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Simple improvements to Gilch synthesis and molecular weight modulation of MEH-PPV

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The solvent and temperature used in the Gilch synthesis of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) were varied to achieve an improved set of reaction conditions. A range of molecular weights from 20 to 500 kg/mol were obtained in moderate to near-quantitative yields. The best conditions for producing low molecular weight MEH-PPV (32 kg/mol, 97% yield) was to use n-pentane as the reaction solvent at 25 °C. For high molecular weight (397 kg/mol, 65% yield), toluene at 55 °C gave the best result. The photophysical properties for all MEH-PPV samples were examined and no significant variation was found between samples obtained under different polymerization conditions.

Introduction

Poly(p-phenylenevinylenes) (PPVs) were the first materials used in organic light emitting diodes (OLEDs),[1] as well as bulk heterojunction (BHJ) organic photovoltaic cells (OPVs).[2, 3] Many polymerization methods for the production of PPVs) exist,[4] such as the Horner-Wadsworth-Emmons (HWE) polymerization,[5] the Wessling route,[6] Stille polymerization,[7] Heck polymerization,[8] ring opening metathesis polymerization (ROMP),[9] and the Gilch polymerization.[10] The Gilch polymerization method is used extensively in particular, since it supports the use of a variety of monomers,[11] which can be easily synthesized in as little as two steps on large scales,[12] and often produces solution processable polymers in high yields. The mechanism for the Gilch polymerization method involves deprotonation of the bis-α,α-substituted xylene monomer to form a quinodimethane intermediate (Figure 1).[11, 13, 14] This can then dimerize to form a biradical initiator. With more of the quinodimethane intermediate the chain can propagate via a radical polymerization process. Subsequently, the PPV is then generated via an elimination reaction with base. An anionic polymerization was proposed as an alternative pathway for the Gilch mechanism,[12] however this is often disputed and the radical mechanism is preferred.[11, 15]

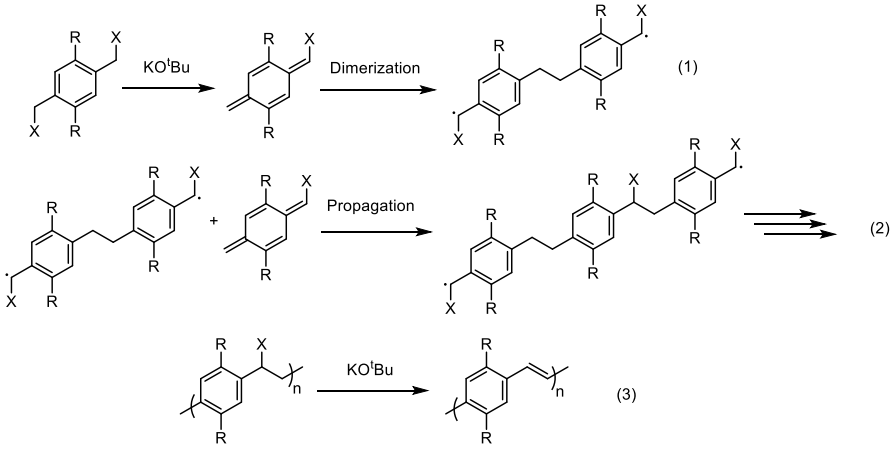

Figure 1. The reaction mechanism for the Gilch polymerization method.

Despite extensive studies into the Gilch polymerization method and mechanism, no procedures have shown the effect of reaction solvent and temperature on the molecular weight outcome. Additionally, previous studies that have modulated the molecular weight have done so using additives which are necessarily incorporated into the endgroups of the polymers to some degree.[12, 15, 16] These additives include; radical traps (e.g. TEMPO), chain transfer agents such as CBr_4, or simple end-capping reagents such as tert-butyl benzyl bromide. Apart from

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studying the effect of reaction solvent and temperature on molecular weight in this study (Figure 2), the photophysical properties of the resulting polymers are also examined and verified.

Results and discussion

MEH-PPV was synthesized via Glich polymerization of bis(bromomethyl) monomer 1 with variations in reaction solvent and temperature (Figure 2). Monomer 1 (79 mM in the chosen solvent) was added via syringe pump at a rate of 10 mL/hr to a flask containing a 70 mM solution of potassium *tert*-butoxide (KO^tBu). If the monomer was added all at once, the monomer concentration in the reaction would be 12 mM. The scale of the reactions was 0.1g of monomer (0.24 mmol). The mixtures were then stirred for 24 or 72 hr depending on the reaction temperature. The polymeric products were then precipitated in methanol and collected via centrifugation. In the case of non-polar reaction solvents, the polymer precipitated from the reaction mixture. Although many reaction solvents are immiscible with methanol, the same precipitation procedure into methanol was used for consistency, and the precipitated polymer was collected via centrifugation. The MEH-PPV samples were washed three times with methanol and hexanes and dried. These samples were subjected to molecular weight and photophysical analysis without further purification (Refer to experimental section for detailed synthesis procedure and characterization methods).

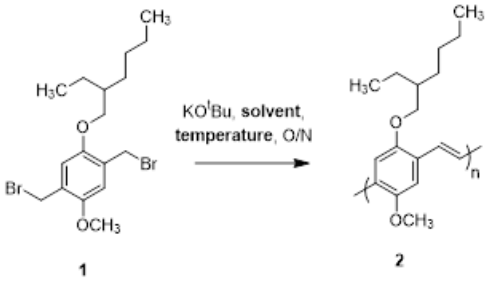
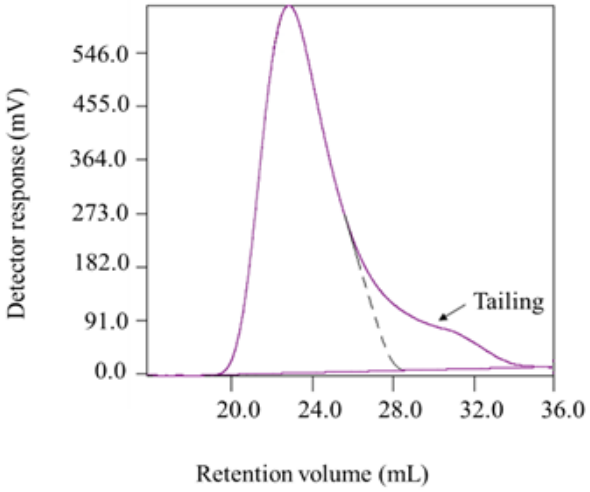


Figure 2. Reaction conditions used to produce MEH-PPV.

Reaction solvents

The most commonly used solvent for the Gilch polymerization is THF, which serves as a good comparison between solvents. The reaction in THF at 25 °C gave a polymer sample with number average molecular weight (M_n) of 50 kg/mol, weight average molecular weight (M_w) of 371 kg/mol, peak molecular weight (M_p) of 311 kg/mol and dispersity (Đ) of 7.37 (Table 1, entry 11). This high dispersity number can be partly attributed to the simple isolation procedure without purification steps one typically encounters for conjugated polymers. Additional purification can be performed to remove "tailing" via reprecipitations or Soxhlet extractions, which has been shown to significantly reduce dispersity.[12] Table 1 shows the effect of solvent on the reaction yield as well as the change in average molecular weights and dispersities. The molecular weight of polymers is often reported and compared using the number average molecular weight, M_n. However with broad dispersities due to "tailing" as seen in the GPC trace (Figure 3), there was a bias towards a lower M_n as compared to the most abundant



molecular weight polymer. In the following discussions, the peak molecular weight, M_p, was mainly used for comparisons.

Figure 3. GPC trace showing the effect of "tailing" upon the molecular weight distribution.

Table 1. The effect of solvent upon the molecular weight distribution and reaction yield carried out at 25 °C.

Entry	Solvent	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	Đ	Yield
1	DMF	12,100	20,400	19,400	2.52	7%
2	DMAc	18,100	59,800	42,600	3.30	6%
3	n-Pentane	10,200	31,800	19,400	3.10	97%
4	Hexanes	14,300	55,800	21,600	3.92	45%
5	n-Hexane	12,600	46,100	25,500	3.83	57%
6	Cyclohexane	23,000	102,000	77,000	4.43	59%
7	Perfluorodecalin / n-hexane (3:1)	18,600	69,500	50,900	3.74	46%
8	α,α,α-Trifluorotoluene	23,500	71,000	54,100	3.02	55%
9	Chlorobenzene	26,400	108,000	80,100	4.07	80%
10	Toluene	68,600	502,000	319,000	7.31	62%
11	THF	50,300	371,000	311,000	7.37	65%
12	Diethyl ether	15,000	48,900	36,200	3.27	82%
13	MTBE	20,000	98,500	75,600	4.94	73%
14	1,4-Dimethoxyethane	23,400	125,000	82,800	5.34	quant.
15	1,4-Dioxane	43,400	361,000	202,000	8.33	85%
16	Methanol	-	-	-	-	NR
17	Acetonitrile	-	-	-	-	NR
18	tert-Butanol	-	-	-	-	NR

1,4-Dioxane is the only other commonly used solvent used in the Gilch polymerization of MEH-PPV and has been shown previously to give improved dispersity and yield compared to THF.[15] Under our experimental conditions, the polymerization with dioxane gave slightly lower molecular weight range and better isolated yield compared to THF (Table 1, entry 15). Various other solvents were then trialed in the reaction with differing functionality, such as amides (DMF, DMAc), alkanes (hexanes a.k.a petroleum spirits, n-hexane, n-pentane, cyclohexane), fluorinated solvents (perfluoromethyldecalin, α,α,α-trifluorotoluene), aromatics (toluene, chlorobenzene), ethers (diethyl ether, methyl tert-butyl ether (MTBE), 1,4-dimethoxyethane, THF, 1,4-dioxane), alcohols (methanol and tert-butanol), and a nitrile (acetonitrile). Solvents containing amides were found to work poorly with low yields 6-7% and with lower molecular weights (Table 1, entries 1 and 2). Alkanes, with the exception of pentane, produced MEH-PPV in lower yields (45-59%), as well as lower molecular weights (M_p 19 to 77 kg/mol) and lower dispersities (3.1 to 4.4) when compared to THF (Table 1, entries 4-6). n-Pentane was the standout solvent for producing low molecular weight range MEH-PPV in the lower dispersity and very good yield of 97% (Table 1, entry 3). The results with fluorinated solvents were similarly to alkanes (Table 1, entries 7 and 8). For perfluoromethyldecalin, a mixture with n-hexane (3:1) was needed to dissolve the monomer, otherwise the reaction proceeded very slowly with only perfluoromethyldecalin as the solvent. Polymerizations in aromatic solvents produced much higher M_p values than alkanes (80-319 kg/mol), with higher yields and modest dispersities (Table 1, entries 9 and 10). In the case of chlorobenzene, the isolation yield of the product was higher than that of THF at 80%. Ethers provided higher yields with lower M_p values and dispersities, with 1,2-dimethoxyethane giving quantitative conversion (Table 1, entries 12-14). Reactions with methanol, *tert*-butanol, and acetonitrile as solvent did not produce polymeric products. Yellow solutions were produced for acetonitrile and tert-butanol indicating the formation of oligomeric products. It is possible that the significantly lower basicity of KO^tBu in tert-butanol and acetonitrile hinders the elimination step needed to generate both the quinodmethane intermediate and the final polymer. Additionally, should any polymers be formed, the lack of solubility of these polymers in either tert-butanol or acetonitrile would inhibit further growth. No colour change or any other indication of MEH-PPV formation was observed for methanol. A control experiment was performed using sodium methoxide in THF. It was expected that KO^tBu in methanol would form the corresponding methoxide base. Due to the difference in the nucleophilicity of the base, methoxide was more likely to undergo a substitution reaction with any halide functional groups rather than the tert-butoxide base. This would result in a saturated methoxide functionalized polymer and hence showed no colour change in the reaction. Previous literature showed that the substitution reactions to form methoxide functionalized polymers occurred in methanol at 50 °C, but then

required 220-300 °C under vacuum to eliminate methanol and generate the conjugated PPV backbone.[1, 17, 18]

Even though the results show trends among some solvents, there exists some outliers. For example, n-pentane produces a similar molecular weight polymer to n-hexane but in a much higher reaction yield of 97% versus 57% for n-hexane. Batch-to-batch variations may play a significant role in the consistency of results, and so further work is required to show the statistical significance of these values. Instead this study may be used as a guide to produce low molecular weight polymers (<100 kg/mol) or high molecular weight polymers (>100 kg/mol) in moderate to good yields (>50%) or in poor yields (<50%).

The effect of temperature

MTBE was chosen to perform a temperature study ranging from -78 to 55 °C (Table 2), since it performed roughly as the median solvent in M_p, dispersity and yield at 25 °C. MTBE also offered a large temperature range between its melting point and boiling point at atmospheric pressure. The reaction yield decreased when the temperature was lowered and increased when the temperature was raised. Upon lowering the temperature, longer reaction times were needed to reach a steady state in molecular weight distributions via GPC analysis. At 0 °C, bimodal distributions in the GPC data were observed after 24 hr. After 72 hr reaction time, a typical single broad distribution was recorded. At -78 °C, the reaction slowly became pale yellow in colour and no polymeric material was isolated on workup. This suggested that the rate of propagation reduced significantly at lower temperatures, and hence longer reaction times were needed to grow larger polymer chains. It is interesting to note that polymerization at temperatures as low as -100 °C has been observed.[19] However, this was achieved through continuous photopolymerization and the yield of the polymer was not report and expected to be low. This is consistent with the results shown in Table 2 as a general trend, whereby the yield decreases as the temperature decreases. This may be due to the reduction in the elimination rate with the alkoxide base, thereby reducing the overall availability of the quinodimethane monomer concentration in the polymerisation solution at any given time. Surprisingly, the M_p decreased as the reaction temperature increased above room temperature (Table 2, entries 1 and 2). Upon decreasing the reaction temperature below 25 °C, the M_p decreases to 23 kg/mol and then remained unchanged as the temperature was reduced further. It is worthwhile to note that at 40 °C, the dispersity is much higher than any other values obtained, with a value of 8.31, although this may be an outlier from simple batch-to-batch variations.

To test whether this temperature related trend seen for MTBE would occur independent of solvent choice, a study was performed with different solvents run in parallel at both 25 and 55 °C (Table 3). THF, toluene and chlorobenzene were chosen since they offer distinct solvent properties baring different functional groups whilst large M_p values were obtained at 25 °C (Table 1). This would then produce a noticeable decrease if the same trend applies as seen with MTBE. Interestingly, chlorobenzene showed lower M_p at 25 °C (80 kg/mol) when compared to the result at 55 °C (151 kg/mol) while THF and toluene showed higher M_p at 25 °C. The factors affecting molecular weight and product yield outcomes include solubility of monomers, reagents and resulting polymers in the solvent, rate of chain propagation and stability of radical intermediates. While it is difficult to say which of these factors are more important, it is clear that MEH-PPV from low to high molecular weights can be obtained in high isolated yields simply by adjusting solvent and temperature without the use of additives.

Table 2. The effect of temperature upon the molecular weight distribution and reaction yield using MTBE as the solvent. *Reactions left for 72 hrs.

Entry	Temperature (°C)	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	Đ	Yield
1	55	18,500	78,600	37,700	4.24	quant.
2	40	21,200	176,000	54,200	8.31	quant.
3	25	20,000	98,500	75,600	4.94	73%
4	0*	13,800	40,500	23,500	2.94	40%
5	-15*	15,300	41,200	22,900	2.70	49%
6	-30*	16,600	35,100	23,600	2.11	21%
7	-78*	-	-	-	-	NR

Table 3. The effect of temperature upon the molecular weight distribution and reaction yield for different reaction solvents.

Entry	Solvent	Temperature (°C)	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Đ	Yield
1	THF	55	49,600	194,000	167,000	3.92	62%
2	THF	25	50,300	371,000	311,000	7.37	65%
3	Toluene	55	70,700	397,000	300,000	5.61	65%
4	Toluene	25	68,600	502,000	319,000	7.31	62%
5	Chlorobenzene	55	54,100	474,000	151,000	8.77	64%
6	Chlorobenzene	25	26,400	108,000	80,100	4.07	80%

Ranking conditions

Given these results, two sets of ideal conditions can be used for a Gilch polymerization. One set of conditions can be used to target polymers at lower molecular weight range. Lower molecular weight materials are sometimes desirable where greater ease of dissolution and lower solution viscosity are required in applications.[20] Alternatively, high molecular weight polymer can be achieved in high yield with a different solvent and temperature combination. This could be particularly advantageous for monomers that do not polymerize efficiently in conventional Gilch reaction conditions. To quantify these two sets of conditions, we assigned a rank based off the dispersity, M_p, and reaction yield:

$$Rank_{High} = \frac{yield \times M_p}{Đ}, \; Rank_{Low} = \frac{yield}{Đ \times M_p}$$

These ranks assign arbitrary values which increase when a high weight polymer or low weight polymer is favoured. The dispersity is also desired to be low in all cases, and the yield should be high in all cases. Table 4 and Table 5 summarizes these ranks in the form of a normalized rank as a ratio of the lowest obtained value (See supporting information Table S1 and Table S2 for the complete results). Alkanes and ethers tend to produce very high values for $Rank_{Low}$ (Table 4), with n-pentane at 25 °C giving the best result with a value of 61, compared to toluene at 25 °C (the lowest rank). Aromatic solvents gave low $Rank_{Low}$ values ranging from 1 to 13, reflecting the fact that they enabled the production of high molecular weight polymers. DMF and DMAc gave low $Rank_{Low}$ and low $Rank_{High}$ values due to the poor yields of those reactions.

Toluene was found to be the best performing solvent for producing a high weight polymer with a $Rank_{High}$ value of 65 compared to that of DMF (Table 5). As expected, the values and trend of $Rank_{High}$ mirror that of $Rank_{Low}$ in general, whereby alkanes have low values (5 to 19) and aromatic solvents have high values (18 to 65). From this, the best set of condition for producing a high weight polymer was with toluene as the solvent at 55 °C, and the best condition for producing a low weight polymer was with n-pentane as the solvent at 25 °C.

Table 4. Selected examples of normalized ranking for reaction conditions (ranked from highest to lowest) for the production of low molecular weight polymers with high reaction yields.

Entry	Solvent	Temperature (°C)	Normalized Low Rank
1	n-Pentane	25	61
2	MTBE	-15	30
3	n-Hexane	25	22
4	α,α,α-Trifluorotoluene	25	13
5	Chlorobenzene	25	9
6	DMAc	25	2
7	THF	25	1
8	Toluene	25	1

Table 5. Selected examples of normalized ranking for reaction conditions (ranked from highest to lowest) for the production of high molecular weight polymers with high reaction yields.

Entry	Solvent	Temperature (°C)	Normalized high rank
1	Toluene	55	65
2	THF	25	51
3	Chlorobenzene	25	29
4	MTBE	25	21
5	α,α,α-Trifluorotoluene	25	18
6	n-Pentane	25	11
7	MTBE	-15	8
8	DMF	25	1

Reproducibility

To test the reproducibility of the polymerisation conditions developed in this work, four of these conditions were repeated in quadruplicate. These conditions include: n-pentane (25 °C), α,α,α-trifluorotoluene (25 °C), MTBE (25 °C), and toluene (55 °C). All conditions can be reproduced to some degree, with MTBE being the least reproducible solvent in terms of molecular weights (see Table S3). These conditions were chosen since they represent both a variety of molecular weight ranges and classes of solvents, as well as some temperature variations. Firstly, Table 1 shows the extent of reproducibility when using n-pentane as a solvent. The molecular weight values and dispersities appear to all be easily reproducible, however the reaction yields vary significantly. This was suspected to be due to the polymers being significantly more soluble due to their low molecular weight, and hence may be lost during successive washing cycles with hexanes. Several batches were prepared under the same conditions, and then washed 3 times with methanol and then washed either 0, 1, 2, 5, or 10 times with hexanes. However, the reaction yields remained mostly unchanged, ranging from 50% to 61%. There may still exist some ideal workup conditions that can ensure greater reproducibility of the reaction yield.

Table 6. GPC data for polymers produced using n-pentane as a solvent at 25 °C, where entry 1 is the previously shown value from Table 1.

Entry	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Đ	Yield
1	10,200	31,800	19,400	3.10	97%
2	9,200	19,800	14,200	2.16	77%
3	8,610	17,900	13,200	2.08	39%
4	9,390	20,600	14,700	2.20	74%
5	9,400	24,500	14,400	2.60	17%

For α,α,α-trifluorotoluene (Table 7) the molecular weight values are fairly consistent despite having a slight offset when compared to the previously obtained value. This may be attributed to a drift retention time from the previous GPC runs on another calibration curve.

Table 7. GPC data for polymers produced using α,α,α-trifluorotoluene as a solvent at 25 °C, where entry 1 is the previously shown value from Table 1.

Entry	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Đ	Yield
1	23,500	71,000	54,100	3.02	55%
2	12,300	33,000	26,600	2.69	74%
3	14,500	37,900	38,200	2.61	60%
4	12,900	34,100	27,600	2.64	52%
5	12,600	26,100	23,300	2.07	73%

When using toluene as the solvent at 55 °C (Table 8), high molecular weight polymers can be consistently produced with moderate to good reaction yields.

Table 8. GPC data for polymers produced using toluene as a solvent at 55 °C, where entry 1 is the previously shown value from Table 3.

Entry	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Đ	Yield
1	70,700	397,000	300,000	5.61	65%
2	83,600	573,000	252,000	6.85	59%
3	89,200	671,000	399,000	7.52	74%
4	72,000	621,000	385,000	8.63	65%
5	56,200	477,000	219,000	8.49	77%

Optical properties

The UV-Vis absorption and photoluminescence (PL) spectrum of the polymer samples were obtained in chloroform solution to confirm the typical photophysical properties of MEH-PPV. Approximately 1 mg of each polymer sample was dissolved in chloroform and stirred for several hours. The solutions were then filtered through a 0.4 µm syringe filter and diluted by a factor of 100 in chloroform (or until the measured absorbance value was approximately 0.1). The PL spectra were obtained using 490 nm excitation. The UV-Vis absorption spectrum of the polymer produced by each set of polymerization conditions only vary slightly in the peak maxima 482 to 502 nm (Figure 4 and Figures S2 to S6). Similarly, the PL spectrum of the polymers showed little variation between samples obtained from different polymerization conditions with peak maxima ranging between 554 to 559 nm (**Error! Reference source not found.** and Figures S2 to S6). Selected examples of the UV-Vis and PL spectra are shown in Figures 4 with the data summarized in Table S4. The photoluminescence quantum yield (PLQY) for each polymer was measured relative to Rhodamine 6G in chloroform.[21] The values of the PLQY are consistent with those reported in the literature,[22, 23] varying from 0.28 to 0.21. In summary, the photophysical properties of the MEH-PPV samples display very little dependence on the molecular weight variations as a result of the different polymerization conditions.

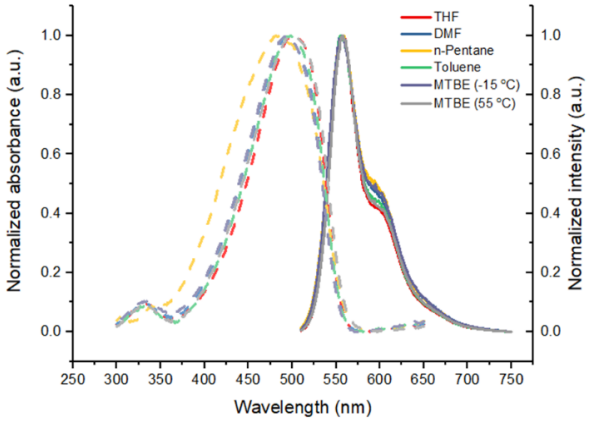


Figure 4. Selected examples of UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra of polymers produced under different polymerization conditions.

Literature comparison

Previous methodologies used to produce MEH-PPV often fail to achieve high reactions yields, particularly when low molecular weight polymers are produced (Figure 5). Given that peak molecular weights are not often reported, the M_w values were used as a suitable comparison. Various Gilch polymerization techniques such as ball milling,[24] or flow chemistry,[25] or even different monomers,[11, 26] are unable to produce low molecular weight polymers (<100 kg/mol) with high isolated product yields. In this work, polymerization conditions were found to produce low molecular weight polymers in up to quantitative conversion. The best conditions to produce a low weight polymer in high yield was the use of n-pentane at 25 °C giving MEH-PPV with M_w of 31.8 kg/mol and 97% yield. The conditions for the best yield of a high molecular weight polymer in this work was obtained with 1,4-dioxane at 25 °C achieving M_w of 361 kg/mol and 85% yield, although the dispersity for this sample is 8.35.

From the previous ranking table (Table 5), it is suggested that toluene at 55 °C should be used instead of 1,4-dioxane, due to the lower dispersity achieved with toluene. From previous methodologies, the best conditions for both high molecular weight (3,160 kg/mol, 94% yield) and low molecular weight (85 kg/mol, 83% yield) were obtained by Vanderzande and coworkers.[15] For the lower molecular weight polymer, Vanderzande used 50 mol% CBr_4 as an additive with 1,4-dioxane as the solvent at 25 °C while the higher molecular material was obtained without the CBr_4 additive. It is worthwhile to note that the monomer concentration in that work was 25 mM, which is more than double the maximum monomer concentration in this work at 12 mM. This may explain the difference in molecular weights obtained between this work and by Vanderzande when using 1,4-dioxane as a solvent.

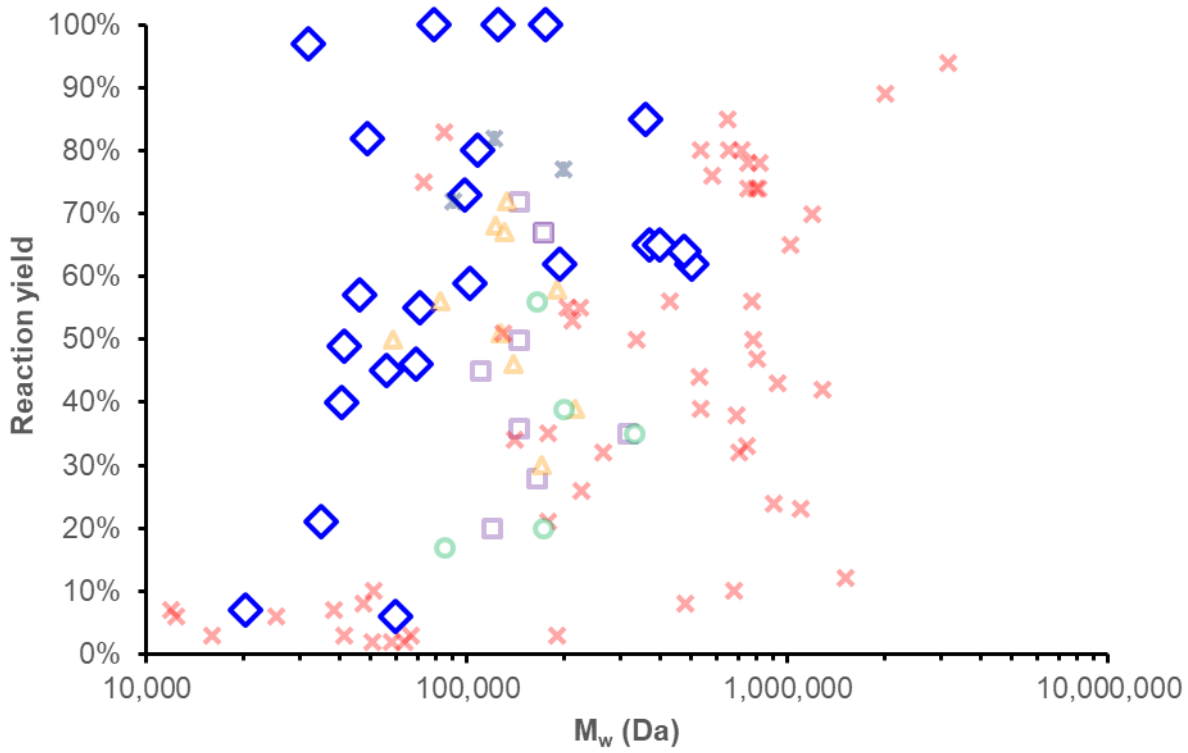


Figure 5. Comparison of reported MEH-PPV synthesis by Gilch reaction showing reaction yield and molecular weight for different polymerization conditions. Blue diamonds = this work, red crosses = Vanderzande et. al.,[15] purple squares = Swager et. al.,[24] green circles =Hsieh et. al.,[26] yellow triangles = Ferraris et. al.,[12] black stars =Wong et. al.[25]

Conclusions

An improved set of reaction conditions for the Gilch polymerization of MEH-PPV were developed by altering the reaction solvent and temperature. The best condition for producing low weight MEH-PPV was using n-pentane as the solvent at 25 °C to produce polymer with M_p of 19.4 kg/mol in 97% yield. However, the reaction yield for this set of conditions was found to be difficult to reproduce despite having very consistent molecular weight values. Toluene at 55 °C was found to produce higher molecular weight material very consistently (M_p 300 kg/mol) in 65% yield. The UV-Vis absorption spectrum, PL spectrum and PLQY of the MEH-PPV samples synthesized in all conditions were found to be very similar indicating that the reaction condition variations did not adversely affect the photophysical properties of the samples. This work showed molecular weight of MEH-PPV can be tuned by simply adjusting solvent and temperature of the Gilch reaction. Lower molecular weight range material was obtained in very high isolated yield which was difficult to achieve using previously reported methods.

Conflicts of interest

There are no conflicts to declare.

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Abbreviations

MEH-PPV, methoxyethylhexyloxy-poly(p-phenylenevinylene); PPV, poly(p-phenylenevinylene); UV-Vis, ultraviolet-visible; OLEDs, organic light emitting diodes; BHJ, bulk heterojunction; OPVs, organic photovoltaics; HWE, Horner-Wadsworth-Emmons; ROMP, ring opening metathesis polymerization; KO^{t}Bu, potassium tert-butoxide; THF, tetrahydrofuran; DMF, dimethylformamide; DMAc, dimethylacetamide; MTBE, methyl tert-butyl ether; PLQY, photoluminescence quantum yield; NMR, nuclear magnetic resonance; GPC, gel permeation chromatography; TLC, thin layer chromatography.

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