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Ultrasonic synthesis of poly(2-methoxy-5-butoxy) phenylene vinylene

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Abstract **A new method was developed using ultrasonic irradiation to synthesize poly(2-methoxy-5-butoxy) phenylene vinylene from *p*-methoxy phenol (MOPh) and $CH_3(CH_2)_3Br$. Ultrasonic irradiation catalyzes the reactions through three major steps of etherification, bischloromethylation and elimination. Results showed that our ultrasonic irradiation method could significantly enhance production yield and reduce process time of the synthesis compared with reflux agitating method.**

Keywords: ultrasonic synthesis, poly(2-methoxy-5-butoxy) phenylene vinylene.

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Poly(*p*-phenylene vinylene)(PPV) and its derivatives are copolymers with a one-dimensional linear chain structure. Their characteristic band gaps have the same energy as visible light. They are good conductive polymers and excellent electroluminescence materials[1—4]. For example, poly(2-methoxy-5-butoxy) phenylene vinylene (PMOBOPV) is an excellent photoluminescence (e.g. fluorescence), electroluminescence materials in the visible range. PMOBOPV is also a good photoelectric material[5].

There are many methods for synthesizing PPV and its derivatives, e.g. Wittig, G. Reaction, dehydrochlorination, polycondensation, and soluble prepolymerization (Wessling, etc.). Two major problems with the soluble prepolymerization method[6] are: (1) poor soluble polymers stability at ambient temperature and (2) low production yield. In previous studies, we tried to improve the dehydrochlorination method to synthesize PMOBOPV. We found that the PMOBOPV could be prepared in a simple way by the dehydrochlorination method only by three steps. However, it not only took quit a long time for the reaction but also had poor yield.

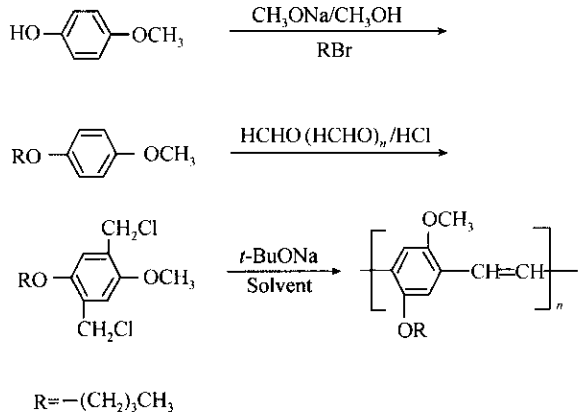
In this report, we describe a new method for synthesizing PMOBOPV with high yield (up to 80%) and shorter reaction time. We used *p*-methoxy phenol and $CH_3(CH_2)_3Br$ as raw and starting materials. Reactions of etherification, dichloromethylation and elimination took place by ultrasonic irradiation under nitrogen. With less than 10 h ultrasonic irradiation, the reaction yield of PMOBOPV could be as high as 80%.

1 Materials and methods

(i) Instruments and reagents. CQ-250 ultrasonic purifier, frequency (33 ± 2) kHz. HITACHI 270-30 infrared spectrometer. FX-90 Q NMR spectrometer. RF-5000 Fluorospectro-photometer (assaying the character of fluorescence and electroluminescence). KBr tabulating, $CDCl_3$ (solvent), TMS (internal standard), $CHCl_3$ (solvent), *p*-methoxyphenol (analytical grade), methanol, sodium, butyl bromide, formaldehyde solution (36%), paraformaldehyde, *tert*-butyl alcohol, dioxane, ethanol, hydrochloric acid (chemical pure), high-purity nitrogen.

(ii) Methods of PMOBOPV synthesis

(1) Synthetic route



R= —$(CH_2)_3CH_3$

(2) Preparation of MOBOB. For comparison, we prepared MOBOB using two different methods,i.e. ultrasonic irradiation and reflux-agitating.

p-methoxyphenol (MOPh, 0.2 mol) and a solution of sodium methoxide (2.0 mol/L) in methanol were added to a 500 mL three-necked flask equipped with a spherical condenser and filled with nitrogen gas. After the mixture was cooled down to room temperature, $CH_3(CH_2)_3Br$ (0.2 mol) was slowly added to the flask. The reaction was processed for several hours by either the ultrasonic irradiation method or the reflux-agitating method. The reaction mixture was then distilled under reduced pressure to remove methanol. The remainder was washed with 10% NaOH solution followed by distilled water. 1-methoxy-4-butoxy benzene (MOBOB) was finally obtained by recrystallization in ethanol.

(3) Preparation of BCMMOBOB. Dried MOBOB (0.02 mol) was dissolved in 80 mL of dioxane. Then paraformaldehyde (0.0025 mol) was added at room temperature, followed by formaldehyde (0.0025 mol) and finally concentrated hydrochloric acid (100 mL). The mixture was heated and refluxed for 5 h, then cooled

down to room temperature. After filtration the product was washed with ethanol (2 times), then distilled water (2 — 3 times). 1,4-bis(chloromethyl)-2-methoxy-5-butoxy benzene (BCMMOBOB) was recrystallized in ethanol.

(4) Preparation of PMOBOPV. BCMMOBOB (0.002 mol) was dissolved in a polar solvent. Sodium *tert*-butoxide (*t*-BuONa, 0.018 mol) in the same solvent (50 mL) was slowly added. The reaction took place for several hours by either ultrasonic irradiation at room temperature or reflux-agitating at the boiling point. The product was red precipitates which were separated by using a proper amount of methanol/water (V_{MeOH} : V_{H_2O} = 1 : 1) solvent. The red precipitates were then dipped in a warm ethanol solvent for 2 h and finally were washed with ethanol and followed by distilled water for 3 times. Pure poly(2- methoxy-5-butoxy)phenylene vinylene (PMOBOPV) was obtained.

2 Results and discussions

(i) Impact of ultrasonic irradiation and reflux-agitating to the production yield

(1) MOBOB. Two different methods, ultrasonic irradiation and reflux-agitating, were used in the preparation of MOBOB. A significant difference in the production yield of MOBOB was observed as shown Table 1.

Table 1 shows that compared to the reflux-agitating method the ultrasonic irradiation method took much less time and produced more MOBOB.

(2) PMOBOPV. PMOBOPV was synthesized by dehydrochlorination at alkali condition (pH =12 — 14) in a polar solvent. The production yield increased while reaction time prolonged during the reaction for both methods of ultrasonic irradiation and reflux agitating. The results are summarized in Table 2.

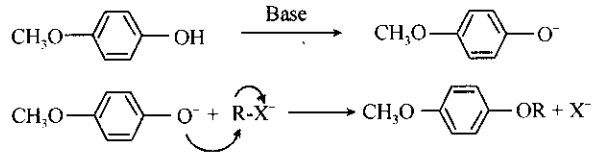
As expected, the concentration of PMOBOPV increased as time prolonged for both methods. However, the ultrasonic irradiation method resulted in a yield as high as 80% in 10 h while reflux-agitating method 62.5% in a much longer time of 18 h.

In addition, we noted that ultrasonic irradiation showed no catalytic action to the production of BCMMOBOB by the chloromethylation of MOBOB.

(ii) Mechanism of ultrasonic irradiation synthesis. Synthesis of PMOBOPV was completed in three steps.

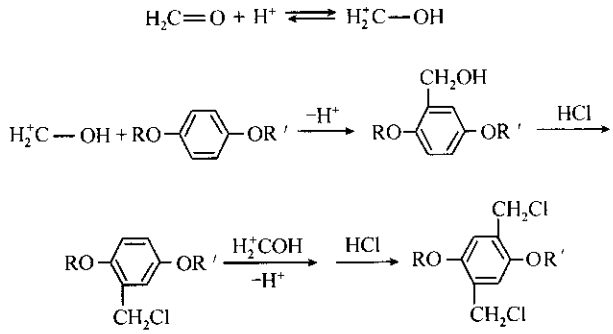
Step 1. Synthesis of MOBOB by Williamson method

Etherification of phenol is a type of nucleophilic substitution reaction. Under alkali condition, MOPh converts into phenoxy anion. As a nucleophile, phenoxy anion attacks the alpha-carbon atom that links to halogen atom in RX. As halogen anion leaves, MOBOB forms. The scheme of the process is shown as follows:



Step 2. Preparation of BCMMOBOB

In the presence of acid (as a catalyst), formaldehyde combines with hydrion to form $^{+}CH_2OH$. $^{+}CH_2OH$ is stronger in electrophilic than formaldehyde and therefore it has advantages to have an electrophilic substitution reaction on benzene to produce BCMMOBOB.



Step 3. Synthesis of PMOBOPV

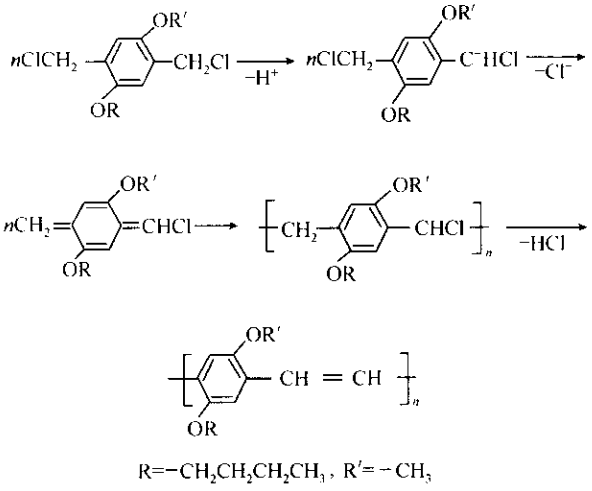
In an alkali solution, BCMMOBOB converts into carbanion by losing a hydrion on the chloromethyl. By ultrasonic irradiation, benzene combines with carbanion to form a more stable quinoid structure (resonance effect) which polymerizes into PMOBOPV in the presence of strong base.

Table 1 Comparison of MOBOB yield between ultrasonic irradiation and reflux-agitating methods.

Synthetic method	Synthesis	Reaction time/h	Color	Yield (%)
Ultrasonic irradiation	MOBOB	5	white	89
Reflux-agitating	MOBOB	16	white	80

Table 2 The effect of reaction time on PMOBOPV production yield

Synthesis	Yield in different reaction time (%)						
	5 h	6 h	8 h	10 h	12 h	18 h	24 h
Ultrasonic irradiation	51.5	64.0	72.0	80.0	81.0	81.2	81.5
Reflux-agitating	25.0	30.0	37.5	46.2	54.4	62.5	63.0



The mechanism of reactions described above is that by ultrasonic irradiation it creates cavitation in the low cohesive force solvent, the so-called ultrasonic cavitation effect. Average lifetime of cavitation bubbles was about 0.1 μs. in the moment of bubble blow-out, it could raise the partial temperature to as high as about 4000 K and the partial pressure to as high as about 100 MPa. Cooling speed could reach 10^9 k·s^{-1}. Cavitation bubble could release tremendous energy and produce micro – jet flow at a speed of about 110 m·s^{-1} and collision density could reach 1.5 kg·cm^{-3}[7] .Under these conditions the chemical bonds of MOPh and BCMMOBOB in cavitation bubble could be easily broken ,which would benefit to promote the formation of phenoxy anion and carbanion. Phenoxy anion, as a nucleophile, attacks to RX that produces phenolic ether MOBOB. Due to the resonance effect, Carbanion and benzene form a more stable quinoid structure. Under alkali condition, the quinoid structure could form prepolymers which then convert into PPV by dehydrochlorination[8].

Further, ultrasonic irradiation could promote disturbance of heterogeneous boundary surface. Renewal of boundary surface accelerated transfer of mass and heat, which speeded chemical reaction. The ultrasonic irradiation catalysis was probably due to energy effect and mechanical effect by ultrasonic cavitation in liquid.

We also found that ultrasonic irradiation had no impact to the synthesis of BCMMOBOB, in the chloromethylation of MOBOB . This is probably due to a great difficulty in forming stable active intermediate under condition of ultrasonic irradiation.

(iii) Characteristics of the destination product.

Infrared Spectra. The characteristic absorption peaks of benzene ring are at 1450 cm^{-1} and 1510 cm^{-1} . The strong characteristic peaks at 879 cm^{-1} and 1740 cm^{-1} suggest that there are 4 substituents on the site of 1,2,4,5 on benzene. The absorption at 3050 cm^{-1} is the superposition peak of C—H expansion and contraction vibration on benzene and vinyl .

^{1}HNMR: the subordinations of peaks are: chemical shift of H proton 7.40 (s, 2H, Ph-H), 7.20 (s, 2H, —CH = CH—) and 3.94 (s, 3H, OCH_3). There are four types of H proton in —$OCH_2CH_2CH_2CH_3$, chemical shift of H protons are: 4.0 (t, 2H), 1.80 (m, 2H), 1.50 (m, 2H)and 0.95 (t, 3H), respectively.

Measurements of excitation, photoluminescence and electroluminescence spectra of PMOBOPV showed that the fluorescence excitation peak, photoluminescence peak and electroluminescence peak are at 517 nm, 547 nm, 525 nm, respectively, which are all in the range of visible light.

Results of IR, ^{1}HNMR, fluorescence, and electroluminescence measurements of our destination product are in agreement with reference[6] results of PMOBOPV synthesized by other methods.

3 Conclusion

Using *p*-methoxyphenol and $CH_3(CH_2)_3Br$ to synthesize poly(2-methoxy-5-butoxy) phenylene vinylene (PMOBOPV), compared to classic methods our ultrasonic irradiation method significantly improves the efficiency of the synthetic process with a higher production yield and a shorter process time.

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