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ФУНКЦИОНАЛЬНЫЕ ПОЛИМЕРЫ

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SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF POLY(2-METHOXY-5-(2'-ETHYLHEXYLOXY)-*p*-PHENYLENE VINYLENE-*co*-STYRENE) COPOLYMERS[1]

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Abstract – A series of conjugated and non-conjugated copolymers of poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene-*co*-styrene) were synthesized via a typical chlorine precursor route. The obtained copolymers were characterized by FTIR spectra, Uv-vis spectra, ^{1}H NMR and GPC. The results obtained indicated that the introduction of non-conjugated PS segments in MEH-PPV led to the interruption of conjugation structure and shortened the effective conjugated length, by which the optical properties of the conjugated polymer can be adjusted.

INTRODUCTION

Since the discovery of electroluminescence of conjugated polymers, the researches on conjugated polymers have attracted considerable attention in versatile applications, such as electroluminescene, photovoltaics and optical sensors [1–5]. Poly(*p*-phenylenevinylene) (PPV) as the first electroluminescent material discovered in 1990 [6], has received a great deal of interest because of its unique photoelectronic properties and variety of derivatives [4, 7–10]. Now, PPV and its derivatives have become the most classical conjugated polymers used in organic light-emitting diodes (OLEDs), solar cells, and biosensor, etc. [11–13]. In particular, poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) is one of the most widely studied and utilized polymer in different fields due to its relatively good solubility and easy processability [14–17].

In organic conjugated system, the conjugation length influences on the band gap from HOMO to LUMO. Generally speaking, a shorter conjugation length makes a larger band gap. Therefore, when a non-conjugated segment is incorporated into a conjugated chain, the conjugation will be interrupted, and the resultant copolymer will have a blue-shifting luminescence. Many conjugated/non-conjugated copolymers based on PPV and its derivatives comprising a combination of different aryl units have been studied [18–22]. But these copolymers may be easily transformed into the fully conjugated copolymer by acid or thermal disposal. Tang J. et al. have reported a new method to incorporate the non-conjugated polystyrene segments into the PPV backbone [23–26]. However, the studies aimed at the improvement of the synthetic strategy of non-conjugated segments incorporation to PPV or its derivatives are relatively rare. In view of the importance of MEH-PPV and its low solubility in organic solvent, we report about successful synthesis of the copolymer with the conjugated MEH-PPV and the non-conjugated polystyrene with adjustable optical property and excellent solubility. The structure and composition of the obtained copolymers were characterized by FTIR spectra, ^{1}H NMR spectra and GPC. The PL properties of these copolymers were also investigated.

EXPERIMENTAL

2-Ethylhexyl bromide (95%) was purchased from Acros. Styrene was distilled under reduced pressure before use. 1,4-Dioxane was purified by distillation in the presence of sodium and stored over silica gel-self indicator. *tert*-BuOK was freshly prepared by reaction of *tert*-BuOH with potassium. 4-Methyloxyphenol, tetrabutyl ammonium bromide and other chemical reagents were used as received.

Synthesis of methoxy-4-(2-ethylhexyloxy)benzene (**1**) was carried out according to procedure described in [27]. To a stirred mixture of 4-methyloxyphenol (10.0 g, 81 mmol), KOH (5.6 g, 0.1 mol), tetrabutyl

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[1] Статья печатается в представленном авторами виде.

Properties of the resultant copolymers synthesized from the copolymerization by changing the amounts of styrene

Sample	Styrene[a], ml	Styrene/compound **2** (mol ratio)	Styrene units content[b], mol %	M_n^c	PD[d]	Color[e]	Emission peaks[f], nm
MEH-PPV	0	–	–	2.63×10^4	3.68	red	565
$\mathbf{P_1}$	3	10	46.21	4.45×10^4	1.89	red-orange	558
$\mathbf{P_2}$	6	20	54.72	3.61×10^4	2.95	orange	554
$\mathbf{P_3}$	12	40	62.33	4.01×10^4	3.51	yellow	548

[a] Volume of styrene adding to the reaction.

[b] Styrene units molar content in the copolymers calculated by equation (1).

[c] Number-average molecular weight.

[d] Polydispersity index (M_w/M_n).

[e] The color of the solid powders of the polymers.

[f] Emission peaks of the polymers in $CHCl_3$ with a concentration of 0.01mg ml^{-1}.

ammonium bromide (0.5 g, 17 mmol) and water (30 ml) 2-ethylhexyl bromide (15.4 g, 80 mmol) was added. The reaction mixture was then heated to reflux for 3 days under N_2 atmosphere. After cooling to room temperature the resulting mixture was extracted with 150 ml of diethyl ether and the organic layer was washed with 100 ml of 0.5 M NaOH and 100 ml water respectively, then it was dried over anhydrous Na_2SO_4 and finally, diethyl ether was eliminated in vacuum. Residual was purified by column chromatography (silica gel; petroleum ether/diethyl ether (3/1) as an eluent). The light yellow liquid product **1** (14.9 g) was obtained by vacuum distillation (78% yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.84 (s, 4H, aromatic H), 3.8 (s, 2H, $-OCH_2-$), 3.78 (s, 3H, $-OCH_3$), 0.9–1.7 (m, 15H).

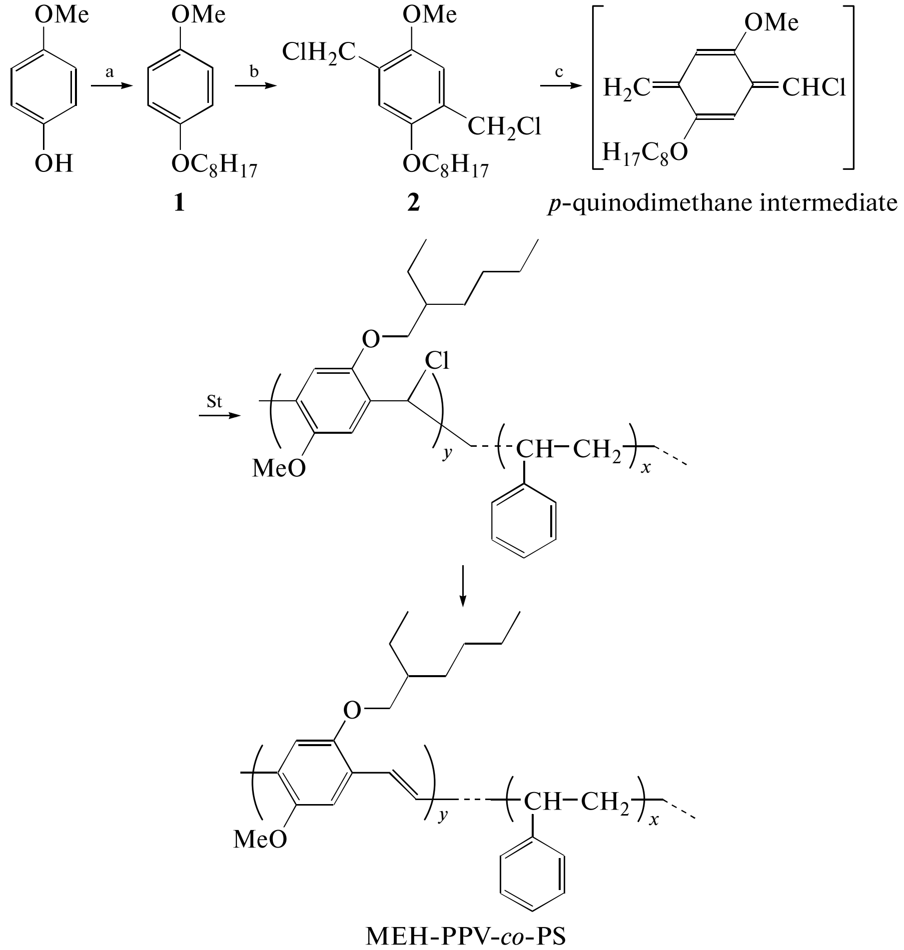
1,4-Bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxy-benzene (**2**) was synthesized by reacting 10 g (43 mmol) of compound **1** with 20 g of formaldehyde and 40 ml of concentrated hydrochloric acid in 30 ml of 1,4-dioxane [20, 28]. After that the solution was heated at 90°C for 3 days, then cooling ethyl acetate and water were added into the reaction mixture, a mass of white precipitates were emergent. After filtration, the crude solid was dissolved in a small amount of hot cyclohexane, and then the solution was poured into ice-cold methanol. The white solid was obtained after filtration and vacuum drying (6.06 g, 43% yield, mp 47–48°C). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.92 (d, 2H, aromatic H), 4.64 (s, 4H, $-CH_2Cl$), 3.88 (d, 2H, $-OCH_2-$), 3.86 (s, 3H, $-OCH_3$), 0.9–1.75 (m, 15H).

For synthesis of MEH-PPV and copolymers to a round-bottom flask 3.5 g of *tert*-BuOK, 20 ml of dry 1,4-dioxane and different volume of styrene (see table) were added. Under N_2 atmosphere, a solution of compound **2** (1.0 g) in dry 1,4-dioxane (10 ml) was added dropwise into the above reaction system. During this procedure, the solution gradually turned from colorless to orange-red. The reaction mixture was stirred at 60°C for 4 h, then the solution was cooled to room temperature and poured into a large amount of methanol. The precipitate was collected and washed with diethyl ether several times. The product was further purified by re-precipitating from $CHCl_3$/MeOH and dried in vacuum. By dosage of styrene with 3, 9, 12 ml, three kinds of copolymers ($\mathbf{P_1}$, $\mathbf{P_2}$ and $\mathbf{P_3}$) were obtained, respectively. Elemental analysis. $\mathbf{P_1}$: C, 83.2%, H, 9.0%; $\mathbf{P_2}$: C, 80.8%, H, 9.0%; $\mathbf{P_3}$: C, 84.0%, H, 8.6%.

FTIR spectra were recorded on a Magna 560 FT-IR spectrometer. ^{1}H NMR spectra were obtained from an AVANCE 500MHz Bruker spectrometer in $CDCl_3$ solution. UV-vis absorption spectra were recorded on a Vary 500 UV-vis-NIR spectrometer in the range 200–800 nm. The photoluminescent properties of MEH-PPV and copolymers were measured on a Cary Eclipse fluorescent spectrometer. The molecular weights of polymers were estimated at a flow rate of 1.0 ml min^{-1} at 25°C by GPC on a Waters instrument, using $CHCl_3$ as eluent, and the molecular weights were determined using polystyrene standards. Elemental analysis was performed using a Perkin-Elmer 2400 series II analyzer.

RESULTS AND DISCUSSION

The preparation process of copolymer is illustrated in scheme. The mechanism of the copolymerization is possible free-radical copolymerization [25]. Firstly, compound **2** eliminates HCl and forms *p*-quinodimethane intermediate in the presence of *tert*-BuOK. The *p*-quinodimethane intermediate being both initiator and monomer possesses high activity in self-polymerization at low temperature. Styrene and *p*-quinodimethane is a couple of isomers. However, Styrene needs elevated temperature to undergo self-polymerization. When the content of styrene in the reaction system is low, we can only obtain MEH-PPV homopolymer. So in order to obtain the copolymers with high content of styrene units, extremely large amount of styrene is added into the reaction system. The decrease of the *p*-quinodimethane intermediate concentration leads to suppression of the *p*-quinodimethane self-polymerization. Evidently, the two kinds of structural units are most possibly randomly arranged in the main chain of the copolymers. The detailed structure and sequence distribution of the two units in the main chain of copolymers are difficult to confirm [24, 25]. This needs further study. The obtained copolymers have excellent solubility in $CHCl_3$ and THF. The color of the copolymers gradually becomes lighter with increasing amount of styrene in the reaction of the copolymerization.



Scheme. Synthetic route of MEH-PPV-*co*-PS copolymers: a) 2-Ethylhexyl bromide, KOH, TBABr, H_2O, N_2, reflux, 3 d; b) HCHO, HCl, 1,4-dioxane, 90°C, 72 h; c) styrene, *tert*-BuOK, 1,4-dioxane, N_2, 60°C, 4 h.

Figure 1 shows the FTIR spectrum of MEH-PPV (curve *a*) and copolymer $\mathbf{P_2}$ (curve *b*). The peaks at 3033, 1614 and 1502 cm^{-1} are characteristic of benzene ring. The peaks at 2954, 2924, 2862, 1462 and 1386 cm^{-1} belong to the characteristic vibrations of CH_2 and CH_3 groups of the side chains for MEH-PPV and the main chains for PS. The peaks at 3058 and 966 cm^{-1} are assigned to the olefinic C–H stretching and trans-substituted olefinic C–H bending of MEH-PPV, respectively [29]. The characteristic peaks at 769

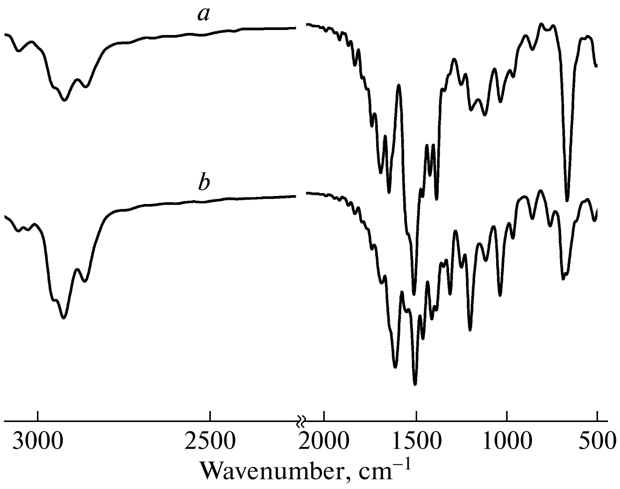


Fig. 1. FTIR spectra of (*a*) MEH-PPV and (*b*) $\mathbf{P}_2$.

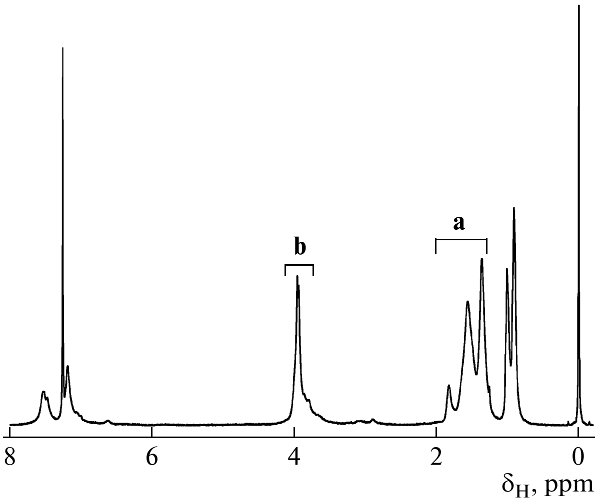


Fig. 2. ^{1}H NMR spectra of $\mathbf{P}_1$. Region **a** – the resonance of $-OCH_3$ and $-OCH_2-$ groups of the alkoxy chains of MEH-PPV unit; Region **b** – the resonance of methylene and methenyl groups for both MEH-PPV and styrene units.

and 692 cm^{-1} are attributed to the C–H bending of mono-substituted benzene of pure polystyrene [25], however, these peaks can not be observed in the spectrum of pure MEH-PPV. These results confirm that the PS segments as non-conjugated spacers have been successfully copolymerized in the conjugated MEH-PPV backbone chains.

The structure of the obtained copolymers was determined by ^{1}H NMR (see table) and all the copolymers exhibited similar spectrum profiles. Figure 2 shows ^{1}H NMR spectrum of copolymer $\mathbf{P}_1$ in $CDCl_3$. The resonance (region **b**) at 3.75–4.1 ppm is assigned to the $-OCH_3$ and $-OCH_2-$ groups of the alkoxy chains of MEH-PPV unit. The peaks at 1.01 and 0.91 ppm belong to the $-CH_3$ of the ethylhexyloxy substitute. The peaks at lower field can be attributed to the conjugated benzene rings and vinyl units [30, 31]. The resonance (region **a**) at 1.23–1.89 ppm belong to methylene and methenyl groups for both MEH-PPV and styrene units, which can be used to affirm the composition of the copolymer [25]. We presume that the structures of MEH-PPV and styrene units in the copolymer are the same as in their homopolymers, the molar content of styrene units in the copolymers can be calculated by the following equation:

$$St\% = [(5I_a - 9I_b)/(5I_a - 6I_b)] \times 100\%, \qquad (1)$$

where I_a and I_b represent the peak integrals in the region **a** and **b**, respectively. The calculated results are listed in table. It can be seen that the content of styrene unit in the copolymers increased with increasing amounts of styrene. But the enhanced ratio of styrene unit in the copolymers is not linear with the adding amount of styrene. This result indicates that *p*-quinodimethane intermediate also has high activity at low concentration, even when the content of styrene is 40 times more than *p*-quinodimethane ($\mathbf{P}_3$). The elemental analysis results are in accordance with that of ^{1}H NMR analysis (see experimental part).

The molecular weights of MEH-PPV and MEH-PPV-*co*-PS copolymers were measured with GPC in $CHCl_3$ using mono-dispersed polystyrene as the relative standards, and the results are listed in table. All the GPC curves exhibit a single peak profile, indicating that the obtained copolymers are not the simple blend of MEH-PPV and PS. It can be seen from table that the number-average molecular weights of the MEH-PPV and MEH-PPV-*co*-PS copolymers have the same order of magnitude, which are among twenty thousand and forty thousand.

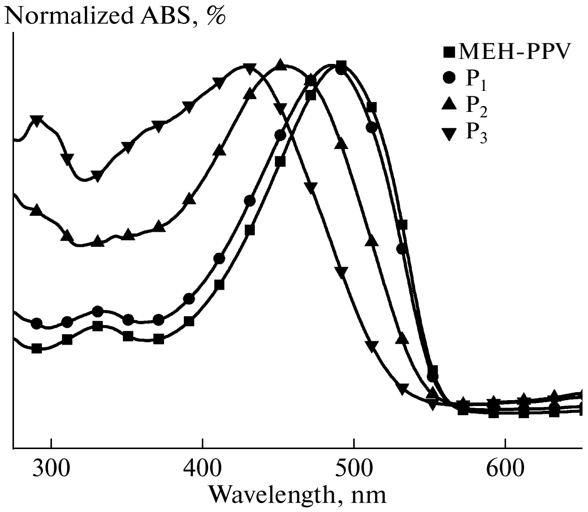


Fig. 3. UV-vis absorption spectra of MEH-PPV and MEH-PPV-*co*-PS polymers.

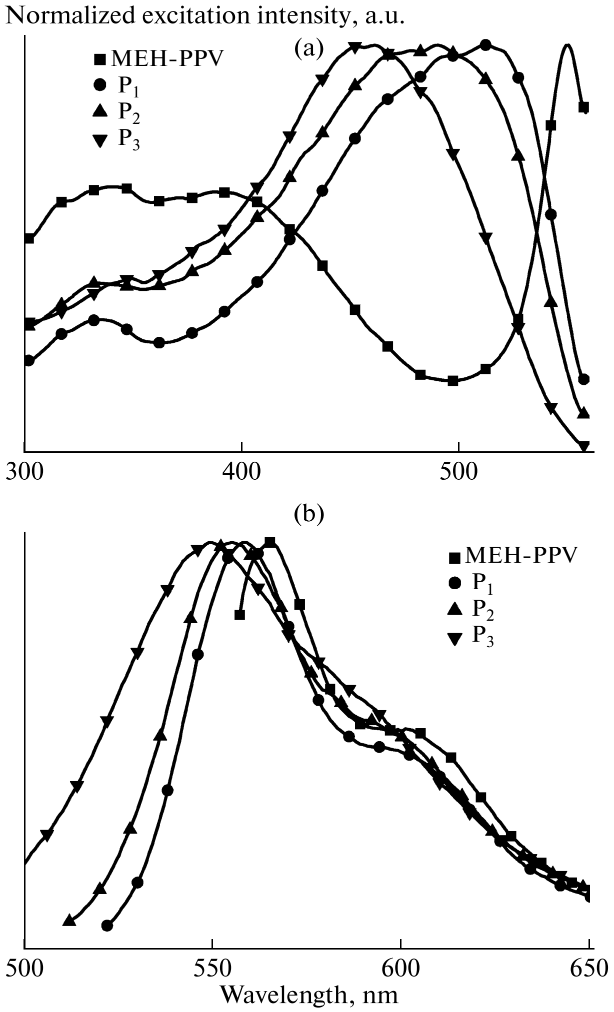


Fig. 4. (a) Photoluminescence excitation spectra of MEH-PPV and MEH-PPV-*co*-PS polymers. (b) Photoluminescence emission spectra of MEH-PPV and MEH-PPV-*co*-PS polymers.

UV-vis spectroscopy is a useful technique to characterize the conjugated system. Figure 3 shows the absorption spectra of MEH-PPV and MEH-PPV-*co*-PS copolymers in $CHCl_3$ with a concentration of 0.01 mg ml^{-1}. The maximum absorption peaks for the four samples were observed at 489, 483, 450 and 428 nm, respectively. In addition, there is a shoulder peak at around 300 nm for the copolymers $\mathbf{P}_2$ and $\mathbf{P}_3$, and this satellite peak can be assigned to B band absorption of the aryl ring. From the spectra, it can be seen that the maximum absorption peak had a clear blue-shift. Generally speaking, the peak value of the UV-vis spectrum correlates to the length of conjugated blocks in the polymer chain. It indicated that with increasing the amount of styrene added into the reaction, the content of styrene units in the copolymer gradually became higher, and the length of the conjugated chain gradually became shorter. The ^1H NMR analysis also supported this result as discussed above.

Figures 4a and 4b show the PL excitation and emission spectra of pure MEH-PPV and MEH-PPV-*co*-PS copolymers in $CHCl_3$ with a concentration of 0.01 mg ml^{-1}, respectively. The maximum emission of MEH-PPV and its copolymers appears at 565, 558, 554 and 548 nm, respectively. There are obvious blue-shifts for both the excitation and emission spectra with increasing styrene content. This may be attributed to the presence of the different length of the conjugated chain. We know that a peak with shorter maximum emission wavelength corresponds to a shorter conjugated length and a higher HOMO-LUMO energy gap [25]. Therefore, it can be inferred that a copolymer with a higher content of styrene units should have a shorter conjugated length in the polymer chain. In other words, the PL property of the copolymer can be tuned by controlling the amount of styrene added into the copolymerization reaction. It still needs more efforts to incorporate higher content of interruptions (defects) into the conjugated chains in order to achieve the larger light-emitting blue shift.

CONCLUSIONS

Poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene-*co*-styrene) copolymers were synthesized via *p*-quinodimethane intermediate route. The molar content of styrene units in the copolymer chain can be adjusted by controlling the amount of styrene added into the copolymerization reaction. Both the UV-vis spectra and PL spectra of the copolymers revealed the obvious blue-shifts, because the incorporation of non-conjugated styrene units in the polymer chain interrupted the conjugated structure of the polymer and shortened its effective conjugated length. The obtained copolymers could be potentially used in LEDs because of their excellent solubility in non-polar solvent and controllable optical properties. We also expect that the detailed structure of copolymers can be further determined, and the electroluminescent properties based on these novel copolymers can be further studied in the future.

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