

SYNTHESIS AND CHARACTERIZATION OF FULLY SOLUBLE POLYPHENYLENEVINYLENE

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Abstract Fully soluble poly[2-methoxy-5-(2'-ethylhexyl)-oxy]-*p*-phenylenevinylene] (MEH-PPV) was synthesized by the addition of molecular weight modifiers (chain stopper, free radical scavengers) to a polymerization system containing monomer, catalyst and a solvent. These PPV products synthesized in this work were characterized by IR, NMR, UV-visible spectroscopy and GPC. Results show that the M_w of polyphenylvinylene (PPV) can be controlled by the addition of chain stopper (benzyl bromide) and radical inhibitor (2,6-di-*tert*-butyl-4-methyl phenol). The polymerization mechanism in the presence of these additives was also discussed. A dual mechanism involving carbene for PPV polymerization was proposed.

Keywords Polyphenylenevinylene, Light emitting polymer, Conjugation polymer, Conducting polymer, Polymerization of PPV

INTRODUCTION

Modern electronic industries require new display devices and information storing materials with higher resolution and easy processability. Organic light emitting diode (OLED) is one of the most promising candidates; it possesses better processing ability, flexible and low threshold voltage. However, low molecular weight organic compounds as electro-luminescence materials have some deficiencies, e.g. the film formed is fragile, crystallizable easily and has poor stability. In comparison with low molecular weight organic compounds, light-emitting polymer used for polymer light emitting diode (PLED) device is more attractive.

Extensive studies have been done for PLED, since the first PLED device fabricated from PPV was reported in 1990^[1, 2]. Numerous reviews, patents and papers about PLED were published^[3-14]. So far, PPV and its analogues remain the most important polymer for PLED applications owing to its good light emitting performance, ease of synthesis and better environmental stability. There are two approaches to achieve successful application of PPV in PLED devices. One is the precursor approach, in which a soluble precursor of PPV is coated on the substrate, then heated over 300°C to convert this precursor into the final PPV film. Another one is the soluble PPV approach, in which soluble side chains are introduced into the phenyl ring of PPV and make the derived PPV soluble, and then the solution coating processing can be used. The former approach has some problems for the final PPV film such as the oxidation of film owing to high processing temperature, structural defects arising from incomplete thermal conversion, producing random copolymer and side reactions. These disadvantages can cause the devices to have poor performance and poor manufacturing reproducibility. The latter approach has some more attractive advantages, for example solution processing avoids high temperature oxidation and the final molecular structure of PPV can be controlled. Poly[2-methoxy-5-ethylhexyloxy]-*p*-phenylenevinylene] (MEH-PPV) prepared from the monomer (2-methoxy-5-ethylhexyloxy-*p*-bis(halomethyl)

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benzene) MEHDMB is a successful example. Among PPV analogues, MEH-PPV has the best solubility in common organic solvents. Unfortunately, in actual practice, gels or micro-gels were always formed during the polymerization process. Therefore, gelation becomes a very serious problem for PPV used in PLED. Too high molecular weight which is associated with the very fast rate of polymerization reaction and too fast to increase the kinetic chain length are the principal reasons for PPV gel or micro-gel formation in organic solvent. Therefore, by adding compounds which can retard the polymerization rate or can control the kinetic chain length in the polymerization system, fully soluble PPV with optimal MW can be obtained. Therefore, we used the above idea to synthesize fully soluble PPVs. The additives involve chain stopper (benzyl bromide) and radical inhibitor (2,6-di-*tert*-butyl-4-methyl phenol). In this paper, the synthesis of monomer (2-methoxy-5-(2'-ethylhexyloxy)-*p*-bis-bromomethylbenzene) MEHDBMB, and its polymerization in the presence of a catalyst, potassium *tert*-butoxide (*t*-BuOK) in THF, as well as the characterization of final PPV products by IR, NMR, UV-, PL spectroscopies and GPC are reported.

EXPERIMENTAL

Materials

p-Methoxyphenol and 2-ethylhexyl bromide were supplied by the Aldrich company, paraformaldehyde was a product of Merck company. Hydrogen bromide (HBr) was a 30% solution of HBr in acetic acid and *t*-BuOK was a 1.0 mol/L solution in tetrahydrofuran (THF), both were available from Aldrich. THF was re-distilled before use.

Synthesis

Synthesis of monomer

p-Methoxy-2-ethylhexyloxy benzene (MEHB) was synthesized from the reaction of *p*-methoxyphenol with 2-ethylhexyl bromide in the presence of K_2CO_3 . The monomer, 2-methoxy-5-(5-ethylhexyloxy)-*p*-bisbromomethylbenzene (MEHDBMB) was prepared by bromomethylation of MEHB in the presence of paraformaldehyde and HBr in acetic acid solution. A typical bromination of MEHB proceeds as follows. To a three-necked flask equipped with a condenser, an argon inlet and a magnetic stirrer, 10.0 g (0.0427 mol) of MEHB and 9.6 g (0.24 mol) of paraformaldehyde were added and well mixed. Then 132 mL of HBr-HAc solution (HBr 0.6628 mol) was added. The reaction was run at 35°C, under stirring for 19h. Then, 180 mL of distilled water was added to precipitate the reaction product. The precipitate was filtered, and washed with distilled water till pH 7. After drying, the product was purified by recrystallization from hexane. A yield of 94.05% was obtained.

Polymerization of monomer

Polymerization of the above monomer (MEHDBMB) was carried out in THF solution with *t*-BuOK as the catalyst. A typical polymerization of monomer in this work is described as follows. To a three-necked flask equipped with a condenser, an argon inlet and a magnetic stirrer, 0.30 g (0.71 mmol) of MEHDBMB, 60 mg of benzyl bromide (chain stopper) and 30 mL of newly distilled THF were added. Then *t*-BuOK 2.13 mL (2.13 mmol) was added and the reaction run at ambient temperature for 3h with stirring. The reaction product was precipitated by adding 40mL methanol under stirring. This precipitate was filtered, washed with distilled water till pH 7, and then washed with methanol (3 × 30 mL). After drying, a solid product with a deep red colour was obtained. The yield was 44.84%.

Characterization

IR spectra were recorded using a Bio-Rad. Win. FT-IR spectrometer. Elemental analysis was obtained using a Perkin-Elmer 2400 CHN Elemental Analyzer.

^1H -NMR spectra were recorded using a Bruker ACF 300 spectrometer with $DCCl_3$ as the solvent and tetramethyl silane (TMS) as an internal standard. UV spectra were determined using an UV-3101 UV-visible spectrophotometer with chloroform as the solvent. Photoluminescence spectra (PL) of the samples were

performed on a Perkin-Elmer LS50B luminescence spectrometer. A coating film of sample on glass plate was used. Molecular weight was determined on a Waters 2696 Module Gel Permeation Chromatograph (GPC) using a Styragel column and THF as the eluant.

RESULTS AND DISCUSSION

Structural Characterization

The IR spectra and ^1H -NMR spectra of monomers shown in are Figs. 1 and 2.

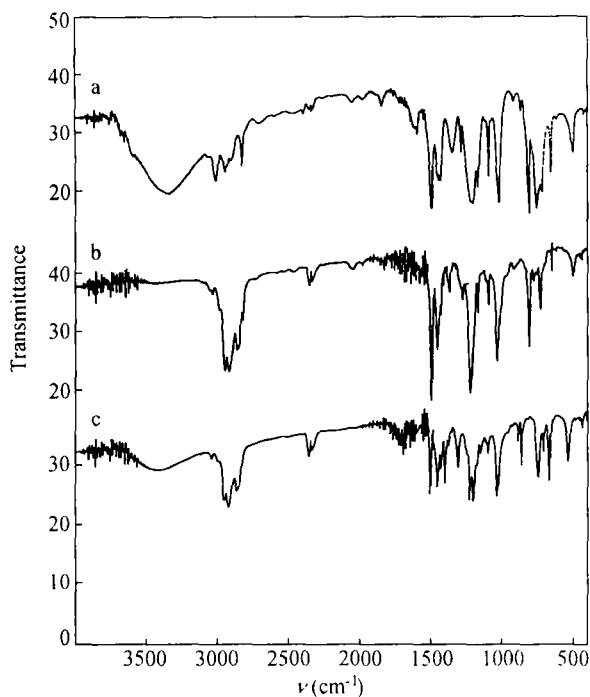


Fig. 1 IR spectra of compounds
a) *p*-Methoxyphenol
b) *p*-Methoxy-2-ethylhexyloxybenzene
c) 2-Methoxy-5-(2-ethylhexyl)-oxy-*p*-bis-bromo-methylbenzene (MEHDBMB)

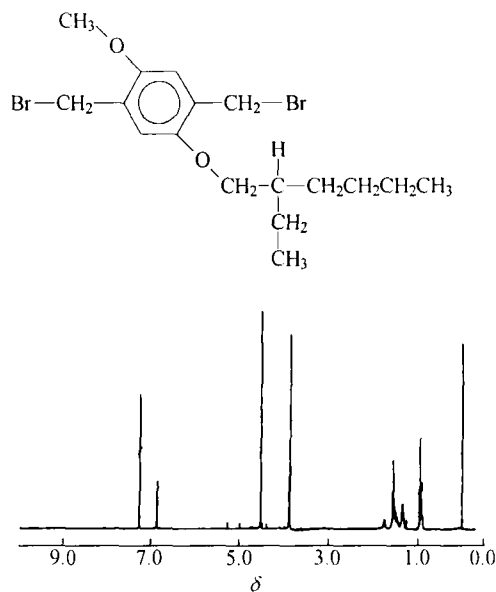


Fig. 2 ^1H -NMR spectrum of monomers

From Fig. 1 it can be seen that after introducing the 2-ethylhexyloxy side chain, the stretching vibration of OH (3358 cm^{-1}) on the phenyl ring of *p*-methoxyphenol disappeared, while the intensities for the methyl peak and the new peak of the methylene group from 2-ethylhexyloxy side chain (curve b, $2949, 2963\text{ cm}^{-1}$) became stronger. After bromomethylation, the Br—C stretching vibration (547 cm^{-1} , and 1200 cm^{-1}) in Fig. 1c appeared. These data indicate that the reactions (Scheme 1) have taken place.

From Fig. 2 it can be seen that the new monomer contains the chemical shifts for benzene ring ($\delta = 6.85$, 2H), bromomethyl on phenyl ($\delta = 4.55$, 4H, singlet), methoxy group ($\delta = 3.85$, 3H, singlet) and 2-ethylhexyloxy group ($-\text{O}-\text{CH}_2-$ at $3.85, 3.90$, 2H, 2CH_3 at $\delta = 0.90\text{--}0.94$, methylene at $\delta = 1.30\text{--}1.54$, tert-H, at $\delta = 1.77$, 1H). These NMR data coincide with those of the IR spectra.

Elemental analysis shows that the found values agree with the values calculated from the formula (found: C 48.48%, H 6.26%, Br 38.12%; calculated: C 48.36%, H 6.16%, Br 37.89%).

The IR spectrum and ^1H -NMR spectrum of PPV product are shown in Figs. 3 and 4.

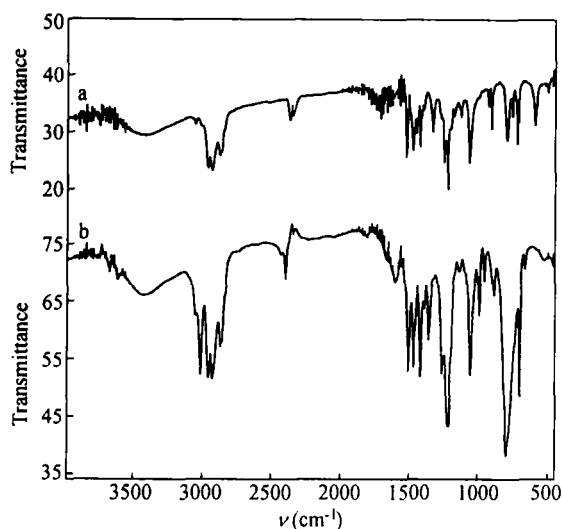
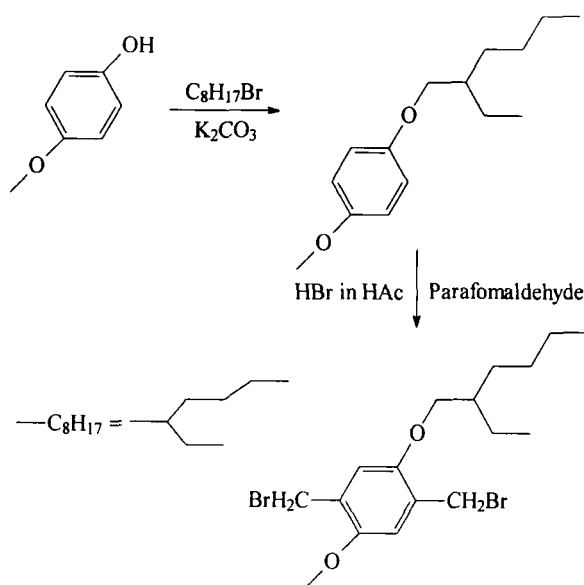


Fig. 3 IR spectra of PPV (a) and METH-PPV (b)

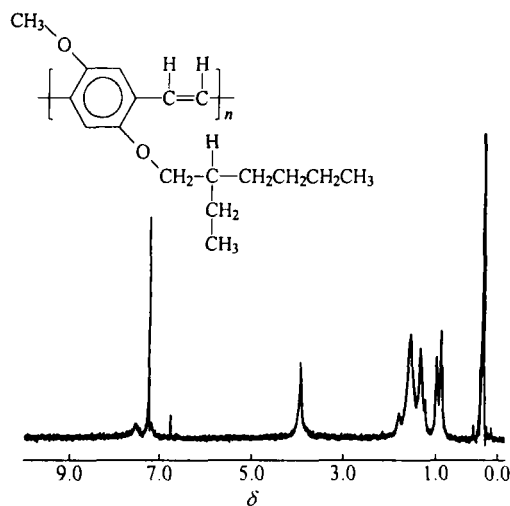


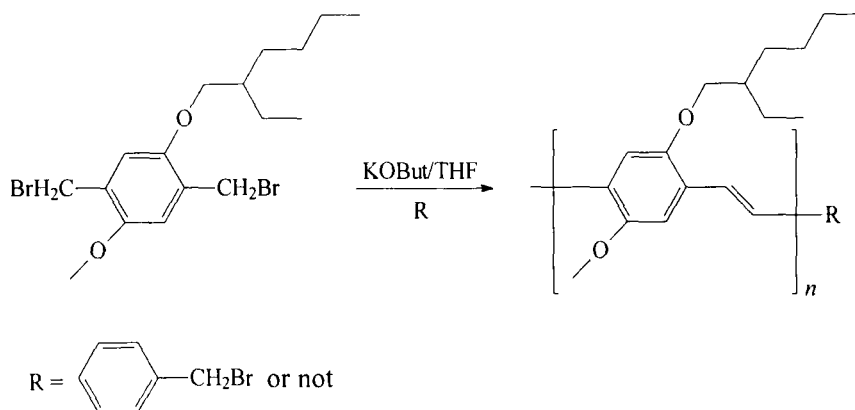
Fig. 4 ^1H -NMR spectrum of PPV

From Fig. 3 it can be seen that after polymerization, the absorption of Br-C at 547 cm^{-1} in the monomer disappeared, and a new absorption at 1590 cm^{-1} belonging to long conjugated double bond appeared. This indicates that the polymerization reaction has occurred (Scheme 2).

From Fig. 4 it can be seen that after polymerization, the NMR peak for $-\text{CH}_2-\text{Br}$ ($\delta = 4.55$) in the monomer disappeared, and the new poly(phenylenevinylene) with long conjugated structure (phenylene, $\delta = 7.20$, 2H; vinylene, $\delta = 7.40\sim 7.60$, 2H) was formed. The product of PPV contains methoxy ($\delta = 3.96$), 2-ethylhexyloxy group ($-\text{O}-\text{CH}_2-$, $\delta = 3.92, 3.96$, 2H; 2CH_3 , $\delta = 0.90\sim 1.00$; methylene, $\delta = 1.36\sim 1.60$, 4 CH_2 ; tert-proton, $\delta = 1.85$, 1H).

The results of NMR determination further support the conclusion drawn from the IR study. Figure 5 shows the UV- spectra of monomer (a) and its PPV (b). After polymerization, a strong absorption at 500 nm is evidenced in PPV product; this is very different from monomer. Moreover, the monomer is white in colour but

becomes deep red after polymerization, which is associated with the long conjugated structure in PPV. The UV results further support the conclusion drawn from IR and NMR analysis.



Scheme 2

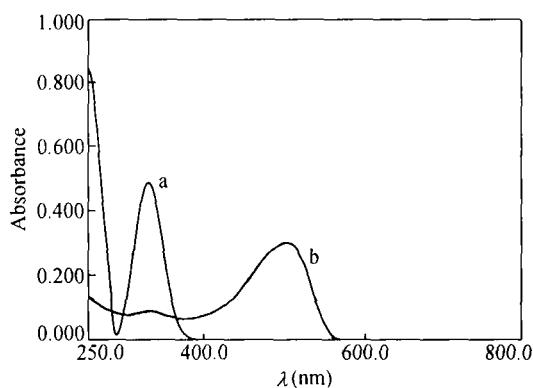
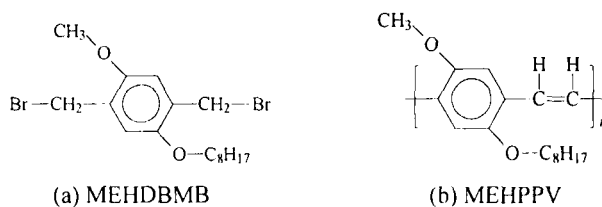


Fig. 5 UV-spectra of monomer (a) and its polymer (b)



Molecular Weight and Solubility of PPV

The M_w and the solubility of PPV are shown in Tables 1 and 2. From Table 1 it can be seen that chain stopper can effectively lower the M_w of PPV, and makes it fully soluble in common organic solvents. It is very interesting to observe that a typical radical inhibitor (2,6-di-*tert*-butyl-4-methyl phenol, an antioxidant) which operates the mechanism of stopping free radical chain reactions (scavenger) can effectively lower the M_w of PPV. And our recent research results show that 2,6-di-*tert*-butyl-4-hydroxymethylphenol (a radical inhibitor too) has a similar effect on lowering the M_w of PPV. These results imply that free radical polymerizing behaviour is involved in this polymerization process.

From Table 2 and Table 1 it can be seen that the molecular weight of PPVs can be controlled by adding

molecular weight modifiers, making these PPV more readily soluble in common organic solvents.

Table 1. Molecular weight and polydispersity of PPV *

Sample	Monomer (g/mmol)	Additives	<i>t</i> (h)	<i>M_w</i> / <i>M_n</i>	Polydispersity	Yield (%)
A	0.300/0.71		3.0	Gel		52.15
B	0.300/0.71		1.5	Gel		91.63
C	0.300/0.71	Stopper 30mg	3.0	252395/47289	5.34	63.36
D	0.300/0.71	Stopper 60mg	3.0	218866/49939	4.38	44.84
E	0.300/0.71	Stopper 120mg	3.0	147324/38841	3.79	52.64
F	0.300/0.71	Antioxidant, 70mg	3.0	201974/50197	4.00	45.55

* Every sample (A, B, C, D, E and F) was polymerized in the presence of 30 mL THF (solvent) and 2.13 mmol *t*-BuOK (catalyst)

Table 2. Solubility of PPV *

Solvent	Sample					
	A	B	C	D	E	F
THF	Gel	Gel	S	S	S	S
Chloroform	Microgel	Microgel	S	S	S	S
Xylene	Gel	Gel	S	S	S	S

* Samples A-F are the same as Table 1.

The solubility of PPVs was examined by adding 5 mg of PPV into 1 mL of solvent at room temperature for 0.5 h.

Samples C, D, E, F can directly dissolve in chloroform and THF at room temperature, but samples C, D, E, F often need heating to dissolve in xylene, then keep the solution at room temperature.

Sample A or B is a gel (microgel) in the above solvent even it is heated for days.

Optical Properties of PPV

The UV- spectra of PPVs prepared by adding different amounts of additives are shown in Fig. 6. All PPVs have a very strong absorption at 500 nm and a weak absorption at 330 nm, the former is attributed to the long conjugated double bond connecting with the structures of styryl and stilbenyl groups^[15]. By comparing the UV- spectra of PPVs, one can see that the additives in the PPV have no obvious effect on their UV spectra. This may be associated with the very small amount of additives capping the ends of PPV molecular chains.

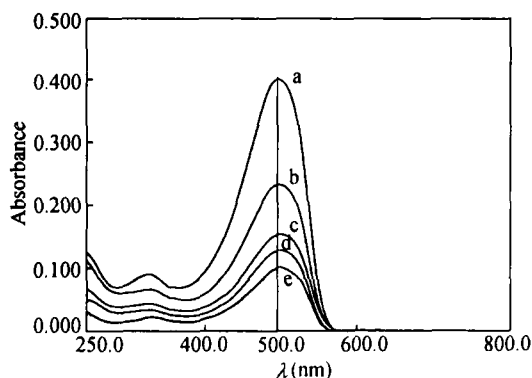


Fig. 6 UV of PPVs

a) Stopper 30 mg; b) Stopper 60 mg; c) Stopper 0 mg; d) Stopper 120 mg; e) antioxidant 70 mg

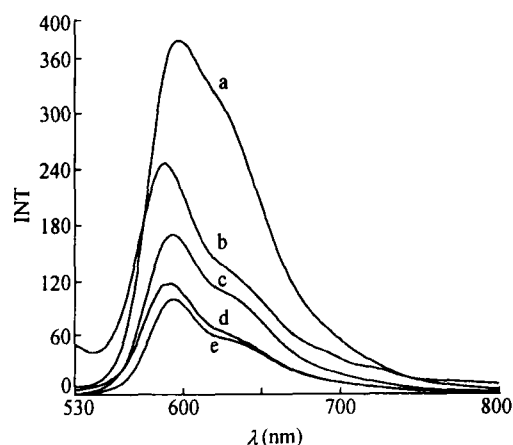


Fig. 7 Photoluminescence of PPVs

a) Stopper 120 mg; b) antioxidant 70 mg; c) stopper 30 mg; d) no stopper; e) stopper 60 mg

The photoluminescence spectra of PPVs are shown in Fig. 7. Pure PPV has a strong light emission at

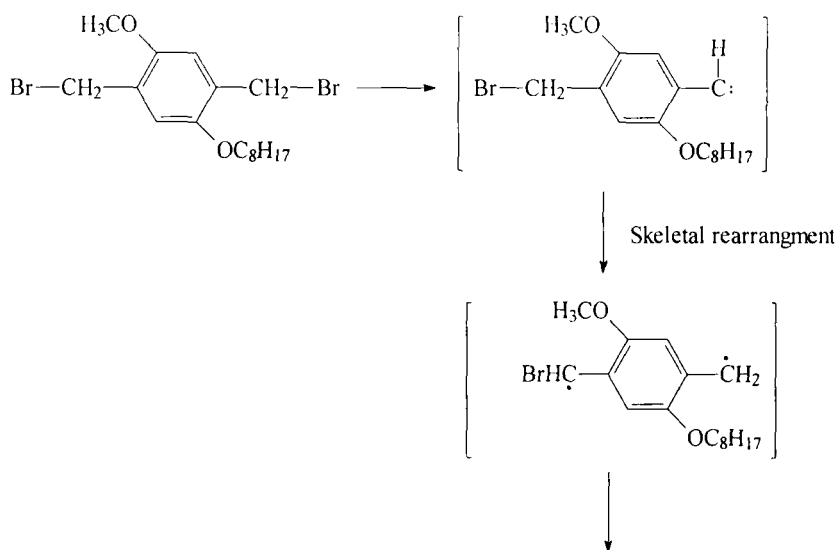
590 nm when it is excited by 490 nm light. Some red shifts of the luminescence spectra of PPV capping additives have been observed. In the spectrum of PPV capping 2,6-di-tert-butyl-4-methylphenol the absorption band at 590 nm shifts to 592 nm, and the band for benzyl bromide even shifts from 590 nm to 600 nm.

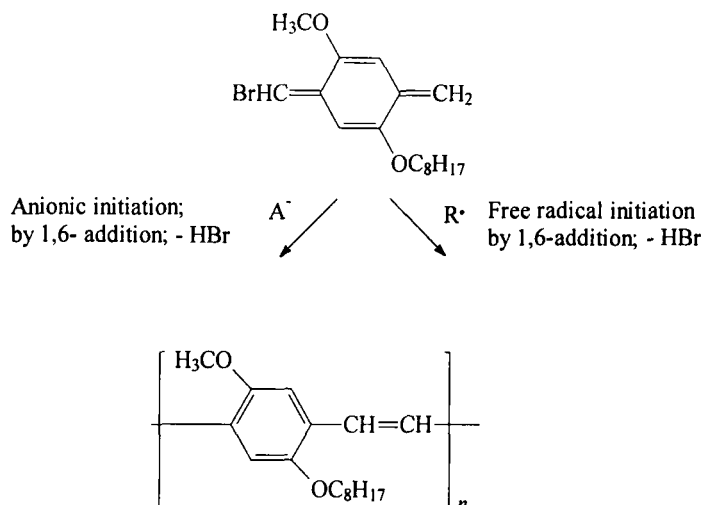
Polymerization Mechanism of PPV

The polymerization mechanism of PPV is still not clear, and two mechanisms, radical and ionic, have been proposed. Wessling and coworkers^[16, 17] have prepared high molecular weight PPV using a series of dialkylsulfonium salts (SR_2^+X^-). They observed that the radical initiator can accelerate the polymerization rate and increase the viscosity of resultant PPV, but oxygen can affect the polymerization rate and lower the viscosity of resultant PPV. Therefore, they proposed a radical polymerization mechanism. However, this mechanism can not explain why the polymerization continues to proceed without radical initiator. Obviously, besides the free radical mechanism, other mechanisms should take effect. In a later study, Garay and Lenz^[10, 18, 19] proposed an anionic polymerization mechanism through the formation of a highly reactive *p*-xylylene intermediate, which was confirmed by UV and $^1\text{H-NMR}$ spectroscopies^[15]. However, this mechanism can not explain the fact that the polymerization rate was accelerated by adding free radical initiator.

Our results show that a radical inhibitor which operates the mechanism of stopping free radical chain reaction can inhibit the increase of molecular chain length and lower the M_w of PPV; and our recent studies also show that free radical scavengers such as 2,2,6,6-tetramethyl piperidinol-4,4-amino-2,2,6,6-tetramethyl piperidine and nitroxy stable free radical prepared oxidation by of the copolymer of 2,2,6,6-tetramethylpiperidinyl methacrylate and styrene can more effectively control the polymerization reaction and lower the M_w of PPV. This work is still in progress and will be reported in another paper. We have also observed that the polymerization of PPV proceeds rapidly without free radical initiator. Therefore, it seems that in the polymerization of PPV there are dual mechanisms, both radical and ionic. This is not surprising since the dual mechanisms always exist in the reaction of hydrogen halide, e.g. dehydrochlorination of polyvinylchloride (PVC) possesses the ionic or radical mechanism, which depends on the experimental condition^[20]. Hydrogen bromide adds to propene to give a 1-bromide product (radical mechanism, anti-Markovnikov rule), and HCl adds to propene to yield a 2-chloride product (ionic mechanism, Markovnikov rule)^[21].

Based on the literature and our results as well as considering the fact that the benzylcarbene can be formed from benzyl halide by the action of base and the characteristics of radical homolysis of the C-Br bond^[21-23], we propose a dual polymerisation mechanism for PPV, in which the monomer forms a *p*-xylylene intermediate through benzylcarbene rearrangement and then polymerizes through 1,6-addition:





In the above mechanism, bisbromomethylbenzene monomer was turned into benzylcarbene through base-promoted dehydrobromination. This benzylcarbene was converted into *p*-xylylene intermediate by skeletal rearrangement and structure stabilization, then it was polymerized by 1,6 addition of either radical or ionic nature depending upon the reaction conditions and the structure of the monomer. Under our experimental condition for bisbromomethylbenzene monomer with *t*-BuOK as a catalyst, the free radical polymerization mechanism is somewhat predominant but can not exclude the ionic polymerization mechanism.

This dual polymerization mechanism can better explain the fact that the polymerization rate can be accelerated by free radical initiator and retarded by free radical scavenger. Also it can better explain the fact that the polymerization can proceed without free radical initiator.

CONCLUSION

Based on the above results, we can conclude that some soluble MEH-PPVs have been synthesized. Their molecular weight can be controlled by the addition of molecular weight modifier, and the chain stopper (benzyl bromide) as well as free radical scavengers (2,6-di-*tert*-butyl-4-methyl phenol and some hindered piperidines) are effective molecular weight modifiers for PPV preparation under these experimental conditions.

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