Superlattices and Microstructures 65 (2014) 91–105

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

On the mechanism of electrical conduction in thin films of some polysulfone-poly(alkylene oxide)-poly(dimethylsiloxane) block copolymers

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ARTICLE INFO

Article history:
Received 22 July 2013
Received in revised form 26 September 2013
Accepted 23 October 2013
Available online 29 October 2013

Keywords:
Organic semiconductors
Activation energy
Electronic transport
Thermistor thin films

ABSTRACT

Polysulfone poly(alkylene oxide)-poly(dimethylsiloxane) block copolymers have been prepared by the hydrosilylation reaction of allyl endcapped poly[(ethylene oxide) (propylene oxide)] oligomers with Si–H terminated polydimethylsiloxane in chlorobenzene using an isopropanol solution of hexachloroplatinic (IV) acid as catalyst for hydrosilylation.

The temperature dependences of electrical conductivity and thermoelectric power (Seebeck coefficient) of copolymers were studied using thin-film samples deposited from dimethylformamide (spin coating technique) onto glass substrates. Organic films with reproducible electronic transport and optical properties can be obtained if, after deposition, they are submitted to a heat treatment consisting of several successive heating/cooling cycles within temperature range of (295–485) K. Investigated copolymers presents typical semiconducting characteristics. The values of some fundamental parameters (activation energy of electrical conduction, ratio of carrier mobilities, optical energy bandgap) have been determined. The mechanisms of electronic transport are identified in different temperature domains. Transmission and absorption spectra have been recorded and optical energy bandgaps are calculated from the absorption spectra. The thermistor effect of investigated copolymers is also discussed.

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http://dx.doi.org/10.1016/j.spmi.2013.10.033

1. Introduction

In recent years the organic semiconducting compounds are one of theoretical and experimental areas of the solid-state science and technology [1–5]. Particularly, the investigations of the electronic transport mechanism in organic semiconducting polymers have been much intensified [1–4]. Developing new materials for organic semiconductors and improving the performance of recent prepared organic compounds have been two major research topics over the past two decades. The performance of novel semiconducting devices depends on the particularities of the electronic transport and optical properties of respective organic semiconductors, which strongly depend on their molecular structure. Organic semiconductors show remarkable characteristics (high processability and versatility, as well as compatibility with mechanically flexible substrates, etc.) which can be modified thanks to their chemical structure [2–5]. The mentioned characteristics make organic semiconductors very attractive and promising candidates for a wide range of applications in solid-state device technology (thermistors, Schottkey diodes, organic solar cells, sensors, flexible displays, smart cards, etc.) [5–8].

The understanding of the mechanism of the electrical conduction in polymeric semiconducting films continues to progress, but a unitary theory on this process has not yet advanced [4,6,9,10]. Generally, the obtained experimental results on the electronic transport properties in different organic polymers are interpreted in terms of various models, elaborated for inorganic semiconductors, such as band conduction, qualitative molecular orbital theory (QMOT), variable range hopping conduction and trapping model [9–14].

It is known, that the block copolymers are attractive materials because they join the properties of the corresponding homopolymer systems and also give the possibility to control the physico-chemical properties and processibility in order to obtain novel engineering materials for specific applications. Chemical nature of the copolymers (diblock, triblock, etc.), the length of the blocks, individually or, in relation to one other, have an important role in determining the characteristics of block copolymers and often new properties are generated by the combination of the properties present in homopolymers [10,15,16].

In the last years a considerable number of solid-state devices are made by using thin films of thickness $d < 4$ μm [2,3,16]. It is well know that the structure, electronic transport and optical properties of a certain organic semiconductor in thin films strongly depend on the thickness deposition method and preparation conditions [3,9,10]. Therefore, it is important to establish a correlation between deposition technique and values of characteristic parameters for a great number of thin-film samples prepared from a certain method [8–11].

Generally, by studying the electronic transport and optical properties of the organic polymers, very useful information can be obtained about the mechanism of electrical conduction, mobilities of the charge carriers, predominant scattering mechanism, etc.

In a series of previous papers [9,10,17] we have investigated the electronic transport (temperature dependence of electrical conductivity and Seebeck coefficient) and optical (transmission and absorption spectra) properties of some polysulfone block copolymers containing polydimethylsiloxane. In these copolymers the soft segments of polydimethylsiloxane were incorporated into the rigid high molecular weight polysulfone [17]. All studied polymers exhibited semiconducting behavior. The values of some characteristic parameters (thermal activation energy of electrical conduction, concentrations and mobilities of charge carriers, etc.) have been correlated with their molecular configurations.

In the present paper, we extended these studies on a class of six recent synthesized block copolymers, namely polysulfone-poly(alkilene oxide)-poly(dimethylsiloxane). Our aim is to establish the deposition conditions in order to prepare samples having homogeneous solid-state structure, uniform thickness on large area of the substrate and a good substrate adherence. We also found the experimental conditions for obtaining samples with reproducible properties. We have established some correlations between molecular structures of the examined copolymers and the values of their characteristic parameters (activation energy, ratio of carrier mobilities, etc.).

The mechanism of electrical conduction in the studied copolymers is also discussed. The performed experiments indicated that temperature dependence of the electrical conductivity and transmission