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Synthesis of Exfoliated MEH-PPV /Clay Nanocomposites

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Abstract: The synthesis of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) in the presence of organophilic montmorillonite (OMMT) was reported and the exfoliated MEH-PPV/OMMT nanocomposites was obtained by controlling the ratio of the monomer to the OMMT.

Keywords: MEH-PPV, nanocomposite, *in-situ* polymerization.

Currently, a great deal of attention is being paid to the study of organic and inorganic nanoscale hybrid materials. There were several works[1-6] on the investigation of the nanocomposites of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene), MEH PPV, a semiconducting polymer with a conjugated backbone. Different kinds of inorganic particles, including CdSe[1-3], SiO_2, TiO_2[4], porous silicon[5], porous gallium phosphide[6], and layered silicates[7] were integrated with the polymer. For polymer/layer silicate composites, two different synthetic strategies, *i.e. ex-situ* route and *in-situ* route could be used to integrate the polymer with inorganic matrixes. Essentially, the *ex-situ* route is a physical intercalating process while the *in-situ* route is polymerization reaction. Lee *et al.* have prepared MEH-PPV/OMMT intercalated composite using *ex-situ* approach and reported that could lead to both high electroluminescence and photo luminescence properties[7]. So far the *in-situ* synthesis and the properties of MEH-PPV/ OMMT nanocomposite have not yet been reported.

Experimental

We adopted the Gilch's method[8] to synthesize MEH-PPV/clay nanocomposite as shown in **Scheme 1**. *p*-Xylene was distilled from sodium benzophenone *prior to* use. The organophilic montmorillonite(OMMT) was provided by Key Laboratory of Engineering Plastics, CAS[9]. 1,4-Dibromo-2-methoxy-5-(2'-ethylhexyloxy)xylene **3** was prepared as described by Neef and Ferraris[10].

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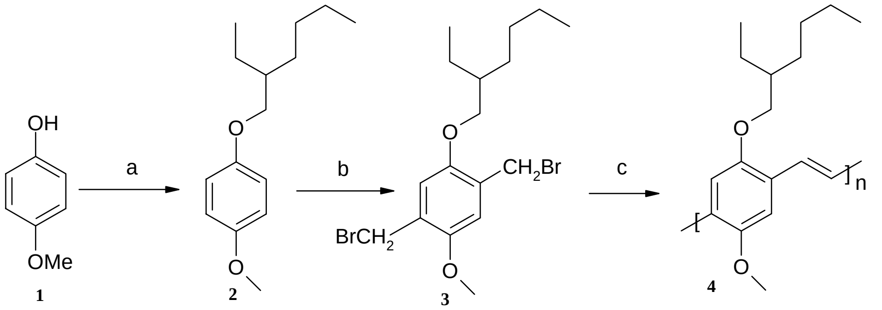
Scheme 1 Gilch route for MEH-PPV polymerization



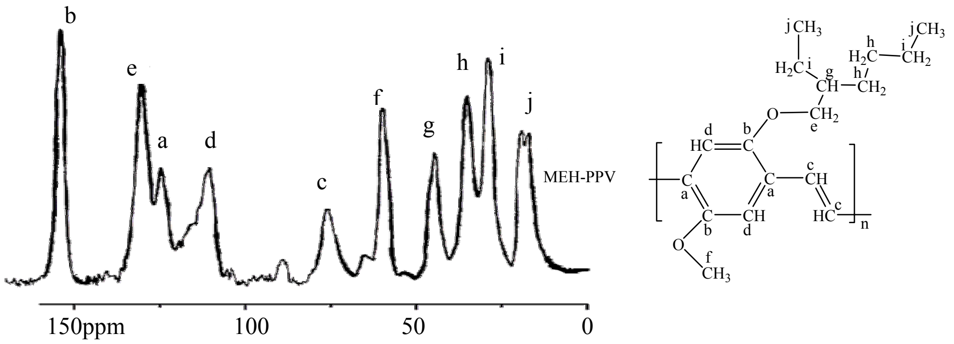
a $BrCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$ b nCH_2O/HBr c *t*-BuOK/xylene

The required amount of dried OMMT was mixed with **3** in *p*-xylene in a round bottom flask with stirring, flushed with high purity nitrogen. The suspension was sonicated for 1.5 h in ultrasonic bath then agitated for 36 h at room temperature. Subsequently the reactive vessel was thermostated at 100 °C under inert atmosphere and a solution of potassium *tert*-butoxide in *p*-xylene was added. After an additional 24 hour agitation, ten times of methanol was poured into the reaction mixture under stirring at room temperature. The deposition was collected by suction filtration, and then washed with methanol/water (1/1, v/v) for three times, the purified MEH-PPV/ OMMT was dried in vacuum.

Results and Discussion

A chemical shift at δ 4.5 - 4.6 on the ^1H NMR spectrum of monomer **3** was assigned to CH_2Br hydrogen, which would disappear after polymerization. On the ^1H NMR spectrum of the final product, there was a new peak at δ 7.5 assigned to the conjugated aromatic hydrogen of MEH-PPV. Besides, the colors of compound **3** and MEH-PPV were different, the former was colorless, the later was deep yellow, thereby it is easily to

Figure 1 ^{13}C NMR spectrum of solid-state MEH-PPV/OMMT nanocomposite.



[a] Weight percentage of MEH-PPV in the nanocomposite is 70. In measurement, CP/MAS techniques were used, the π/2 pulse length 5.1 μs and the recycle delay time 4s, spinning rate 5k.

Table 1 Experimental parameters and results for *in-situ* polymerization.

Experiment No.	Reaction Dose monomer/OMMT (mg)	Product Compositions		Exfoliated (+) not (-)
		Organic contribution （wt%）	Inorganic contribution （wt%）	
1	1000 : 100	70	30	+
2	1000 : 150	69	31	+
3	1000 : 200	67	33	+
4	1000 : 1350	36	64	-

a For experiment 1 ~ 4, the solvent is *p*-xylene.

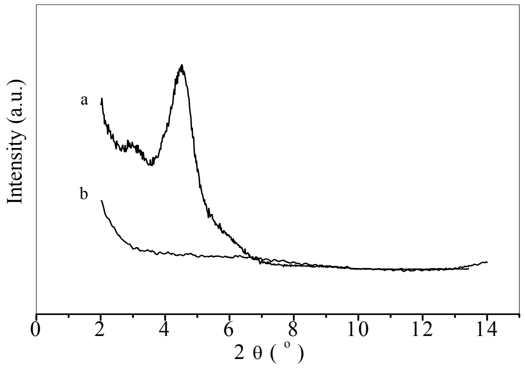
b The weight percents of MEH-PPV and clay in the produced composites were determined by thermogravimetric analysis. The TGA experiment was performed under nitrogen condition with a heating rate of 20 oC/min from 25 to 800 o C.

c The morphologies in the final composites were examined by XRD.

determine whether the reaction occurred or not. Further chemical information about the polymer in the composites can be gained by ^{13}C NMR measured in solid-stated. **Figure 1** shows the ^{13}C NMR spectrum of the MEH-PPV/OMMT nanocomposite measured by CP/MAS techniques in solid state. Taking into account of the possible deviation, the experimental result is consistent with that of the calculated one based on the group additivity rule.

The effect of the ratios of monomer **3** to OMMT on the structure of the final composites was investigated and the results were listed in **Table 1**. It was found that, when the monomer component is much more than that of OMMT, for example the monomer/OMMT weight ratios of 100/10, 100/15 and 100/20 (reaction 1, 2 and 3 in **Table 1**), the composites with exfoliated structures in nanoscale were obtained. When the OMMT proportion was significantly increased, such as 100/135 (monomer/OMMT) in reaction 4, the dehydrohalogenation reaction happened, but the morphology of composite is not exfoliated anymore.

Figure 2 X-ray diffraction patterns of OMMT (**a**) and MEH-PPV/OMMT nanocomposite (**b**).

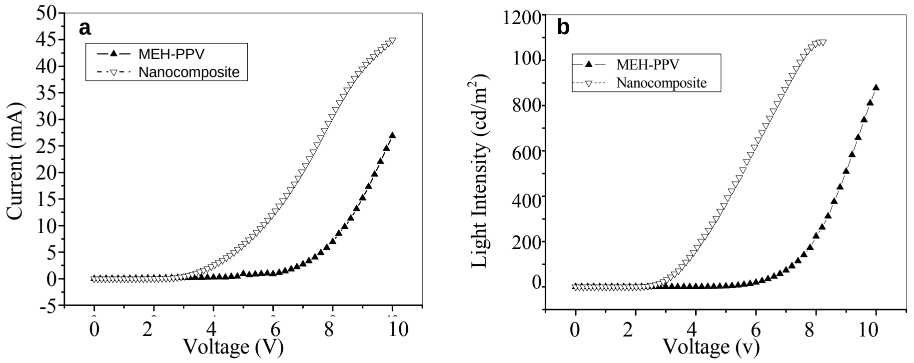


[a] The experimental data of the powder samples were collected on a Rigaku D/Max-2500 Diffractometer. [b] Weight percent of MEH-PPV in nanocomposite is 70 %, determined by TGA.

Figure 2 exhibited the XRD patterns of OMMT (**a**) and MEH-PPV/OMMT nano composites (**b**). In a representative XRD pattern obtained at room temperature, curve a displays a diffraction peak at $2\theta = 4.5^{\circ}$, corresponding to an interlayer gallery of 3.9 nm. Curve b showed no distinct diffraction peak suggesting that the gallery of OMMT was expanded to exfoliated in the process of polymerization, therefore the clay layers were chaotically dispersed in the polymeric structure.

The nanocomposite materials show enhanced electroluminescence behavior tested on the LED devices. The current-voltage curves and radiance-voltage curves (**Figure 3**) showed that both current and luminescent intensity of nanocomposites devices are significantly higher than that of the pure polymer devices under the same electric field. Furthermore, for the nanocomposite device, a lower turn-on voltage was observed.

Figure 3 Current-voltage (**a**) and radiance-voltage (**b**) curves of MEH-PPV/OMMT nanocomposites and MEH-PPV.



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