



New copoly(ether sulfone)s containing azobenzene crown-ether and fluorene moieties



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ABSTRACT

New soluble and thermally-resistant copoly(ether sulfone)s, containing both azo-crown-ether and fluorene units, have been synthesized by using the Williamson reaction. In this respect the 4,4'-sulfonylbis(*p*-chlorophenyl) monomer was reacted with two bisphenols, namely 9,9-bis(4-hydroxyphenyl)fluorene and 4,4'-bis(4-hydroxyphenylazo)dibenzo-18-crown-6. The polymers synthesized were confirmed as chemical structures by FTIR and ¹H NMR spectra and characterized by X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, solubility and solution viscosity. The copolymers have been complexed with KSCN and the atomic potassium content was determined by EDX. A study of the photoisomerization process as well as the thermal relaxation of azoaromatic chromophores in the copoly(ether sulfone)s in dimethyl sulfoxide solution and of the corresponding complexes with KSCN was also presented.

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1. Introduction

Aromatic polysulfones are a family of amorphous thermoplastics that possess unique high performance properties as engineering materials, proved by their continuous commercialization since 1965 [1–3]. The aromatic polysulfones are recognized as polymers that have a variety of desirable characteristics including high thermooxidative and dimensional stability, excellent mechanical properties and good hydrolytic stability. There is a growing demand for new materials to meet increased performance requirements in many practical application areas. Thus, considerable research effort has been made toward the modification of known polysulfone structures, as well as the design of polymers with novel structures [4–6].

In recent years different polymers and copolymers containing both photochromic molecules such as azobenzene and crown ether units have been synthesized [7–9]. The crown ethers have enjoyed a considerable interest because of their potential for a large number of applications. Reasons for their current development are based on their powerful and selective complexation properties with a variety of cations [10–12].

Azobenzene and many of its derivatives have been known and studied for a long time. One of the most important and known properties of these chromophores however, is the photochemical *trans* ↔ *cis* isomerization induced by either UV or visible light [13,14]. In azopolymers, the photoisomerization induces conformational changes in the polymer chains, which in turn lead to macroscopic variations in the chemical and physical properties of surroundings and media [15,16]. If a photosensitive moiety, that either it is incorporated into a polymer chain or not, is combined with a crown ether, conformational changes in response to photoirradiation will occur as well as a change in the complexation ability [17]. In the case of photoresponsive macrocyclic systems, it is possible to control the ion-binding and transport processes by an on–off light switch, which would lead to the photoregulation of these processes [18–21]. Kahana et al. reported the synthesis of some polysulfones modified with benzo-18-crown-6 which have been employed to successfully transport of KSCN [22].

In order to combine the advantages of polysulfone polymers with that of crown ethers as complexant molecules and also with photosensitivity of azobenzene units, this paper has as main goal the synthesis and characterization of new copoly(ether sulfone)s, containing the above mentioned moieties. A second goal was the investigation, by UV photoirradiation, of the photosensitive response of both virgin and KSCN complexed copolymers, rendering such copolymers interesting materials for optical applications.

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2. Experimental

2.1. Materials

4,4'-Sulfonylbis(*p*-chlorophenyl) (**M1**, Aldrich) was recrystallized from toluene, mp. 147–149 °C. 9,9-Bis(4-hydroxyphenyl)fluorene (**M2**) and all the solvents used for the reactions (Aldrich) have been used as received. Anhydrous potassium carbonate (Fluka) was dried before use, in vacuum, at 120 °C for 24 h.

2.2. Measurements

Fourier Transform-Infrared (FTIR) spectra were measured on a FT-IR Bruker Vertex 70 spectrophotometer in transmission mode, by using KBr pellets. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a BRUKER Advance DRX 400 MHz spectrometer, in either DMSO-*d*₆ or CHCl₃-*d*₃ as solvent with tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm). Thermogravimetric analysis (TGA) was carried out under an inert atmosphere, by using a TG-DSC-FTIR-MS complex system analysis instrument composed from the following modules coupled to each other: TG/DSC instrument, model STA 449F1 Jupiter (Netzsch, Germany); mass spectrometer QMS 403C Aëolos (Netzsch, Germany); FTIR spectrometer Vertex 70 (Bruker, Germany). Samples of 7–10 mg were heated from 25 °C to 600 °C with a heating rate of 10 °C/min. Temperatures corresponding to 5% (*T*₅) and 10% (*T*₁₀) weight loss, and the temperature of maximum decomposition rate, corresponding to the peak in DTG curve (*T*_{dec}), have been taken as representative criteria when discussing the thermal stability. Differential scanning calorimetry (DSC) measurements were performed with a Pyris Diamond DSC Perkin Elmer USA instrument, at a heating rate of 10 °C/min, under nitrogen atmosphere. The second heating cycle was used to determine the glass transition temperature (*T*_g) of the samples. Softening behavior of polymers was investigated by using polarizing optical microscopy (POM), with an Olympus BH-2 microscope equipped with a THMS 600/HSF91 hot stage. Wide angle X ray diffraction (WAXD) measurements were performed on powder samples, by using a Bruker D8 ADVANCE Diffractometer, using the Ni-filtered Cu-*K*_α radiation ($\lambda = 0.1541$ nm). The working conditions were 36 kV and 30 mA. All the diffractograms were investigated in the range of 1.5 ÷ 40 (2 theta degrees), at room temperature and reported as observed. Chemical composition of the complexed copoly(ether sulfone)s was investigated by an energy dispersive X-ray (EDX) system attached to an environmental scanning electron microscope (ESEM) Quanta 200 at an accelerating voltage of 20 kV. UV–Vis absorption spectra were carried out by using Shimadzu UV3600 or SPECORD 200 Analytik Jena spectrophotometers in 10 mm quartz cells fitted with poly(tetrafluoroethylene) stoppers. Fluorescence spectra were taken from Perkin Elmer LS55 luminescence spectrometer in DMSO solution. The UV irradiation experiments were performed with a 500 W high-pressure mercury lamp (HBO Osram) in quartz cuvettes at room temperature. The appropriate irradiation wavelengths were selected using corresponding filters. The photoreaction extent was estimated by the relation $G = (A_0 - A_t)/A_0$, where *A*₀ and *A*_{*t*} are the absorbances corresponding to trans azo isomer at *t* = 0 and after irradiation time *t*. The solvents used were of spectrophotometric grade purity (Aldrich). The solubilities of the polymers were determined in a series of common solvents like: acetone, methanol, chloroform (CHCl₃), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N*-methyl-pyrrolidine-2-one (NMP). Reduced viscosities (η_{red}) of the polymers were measured by using Schott CT 52 viscometer at a concentration of 0.5 g/dL in NMP at 25 °C.

2.3. Monomer synthesis

The photosensitive monomer (**M3**) containing the azobenzene chromophore and the dibenzo-18-crown-6 moiety was prepared via coupling reaction of phenol with the diazonium salt of 4,4'-diaminodibenzo-18-crown-6 in the presence of triethylamine, according to previously reported methods [9].

2.4. Copolymers synthesis

All the copolymers were prepared by the same procedure, as described below for sample **P1:M1** (0.29 g, 1.0 mmol), **M3** (0.6 g, 1.0 mmol), anhydrous K₂CO₃ (0.16 g, 0.0012 mol) and DMSO (5 mL) were charged into a round bottom flask fitted with thermometer, condenser, nitrogen inlet and outlet and magnetic stirrer. The temperature was increased gradually to 100 °C during 1 h. Then, it was increased quickly to 160 °C and maintained under stirring for 7 h. After cooling to room temperature, the orange reaction mixture was poured into cold water. The precipitated polymer was washed three times with cold water and once with methanol. Finally, the solid was filtered and dried under vacuum at 60 °C for 24 h. Yield 0.75 g, 93%. ¹H NMR (400 MHz, CDCl₃, ppm) δ : 7.92–7.90 (d, 4H, *J* 8 Hz), 7.89–7.87 (d, 4H, *J* 8 Hz), 7.60–7.58 (d, 2H, *J* 8 Hz), 7.47 (m, 2H), 7.15–7.09 (m, 8H), 6.98–6.96 (d, 2H, *J* 8 Hz), 4.27–4.07 (d, 16H).

2.5. Complexation reaction of copolymers **P1–P4**

The copolymers containing crown ether moieties (**P1–P4**) were complexed with KSCN as follows: 0.2 g copolymer was solved in 2 mL DMF with heating. Then, 0.35 g KSCN were added and the reaction mixture was heated at 100 °C under vigorous stirring for 48 h. At the end the reaction mixture looks like a clear solution. After cooling, the reaction mixture was poured into 100 mL abs. methanol and the precipitate formed was filtered, washed with methanol and dried into a vacuum oven at 60 °C overnight.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathway to prepare the polymers was the classical Williamson reaction, in which 4,4'-sulfonylbis(*p*-chlorophenyl) (**M1**) reacted with two bisphenols, namely 9,9-bis(4-hydroxyphenyl)fluorene (**M2**) and 4,4'-bis(4-hydroxyphenylazo)dibenzo-18-crown-6 (**M3**). The ratio between the **M2** and **M3** monomers varied from 0/100 (**P1**) to 100/0 (**P5**) and their corresponding chemical structures are presented in Scheme 1.

The resulting copoly(ether sulfone)s were characterized by using both FTIR and ¹H NMR spectroscopy. As shown in their FTIR spectra (Fig. 1) the presence of the strong absorption band at about 1243 cm⁻¹ indicated the formation of new aryl ether linkage. The absorption bands occurring at 1324 cm⁻¹ and 1151 cm⁻¹ are characteristic of both asymmetric and symmetric SO₂ stretching vibrations, respectively. Also, the spectra showed the presence of two absorption bands at 2925 and 2874 cm⁻¹, corresponding to C–H stretching vibration of CH₂ moieties from **M3** bisphenol. The absorption bands at 3436 cm⁻¹ (O–H) and 1073 cm⁻¹ (*p*-Ph-Cl) showed the presence of terminal –OH and –Cl functional groups.

The chemical structure of the obtained copoly(ether sulfone)s was further identified by the ¹H NMR measurements. Representative ¹H NMR spectra of **P1**, **P3** and **P5** samples, together with the assignments of all the protons are illustrated in Fig. 2. The signals corresponding to the aromatic protons are centered in the region 7.92–6.98 ppm. The spectrum shows a multiplet signal at 7.92–

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