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Monomer synthesis 2.2'-(1,4 -phenylene)-bis (2-oxazoline) polymer precursor and their application to the synthesis of copolymer

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ABSTRACT — This work is concerned the cyclic imino ether (coupler chains) synthesis, namely, 1, 4 (phenylene) bis (2-oxazoline) (PBO) from condensation reaction of a nitrite derivative dicyanobenzene (DCB) with ethanolamine (EA). The reaction is carried out in bulk at elevated temperature 130 ° C in the presence of zinc acetate catalyst. The PBO was characterized by infrared spectroscopy (IR), ^{1}H NMR spectroscopy and differential scanning calorimetry (DSC).

In the second part, the polyaddition reaction between chain coupler 1.4 (phenylene) bis (2-oxazoline) and oligomere with carboxy end groups, were established the structural analysis by ^{1}H NMR and IR show the feasibility these coupling reactions.

***Keywords**: 1.4 (phenylene) bis (2-oxazoline), ring opening, polyaddition, carboxyl group.*

I.Introduction

Known for over a century [1], the 2-oxazolines are simple cyclic imino ethers, containing the sequence –N=C-O-.

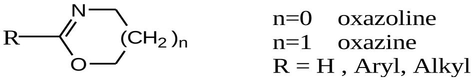

Fig. 1 General structure of oxazoline and oxazine

Oxazolines are prepared by various methods; reviews have detailed each of its synthesis methods proposed by Elderfield [2] and Frump [3]. Oxazolines different synthesis methods may be considered (Fig.2) [4- 5]. It is always condensing an amino alcohol with a carboxylic acid or acid derivative.

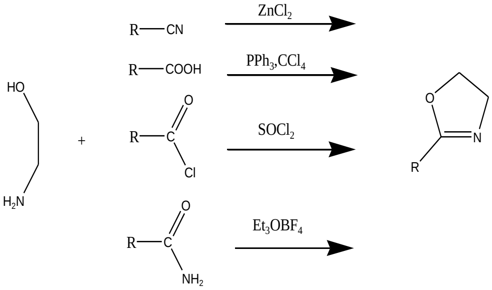

Fig. 2 Synthesis of oxazoline ring

All the cyclic imino ethers, they appear the most used. This is due to their high reactivity. Thus, this heterocycle has been widely used in organic synthesis such as precursor in the design of complex compound [6-7].

It served as activating group, such as coordinating ligand, as protecting group, but also as a reactant in addition reactions with organic acids, phenols, thiols or anilines [8-12]

The purpose of using these reactions to subsequently synthesize copolymers (ester-amide) (PEA) from bisoxazoline that structure is reported (Fig. 3).

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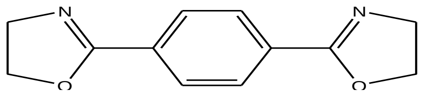


Fig. 3 1, 4 (phenylene) bis (2-oxazoline) (PBO)

II. Experiment section

1. *Materials and methods*

Zinc acetate dihydrate, ethylene glycol (EG) were purchased from Fluka, phthalic anhydride (PA), dicyanobenzene (DCB) and chloroform were obtained from Reedel-de Haen, ethanolamine (EA)and tetrahydrofuran (THF) were purchased from Aldrich.

The Infrared spectrum of the PBO were recorded on a BRUCKER Alpha FT-IR spectrometer (equipped with Alpha's Platinum ATR single refection diamond ATR module), and other FTIR spectra were recorded using an FTIR-8300 Shimadzu spectrophotometer (Shimadzu, Japan). Samples were prepared in KBr disks and transmittance was measured from 400 to 4000 cm^{-1}.

The proton magnetic resonance (^1H NMR) spectra of polymers were obtained on a BRUCKER at 300 MHz; sample was recorded in chloroform d6.

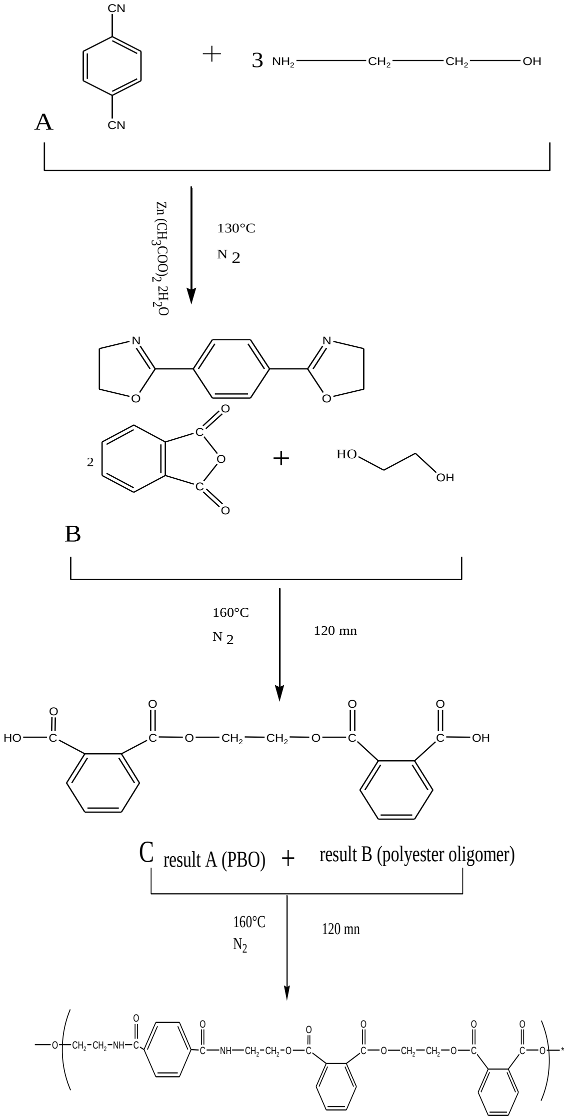
Differential scanning calorimetry (DSC) was performed on a device type DSC 204 F1 Phoenix- NETZSCH.

2. *Monomer synthesis (PBO)*

One mole of dinitrile (DCB) was dissolved in three moles of ethanolamine (EA) in the presence of Zinc acetate dihydrate at 2.5 mole% (scheme1.A). The mixture was refluxed for 4 hours under inert atmosphere (N_2) and maintained at a temperature of around 130 ° C. Release of ammonia (NH_3) was observed at the end of reaction product was recovered a green-yellow color. The product collected was dissolved in THF heating with magnetic stirring, after drying yielded of yellow powder.

3. *Synthesis of poly (ester-amide)*

The PEA was prepared by coupling reaction of polyester oligomer with ωω'diacides and the bizoxazolines 1,4 (phenylene) bis (2-oxazoline). We performed the polyaddition reaction of an equimolar ratio between the diacid and coupler of chains PBO under inert atmosphere (N_2) (scheme1.C). The temperature of the mixture is raised slowly from 120 ° C to 160 ° C. Poly (ester-amide) obtained was dissolved in chloroform and then precipitated with heptanes , then dried under vacuum at 40 °C up to constant weight.



Schema 1: A) Synthesis of bisoxazoline with polycondensation method, B) polyester oligomer, C) coupling reaction between polyester oligomer ω ω'diacides and PBO.

III. Results and discussion

Interpretation of the IR spectrum

Fig. 4 (a) shows the FTIR spectrum of the In the PBO. The peaks at 1639.68 cm^{-1} indicate the presence of the function -C = N. Other peaks were observed at 3047.58-3072.73 cm^{-1} and

2873.29-2981.59 cm^{-1} correspond to -CH$_2$ -CH aromatic protons and aliphatic protons, respectively. This peaks confirmed the presence of an aromatic ring. The characteristic absorption band at 1412.26 cm $^{-1}$ was assigned to CH $_2$ (s) oxazoline which appear in a range of 1410-1420 cm^{-1}. Cyclic ether appears around 1250 cm $^{-1}$.The spectrum is consistent with the desired structure allowed.

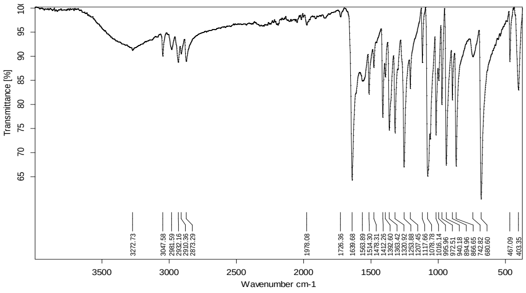


Fig. 4 IR spectrum of PBO

2. ^{1}H NMR

The ^{1} H NMR showed the existence of three different methylene groups. The peak in the region δ 4.49- 4.4 ppm corresponding to CH$_2$ group protons attached to oxygen, peak in the region δ 3.98- 3.44 ppm corresponds to other CH$_2$ group protons attached to nitrogen and at δ 7.95 ppm corresponding to aromatic ring protons. The other peaks are attributed to ethanolamine (δ 3.82 ppm, δ 1.82 ppm) (Fig. 5).

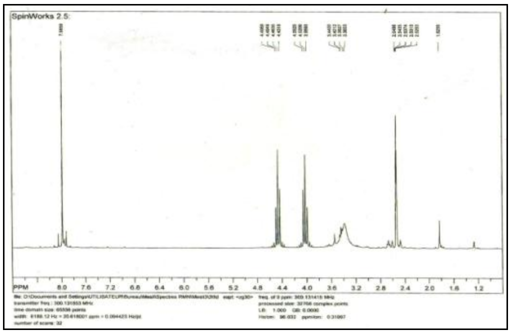


Fig. 5 ^{1}H NMR spectrum of PBO

3. Thermal analysis (DSC)

4. The DSC thermogram was recorded from 25°C to 300 ° C at a heating rate of 10 ° C per minute under nitrogen atmosphere. Fig. 2 gives DSC scan of PBO, which indicates that the melting point of the compound is 245 ° C (mp 243 ° - 246 ° C).

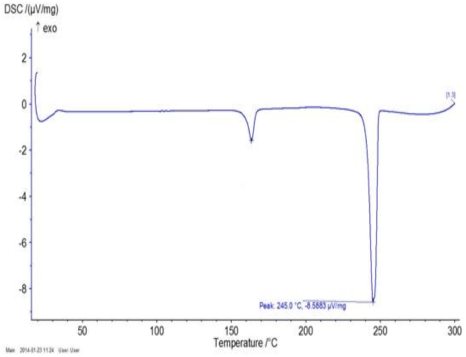


Fig. 6 thermogram of PBO

5. *Infrared spectral studies*

Poly (ester-amide) PEA was prepared by the coupling reaction between PBO and polyester oligomer as illustrated in Scheme 1. PBO react with carboxylic acids through the ring opening between positions 1 and 5 of the oxazoline, producing compounds possessing both amide and ester bonds. This has been confirmed by both FT-IR spectral analyses, as shown in Fig. 7 (b).The FTIR spectra shows the absorption bands at 1731.76 cm^{-1} and 1448.28 cm^{-1} that were attributed to the linear ester and carboxyl terminal groups respectively. There are wide bands stretching vibration at 3407.6cm^{-1} which characterize the absorption of the bond N-H amide. The amide bands were noted respectively at 1539.88 cm^{-}1. The signal at 1649.89 cm^{-1} was attributed to the C-O of the amide.

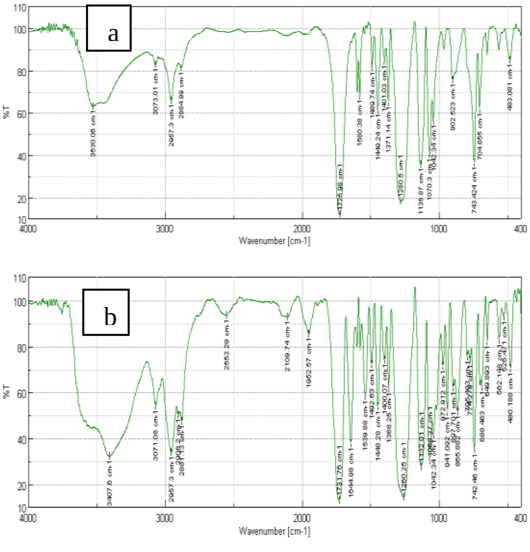


Fig.7 a) IR spectrum of the polyester oligomer b) IR spectrum of the polyesteramide PEA

6. ^{1}H NMR

According to the ^{1} H NMR spectrum corresponding to the polyester coupled with the bisoxazoline, there is the appearance of a triplet at δ 7.99 ppm corresponding to the proton NH formed after opening the oxazoline ring. They also note the occurrence of a triplet and a quadruplet to δ = 4.08 and δ = 3.71ppm ppm corresponding to the protons of two groups CH_2-OCO and open heterocycle-CH $_2$ NHCO. The aromatic rings give signals to δ = 7.28 ppm. This spectrum shows that the coupling reaction is by ring opening (fig. 8).

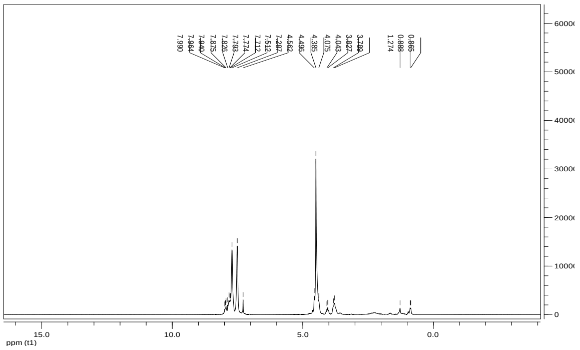


Fig. 8 1H-NMR spectrum of the PEA

IV. Conclusions

In this study we synthesis 1.4 (phenylene) bis (2-oxazoline) (PBO) by condensation of ethanolamine with the dicyanobenzene by weight in the presence of zinc acetate as catalyst. The structural analysis by ^{1} H NMR and IR consistent with the structure recommended.

These results later use bisoxazoline prepared as chain coupler with polyesters acids end groups
PBO finds application in polymer synthesis as a chain extender/ chain coupling.

The coupling reaction was confirmed by structural analyzes ^{1}H NMR and IR. It allows us to achieve the ester amide structure in the main chain by ring-opening reaction with carboxyl acid. The results were satisfactory

V. References

[1] M. Tilliet, *Synthesis and study of new oxazoline-based ligands,* Ph.D. dissertation, Dept. Chem. Sci. Eng., Stocklom Univ., 2008

[2] *R. C. Elderfild, Heterrocyclic Compounds* (J. Wiley,1977, pp. 376- 391)

[3] *J. A. Frump,* Oxazolines. Their preparation, reactions, and applications, *Chemica Reviews* 5 *(1971) 483 -505.*

[4] T. Loontjens, W. Belt, D. Stanssens, P. Weerts, Synthesis of 1,2-bis(2-oxazolinyl-2)ethane and its application as chain extender for poly(ethylene terephthalate), Polymer Bullettin 30 *(1993) 13- 18.*

[5] J l Jie, *Meyers Oxazoline Method, Name Reaction* (Springer ,2014, pp. 393-394)

[6] A. I. Meyers, E. D. Mihelich , The Synthetic Utility of 2-Oxazolines, Journal of the Gesellschaft Deutscher Chemiker 15 *(1976) 270-281.*

[7] *T. Gant, A. I. Meyers,* The chemistry of 2-oxazolines, *Tetrahedron* 50 *(1994) 2297-2360.*

[8] *G. Odian, F. Shi,* Thermal polymerization of hydroxy- and mercapto-substituted 2-oxazolines, *Macromolecules* 26 *(1993) 17-23*

[9] *F. Böhme, D. Leistner, A. Baier,* Comparison of the coupling behaviour of diisocyanate and bisoxazolines in modification of liquid crystalline poly(ethylene terephthalate-co-oxybenzoate)s, *Macromolecular Materials and Engineerning* 224 *(1995) 167-178.*

[10] *I. Ben Mansour, K. Alouani, R. Mercier,* synthèse de monomères bisoxazolines précurseurs de polymères et étude des réactions oxazoline/acide carboxylique et oxazoline/phénol par réactions modèles, *Journal de la Société Chimique de Tunisi* 11*(2009) 145-157.*

[11] J. Lustoň, J. Kronek, O. Markus, I. Janigová, F. Böhme, Synthesis and polymerization reactions of cyclic imino ethers. 3. Poly (ester amide)s of the AA + BB type on the basis of 2-oxazolines, Polymers for Advanced Technologies 18 *(2006) 165-172.*