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Synthesis and Luminescence Property of Poly (phenylenevinylene) with Alkoxyl Substituents under the Ultrasonic irradiation

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Abstract. In this paper, poly [(2-methoxyl-5-octyloxy) Phenylene Vinylene] (MO-PPV) was synthesized by Gilch route under ultrasonic irradiation. The molecular structure, thin film and luminescence property examined through FT-IR, SEm, AFM, UV-Vis spectroscopy and fluorescent spectroscopy, the results showed that the 'cavitations effect' caused by the ultrasonic irradiation not only accelerate the reaction speed but also reduce structural defects of the polymer thin film, the synthesized MO-PPV is free of gelatins which is harmful for the polymer's thin films act as active layer in polymer light-emitting diodes (PLED).

Introduction

Since dialkoxy-PPVs with a solubilizing side-chain linked to the polymer backbone exhibit excellent electroluminescent activity and nonlinear optical responses and great advantages in processing which can be cast directly into thin film, various synthetic approaches to soluble dialkoxy-PPVs have been researched, such as the Gilch route, the Wittig reaction, aryl–ethylene coupling via Heck or Suzuki reactions. But polymers synthesized by these methods contain a number of structural defects as a result of incomplete elimination, cross-linking or other side-reactions during polymerization, which was harmful for polymer thin films used in device by solution processing.

In order to reduces structural defects in the polymer, ultrasonic irradiation method was used in this paper, the Poly (2-methoxy-5-octanoxy-1, 4-phenylenevinylene) (MO-PPV) was synthesized with Gilch route under ultrasonic energy field. IR spectroscopy and transmission spectrum were used to figure out the structure of the polymers that synthesized by ultrasonic irradiation method and conventional mechanical stirring method respectively. Photo-luminescent spectroscopy was used to figure the luminescent characteristic of the polymers that synthesized by ultrasonic irradiation method and conventional mechanical stirring method respectively. It can be concluded that ultrasonic irradiation caused the 'cavitation effect', which not only accelerate the reaction speed but also reduce structural defects in the polymer. Ultrasonic synthesis is probably a good way to provide a prescription for optimizing polymer films used in devices by solution processing.

2 Experiment Section

2.1 Agent

All the solvents used in the experimentl are analytical pure without purification further. The agent and chemical medicine used in the experiment are purchased from the Beijing chemical medicine company or Xi'an chemical medicine company, list as follows: hydroguinone，1,4－Dioxane，Tetrahy drofuran, n-Butyl bromide，n- octyl bromide, Methyl alcohol，Sulfuric Acid

2.2 Gilch route synthesis of poly [(2-methoxyl-5-octyloxy) Phenylene Vinylene] (MO-PPV)

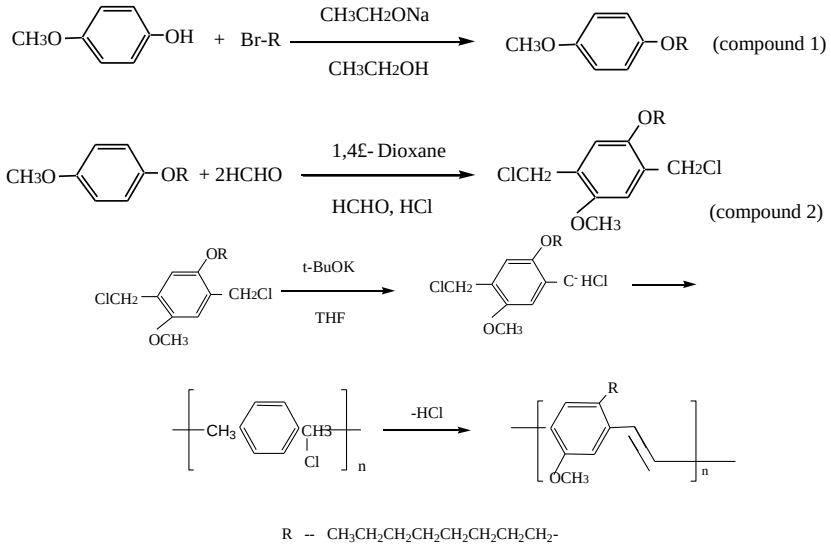


Fig.1 Scheme Gilch route of MO-PPV

2.3 Preparation

The preparation of MO-PPV is according to the Gilch route, the difference is ultrasonic irradiation replace the mechanical stirring heating. Detail is as follows;

2.3.1. 1-methoxy-4-octyloxybenzene (compound 1)

1-methoxy-4-octyloxybenzene was prepared according to a known procedure[7] that was modified as follows. Hydroguinone was added portion wise to CH_3CH_2ONa/CH_3CH_2OH mixture filled with inert gases N_2, after 10 mimute, instill the n-octyl bromide reagent then ultrasonic irradiation 6h in the inert gases atmosphere, the mole ratio of hydroguinone and n-Bromooctane reagentis 1:1.2. the 1-methoxy-4-octyloxybenzene was obtained. yield 88%, 15g, mp 40~42℃. IR (KBr):; 2994 cm^{-1} ; 1510 cm^{-1} ; 825 cm^{-1})

2.3.2 1,4-bis (halomethyl) -2-octyloxy- 5-methoxybenzene (compound 2)

Compound 1 and hydrochloric acid, formaldehyde, polyformaldehyde was added in1,4-Dioxane solution in turn, the reaction continued for 6h at 60-70℃ under the ultrasonic irradiation with HCl gas atmosphere. The 1,4-bis (halomethyl) -2-octyloxy- 5-methoxybenzene (compound 2) can be abstained after evaporated the formaldehyde, cooled, filtrated, and drying. yield 85%, 13.9 g, mp 65~67℃. IR (KBr): 2292cm-1, 1270 cm-1 ;872cm-1;611 cm-1.;

2.3.3 MO-PPV

Compound 2 was dissolved in 100 mL of tetrahydrofuran (THF) first. THF was freshly distilled over sodium before it was used. Then, 3 g (~4.5 equiv) of potassium tert-butoxide dissolved in 150 mL of THF was added slowly to the monomer solution under a nitrogen atmosphere. After the complete addition of the base, the reaction proceeded under the ultrasonic irradiation at 60℃temperaturefor 5~6h. At the end of the reaction, lots of resulting polymer (~1.5 g red precipitate) was obtained. IR (KBr): 3061cm^{-1}, 1610 cm^{-1} ;965cm^{-1}.

3. Results and discussion

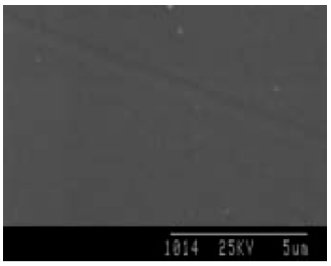
3.1 Ultrasonic polymerization property

Compared with traditional heating method, the every reaction temperature is reduced, and the reaction time has been reduced to a half. The reason maybe lie in as follows, first ultrasonic irradiation gives the reactant great acceleration so that the collision chances between reactant are increased. Second, the ultrasonic irradiation also causes the cavitation effect, which makes the activation energy to be reached at a lower temperature. Cavitation effect means the fluid continuation was destroyed by the ultrasonic energy field and produced cavitation in the fluid, many cavitations in the fluid collapse

rapidly, for example if the diameter of bubble is $1*10^{-4}$m, the collapse rate will be$5*10^{-9}$S, because the high temperature high pressure which produced in the process of collapsing can not transfer to in liquid medium in time, it will forming many micro- reactor, so the activation energy will be reduced, the reaction can be completed under the lower temperature and fast.

3.2 Thin film property

The high frequency and high energy of the ultrasonic field not only accelerate the polymerization but also reduce structural defects of the polymer thin film, as Fig.2 and Fig.3 shown. Fig.2 is SEM of MO-PPV thin film, Fig.3 is the AFM of the thin film. The thin film was deposited from the solution at the concentration 5mg/mL and spin speed 1000rmp.From the figure, it can be see that the film is smooth and has little defect.



Fg. 2 SEM of PMOCOPV film

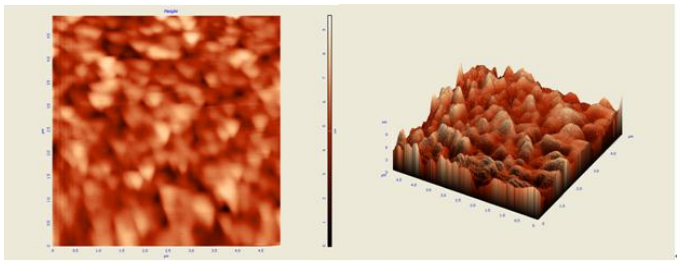


Fig.3 AFM phase image of MO-PPV thin film

The cavitation effect of the ultrasonic irradiation not only accelrate the polymerization but also has special characters. Ultrasonic irradiation also can induce the polymer degradation, so we can supposes under the ultrasonic irradiation the polymerization and degradation happened at the same time. According to the theory of McCoy etc the polymer molecular has bimodal distribution, and the molecular distribution is given as follows;

$$P_{tot}(x,t)=p(x,t)+q(x,t)=p_0(x)\exp[-\theta(x-x_f)]+2p_0(2x)\{1-\exp[-\theta(2x-x_f)]\}.$$

In the equations, $\theta=kt$， is reaction time.P_0 is the molecular distribution at the time degaradation happened， x_f is the molecular weight lower limit, when the molecular weight lower than the x_f the degaradation won't happened.

At the begaining of our experiment, the poylmerziration happened, the moleculer weight increased quickly, when some molecular weight over x_f , the degaradation happened, the shearing action limit the molecular becoming more large，then limit the gelatins appear, so the MO-PPV thin film is smooth and has little defect.

X_f should be affacted by the ultrasonic power and frequency, the reaction temperature, solvent alkalescence etc many factors. We will discuss in another paper.

3.3 photoluminescence property

Photoluminescence spectrum of the MO-PPV solution and thin film were measured on Gilden Photonics SENS-9000 fluorometry under room temperature. The liquid sample is the complexes dissolved in dichloromethane loading in the 1 cm×1 cmquartz glass. The thin film is made by spin coating with concentration 5mg/mL solution , 1000rmp. The measurement results are show in Figure 4. and Fig .5

Figure 4 and Figure 5 showed photoluminescence spectrum of the MO-PPV. It can be observed from the figure that the thin film luminescence peak is slight red shift. The max emission of the MO-PPV solution is 544~560 nm, the max emission of MO-PPV thin film is 604nm. With out gelatins, the thin film photoluminescence peak becomes narrow and pure. And it act as active layer in polymer light-emitting diodes (PLED), its EL property has been be researched in another pape r.

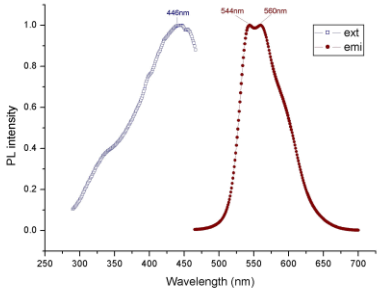


Fig.4 Photoluminescence spectrum of the MO-PPV solution

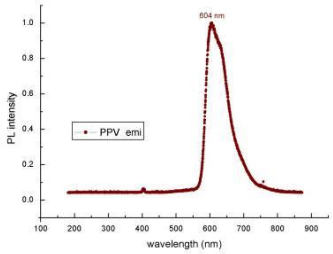


Fig.5 Photoluminescence spectrum of MO-PPV thin film

4 Conclusions

In conclusion, we have synthesized MO-PPV under ultrasonic energy field. Because "cavitation effect"of the ultrasonic irradation reduced activation energy, the polymerization can be complete at a lower temperature and fast.

Ultrasonic irradiation can induced polymerization and degradation together, the shearing action limit the polymer molecular becoming more large, limit the gelatins appear, so the polymer's thin film become less defect, and its photoluminescence peak become narrow and pure.

Acknowledgements

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