Effect of chain conformation on micro-mechanical behaviour of MEH–PPV thin film

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Abstract. The morphology, photoluminescent properties and micro-mechanical character of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH–PPV) thin films prepared from toluene (T film) and chloroform (C film) were studied by transmission electron microscopy (TEM), absorption, photoluminescence spectrophotometry and nanoindentation test. The morphological feature of worm-like entities which appeared in T film was ~10–20 nm in length and 3–5 nm in width. The C film displayed the continuous cotton fibre-shaped morphology. In contrast with C film, the band-edge absorption and maximum emission for T film shifted to the longer wavelength. An analysis from TEM photograph, absorption and photoluminescence spectra indicated that different chain conformation presented in these two kinds of films. The nanoindentation test showed that the elastic modulus and indentation hardness of T film under the same experimental parameter (load: 50–200 μN , loading rate: 20 $\mu\text{N/s}$ and holding time: 20 s) decreased by 33.3 ± 0.3 and $8.9 \pm 0.5\%$, respectively comparing with C film. In addition, critical bending radius of these two films based on the flexible base was also evaluated from the obtained experimental results.

Keywords. MEH–PPV; morphology; nanoindentation; mechanical properties; chain conformation.

1. Introduction

Aggregated structure of macromolecular chain in π -conjugated polymers is one topic of great significance, since it determines the performance of the materials when used as components of organic electrooptical devices (Nguyen *et al* 2000; Jeng *et al* 2005). An impressive number of research groups have expended considerable efforts in attempting to probe into the effects of chain aggregation on the spectroscopy, excited state dynamics, emission yields and charge transport characteristics of these materials (Traiphol *et al* 2006). One of the most extensively studied classes of π -conjugated polymers for optoelectronic applications is poly(*p*-phenylene vinylene) (PPV) and its derivatives because of its stability, easy processability and good electrical and luminescent properties (Nguyen *et al* 1999). The research of chain conformation of MEH–PPV dissolved in different solvents begins early. For example, tetrahydrofuran and dichloromethane have a preferential salvation of the lateral groups, resulting in coiled chain conformation, while chlorobenzene, xylene and toluene mainly solvate MEH–PPV backbone, resulting in straight chain conformation (Nguyen *et al* 1999). The different chain conformation in solution can be ‘memorized’ by the polymer film through the spin-coating technic and show different chain aggregated structure in thin film (Liu *et al* 2000; Shi *et al* 2000). So the investigation on an aggregated structure and the

micro-mechanical property of spin-coating films prepared from dichloromethane and toluene can increase our understanding for the interrelation between the macromolecular chain conformation and the micro-mechanical property, results of which may provide experimental evidence for the application of conjugated polymers in photoelectric field.

Recently, nanoindentation is used to study mechanical property of polymers extensively, even including surface mechanical characterization (Frontini 2007; Fasce *et al* 2008). Mechanical properties of polymers on microscale have been successfully linked to their structure, macroscopic creep behaviour and Young’s modulus (Tranchida *et al* 2009). Shen *et al* (2006) probed into the hardness and modulus of different crystal forms of nylon 6 by nanoindentation technique (Shen *et al* 2006). Moniruzzamana *et al* (2006) investigated reversible photo-mechanical properties of azobenzene-based polymer by nanoindentation. They demonstrated that *trans-cis* isomerization of the chromophores in the polymer chains resulted in the difference of mechanical properties (Moniruzzamana *et al* 2006). Flores *et al* (2000) discussed crystalline polymers which had different chain-folded and chain-extended morphologies (Baltá Calleja *et al* 2000; Flores *et al* 2000). Tranchida *et al* (2009) investigated several PE samples with different degrees of crystallinity, who successfully linked the mechanical properties of the semicrystalline polymeric material with its microstructure through nanoindentation experiments (Tranchida *et al* 2009). Although a number of research groups focus on correlation between different microstructure of polymers and local mechanical properties by

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nanoindentation, no one reported solvent-induced mechanical property of thin film of π -conjugated polymers.

In this paper, we report the morphology, photoluminescent behaviour and micro-mechanical properties of MEH-PPV thin films prepared from toluene and chloroform in order to understand better the correlation between an aggregated structure of conjugated polymer and micro-mechanical properties.

2. Experimental

2.1 Sample fabrication and characterization

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was prepared using an improved synthesis method (In order to increase solubility of MEH-PPV in organic solvent, the polymerization inhibitor (4-methoxyphenol) was added in reaction system. The 4-methoxyphenol was used in amounts (1 mol%) to control molecular weight and to circumvent the problem of self-condensation of 4-tert-butylbenzyl bromide.) described by Neef and Ferraris (2000). MEH-PPV ($M_n = 85,000$ g/mol, $M_w/M_n = 2.57$) was dissolved in toluene and chloroform with a concentration of 30 mg/ml.

MEH-PPV thin films were prepared by spin-coating on quartz substrates. Before preparing the thin film, quartz substrates were cleaned ultrasonically in acetone and isopropanol for ten min, respectively and were spin-coated using a spin coater (Optical Dynamic Corporation, Louisville, KY) at 1800–2000 rpm to obtain MEH-PPV films. The solvent was allowed to evaporate in the dark at room temperature for one day. Film thickness measurement was obtained with an Alpha-Step IQ surface profilometer (XP-2, American Ambilab) of vertical resolution equal to 10 nm. Transmission electron microscopy (TEM) studies were performed by JEM-2010 instrument with an acceleration voltage of 200 kV. UV-Vis and fluorescence spectra were recorded on UV-3100 spectrophotometer and RF-5301PC spectrofluorophotometer, respectively.

2.2 Nanoindentation experiment

The micro-mechanical behaviour of MEH-PPV films was determined by nanoindentation experiments, which were performed using a nanoindenter (Triboindenter, American Hysitron) with a diamond probe. A diamond Berkovich indenter with a tip radius of 50 nm and a maximum load ranging from 50 to 200 μ N were used for evaluating the effective elastic modulus and hardness of MEH-PPV films. A trapezoidal loading function was used in all the experiments. The contact load was first increased to a set maximum value at a constant rate, keeping at this level for a fixed period (holding time) and finally, decreased to zero at the same rate. In extreme cases of viscoelasticity, a 'nose' appears in the unloading load-displacement curve (Tsui and Pharr 1999; Chudoba and Richter 2001; Elmustafa and Stone

2002; Feng and Ngan 2002; Ngan and Tang 2002; Tang and Ngan 2003). The 'nose' phenomenon can overcome by performing the nanoindentation at a high unloading rate with long holding time (Elmustafa and Stone 2002). In our experiment, the holding time was fixed at 20 s and the loading and unloading rate were all fixed at 20 μ N/s to avoid the 'nose' phenomenon.

The indentation depth should not only be deep enough to minimize the surface effect, but also should be less than 10% of the film thickness, when the sample is mounted on a hard substance (Geng et al 2005; Jee and Lee 2010). Therefore, appropriate applied load and loading rate were applied to thicker MEH-PPV films in this work and the thickness of T and C films are 1350 and 1310 nm, respectively.

3. Results and discussion

3.1 Chain aggregated structure of T and C films

The absorption and photoluminescence spectra of T and C films are shown in figure 1. The maximal absorption spectra of the two films have a relative sharp peak at 492 and 493 nm with the band-edge absorption at 585 and 600 nm, respectively. In contrast with C film, the band-edge absorption of T film with red shift of 15 nm is attributed to the straight main chain conformation, which increases the effective conjugated chain of MEH-PPV molecule. This phenomenon indicates that the chain conformation of MEH-PPV molecule survives from solution to spin-coating film. The maximum PL peak of the C and T films appear at 578 and 586 nm with shoulder peak 623 and 630 nm, respectively. A number of evidences have suggested that the presence of a particular emission at wavelength $\lambda_{em} = ca$ 640 nm from aggregated chains in solution-cast MEH-PPV films, which competes with single-chromophore emission $\lambda_{em} = ca$ 590 nm (Collison et al 2001; Tan et al 2002). Hence, increasing

Figure 1. Normalized absorption and emission spectra of T film (red line) and C film (black line) (excited wavelength: 490 nm).

Figure 2. Representative TEM bright field image of T film (a) and C film (b).

photoluminescent peak around 590 nm in T film is correlative with single chain conformation of MEH-PPV molecule, which indicates that the effective conjugation length of MEH-PPV molecule in T film increases when compared with C film and it also suggests that the polymer chain extends more in T film. This result can be further unequivocally confirmed by TEM images study.

Figure 2 shows TEM images of the T film (a) and C film (b). The continuous cotton fibre-shaped morphology appears in TEM image of the C film. The most prominent morphological feature is the abundance of worm-like entities, which are ~ 10 – 20 nm in length and 3 – 5 nm in width for the T film. It shows a good agreement with previous research (Petrella *et al* 2004). The different morphological features of MEH-PPV thin films are correlative with main chain conformation. It is reasonable that the cotton fibre-shaped morphology arises from the coiled chain conformation and the worm-like morphology may be correlative with the straight chain conformation. An analysis from TEM photograph, absorption and photoluminescent spectra indicates that the coiled and straight chain conformations are in C and T films, respectively.

Figure 3. Force–displacement curves of C (solid line) and T films (dash line) under applied load of 100 and 200 μN (loading rate: 20 $\mu\text{N/s}$; holding time: 20 s).

3.2 Effect of chain conformation on micro-mechanical behaviour of MEH-PPV film

The force–displacement curves of T and C films under the same experimental parameter except load are shown in figure 3. According to the force–displacement curves, we find the maximum indentation displacement of the T film increases to 18 nm compared with the C film during loading segment in figure 3(a) (B1 and B). Furthermore, the T film shows larger deformation than the C film under the same holding time and loading force (here, $BC = 13$ nm, $B1C1 = 18$ nm, respectively). In addition, the residual indentation depth (A1D1) of the T film is nearly consistent with the C film (AD) after unloading. In order to eliminate the effect of different loading force on micro-mechanical behaviour of T and C films, we choose the applied load: 50, 80, 100 and 200 μN (here we only provide the force–displacement curves with loads of 100 and 200 μN), all the results prove that the changing trend of micro-mechanical behaviour of

T and C films are similar. The difference between them is that a change in the displacement at loading and holding periods increases with increasing loading force. When loading force is increased, the estimated value of the elastic modulus and hardness from higher loading force will deviate from the true value because of the effect of substrate, which will be discussed in the following section.

The elastic modulus and hardness of T and C films are obtained by analysing the unloading part of the force–displacement curve (figure 4). All the experiments are operated under the same condition (load: 50–200 μN ; loading

rate: 20 $\mu\text{N/s}$; holding time: 20 s). To reduce experimental error, at least five indentations were made for each specimen.

Figure 4(a) shows relationship between applied load and effective modulus. The elastic modulus of T and C films are nearly constant, when the applied load changes from 50 to 100 μN ; when applied load is increased to 200 μN and elastic modulus increases distinctly. According to previous literature, the indentation depth should be limited to less than 10% of the film thickness (Geng *et al* 2005), thus elastic modulus and hardness can be thought to be exact. For the indentation load less than or equal to 100 μN , the elastic moduli are 4.5 ± 0.2 and 6.75 ± 0.18 GP for T and D films, respectively which is constant and can be thought to be the true value. The high elastic modulus for the applied load at 200 μN may be due to the effect of substrate (Geng *et al* 2005). As seen in figure 3(b), increasing the load leads to a larger indentation depth, which has exceeded 10% of film thickness, so the effect of substrate cannot be neglected and leads to a higher elastic modulus. The hardness of T and C films has the similar trend compared with the elastic modulus as depicted in figure 4(b), the hardness of T and C films are 0.305 ± 0.015 and 0.335 ± 0.017 GP, respectively. The hardness of these two films has a relatively small change. In contrast with C film, the elastic modulus and hardness of T film decrease by 33.3 ± 0.3 and $8.9 \pm 0.5\%$, respectively. As we can all see, the elastic modulus is dramatically different between C and T films. A stronger atomic or molecular bonding can result in a higher Young's modulus (Wang and Shi 2000). Since the molecular chain in D film is coiled, the molecular bonding in C film may be stronger than T film, which may result in a higher elastic modulus for C film.

Figure 4. (a) Relationship between applied load and effective elastic modulus at a loading rate of 20 $\mu\text{N/s}$ with 20 s holding period and (b) relationship between applied load and hardness at a loading rate of 20 $\mu\text{N/s}$ with 20 s holding period.

3.3 Effect of MEH–PPV chain conformation on critical bending radius

The critical bending radius is a critical condition for application as flexible displays. The critical bending radius based on the flexible base is evaluated from the obtained mechanical parameters. The thickness of the hypothetical flexible is 100 μm and the analysis of critical bending radius is based on (1) (Suo *et al* 1999):

$$r_c = \frac{E_f (2 + \pi) (d_f + d_s)}{2\sqrt{3}H_{IT}}. \quad (1)$$

In equation (1), d_f is the thickness of MEH–PPV films, d_s the thickness of base film. E_f the Young's modulus and H_{IT}

Table 1. Critical bending radius of MEH–PPV thin film prepared from toluene and chloroform.

Solvent	Young's modulus (GPa)	Indentation hardness (GPa)	Thickness of MEH–PPV film (nm)	Thickness of base (μm)	(mm)
Chloroform	6.75 ± 0.18	0.335 ± 0.017	1310	100	3.04 ± 0.22
Toluene	4.50 ± 0.20	0.305 ± 0.015	1350	100	2.22 ± 0.21

the indentation hardness. The critical bending radius of the MEH-PPV film prepared by different solvents is shown in table 1.

The critical bending radius (r_c) of the T film decreased a lot in contrast with the C film. The relative comparison of the critical bending radius can offer us useful information for flexible display. The result indicated that MEH-PPV thin film prepared from toluene can bear a larger bending stress.

4. Conclusions

In summary, MEH-PPV thin films prepared from toluene and chloroform exhibit distinct morphology, photoluminescent properties and micro-mechanical character. The different macromolecular chain conformation is responsible for inducing these results. Furthermore, elastic modulus, hardness and critical bending radius of the MEH-PPV thin film prepared from toluene decreases compared with the thin film prepared from chloroform under the same experimental parameter.

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