Polymer 53 (2012) 4843–4854

Contents lists available at SciVerse ScienceDirect

Polymer

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

Conformational structure and aggregation behavior of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] in toluene/nonane solutions

Jean-Hong Chen*, Ching-Wan Chiu, Lung-Chuan Chen, Shin-Yi Lai, Chia-Cheng Lee

Department of Materials Engineering, Kun Shan University, Tainan 71003, Taiwan, ROC

ARTICLE INFO

Article history:
Received 28 March 2012
Received in revised form
10 August 2012
Accepted 21 August 2012
Available online 30 August 2012

Keywords:
Conformational structure
Aggregation behavior
Photophysical properties

ABSTRACT

We identified the conformational structure, aggregation behavior and photophysical properties of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in various toluene/nonane solutions dependent on nonane content. In dilute solution region (*e.g.*, below the overlap concentration, c^*), static light scattering (SLS) revealed that the stiffness of MEH-PPV decreased as nonane content was increased, attributed to a stronger interaction force between MEH-PPV backbones. However, MEH-PPV chains presented a more extended-wormlike conformational structure in toluene. Therefore, a looser intermolecular micellelike aggregates occurred easily between the ether side chains of MEH-PPV at the concentration exceeded the overlapping concentration in toluene and toluene/nonane solutions. Nevertheless, at higher nonane content, the micellelike aggregates were became highly compacted by the π–π complex force between MEH-PPV backbones, dominating the dynamic behaviors and photophysical properties of MEH-PPV in toluene/nonane solution. These results proved that two types of segmental association with distinct stability were identified for the MEH-PPV/toluene/nonane solutions upon prolonged aging. The highly stable, which could not be disrupted by heating, was attributed to the interaction force between ether side chains of MEH-PPV in both solutions. Other type was a weaker affinity force through π–π complex, which could be disrupted thermally, making the micellelike aggregates more compact to form the network structure in MEH-PPV-enriched at higher nonane content.

1. Introduction

Π-Conjugated polymers constitute a family of organic optoelectronic materials for applications such as light-emitting diodes and photovoltaics [1–6]. To realize its potential application, researchers have investigated molecular parameters that dictate photophysical behaviors of conjugated polymers. In this work, we investigate relationship between local structure of conjugated polymers, controlled by tuning local polymer–solvent interactions and their aggregation behavior. The poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, see Scheme 1 for its chemical structure) is frequently used as model material to gain basic understanding of the photophysics of a typical conjugated polymer [3,7–9]. Moreover, spectroscopic studies have indicated conjugated polymers undergo interchain aggregation in the solution state, even at large dilution [10–15]. The intrinsic chain stiffness coupled with the amphiphilic nature (due to the solubility difference between the backbone and the side chain of conjugated polymer) and π–π interaction makes the solution behavior of conjugated polymers highly complex. Conjugated polymer chains are seldom completely dispersed in solution, even at large dilution (*e.g.*, below the overlap concentration, c^*). Abundant experimental studies have demonstrated the existence of sub-micrometer or micrometer micellelike aggregates in the solutions [16], and their presence drastically modifies the photophysical properties of the system [10,17].

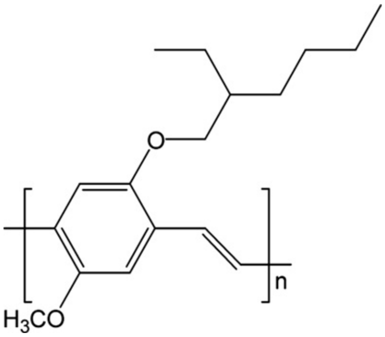
The conformational structure and aggregation behavior of conjugated polymers in solution also exhibit strongly time dependence due to the slow dynamics to attain equilibrium or metastable equilibrium state upon polymer dissolution. Such time dependence is sometimes manifested by slow gelation, where the initially viscous liquid solution transforms into gel upon prolonged aging at ambient or subambient temperatures [13–15,18–21]. This gelation phenomenon is prevalent among different types of conjugated polymers (*e.g.*, poly(phenylene ethynylene)s [18], poly(phenylenevinylene)s [19,20], polythiophenes [21,22], and polyfluorenes [13,15]), but the underlying mechanism and gel structure may vary from system to system.

Recently, several studies have addressed the factors controlling the conformational structure of conjugated polymers in solution

---

* Corresponding author. Tel.: +886 6 205 5138; fax: +886 6 205 0493.
E-mail address: kelvench@mail.ksu.edu.tw (J.-H. Chen).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.08.048



Scheme 1. Chemical structure of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).

[23–28]. The delocalization of the conduction electrons in conjugated polymer systems and steric effects of the side chains serve to extend the polymer chain in the solution. Aime et al. found the steric effect of the side chains induced significant expansion of the polymer chains [23]. The fact such a steric effect played a strong role in the conformation of conjugated polymers has also been confirmed experimentally from the solution properties of poly(-alkythiophenes) [24–26]. Gettinger et al. reported increasing the size of the solubilizing side chains increased the intrinsic persistence length of the poly(phenylenevinylene) (PPV) backbone, and the resulting change in chain stiffness exerted a strong effect on the photoluminescence of the polymer [27]. Recently, we reported the interchain aggregation behavior of poly(2,3-diphenyl-5-hexyl-1,4-phenylenevinylene) (DP6-PPV) bearing hexyl side chains in the solutions with chloroform and toluene [28]. We revealed the aggregation of DP6-PPV in chloroform and toluene yielded network aggregates whose internal structure could be characterized by certain fractal dimensions. Two types of segmental association with distinct stability were identified for the toluene solution. The highly stable segmental association was attributed to the π–π complex already present in the DP6-PPV powder, while the other type of labile segmental association was ascribed to the poor affinity of the aliphatic side chains of DP6-PPV to toluene.

However, the incorporation of the longer decyl side chains in poly [2,3-diphenyl-5-decyl-1,4-phenylenevinylene] (DP10-PPV) should impose a stronger steric hindrance (relative to that of DP6-PPV) against the interchain aggregation of the polymer; therefore, the aggregate structure of DP10-PPV differed from that of DP6-PPV. The conformational structure of DP10-PPV in the dilute regime, where the interchain aggregation was not significant, has been investigated by means of static light scattering (SLS). It indicated although DP10-PPV displays a weaker tendency toward aggregation than DP6-PPV, this polymer was able to aggregate in semi-diluted solutions, generating aggregates with hydrodynamic radii of sub-micrometer to 10 μm in size depending on the concentration of the semi-diluted solutions. However, these aggregates are loosely bound by the micellelike association of segments that can be easily disrupted by moderate heating [14,20–22]. Recently, the gel formation of MEH-PPV in dichlorobenzene solution by addition of nonane was reported by Wang et al. [19]. They proposed the gel formation of MEH-PPV caused the interchain physical cross-linking by interaction between neighboring alkoxy side chains with alkane as a bridge. The intrachain aggregates of MEH-PPV in solution have also been found to form during the gel formation, due to the adoption of a contract coil conformation in the solution as the nonane is added. However, the branch ether side chain possibly disrupts the interchain aggregation/π–π complex between the MEH-PPV chains and may enhance the solubility of the polymer in the solution. These issues are important to understand the optical and electro-optical properties of conjugated polymers dependence on the solubility of the mixed solvents that is a mixture of a poor solvent nonane in toluene, therefore, the conformation structure and aggregation behavior of conjugated polymers in a mixed solution is highly complex. Apart from the effects of the conventional parameters such as solvent quality and concentration, the structure also displays strong time dependence as the dynamics of the system to attain the equilibrium or the metastable equilibrium structure upon the polymer dissolution are usually very slow. Some recent studies have demonstrated even the presence of π–π complex in the solution greatly influenced the aggregation behavior and photophysical properties of the polymer in solution [14,15,22,28].

The present study, we consider toluene is a relatively good solvent, whereas nonane is poorer one for MEH-PPV. The former solvent is a poor and good solvent, respectively, for the ether side chains and backbone of MEH-PPV [16], whereas the latter one is a good and poor solvent for the ether side chains and backbone of MEH-PPV, respectively [19]. The influence of nonane on the conformational structure, gelation behavior and photophysical property of MEH-PPV in toluene/nonane mixed solutions will be discussed in connection with the existence of two types of segmental associations; an unstable interaction force of π–π complex between MEH-PPV backbones, which is dissipated by heating [13–15,22,28]. Other one is more stable micellelike segmental association could be ascribed to the strong affinity between the ether side chains of MEH-PPV in solutions [16]. For clear discussion of the study, we will realize the conformational parameters of MEH-PPV in dilute toluene solutions ($c < c^*$) at 50 °C deduced by static light scattering (SLS), on the other hand, the aggregation, gelation and photophysical behaviors of the polymer over a broad concentration range (from $c < c^*$ to $c > c^*$) was probed by dynamic light scattering (DLS), UV–vis absorption (UV–vis) and photoluminescence (PL) spectra.

2. Experimental section

2.1. Materials and solution preparation

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) was obtained from American Dye Source Inc. The weight-average molecular weight (M_w) and the polydispersity were *ca.* 1330 kg/mol and 4.5, respectively, as determined via size exclusion chromatography (SEC) using polystyrene standards in THF at 50 °C. The polymer solutions with various concentrations were prepared by dissolving appropriate amounts of the polymer in various ratio of toluene/nonane (100/0, 90/10, 80/20, and 70/30 vol %) mixed solvents. The mixtures of polymer and solvent were stirred at *ca.* 70 °C for 4 h, where macroscopically homogeneous solutions were observed by the naked eye after the stirring and then filtering through 0.45 μm PTFE filters (Millipore) to remove dust in the dilute solutions ($c < 0.006$ mg/mL). Polymer solutions used for static light scattering measurement at dilute solution; *e.g.*, the concentrations below the critical overlap concentration c^* (c^* is *ca.* 0.103 and 0.135 mg/mL for toluene and 70/30 vol% toluene/nonane solutions, respectively, as estimated via $c^* \sim 3M/4\pi N_A(R_g)^3$, with M being the molecular weight of the polymer and R_g the radius of gyration of MEH-PPV in toluene and 70/30 toluene/nonane diluted solution, are *ca.* 78.0 and 65.8 nm, respectively, at 50 ± 0.1 °C).

Static light scattering. The SLS measurement were carried out using a commercial light scattering spectrometer (ALV/CGS-3 with an ALV/LSE-5003 multiple-τ digital correlator) with a JDS-Uniphase solid-state He–Ne laser output power *ca.* 22 mW at an operating wavelength of 632.8 nm as the light source. The reciprocal reduced scattering intensity, $Kc/\Delta R_\theta$ was derived, where c is the concentration of polymer and ΔR_θ is the excess Rayleigh ratio (R_θ(solution) − R_θ(solvent)) where R_θ is the Rayleigh ratio at a scattering angle θ.