

Use of DMF as Solvent Allows for the Facile Synthesis of Soluble MEH–PPV

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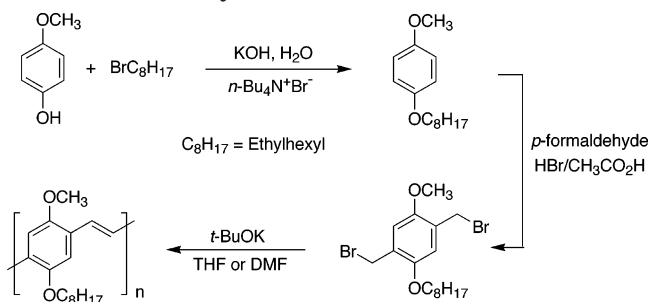
ABSTRACT: A new method is described for the synthesis of soluble poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH–PPV) using *N,N*-dimethylformamide (DMF) as the solvent. Based on a modification of the traditional Gilch method, the polymerization of α,α' -dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene was conducted in DMF under a variety of experimental conditions. The resultant MEH–PPVs were characterized and compared to those prepared using analogous syntheses in tetrahydrofuran (THF). Characterization techniques included ¹H NMR spectroscopy, UV–vis spectroscopy, and gel permeation chromatography (GPC). Although the molecular weights of the polymers prepared in DMF were routinely lower than those prepared in THF, the polydispersities were as low as (and in most cases lower than) those obtained using THF. Significantly, the use of DMF in polymerizations conducted at 100 °C led to no gelation of the polymer, which circumvented the need for any controlled addition of monomer during the reaction. Moreover, control over the polymer molecular weights in DMF could be achieved using chosen aliquots of the molecular weight modifier 4-(*tert*-butyl)benzyl bromide and/or by controlling the concentration of the reactants.

Introduction

Poly(*p*-phenylenevinylene)s (PPVs) have received a great deal of interest due to their unique physical properties such as conductivity, electroluminescence, and solubility of selected derivatives, which allows for facile processing in the manufacture of microelectronic devices.¹ Moreover, PPVs and their derivatives are currently the most popular class of conjugated polymers used in organic light-emitting diodes (OLEDs).² These polymers are also being developed for use in photovoltaic diodes,³ light-emitting electrochemical cells,⁴ laser devices,⁵ photodetectors, and image sensors.⁶ Perhaps the most widely studied and utilized polymer in this class is poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH–PPV). The presence of the long branched ethylhexyloxy substituent on the aromatic ring imparts remarkable solubility and processability to this conjugated polymer.

Three predominant approaches are used for the synthesis of PPV: Wittig condensations,^{7,8} the Wessling route,⁹ and the Gilch route.¹⁰ In the Wittig route, aromatic bisphosponium salts are treated with aromatic bisaldehydes in ethanol to afford typically insoluble polymer. In the Wessling route, *p*-xylene sulfonium salts are treated with an equimolar amount of base to obtain a soluble precursor polymer, which is then thermally treated to obtain the conjugated PPV. In the widely preferred Gilch route, α,α' -dihalo-*p*-xylenes are treated with potassium *tert*-butoxide in organic solvents (e.g., THF), where the polymerization is carried out either by the controlled addition of monomer to a solution of base or by the controlled addition of base to a solution of

Scheme 1. Synthesis of MEH–PPV in DMF



monomer. One of the major problems associated with the latter route is gel formation.^{11,12} Indeed, if the rate of addition of monomer to base or base to monomer is not controlled precisely, the reaction typically leads to the formation of a gel, which limits the yield, molecular weight, polydispersity, solubility, and processability of the polymer.

To overcome the problems associated with gel formation, researchers have explored several modifications of the Gilch route. For example, the use of additives, such as benzyl bromide,¹⁰ 2,6-di-*tert*-butyl-4-methylphenol,¹¹ and poly(ethylene glycol),¹³ has been shown to reduce gel formation in polymerization reactions. However, the use of these additives fails to produce MEH–PPVs with low polydispersities.

Given these limitations, we sought to develop a facile and general method for the synthesis of MEH–PPV using *N,N*-dimethylformamide (DMF) as the solvent rather than the traditionally used solvent tetrahydrofuran (THF). We chose to explore the use of DMF due to the known solubility of MEH–PPV in this solvent. To this end, we report here the synthesis of soluble MEH–PPV via the base-promoted polymerization of α,α' -dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene (**1**) in DMF (Scheme 1) under a variety of experimental

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conditions and compare the resultant polymers to those prepared similarly in THF. Specifically, we compare the molecular weights, polydispersities, and UV-vis absorption spectra. We also examine the use of 4-(*tert*-butyl)benzyl bromide as a molecular weight modifying agent in the polymerizations in DMF.

Experimental Section

All reagents were commercially available and used as received unless otherwise stated. The monomer α,α' -dibromo-2-methoxy-5-(2-ethylhexyloxy)xylene was either obtained from Polyorganix Inc. or synthesized using a literature procedure.¹⁴ The reagent 4-methoxyphenol was purified by sublimation. Prior to use in the polymerization reactions, THF was freshly distilled from sodium benzophenone, and DMF was freshly distilled from calcium hydride. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer (¹H: 300 MHz) using THF-*d*₆ as solvent. The data were processed using NUTS-NMR Utility Transform software (Acron NMR). Molecular weights of the polymers were measured in THF against polystyrene standards with a solvent flow rate of 1 mL/min on a Waters Styragel HR 5E (7.8 × 300 mm) column and using both a Waters 410 differential refractometer and a Waters 996 photodiode array detector. The resultant data were analyzed using a Waters Millennium 2010 Chromatography Manager, GPC software version 2.0. No effort was made to correct the molecular weight for differences in the Mark-Howink coefficient and exponent for MEH-PPV in comparison to polystyrene. UV-vis spectra were collected in THF on a Varian Cary Scan UV-vis spectrophotometer using Cary Scan software version 01.00(6).

Polymerization of 1 in THF: Bulk Addition at 23 °C, Method A. A 100 mL Schlenk flask equipped with a magnetic stirring bar was charged with potassium *tert*-butoxide (0.28 g, 2.5 mmol) and flushed with argon. After dilution with 12.5 mL of freshly distilled anhydrous THF, a solution of 0.25 g (0.59 mmol) of monomer **1** in 2.5 mL of anhydrous THF was added to the reaction mixture all at once. After stirring the reaction mixture for an additional 16 h at room temperature, a bright red gel was obtained, which was then precipitated into rapidly stirring methanol. The polymeric precipitate was collected by centrifugation followed by decanting the solvent mixture.

Polymerization of 1 in THF: Controlled Addition, Method B. Five 100 mL Schlenk flasks equipped with magnetic stirring bars were charged with potassium *tert*-butoxide (0.28 g, 2.5 mmol) and flushed with argon. To the flasks were then added 0, 2, 4, 6, and 8 mL (0, 0.5, 1.0, 1.5, and 2.0 mol %, respectively) of 1.48 mM 4-methoxyphenol stock solution (prepared by dissolving 45.87 mg of 4-methoxyphenol in 250 mL of anhydrous THF) and 12.5, 10.5, 8.5, 6.5, or 4.5 mL, respectively, of freshly distilled anhydrous THF to make the total reaction volume 12.5 mL. At room temperature (23 °C), a solution of 0.25 g (0.59 mmol) of monomer **1** in 2.5 mL of anhydrous THF was then added to the reaction mixture over 1 h using a syringe pump. In some cases, gel formation was observed at the end of the monomer addition, and the reaction was repeated. The reaction mixture was stirred for an additional 16 h at room temperature. At the end of the reaction period, a bright red solution was obtained, which was then precipitated into rapidly stirring methanol. The polymeric precipitate was collected by centrifugation followed by decanting the solvent mixture. Purification was effected by dissolving the residue in THF, filtering the solution through a 0.45 μm filter, and precipitating the mixture into hexanes. The process was then repeated but precipitated into methanol rather than hexanes. The resulting residue was dried under vacuum to afford 65–91 mg (42–59%) of MEH-PPV as a bright red powder.

Polymerization of 1 in THF: Bulk Addition at 67 °C, Method C. A 100 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with potas-

sium *tert*-butoxide (0.28 g, 2.5 mmol) and flushed with argon. After dilution with 12.5 mL of freshly distilled anhydrous THF, the reaction mixture was brought to reflux. A solution of 0.25 g (0.59 mmol) of monomer **1** in 2.5 mL of anhydrous THF was added to the reaction mixture all at once. After stirring the reaction mixture for an additional 16 h under reflux, a bright red gel was obtained, which was then precipitated into rapidly stirring methanol. The polymeric precipitate was collected by centrifugation followed by decanting the solvent mixture.

Polymerization of 1 in THF: Controlled Addition at 67 °C, Method D. A 100 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with potassium *tert*-butoxide (0.28 g, 2.5 mmol) and flushed with argon. After dilution with 12.5 mL of freshly distilled anhydrous THF, the reaction mixture was brought to reflux. A solution of 0.25 g (0.59 mmol) monomer **1** in 2.5 mL of anhydrous THF was added to the reaction mixture over 1 h using a syringe pump. After stirring the reaction mixture for an additional 16 h under reflux, a bright red solution was obtained, which was then precipitated into rapidly stirring methanol. The polymeric precipitate was collected by centrifugation followed by decanting the solvent mixture. Purification was effected by dissolving the residue in THF, filtering the solution through a 0.45 μm filter, and precipitating the mixture into hexanes. The process was then repeated but precipitated into methanol rather than hexanes. The resulting residue was dried under vacuum to afford 79 mg (51%) of MEH-PPV as a bright red powder.

Polymerization of 1 in DMF: Controlled Addition, Method E. The same experimental procedure was followed as the one described in method D except that freshly distilled DMF was used as the solvent rather than THF, and because of the temperatures employed, no solvent reflux occurred. Furthermore, the reaction was conducted at three separate temperatures: 23, 67, and 100 °C, where the intermediate temperature was chosen to be that of refluxing THF. In all cases, the reaction yielded a bright red solution containing bright red precipitates. The product mixture was processed as described in method D to afford 39–62 mg (25–40%) of MEH-PPV as a bright red powder.

Polymerization of 1 in DMF: Bulk Addition, Method F. Nine 100 mL Schlenk flasks equipped with magnetic stirring bars were charged with potassium *tert*-butoxide (0.28 g, 2.5 mmol) and flushed with argon. Respective aliquots of 0, 1, 2, 3, 5, and 10 mol % 4-(*tert*-butyl)benzyl bromide in 12.5 mL of anhydrous DMF were added to six of the nine flasks. To the remaining three flasks were then added respective aliquots (1.5, 5.0, and 17.5 mL) of anhydrous DMF. Each of the reaction mixtures was then heated to 100 °C, and a solution of 0.25 g (0.59 mmol) of monomer **1** in 2.5 mL of anhydrous DMF was added all at once. The reaction mixture was allowed to stir for an additional 16 h at 100 °C. At the end of the reaction period, a bright red solution containing bright red precipitates was obtained. The mixture was precipitated into rapidly stirring methanol, and the residue was collected by centrifugation. Purification was effected by dissolving the residue in THF, filtering the solution through a 0.45 μm filter, and precipitating the mixture into hexanes. The process was then repeated but precipitated into methanol rather than hexanes. The resulting residue was dried under vacuum to afford 42–51 mg (27–33%) of MEH-PPV as a bright red powder.

Results and Discussion

Synthesis of MEH-PPV in THF. As previously reported,¹⁰ the simple bulk addition of monomer **1** to a solution containing potassium *tert*-butoxide in THF led to the formation of an insoluble polymer gel (Table 1, entry 1). We then examined the polymerization of **1** according to literature procedures¹⁴ by slowly adding the monomer to the *tert*-butoxide/THF solution over a period of 1 h at room temperature (Table 1, entry 2). Although the slow addition of monomer reduced the formation of

Table 1. Characteristics of Soluble MEH-PPV Prepared in THF under Various Conditions

entry	method	solvent	total vol (mL)	monomer addition	temp (°C)	MWM ^a (mol %)	M _n ^b	PDI ^c	% yield
1	A	THF	15.0	at once	23	0.0	insoluble gel produced		
2	B	THF	15.0	over 1 h	23	0.0	80 000	4.1	42
	B	THF	15.0	over 1 h	23	0.0	89 000	3.0	50
	B	THF	15.0	over 1 h	23	0.0	88 300	2.4	43
3	B	THF	15.0	over 1 h	23	0.5	70 100	4.6	58
	B	THF	15.0	over 1 h	23	0.5	88 300	4.4	35
	B	THF	15.0	over 1 h	23	0.5	88 300	3.2	54
4	B	THF	15.0	over 1 h	23	1.0	62 000	4.3	42
	B	THF	15.0	over 1 h	23	1.0	88 300	3.7	53
	B	THF	15.0	over 1 h	23	1.0	88 300	4.1	55
5	B	THF	15.0	over 1 h	23	1.5	49 000	4.1	53
	B	THF	15.0	over 1 h	23	1.5	40 100	3.4	45
	B	THF	15.0	over 1 h	23	1.5	45 700	2.8	43
6	B	THF	15.0	over 1 h	23	2.0	38 700	5.3	58
	B	THF	15.0	over 1 h	23	2.0	38 500	3.3	47
	B	THF	15.0	over 1 h	23	2.0	37 000	3.6	53
7	C	THF	15.0	at once	67	0.0	insoluble gel produced		
8	D	THF	15.0	over 1 h	67	0.0	80 000	2.3	51
	D	THF	15.0	over 1 h	67	0.0	85 300	2.1	55

^a Molecular weight modifier: 4-methoxyphenol. ^b Number-average molecular weight. ^c Polydispersity index (M_w/M_n).

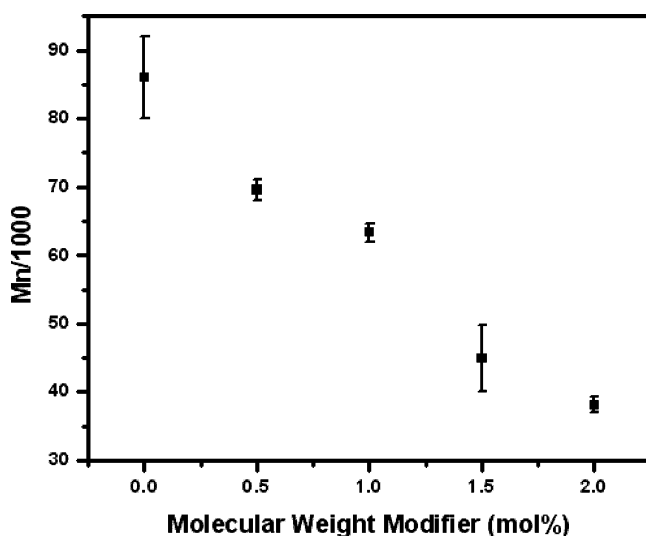


Figure 1. Plot showing the decrease in molecular weight of MEH-PPV as a function of increasing amounts of 4-methoxyphenol (for THF at 23 °C). The error bars indicate the observed variation among duplicate runs.

polymer gel compared to cases in which the monomer was added all at once, the technique still led to gel formation in about 10% of the runs. Using the method of slow addition, we systematically added increasing amounts of the molecular weight modifier, 4-methoxyphenol,¹⁴ to examine the influence of this agent on the molecular weights of the resulting MEH-PPVs. As described in the literature,¹⁴ the molecular weights of the polymer were observed to decrease with increasing amounts of 4-methoxyphenol (Table 1, entries 2–6). A graphical presentation of these data is provided in Figure 1, which shows the systematic relationship between number-average molecular weight (M_n) and the quantity of 4-methoxyphenol employed.

Using refluxing THF, we repeated the reactions in entries 1 and 2 to evaluate the role of elevated temperature in these polymerizations (Table 1, entries 7 and 8). Examination of entries 1 and 7 reveals that gel formation occurs at both room temperature and at 67 °C when the monomer is added all at once. In contrast, entries 2 and 8 demonstrate that gel formation can be avoided at either temperature by using the controlled addition of the monomer **1** to the *tert*-butoxide solution.

Furthermore, comparison of these latter data suggests that temperature plays no significant role in influencing the molecular weights of the polymers synthesized in THF.

Synthesis of MEH-PPV in DMF. On the basis of the results in THF, we chose to examine the polymerization of **1** in DMF using the method of slow addition. Entries 1–3 in Table 2 show the resultant data for a series of MEH-PPVs prepared at three temperatures (23, 67, and 100 °C). In all cases, these trials gave polymers with relatively low dispersities, and their molecular weights were substantially lower than any of those prepared in THF. Although the increase in temperature from 23 to 100 °C appears to correlate with an increase in the average molecular weight, the magnitude of the increase is quite small. Pang and co-workers also noted an increase in polymer molecular weight with increasing temperature in the synthesis of PPVs by Wittig condensation in THF and a mixture of chloroform and THF.¹⁵ The authors attributed this phenomenon to an enhanced solubility of the polymers at elevated temperatures, which facilitates the growth of longer chains.

Given the relatively low molecular weights of MEH-PPV obtained from the preceding studies, we chose to explore the polymerizations of **1** in DMF by adding the monomer in bulk to a solution of *tert*-butoxide in DMF (i.e., method F). Entry 4 in Table 2 shows the data for the polymer produced by adding an aliquot of **1** all at once to a basic solution of DMF maintained at 100 °C. In this reaction, no gel formation was observed, and the resultant polymer was completely soluble in common organic solvents; for example, solutions of the polymer in THF, benzene, chloroform, toluene, and xylene were easily filtered through 0.45 μ m filters. Moreover, the average molecular weight of the MEH-PPV was substantially higher than those produced using method E (~30 000 vs ~5000). By analogy to Hontis et al.,¹⁶ the fact no gelation occurs in DMF might be due to an unraveling of the polymer “physical network” that only occurs at elevated temperatures (98 °C in their case; 100 °C in ours).

Given these encouraging results, we then explored the use of a molecular weight modifying agent that would allow precise control over the molecular weights of the MEH-PPVs produced in DMF. Initial attempts using

Table 2. Characteristics of Soluble MEH-PPV Prepared in DMF under Various Conditions

entry	method	solvent	total vol (mL)	monomer addition	temp (°C)	MWM ^a (mol %)	M _n ^b	PDI ^c	% yield
1	E	DMF	15.0	over 1 h	23	0.0	2 500	2.4	25
2	E	DMF	15.0	over 1 h	67	0.0	3 800	1.8	34
3	E	DMF	15.0	over 1 h	100	0.0	5 500	1.5	40
4	F	DMF	15.0	at once	100	0.0	27 800	1.9	30
	F	DMF	15.0	at once	100	0.0	26 100	2.1	38
	F	DMF	15.0	at once	100	0.0	26 800	1.8	37
5	F	DMF	15.0	at once	100	1.0	21 400	3.2	31
	F	DMF	15.0	at once	100	1.0	22 200	2.2	37
	F	DMF	15.0	at once	100	1.0	21 500	1.9	40
6	F	DMF	15.0	at once	100	2.0	18 200	3.9	33
	F	DMF	15.0	at once	100	2.0	19 000	2.2	27
	F	DMF	15.0	at once	100	2.0	18 600	2.8	39
7	F	DMF	15.0	at once	100	3.0	16 100	4.7	29
	F	DMF	15.0	at once	100	3.0	16 500	2.5	38
	F	DMF	15.0	at once	100	3.0	16 500	3.1	34
8	F	DMF	15.0	at once	100	5.0	11 500	2.8	30
	F	DMF	15.0	at once	100	5.0	11 200	2.9	34
	F	DMF	15.0	at once	100	5.0	10 600	3.3	35
9	F	DMF	15.0	at once	100	10.0	5 500	1.9	27
	F	DMF	15.0	at once	100	10.0	5 000	2.5	39
	F	DMF	15.0	at once	100	10.0	4 900	1.8	33
10	F	DMF	4.0	at once	100	0.0	19 200	3.2	28
	F	DMF	4.0	at once	100	0.0	18 800	2.1	36
11	F	DMF	7.5	at once	100	0.0	24 500	2.7	33
	F	DMF	7.5	at once	100	0.0	25 400	2.6	27
12	F	DMF	20.0	at once	100	0.0	31 500	4.3	35
	F	DMF	20.0	at once	100	0.0	32 000	2.2	39

^a Molecular weight modifier: 4-(*tert*-butyl)benzyl bromide. ^b Number-average molecular weight. ^c Polydispersity index (M_w/M_n).

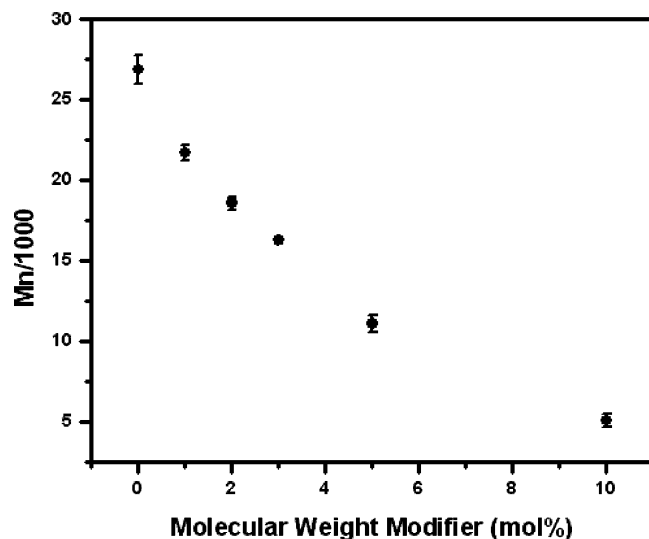


Figure 2. Plot showing the decrease in molecular weight of MEH-PPV as a function of increasing amounts 4-(*tert*-butyl)benzyl bromide (for DMF at 100 °C). The error bars indicate the observed variation among duplicate runs.

4-methoxyphenol as a molecular weight modifier were unsuccessful; the molecular weights were insensitive to this reagent at concentrations as high as 10 mol % (data not shown). In contrast, the use of 4-(*tert*-butyl)benzyl bromide was remarkably effective.^{17,18} Entries 4–9 in Table 2 show that the use of increasing amounts of this agent led to a systematic reduction in the molecular weights of the MEH-PPVs produced. These data are graphically presented in Figure 2, which indicates an inverse relationship between the molecular weights and the amount of 4-(*tert*-butyl)benzyl bromide added.

In separate studies, we found that it was possible to modify the molecular weights of MEH-PPVs produced in DMF simply by adjusting the total volume of the reaction. When the amount of DMF used in the reaction was varied from 4 to as high as 20 mL, but the amount

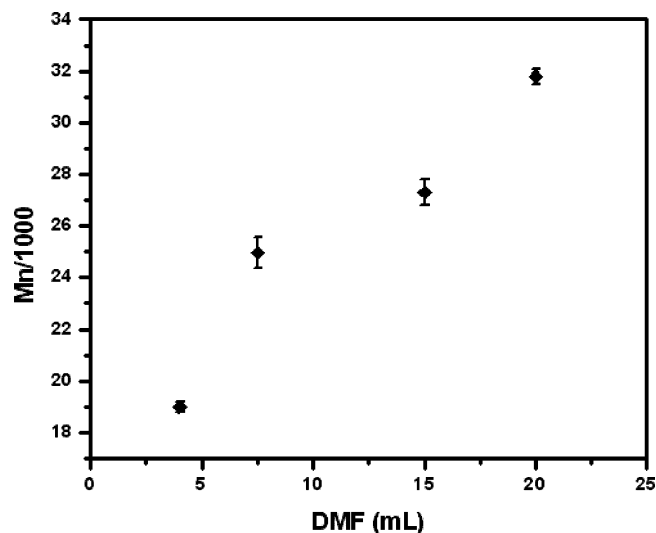


Figure 3. Plot showing the increase in molecular weight of MEH-PPV as a function of increasing volume of DMF. The error bars indicate the observed variation among duplicate runs.

of base and monomer were kept constant under the same experimental conditions, the average molecular weights of the MEH-PPVs produced varied systematically from ~19 000 to ~32 000 (Table 2, entries 4, 10, 11, and 12). The linear relationship between molecular weight and reaction volume is illustrated in Figure 3.

Comparison of the MEH-PPVs synthesized using THF and DMF reveals that those synthesized in THF exhibit notably higher molecular weights than those synthesized in DMF (Table 1 vs Table 2). The difference in molecular weights probably arises from differences in solubility of MEH-PPV in these two solvents, where an enhanced solubility in THF relative to DMF facilitates the growth of longer chains—a hypothesis supported indirectly by the work by Pang and co-workers (*vide supra*).¹⁵ Our polymerization trials in DMF at

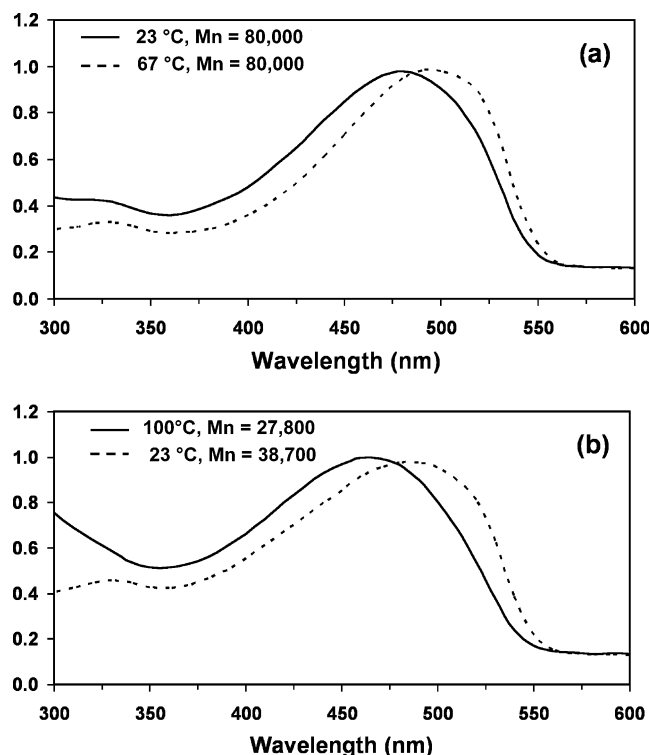


Figure 4. UV-vis absorption spectra of MEH-PPV solutions in THF (a) constant molecular weight prepared in THF at various temperatures, and (b) similar molecular weight prepared in DMF (100 °C) and THF (23 °C).

systematically chosen temperatures are further consistent with this hypothesis. Entries 1–3 in Table 2 show, for example, that increasing the temperature without varying other experimental parameters leads to a systematic increase in the molecular weights of the MEH-PPVs produced.

Analysis of the MEH-PPVs by UV-Vis Spectroscopy. We collected the UV-vis spectra of selected samples of the polymers to examine whether the conjugation length varies with the polymerization method employed. For all samples, we observed a broad absorption band with absorption maxima ranging from 460 to 510 nm (Figure 4); these bands arise from transitions between states delocalized along the MEH-PPV backbone.¹¹ Parts a and b of Figure 4 separately compare the UV-vis absorption of MEH-PPVs with approximately the same molecular weight but prepared at different temperatures and/or using different solvents and addition methods. Although the data indicate moderate shifts in the positions of the absorption maxima, the overall spectral features are quite similar, suggesting that the various synthetic methods afford MEH-PPVs having similar conjugation lengths.

Conclusions

Using a modified version of the traditional Gilch reaction, the work presented here demonstrates a new and simple method for the synthesis of soluble MEH-

PPV. Coupled with the bulk addition of monomer to the reaction mixture, replacement of the solvent THF with DMF leads to MEH-PPVs without polymer gelation. While the polydispersities of the polymers prepared in DMF are as good or better than most of those prepared in THF, the molecular weights of the polymers prepared in DMF are routinely lower than those prepared in THF. Furthermore, the molecular weights of the polymers prepared in DMF can be systematically controlled by adding selected aliquots of 4-(*tert*-butyl)benzyl bromide and/or by varying the concentration of the reactants. Importantly, polymerizations in DMF can be conducted without needing to carefully control the slow addition of monomer to the reaction mixture, which is an essential feature of successful polymerizations in THF.

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Supporting Information Available: Gel permeation chromatograms illustrating the molecular weight distributions of selected polymerization trials listed in Tables 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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