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Synthesis and Analysis of poly (1, 3, 4-oxadiazole)

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Abstract: *Polyamide hydrazide is synthesized by from IPC and BABH poly amide hydrazide is analysed by X-ray diffraction show crystalline in polymer. Thermal properties by TGA. Synthesis of poly (1,3,4 triazole)s from orthophosporic acid P_2O_5, polyhydrazide and aniline analysis of poly(1,3,4-triazole)s by IR spectrum absorption bands of triazole ring breathing vibrations with disappearance of hydrazide bands. Synthesis of poly (1, 3, 4 oxadiazole)s from poly (amide hydrazide) and $PoCl_3$. Convesion of hydrazide group into 1,3,4 oxadiazole ring is monitored by FTIR.*

Keywords: *Polyhydrazide, Polyamide hydrazide, Polyoxadiazoles, Poly (1, 3, 4-Oxadiazole)s.*

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I. Introduction

Preparation of Polyhydrazide: A preferred technique for high molecular weight polyhydrazides containing the $-R_1CONHNHCOR_2-$ groupis low temperature solution polycondensation under anhydrous conditions. A diacid chloride is allowed to react with the dihydrazides in amide solvent that functions as both acid accepter and solvent for the polyhydrazide.

Application of Polyhydrazides:

1.Polyhydrazide fibers having high tensile properties are useful as reinforcing elements in plastics and rubbers.
2.Zinc chelates of polyhydrazides are flame retardant and practically nonsoftening.
3.Phosporus containing fibrous polyhydrazide is flame retardant.
4.Polyhydrazide yarns are used as belts for absorbing energy during automobile and air craft accidents.
5.Polyhydrazides are useful for immobilization of proteins. Acrylic hydrazide resins which are soluble are useful as protective and decorative coatings.

POLYAMIDE-HYDRAZIDES

Preparation of Polyamide hydrazide: polyamide-hydrazide is usually prepared from dicarboxylic acid chlorides and aminohydrazides such as p-aminobenzhydrazide by the low temperature solution polycondensation method, salts such LiCl may be added to aid the solubility of polymers.When p-aminobenzhydride is used, the polymer obtained may be highly or sequentially ordered, depending upon the mode of addition of the acid chloride. This difference is trackable to the different reactivities of the amino and hydrazide groups towards the acid chloride.

Properties of Polyamide hydrazide:

Most of the polymers in the class are soluble in dimethyl sulphoxide which is used for spinning. Light scatteing, Sedimentation, Rheological studies on X-500 class. Polyamide hydrazide show that they are semi-flexible polymers and undergo phase transition induced by the shear in H_2SO_4 from isotropic to the anisotropic state.

Application of Polyamide hydrazide:

1.Excellent mechanical properties.
2.Polyamidehydrazide containing group 1A, 2A, 2B, 3B, 5B metals are fire resistant.
Polyoxadiazoles: Polymer containing oxadiazole units are known to have excellent thermal and hydrolytic stability, in addition to their capacity to form fibre, film and membranes.

Poly (1,3,4-Oxadiazole)

Preparation of Poly(1,3,4-Oxadiazole) : This can be prepared by cyclodehydration of polyhydrazide containing the (-CO-NHNH-CO-) group. This can be done either thermally near $T_g$of polyhydrazide or in solution by using dehydrating agents such as chlorides, anhydrides, sulphuric acid and phosphorus oxychloride.
The thermal method is usually preferred because of its simplicity and quantitative yield. The polyhydrazide are heated at 100^0C for 1-2 hours at 67 Pa. Certain catalyst accelerates the cyclodehydration reaction e.g. Carbodiimide, isocyanate, thionylchloride, ortho-formate ester and phosphorus dihalo nitrile timmers.

The course of cyclodehydration reaction can be followed by IR spectroscopy by observing the increase in absorption peak at 970 cm^{-1}characteristics of (1,3,4-oxadiazole) ring and decrease in peak at 1670 cm^{-1}characteristics of the carbonyl of hydrazide. The kinetics of conversion of polyhydrazides to poly (1,3,4-oxadiazole) indicate a first order process upto 90% reaction with activation energies in the order of 209KJ/Mole. The rate of cyclodehydration depend on physical state of polymer. The degree of cyclodehydration varies inversely with the crystallinity suggest that thermal cyclodehydration below the m.p. of polymers occur only in amorphous state.

Properties of Poly (1,3,4-oxadiazole): Poly(1,3,4-oxadiazoles) has densities in the range 1.2-1.4 g/cm^3. It is thermally more stable than polyhydrazides and has good stability towards hydrolytic attack. Aliphatic oxidiazole degrade at about 400^oC-450^oC and are soluble in solvent such as formic acid, dimethyl acetamide, dichloroethane etc. Aromatic oxidiazoles are thermally and oxidatively stable. They decompose between 450^oC-500^oC. These are soluble in sulphuric acid, trifluroacetic acid and phosphoric acid and may exhibit liquid crystalline behavior.

Properties of poly(1,3,4-oxadiazole) : The properties of poly(1,3,4-oxadiazole have been investigated. The all aromatic poly(1,2,4-oxadiazole) are soluble only in strong acids such as trifluroacetic acid, sulphuric acid and slow extremely good hudrolytic stability in both acidic and basic medium. They have good resistance to UV catalyzed oxidative attack and have lower melting temperature than their precursors namely poly (o-acyamidoxime). When suitably compounding these polymers may be used as adhesives, caulking compounds, channel sealants and fuel tank liners.

Synthesis of poly(1,3,4-oxadiazole) : Into a 100mL round bottom flask equipped with a magnetic stirrer, a calcium chloride guard tube was placed poly(amide hydrazide) (PAHI-3) 0.1 gm, $POCl_3$(99%) 10mL and the reaction mixture was refluxed with stirring for 5hrs in oil bath at 80^oC. Then the whole reaction mixture was poured in 200mL distilled water with stirring. White precipitate of poly(1,34-oxadiazole) was obtained. The precipitated polymer was filtered, washed with water, methanol and dried under vacuum at 80^oC for 2hrs. Yield 0.9g (94.83%).

Application of Poly (1,3,4-oxadiazole)

1.Poly(1,3,4-oxadiazole fibers have combination of properties i.e. they have good strength, stiffness, good fatigue resistance and low denstity.

2.Oxidiazoles containing polar group like $–OCH_3$ and –CN have a high degree of semi permeability to water, therefore can serves as reverse osmosis membranes, useful in sea water desalination with salt rejection capacities as high as 93%

3.Poly(1,3,4-oxadiazole) copolymer prepared from 5-tert-butyl isophthalic acid and hydrazine sulphate were useful for fibers, films coatings, laminates and molded objects.

4.Material for filtering gases and liquid at temperature upto 350^0C can be produced from polyoxadiazole fibers.

II. Conclusion

Preformed hydrazide and methylene linkage containing aromatic diamine, viz, bis (4-amino benzyl) hydrazide (BABH), was successfully synthesized. A series of poly (amide hydrazide)s and copoly (amide hydrazide)s and the related polyamide were synthesized from BABH or ODA with IPC by low temperature solution polymerization method. Polymers had inherent viscosities in the range of 0.18-0.93 dL/g indicating formation of medium to high molecular weight polymers. XRD analysis of polymers showed partially crystalline nature possibly due to high level of hydrogen bonding in hydrazide units incorporated. The polymers having higher mol % of BABH.

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