MEH–PPV: Improved Synthetic Procedure and Molecular Weight Control

2 AUTHORS:

Charles J. Neef
Pittsburg State University
23 PUBLICATIONS **582** CITATIONS

SEE PROFILE

John P Ferraris
University of Texas at Dallas
229 PUBLICATIONS **9,418** CITATIONS

SEE PROFILE

Articles

MEH-PPV: Improved Synthetic Procedure and Molecular Weight Control

C. J. Neef and J. P. Ferraris*

The University of Texas at Dallas, P.O. Box 830688, MS/BE26, Richardson, Texas 75083-0688

*Received September 8, 1999; Revised Manuscript Received February 3, 2000*

ABSTRACT: Mechanistic studies on the polymerization of α,α'-dibromo-2-methoxy-5-(2-ethylhexyloxy)-xylene have been performed. Polymerizations were initially carried out by adding potassium *tert*-butoxide to monomer in the presence of a chain transfer agent, anthracene. Anthracene showed little effect on the molecular weight of the resulting polymer, suggesting that the major polymerization route was not radically initiated. Polymerizations were also carried out by adding monomer to potassium *tert*-butoxide in the presence of a nucleophile, 4-methoxyphenol. The molecular weight of the resulting polymer scaled linearly with the amount of 4-methoxyphenol, suggesting an anionic mechanism. In addition, each polymerization was monitored by in-situ torque measurements to further elucidate the polymerization mechanism and optimize polymerization conditions.

Introduction

Poly(*p*-phenylenevinylene)s (PPVs) continue to receive considerable interest for applications such as light-emitting diodes,[1] field effect transistors,[2] and photovoltaic devices.[3] Two approaches are generally used for the synthesis of PPVs: the Wessling[4] route and the Gilch[5] route. The Wessling route involves treatment of *p*-xylylene sulfonium salts with an equal molar amount of base to form a soluble precursor polymer. The precursor polymer is then thermally treated to give the conjugated PPV. The Gilch route employs the treatment of α,α-dihalo-*p*-xylenes with potassium *tert*-butoxide in organic solvents. Alkyl or alkoxy substituents on the aromatic ring are often used to impart solubility to the PPV. One of the most widely studied PPVs is poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) due to the enhanced solubility of this polymer.[6]

The mechanism of this polymerization is not fully understood, and several processes have been suggested.[7] The polymerization is believed to proceed through a reactive quinodimethane intermediate that has been observed from UV spectra.[8,9] However, the nature of the propagating species, radical or anionic, is not firmly established (Scheme 1). Several reports have suggested a radical polymerization due to decreases in molecular weight with the addition of chain transfer agents such as anthracene or TEMPO.[10,11] In contrast, the addition of 4-*tert*-butylbenzyl chloride resulted in an inverse relationship between the amount of benzyl chloride and molecular weight, suggesting an anionic polymerization.[12,13] Also, both radical and anionic mechanisms have been observed for the polymerization of chloromethyl-4-(*n*-butylsulfinyl)methylbenzene.[14] Due to the ambiguity in this polymerization process, further research is warranted to obtain a better understanding of the mechanism. Understanding the polymerization mechanism may provide the means to control molecular

Scheme 1. Polymerization Mechanism of α,α'-Dibromoxylene by Anionic and Radical Initiation
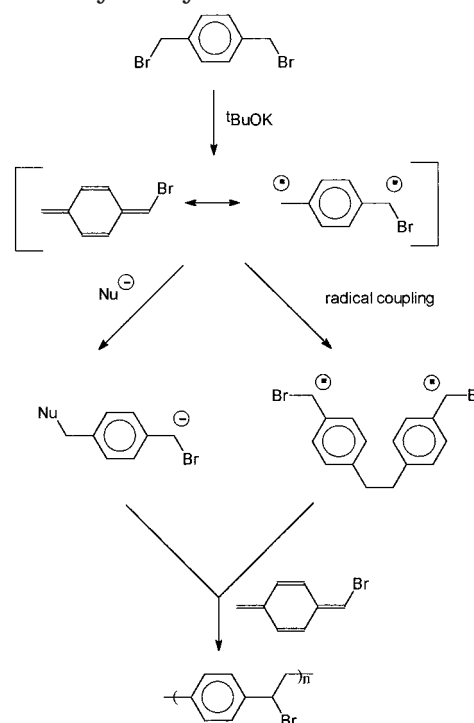
weight and circumvent polymerization problems such as gelation or precipitation of polymer products during polymerization.

In this paper, we describe several experiments to further elucidate the polymerization mechanism of α,α'-dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene. The effects of a chain transfer agent and a nucleophile on the molecular weight of the resulting polymer were evaluated. Also, the order of addition of reagents, base to

monomer or monomer to base, was studied. In addition, a rheostat was used as the mechanical stirrer to detect in-situ changes in viscosity and to follow the polymerization process.

Experimental Section

All reagents were commercially available and used as received unless otherwise stated. THF was distilled from sodium benzophenone prior to use. ^{1}H NMR spectra were obtained on a JEOL FX-200 or FX-270 MHz instrument using TMS as an internal standard. Torque measurements were recorded with a Contraves model 115 rheomat/rheostat and plotted with a strip chart recorder. Molecular weights were measured with a Phenomenex phenogel (5 μm) column using a Viscotek T60 and LR40 triple detector and analyzed with TriSEC GPC Viscometry software (version 3.0).

Synthesis of Methoxy-4-(2-ethylhexyloxy)benzene (1). To a round-bottom flask were added 4-methoxyphenol (100 g, 0.81 mol), KOH (56 g, 1 mol), tetrabutylammonium bromide (5 g, 0.17 mol), and water (300 mL). To this solution was added 2-ethylhexyl bromide (154 g, 0.80 mol), and a N_2 atmosphere was established. The reaction was then heated to reflux for 3 days. After allowing the reaction to cool to ambient temperature, the layers were separated followed by extraction of the organic layer with water. Purification by distillation afforded 157 g (83%) of **1**. The ^{1}H NMR spectrum was consistent with that previously reported.[6] ^{1}H NMR (200 MHz, CDCl$_3$): 6.84 (s, 4H), 3.90 (s, 5H), 1.9−0.8 (m, 15H).

Synthesis of α,α′-Dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (2), To a round-bottom flask were added **1** (50 g, 0.21 mol), paraformaldehyde (30 g, 1 mol), acetic acid (100 mL), and 30% HBr in acetic acid (100 mL). A N_2 atmosphere was established followed by heating the reaction to 70 °C for 4 h. After allowing the reaction to cool to ambient temperature, the reaction was diluted with chloroform followed by extraction with water and NaHCO$_3$(aq). The chloroform solution was dried over MgSO$_4$ followed by removal of the chloroform under reduced pressure. Purification by recrystallization from hexane afforded 71 g (80%) of **2**; mp = 81−82 °C. EA: calculated 48.36% C, 6.21% H; found 48.34% C, 6.12% H. IR (KBr), cm^{-1}: 3048, 2956, 2926, 2871, 1512, 1461, 1407, 1315, 1232, 1204, 1038, 871, 718, 680, 547. ^{1}H NMR (270 MHz, CDCl$_3$): 6.86 (s, 4H), 4.53 (s, 4H), 3.86 (s, 5H), 1.8−0.8 (m, 15H). [13]H NMR (270 MHz, CDCl$_3$): 151.09, 151.04, 127.54, 127.40, 114.37, 113.85, 71.02, 56.32, 39.68, 30.72, 29.19, 28.76, 28.70, 24.10, 23.12, 14.17, 11.33.

Polymerizations of α,α′-Dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (MEH-PPV), Method A. To a round-bottom flask, well flushed with N_2 and equipped with a rheostat as the mechanical stirrer, were added **2** (2.0 g, 4.7 mmol), anthracene (0, 2, 4, 10, or 50 mol %), and THF (100 mL). A solution of potassium *tert*-butoxide in THF (20 mL, 1.0 M) was then added at a rate of 20 mL/h via a syringe pump. After complete addition of the base, the reaction was stirred for an additional 16 h. The reaction was poured into rapidly stirred methanol, and the resulting polymer was collected by suction filtration. The polymer was purified by continuous extraction with hexane followed by continuous extraction with toluene. The toluene was removed under reduced pressure. The polymer was then dissolved into THF, precipitated into rapidly stirred methanol, collected, and dried under reduced pressure to give 0.55−0.78 g (45−63%) of MEH-PPV.

Polymerizations of α,α′-Dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (MEH-PPV), Method B. To a round-bottom flask, well flushed with N_2 and equipped with a rheostat as the mechanical stirrer, were added a solution of potassium *tert*-butoxide in THF (20 mL, 1.0 M), 4-methoxyphenol (0, 0.5, 1.0, 1.5, or 2.0 mol %), and dry THF (80 mL). A solution of **2** (2.0 g, 4.74 mmol) in dry THF (20 mL) was then added at a rate of 20 mL/h with a syringe pump. After complete addition of the monomer, the reaction was stirred for an additional 16 h. The reaction was poured into rapidly stirred methanol, and the resulting polymer was collected by suction filtration. The polymer was purified by two additional pre-
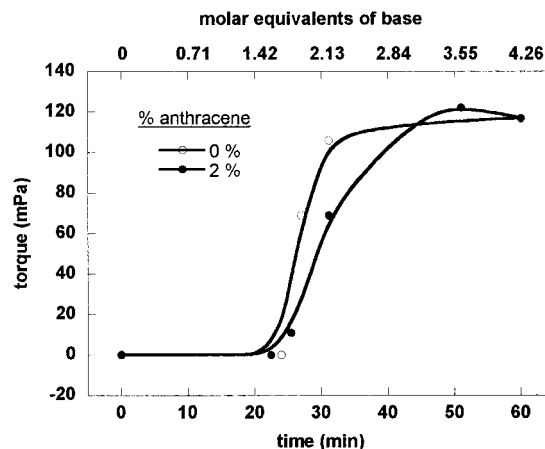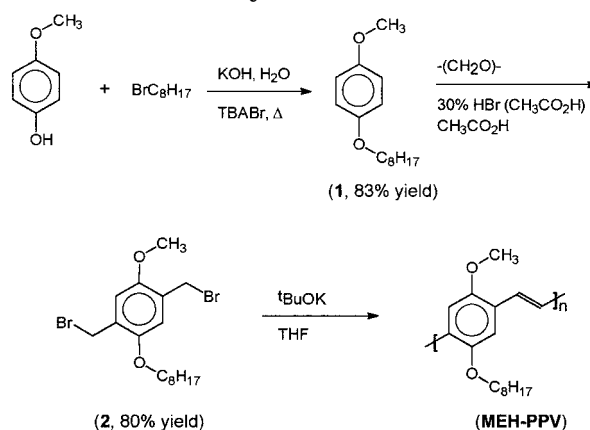

Figure 1. Torque measurements of polymerizations under method A conditions without and with (2 mol %) the addition of anthracene.

Scheme 2. Synthesis of MEH-PPV

cipitations, from THF into hexane and from THF into methanol. The polymer was then collected and dried under reduced pressure to give 0.62−0.88 g (50−72%) of MEH-PPV.

Results and Discussion

Synthesis of 2. The synthesis of **2** was accomplished in two steps from 4-methoxyphenol (Scheme 2). 4-Methoxyphenol was reacted with 2-ethylhexyl bromide under phase transfer conditions to give **1** in an 83% yield. **1** was then treated with paraformaldehyde and HBr in acetic acid to give **2** in an 80% yield, resulting in an overall yield of 66%. The synthesis of **2** was more convenient than the chloromethyl derivative since gaseous HCl was not used in the synthesis. Also, the yield of **2** was higher than the reported yield of the chloromethyl derivative.[6] Spectral analyses and elemental analysis of **2** were consistent with the proposed structure.

Synthesis of MEH-PPV (Method A). Initially, experiments on the synthesis of MEH-PPV were performed by adding potassium *tert*-butoxide to **2** (method A) over a period of 1 h. Various amounts of anthracene (0, 2, 4, 10, and 50 mol %) were also used in the polymerization since anthracene is a known chain transfer agent for the polymerization of 1,4-bis(tetrahydrothiophenomethyl)benzene.[10] During each polymerization, the torque was monitored in order to detect changes in viscosity, and the results for 0 and 2 mol % anthracene are shown in Figure 1. Polymerization of **2** in the absence of anthracene showed no change in

Table 1. Polymerization Results versus the Amount of Anthracene under Method A Conditions

| % anthracene	Δtorque (mPa)[a]	% yield	M_n[b]	PD[c]
0	117	51	108 600	1.17
2	122	39	95 500	2.27
4	69	46	120 800	1.15
10	85	58	73 000	2.61
50	148	30	58 400	2.92

[a] Difference between initial and final torque. [b] Number-average molecular weight. [c] Polydispersity.

torque until 8–9 mL (ca. 2 mol equiv) of base was added. At this point, a significant change in torque was observed which increased rapidly and leveled off within minutes. These results showed that significant polymerization did not occur until 2 mol equiv of base was added and that it occurred very quickly at this point. The resulting toluene-soluble polymer had a molecular weight (M_n) of 108 600.

Torque measurements for polymerizations with anthracene were similar to the polymerization without anthracene. No significant change in torque was observed, until ca. 2 mol equiv of base was added, which was followed by a very rapid increase. The steplike change in torque observed at 8–9 mL and the small effect of anthracene suggest that the polymerization of **2** is not primarily radical in nature. Also, the difference between the final torque and initial torque (Δtorque) did not correlate well with the M_n of the corresponding polymer. The lack of correlation between Δtorque and M_n may be a result of incomplete dehydrobromination due to the rapid polymerization. The viscosity of the solution would therefore be due to a combination of polymers at various stages of dehydrobromination.

The effects of anthracene on the M_n of the resulting polymers are given in Table 1. The addition of small amounts of anthracene, 2 or 4 mol %, to the polymerization of **2** resulted in polymers with M_n's of 95 500 and 120 800, respectively. These results are similar to the polymerization of **2** in the absence of anthracene and suggested that small amounts of anthracene have a minimal effect. Larger amounts of anthracene in the polymerization, 10 or 50 mol %, gave polymers with M_n's of 73 000 and 58 400, respectively. Despite some diminution of M_n, the effect of anthracene was much smaller than expected. For example, in the polymerization of 1,4-bis(tetrahydrothiophenomethyl)benzene, a decrease in molecular weight from 222 000 to 12 000 was observed with the addition of 10% anthracene.[10] Although a radical mechanism cannot be entirely eliminated, these data were not consistent with this type of mechanism and illustrated the difficulty of controlling the M_n under method A conditions.

Synthesis of MEH-PPV (Method B). If the polymerization of **2** is anionic in nature, then initiation and molecular weight might be controlled by the addition of **2** to excess base (method B) in the presence of an initiator. Also, anionic polymerization of the quinodimethane should show a slow increase in viscosity as **2** is added. Previous studies have shown that 4-*tert*-butylbenzyl chloride can be used as an anionic initiator to reduce M_n, but precise control of molecular weight was limited due to self-condensation of the benzyl chloride.[12] For this study, the initiator 4-methoxyphenol was used in various amounts (0, 0.5, 1.0, 1.5, and 2.0 mol %) to control molecular weight and to circumvent the problem of self-condensation observed for 4-*tert*-
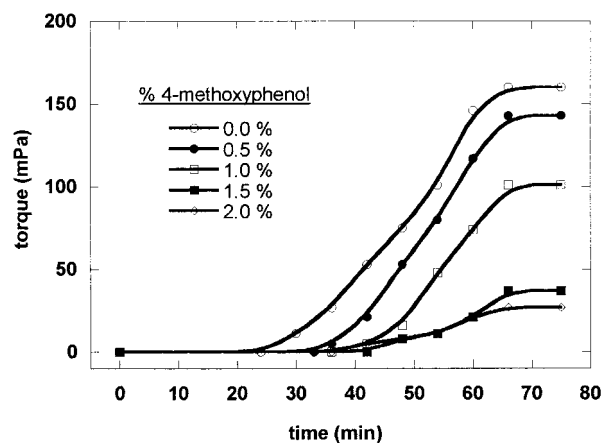
Figure 2. Torque measurements of polymerizations under method B conditions with various amounts (0, 0.5, 1.0, 1.5, and 2.0 mol %) of 4-methoxyphenol.

Table 2. Polymerization Results versus the Amount of 4-Methoxyphenol under Method B Conditions

% 4-methoxy-phenol	Δtorque (mPa)[a]	% yield	M_n[b]	PD[c]
0	160	72	125 700	1.06
0.5	143	68	118 200	1.04
1.0	101	67	86 200	1.52
1.5	37	56	57 700	1.43
2.0	27	50	51 300	1.14

[a] Difference between initial and final torque. [b] Number-average molecular weight. [c] Polydispersity.

butylbenzyl chloride. The pK_a of 4-methoxyphenol allows for complete deprotonation by *tert*-butoxide, and the resulting phenoxide is expected to act as a nucleophile to initiate polymerization but not be sufficiently basic to form the quinodimethane from **2**.

For the polymerization with 0% 4-methoxyphenol, a change in torque was observed at ca. 25 m which continued to rise at a gradual rate, leveling off after complete addition of monomer. These results are shown in Figure 2 and are qualitatively different from the torque profile obtained under method A conditions. The gradual rise in torque under method B conditions suggests a change in polymerization process and is consistent with an anionic polymerization. If this mechanism is operating, then the molecular weight of the polymer should be controllable by the addition of an appropriate amount of initiator.

Differences in the Δtorque and molecular weight as a function of the amount of 4-methoxyphenol were observed, and these results are reported in Table 2. As the amount of 4-methoxyphenol was increased, the Δtorque and M_n showed a decrease. Also, the polydispersities of the resulting polymers were low, ranging from 1.04 to 1.52. These results were consistent with anionic initiation since anionic polymerization is known to have an inverse relationship between M_n and initiator and to result in low polydispersity. Plots of Δtorque and M_n versus percent 4-methoxyphenol are shown in Figure 3. These plots show linear relationships between Δtorque and M_n with percent 4-methoxyphenol and clearly illustrate the control of molecular weight by this polymerization method. Also, the Δtorque was consistent with the M_n of the corresponding polymer and suggested that the viscosity of the solution was due to MEH-PPV and not from polymer at various stages of dehydrobromination.
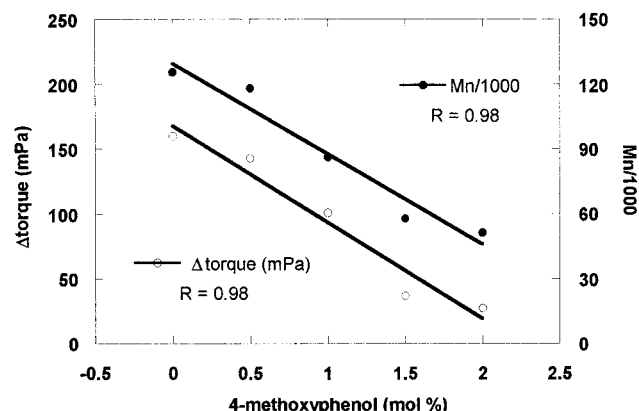
Figure 3. Molecular weight and Δtorque versus % 4-methoxyphenol for polymerization experiments under method B conditions.

In addition to molecular weight control and low polydispersity, this polymerization method offers several advantages over the current literature method of PPV synthesis: addition of base all at once to the monomer. Addition of monomer to excess base provides a steady concentration of in situ generated quinodimethane, resulting in better control of the polymerization kinetics. The control of molecular weight circumvents the problem of microgel formation observed with MEH-PPV.[12] Also, this method may be useful for electron-deficient monomers that are difficult to polymerize using the current method of PPV synthesis.

Conclusion

An improved polymerization method has been illustrated for the synthesis of MEH-PPV. This method utilizes a reversal in the addition of reagents, **2** to

potassium *tert*-butoxide, and the addition of an initiator to control the anionic polymerization. In addition, the molecular weight of the resulting polymer was linearly dependent on the amount of initiator, and the molecular weight decreased as the amount of initiator was increased. These results were consistent with an anionic polymerization of **2**.

References and Notes

(1) Friend, R. H.; Greenham, N. C. *Handbook of Conductive Polymers*; Marcel Dekker: New York, 1998; p 823.
(2) Parker, I. D.; Gymer, R. W.; Harrison, M. G.; Friend, R. H.; Ahmend, H. *Appl. Phys. Lett.* **1993**, *62*, 1519.
(3) Antoniadis, H.; Hsieh, B. R.; Abkowitz, M. A.; Jenekhe, S. A.; Stolka, M. *Synth. Met.* **1994**, *62*, 625.
(4) Wessling, R. A.; Zimmerman, R. G. U.S. Patents 3,401,152, 1968, and 3,532,643, 1970.
(5) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 1337.
(6) Wudl, F.; Srdanov, G. U.S. Patent 5,189,136, 1993.
(7) Moratti, S. *Handbook of Conductive Polymers*; Marcel Dekker: New York, 1998; p 343.
(8) Lahti, P. M.; Modarelli, D. A.; Denton, F. R.; Lenz, R. W.; Karasz, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 7258.
(9) Denton, F. R.; Sarker, A.; Lahti, P. M.; Garay, R. O.; Karasz *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2233.
(10) Denton, F. R.; Lahti, P. M.; Garay, Karasz *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2223.
(11) Issaris, A.; Vanderzande, D.; Gelan, J. *Polymer* **1997**, *38*, 2671.
(12) Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094.
(13) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 231.
(14) Hontis, L.; Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1999**, *40*, 6615.

MA991521D