

History of arylidene polymers from chemistry point of view

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Mahmoud A Hussein

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About the authors

Mahmoud A Hussein,^{1,2} Khalid A Alamry,¹ Samar J Almehmadi,¹ Mona A Abdel-Rahman,² Kamal I Aly,² Abdullah M Asiri^{1,3}

¹Department of Chemistry, King Abdulaziz University, Saudi Arabia

²Department of Chemistry, Assiut University, Egypt

³Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Saudi Arabia

*Corresponding author details

Mahmoud A Hussein

Chemistry Department, Faculty of Science, King Abdulaziz University,
PO Box 80203, Jeddah, Saudi Arabia, Email maabdo@kau.edu.sa,
mahmali@aun.edu.eg, mahussein74@yahoo.com

Kamal I Aly

Polymer Chemistry Lab 122, Chemistry Department, Faculty of Science,
Assiut University, PO Box 71516, Assiut, Egypt,
Email kamalaly@yahoo.com

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Abstract

Arylidene polymers or by other words polyarylidenes have been prolonged studied over wider range of years with a significant attentions in the past few decades. The preparation of such polymers produces a variable number of polymers that mainly containing different functional groups. The type of these polymers is also mainly based on significant developments in the synthesis methods. A versatile number of arylidene monomers and pre-monomers are reported in the literature which illustrated in producing different types of polyarylidene. Arylidene Polymers can be utilized and applied over a floppy range of applications, such as in chemistry, materials science, chemical engineering, biology and recently in environmental remediation. Therefore, the current work shows a simple introduction to the chemistry of arylidene polymers and their variable characteristics. The work describe in this work focus on the syntheses and characterization of arylidene polymers as a continuation of our study on the synthesis and properties of different new polymers based on diarylidenecycloalkanones possessing some interesting properties, attractive morphology, liquid crystalline behavior, conducting properties and many other properties. Such variable types of arylidene polymers can be easily applied in different field of applications. A comprehensive overview to the synthesis and characterization of various types of arylidene polymers with a special attention to arylidene based unsaturated polyesters, polyketons, polyurea derivatives, polyamides, organometallic and other arylidene based polymers have been presented from chemistry point of view. More particularly, a special attention has been given to the morphological changes that have been detected upon changing the type of arylidene segments and its corresponding functional groups as well. In addition to solubility, viscosity, thermal behavior and other properties that may also changed upon polymerization.

Keywords: arylidene polymers, cycloalkanones, synthesis, characterization, polycondensation technique, polyketons, polymerization, biological chemistry, materials science, electronic conductivity, fluorescence, high thermal stability, polycondensation, diarylidenecycloalkanones, piperidinone ring, solubility, viscosity, crystallinity, friedel–crafts conditions, x-ray diffraction, gram positive, gram negative bacteria, monomers, antibacterials acidity, water repellency, corrosion inhibitors, DTA measurements, micropores, thermal analyses, protonic, multifunction, thermal property, mechanical properties, corrosion, polymers chains, hybrid type, morphology, cyclohexanone moiety

List of Abbreviations

AlCl ₃	aluminum chloride
BF ₃	boron trifluoride
CH ₂ Cl ₂	ichloromethane
DCH	2,6-dibenzylidenecyclohexanone
DCP	2,5-dibenzylidenecyclopentanone
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTG	differential thermal gravimetry
IR	infrared spectroscopy
K ₂ CO ₃	potassium carbonate
KOH	potassium hydroxide
LiCl	lithium Chloride
NaOH	sodium hydroxide
NMP	n-methylpyrrolidone
OPM	optical polarizing microscopy
PAKAS	polyarylidene(keto amine)s
SEM	sacanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis

Introduction

Arylidene Polymers have been extensively investigated in recent years. There are many studies dealing with preparation of arylidene polymer all these studies show significant developments in the synthesis methods. Arylidene monomers and pre-monomers are very important precursors which have been utilized to synthesize different types of polyarylidene in the last few decades.¹ These polymers can be used and applied in, chemistry, biological chemistry, materials science, engineering, variable fields of industries and other areas of life. Synthesis of the new arylidene polymers has based on diarylidene cycloalkanone moieties. Which are named versatile photoactive molecules because it's have both mesogenic and photoactive properties, also its have some extent of conjugation in the main chain and that explain the electrical properties.² The diarylidene cycloalkanone have many other properties, such as attractive morphology, liquid crystalline behavior, anti-microbial activity, conducting properties, corrosion protection, higher thermal stability.^{3,4}

This compound demonstrated potential applications in biology, chemistry, materials science, technology and medical applications, especially when incorporated with polymer architectures due to its harnessing properties as a photoactive and mesogenic unit, also its introduced to the macromolecular architecture by Borden et al.,^{5,6} Arylidene polymers are extensively used in various areas of interests, as they have special features. Some of these features included electronic conductivity, fluorescence, high thermal stability, and photocuring ability (for adhesives, photoresists, and holography).⁷ On the other hand, there are some disadvantages of polyarylidene such as its resistance against water and moisture, fast photo response, poor dimensional stability, low heat distortion temperature and poor low-temperature impact strength.⁸ In this review will mention different type of arylidene polymers such as unsaturated polyester, polyamides, polyketones, polyazomethines, polyurea derivatives, polyethers, and other types of polyaryldiene hybrid polymers such as poly(keto-amine)s, poly(phosphate-ester)s, poly(ether-ketone)s, poly(ester-amide)s, poly(arylidene-ether)s, poly(azomethine-ether)s in addition to organometallic arylidene polymers.

Methods of preparation

Polycondensation refers to a process of creating compounds from functional clusters and proceeds pairs of functional clusters without small molecules in which the product of the recurring component is different from that of the exiting monomer. Polycondensation takes place in stages, and is distinguished by the speed at which the reaction will make the monomers fade. In addition, there is a difference between polycondensation of bifunctional and polycondensation of tri-and higher functional compounds. Polycondensation of bifunctional compounds causes the creation of linear polymers. On the other hand, polycondensation of tri-and higher functional compounds produces branched and crosslinked polymers.

Conditions of polycondensation

Several conditions are common for polycondensation for achieving high molecular weight. These conditions are described as follows:

- I. There is a reduction in the weight of molecules when there is more reaction than the stoichiometric amount in one of the components. This is because the excess reaction blocks a polymer's end functional groups, creating a polymer with similar end groups, and preventing continuous development of the polymer molecule.
- II. There is a possibility of increased side reactions due to the existence of atmospheric oxygen, particularly if the components are made up of unsaturated groups. As a result, polycondensation is normally undertaken where there is no atmospheric oxygen.
- III. A polymer with decreased molecular weight is formed due to the existence of monofunctional monomer or impurities which restricts the polymerization of bifunctional monomers. This is mainly because of the reaction with expanding polymers and yield chain ends which do not have the capacity to react.

Melt polycondensation:⁹ It is applied if the reactants and the polymers are stable at the melting point. The mechanisms are frequently heated under inert gas for extended period at great temperature and condensed pressure. The benefit of this method is that there is no necessity to use solvent, which lowers the rate of polycondensation and increases the probability of forming the ring.

Solution polycondensation:¹⁰ It is applied if the reactants and the polymers are will not be stable at the melting point. The components are heated in an inert solvent below addition of this procedure is that the reaction can be carried out at a lower temperature.

Interfacial polycondensation:^{11,12} The reaction between a diamine and a diacid chloride, or a dihydroxy compound and a diacid chloride provide a clear explanation of the process of interfacial polymerization. An interfacial polymerization occurs when two monomers are found in two immiscible solvents. The result is a reaction which takes place when the two liquids mix. This largely differs from the procedures used for polycondensation, and can only be applied to reactions which are extremely quick. The results of these reactions are exceedingly high molecular weights. The polymer film inhibits further diffusion into the acid chloride solution, thus controlling the number of new chains which can form high molecular weights are also dependent on a stoichiometric balance and that because the reaction is diffusion-controlled.

Unsaturated polyesters containing arylidenes

The initial resins of comparable sort as utilized today were orchestrated in the 1930's. Carlton Ellis clarified how one could get a rigid polymer after copolymerized the blend

of unsaturated polyester prepolymers with styrene. These pitches turn out to be economically essential the following decade when they were reining constrained with glass filaments giving auxiliary items with high mechanical quality and low thickness. Today unsaturated polyesters are a standout amongst the most imperative matrix resins for composite materials.¹³ As a continuation of our examination on the blend and properties of various new polymers in view of diarylidenecycloalkanones having diverse properties, alluring morphology, fluid crystalline conduct, directing properties and numerous different properties, which have been distributed in our past work. The primary item regions for unsaturated polyester are marine mechanized, electric and electronic, building, development, game, and recreation, household and clean machines, furniture, and military applications. An exceptional use in gel coats, which are utilized as hued and securing surface coatings in composites.¹⁴

Experimental results

Some examples of these important polymers can be summarized as follows: Unsaturated polyesters based of diarylidenecyclopentanone 2a-f were integrated from

the polymerization of 2,5-bis(4-hydroxy-benzylidene)cyclopentanone and 2,5-bis(4-hydroxy-3-methoxy-benzylidene)-cyclopentanone monomers 1a,b with various diacid chlorides utilizing interfacial polycondensation technique.¹⁵ Monomers 1a,b can be obtained by the response of cyclopentanone with the given aldehyde derivatives (i.e. p-hydroxy-benzaldehyde or vanillin respectively) as showed in Figure 1. The best environments for interfacial polycondensation method beside other characteristics including: viscosity, thermal stability, and electrical properties of the gained unsaturated polyesters were studied. Also, there is another kind of unsaturated polyesters based on diarylidenecyclohexanone moieties 4a-f were synthesized¹⁶ using also interfacial polycondensation technique. The polymers were synthesized by the polymerization of 2,6-bis(4-hydroxybenzylidene)cyclohexanone 3a and 2,6-bis(4-hydroxy-3-methoxybenzylidene)-cyclohexanone 3b with various aromatic and aliphatic diacid chlorides as shown in Figure 2. More studies were carried out on the obtained polymers, showing their thermal stability, X-ray analysis, and morphological properties. The morphological properties of some chosen cases of polymers were analyzed by TEM showing an aggregated globules and crystal lattice (Penta and hexagonal) inter chains.

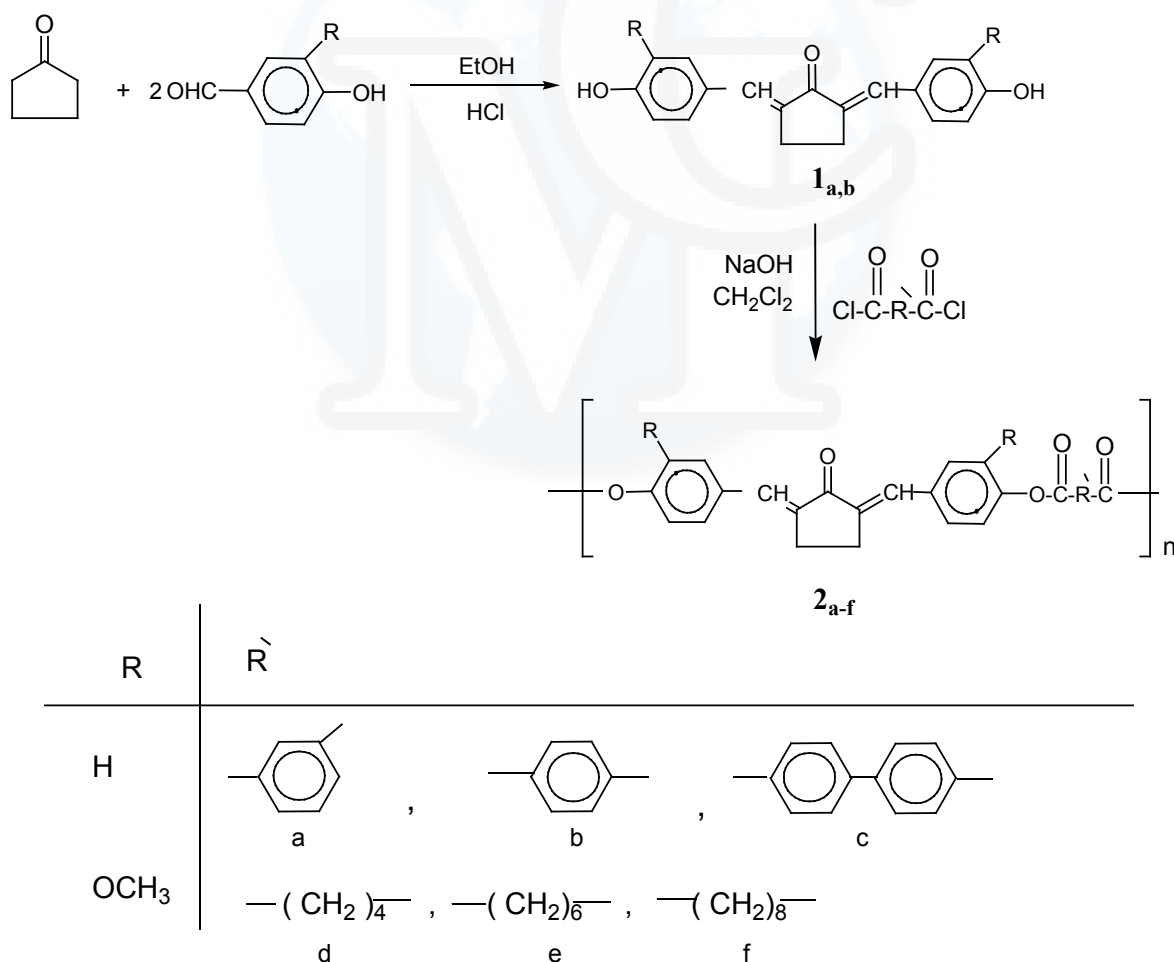


Figure 1 Synthesis of polyarylidenes 2_{a-f}.

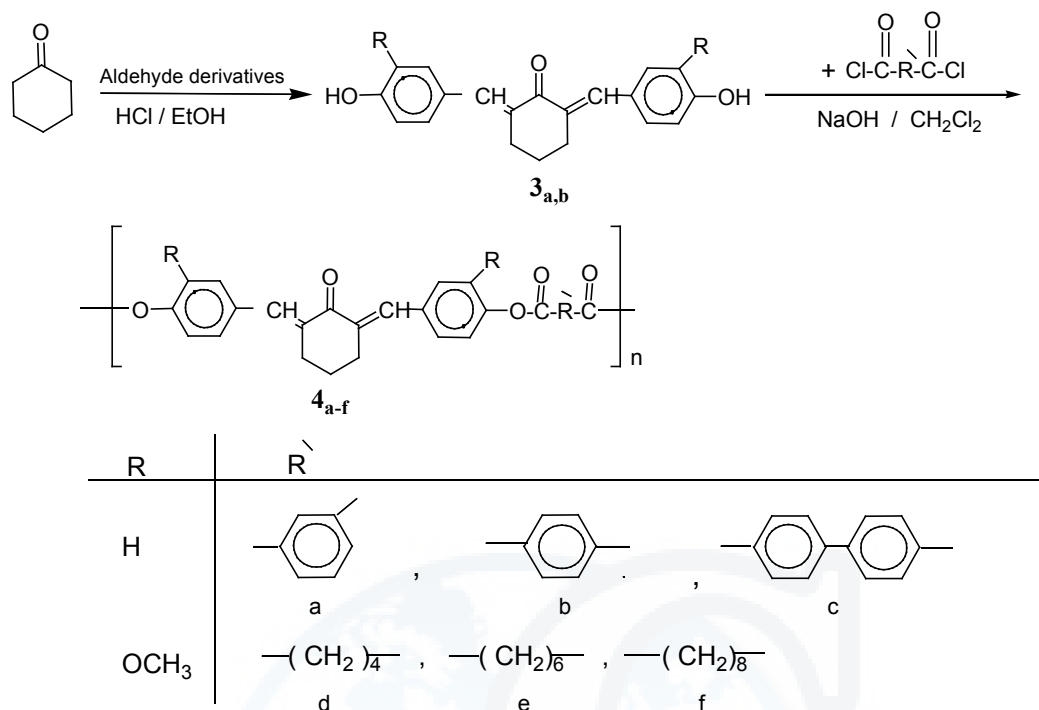
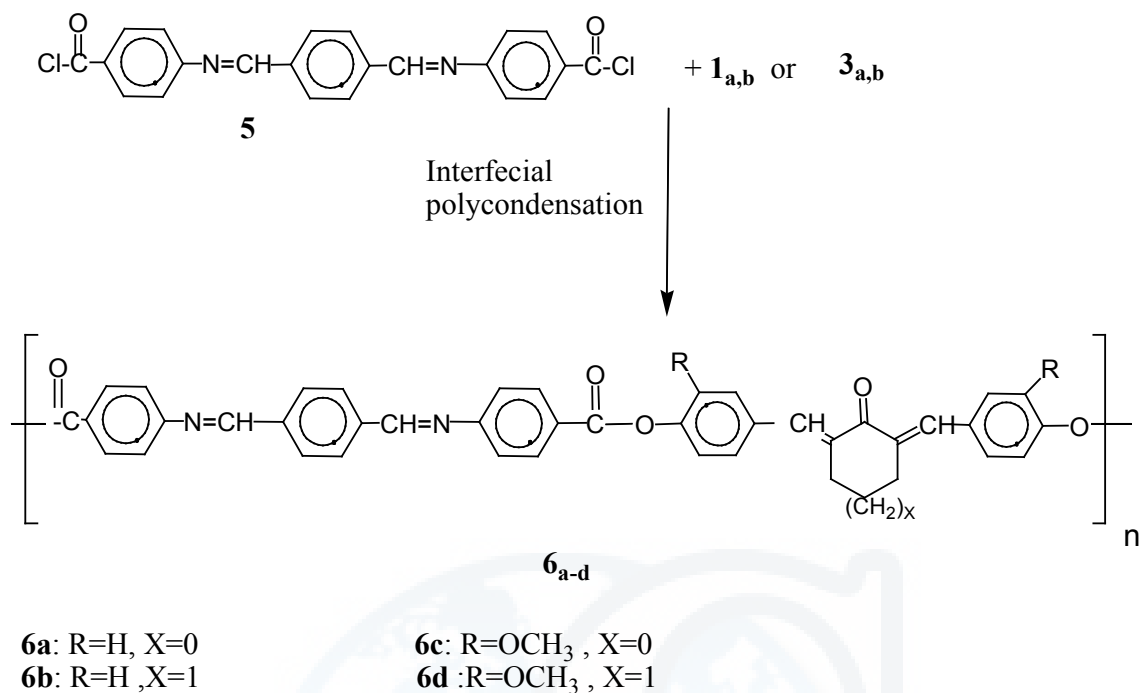
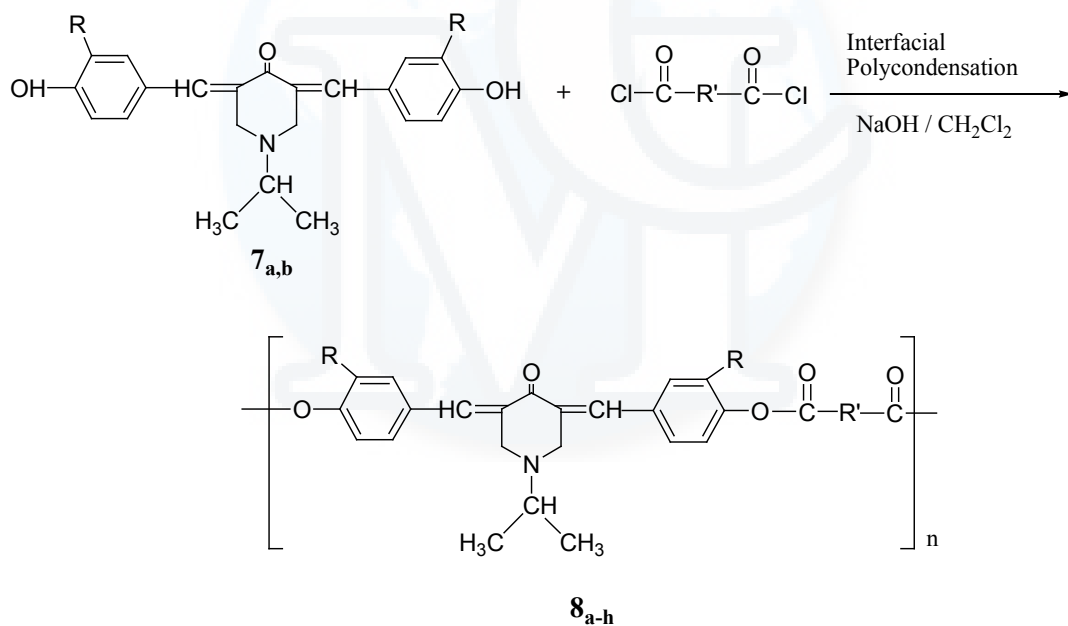


Figure 2 Synthesis of polyarylidene 4_{a-f}.

Moreover, interfacial polycondensation of 4,4'-[1,4-phenylene-bis(methylidene)nitri]o]-dibenzoyl chloride 5 with diarylidene-cycloalkane derivatives 1a,b, 3a,b will yield poly(arylidene-ester)s 6a-d hybrid polymer which carry azomethine group in the polymer main chain, as appeared in.¹⁷ Figure 3 The thermal stability, crystallinity, and electrical properties of these polymers were evaluated by different measurements, and the data obtained were discussed. Aly & Geies¹⁸ synthesized a novel unsaturated polyesters 8a-h by reacting of 3,5-bis(p-hydroxybenzylidene)isopropylpiperidinone and 3,5-divinylideneisopropylpiperidinone 7a,b as new starting materials for preparing. The unsaturated polyesters 8a-h they aimed were prepared by interaction of monomers 7a or 7b with adipoyl, sebacoyl, isophthaloyl or terephthaloyl dichlorides that done over the interfacial polycondensation technique (Figure 4). Most of these polyesters were dissolvable in dimethyl sulfoxide. Thermogravimetric examinations verified that the aromatic based polyesters were to some degree less thermally stable than their aliphatic partners. The examinations of X-ray diffraction confirmed that the inclusion of piperidinone ring in the polymer chain causes a small decrease in the degree of crystallinity. The preparation of unsaturated polyesters 9a-d will be by the reaction between 3,5-bis(p-hydroxybenzylidene)isopropylpiperidinone 7a or 3,5-divinylideneisopropylpiperidinone 7b with 4,4'-azodibenzoyl chloride and 3,3'-azodibenzoyl chloride the yielding unsaturated polyesters 9a-d will be containing an azo group which will be in the main chain¹⁹ as shown in Figure 5.

In 2001, Giana et al.,²⁰ synthesized a new polyesters

contain an aliphatic and aromatic unit together at the same time in the back bone were prepared by polycondensation of 4,4'-[hexane-1,6-diyl-bis(2,4,5-trioxoimidazolidine-1,5-diyl)]dibenzoyl chloride 10 with various biphenols 12a-f. Monomer 10, model compound 11 and polymers 13a-f then studied their viscosities, solubility and thermal properties (Figure 6 & Figure 7). In 2014 Alkskasa et al.,²¹ synthesized a novel category of unsaturated polyesters 14a-d based on diethyl ketone segments in the polymers backbones. Polyesters 14a-d were prepared using interfacial polycondensation technique through the reaction of 2,4-bis(4-hydroxybenzylidene)-3-pentanone (a) and 2,4-bis(4-hydroxy-3-methoxybenzylidene)-3-pentanone (b) with 3,3'-azodibenzoylchloride or 4,4'-azodibenzoylchlorid with azo diacid chlorides in the presence of NaOH/CH₂Cl₂ as shown in Figure 8. Almost all characterization tools were examined for these polymers including: thermal properties which were evaluated by DSC and TGA measurements. Also, the morphological behavior of the synthesized polyester 14c as an example was examined by SEM as shown in Figure 9. Furthermore, Alkskasa et al.,²² prepared a new class of unsaturated polyester 15a-d, 16a-d using the same interfacial polycondensation technique through the reaction between 3-p-hydroxyphenyl-6-p-hydroxybenzylidene cyclopentapyrazoline or 3-vanillyl-6-vanillylidene cyclopentapyrazoline with different aliphatic and aromatic diacid chlorids in the presence of NaOH/CH₂Cl₂. Acid chlorides including: adipoyl, sebacoyl, isophthaloyl, or terephthaloyl dichlorides as shown in Figure 10. The same characterization tools were investigated including thermal behaviors (thermal behavior and stability) which were evaluated by DSC and TGA measurements. DSC curve for polymer 16c as selective example is shown in Figure 11.


 Figure 3 Synthesis of poly(arylidene-ester)s **6_{a-d}**.


R	R'
H	
OCH ₃	a b c d e f g h

 Figure 4 Synthesis of polyesters **8_{a-h}**.

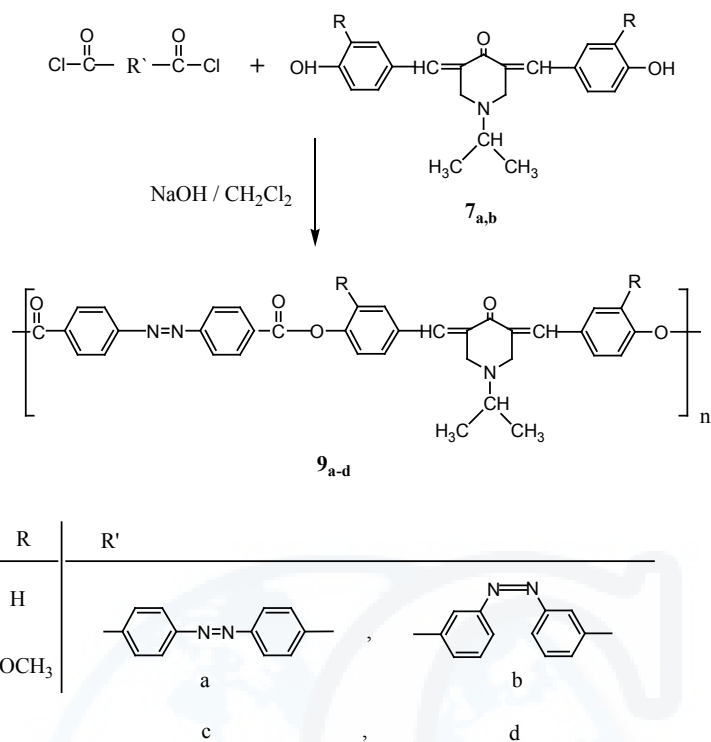
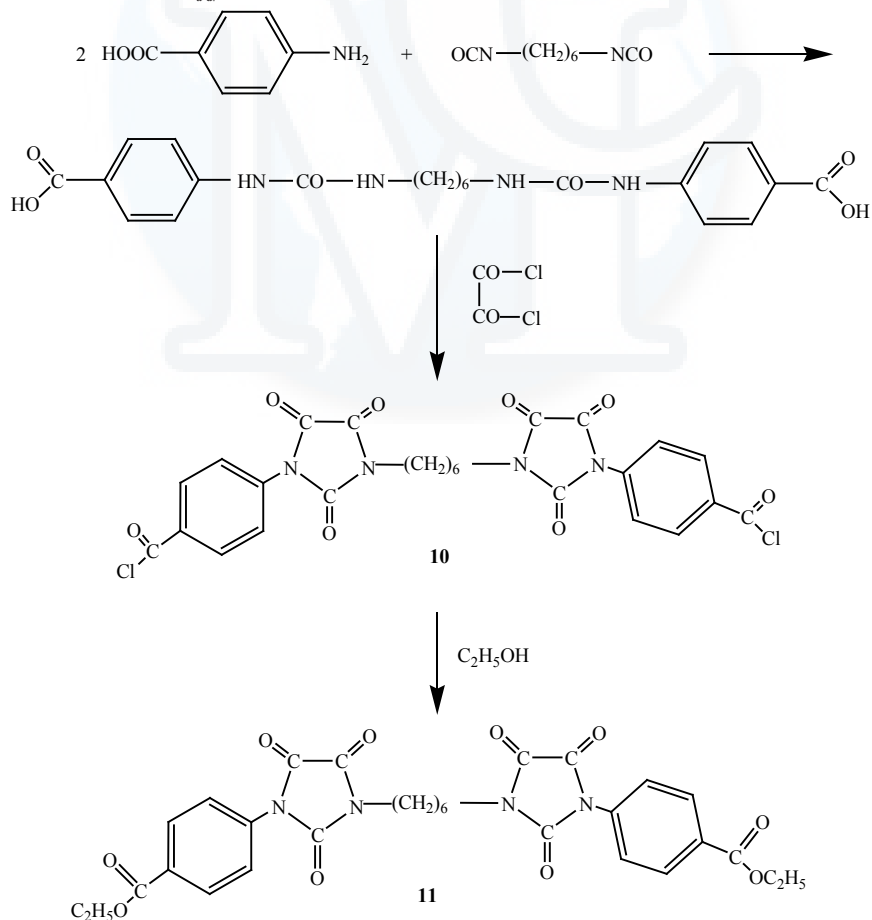
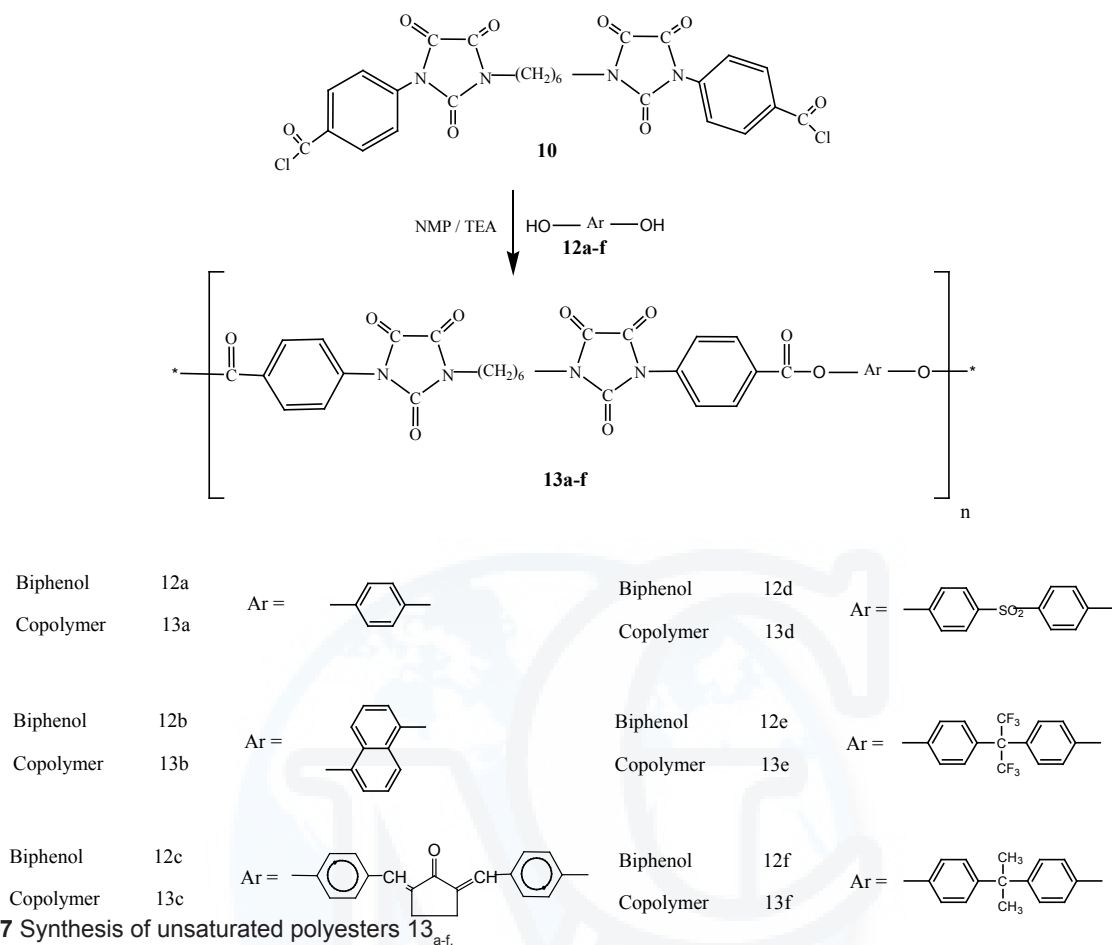
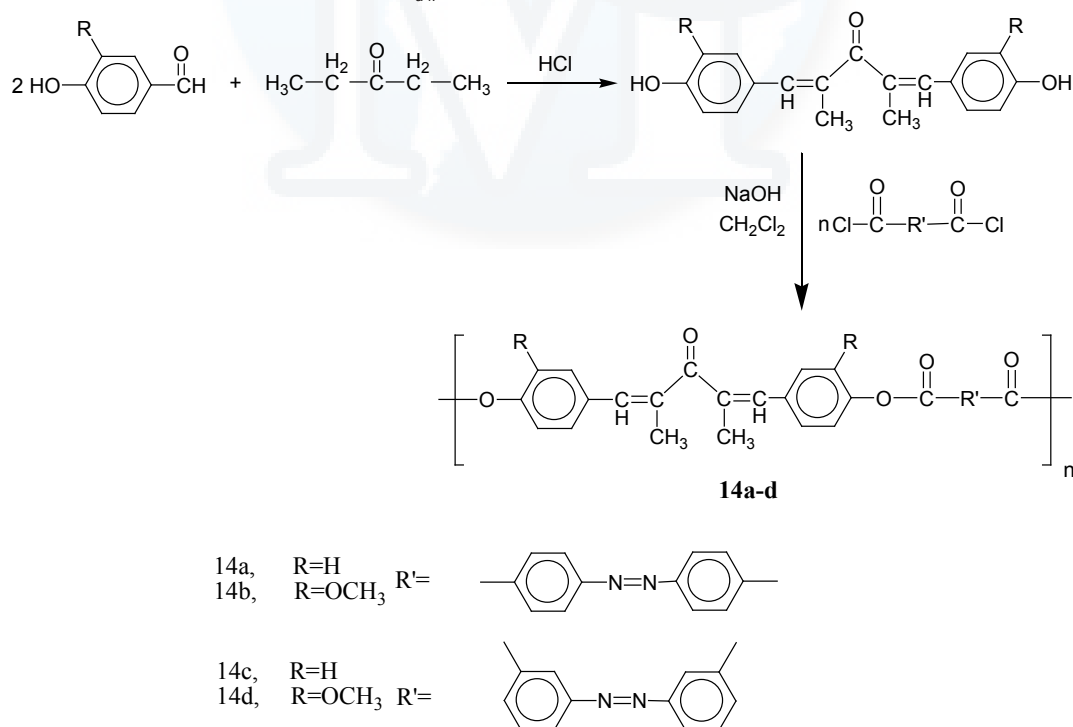

 Figure 5 Synthesis of unsaturated polyesters 9_{a-d}.


Figure 6 Synthesis of model compound 11.


 Figure 7 Synthesis of unsaturated polyesters 13_{a-f}.

 Figure 8 Synthesis of unsaturated polyesters 14_{a-d}.

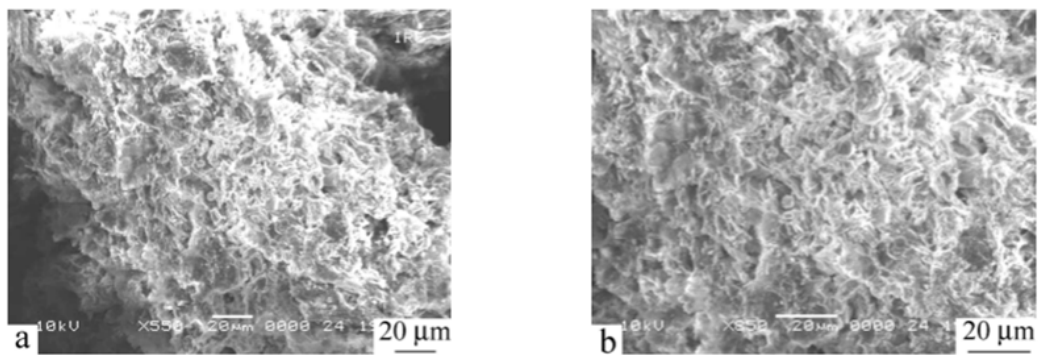


Figure 9 SEM micrographs showing the morphology of the polyester 14c; (A) at x=550; (B) at x=850.²¹

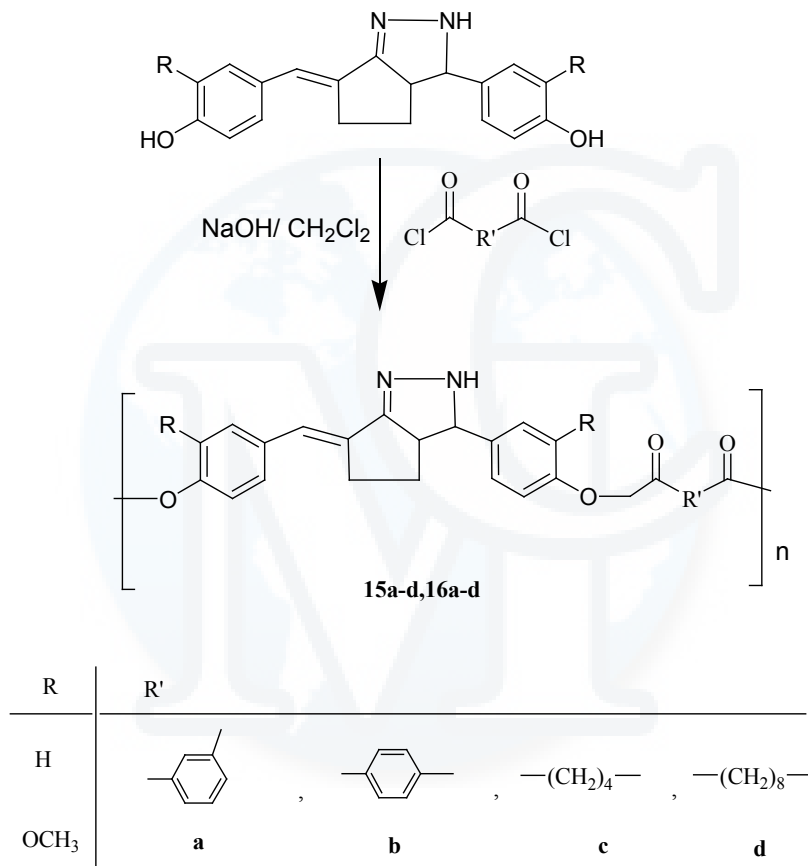


Figure 10 Synthesis of unsaturated polyesters 15_{a,d} & 16_{a,d}.

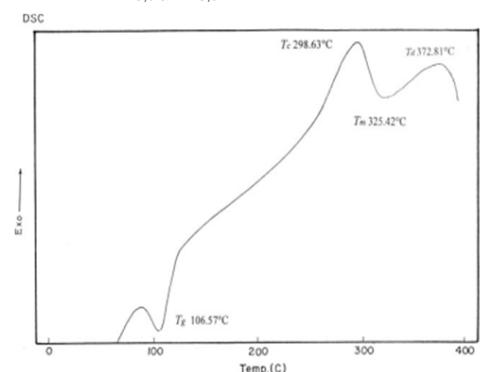


Figure 11 The DSC curve of polyester 16c.²²

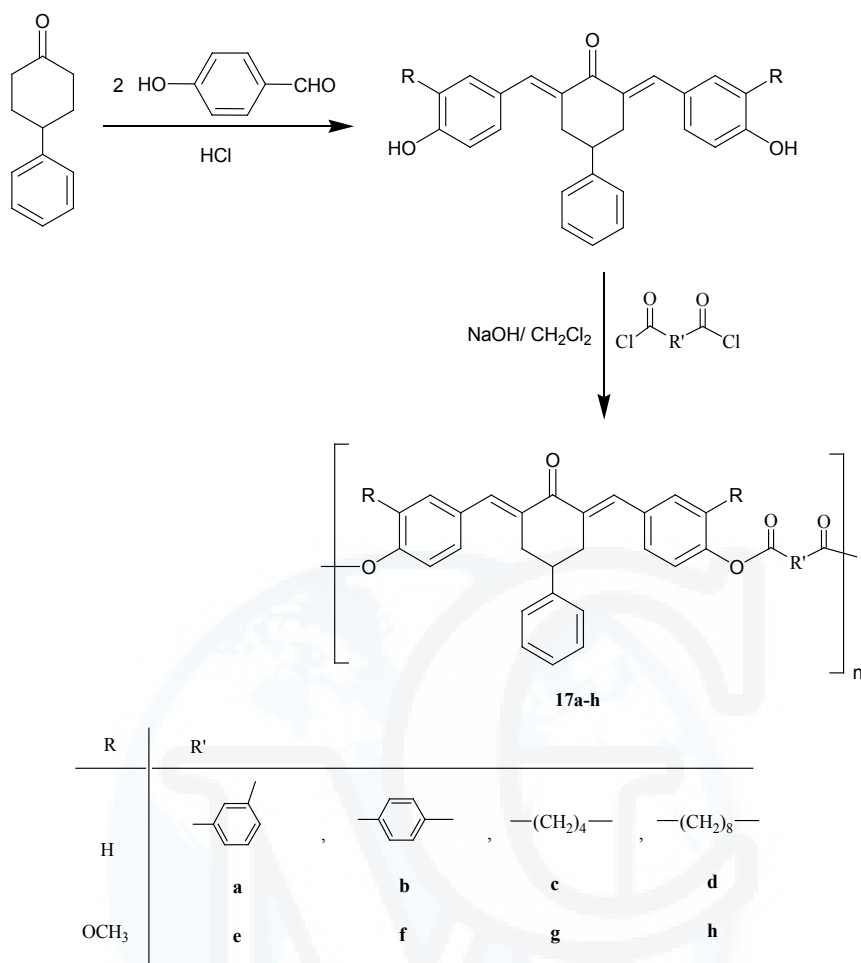


Figure 12 Synthesis of unsaturated polyesters 17_{a-h}.

Alkskasa & Esbata²³ synthesized a new class of unsaturated polyesters 17a-h using interfacial polycondensation technique. The reaction between 2,6-bis(p-hydroxybenzylidene)-4-phenylcyclohexanone and 2,6-divanillylidene-4-phenylcyclohexanone with adipoyl, isophthaloyl, sebacoyl and terephthaloyl dichlorides in the presence of NaOH/CH₂Cl₂ at ambient temperature yielded the required polymers in good conditions as shown in Figure 12. Solubility, viscosity, crystallinity and morphology were investigated as characterization tools. Besides, thermal properties (thermal behavior and stability) which were evaluated by TGA, DTG and DSC measurements and the results are linked to the polymers structures as shown in Figure 13 for polymers 17b, 17f as an examples.

Experimental discussions

Generally, when we compare the unsaturated polyesters which have been prepared based on diarylidene cyclohexanone derivatives we found they prepared in most cases throughout interfacial polycondensation technique at ambient temperature. In addition, all the polymers are insoluble in common organic solvents; whereas, most of them are soluble in polar aprotic solvents and sulfuric acid. Thermogravimetric studies presented that the aromatic

based polyesters showed significantly higher thermal stability compared to the aliphatic counterparts. As well the x-ray diffraction studies presented that the presence of pendant groups in the polymers chains causes a noticeably decrease in the degree of crystallinity while comparing these properties to its similar ones in the open literature.¹³⁻²³

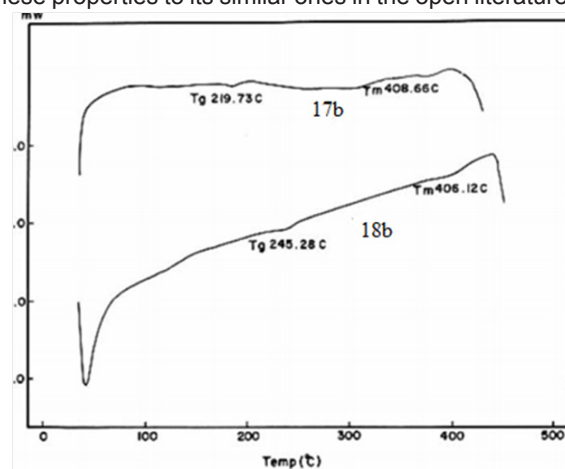


Figure 13 The DSC curves of polymers 17b, 17f.²³

Polyketones

Polyketones are an important kind of polymers which have thermal properties and chemical resistance. Polyketones have been widely used in different areas of life such as medical, chemical, applications. In this review will mention some of polyketones synthesis by different monomers.

Experimental results

In 2013 Alkskasa et al.,²⁴ prepared a series of polyketone 18a-f using Friedel-Crafts polymerization technique through the reaction between dithiophenylidene cycloalkanones with three different diacid chlorides including: adipoyl, sebacoyl and terephthaloyl dichlorides in the presence of BF₃ as illustrated in Figure 14. The thermal properties as

well as all other properties were examined and discussed in details. More particularly, the morphological characters of the synthesized polyesters were examined by SEM as shown in Figure 15 for polymer 18c as an example. On the other hands, the synthesized polymers showed a significant biological activity against all tested bacteria and fungi. In 2003 Aly et al.,²⁵ prepared a new class of polyketones 19a-h & 20a-h using also Friedel-Crafts polymerization method. The polymerization was carried out between diarylidene cycloalkanones (DCP or DCH) with aromatic or aliphatic diacid chlorides in the presence of anhydrous AlCl₃ and CH₂Cl₂ as given in Figure 16. TGA, DTG and DTA were used to evaluate the thermal properties of these polymers and the results were correlated to the original structures as shown for polymer 19a in Figure 17.

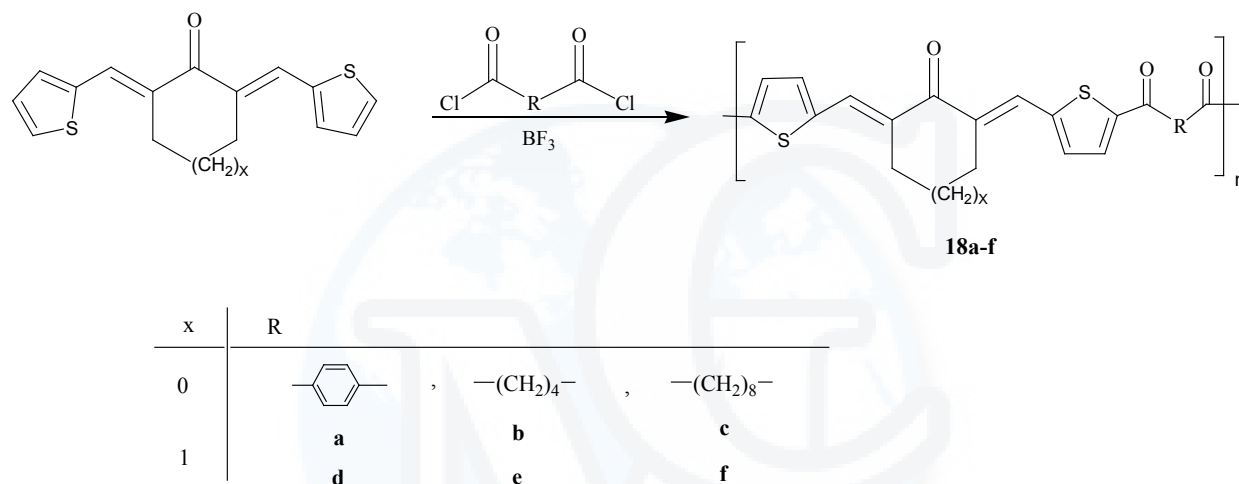


Figure 14 Synthesis of polyketones 18_{a-f}.

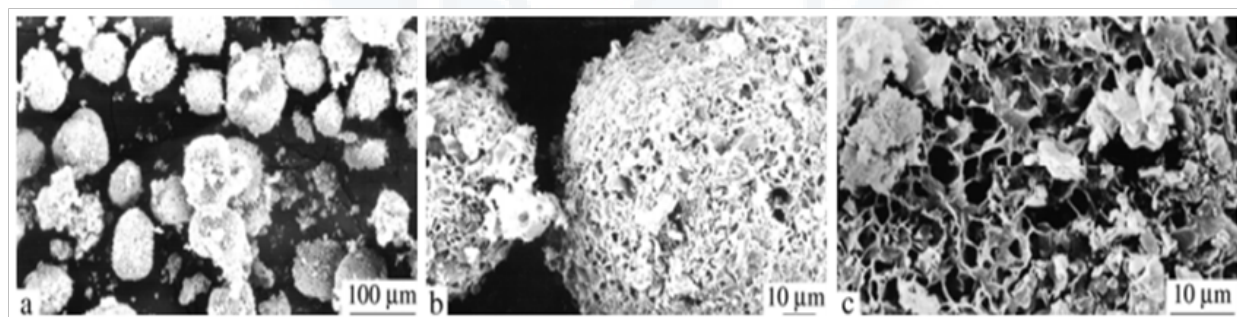


Figure 15 SEM micrographs of polymer 18c at (A) low magnification; (B) at x=1000; (C) at x=2000.²⁴

Al-Muaikel & Aly²⁶ synthesized a new class of polyketones 21a-d containing N-methylpiperidinone using in the polymers main chains using normal Friedel-Crafts technique. Polycondensation reaction between 2,6-bisfurfurylidene N-methyl piperidone and various diacid chlorides in the presence of AlCl₃ and carbon disulphide as a solvent yielded the desired polyketones as shown in Figure 18. This study was mainly aimed to examine the biological activity for the prepared polyketone selected types of bacteria and fungi. In addition, all other properties were also investigated including solubility, viscosity, crystallinity and thermal properties.

The thermal stability for polymer 21a was evaluated by TGA, DTG and DTA measurements is given in Figure 19. In addition, the morphology of the prepared polymer 21a was also tested using SEM showing an interesting surface morphology as shown in Figure 20. More particularly, Hussein et al.,²⁷ synthesized a new class of polyketones 23a-h containing naphthalene moieties along the polymers main chains using the ordinary Friedel-Crafts preparation procedures and conditions. Dinaphthylidene cycloalkanone monomers 22 interact with different aliphatic and aromatic diacid chlorides produce a high yield polyketones of variable

colors as shown in Figure 21. The work aimed to examine the biological activity for the desired polyketones including selected types of Gram positive, Gram negative bacteria and selected fungi. Therefore, the produced monomers as well as polymers were screened for their antibacterial and antifungal activities. The results showed a significant antibacterial activity against tested Gram-negative and Gram-positive bacteria and no significant influence against the selected fungi species except monomer based

cyclohexanone moiety and two other polymers 23a and 23f respectively. All other properties were also tested, and evaluated including the polyketones thermal properties which evaluated by TGA, DTG and DTA measurements. The polymers crystal structures were estimated by x-ray diffraction patterns. Also, selected samples were scanned by (SEM) to study the morphology features for these polymers as well.

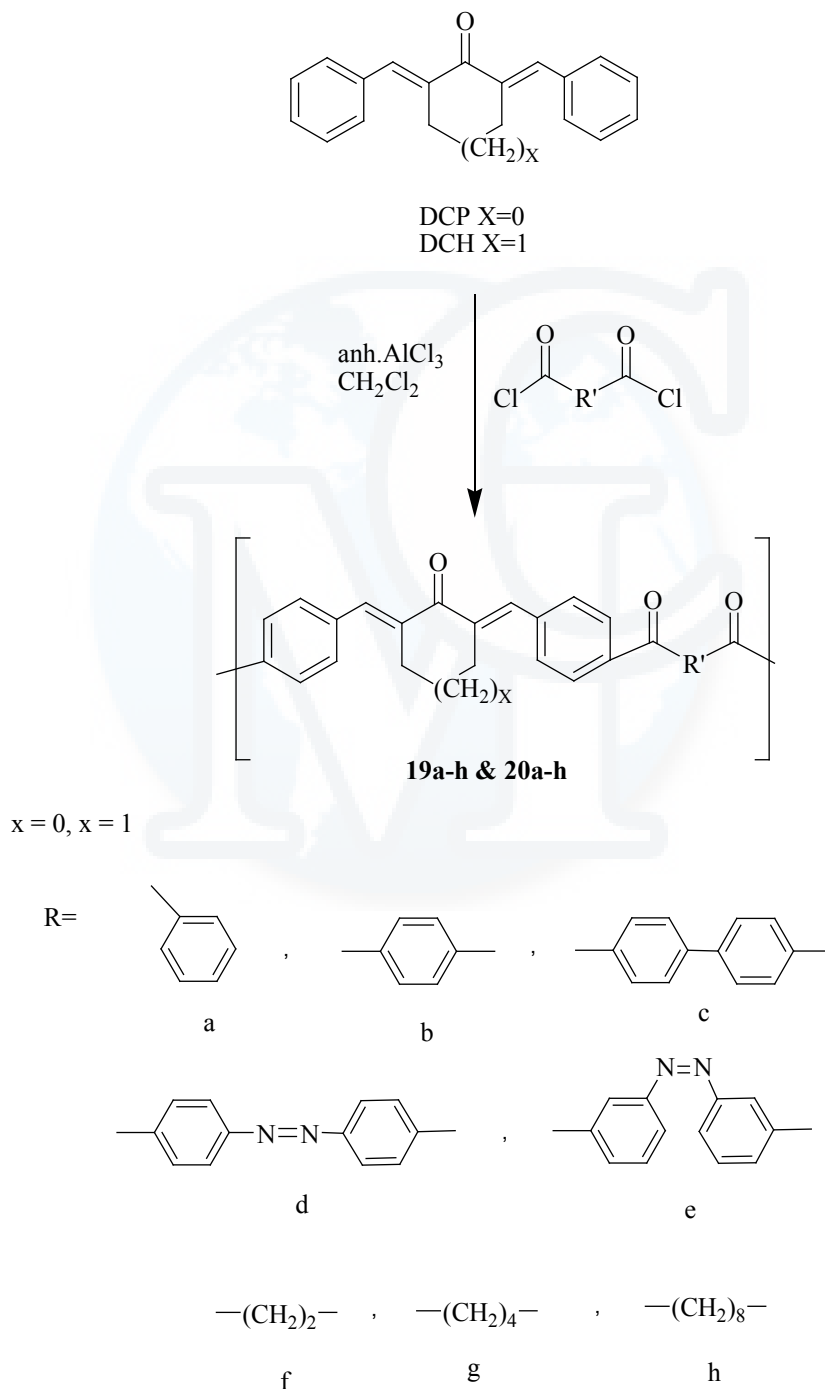


Figure 16 Synthesis of polyketones 19_{a-h} & 20_{a-h}.

Experimental discussions

This section discusses the preparation methods, characterization tools and some possible application of selected polyketones based arylidene monomers. All types of these different polyketones that mainly based diarylidene cycloalkanone moieties were prepared using normal Friedel–Crafts conditions using AlCl_3 in a suitable solvent like carbon disulphide or methylene chloride. The properties of these different polyketones were highly affected by their chemical structural differences and based on the building constituent that are presented in each type. Most polymers give a moderate viscosity values which are directly related to the higher molecular weights of these polymers. Solubility character also affected by the pendent group in most cases which enhance the solubility in certain solvents. The thermal stability studies also showed considerable difference in their stability according to the main cycloalkanone core unit. In which, cyclohexanone based polyketones show thermally stably stable polymers than cyclopentanone counterparts polymers. In addition, the aliphatic based polymers show less thermally stable than the aromatic based ones. X-ray crystal structures confirm

that the majority of these polyketones are semi crystalline in nature. As reported in the literature almost all polyketones show antibacterials acitly. Therefore, the previous examples aimed also to test the biological activity for the different types of polyketones including selected types of Gram positive, Gram negative bacteria and selected fungi. Almost in all cases the polymers give moderate activity against the tested microorganisms compared to the open literature results.^{24,27}

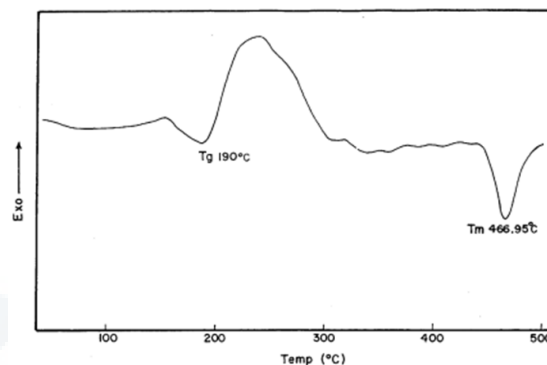


Figure 17 The DSC curves of polymers 19a.²⁵

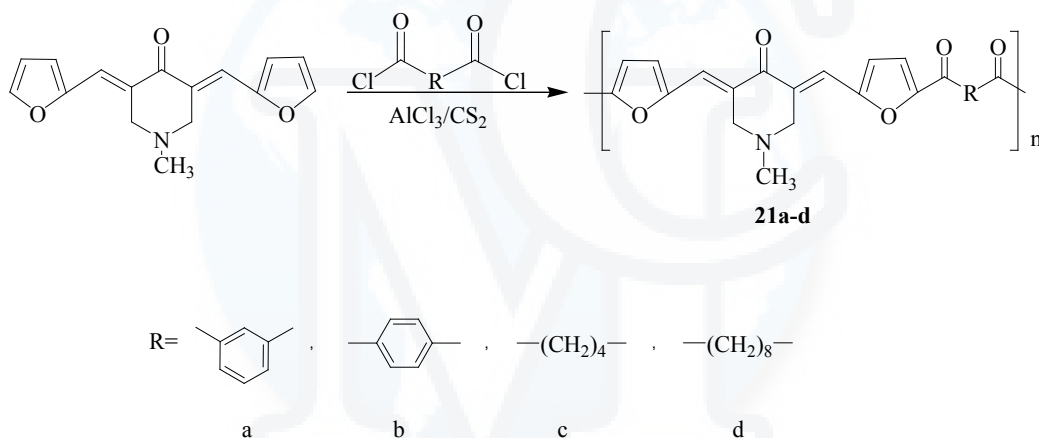


Figure 18 Synthesis of polyketones 21_{a-d}.

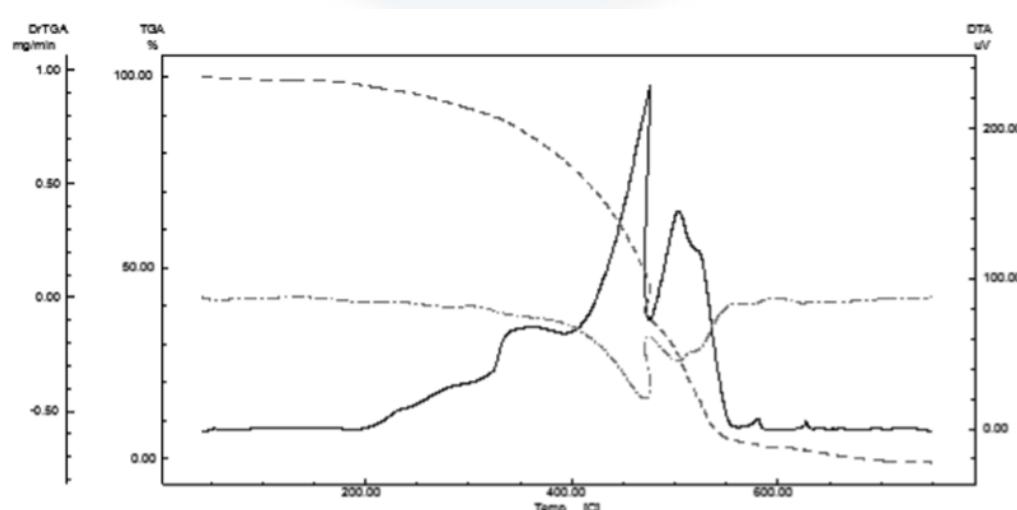


Figure 19 TGA, DTA and DTG curves of polyketone 21a.²⁶

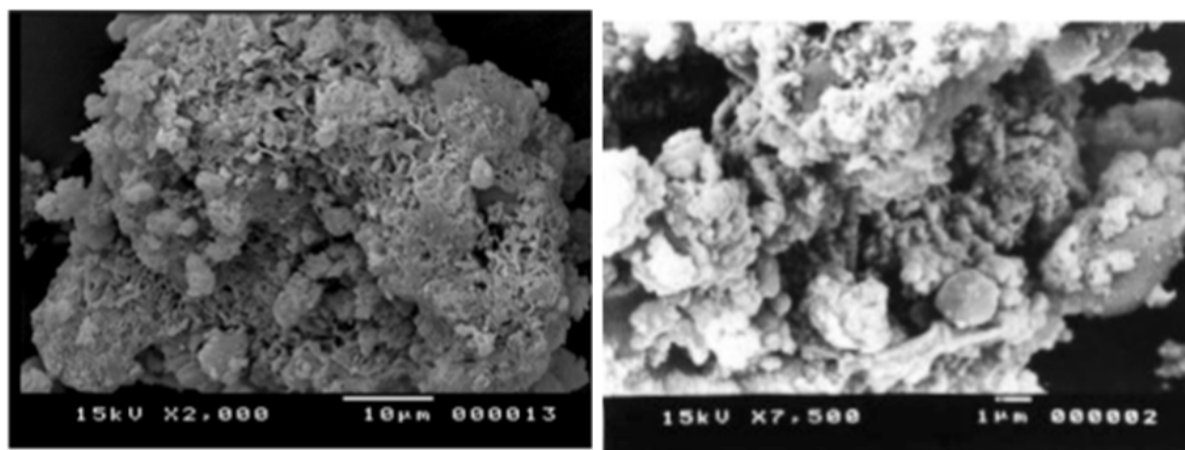
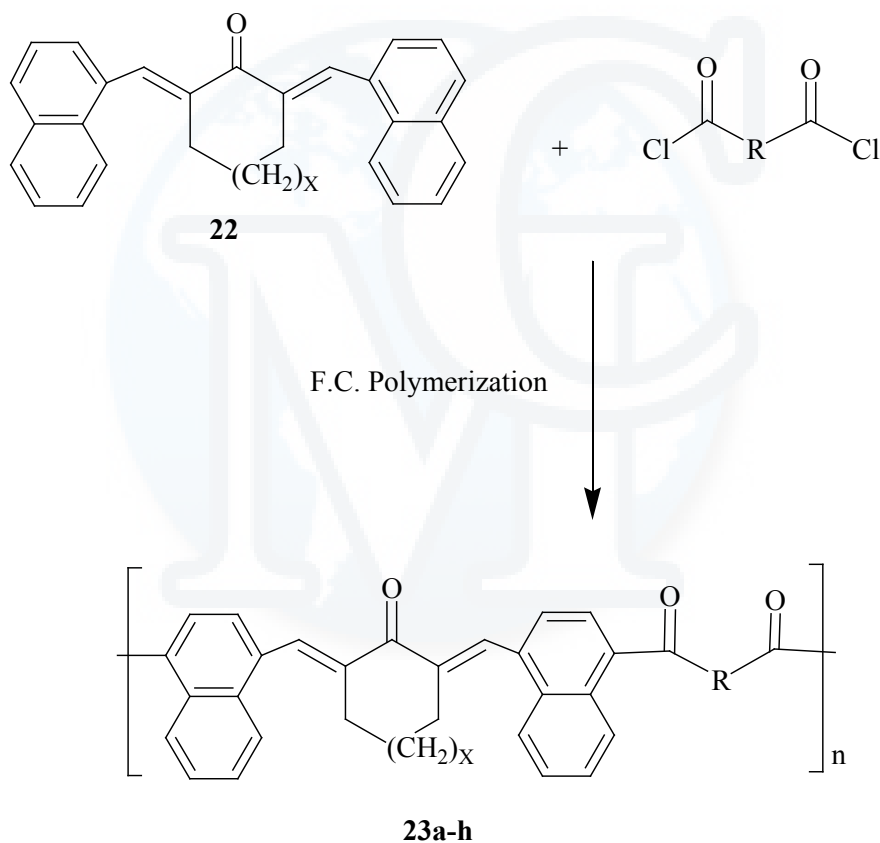


Figure 20 SEM images of polyketone 21a: (A) $x=2000$ and (B) $x=7500$.²⁶



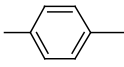

x	R
0	$-(CH_2)_4-$, $-(CH_2)_8-$,  , 
1	a b c d e f g h

Figure 21 Synthesis of polyketones 23_{a-h}.

Polyurea derivatives and polyurethanes

Polyurea is an important kind of hard materials which can be prepared by the reaction of isocyanate moieties with an amine under high temperature conditions. Also, it has an amazing physical and chemical properties for example water repellency, leather appearance and chemical resistance.^{28,29} In this section we will mention some of these polyurea derivative synthetic routes through different diarylidene monomer.

Experimental results

Aly & Hussein²⁸ synthesized a new class of polyurea derivatives 25a-c and 26a-c based on diarylidencycloalkanone moieties in the polymers backbone as highly appreciated corrosion inhibitors. The synthetic route done using polycondensation reaction of bis(2-aminothiazol-4-ylbenzylidene)cycloalkanones monomers 24a,b with diisocyanate compounds including: 1,6-hexamethylene diisocyanate, toluene-2,4-diisocyanate and diphenylmethane-4,4'-diisocyanate in the presence of pyridine as a reaction solvent as illustrated in Figure 22. All characterization tools were tested such as solubility, viscosity, crystallinity, thermal analyses. In addition to some other properties such as electrical properties, were also tested. The surface morphology of selected samples of polyurea derivatives were also measured using scanning electron microscopy measurements. Figure 23 shows the surface morphology of polymer 26a at magnifications $\times=1,500$ and $\times=3,500$ in which the morphology shows porous micropores along the surface. Furthermore, the corrosion inhibitive properties of diarylidencycloalkanone monomers and selected examples of these polyurea derivatives were studied in details. The synthesized polymers show excellent efficiency as corrosion inhibitors in mild acidic solutions 0.5 M H₂SO₄ at 40°C giving all types of protections (cathodic, anodic and mixed) inhibition.

Aly et al.²⁹ synthesized another new category of polyurea derivatives 28a-c via solution polycondensation technique. The preparation done by the reaction of 4,4'-bis(2-aminothiazol-4'-yl)diphenyl ether monomer 27 with diisocyanate compounds in the presence of pyridine as a solvent (Figure 24). All the polymers properties were tested and studied in details. The thermal properties were also tested by TGA, DTG, and DTA measurements showing higher thermal stability. Additionally, the morphological properties were also tested for selected samples by SEM. Figure 25 shows the morphological property of polyurea 28c. The corrosion inhibition properties of these polymers were also tested as an important application for these polymers. The inhibitive property was carried out on steel and gave good results in which these polymers have been considered as cathodic good inhibitors in 0.5 M H₂SO₄ at 40°C.

Polyurethanes or polycarbamate's as well (from carbamic acid, RNHCO₂H), are ester-amide derivatives of carbonic acids. It has many different applications including fibers (especially the elastic type), adhesives, coatings, elastomers, flexible and rigid foams, and thus have gotten extensive consideration in the literature.^{30,31} Polyurethanes 29a-d and

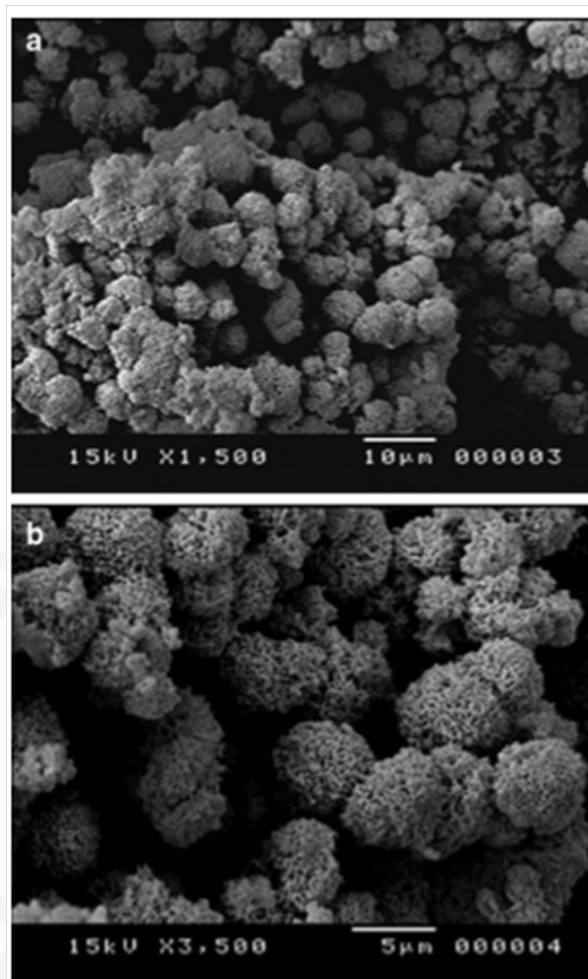


Figure 23 The SEM images of the polymer surface of polyurea 26a (A) $\times=1,500$ and (B) $\times=3,500$.²⁸

30a-d were synthesized³² through advanced development arrangement polymerization, by the polymerization of diisocyanates with diarylidene monomers 1a, b and 3a, b, in DMF, as illustrated in Figure 26. The requirement for particularly polymers with improved electrical properties (conductivity) has run a lot of researches in this field.^{33,34} Some of these materials were prepared beforehand in our lab and all the thermal properties were evaluated, and morphology properties for selected samples were examined.

Experimental discussions

Polyurea derivatives and polyurethanes based on diarylidencycloalkanone moieties were prepared via solution polycondensation technique in pyridine. All characterization tools of these polymers were tested such as solubility, viscosity, crystallinity, thermal analyses. In addition to some other properties such as electrical properties, were also tested. Most of these polyurea derivatives were soluble in aprotic solvents like DMSO and DMF and protic solvents like formic and concentrated sulfuric acids. X-ray examination showed the polyurea

derivative polymers had higher degree of crystallinity compared to those of polyurethanes. Also, the crystallinity of polyurea based on diarylidene cyclohexanone is found to be higher than polyurea based on diarylidene cyclopentanone. The conductivity test is considered an important tool for all types of polyurea derivatives. The conductivity test of these polyurea derivatives was measured and the values

are found in the range of insulator materials. Moreover, the corrosion inhibitive properties of diarylidene cycloalkanone monomers and different types of polyurea derivatives were studied in detail. The synthesized polymers show excellent efficiency as corrosion inhibitors in mild acidic solutions 0.5 M H₂SO₄ at 40°C giving all types of protections (cathodic, anodic and mixed) inhibition.²⁸⁻³²

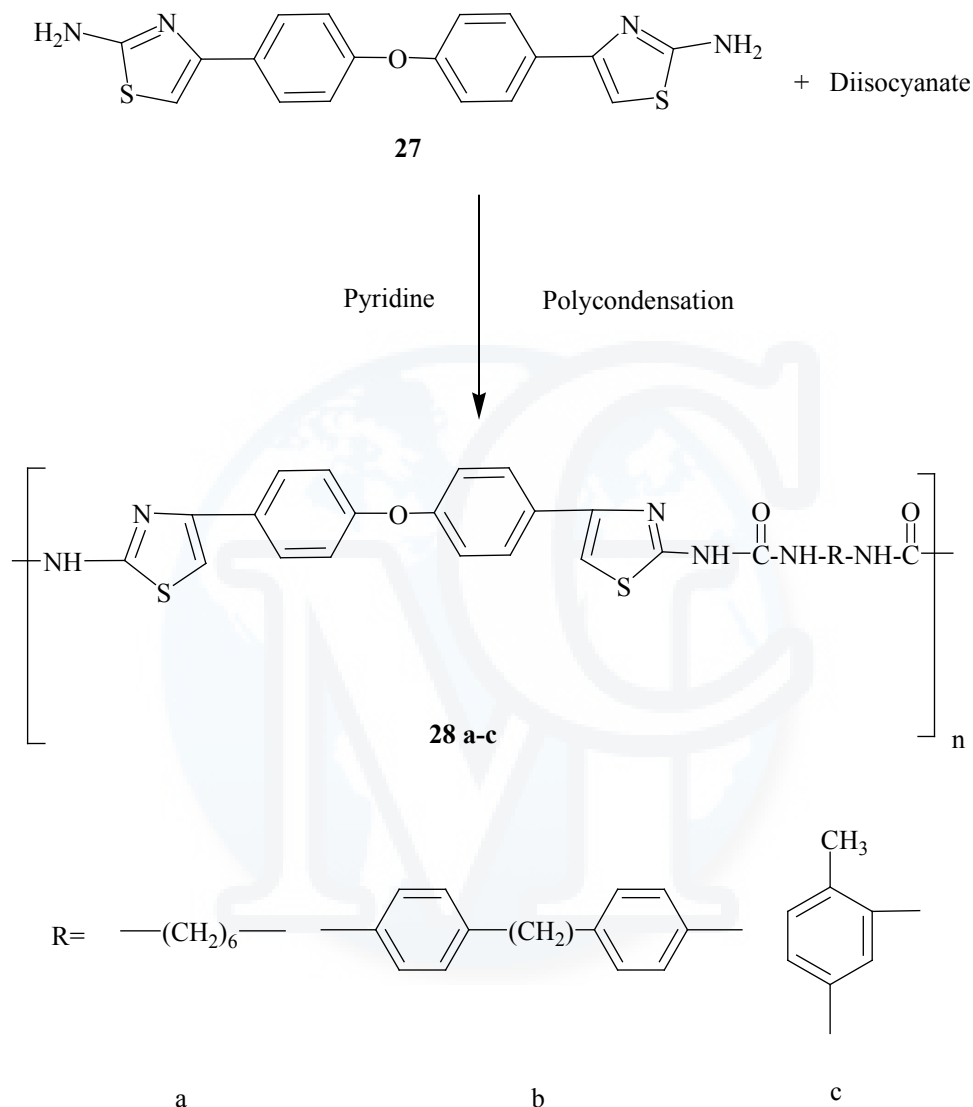


Figure 24 Synthesis of polyurea derivative 28_{a-c}.

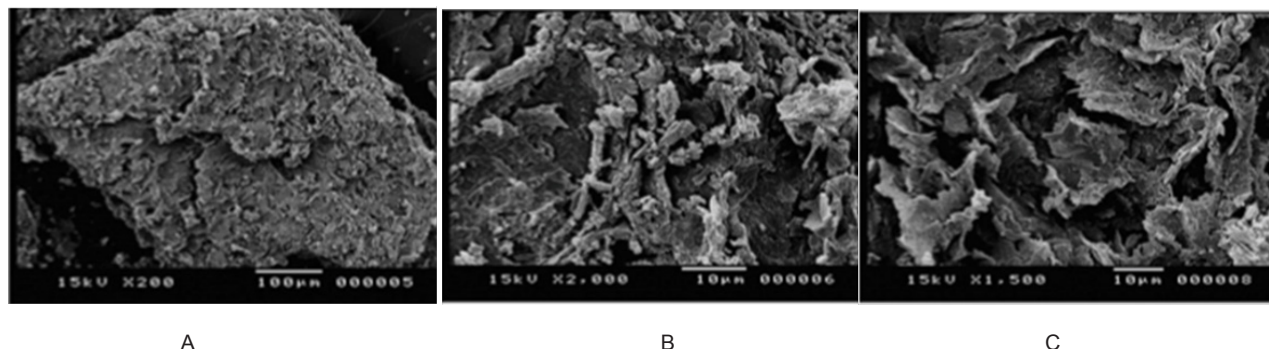


Figure 25 The SEM images of the polymer surface of polyurea 28c. (A) X=200, (B) X=1500 and (C) X = 2000.²⁹

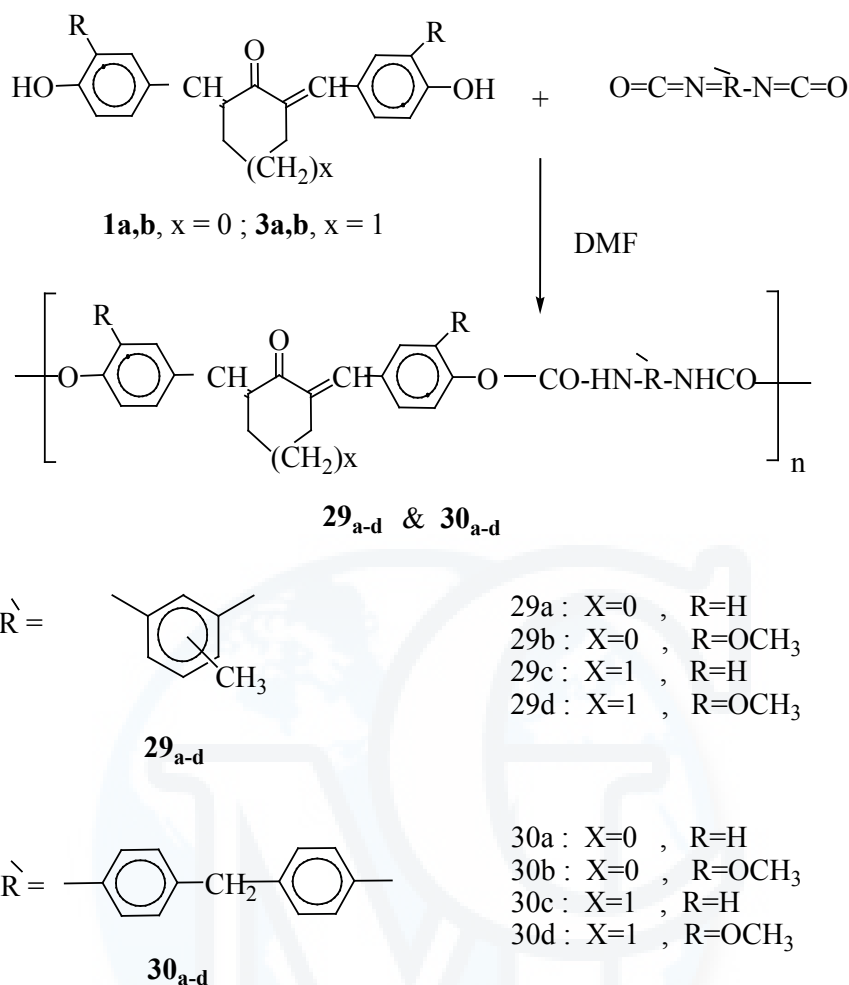


Figure 26 Synthesis of polyurea derivatives 29_{a-d} & 30_{a-d}.

Polyamides

Polyamides are multifunctional synthetic polymers which contain amide groups that link the monomers together. Polyamides have different applications in many areas of life especially in variable industries and it has unique properties such as the thermal property, mechanical properties, and chemical resistance.³³⁻³⁵ In this section we will mention different polyamide preparation methods by diverse arylidene monomers.

Experimental results

In 2015 Aly & Hussein³⁶ work on synthesized a new and interesting series of thiazole based polyamides 31a-f containing diarylidene cyclohexanone moiety, through a well known technique called "low temperature solution polycondensation." The main purpose of this study is to investigate the corrosion inhibitive properties of the selected thiazole-based polyamides. Polyamides are known as groups of engineering thermoplastics that are used in wide range of applications under polycondensation procedures of bis(2-aminothiazol-4-ylbenzylidene)cyclo-

hexanone 24b monomer with diacid chlorides to get the desired polyamide 31a-f as shown in Figure 27. Adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl dichlorides and biphenyl dicarbonyl dichloride were used as diacid chlorides. Polyamides 31d & 31f and monomer 24b were utilized as selected examples to measure the corrosion inhibitive performance in the presence of carbon-steel electrode under the condition (0.5 mol/L H₂SO₄ and at a fixed temperature of 40°C). The calculated inhibition efficiency (IE%) for polymer 31d was in the range (82±6)% in all selected concentrations. The best IE% value was obtained at 1 mg/L to reach 98.24% for polymer 31d and whereas, polymer 31f reaches 87.75% at concentration of 0.5 mg/L. In addition, they measured the thermal properties by TGA and DTG besides, other properties including solubility, viscosity, electrical properties, crystallinity and morphological properties. All the results were correlated to the polymers structures and compared to the previous synthesized polymers. The inherent viscosities for these polymers gave an indication for the lower molecular weight of these polymers where the values were in the range of 0.6–1.03 dL/g.

Aly et al.,³⁷ synthesized a new category of polyamides 32a-d based on the diarylidene cycloalkanone monomers containing azo groups in the polymers backbone. The synthetic steps were ended by the formation of four novel polyamides based on diarylidene cycloalkanone moieties as final products. Polyamide 32a-d were produced by the reaction of diamino arylidene monomers 24a,b with diacid chlorides (4,4'-azodibenzoyl dichlorides and 3,3'-azodibenzoyl dichlorides) in NMP as a solvent

and in the presence of LiCl anhydrous under solution polycondensation technique as shown in Figure 28. The desired polymers were identified and characterized by elemental and spectral analyses, besides solubility and viscometry measurements. The thermal properties were also examined by TGA, DTG and DTA measurements and linked to the polymers structural units as previously mentioned. Also, all the other characters and properties were also examined and studied in details.

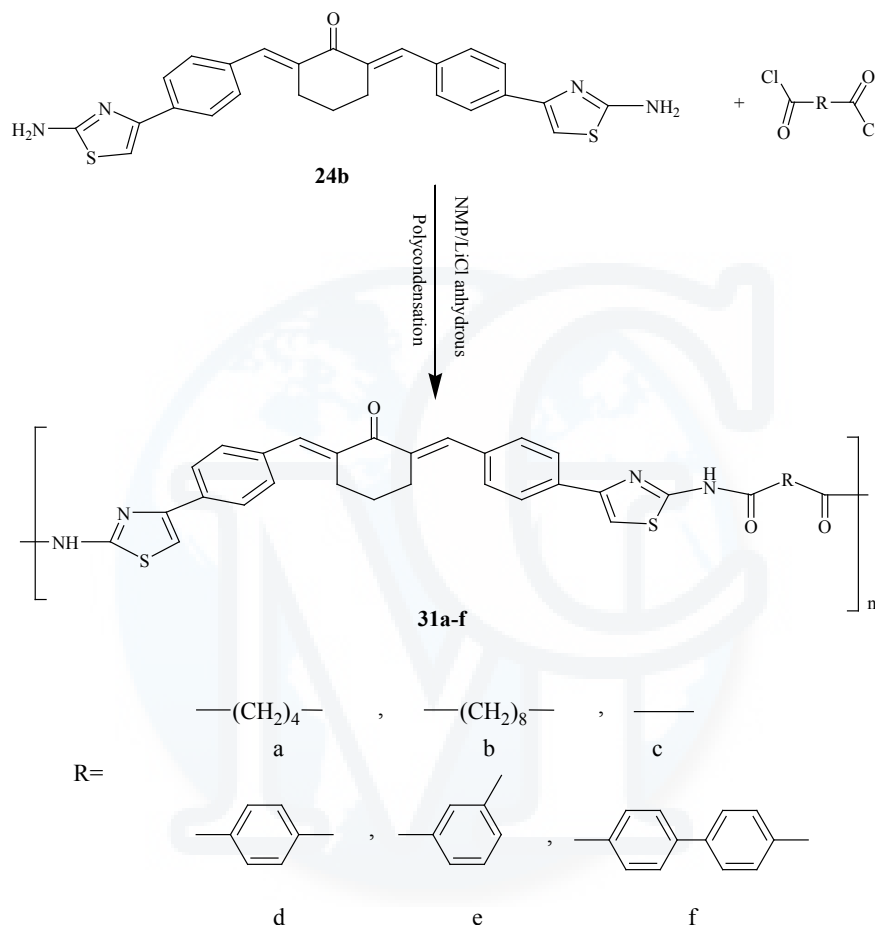


Figure 27 Synthesis of polyamides 31_{a-f}.

Aly et al.³⁵ also synthesized a novel class of polyamide polymers 33a-f containing diarylidene cyclopentanone moieties in the main chains. The synthetic procedures for the preparation of these polyamides were done by polycondensation reaction of bis(2-aminothiazol-4-ylbenzylidene)cyclopentanone monomer 24a and selected diacid chlorides (including adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl, biphenyldicarbonyl) under the same previous conditions in the presence of LiCl/NMP as illustrated in Figure 29. The resulting polymers were characterized by elemental and spectral analyses, beside solubility and viscometry measurements. Also, the thermal properties were studied by TGA, DTG, and DTA measurements and the results linked to the polymers structures. Besides that, the produced polymers show

effective corrosion inhibition behavior under the mild acidic conditions 0.5M H₂SO₄ and in the presence of carbon-steel electrode at a temperature of 40°C. Finally, Hussein et al.,³⁸ synthesized another new category of polyamides 35a-e using similar conditions of polycondensation technique through the reaction of 4,4'-bis(aminoacetyl)diphenyl ether dihydrochloride 34 and different aliphatic and aromatic diacid chlorides (including adipoyl, sebacoyl, oxaloyl, 4,4'-azodibenzoyl and 3,3'-azodibenzoyl dichlorides) in DMF as solvent and potassium carbonate anhydrous as catalyst as shown in Figure 30. The thermal properties of these polymers were evaluated by TGA, DTG and DTA measurements. The final decomposition temperatures (FDT) for polymers were nearly complete at around 730-750°C, indicating the higher thermal stability of these category of

polyamides. Moreover the glass transition temperatures (T_g) for the selected polymers were measured and found to be in the range of 47–74°C, while T_m values were in the range of 156–315°C. Also all other properties were studied

and discussed. In addition to the morphological behavior of polymer 35d as selected sample was tested by SEM as shown in Figure 31.

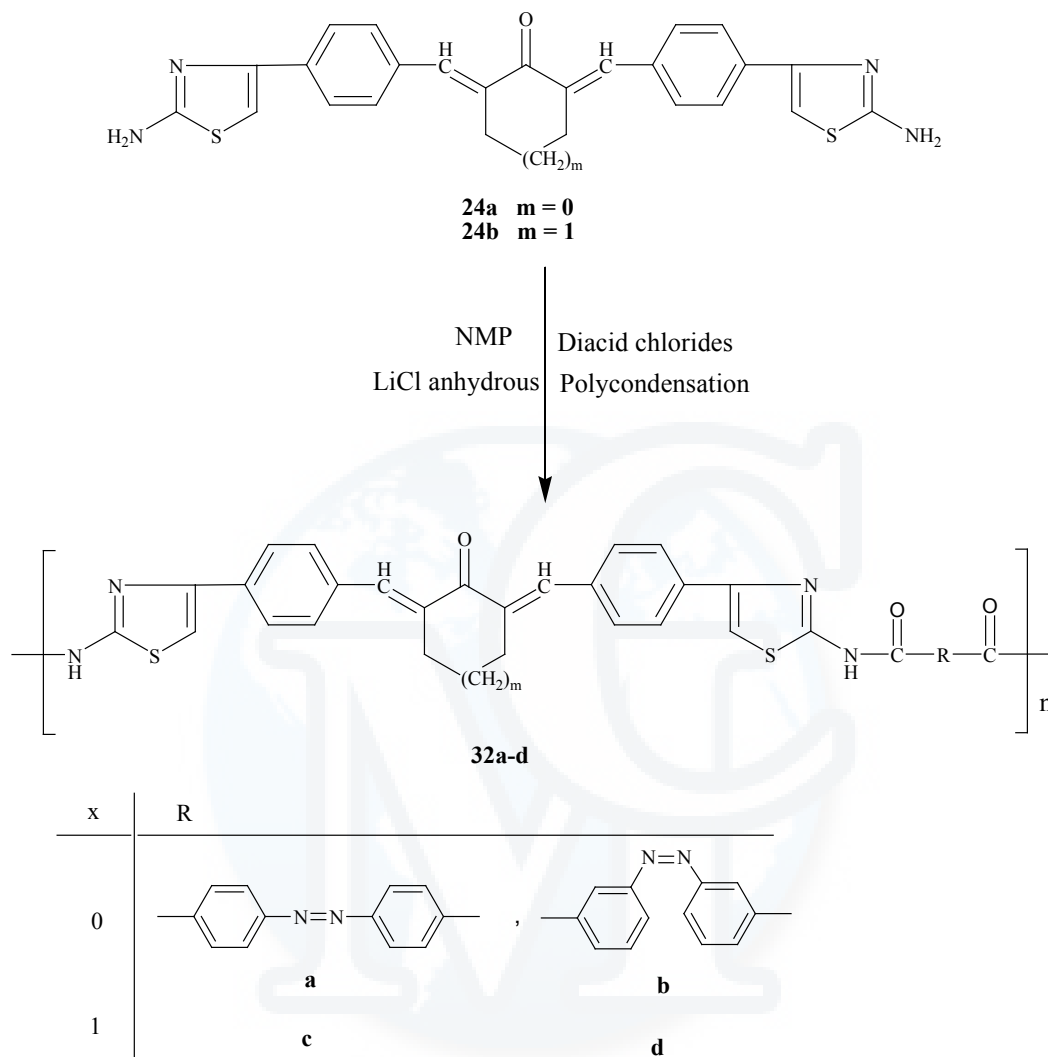
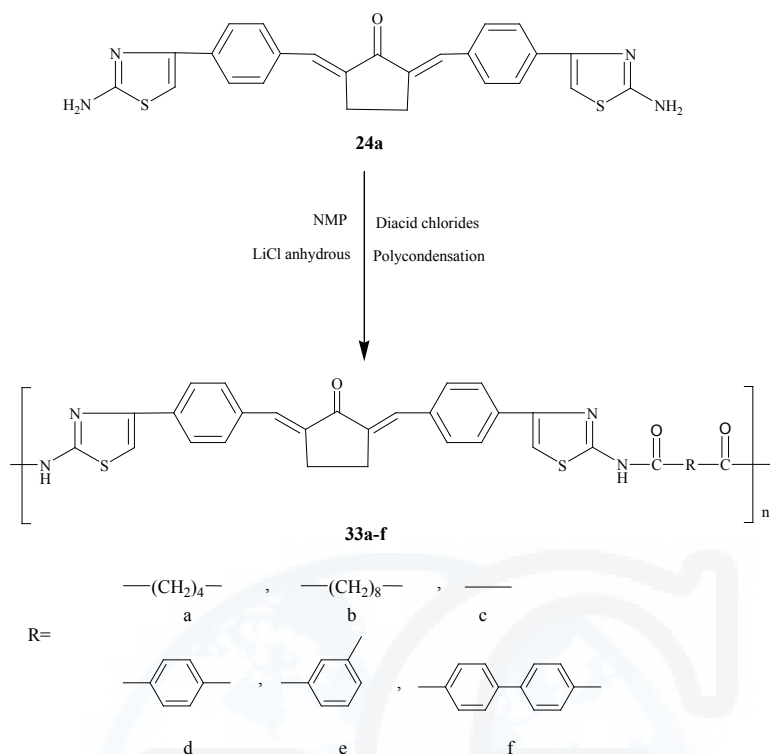
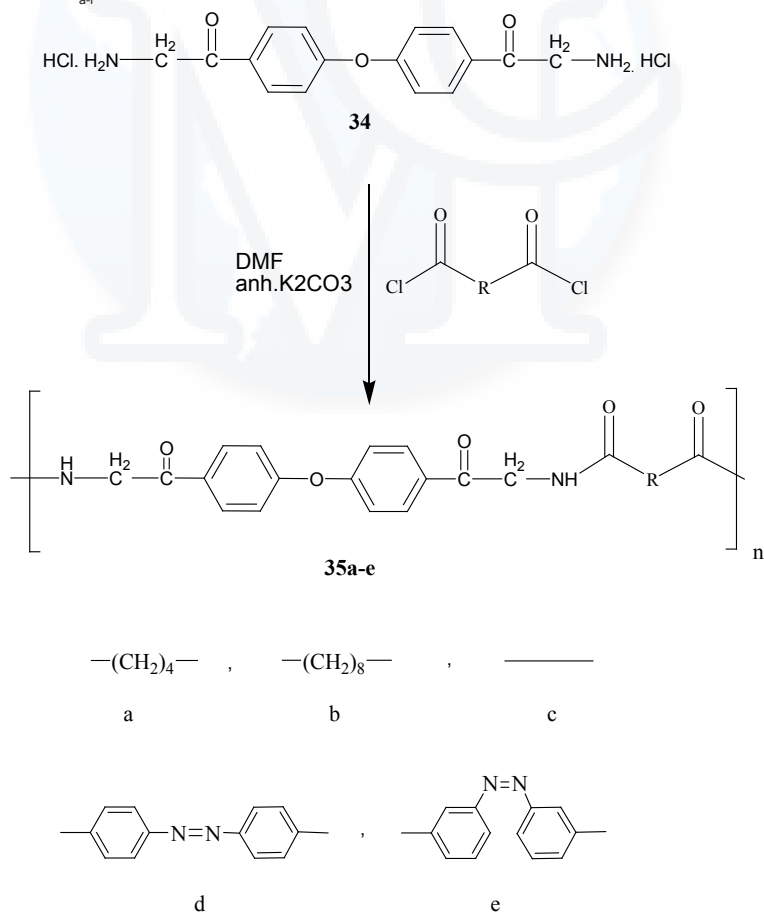


Figure 28 Synthesis of polyamides 32_{a-d}.

Experimental discussions

Different types of polyamides based on diarylidene cyclopentanone moieties were synthesized in good yield through solution polycondensation techniques at low temperature in the presence of anhydrous potassium carbonate or lithium chloride anhydrous as catalysts. Some polyamides were completely soluble in DMSO and DMF and the rest are partially soluble. In addition the polymers did not show any significant sign of solubility on the common organic solvent like acetone, ethanol, methanol and other common solvents. Aliphatic based polymers were more soluble aromatic based polymers in all cases. The thermal stability of polyamides of aliphatic based chains are less thermally stable than the polymer of

aromatic based. X-ray analyses of these polymers found that, aromatic based polymers were amorphous in nature. Moreover, polyamides based on para-azo linkage have a higher degree of crystallinity than those based on meta-azo linkage whenever it is attached to the polymers chains. A comparative SEM studies were also carried out between different polyamides to confirm the morphological changes. Comparative corrosion inhibition studies of different types of polyamides were studied in details. These polymers also show highly effective products as corrosion inhibitors under the same previously mentioned conditions giving IE% value up to 98.24% at concentration of 1 mg/L for polymer 31d. such result indicate that polyamides are consider as corrosion inhibitors better than polyurea derivative as illustrated in the previous section.^{33–38}


Figure 29 Synthesis of polyamides 33_{a-f}

Figure 30 Synthesis of polyamides 35_{a-f}

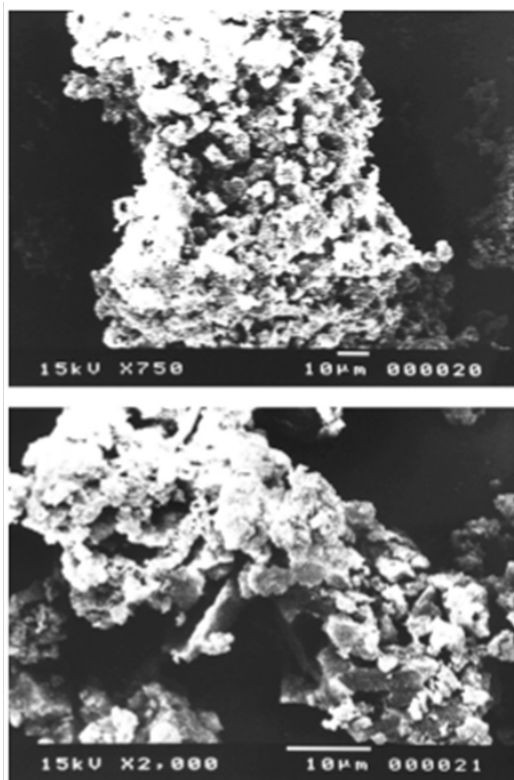


Figure 31 SEM images of polyamide 35b at magnifications $x=750$ and 2000 .³⁸

Other arylidene polymers

As an extraordinary significance for the use organic–organic or organic–inorganic polymers, such as polyphosphate esters, this used mainly as flame–retardant materials, beside its amazing plasticizer properties.³⁹ The majority of polymers in this section are found to be hybrid type which mainly appreciated from numerous number of researchers due to gaining some extra properties that presented for the first time due to such hybridization occurred. In this section we will summarize the most important types of other polymers containing arylidene moieties in the main chains.

Experimental results

Poly(phosphate-ester)s containing diarylidenecycloalkanone moieties 36a-d were obtained in considerable yield⁴⁰ by the polymerization of 1a,b or 3a,b with phenyl phosphorodichlorate in the presence of methylene chloride as a solvent, and sodium hydroxide as a basic medium as shown in (Figure 32). The reaction between isophthaloyl chloride or sebacoyl chloride with monomers 1a,b, or 3a,b and 2,7-bis(p-hydroxybenzylidene)cycloheptanone 37 monomer at ambient temperature lead to the formation of linear unsaturated copolyesters 38a-d and 39a-d based dibenzylidene-cycloalkanones⁴¹ through interfacial polycondensation technique as illustrated in Figure 33. In view of this polymerization process, the final products were characterized by elemental and spectral analyses, IR spectroscopy, solubility, and inherent viscosity. In addition, interesting thermal properties were also studied

and measured by TGA and DSC instruments. Also, they studied the other properties including: electrical properties, crystallinity and morphological properties were also investigated in more specifications. Another synthetic technique was used to prepare a high molecular weight copoly(ester-thioester)s⁴² 41a-c and 42a-c polymers through the polymerization of 4,4'-(terphthaloyl dithio) diacetic acid 40a, 3,3'-(isophthaloyl dithio)diacetic acid 40b, and 1,8-(sebacoyl dithio)diacetic acid 40c with 2,6-bis(benzylidene)cyclohexanone derivatives 3a, b in the presence of pyridine and thionyl chloride as shown in Figure 34. Abd-Alla et al.,⁴³ synthesized a series of conjugated poly(arylidene)cycloalkanones 43a,b and copoly(arylidene)cycloalkanones 44 using similar synthetic routes as previously mentioned; and examined the available properties for these products including: thermal stability, solubility, crystallinity and electrical properties (Figure 35). Aly⁴⁴ synthesized different types of conjugated polymers, copolymers and terpolymers 45a,b holding piperidone moiety in the main chain through the polymerization of N-isopropylpiperidone, cyclopentanone and cyclohexanone with terephthalaldehyde in ethanol and using KOH as a catalyst a (Figure 36). The thermal properties, crystallinity, morphology and electrical properties for the produced materials were discussed and evaluated by different available instruments. Aly & Khalaf⁴⁵ also synthesized different types of conducting polymer which named as azomethine polymers 46a-d due to the presence of azomethine linkage in the polymers main chains. Such polymers built based on cycloalkanones and pyridene moieties as cornerstones during the polymerization. The synthesis has been carried out by polycondensation of 2,5-bis(m-aminobenzylidene) cyclopentanone, 2,6-bis(m-aminobenzylidene)cyclohexanone, 2,6-bis(p-aminobenzylidene) cyclohexanone, and 2,6-bis(m-aminobenzylidene)pyridine at room temperature with terephthalaldehyde and in the presence of ethanol (Figure 37).

The thermal examinations proved that these polymers are highly stable up to around 400°C and there is no thermal and thermo-oxidative degradation observed before these temperature ranges. Upon doping with iodine, the synthesized polymers became semiconductors and the conductivity values become very high and appeared in the range of (10⁻⁷-10⁻⁸ Scm⁻¹). In 2008 Al-Muaiikel et al.,⁴⁶ intended to investigate the potential influence of inclusion of cycloalkanone moieties to the polymers properties. They also aimed at identifying new synthetic route for this preparation. They synthesized and characterized some new poly(ether-ketone)s and copoly(ether-ketone)s based diarylidenecycloalkanones hybrid polymers through solution polycondensation method. Monomer 47 reacts with sodium phenoxide in DMF and K₂CO₃ was used as catalyst to synthesize the desired polymers 48a-d. Elemental and spectral analyses were used to confirm the products chemical structures. The new polymers show great antibacterial while treating with some Gram positive, Gram negative bacteria and fungi. The rationale for conducting the research is highly growing popularity of these polymers

to the researchers as shown in Figure 38. The thermal properties and all other properties such as electrical

properties, crystallinity and morphological properties were studied and discussed briefly.

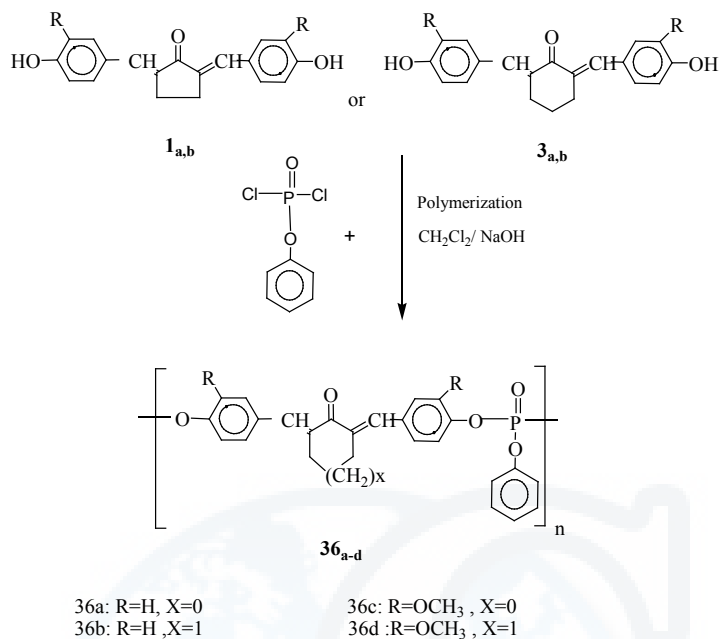


Figure 32 Synthesis of polymers 36_{a-d}.

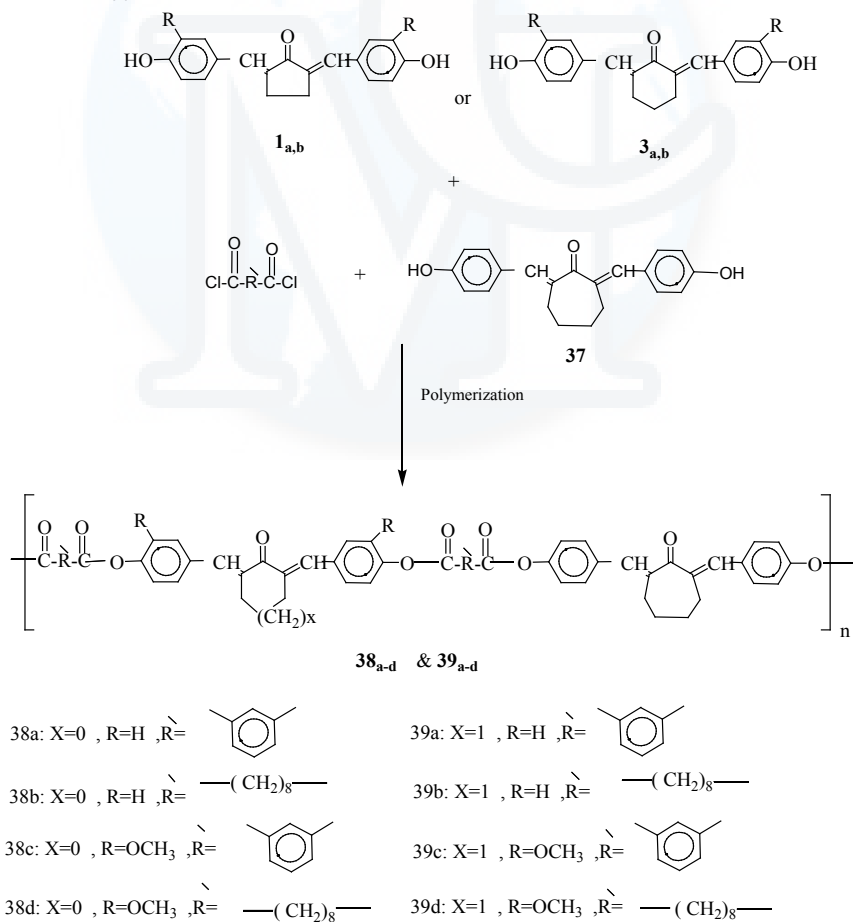
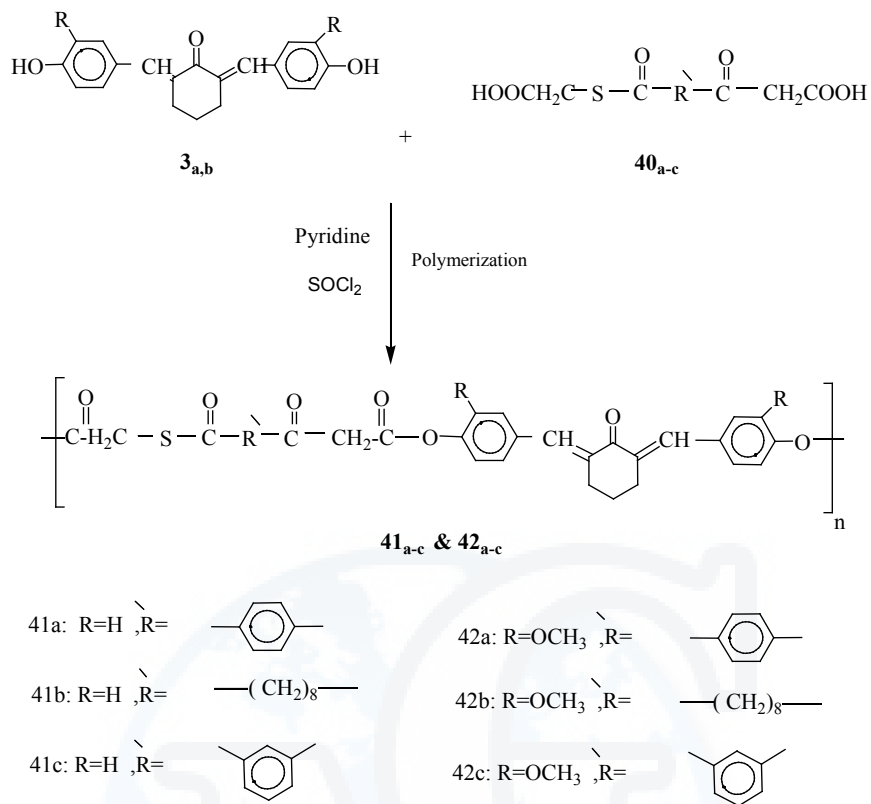
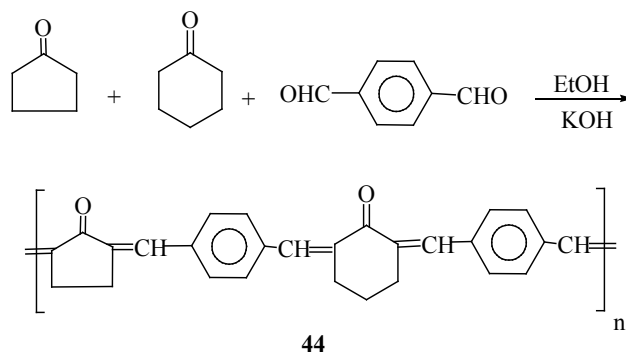
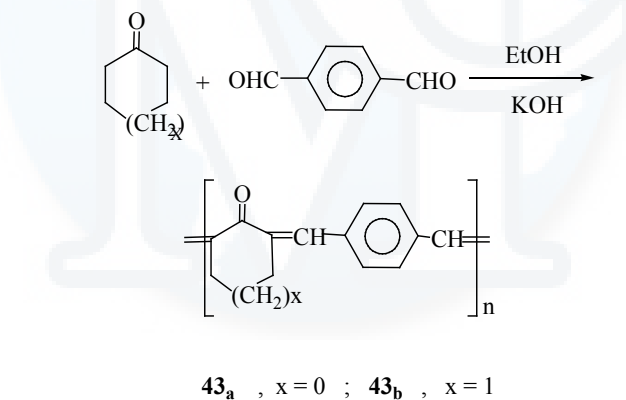
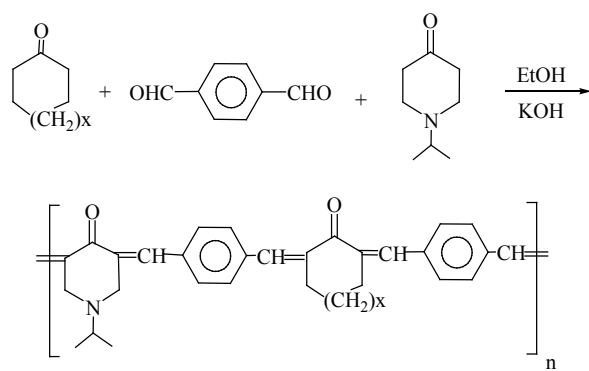


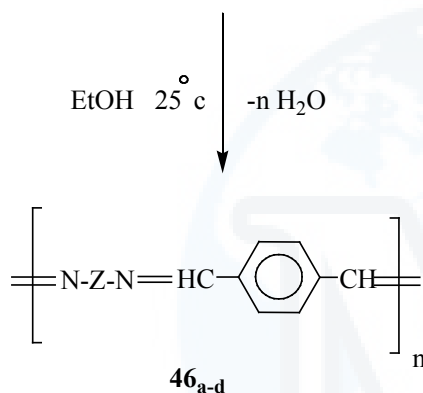
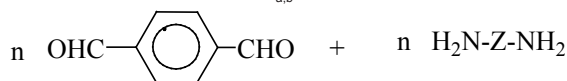
Figure 33 Synthesis of polymers 38_{a-d} & 39_{a-d}.


 Figure 34 Synthesis of polymers 41_{a-c} & 42_{a-c} .

 Figure 35 Synthesis of polymers $\text{43}_{a,b}$ & 44 .

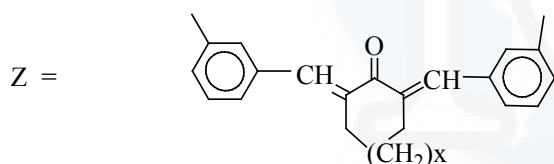


45a, x=0; 45b, x=1

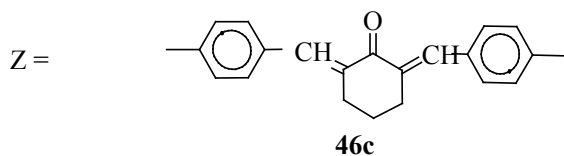
Figure 36 Synthesis of polymers 45_{a,b}.



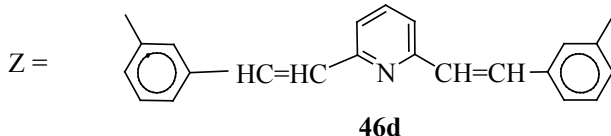
46_{a-d}



46a: X=0; 46b: X=1



46c



46d

Figure 37 Synthesis of polymers 46_{a-d}.

Hussein et al.,⁴⁷ synthesized another series of hybrid polymers namely polyarylidene(keto-amine)s (PAKAs) polymers 50a-e using solution polycondensation technique. The rationale of this study was mainly based on the

attractiveness of PAKAs as it has been typically classified as a hybrid class of polymers. These polymers gather attractive properties from all substituent's, such as collecting properties of polyketones, polyamine and arylidene polymers as well. For this study, a new series of PAKAs was synthesized based on thiophene moieties in polymers main chains. Polymers 50a-e were synthesized by the reaction of the new synthesized monomer 49, with diverse diamines using polycondensation method. A schematic illustration is shown in Figure 39. The properties were identified and evaluated by thermal properties, electrical properties, crystallinity and also morphological properties for polymer 50b as a selected sample were tested by scanning electron microscopy SEM as shown in Figure 40.

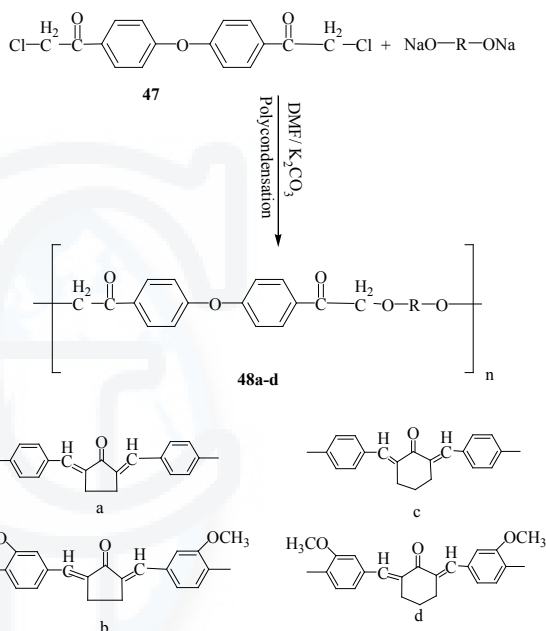


Figure 38 Synthesis of polymers 48_{a-d}.

Khairou KS et al.,⁴⁸ aimed to investigate the effect of inclusion of cyclohexanone moiety on the polymers properties. Their work focused on synthesized a new class of poly(ester-amide)s, as another hybrid class of polymers with main chains based on diarylidene-cyclohexanone. The synthetic procedure for this poly(ester-amide)s 52a-c done through interfacial polycondensation of 2,6-bis(4-hydroxybenzylidene)cyclohexanone 3a and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone 3b monomers with diacid chlorides 51 as shown in Figure 41. Thermal properties were tested by TGA and DSC measurements; besides, electrical properties, crystallinity and morphological properties were all examined and all the results were linked to the polymers structures. Sidharthan & Amaladhas⁴⁹ used acid-catalyzed Claisen-Schmidt procedures to synthesize the common diol and the six arylidene diols 54. The six arylidene diols were varied and has a ratio of 2:1:1. The common diol used to prepare the polymers 55 using polycondensation as shown in Figure 42. The authors performed this research due to lack of data about the synthesis and characterization of copolyesters containing bischalcone and keto-arylidene moiety in the

main chain. All the properties such as Thermal properties electrical properties, crystallinity and morphological properties be examined and discussed. Abdel-Rahman & Hussein⁵⁰ synthesized and studied the properties of different new polymers based on diarylidene cycloalkanones possessing interesting properties. The new class of photoactive polymers was categorized using elemental and spectral analyses. The syntheses of polymers 59a,b - 61a,b done via condensing polymerization of different diarylidene

monomers 56a,b-58a,b with 1,2-bis(chloromethylsilyl) ethane in tetrahydrofuran and in the presence of butyllithium as a catalyst as given in Figure 43. The structure was determined by x-ray diffraction patterns. The polymers also showed good electron transport and on the other hands thermal properties were evaluated by TGA and DSC measurements electrical properties, crystallinity and morphological properties be also examined.

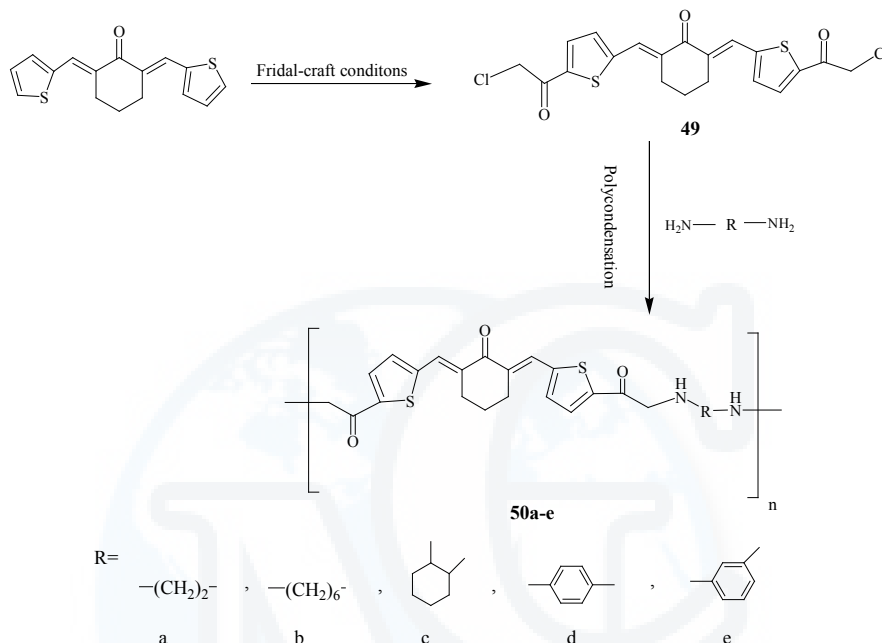


Figure 39 Synthesis of polymers 50_{a-e}.

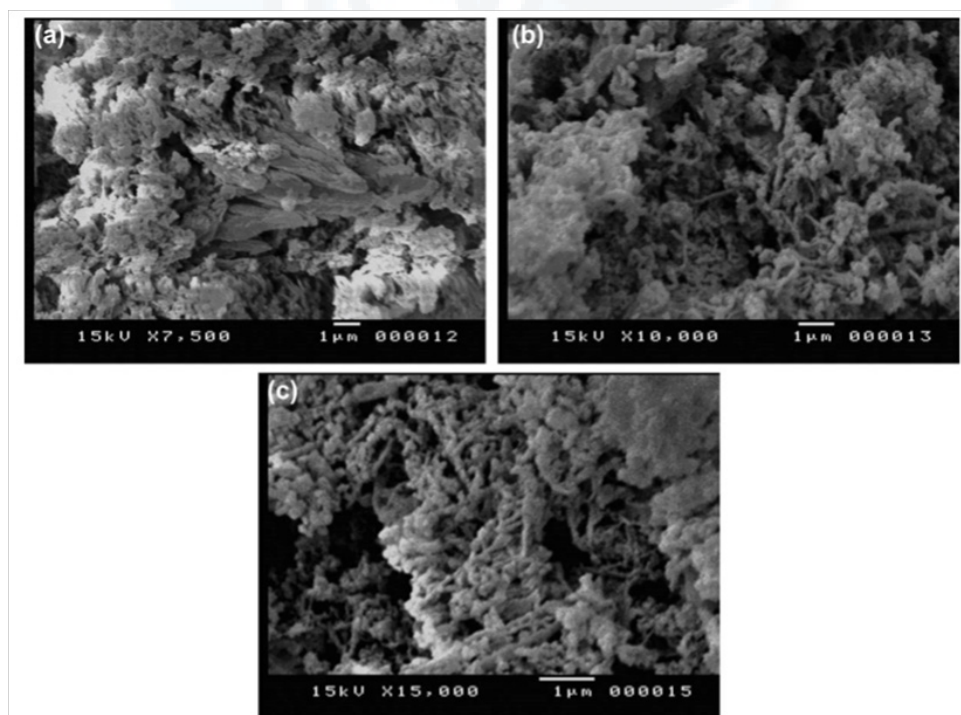


Figure 40 SEM images of the polymer surface of PAKA 50b at different magnifications: (A) 7500, (B) 10,000, and (C) 15,000.⁴⁷

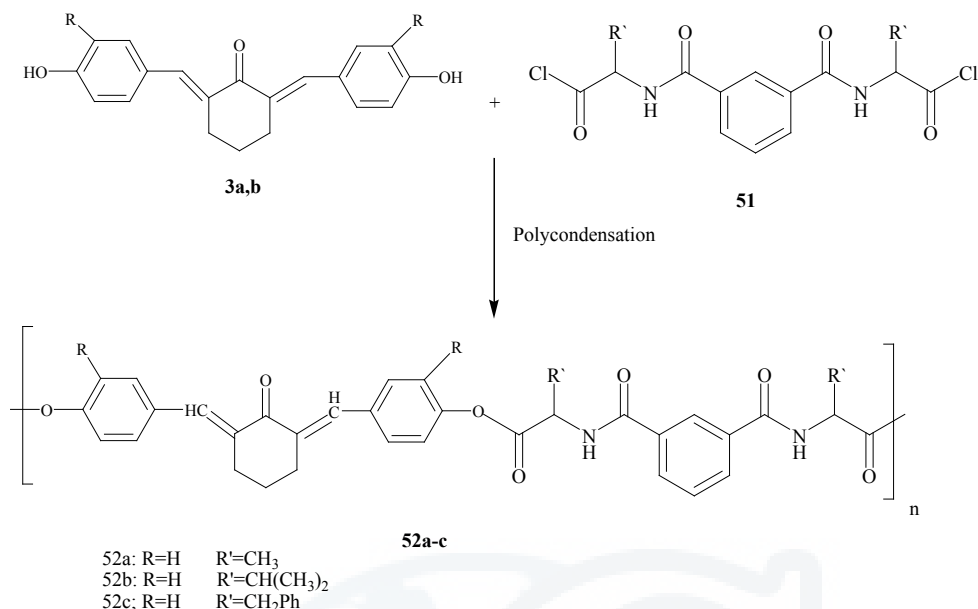


Figure 41 Synthesis of polymer 52_{a-c}.

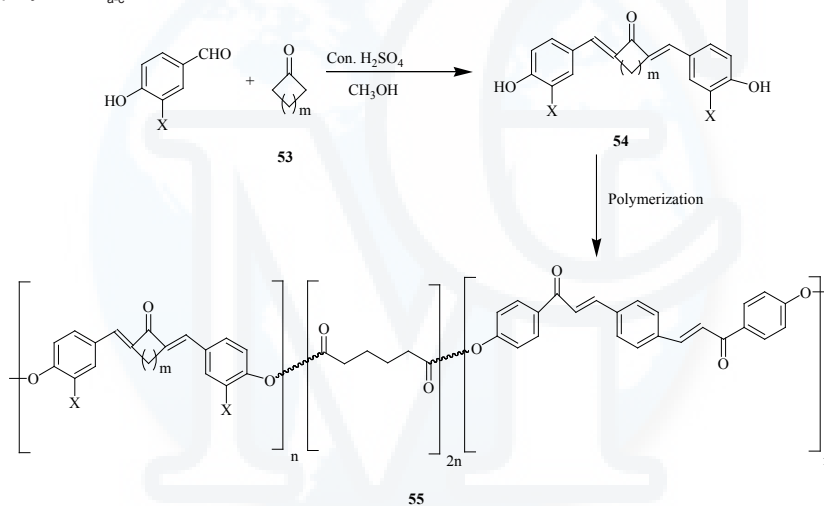


Figure 42 Synthesis of polymers 55.

Aly et al.,⁵¹ synthesized a new series of liquid crystalline poly(arylidene-ether)s containing a flexible spacer. The polyarylidene they synthesized be based on cyclopentanone moiety. Synthesis of the poly(arylidene-ether)s 64a-e & 65a-e done by polycondensation of 4,4'-diformyl- α,α' -diphenoxy alkanes 62a-e and 4,4'-diformyl-2,2'-diphenoxyalkanes 63a-e with cyclopentanone in ethanol and KOH (Figure 44). The polymers structures examined by x-ray analysis and the crystallinity of some polymers showed some degree of crystallinity; in addition the morphological properties for selected sample were examined by SEM testing. Additionally, new thermotropic liquid crystalline (LC) properties were examined and evaluated by DSC, optical polarizing microscopy giving an interesting LC phases. Such thermotropic LC properties of polymers 65b and 64b are shown in Figure 45 & Figure 46 respectively. As well, Aly⁵² synthesized a novel liquid crystalline poly(arylidene-ether)s polymers 66a-e & 67a-e

and copoly(arylidene-ether)s copolymers 68a-e & 69a-e procedure done by polycondensation of (4,4'-diformyl- α,α' -diphenoxyalkanes 62a-e and 4,4'-diformyl-1,2,2'-dimethoxy- α,α' -diphenoxyalkanes 63a-e with cyclohexanone and/or cyclopentanone novel liquid crystalline polymers as illustrated in Figure 47 & Figure 48 respectively.

The polymers morphology examined by scanning electron microscopy and the results show that polymer 69b surface like the cabbage shape as shown in Figure 49. Also, all the polymers and copolymers showed thermotropic LC properties. The thermotropic LC behavior was examined and evaluated by DSC, and optical polarizing microscopy. LC properties for polymers 69b and 69c (as an examples) were shown in Figure 50 & Figure 51 respectively. Mostly the mesophase extended up to 310°C while the thermal decomposition prohibited more observation. Whereas, the benzene ring having the methoxy substituents caused

the lower of temperature significantly. Aly & El-Kashef⁵³ synthesized two new series based on N-methyl piperidone and/or cyclohexanone namely: poly- and copoly(arylidene-ether)s 71a-e & 72a-e and 73a-e & 74a-e. These polymers were prepared through the reaction of 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-e & 63a-e and N-methylpiperidone 70 as new homopolymers. Whereas, the corresponding copolymers were derived from the interaction between diphenoxyalkanes and N-methylpiperidone and cyclohexanone respectively (Figure 52 & Figure 53). The

polymers had been characterized by DSC measurements and OPM microscope images showed the poly(arylidene-ether)s nematic mesophase over a wide temperature range on the other hands the corresponding copoly(arylidene-ether)s showed opposite result that because the polarized light. Also, both the Polymers and the copolymers showed thermotropic liquid crystalline properties. Also the polymers surfaces examined by scanning electron microscopy show that the polymers surfaces as shown in Figure 54 & Figure 55 for polymers 71b and 73b.

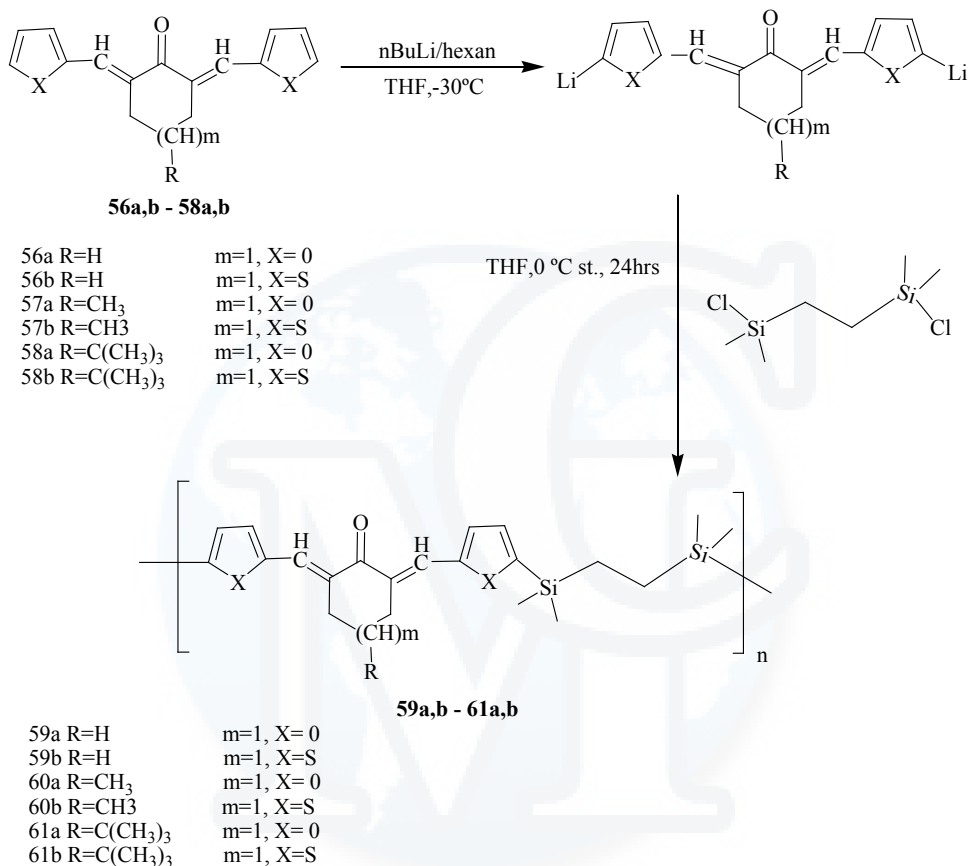
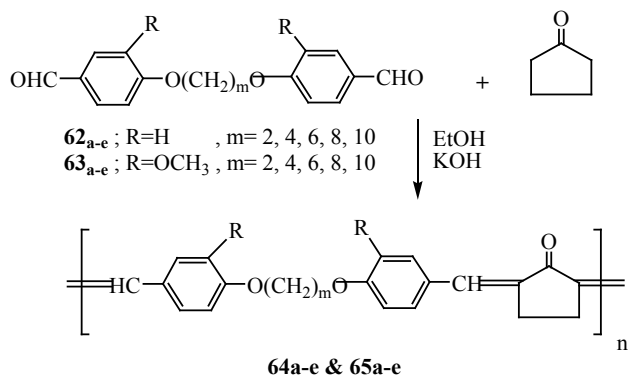


Figure 43 Synthesis of polymers 59_{a,b} - 61_{a,b}.



R=H, m= 2, 4, 6, 8, 10
 R=OCH₃, m= 2, 4, 6, 8, 10

Figure 44 Synthesis of polymers 64_{a-e} & 65_{a-e}.

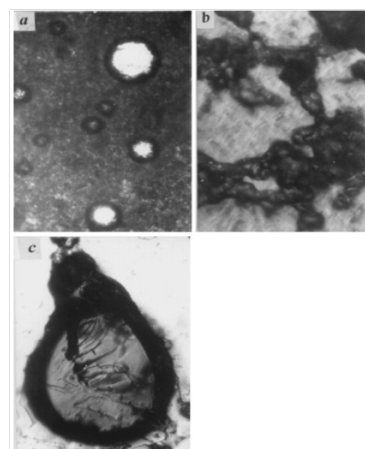


Figure 45 Photomicrographs of the polymer 65b in heating cycle at (A) 185°C (B) 190°C and (C) after cooling.⁵¹

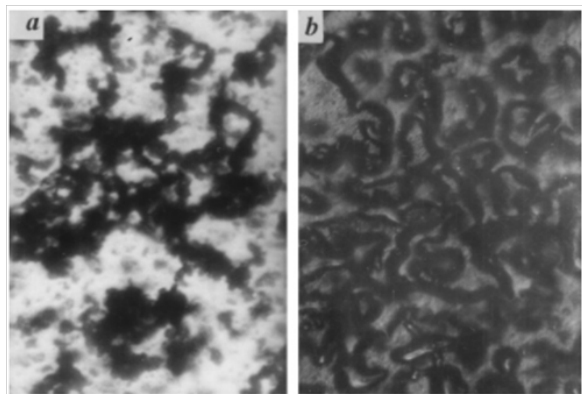


Figure 46 Photomicrographs of the polymer 64b in the heating cycle at 317°C.⁵¹

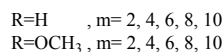
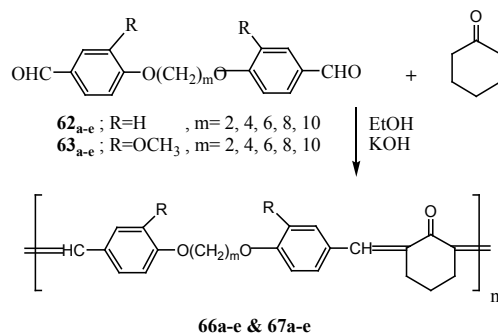


Figure 47 Synthesis of polymers 66_{a-e} & 67_{a-e}.

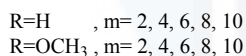
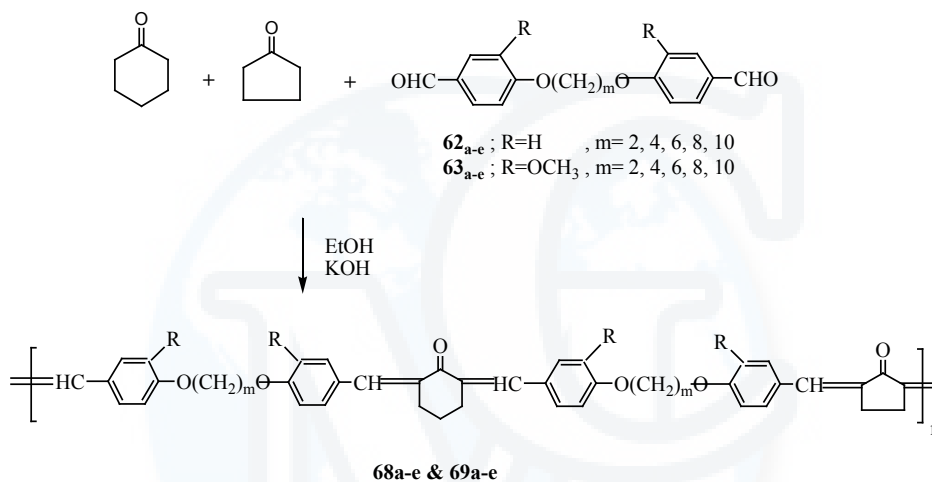


Figure 48 Synthesis of copolymers 68_{a-e} & 69_{a-e}.

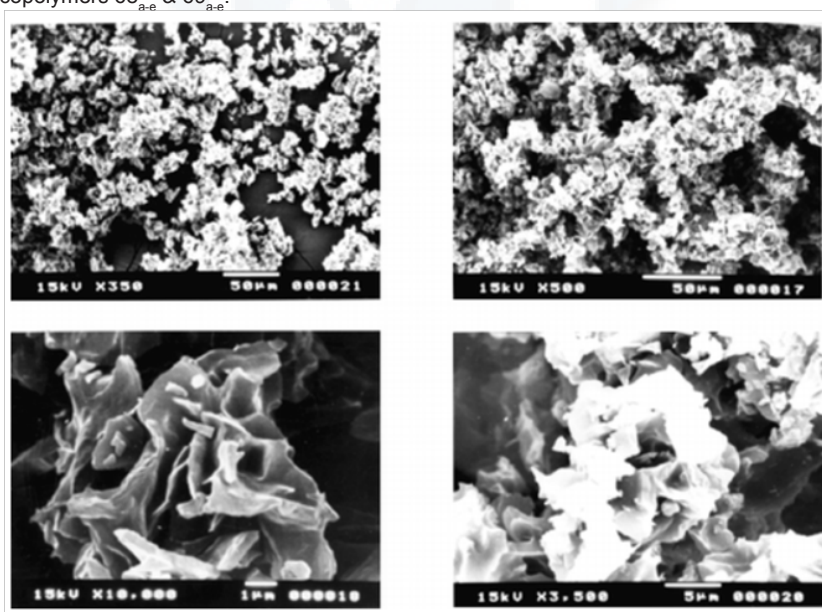


Figure 49 SEM images of polymer 69b at magnifications x=350, 500, 10000 and 3500 respectively.⁵²

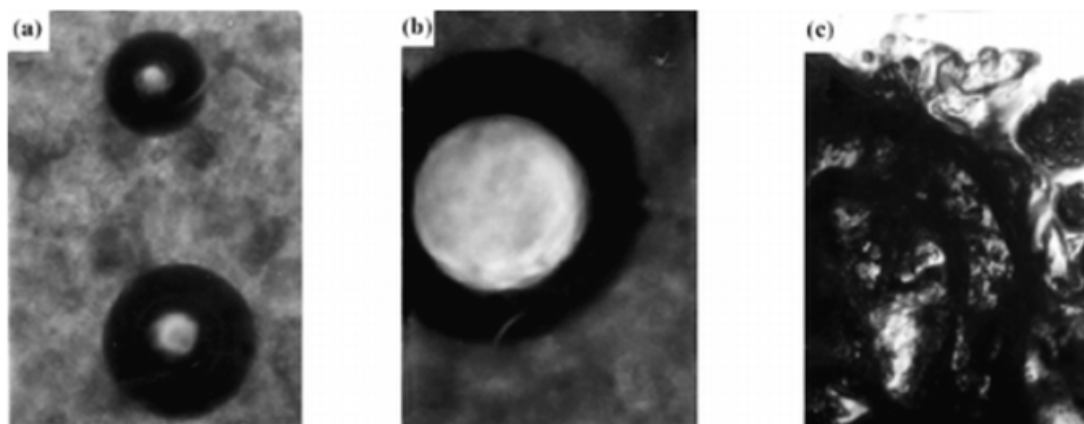


Figure 50 Photomicrographs of polymer 69b in the heating cycle at (A) 135°C; (B) 148°C; (C) after cooling.⁵²

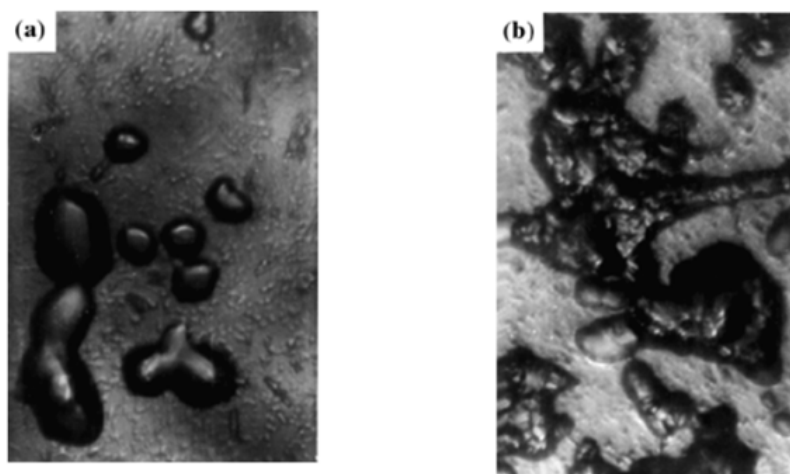


Figure 51 Photomicrographs of polymer 69c in the heating cycle at (A) 158°C; (B) 185°C.⁵²

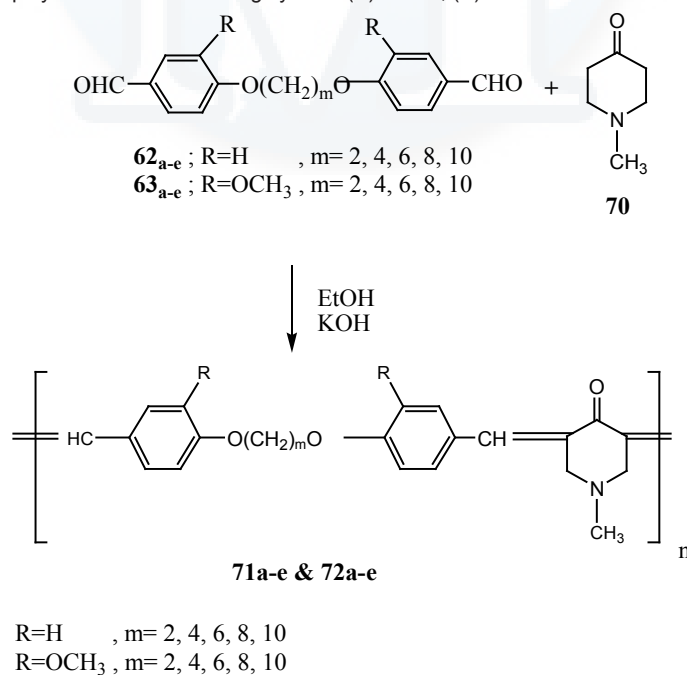


Figure 52 Synthesis of polymers 71_{a-e} & 72_{a-e}.

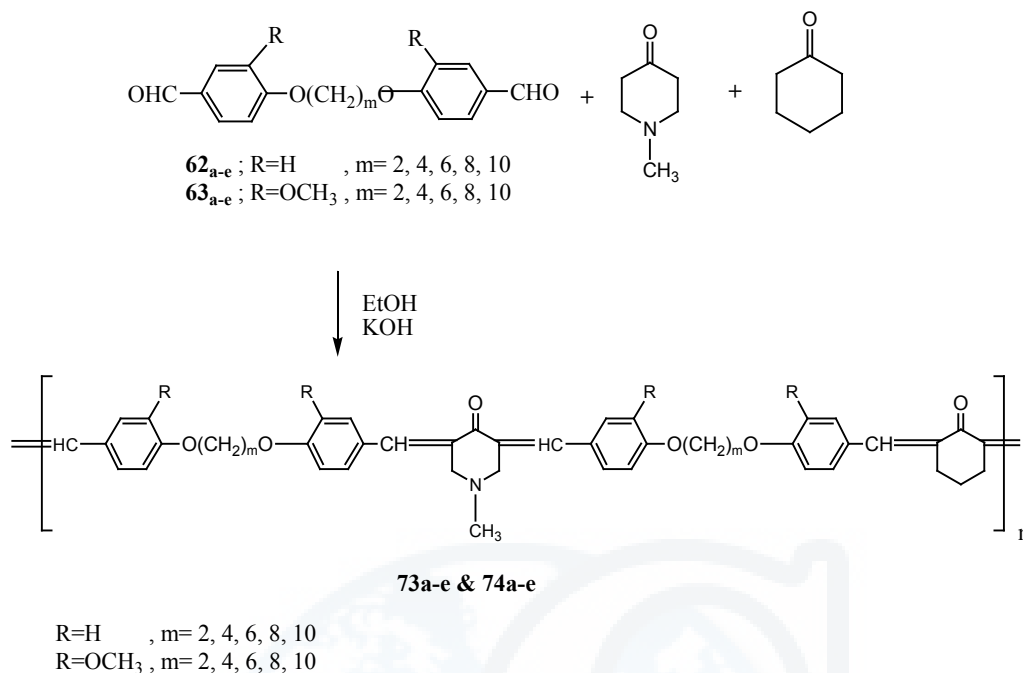


Figure 53 Synthesis of polymers 73_{a-e} & 74_{a-e}.

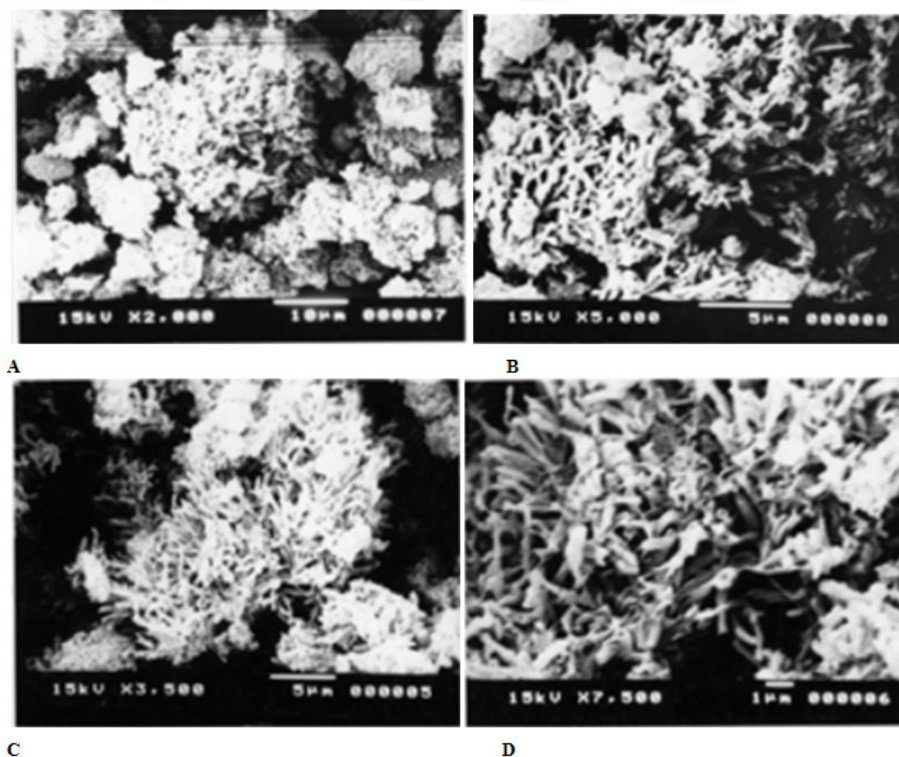


Figure 54 SEM images for polymer 71b at magnifications (A) x=2000; (B) x=5000; (C) x=3500; (D) x=7500.⁵³

In 2005 Sakthivel et al.,⁵⁴ synthesized a two new series of crystalline-cum-photocross linkable divanillylidene cyclohexanone containing macromolecules. Monomers 2,6-bis[m-hydroxyalkoxy(vanillylidene)] cyclohexanone 76a-c was prepared firstly by the interaction of diarylidene

compound 3b with variable bromo, hydroxyl alkanes 75a-c using DMF as solvent. Polymers 77a-c were prepared by interaction between monomer 76a-c with different arylphosphorodichloridates (naphthyl, biphenyl) at ambient temperature then using polycondensation technique Figure

56. Furthermore, the thermal properties were measured by TGA and DSC measurements; also, they studied the other properties such as electrical properties, crystallinity and morphological properties. In 2008 Alkskasa et al.,⁵⁵ synthesized a new class of conjugated polymer 78 using polycondensation technique by the reaction of 4-phenylcyclohexanone and terephthalaldehyde in the presence of sodium hydroxide as shown in Figure 57. The

thermal properties (thermal behavior and stability) for all the synthesized polymers were evaluated by TGA, DTG and DTA measurement and the analyses are linked with the corresponding polymers structures. Also, the polymers morphologies for selected examples were tested by a scanning electron microscope (SEM) as shown in Figure 58.

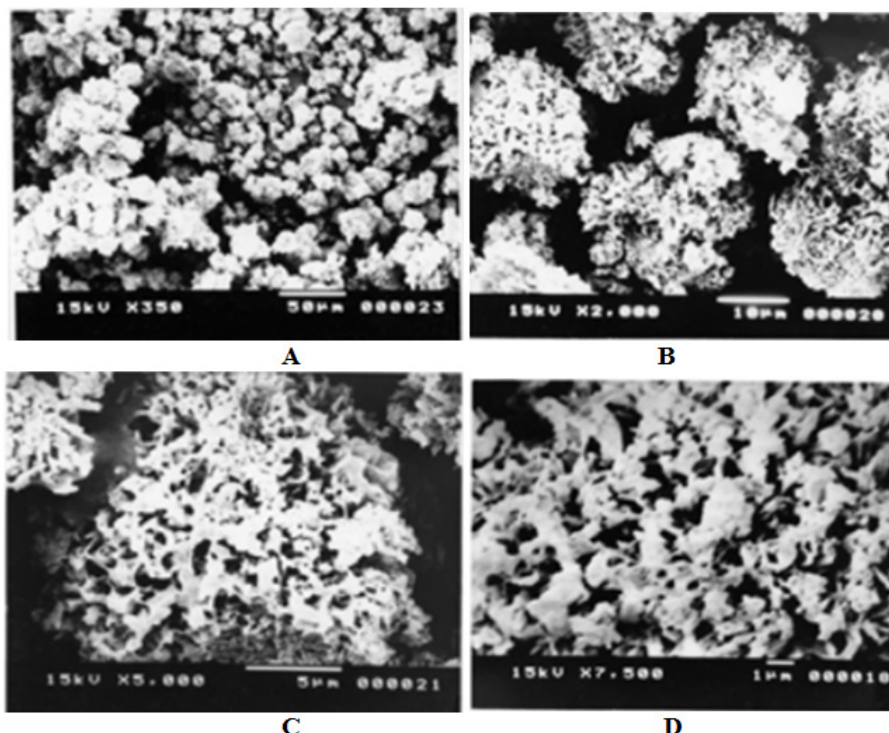


Figure 55 SEM images for polymer 73b at magnifications (A) x=350; (B) x=2000; (C) x=5000; (D) x=7500.⁵³

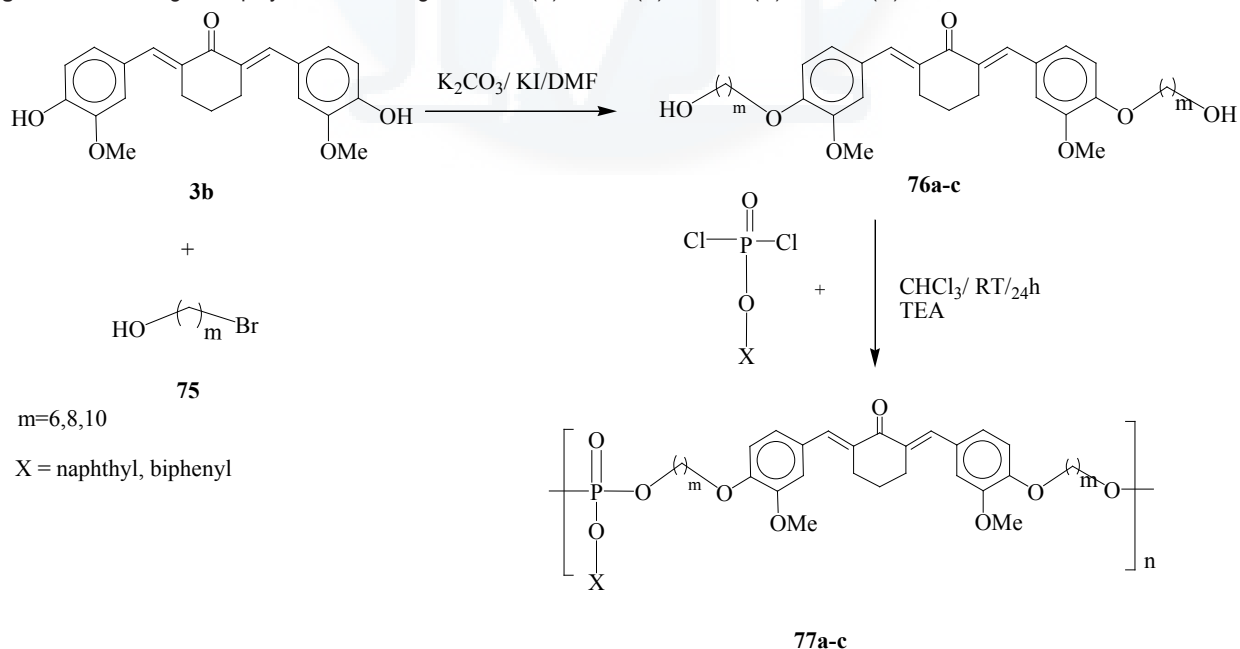


Figure 56 Synthesis of polymers 77_{a-c}.

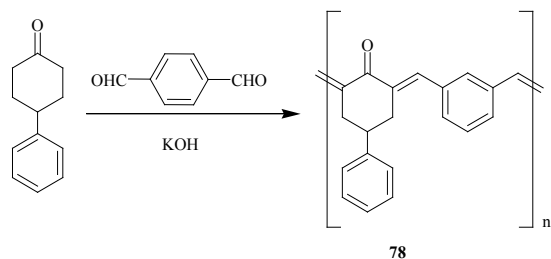


Figure 57 Synthesis of polymer 78.

Alkskasa & El-Gnidi⁵⁶ synthesized a new class of poly(azomethine-ether)s 79a-d & 80a-d using polycondensation technique by the interaction between 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-d & 63a-d, with 2,6-bis(m-aminobenzylidene)-4-phenylcyclohexanone in ethanol as shown in Figure 59. All the polymers thermal properties including: thermal behavior and stability were evaluated by DSC, TGA and DTG measurements and the results are linked to the corresponding polymers structures.

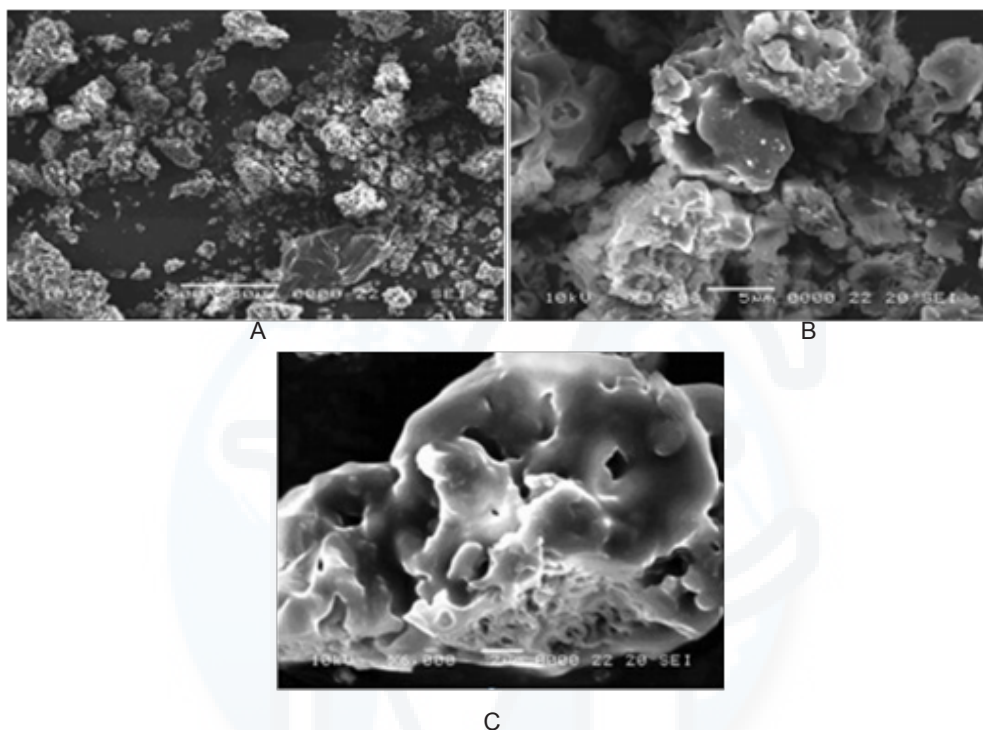


Figure 58 SEM micrographs of polymer 78 at (A) low magnification, (B) at magnification $x=3500$, (C) at magnification $x=6000$.⁵⁵

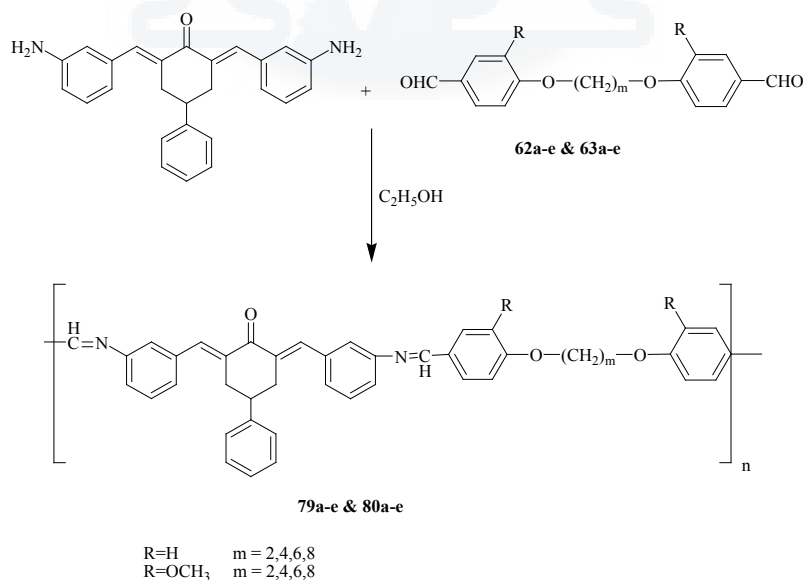


Figure 59 Synthesis of polymers 79_{a-e} & 80_{a-e}.

In 2003 Aly et al.,⁸ synthesized two novel series of poly(azomethine-ether)s 81a-e & 82a-e and 83a-e & 84a-e using polycondensation technique by the reaction between 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-d & 63a-d, with 2,7-bis(m-aminobenzylidene) cycloheptanone or bis-(m-aminobenzylidene)acetone respectively using ethanol as solvent as shown in Figure 60. All expected properties including thermotropic LC properties were examined and evaluated by DSC and OPM measurements. The Texture for the polymer 81c is observed and seemed to have low melts viscosities shown in Figure 61. Aly et al.,⁵⁷ synthesized a new series of liquid crystalline poly(arylidene-ether)s 85a-g & 86a-g. The synthesized polymers based mainly on 4-methyl cyclohexanone moiety. The synthesis of these polymers was done by the interactions of 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-g & 63a-g with the 4-methyl-cyclohexanone monomer in the presence of KOH as shown in Figure 62. All the properties such as thermotropic

liquid crystalline were examined and evaluated by DSC in addition to optical polarizing microscopy. All the results were correlated to the polymers structures as shown in Figure 63 for polymer 86b as an example. Additionally, the polymer structure examined by x-ray analysis and the results showed that, the crystallinity of some polymers was highly enhanced. In addition, the morphological properties for selected samples were also examined by SEM. Aly & Sayed⁵⁸ synthesized a new category of liquid crystalline copoly(arylidene-ether)s 87a-g & 88a-g. The synthesized polyarylidene copolymers basically based on cyclohexanone derivative moiety and the polymerization procedures was carried out between 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-g & 63a-g with methyl-cyclohexanone and 4-tertiary-butyl-cyclohexanone as shown in Figure 64. All the properties such as thermotropic LC were examined and evaluated by DSC & OPM characterization tools and all the obtained results were correlated to the polymers structures.

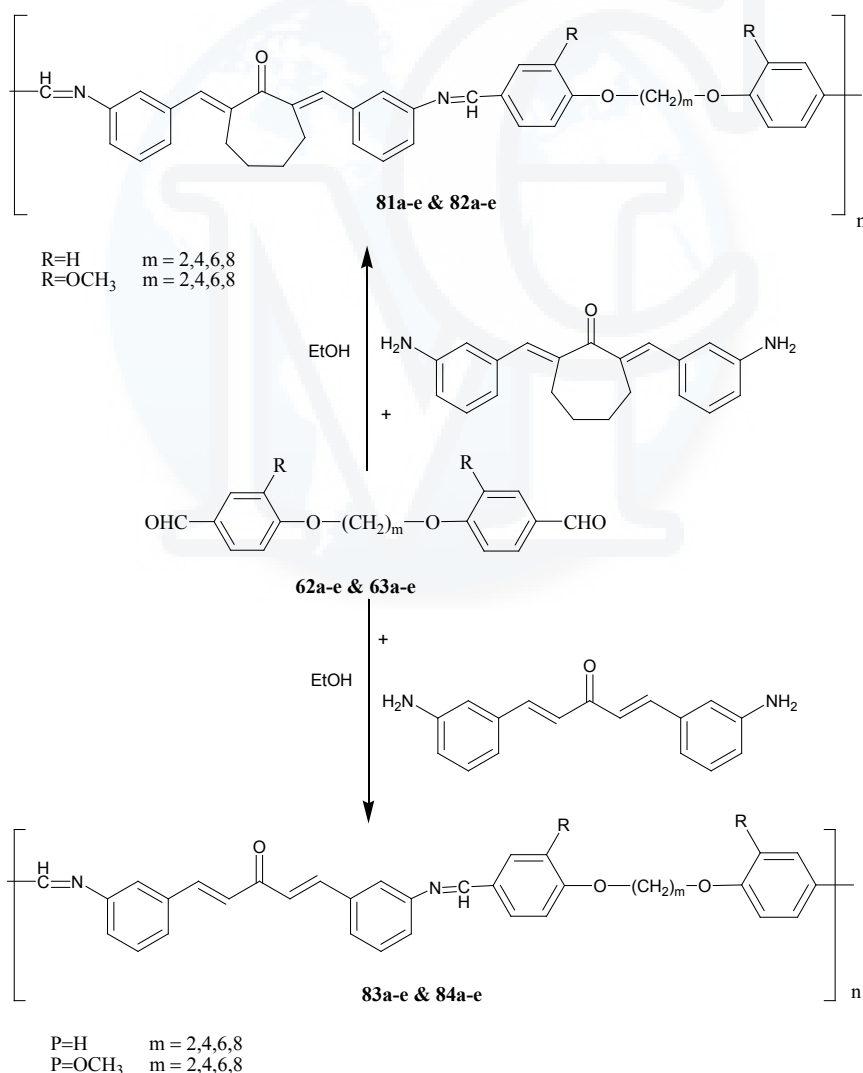


Figure 60 Synthesis of polymers 81_{a-e} & 82_{a-e} and 83_{a-e} & 84_{a-e}.

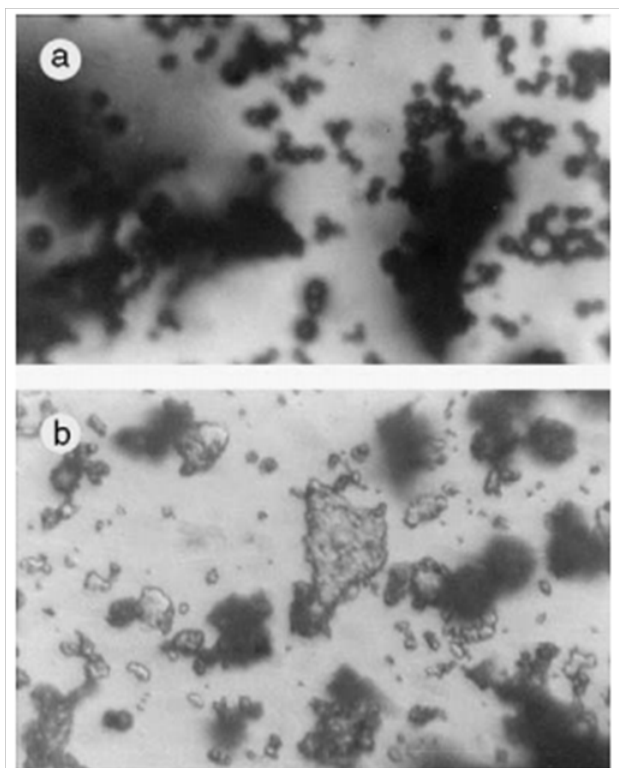


Figure 61 Photomicrographs of the polymer 81c (A) at 243°C (before melting) and (B) 294°C.⁸

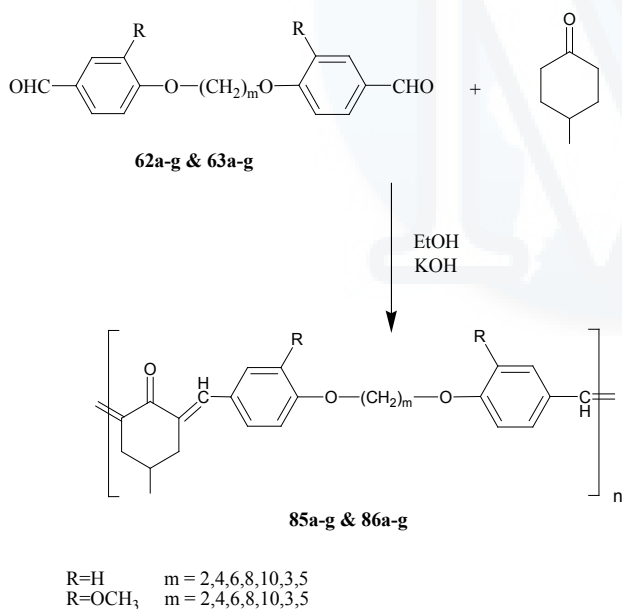


Figure 62 Synthesis of polymers 85_{a-g} & 86_{a-g}.

In addition, the morphological properties for selected samples were examined by scanning electron microscopy and the degree of crystallinity of these polymers was examined by X-ray showing better degree of crystallinity for some of them. Aly et al.,⁵⁹ synthesized a new class of liquid crystalline poly(arylidene-ether)s 89a-g & 90a-g. The synthesized polymers officially based on

cyclohexanone moiety and 4-tert-butylcyclohexanone and the polymerization was carried out by the reaction between 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-g & 63a-g with cyclohexanone and 4-tertiary-butyl-cyclohexanone in ethanol and in the presence of KOH as shown in Figure 65. All thermotropic LC properties were also examined and evaluated by DSC the result was correlated to the polymers structures. In addition, the morphological properties for selected sample was examined by scanning electron microscopy (Figure 66) also the polymers structures were examined by X-ray and some polymers showed higher degree of crystallinity. Aly & Ahmed⁶⁰ synthesized thermotropic LC poly(azomethine-ether)s 91a-d & 92a-g and 93a-d & 94a-d by polycondensation reaction between different 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-d & 63a-d with 2,5-bis(m-aminobenzylidene) cyclopentanone, and 2,6-bis(m-aminobenzylidene) cyclohexanone as shown in Figure 67. In addition, they evaluated the thermal properties by (TGA) and (DTG) for these polymers and other properties such as electrical properties, crystallinity and morphological properties and all the result were also correlated to the polymers structures.



Figure 63 Photomicrographs of polymer 86b in heating cycle at (A) <109°C, (B) >112°C.⁵⁷

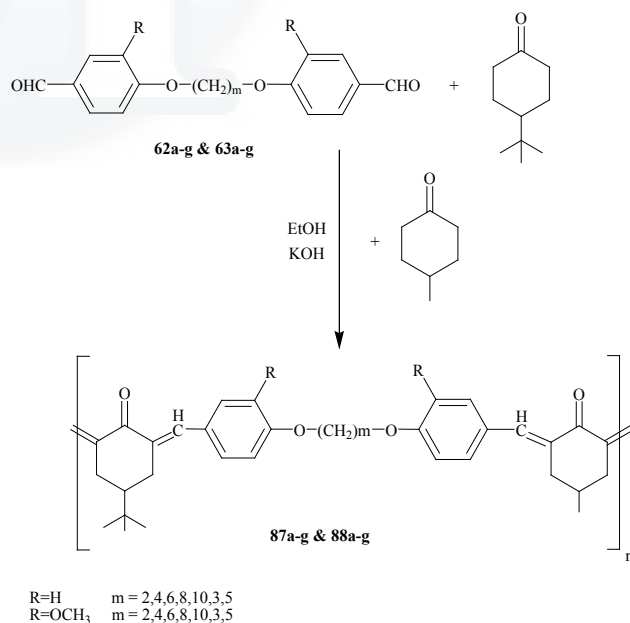


Figure 64 Synthesis of polymers 87_{a-g} & 88_{a-g}.

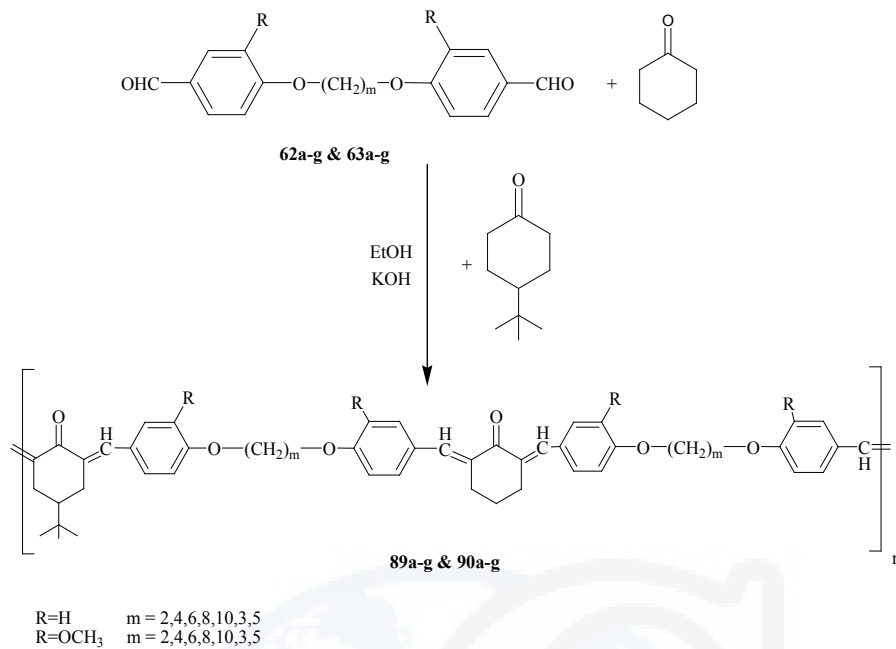


Figure 65 Synthesis of polymers 89_{a-g} & 90_{a-g}.

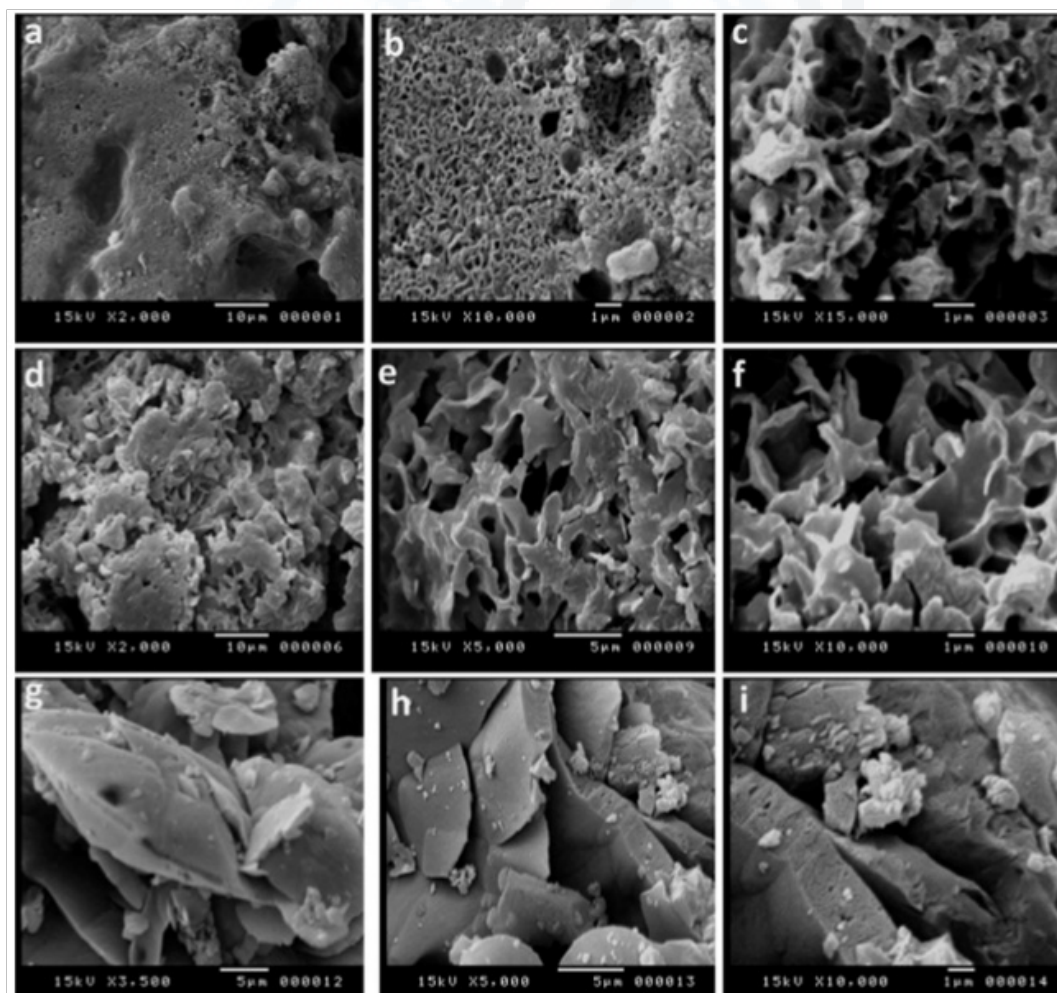


Figure 66 SEM images of polymers 89e at different magnifications (A) x=2000, (B) x=10000, (C) x=15000, (D) x=2000, (E) x=5000, (F) x=10000, (G) x=3500, (H) x=5000, (I) x=10000.⁵⁹

More particularly, Abbady et al.,⁶¹ synthesized a new category of polyketoamine polymers 96a-j, 97a-j and 98a-j which contain ether, sulphide and sulphone moieties in the main chain respectively. The preparation procedure for this polymers was carried out by polycondensation reaction of 4,4'-bis(chloroacetyl)diphenyl ether, 4,4'-bis(chloroacetyl)diphenyl sulfide and 4,4'-bis(chloroacetyl)diphenyl sulfone 95a-c with different aliphatic or aromatic diamines as shown in Figure 68. The thermal properties for the polymer were evaluated by DSC and OPM. In addition, the morphological properties for selected sample of the polymer were examined by scanning electron microscopy. Also' the polymers structures were examined by X-ray diffraction patterns and some these polymers showed some degree of crystallinity. In 2002 Aly et al.,⁶² synthesized a new category of polyketoamines 99a-j and 100a-j. The method of preparation for these polymers was carried out using suspension polycondensation technique. This polyketoamines were prepared by polymerization of the reaction between 2,5-bis(4-chloroacetylbenzylidene)-cyclopentanone and 2,6-bis(4-chloroacetylbenzylidene)-

cyclo-hexanone 98a,b with various aliphatic or aromatic diamines as shown in Figure 69. The thermal properties for the polymer were evaluated by DSC and OPM. In addition, the morphological properties for selected sample of the polymer was examined by scanning electron microscopy and the electrical conductivity give result for some samples about 10-12 ohm/cm. Also' the polymer structure examined by X-ray the crystallinity of some sample of the polymer and showed some degree of crystallinity. In 2007 Hammam et al.,⁶³ synthesized through advance development arrangement polymerization poly(hydrazone-ether)s 102a-e & 103a-e, by the polycondensation 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarbohydrazide 101, and different 4,4-diformyl- α,ω -diphenoxyalkanes, or 4,4-diformyl-2,2-dimethoxy- α,ω -diphenoxyalkanes 62a-d & 63a-d in the presence of ethanol, as appeared in Figure 70. All the thermal properties were evaluated by (DSC) (Figure 71) and (OPM) using a hot stage and (TGA), and morphology properties for selected samples were examined as shown in Figure 72.

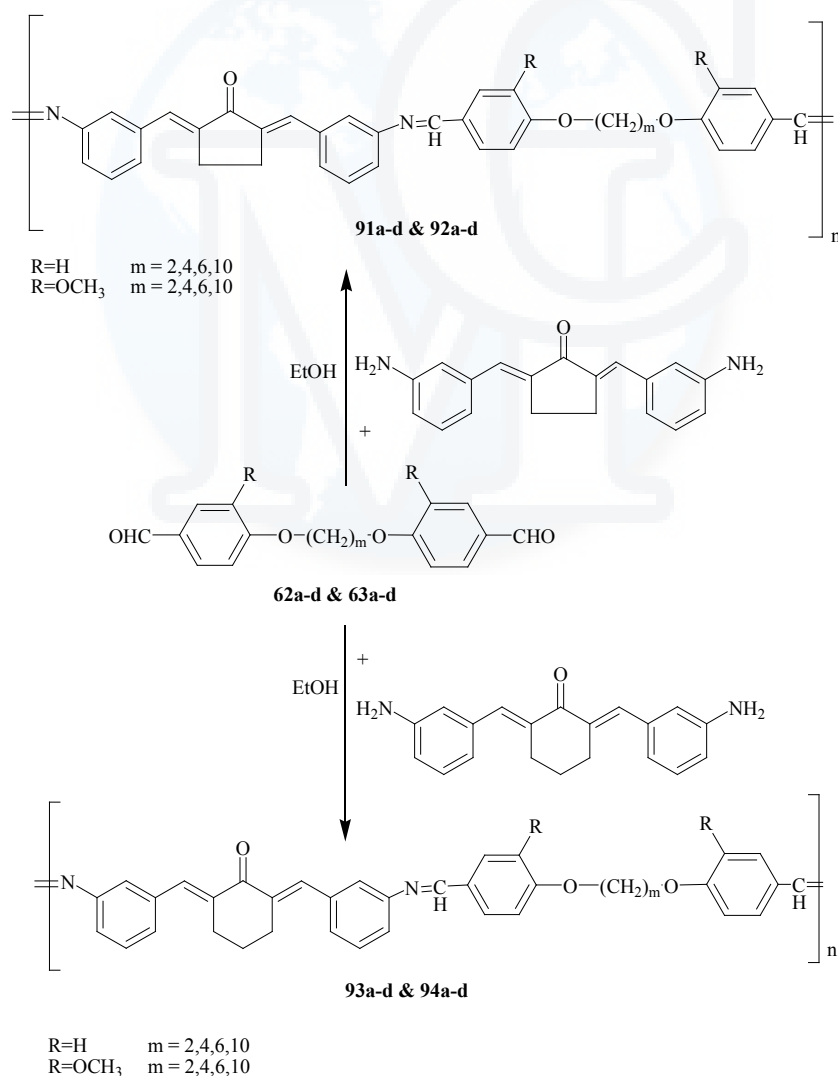
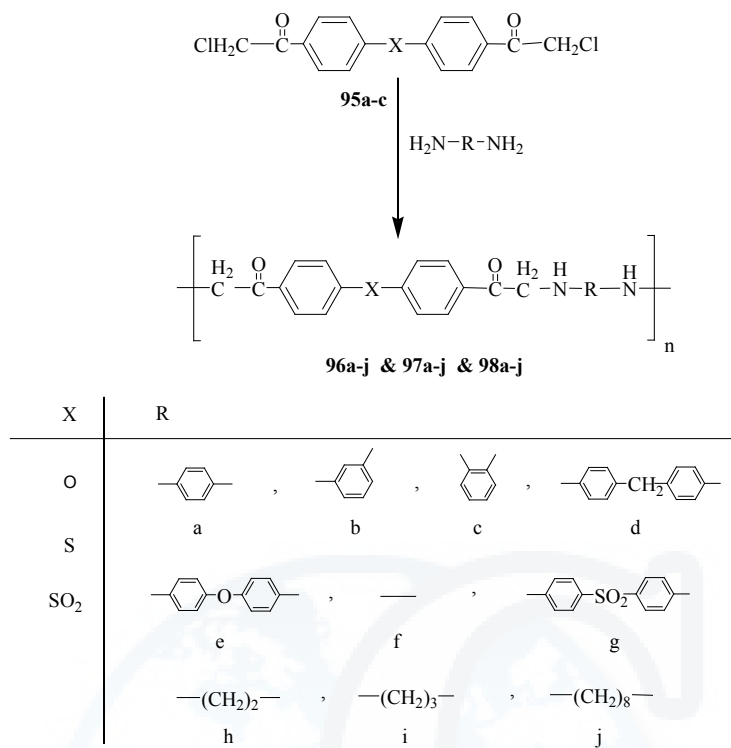
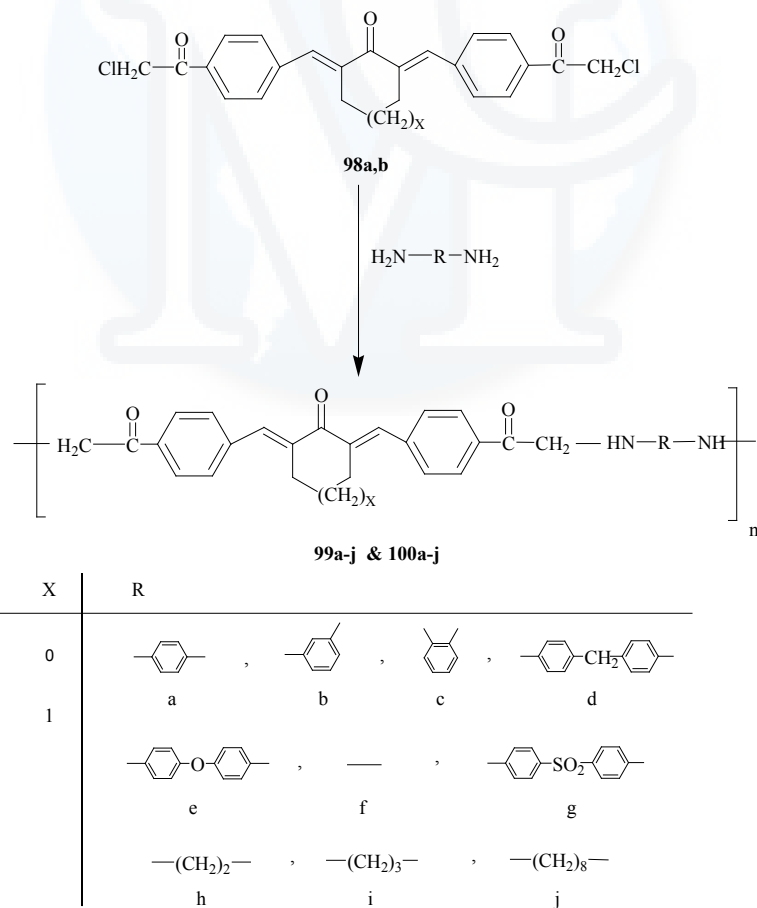


Figure 67 Synthesis of polymers 91_{a-d} & 92_{a-d} and 93_{a-d} & 94_{a-d}.


 Figure 68 Synthesis of polymers 96_{a-j} & 97_{a-j} & 98_{a-j}

 Figure 69 Synthesis of polymers 99_{a-j} & 100_{a-j}

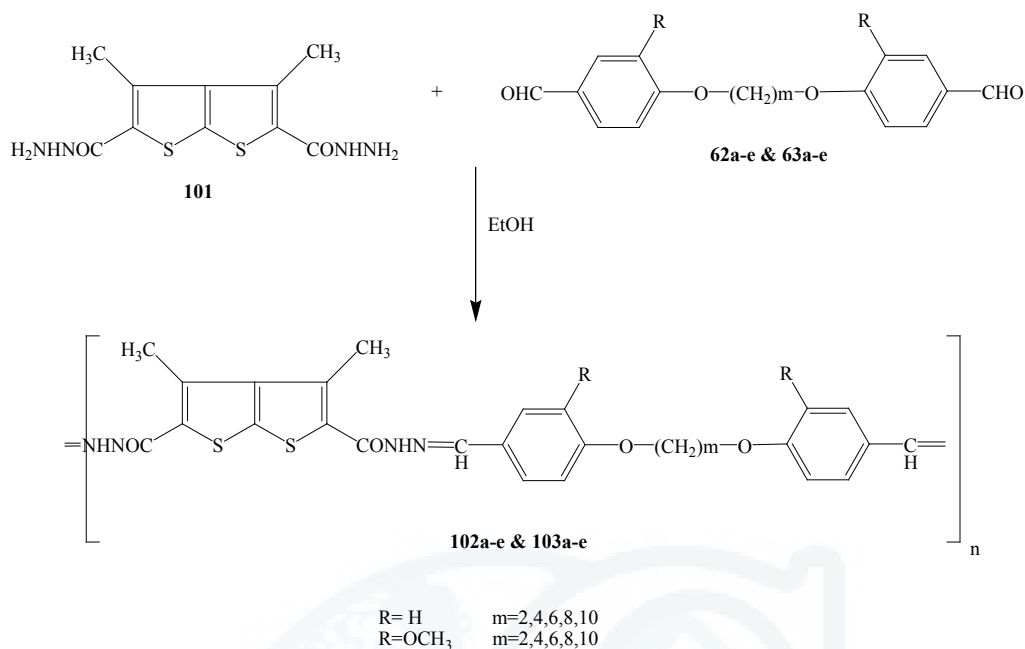


Figure 70 Synthesis of polymers 102_{a-e} & 1-3_{a-e}.

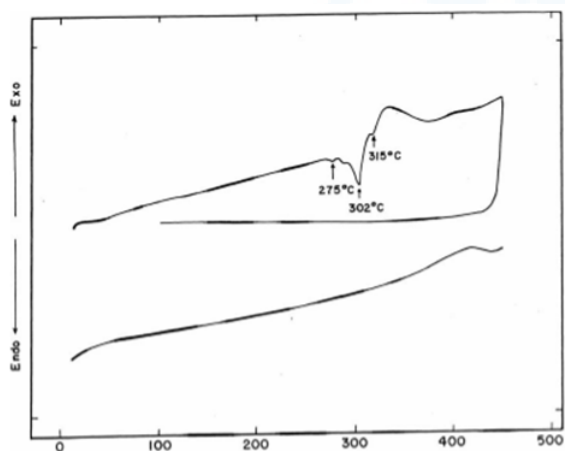
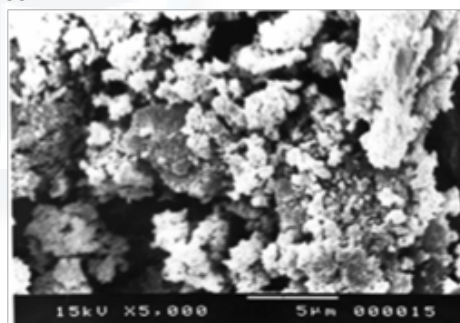


Figure 71 DSC curve of polymer 102e.⁶³

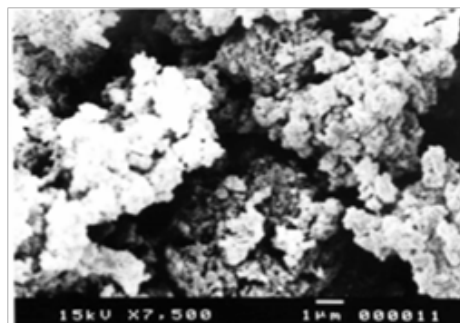
Experimental discussions

The previous section discuss the preparation routs of different types of hybrid polymers which are basically appreciated from large number of researchers due to its interesting properties in addition to some extra properties that appeared for the first time due to these hybrid formation. Interfacial polycondensation, solution polycondensation and acid-catalyzed Claisen-Schmidt synthetic routs were reported for the preparation of variable number of arylidene containing hybrid polymers. All characterization tools were tested discussed and correlated to their chemical structures in order to follow up all available properties to a suitable application. Solubility, viscosity, crystal structures, thermal properties; besides SEM morphological features were all tested, discussed and linked to their structures. The thermal examinations proved that the majority of these polymers are highly stable and there is no thermal and thermo-oxidative degradation observed at early temperature

rang. An addition properties were also investigated as an obvious evidence for this hybrid type interaction such as electrical and thermotropic LC properties. The conductivity values become very high and appeared in the range semiconductors (10⁻⁷-10⁻⁸ Scm⁻¹) as a result of doping with iodine. Moreover, the thermotropic LC behavior was examined and evaluated by DSC, and optical polarizing microscopy giving an interesting LC nematic phases in all the cases.⁴⁻⁶³



A



B

Figure 72 SEM images of polymer 102d at magnifications (A) x=5000, (B) x=7500.⁶³

Organometallic polymers

Organometallic polymer should contain metal centers, these metal centers attached to each other's by organic legends. It is also consider as new materials that carry both low density structural variance properties and different functional group of organic materials. Besides, many other properties such as: electrical conductivity and high temperature stability. In this section we will show many reported studied for organometallic polyketones, polyesters and their corresponding copolymers as well.

Experimental results

Aly⁶⁴ synthesized a new class of unreported organometallic polyketones 105a-d and copolyketones 106a,b depending on Friedel–Crafts reaction of 2,6-[bis(2-ferrocenyl)methylene]

cyclohexanone monomer 104 with different diacid chlorides in the presence of carbon disulphide and aluminum chloride as a catalyst the reaction done through solution polymerization as showed in Figure 73 & Figure 74. In most cases the polyketones and copolyketones were insoluble in organic solvents, in contrast they soluble in parotic solvents. All the properties such as the thermal properties of these polyketones and copolyketones were examined and linked to their structural units by thermogravimetric analysis and DSC measurements, and they had inherent viscosity of 0.29–0.52 dl g⁻¹. The products show lower thermal stability the observed for previous polykotones. The morphology study using the scanning electron microscopy showed that polymer 106b has both polymorphic globular and subglobular structures as shown in Figure 75.

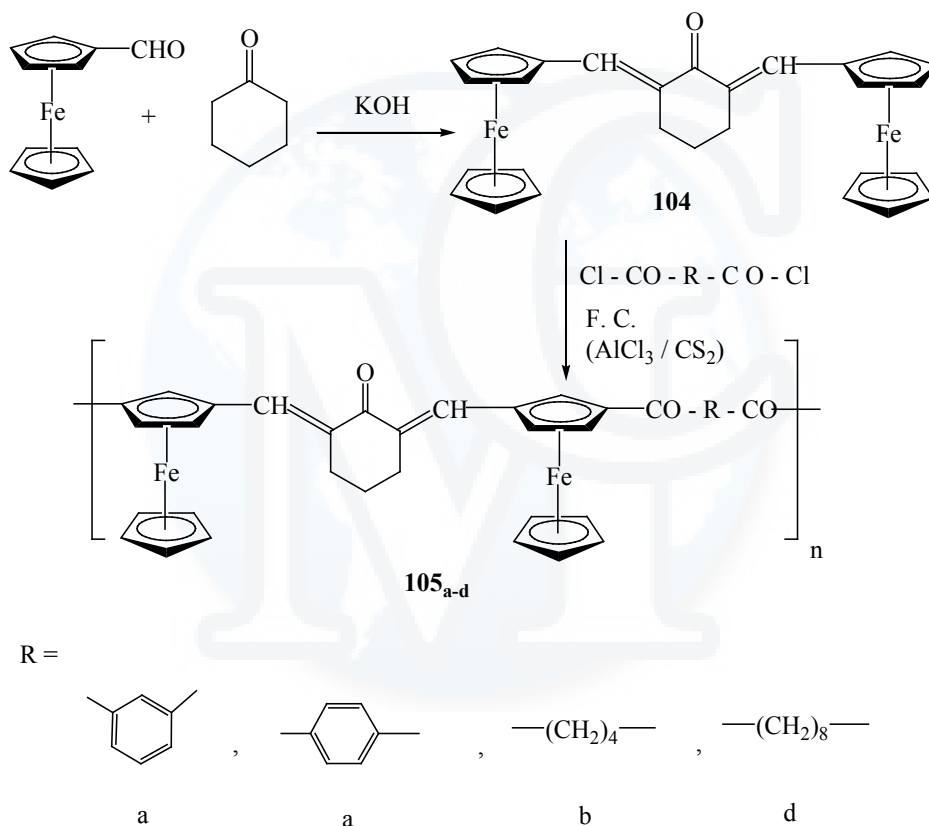


Figure 73 Synthesis of polymers 105_{a-d}.

Moreover, Aly & Abdel Monem⁶⁵ synthesized another new category of organometallic polyketones 108a-d and copolyketones 109a,b through the same condition of Friedel–Crafts reactions of 2,7-bis[(2-ferrocenyl)methylene] cycloheptanone monomer with different diacid chlorides via the solution polymerization as shown in Figure 76 & Figure 77. Thermal properties of these products were examined by common instruments for thermal analyses. The results were linked to their structural units by using TGA and DTG measurements. These polymers had inherent viscosity values in the range of 0.32–0.65 dl g⁻¹ which prove the

lower molecular weight of these series. Nearly similar thermal behaviour was detected for these polymers and copolymers as the previous organometallic polyketones 105a-d and copolyketones 106a,b. Additionally, the electrical conductivity of polyketone 108a and copolyketone 109a was studied above the temperature range (300–500 K) and tracked an Arrhenius equation with activation energy 2.09 eV. Also, the morphological properties of polymer 108b as a selected example of polyketones were detected by scanning electron microscopy as shown in Figure 78.

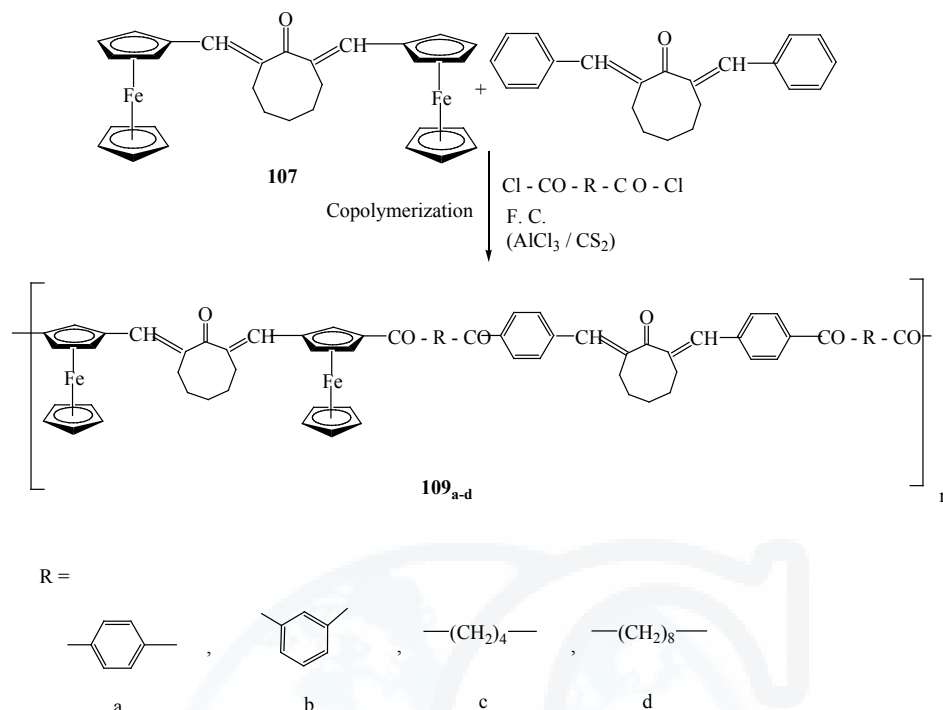


Figure 77 Synthesis of polymers 109_{a-d}.

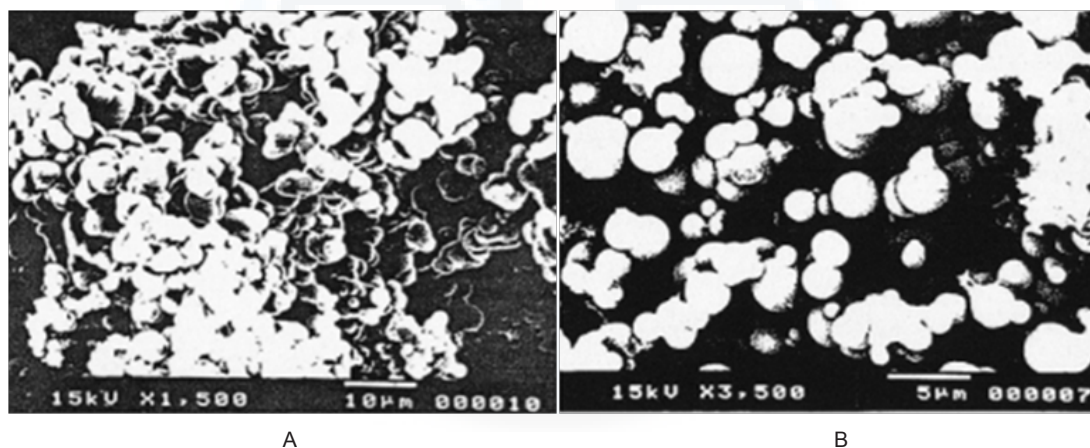


Figure 78 SEM images of polyketone 108b (A) $x=1500$, (B) $x=3500$.⁶⁵

Experimental discussions

The synthetic procedure of two different types of organometallic polyketones and their corresponding copolymers were carried out using the normal conditions of Friedel–Crafts reaction throughout solution polycondensation technique. The mentioned polymers were mainly base on bis(2-ferrocenyl)methylene[cycloalkanone moieties. Similar general properties to the previously mentioned polyketones were mentioned in this section with some extent of enhancement due to the organometallic part that has been inserted in the main chains. X-ray diffraction studies confirm that, most of the polymers show highly order crystal structures and hence their structures seems to be semicrystalline in nature. Whereas, the thermal properties showed a diverse behavior concerning compared to normal polyketones. Besides that, the thermal properties

also studies confirm that the copolymers were less stable than the corresponding polymers.^{64,65} Additionally, the electrical conductivity of all polyketones was studied above the temperature range (300 - 500 K) and tracked an Arrhenius equation with activation energy 2.09 eV. Due to organometallic part these polymers show enhanced electrical properties in comparison to previously mentioned polymers without metallic part.^{28,29,32,64,65}

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