

SYNTHESIS OF NOVEL POLY (ARYLENE ETHER)S AND POLY(ETHER IMIDE)S SUPPORTED WITH TRIFLUOROMETHYL FOR MICROELECTRONIC APPLICATIONS.

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Abstract:

The advanced microelectronic packing requirement are passing on the need to produce increasingly lower dielectric constant materials while maintaining high thermal stability and ease of processing. The efforts have been focused on the direction of synthesis and characterization of novel polymers with the goal of high thermal stability, high mechanical strength, low water absorption rate, solubility in selected organic solvents, low dielectric constant and low coefficient of thermal expansion. These stringent combined goals have been largely achieved by synthesizing novel poly(arylene ether)s and Poly(Ether Imide)s containing rigid terphenyl units in the polymer chain and pendent trifluoromethyl groups. This novel polymer exhibited outstanding thermal stability, tensile strength, negligibly small water absorption rate even after submersion in boiling water for several days. It also exhibited low dielectric constant and have optical clarity. Therefore this novel material can be consider for use in numerous applications which requires for high –performance aerospace material as well as inter layer dielectric for advanced microelectronic applications.

Introduction:

Polyimides and polyethers are of great interest because they exhibit a number of outstanding properties, such as excellent thermo-oxidative stability, mechanical and electrical properties [1-3]. These material have been consider for use in numerous applications, which requires robust organic materials including composites and precursors for high performance aerospace materials and membranes for gas separation. Polyimides and poly(aryl ether)s with low dielectric constant, low water absorption low coefficient of thermal expansion and low refractive index are getting interest for interlayer dielectric in electronic devices such as integrated circuits[4]. Fluorine containing polymers are of great interest because of their possible use as gas selective membranes, low dielectric constant and remarkably low water absorption rate.

The tetrafluoromethyl groups in the polymer backbone enhance the solubility without forfeiture of thermal stability. They also increase the glass transition temperature with concomitant decrease of crystallinity. This group also helps to increase the free volume of the polymer thereby improving various properties of polymers including gas permeability and electrical insulating properties [5] Because of these interesting properties of the fluorinated polymers, considerable attention have been devoted to the synthesis of new classes of fluorinated polymers. The polymers containing terphenyl and quadrephenyl unit in polymer backbone are already reported [6-11]. In this paper few novel poly(aryl ether)s and Poly(Ether Imide)s are reported for the study of their dielectric and mechanical properties.

Experimental:

The elements, C, H, and N were analyzed by elemental analyzer. ¹H-NMR, ¹³C_NMR spectra were recorded on a Bruker ARX 300 instrument and IR spectrum was recorded with Bruker IFS 55 spectrophotometer with KBr pellets. DSC measurement was made using differential scanning calorimeter (

Model- 2920) instrument, at a heating / cooling rate of 20 K / minute under nitrogen atmosphere. The Thermogravimetry was measured on a DTG-6H shimadzu thermal gravimetric analyzer system equipped with a computer with a heating rate of 10 K / Minute for determination of decomposition temperature at 5% weight loss. Mechanical properties of thin polymer film were performed at room temperature on Testometric Micro-350 instrument under strain rate 5 % / min. The glass transition temperature was taken at the middle of the step transition in the second heating run.

Synthesis of polyethers:

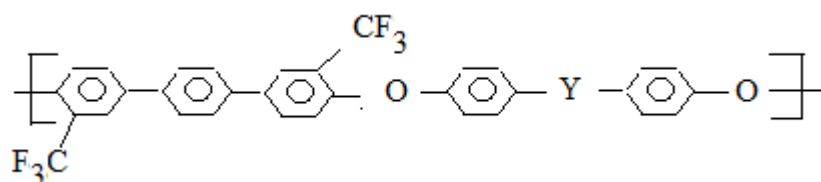
Polymerization of the bisfluoro monomer 1,4-bis(2-fluoro benzotrifluoride) benzene [1] with stoichiometric amount of different bisphenol were carried out in presence of excess of Na_2CO_3 as base NMP. The polymerization was run at solid contents of 25 %, and benzene was used for azeotropic removal of water. Initially the temperature was maintained at 140-160 $^\circ\text{C}$ during polymerization and the water generated by deprotonation of the phenol was removed effectively through a Dean-Stark trap. After completion of bisphenoxide formation and dehydration, the reaction mixture was placed in microwave and the reaction temperature was raised to 190 $^\circ\text{C}$. The high molar mass with dramatic increase in viscosity was obtained after 2 hrs. The resulting polymer solution was coagulated in a large excess of methanol and fibrous solids were isolated. The product obtained was further purified by boiling and washing several times with hot water to remove any inorganic impurities dried in vacuum and dissolved in THF, and the concentrated solution was reprecipitated in excess of methanol. The fibrous polymer recovered by filtration and were dried in vacuum.

Synthesis of polyimides:

The 4,4''-bis(aminophenoxy)-3, 3''-trifluoromethyl terphenyl monomer [2,8] was reacted with pyromellitic dianhydride, benzophenone tetracarboxylic acid dianhydride and 2,2-bis(3,4-dicarboxyphenol) hexafluoropropane to give corresponding poly(imide)s. Two different methods were chosen to achieve the imidization at the final stage of the reaction. One of the most common approach; the diamine was reacted with equimolar amount of pyromellitic dianhydride, benzophenone tetracarboxylic acid dianhydride in DMG at room temperature. Initially, the diamine was dissolved in calculated amount of dry DMG and the dianhydride monomer was added to it slowly. In all cases the reaction mixture become highly viscous within 10-15 minutes, the reactions were continued for 3hrs. The poly(amic acid) solutions were cast on clean glass plates and heated the film throughout the various stages up to 300 $^\circ\text{C}$ to remove solvent and water formed by imidization. The transparent, pale-yellowish film were obtained.

Results and discussion:

These novel polymers are soluble in a number of organic solvents, such as NMP, DMF, THF etc. The detail thermal, mechanical, optical and mechanical properties of these poly(aryl ether)s were studied. These polymers exhibited negligibly small water absorption even after immersing in boiling water for 72 hours. The refractive index of these polymers are very close to that of theoretical values. The poly(ether imide)s also exhibited outstanding thermal stability in air only 5 % weight loss occurred above 516 $^\circ\text{C}$ very low water absorption, low refractive index and low dielectric constant. The high modulus and tensile strength of these polymers are due to more rigid imide backbone compare to poly(aryl ether). All the properties of these polymers are depicted in table -1 and 2.



refractive index and low dielectric constant. Due to these promising properties such polymers can be used as interlayer dielectric for microelectronic applications.

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