** (0.711 g, 1.5 mmol) with 4,4'-diamino diphenyl ether (0.360 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as yellow powder; yield = 45%. FT-IR (KBr): 3362 cm^{-1} (NH and OH), 2958 cm^{-1} (CH aliphatic), 1654 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1599 cm^{-1} (C=C), 1224 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6):δ = 7.57 (s, 2H, CH=C), 7.21 (m, 8H, Ar-H), 6.62 (ddd, 8H, Ar-H), 5.33 (s, 1H, NH), 5.23 (s, br, 1H, OH), 4.23–3.85 (m, 8H, -CH_2-O- and -CH_2-NH-), 3.18 (m, 2H, -CH(OH)-), 3.09–2.95 (d, 4H, CH$_2$ of cyclohexanone), 1.34 (m, 1H, CH middle in cyclohexanone), 0.91 (s, 5H, C(CH$_3$)$_3$).

2.4.8. Synthesis of poly(hydroxyl-amino ether)s **P2d**

According to general procedure C: Compound **2d** (0.801g, 1.5 mmol) with 4,4'-diamino diphenyl ether (0.360 g, 1.8 mmol) in (30 mL) of DMF at 80 ^{o}C for 8h as yellow powder; yield = 57%. FT-IR (KBr): 3346 cm^{-1} (NH and OH), 2934 cm^{-1} (CH aliphatic), 1654 cm^{-1} (C=O of 4-*tert*-butylcyclohexanone), 1595 cm^{-1} (C=C,) 1227 cm^{-1} (C-O-C). ^{1}H NMR (DMSO-d_6): δ = 7.59 (s, H, CH=C), 7.11 (m, 6H, Ar-H), 6.73–6.49 (m, 8H, Ar-H), 5.19 (s, 2H, NH), 4.79 (s, br, 2H, OH), 4.03 (m, 8H, -CH_2-O- and -CH_2-NH-), 3.82 (s, 6H, OCH$_3$), 3.22 (s, 2H, -CH(OH)-), 3.08 (d, 4H, CH$_2$ of cyclohexanone), 1.38 (m, 1H, CH middle in cyclohexanone), 0.93 (s, 9H, C(CH$_3$)$_3$).

3. Result and discussion

3.1. Monomers Syntheses

### 3.1.1. Synthesis of diarylidene cycloalkanone monomers

All diarylidene cycloalkanone monomers **1a-d** which contain 4-methylcyclohexanone, or 4-*tert*-butyl-cyclohexanone as cycloalkanone

moieties were synthesized in a good yield by the condensation of one mole of cycloalkanone derivatives with two moles of 4-hydroxybenzaldehyde or 4-hydroxy-3-methoxy benzaldehyde, respectively, in methanol in the presence of HCl with stirring at room temperature, in yields of 75 – 95% as described in our previous work [55] (Scheme 1).
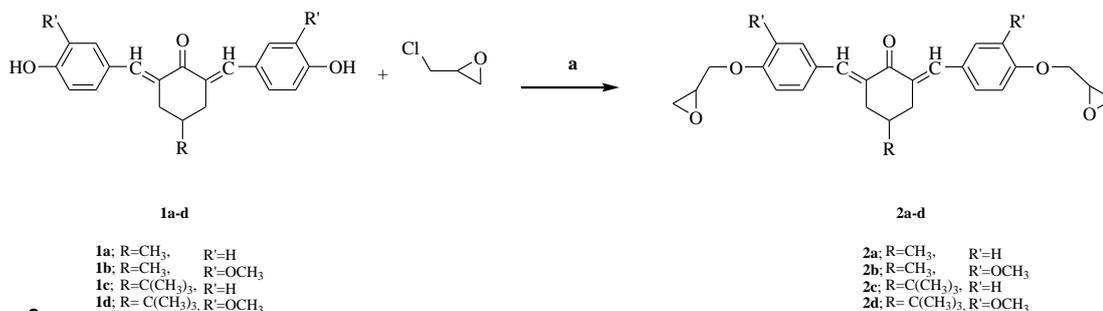
The structures of these monomers were established on the base of elemental and spectral analyses. The FT-IR spectra of all monomers displayed characteristic absorption bands at 1643 –1651 cm^{-1} region attributed to the presence of the (C=O, ketone), 1582 – 1592 cm^{-1} (C=C, benzylidene) and 3332 – 3511 cm^{-1} corresponding to the OH group. These monomers gave fully assignable ^{1}H NMR spectra. They showed the molecular ion peaks in their mass spectra (see the experimental part).

3.1.2. Synthesis of diarylidene-epoxide monomers

All epoxide monomers **2a-d** are prepared diarylidene cycloalkanone derivatives **1a-d** with excess of epichlorohydrin in presence of NaOH (15%) and TBAI as described in our previous work [55] (Scheme 2). The structures of these monomers were confirmed by elemental and spectral analyses. The FT–IR spectra showed a new characteristic absorption band at 911 – 918 cm^{-1} due to the formation of oxirane rings, accompanied with the disappearance of O-H group band at 3332 – 3511 cm^{-1} which confirming the complete formation of the epoxide monomers. Based on ^{1}H NMR spectra the presence of epoxy rings were confirmed by the appearance of two peaks at $\delta = 2.95 - 2.69$ ppm (doublets), at $\delta = 3.43 - 3.33$ ppm (multiplet). The mass spectra of all monomers showed molecular ion peaks which are in agreement with their molecular formulas.

1a; R=CH$_3$,   R'=H
1b; R=CH$_3$,   R'=OCH$_3$
1c; R=C(CH$_3$)$_3$, R'=H
1d; R= C(CH$_3$)$_3$, R'=OCH$_3$
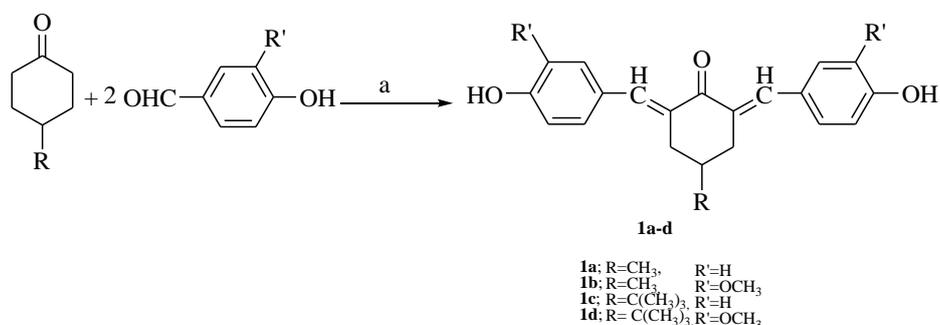
Scheme 1: Synthesis of monomers **1a-d**. Reagents and conditions: (a) MeOH, HCl, room temperature (r.t.).

1a; R=CH$_3$,   R'=H
1b; R=CH$_3$,   R'=OCH$_3$
1c; R=C(CH$_3$)$_3$, R'=H
1d; R= C(CH$_3$)$_3$, R'=OCH$_3$

2a; R=CH$_3$,   R'=H
2b; R=CH$_3$,   R'=OCH$_3$
2c; R=C(CH$_3$)$_3$, R'=H
**2d**; R= C(CH$_3$)$_3$, R'=OCH$_3$

Scheme 2:

Synthesis of monomers **2a-d**. Reagents and conditions: (a) TBAI, NaOH (15%), reflux.

3.2. Polymerization and polymer characterization

Two new interesting series of poly(hydroxyl-amino ether)s based on diarylidene−epoxide moieties in the main chain were synthesized by ring opening polymerization of diarylidene − epoxide monomers **2a-d** during the reaction with 4,4'-diamino diphenyl methane or 4,4'-diamino diphenyl ether, respectively as illustrated in Scheme 3. The structures of the obtained polymers were confirmed by elemental and spectral analyses. The FT-IR spectra of all polymers showed broad band at 3372–3324 cm^{-1} includes overlap of both (NH) and (OH) groups and at 1251–1224 cm^{-1} for (C-O-C) (ether linkages) with the presence of other characteristic absorption bands due to specific groups present in the various polymers. ^{1}H NMR spectra of poly(hydroxyl-amino ether)s showed additional peaks in aromatic region indicating the immerging of the aromatic amines in the polymer main chain. The molecular weights of all polymers were determined by GPC and their data are collected in Table 1 all polymers giving moderate molecular weight except **P1b**. For all polymers the weight-average molecular weight (M_w) are from 8 435 to 23 558. **P1c** gives the highest molecular weight, (M_w) is 23 558 (PDI 8.9). The various characteristics of the resulting polymers including solubility, TGA, SEM, UV-Vis study were also determined and the data are discussed below.
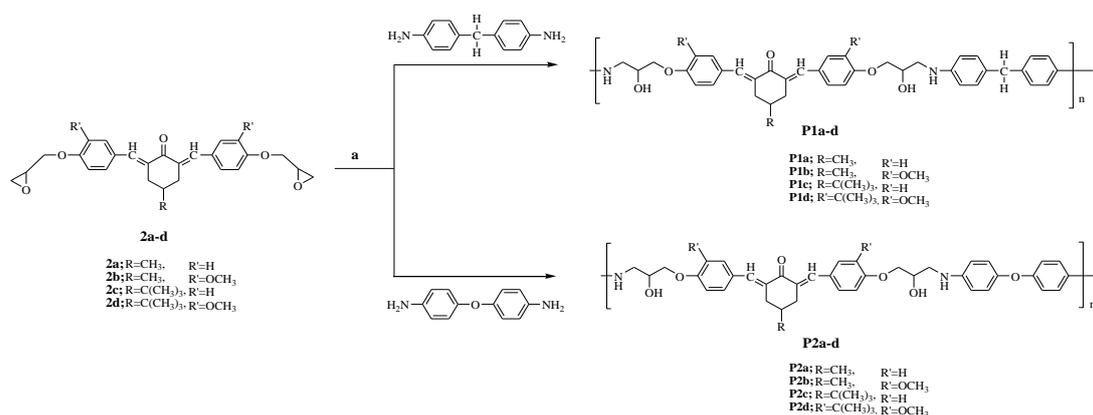
Scheme 3: Synthesis of Poly(hydroxyl-amino ether)s **P1a-d** & **P2a-d**. Reagents and conditions: (a) fusing and DMF at 80°C for 8h.

Table 1: Molecular weight of poly(hydroxyl-amino ether)s **P1a-d** & **P2a-d**

Polymer code	GPC[a]		
	M_w[b]	P_w[c]	PDI[d]
P1a	16731	26	6.4
P1b	8435.1	12	8.6
P1c	23558	34.20	8.9
P1d	12266	16.38	4.5
P2a	16947	7	5.4
P2b	10034	14	5.2
P2c	14738	21	8.6
P2d	22063	29.38	6.8

[a] All GPC measurements were performed at 35°C in THF.

[b] Weight-average molecular weight.

[c] Average number of repeating units.

[d]Polydispersity index.

3.3. Solubility

The solubility of the prepared **P1a**-**d** and **P2a-d** was tested at room temperature using various solvents: dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), chloroform (CHCl₃), dichloromethane (DCM), tetrahydrofuran (THF) and formic acid (HCOOH). 50 mg of the polymer was added to 1mL of the chosen solvent and the solution was analyzed by visual inspection. The results are shown in Table 2. In polar aprotic solvents, such as DMF and DMSO or THF all polymers are completely soluble except **P1a**, **P1c**, **P2a** and **P2c** are partially soluble in THF. The solubility of these polymers in non-polar solvents like CHCl₃ and DCM are not soluble. In HCOOH as an example of polar protic solvent, polymers **P1a-d** are completely soluble but polymers **P2a-d** (contain diphenyl ether moities) is partially soluble. In our previous work, the substituted polymers with methoxy groups in the phenyl rings have better solubility than non-substituted polymers, the presence of methoxy substituents as bulky groups in the polymer main chain decrease the chain packing between the polymer chains, by other way decrease the inter-chains interactions like hydrogen bonding and thereby making solvation easier [56].

2.4. Scanning electron microscope measurements (SEM)

The morphological study of the selected example of poly(hydroxyl-amino ether)s was examined using SEM measurement to show the surface of the polymer using low dose technique [57]. The study of selected examples of polymers **P1a, P1c** and **P2c** showed that the surface of polymer (Figure 1 (a)) (X = 2000) showed that polymer **P1a** has cavity shape with big gapes, the higher magnification (X = 5,000) (Figure 1 (b)) showed layers with some coalescence. (Figure 1 (c)) (X = 2000) showed that polymer **P1c** has amorphous structure sheets, the higher magnification (X = 5,000) (Figure 1 (d)) showed layers with big grooves. (Figure 2 (a)) (X = 2000) showed that polymer **P2c** has aggregates of layer structures, the higher magnification (X = 5,000) (Figure 2 (b)) shows aggregated like columnar shapes.

2.5. TGA study

The thermal behavior of all the synthesized poly(hydroxyl-amino ether)s **P1a-P1d** and **P2a-P2d** was evaluated by TGA and DTG under nitrogen atmosphere at a heating rate of 10 °C/min.

Table 2: Room temperature solubility characteristics of poly(hydroxyl-amino ether)s **P1a-d** & **P2a-d**

Polymer code	DMF	DMSO	THF	CHCl₃	CH₂Cl₂	HCOOH
P1a	++	++	+	−	−	++
P1b	++	++	+	−	−	++
P1c	++	++	++	−	−	++
P1d	++	++	+	−	−	++
P2a	++	++	++	−	−	+
P2b	++	++	+	−	−	+
P2c	++	++	++	−	−	+
P2d	++	++	+	−	−	+

++: soluble at room temperature (RT) according to visual inspection, +: partially soluble, − : insoluble.
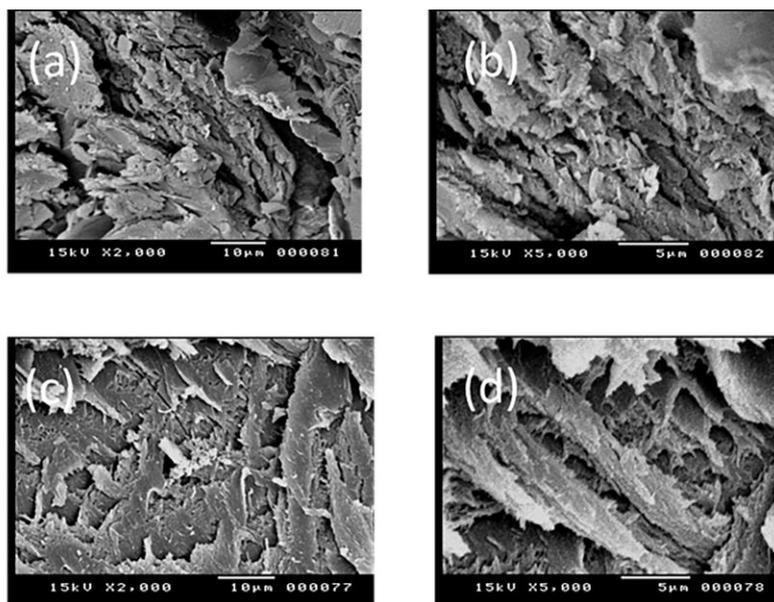
Fig. 1: SEM images of poly(hydroxyl-amino ether)s surface at different magnification; **P1a** (a) X = 2,000, (b) X = 5,000 and **P1c** (c) X = 2,000, (d) X = 5,000.
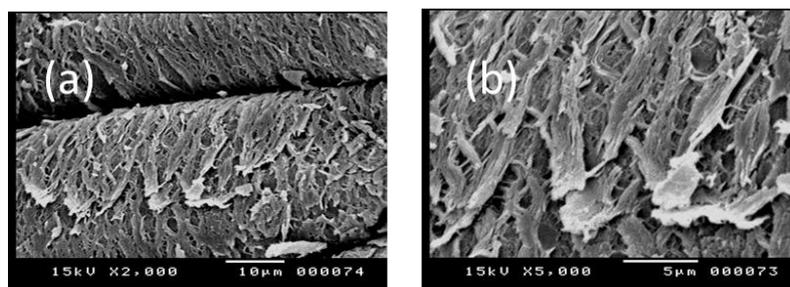

Fig. 2: SEM images of poly(hydroxyl-amino ether)s surface at different magnification; **P2c** (a) X = 2,000, (b) X = 5,000.

The temperatures values corresponding to (10%, 20%, 30%, 40% and 50%) weight loss in addition to char yield and limiting oxygen index (LOI) at 600 °C are shown in Table 3. TGA curves show a small weight loss appeared in the range 0.5 – 5%, this is probably due to the residues of solvents which evaporate at lower temperatures (starting at 27 °C until 100 °C) [58-61]. The initial decomposition temperature (IDT) [62] of these polymers (10% weight loss) that is considered to be the polymer decomposition temperature occurred within the range from 308 to 338 °C for all polymers. The temperature value of 50% weight loss (T$_{50}$%) is one of the main criteria for determining the relative thermal stability of a polymer [61,

63], which occurred within the range from 479 to 547 °C for these polymers. All the polymers showed similar decomposition patterns (one main degradation step or two overlapped steps). TGA curves of these polymers showed degradation steps in the range from 223 to 450 which can be explained due to the cleavage of the ether linkage in the aromatic chains, these results are in agreement with the previous work [63-65]. On the other hand, in most previous studies the thermal behavior of polymers containing substituted methoxy groups instead of hydrogen atoms in the phenyl rings are less thermally stable than that polymers un-substituted in the phenyl rings. However, this phenomenon is not

so clear in the poly(hydroxyl-amino ether)s (see Figure 3). As shown in Table 3, the char residue values of these polymers at 600 °C are high. The limiting oxygen index (LOI) values of all polymers which calculated by using the char residue values, obtained from TGA curves in Van Krevelen's equation [63, 66, 67] are higher than the threshold were obtained with higher char residue values of most polymers indicating that these polymers considered as self-extinguishing materials, which mean that these polymers can reduce the high-temperature transfer between the polymer source and heat source, and suppress the smoke during combustion.

Table 3: Thermal properties of poly(hydroxyl- amino ether)s **P1a-d** & **P2a-d**

Polymer code	Temperature (°C) for various decomposition levels[a]					IDT[b]	(CR)[c] %	LOI[d]
	10%	20%	30%	40%	50%			
P1a	337	404	454	513	547	225	29.35	29.24
P1b	338	363	389	417	479	223	40.47	33.69
P1c	333	382	420	470	551	232	46.00	35.9
P1d	337	366	393	447	516	206	26.35	28.04
P2a	307	370	387	415	446	305	28.55	28.92
P2b	308	374	406	460	499	284	0.356	17.64
P2c	328	372	390	415	454	310	26.61	28.14
P2d	338	374	405	453	524	300	33.63	30.95

[a] The values were determined by TGA at a heating rate of 10 °C min^{-1}

[b] initial decomposition temperature

[c] The values of char residue

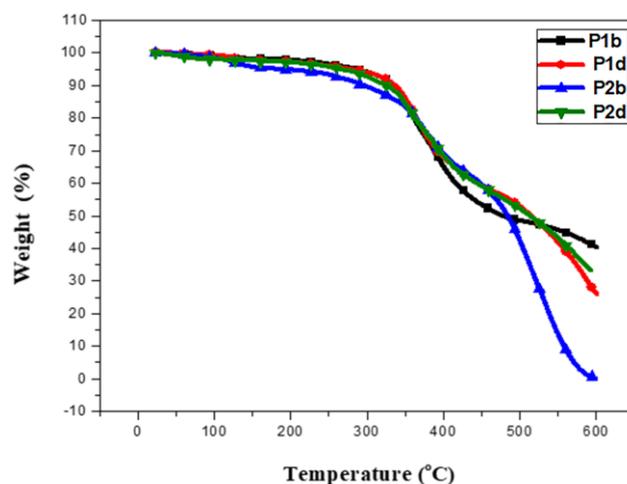[d] LOI at 600 °C = (17.5 + 0.4CR), determined using Van Krevelan's equation.

Fig. 3: TGA analyses of poly(hydroxyl-amino ether)s **P1b, P1d, P2b** and **P2d**.

3.6. Optical properties

3.6.1. UV-Vis absorption study

The ultraviolet and visible spectra of selected examples of the synthesized polymers **P1b**, **P1d**, **P2b** and **P2d** were measured in THF at a concentration of (3.33×10^{-5} g / ml) at room temperature. The UV spectra of these polymers showed an absorption band with λ_{max} 368, 366, 365 and 368 nm respectively, which were due to the π-π* transition in olefinic double bond (C=C) of benzylidene units in the polymer main chains.

3.6.2. Photoresponsive Properties

Photoresponsive properties of selected examples from poly(hydroxyl-amino ether)s were carried out in THF by photolysis under UV irradiation at wavelengths 450 nm at room temperature for different time intervals. This property was investigated by UV-Vis and FT-IR spectroscopy. Previous studies exposed two types of photoresponsive in polymers which contained aryllideneketone moieties in the main chain, namely photoisomerization and photocrosslinking [68]. These polymers contain photocrosslinkable moieties in the main chain due to the presence of olefinic double bond (C=C) in benzylidene moieties in the main chains of the polymers backbones [36]. The UV-Vis spectra of polymers **P1b**, **P1d**, **P2b** and **P2d** after irradiation for various intervals of time show absorption bands at λ_{max} 365−368 nm corresponding to π−π* transition of the olefinic double bond of (C=C) in benzylidene moieties in the polymers main chains (see Figures 4 and 5). By the occurrence of intermolecular cycloaddition in the olefinic double bonds the intensity of π−π* absorption decreases by increasing

in irradiation time and the intensity of δ−δ* absorption of the cyclobutane increases. The degree of photocrosslinking can be calculated by using the following equation [69]:

Degree of photocrosslinking =
$$(1 - A_t / A_o) \times 100$$

Where A_o is the absorbance at λ_{max} before UV irradiation, A_t is the absorbance at time t. The photocrosslinking degrees of the polymers after UV irradiation for 30 minutes were 14%, 11%, 67% and 55% corresponding to **P1b**, **P1d**, **P2b** and **P2d**. We observed that the rate of crosslinking between the polymer chains is faster in the polymers which contain (diphenyl ether) moieties **P2b** & **P2d** in the main chain than that which contain (diphenyl methan) moieties **P1b** & **P1d** in the main chain. This is may be due to the presence of the ether linkage which introduces more flexibility to the polymers, resulting in readily susceptible photocrosslinking [62-64]. Moreover, intermolecular photocycloaddition was confirmed by FT-IR spectroscopy. The IR spectra for the tested polymers **P1b**, **P1d**, **P2b** and **P2d** displayed disappearance of the (C=C) benzylidene bands (after irradiation with VU for 30 minutes) see Figures 6 and 7.

4. Conclusions

In this research two new series of photoactive poly(hydroxyl-amino ether)s **P1a-d** and **P2a-d** based on diarylidene-cycloalkanones were synthesized by ring opening polymerization of different arylidene-epoxide monomers **2a-d** during the reaction with 4,4'-diamino diphenyl methane (DDM) or 4,4'-diamino diphenyl ether (DDE) and obtained in good yield. All the synthesized polymers had good solubility in polar aprotic solvents.
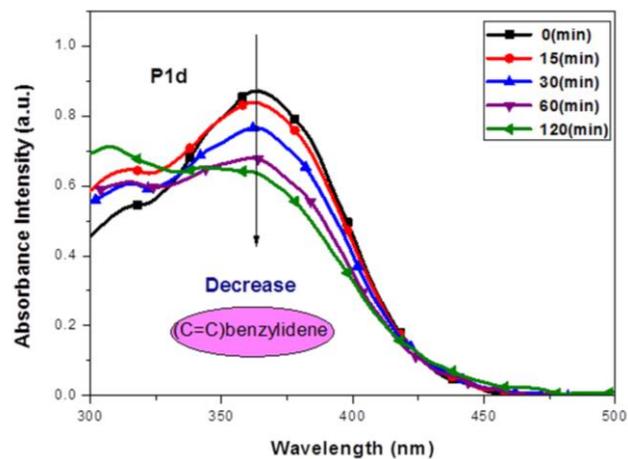
Fig. 4: UV - visible spectra of **P1d** on **U**V irradiation at different time intervals (min).
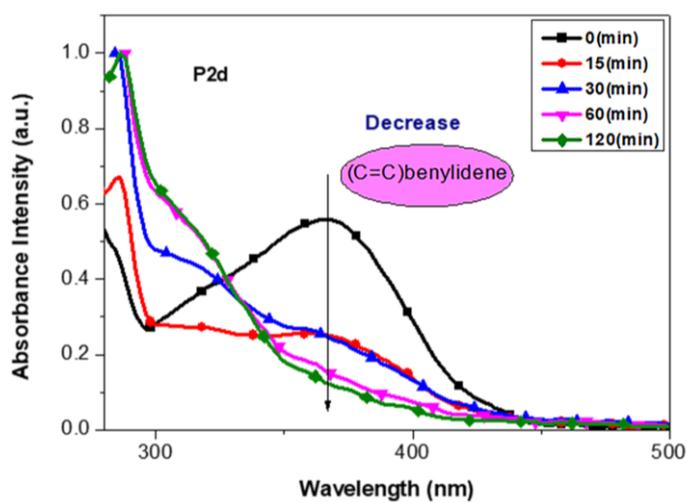

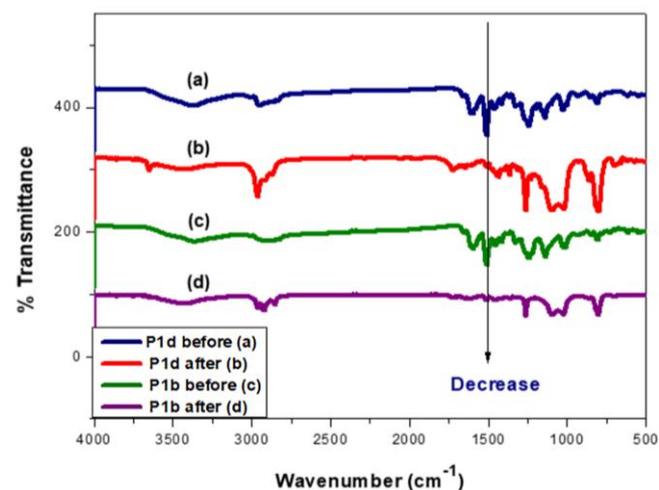**Fig. 5:** UV - visible spectra of **P2d** on UV irradiation at different time intervals (min).

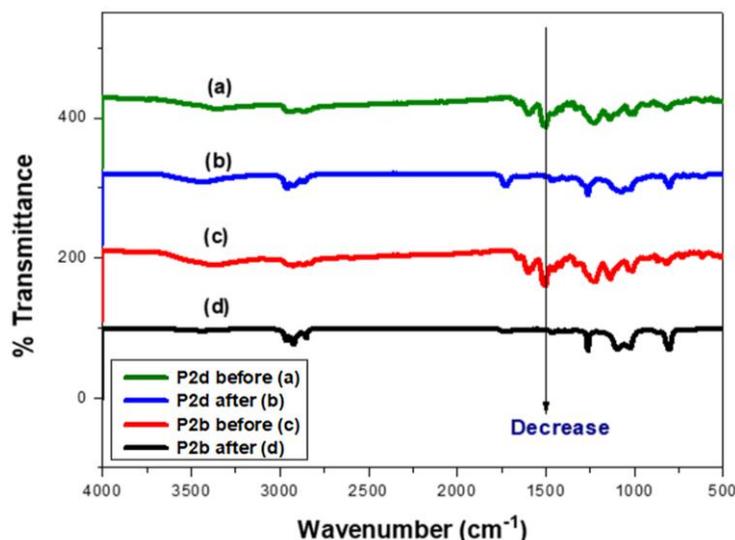**Fig. 6:** FT-IR of poly(hydroxyl-amino ether)s **P1b**&**P1d** before and after irradiation.

Fig. 7: FT-IR of poly(hydroxyl-amino ether)s **P2b&P2d** before and after irradiation.

The IDTs of all of the prepared polymers were in the range 206–310°C. These polymers have high thermal stability with good char yield. The LOI values in most of these new polymers above 25% which demonstrated that these polymers exhibited excellent flame retardancy. Moreover, photocrosslinking property for these polymers was investigated under UV lamp (450), where it was observed that the photocrosslinking ability in the polymers which contain diphenyl ether moieties in the main chain is faster than that which contains diphenyl methane moieties.

Acknowledgements

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