



Synthesis and characterization of novel poly (*p*-methyl styrene) containing azetidinium moieties and their optical and semiconducting properties

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ABSTRACT

The *p*-methyl styrene-based monomer, *p*-methoxy-3-(1-cyclohexyl) azetidinyl styrene (PMAS) was synthesized by reacting *N*-cyclohexylazetidinyl with *p*-chloromethyl styrene in tetrahydrofuran solvent at room temperature in the presence of potassium tert-butoxide (*t*-BuOK). The free-radical initiated polymerization of PMAS was carried out in 1,4-dioxane solution at 70 ± 1 °C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The synthesized monomer and homopolymer have been characterized fully by a range of spectroscopic, thermal analysis and SEM analysis techniques. This homopolymer has been converted into a novel salts by reaction with the iodomethane (CH₃I) at different times (60, 180, 300 min). The electrical conductivity of the poly(PMAS) salts was measured and the poly(PMAS) salts exhibit the semiconducting behavior. The optical band gap and electrical resistance values of this polymers were obtained to be 3.79, 3.77, 3.82 eV, and 6.63×10^8 , 7.09×10^9 , 2.28×10^{10} Ω, respectively.

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1. Introduction

Four-membered heterocyclic analogs of cyclobutane can be derived by replacing a –CH₂ (methylene group) by a heteroatom (NH, O or S). The four-membered saturated heterocycles containing nitrogen, oxygen and sulfur are known as azetidines, oxetanes and thietanes, respectively. Four-membered heterocyclic rings are less strained, and hence more stable than the three-membered rings and, therefore, the ring cleavage is less likely. Moreover, four-membered heterocycles are more difficult to synthesize by direct intramolecular cyclization than the three-membered heterocycles because ring forming ability falls off with the chain length. The molecules of oxetane and thietane are planar, but not

square because of relatively larger size of the oxygen and sulfur atoms than the carbon atom. The planarity of these heterocycles, as compared to cyclobutane which is puckered, has been attributed to the reduction in the number of non-bonded interactions between methylene groups. The small heteroatom containing chiral compounds as oxirane, oxetane, azetidinium and pyrrolidine derivatives are important intermediates of biologically active materials. There are numerous active pharmaceutical ingredients (APIs) among these compounds, such as antibiotics [1], antiviral [2], anticancer agents [3], antidepressants [4], anti-pyretics [5] and cholesterol absorption inhibiting agents [6]. The parent compound, azetidinium was first characterized in 1899 [7,8]. Azetidinium's unusual structure has been the subject of numerous experimental and theoretical studies [9–15]. Establishing the physical and chemical properties of azetidinium and related substituted derivatives remains an active area of research because of the insight provided into the chemistry of small ring systems.

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Semiconducting polymers are now attracting considerable attention as promising materials for the development of optoelectronic devices such as light-emitting diodes, photovoltaic cells, and nonlinear optical systems [16–20]. Organic semiconducting materials such as, monomer, polymer and some organic compounds are interesting as new materials. Organic compounds based on polymers and monomers capable of accepting electrons are potentially useful as semiconductors in a number of new applications in microelectronic and electronic device technology. Among several organic systems, polymers, monomers and some other organic compounds have recently been shown to be a class of interesting organic semiconductors with interesting electrical and optical properties. In general, polymer and monomeric organic compounds having an extended delocalized π -system have intense absorption in the near infrared region and this information is associated with the charge transport properties of organic semiconducting materials [21–24]. Substituted styrene polymers are among the most important commercial polymers, with a very wide range of applications in products as diverse as glazing, lighting housings, bath tubs and structural adhesives. The success of these polymers in many of the applications is dependent on the versatility of the vinylic monomers in copolymerizing to produce a wide diversity of structures, which can be tailored to produce the desired properties. Of particular interest is the synthesis of copolymers with specific functionality, which can act as a locus for further reactions, or furnish the copolymer with specific chemical and/or physical characteristics. In recent years special attention has been dedicated to polymers based on styrene substituted azetidines, since the presence of azetidine groups in the polymer. Furthermore, the nitrogen in the azetidine groups allows to attach charged species, since it can be easily transformed into a quaternary amine creating cationic centres [25–30]. The ionization constants of the monomeric and polymeric ammonium salts were calculated and, from this, the electrostatic free energies of ionization, ΔG_{el} . The structural features of the anions (size, element, e.g. carbon or phosphorus) were observed to have a significant effect on the ionization constants and ΔG_{el} of the salts. It was also noted that the ionization constants for the monomers and polymers were reduced in an aqueous environment compared to an aqueous-ethanolic environment. In the past decade, controlled radical polymerization (CRP) has been the focus of intense research owing to its versatility and potential commercial applications, such as controlled

molar mass, narrow molecular weight distribution and well-defined architecture and functionalities [31–34].

On the other hand, recently, ionomers have been investigated due to the great interest which is both present from the point of view of basic research in polymer science and from practical point of view of designing new composite materials for advanced technologies [35]. We have evaluated that the electrical properties of insulating polymers can be changed to semiconducting polymers by attaching in the structure of their macromolecules. With this aim, we report here the synthesis of PMAS homopolymer. The electrical and optical properties of the synthesized polymer salts have been investigated by conductivity and optical characterization methods.

2. Experimental details

2.1. Materials

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) was purified by successive crystallizations from chloroform–methanol mixture. 1,4-dioxane, dichloromethane, iodomethane, tetrahydrofuran, ethylacetate (Merck), were analytical grade commercial products and used as received. N-cyclohexylazetidinol was prepared by a method adapted from the literature [36,37].

2.2. Synthesis of *p*-methoxy-3-(1-cyclohexyl) azetidiny styrene (PMAS) monomer

To a well-stirred solution of 100 mM N-cyclohexylazetidinol and 100 mM of *p*-chloromethylstyrene in 20 ml tetrahydrofuran. 80 mM of *tert*-BuOK was added dropwise at room temperature under argon atmosphere (see Fig. 1). After the complete addition of *tert*-BuOK, the reaction mixture was stirred for 7 h at room temperature, then filtered and evaporated with a rotavapour. A yellow product was obtained as a yellow solution [38] (yield 80%).

2.3. Homopolymerization

The preparation of homopolymer of monomer PMAS was synthesized by free radical polymerization in 1,4-dioxane solvent using AIBN as a free radical initiator. The polymer were purified by repeated reprecipitation from 1,4-dioxane/*n*-hexane and then filtered and dried until a constant weight was attained.

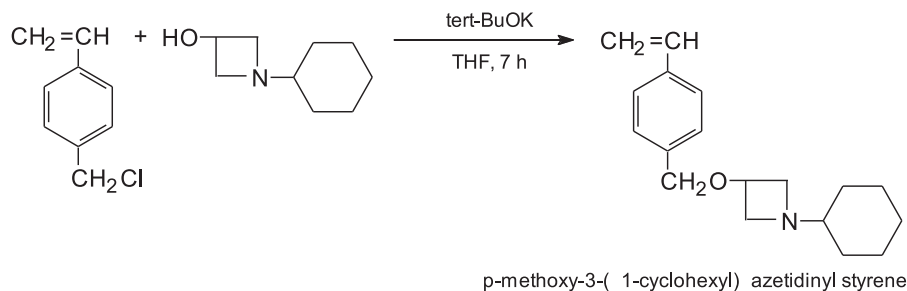


Fig. 1. Reaction scheme of synthesized monomer (PMAS).

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