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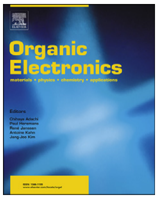

Direct evidence for effect of molecular orientation on thermoelectric performance of organic polymer materials by infrared dichroism

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ABSTRACT

A direct evidence by infrared dichroism is reported for the first time for the effect of molecular orientation on thermoelectric (TE) performance of organic polymer materials. The preferred orientation was induced by mechanical uni-axial stretching of the films of neat polyaniline (PANI) and its nanocomposites with reduced graphene oxide (rGO) or multi-walled carbon nanotube (MWCNT). Five characteristic bands of Fourier transform infrared (FTIR) spectra were chosen, and quantitative investigations were carried out using the dichroic ratios measured by polarized FTIR spectra. The influences of draw ratio and content of inorganic carbon nanoparticles were taken into account. The results show that the TE performance (including anisotropic TE function) can be conveniently tuned by polymer molecular orientation induced by mechanical stretching, which shed light on the understanding of molecular mechanism towards structure-TE performance relationship, and will speed up the applications of organic polymer TE materials.

1. Introduction

Thermoelectric (TE) materials are green energy materials, which are capable of realizing direct energy conversion between heat and electricity under low temperature gradients. Compared with other new energy technologies, TE devices have several advantages, including no moving parts, no noise and long operating lifetime [1]. To date, TE materials have been widely used not only in military, aerospace and other high-tech fields, but also in cogeneration, medical thermostat, micro sensors and other civil areas [1]. Recently, organic TE materials, mainly conducting polymers [2] and their composites [3], have attracted great interest. Because their thermal conductivities are low (usually 0.1–0.5 W m^{-1} K^{-1}) and almost independent of inorganic fillers, power factor ($S^2\sigma$) rather than figure of merit ($ZT = S^2\sigma T/\kappa$) has been often adopted to evaluate their TE performance, where σ, S, κ and T stand for the electrical conductivity, thermopower or Seebeck coefficient, thermal conductivity and absolute temperature, respectively [2–4].

Conducting polymers, including polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy), have been widely used in energy storage and conversion, such as super capacitor [5], and TE materials [6]. Construction of ordered polymeric structures has been regarded as an effective way to simultaneous enhance the electrical conductivity and the Seebeck coefficient (i.e. significant increase in the TE performance), for example, chemical stretching by either organic solvent treatment of pure polymers [6b] or in situ polymerization on inorganic nanoparticle surfaces of conducting polymer/graphene or carbon nanotube (CNT) composites [3,6c–e]. In these studies, Raman, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) have been used to study the interfacial interactions and levels of doping or oxidization. Ultraviolet–visible (UV–vis) spectra were collected to investigate the polaron localization and delocalization as well as the conformational transformation. In addition, the power factor for multilayer films of PANI/graphene/PANI/CNT composite constructed by layer-by-layer assembly was reported to reach 1825 μW m^{-1} K^{-2} [6f]. Nevertheless, direct proof or evidence for the enhancement of TE performance by formation of orientation or ordered structure of polymer macromolecules is scarce, except few X-ray diffraction (XRD) studies. For example, Toshima et al. [7] studied XRD patterns of the doped stretched PANI films and related the results with the enhanced TE performance.

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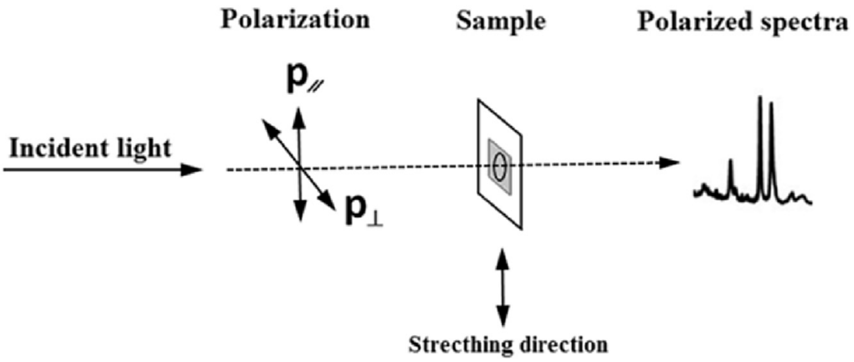

Fig. 1. Schematic illustration of infrared dichroism measurements.

Infrared dichroism is a powerful technique to quantitatively study polymer chain orientation or ordered structure at molecular level, which is effective, convenient, and non-invasive [8]. Indeed, it has been extensively applied to study the macromolecular orientations for film stretching [9] or fiber drawing [10] of polymers and their composites. For example, we have developed an attenuated total reflection (ATR) infrared dichroism technique for the investigation of the orientation of polyamide 6/clay nanocomposite fibers to overcome the difficulty of fiber sample preparation in transmission infrared testing [10]. In addition, we studied the macromolecular orientation changes including main chain and side groups of syndiotactic polystyrene (sPS) [9a,9b] or amorphous polystyrene (aPS) [9c], hard- or soft-segment of polyurethane (PU) [8d] for sPS/CNT [9a,9b], aPS/clay [9c] or PU/clay [9d] nanocomposite films.

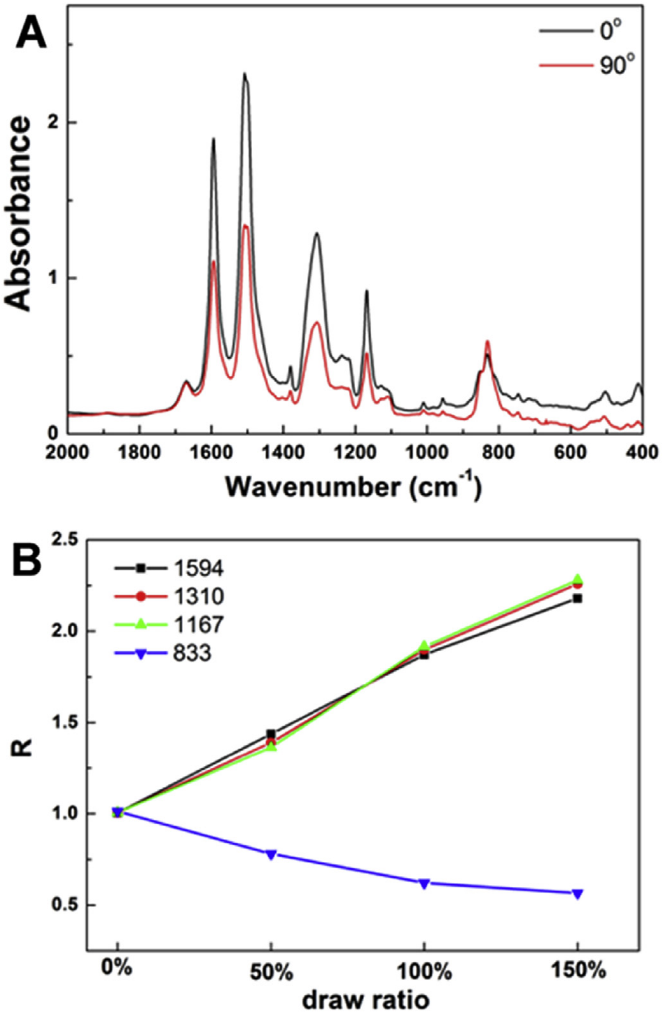

Fig. 2. (A) Polarized FTIR spectra of stretched pure PANI film at draw ratio of 100% with polarized angles of 0° and 90°, respectively. (B) The measured infrared dichroic ratios (R) for the four bands at different draw ratios.

Being a major topic of fundamental science, polymer molecular orientation is a main factor to define the macro-scale properties of polymer materials. Thus, a deep understanding of the relationship between orientation and property or function is of great importance for designing new polymeric materials with superior physical properties or functions. Unfortunately, no infrared dichroism studies have been performed in TE materials of organic polymers and their composites so far. Therefore, it is vital and urgent to carry out these studies to deepen our understandings towards the relationship between orientation and TE performance at the molecular level. In this investigation, by infrared dichroism, we report a direct evidence for the effect of molecular orientation on TE performance (including anisotropic TE performance) of neat PANI, PANI/reduced graphene oxide (rGO) and PANI/multi-walled CNT (MWCNT) nanocomposite films. The stretching-induced anisotropic TE performance has been investigated as well.

2. Experimental

2.1. Reagents and materials

RGO sheets were kindly provided by Professor Wentao Zhai at the Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences. MWCNTs (Baytubes C 150 P) were purchased from Bayer Co., Ltd. PANI (emeraldine base) with an average molecular weight of about 100,000 was bought from Sigma–Aldrich, with a purity of higher than 98%. All of the other reagents, including N-methyl-2-pyrrolidone (NMP) and hydrochloric acid (HCl), were of analytical reagent (A.R.) pure grade, and used without further purification.

2.2. Preparation of self-standing films of PANI/rGO or PANI/MWCNT nanocomposites, and neat PANI

The nanocomposite films were prepared by a simple solution-mixing method conducted in NMP solution. Typically, 4.5 mg rGO (or MWCNT) was first dispersed in 10 mL NMP aided by ultrasonication treatment. Then, 145.5 mg PANI was added into the above dispersion. The mixed solution kept stirring for 72 h to complete the blending process. Subsequently, the mixed solution