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СИНТЕЗ НОВЫХ ПОЛИ (2,2 - БИС(4 - АКРИЛАТОВ ФЕНИЛПРОПАНА НА ОСНОВЕ БИСФЕНОЛА – А)

Аннотация: В данной работе бисфенол - А синтезировали из фенола и ацетона в присутствии кислотного катализатора амперлиста-15, а затем мономер акрилата бисфенола-А синтезировали путем проведения реакции электрофильного замещения (этерификации) между бисфенолом - А и акриловой кислотой в присутствии амберлиста-15 при температуре (135оc). После 60

минут стабилизации при этой температуре было замечено, что цвет раствора менялся от прозрачного до рубиново - красного с увеличением вязкости и образованием полимера (-2,2 Ди (4- акрилат (пропана)).

Предложенная структура мономера и полимера была продемонстрирована с использованием методов инфракрасной (ИК) спектроскопии и протонного магнитного резонанса (1H-ЯМР), а также предложен подходящий механизм образования полимера.

Ключевые слова: Бисфенол - А, Амберлист-15, Бисфенол - А Мономер Акрилат, Акриловая Кислота.

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SYNTHESIS OF NEW POLY(2,2-BIS(4-ACRYLATES PHENYL PROPANE BASED ON BISPHENOL – A)

Annotation: *In this work, bisphenol - A was synthesized from phenol and acetone in the presence of an amberlyst-15 acid catalyst, and then the bisphenol-A acrylate monomer was synthesized by performing an electrophilic substitution reaction (esterification) between bisphenol - A and acrylic acid in the presence of amberlyst -15 at the degree (135°C). After 60 minutes of stabilization at this temperature, it was noticed that the color of the solution changed from transparent to ruby red with the increase in viscosity and the formation of a polymer (-2,2 di (4- acrylate) propane).*

The proposed structure of the monomer and polymer was demonstrated using infrared (IR) spectroscopy techniques and proton magnetic resonance (¹H-NMR), and a suitable polymer formation mechanism was proposed.

Keywords: *Bisphenol- A, Amberlyst-15, Bisphenol- A Monomer Acrylate, Acrylic Acid.*

1. Introduction:

2,2-Bis (4'-hydroxyphenyl) propane (commercial names dian, bisphenol A) is one of the starting materials in the production of epoxy resins and polycarbonates. On an industrial scale it is produced by the acid-catalyzed condensation of acetone and phenol, The kinetics of the synthesis of bisphenol A from acetone and phenol on an ion-exchange catalyst promoted by partial neutralization of acid groups with 2-mercaptoethyl amine was investigated in the temperature range 50-85°C. [1,c.129/2,C.1/3,C.1].

Bisphenol A (BPA) is an environmental contaminant widely used in the plastic industry. BPA has been demonstrated to be an endocrine disruptor and has an adverse effect on the embryonic development of mammals. BPA displays an adverse effect on

porcine early embryonic development through mitochondrial and DNA damage[4,C.23/ 5,c.204].

Direct polymerization of bisphenol- A with CO was carried out using a catalyst system constituted of a Pd carbonylation catalyst, an inorganic redox catalyst, an organic redox cocatalyst, a base and a dehydrating agent. Usage of Cu(OAc)₂ as inorganic redox cocatalyst led to the synthesis of polycarbonate of Mw 3600 but the formation of o-phenylene carbonate (o-PC) and salicylic acid type groups at the chain ends was observed. In an attempt to eliminate end group formation and explore the possibility of higher molecular weight polymer synthesis, various modifications were made in the catalyst system. On replacing Cu with Ce, o-PC formation could be eliminated completely. In addition, the usage of bis(triphenylphosphoranylidene) ammonium bromide (PPNBr) instead of tetrabutylammonium bromide [n(Bu)₄NBr] resulted in elimination of acid group formation leading to the synthesis of polymer of Mw 3:8 × 10³ (determined by GPC), with hydroxy group at both chain termini[6,c.2289 / 7,c.4297].

2. Experimental

2.1. Apparatus and chemicals:

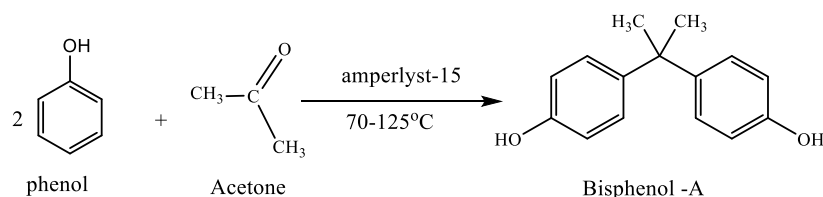
Materials: Phenol, Amberlyst -15, acetone, acrylic acid, ethanol, , hexane (all from Sigma-aldrich), paraffin oil (BDH), Chemic), distilled water.

Instrumentation: ¹H NMR spectrum were recorded on a (Bruker AVANCE) 400 MHz spectrometers and CDCl₃-D₁ was used as NMR solvent, with TMS as an internal standard .FT-IR spectra were recorded on a Jasco FT-IR 4100 and Shimadzu obtained by the KBr disk method.

2.2. Experimental Procedure:

2.2.1. Synthesis of Bisphenol A:

(0.5mol, 4.7gr) phenol is added to the acetone (0,01mole, 0.58g) and (50mg) amberlyst-15 without solvent and the mixture is heated in a flask with reflux on a paraffin oil bath for 24 hours and the temperature is 70-125 °C. The resulting bisphenol-A was dissolved with ethanol well and on cold, and filtered to get rid of the catalyst,(m.p=155-156°C, Y=70%) .



The infrared spectrum of the product was recorded and compared with the reference spectrum of bisphenol- A compatibility between the two spectra was observed Figure 1.

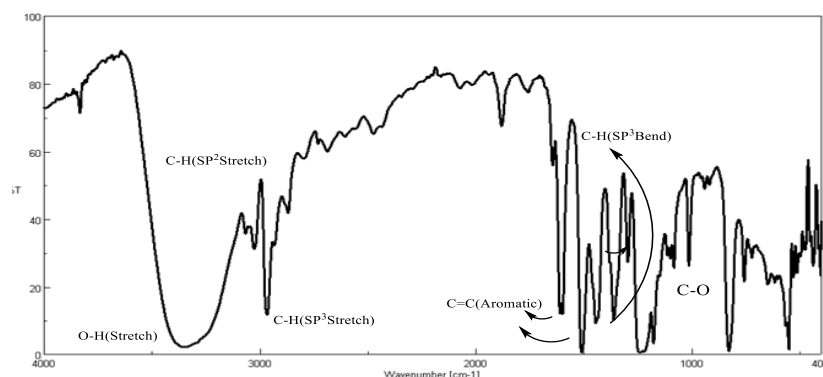


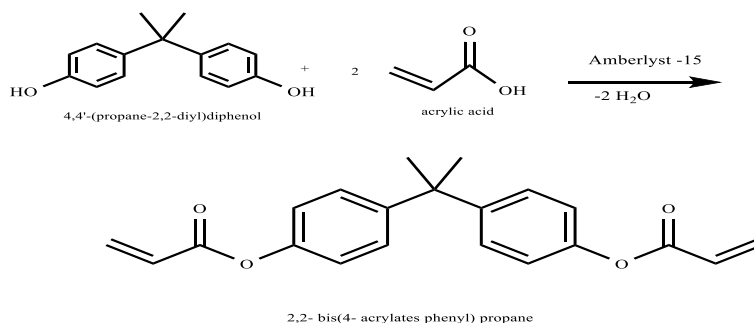
Figure 1. FT-IR absorption spectrum of Bisphenol-A

2.2.2. Synthesis of poly(2,2- bis(4- acrylates phenyl) propane):

It is added to a two-hole vial equipped with an oil bath, a magnetic stirrer, a condenser, and an inlet for nitrogen gas, so that it passes in the form of gas bubbles, a Den stark device, and a thermometer (1mmol, 0.228g) of BPA and (2mmol, 0.144 gr) acrylic acid so that A homogeneous solution is formed) and then 0.012 g of amberlyst-

15 is added, the temperature is raised and fixed at (135°C), and after 60 minutes of stability at this temperature, the color of the solution is observed from transparent to sapphire red and the viscosity increases. Hours no further change was observed.

The product was dissolved with ethanol well and on cold, and filtered to get rid of the catalyst, and the solvent was expelled by evaporation under vacuum, so a ruby red viscous liquid was obtained.



3. Results and Discussion:

3.1. ¹H-spectroscopic measurements:

Figure 2. Explanation of ¹H-NMR (ppm) of poly(2,2- bis(4- acrylates phenyl) propane):

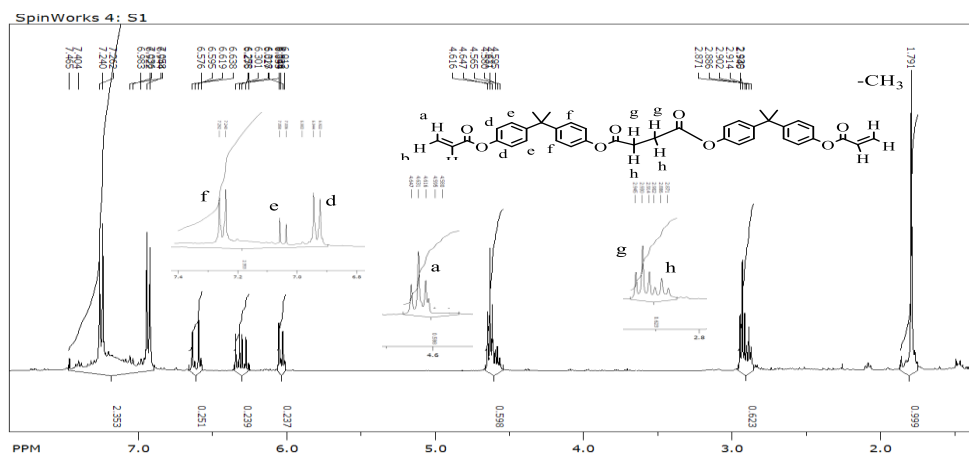
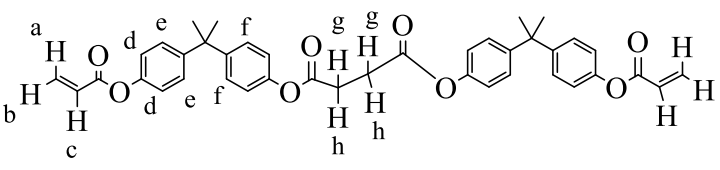


Figure 2. ¹H-NMR spectrum of the poly(2,2- bis(4- acrylates phenyl) propane)in Chloroform

Table1 Explanation of ¹H-NMR (ppm) of poly(2,2- bis(4- acrylates phenyl) propane).

	
$^1\text{H-NMR}(\delta, \text{ppm})$	No
1.75(s, 6H)	-CH ₃
6.576-6.638(dd, 1H, $j_1 = j_2 = 10.4\text{Hz}$)	a
4.647-4.595 (dd, 1H, $j = 6.4\text{Hz}$)	b
6.012-6.053(dd, 1H, $j_1 = j_2 = 6\text{Hz}$)	
6.275-6.344(dd, 1H, $j_1 = j_2 = 7.6\text{Hz}$)	c
6.94(d, 1H, $j = 8.8\text{Hz}$)	d
7.058(d, 1H, $j = 8.8\text{Hz}$)	e
7.24(d, 1H, $j = 8.8\text{Hz}$)	f
2.886-2.945(dd, 2H, $j_1 = 5.6\text{Hz}, j_2 = 6\text{Hz}$)	g, h

3.2. Infrared Spectra:

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} help to indicate regions of absorption vibrations. The main stretching modes are for $\nu(\text{C}=\text{O})_{\text{ester}}$, $\nu(\text{C}=\text{C})$ and $(\text{C}-\text{O}-\text{C})$.

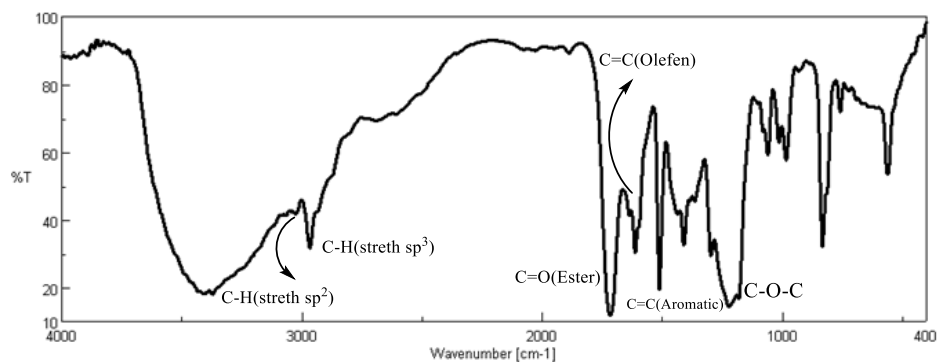
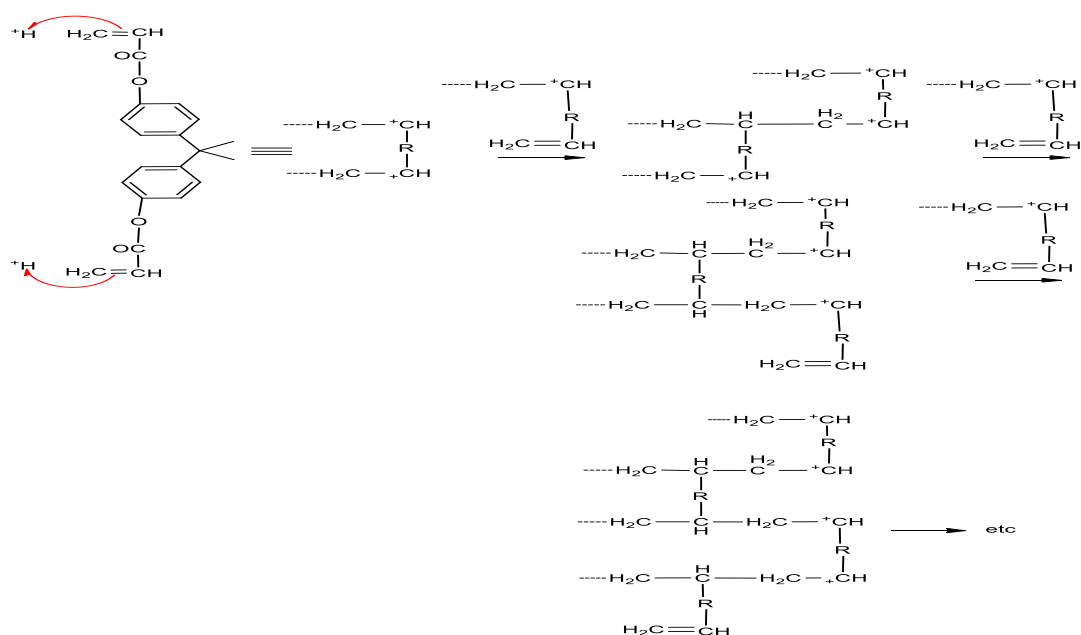


Figure 3. FT-IR absorption spectra of poly(2,2- bis(4- acrylates phenyl) propane)
 Scheme 1 shows mechanism the reactions that lead to the formation of poly(2,2- bis(4- acrylates phenyl) propane)



Scheme 1 mechanism the reactions formation of poly(2,2- bis(4- acrylates phenyl) propane)

4. Conclusion:

The synthesis of a poly(2,2- bis(4- acrylates phenyl) propane)) via reaction bis phenol with acrylic acid, the result was characterized by spectral methods FT-IR, ¹H-NMR.

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