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ПОЛУЧЕНИЕ АЗО ПОЛИМЕРА СВОБОДНОЙ РАДИКАЛЬНОЙ ПОЛИМЕРИЗАЦИЕЙ С ИСПОЛЬЗОВАНИЕМ (AIBN) В КАЧЕСТВЕ ИНИЦИАТОРА

Аннотация: *приготовлен азокраситель, который включает получение соли тетрафторбората диазония. После этого выделенную соль соединяли со стиролом, используя ацетонитрил в качестве растворителя при комнатной температуре. Полученный DYE был радикально полимеризован с использованием (AIBN) в качестве инициатора. Структуры продуктов были идентифицированы с помощью FT-IR, H^1 -ЯМР.*

Ключевые слова: *азополимер, азокраситель, тетрафторборат натрия, свободнорадикальная полимеризация, стирол, AIBN.*

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PREPARATION OF AZO POLYMER BY FREE RADICAL POLYMERIZATION USING (AIBN) AS AN INITIATOR

Abstract: *azo dye has been prepared which includes preparing diazonium tetrafluoroborate salt. Afterward, the isolated salt has been coupled with Styrene using acetonitrile as a solvent at room temperature. The obtained DYE was radically polymerized using (AIBN) as an initiator. The structures of the products were identified by FT-IR, H^1 -NMR.*

Keywords: *Azo polymer, azo dye, tetrafluoroboratesodium, free-radical polymerization, Styrene, AIBN.*

1. Introduction:

Azo polymers (Azo-containing polymers) are polymers that have Azo groups (-N=N-) within the polymer structure. According to the position of the -N=N- group, they can be broadly classified as main-chain and side-chain azo polymers. The synthesis and structures of different azo polymers will be mentioned in this review when necessary. Azo polymers are receiving increasing attention because of their special properties and their potential applications. Various azobenzene derivatives have been utilized as dopants for conventional polymers to form polymer composites and change the polymer properties.[1] Azo polymers comprise a class of both aliphatic and aromatic polymers. Aliphatic azo polymers are thermally unstable and decompose into free radicals, a property that is frequently used in the initiation step of free radical polymerization. aromatic azo polymers stable, due to stabilization by resonance.[2] Recently polymer/azobenzene nonlinear optical (NLO) systems are widely investigated, as they can be of great importance for a variety of applications. The azobenzene moieties can be either doped into the polymer matrixes or covalently attached to the polymer [3] The latter case usually results in more stable systems with increased density of chromophores and enhanced nonlinear optical response [4] The strong nonlinearity emanates from the strong charge transfer taking place within these units.[5]

2. Experimental section:

2.1. Apparatus and materials

¹H-NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer and CDCl₃ was used as NMR solvent. - FT-IR spectra were recorded on a Jasco FT-IR 4100/tybe obtained by KBr disk method. All materials are commercial reagent grade and were obtained from Merck Co.

2.2.1. synthesis 1-(4-nitrophenyl)-2-(3-vinylphenyl)diazene:

A solution of p-nitroaniline (2.76 g, 20 mmol) in water (20 ml) was added dropwise to a solution of 37% conc. HCl (10 mL) and diazotized with an aqueous solution of sodium nitrite (1.38 g, 20 mmol) at 0-5°C. The mixture was stirred for 1h. A yellow transparent diazonium salt solution was obtained. After 30 min at 0-5°C, a

solution of sodium tetrafluoroborate (2.2 g, 20 mmol) in water (10 ml) was added, and after a further 1h, the product was collected by filtration, washed with a small amount of ice-water and then with a large amount of ether. After drying in a vacuum desiccator by P₂O₅.

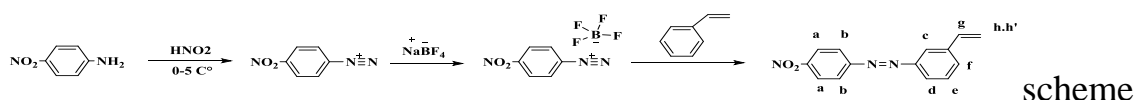
the diazonium tetrafluoroborate (1.91g, 10 mmol), and a Styrene (1.04g, 10 mmol) were dissolved in Acetonitrile, The mixture was stirred at room temperature for 24 h. Then the product was dried to get remove of the solvent. The dye was collected and recrystallized from ethanol to afford a red precipitate product. Yield: 69% m.p = 164 C°

2.2.2. synthesis of polymer:

1-(4-nitrophenyl)-2-(3-vinylphenyl) diazene (5mmol,1.2663g) and (0.1mmol, 0.0165 g) was dissolved in 20 mL of THF. The reaction mixture was heated to 60C° under a nitrogen atmosphere for 24 h. The polymerization was stopped by pouring the reaction mixture into Petroleum ether 40-60 °C. This procedure was repeated several times to ensure the removal of unreacted monomer finally the polymer dried under vacuum overnight.

3. Results and Discussion:

The synthesis of the compound 1-(4-nitrophenyl)-2-(3-vinylphenyl)diazene have been according to the following scheme (1):

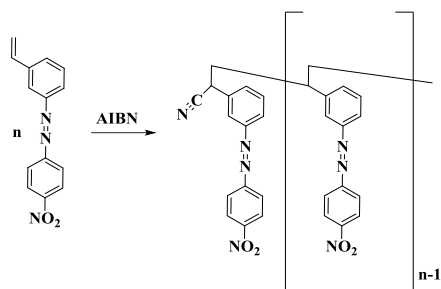


(1): synthesis of 1-(4-nitrophenyl)-2-(3-vinylphenyl)diazene

The structure of the resulting 1-(4-nitrophenyl)-2-(3-vinyl phenyl)diazene and the polymer has been investigated using spectroscopy methods(FT-IR,¹H-NMR). FT-IR ((KBr, cm⁻¹): (C_{SP}²-H, 3030), (-NO₂, 1506-1340), (-N=N-,1486). The ¹H-NMR spectra of the 1-(4-nitrophenyl)-2-(3-vinyl phenyl)diazene using CDCl₃ as solvent show the following peaks: (a) δ= 8.28ppm, dt, J₄=2.08 Hz,J₃ 2.42 Hz,J₂=9.45Hz,2H. (b) δ=8.17ppm,dt, J₄=2.01 Hz,J₃=2.4 Hz,J₂=10.22Hz,2H. (c) δ= 8.10ppm,t, J=3.6 Hz,1H. (d) δ= 7.54ppm, dt, J₄=1.92 Hz,J₃=2.46 Hz,J₂=9.35Hz,1H. (e) δ= 7.44ppm, t, J= 5.92Hz,1H. (f) δ= 7.48ppm, dt, J₄=2.06 Hz,J₃=2.42 Hz,J₂=9.49Hz,1H. (g)

$\delta=6.75\text{ppm},q,1\text{H}$. (h,h') $\delta=5.46\text{ppm},dd,J=2.20\text{Hz},J=13.4\text{Hz},1\text{H}$. $\delta=5.71\text{ppm},dd,J=2.24\text{Hz},J=8.08\text{Hz},1\text{H}$.

The synthesis of the polymer have been according to the following scheme (2):



scheme (2): synthesis of the azo polymer

The ¹H-NMR spectrum of the formed polymers shows the disappearance of the C-H proton peak in the Styrene and the appearance of two new peaks belonging to CH₃- and -CH₂- groups.

4. Conclusion:

The diazonium salt has been isolated as diazonium tetrafluoroborate, which has been coupled with Styrene using acetonitrile as a solvent at room temperature. the azo polymer has been made according free-radical polymerization with AIBN as an initiator.

5. Acknowledgments:

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