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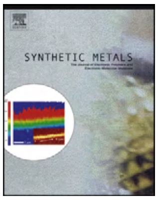

Aliphatic–aromatic poly(azomethine)s with ester groups as thermotropic materials for opto(electronic) applications

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ABSTRACT

We have explored the opto(electronic) and liquid crystal properties of a new series of semiconducting materials based on aliphatic–aromatic poly(azomethine)s. The structures of polymers were characterized by means of FTIR, ^{1}H, ^{13}C NMR spectroscopy, and elemental analysis. UV–vis properties of the thin films of the polymers were investigated on the quartz substrate. The lowest optical energy gap (E_g) at 2.28 eV was found. The polymers were irradiated with a test dose of 2 Gy Co-60 gamma-rays to detect their thermoluminescence properties in the temperature range 25–200 °C. Mesomorphic behavior was investigated via differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) studies. Being into consideration backbone geometry, all polymers, excepted polymer PAZ2, obtained from poly(1,4-butanediol)bis(4-aminobenzoate) and 9-(2-ethylhexyl)carbazole-3,6-dicarboxaldehyde, exhibited liquid-crystalline properties. Moreover, the electrical characterizations of bulk heterojunction (BHJ) and bilayer devices with the following architecture ITO/PEDOT/PAZ:TiO$_2$/Al were investigated. Additionally, devices without and with TiO$_2$ layer such as ITO/PAZ/Al and ITO/TiO$_2$/PAZ/Al were prepared and investigation in the dark and during irradiation with light (under illumination 1000 W/m^2). The sol–gel technique was applied to prepared TiO$_2$ layers and powders. Moreover, impedance spectroscopy at different temperatures for electrical properties measurement was used. Additionally, the compounds were tested using various AFM techniques such as Mode and Phase Imaging and local contrast force–distance curve measurement and roughness (Ra, Rms) along with skew and kurtosis are presented.

1. Introduction

Liquid-crystalline (LC) polymers are investigated broadly and have very wide technological applications due to their self-assembly in the mesophase [1–11]. Applications of such materials range from the production of high-strength materials (fibers) to their use in optical devices [1–11]. For example, Kevlar is applied to make helmets and bullet-proof vests.

Liquid-crystalline mesophases can be formed by polymers with mesogenic moieties in the main chain (MCLCP) or mesogenic units can be bonded to main chain as side groups (SCLCP). SCLCP are sometimes called comb-like LC polymers and exhibit good properties for applications in optically nonlinear devices including optical wave guides and electro-optic modulators in poled polymeric slab wave guides.

Rod like structure of a molecule, consisting of few aromatic rings bonded directly or by various linkages such as ester, imine, azo or ether groups, is known to induce liquid-crystalline (LC) behavior upon heating or in concentrated solution. Among the various linkages, the imine bond is typical [11–33]. These structures built into polymer chains can promote mesophase formation with changes in temperature (thermotropic LC) or at certain concentrations in a suitable solvent (lyotropic LC).

The preparation of thermotropic poly(azomethine)s with moderate melting temperatures has been the goal of several studies [11–36], while lyotropic poly(azomethine)s were not widely investigated [34]. LC poly(azomethine)s with ester groups in the main chain were investigated only in one paper [17], while the polymers having ester and imine bonds in the side chain were described in three papers [22,35,36]. "Banana-shaped" mesogens containing poly(azomethine)s were synthesized and their liquid-crystalline properties were investigated by Choi et al. [17]. Mesophase formation depends on the aliphatic spacer length and substituents on the mesogen ring. In the case of poly(azomethine)s with a shorter spacer ($m = 6$) formation of a nematic phase was observed. Longer aliphatic spacers ($m = 12$) promoted smectic mesophase formation [17].

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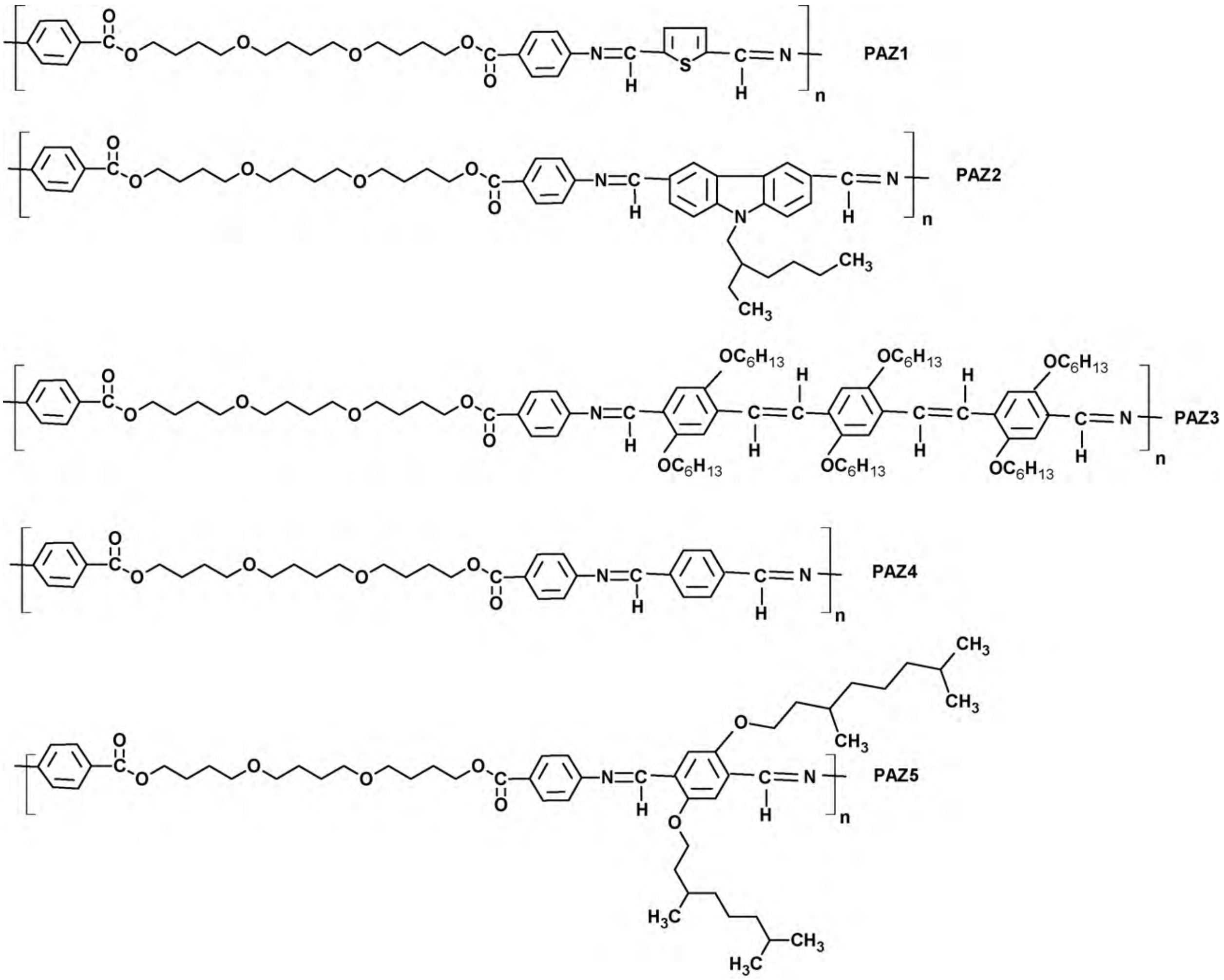

Fig. 1. Chemical structure of the poly(azomethine)s.

Conjugated poly(azomethine)s in neutral (undoped) form are semiconductors or isolators and can be used as polymer light-emitting diodes, polymer lasers, photovoltaic cells and so on [11]. Moreover addition of some substances effecting as redox or acid–base dopant causes dramatic increase of these polymers conductivity changing them into conductive plastics [11]. The phenomenon of polymers conductivity was first described in 1977 by Shirakawa, MacDiarmid and Heeger [37–39] being granted Nobel Prize in 2000 initiated an extensive research devoted to the chemistry and physics of conjugated polymers. Taking into account the electrical properties of the poly(azomethine)s it should be stressed that the conductivities of undoped polymers are low but after doping increase of the electrical properties was observed [40–44]. Ng et al. [40] synthesized poly(azomethine)s with thiophene or furan-moieties and the conductivities of the undoped polymers were $<10^{-9}$ S/cm, while those of the doped with iodine ones were in the range of 10^{-7} to 10^{-6} S/cm. The low conductivity values were attributed to the low degree of conjugation in the polymers caused by non-planarity of the polymer chains [40]. El-Shekeil et al. [41,42] obtained soluble poly(azomethine)s by the condensation of 3,3′-dimethoxybenzidine and 2,6-diamino-3,7-dicyanothien[2,3-f]-4,8-dihydrobenzothiophene with terephthaldehyde and p-diacetylbenzene and the conductivity of the neutral polymers was in the range 10^{-11} to 10^{-10} S/cm. On raising the temperature up to 80 °C, the conductivity increased slightly. At higher temperatures, the polymers showed semiconductor behavior. The polymers were doped with I_2 and concentrated H_2SO_4. At low temperatures, the conductivity of the poly(azomethine)s doped with I_2 and H_2SO_4 was slightly higher than that of the undoped one. At higher temperatures (>80 °C), the conductivity of the doped polymer showed an abrupt increase in conductivity from 10^{-11} to 10^{-7} S/cm [41]. The conductivity of a polyesters containing azomethine linkages was in the range 10^{-9} to 10^{-14} S/cm [43]. Doping of the polymers with silver causes increase in the conductivity many fold (10^{-1} to 10^{-9} S/cm). Electrical and photoelectrical properties of poly(phenyl azomethine furane) thin film devices were investigated by Sharma et al. [44]. We found only one paper where conductance and dielectric anisotropy properties of liquid-crystalline azomethine, that is, salicylaldimine derivative were studied and this compound exhibited large positive dielectric anisotropy was detected and analyzed [45].

In order to investigate the usefulness of aliphatic–aromatic poly(azomethine)s with ester groups for opto(electrical) applications we were synthesized five, new poly(azomethine)s with varied structure of the dialdehyde moiety, as shown in Fig. 1.

By varying the dialdehyde structure we can control the conjugation along the polymer backbone and consequently control the optical and electrical properties of the polymers. In order to investigate the role of the sub-unit of dialdehyde following groups as thiophene, carbazole, stilbene or phenylene were introduced to the poly(azomethine) main chain. Additionally, three of the investigated polymers possessed aliphatic chains in main and side chains. To the best of our knowledge the poly(azomethine)s with thio-