p-Cymene: a Sustainable Solvent that is Highly-Compatible with Direct Arylation Polymerization (DArP)

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ABSTRACT: For over a decade, Direct Arylation Polymerization (DArP) has been demonstrated to be an eco-friendly, facile, and low-cost alternative to conventional methodologies such as Stille polymerization for conjugated polymer synthesis. By accessing through a C-H activation pathway, DArP offers a reduction of synthetic steps while eliminating the generation of stoichiometric, highly-toxic organotin by-products. However, as the major component in these reactions, the solvents most prevalently employed for DArP are hazardous and produced from unsustainable sources, such as dimethylacetamide (DMA), tetrahydrofuran (THF) and toluene. Although the use of sustainable alternative solvents such as 2-MeTHF and cyclopentyl methyl ether (CPME) has recently emerged, drawbacks of ethereal solvents include the need for a pressurized reaction setup as well as potential peroxide formation. While aromatic solvents are superior in solubilizing conjugated polymers, very little has been done in searching for more sustainable, benign alternatives for this class of solvent. Herein, we report the application of a sustainable, naturally-sourced, high-boiling aromatic solvent, p-cymene, to DArP for the first time. p-Cymene was found to display excellent solubilizing ability in the synthesis of a broad scope of alternating copolymers with M_n up to 51.3 kg/mol and yields up to 96.2%, outperforming those prepared using CPME and toluene. Structural analysis revealed the exclusion of defects in these polymers prepared by using p-cymene as the solvent, which in the case of a 2,2'-bithiophene monomer, challenging to access through the use of conventional solvents for DArP, such as DMA and toluene.

π-conjugated polymers are promising electroactive materials widely implemented in various of applications, such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), electrochromic devices, and chemical sensors.[1–5] To prepare these polymers, conventional cross-coupling methods such as Stille-Migita (Stille) and Suzuki-Miyaura (Suzuki) polymerizations are employed, which require the functionalization of monomers with organometallics such as organotin and organoboron.[6,7] Besides the challenging synthetic accessibility, the generation of stoichiometric, acutely toxic, and hazardous by-products from these methods poses significant environmental drawbacks. In vast contrast, the emergence of Direct Arylation Polymerization (DArP) in the past decade offers a streamlined, sustainable, low-cost pathway for the preparation of defect-free, high-performance conjugated polymers, circumventing the necessity for hazardous, pyrophoric reagents and highly toxic byproducts.[8–12]

Despite being established as a "greener" synthetic approach, the sustainability aspect of this methodology still remains problematic.[12] Specifically, DArP protocols are reliant on less earth-abundant Pd catalysts and toxic, hazardous solvents produced from unsustainable, non-renewable sources.[13,14] Recently, progress has been made to potentially replace Pd with earth-abundant, low-cost transition metal catalysts for DArP, such as Cu.[15–18] However, given the fact that the solvent is used in the highest quantity, exploring non-toxic, sustainable solvents for DArP is of the utmost urgency, especially considering the potential of DArP for industrial-scale conjugated polymer synthesis.[19,20] Recently, we identified cyclopentyl methyl ether (CPME) as a sustainable alternative to toxic ethereal solvents such as tetrahydrofuran (THF), providing poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole] (PPDTBT) with excellent molecular weights (M_n) (up to 41 kg/mol) and yields (up to 98%).[21] Subsequently, CPME was demonstrated to be the optimal solvent for the syntheses of amide- and ester-functionalized polythiophenes with exceptionally high regioregularity (>99%).[22,23]

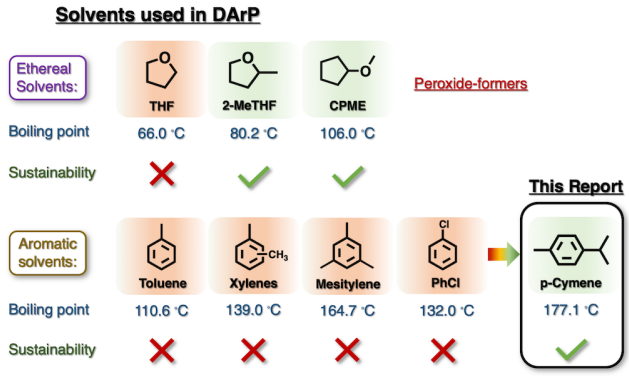


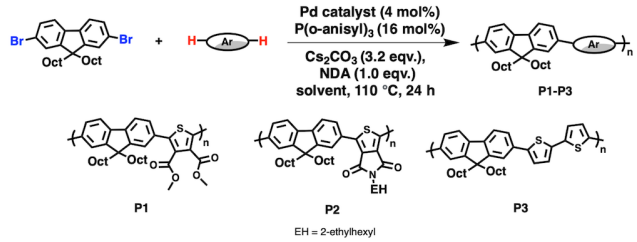
Figure 1. Summary of commonly used solvents in DArP with their boiling points and sustainability.

However, ethereal solvents such as THF, 2-MeTHF, and CPME are classified as organic peroxide-formers over their long-term storage.[24] Furthermore, they possess low boiling points (66.0 °C, 80.2 °C and 106.0 °C for THF, 2-MeTHF and CPME, respectively, see Figure 1), which are typically lower than the temperature required for DArP (typically 100-140 °C).[12,21] Thus, highly-pressurized reaction vessels are generally required when these ethereal solvents are

utilized, and polymerization results carried by these low-boiling solvents might be irreproducible due to the inconsistency in the solvent volume from different reaction setups.[25] Conversely, aromatic solvents such as toluene, xylenes, mesitylene and chlorobenzene are non-coordinating, high-boiling solvents that are also exempt from any peroxide-formation.[14,24,26] More importantly, aromatic solvents are demonstrated to exhibit superior solubility for conjugated polymers synthesized via DArP.[26] What remains unresolved for aromatic solvents, however, is their high toxicity (carcinogenicity in some cases) to human health and the environment, and the intensive energy required for their industrial production from fossil sources.[13,14,24] Therefore, it would be a significant advance for DArP to explore new sustainable aromatic solvents that are sourced from renewable feedstock and do not present toxic hazards to health, while preserving important properties such as high boiling point and good solubility for conjugated polymers.

p-Cymene, a non-toxic aromatic compound that structurally resembles xylenes and mesitylene (Figure 1), can be produced in large quantities as a side product from citrus fruit processing.[14,27,28] As a naturally-occurring compound, p-cymene is present in significant quantity in the essential oils of more than 100 plant species and 200 foods, such as fruit peels, cilantro, and green pepper.[27] Moreover, p-cymene is used in herbal drugs from medicinal plants to prevent coughs, as well as in the cosmetics industry for the production of perfumes and fragrances.[27] Being recognized as a bio-renewable solvent, p-cymene has recently been studied for organic transformations such as esterification and olefin-metathesis, however, the application of p-cymene in the field of conjugated polymer has yet to be exploited.[28,29] Considering the significant potential of p-cymene as a sustainable alternative to conventional aromatic solvents (such as toluene, xylenes) with a high boiling point (177.1 °C), we were emboldened to employ p-cymene for the synthesis of conjugated polymers via DArP. Herein, we disclose for the first time that the high compatibility of the new sustainable solvent, p-cymene, in DArP can be realized by providing conjugated polymers with excellent M_n (up to 51.3 kg/mol) and yields (up to 96.2%) with minimal detectable defects.

Kanbara et al. reported toluene to be the optimal solvent for DArP using 2,7-dibromo-9,9-dioctylfluorene as the monomer paired with various of electron-deficient thiophenes.[30] Hence, as the sustainable alternative to aromatic solvents such as toluene, we first applied p-cymene for DArP using a similar model system (Scheme 1). An electron-deficient thiophene unit, dimethyl 3,4-thiophenedicarboxylate, was selected as the first coupling partner since the ester directing group was found to facilitate the C-H activation of thiophenes.[22,23,31] By using 4 mol% of $Pd(OAc)_2$ as the catalyst, which is the best-performing catalyst in Kanbara's study, in combination with 16 mol% of $P(o\text{-anisyl})_3$ as the ligand, 3.2 equiv. of Cs_2CO_3 as the base, and 1.0 equiv. of neodecanoic acid (NDA) as an additive (Scheme 1), P1 was afforded with a M_n of 22.4 kg/mol and a moderate yield of 69.1% (entry 1). The use of 4 equiv. of $P(o\text{-anisyl})_3$ ligand relative to Pd was inspired from the optimization of DArP protocols by Leclerc et al.[9] Replacing the Pd-catalyst with $PdCl_2(PPh_3)_2$ increased the M_n to 31.9 kg/mol and yield to 75.8% (entry 2). By increasing the concentration of the polymerization to 0.2 M, the M_n of P1 was further improved to 33.8 kg/mol accompanied by a significant improvement in yield (96.2%) (entry 3). It is worth-noting that the optimal M_n of P1 (33.8 kg/mol) synthesized using p-cymene as the solvent is higher than that synthesized using a polar, unsustainable solvent DMA (23.4 kg/mol) via DArP reported by Ling and co-workers.[32]



Scheme 1. Synthesis of P1-P3 using DArP conditions listed in Table 1.

To perform a more complete comparison, we attempted the synthesis of P1 using the sustainable solvent CPME previously disclosed for ester-directed thiophene substrates.[23,31] As a result, P1 was obtained with a lower M_n (20.4 kg/mol) and yield (79.3%) (entry 4), demonstrating the higher compatibility of p-cymene for DArP compared to other sustainable solvents. Another comparison was drawn between p-cymene and the conventional, toxic aromatic solvent, toluene, which provided P1 with a lower M_n of 23.8 kg/mol and a lower yield of 87.1% (entry 5). Significantly, it was observed that during the polymerizations using both CPME and toluene as the solvents, premature precipitation occurred after 24 h, while the reaction using p-cymene as the solvent was conducted smoothly without any polymer precipitation, and the reaction solution displayed a much darker green color. These observations led us to the assumption that p-cymene is a sustainable aromatic solvent highly suitable to solubilize conjugated polymers with high M_n.

This assumption was further supported by the synthesis of P2, a

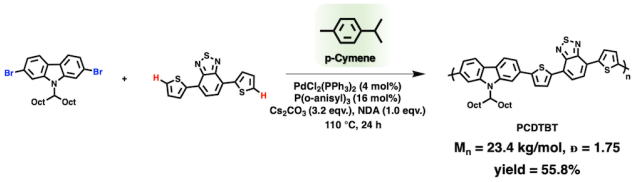
Table 1. DArP conditions for the synthesis of P1-P3 depicted in Scheme 1.[a]

entry	polymer	solvent[b]	concentration (M)	Pd-catalyst	M_n (kg/mol)[c], Đ[c]	yield[d] (%)
1	P1	p-cymene	0.1	$Pd(OAc)_2$	22.4, 1.53	69.1
2	P1	p-cymene	0.1	$PdCl_2(PPh_3)_2$	31.9, 1.49	75.8
3	P1	p-cymene	0.2	$PdCl_2(PPh_3)_2$	33.8, 1.60	96.2
4	P1	CPME	0.2	$PdCl_2(PPh_3)_2$	20.4, 1.53	79.3
5	P1	toluene	0.2	$PdCl_2(PPh_3)_2$	23.8, 1.83	87.1
6	P2	p-cymene	0.2	$PdCl_2(PPh_3)_2$	51.3, 1.73	72.6
7	P2	toluene	0.2	$PdCl_2(PPh_3)_2$	47.4, 1.86	59.3
8	P3	p-cymene	0.2	$PdCl_2(PPh_3)_2$	42.0, 5.21	89.2

[a]Reactions are conducted using the general conditions described in Scheme 1 . [b]CPME = Cyclopentyl methyl ether. All solvents are used in their anhydrous forms followed by 15 minutes of degassing prior to use. [c]Estimated by GPC (80 °C, 1,2,4-trichlorobenzene) calibrated with polystyrene standards. [d]Polymer products were purified via Soxhlet extraction using MeOH, hexanes, and collected by $CHCl_3$. See Supporting Information (SI) for detailed experimental procedure.

5-(2-ethylhexyl)-thieno-[3,4-c]-pyrrole-4,6-dione (TPD)-based conjugated polymer, using p-cymene as the solvent with the optimized DArP condition (entry 3), which afforded P2 with an exceptional M_n of 51.3 kg/mol, and a good yield of 72.6% (entry 6). Consistent with the synthesis of P1, toluene as the traditional aromatic solvent provided P2 with a slightly decreased M_n (47.4 kg/mol) and a significant decrease in yield (59.3 %) (entry 7). The decrease in yield is due to a portion of P2 with lower M_n being removed from the hexanes fraction of the Soxhlet extraction, likely a consequence of premature precipitation of the polymer in toluene during the reaction. On the contrary, similar to our observations with P1, p-cymene also displayed an excellent solubilizing ability for P2 by allowing the polymerization to be conducted without any obvious precipitation of polymer. Interestingly, several sustainable constituents of essential oils including p-cymene have been demonstrated to be the most suitable solvents to dissolve high M_n polystyrene for waste recycling process.[33] This might explain the high dissolution ability of p-cymene for conjugated polymers exhibited in this report. It is also imperative to note that the boiling point of p-cymene (177.1 °C) is much higher than the reaction temperature (110 °C), which allows these reactions to run without being pressurized, as opposed to those employing conventional DArP solvents such as THF, CPME, or toluene (Figure 1). For this reason, p-cymene is highly advantageous among all the sustainable solvents available for DArP, especially in a large, industrial scale setting.

Encouraged by these results, we were interested to examine the capacity of p-cymene as a sustainable solvent for DArP using a 2,2'-bithiophene monomer without any electron-withdrawing substituent or carbonyl directing groups on the thiophene substrate (Scheme 1, P3). The synthesis of P3 via DArP was found to be extremely challenging due to the absence of orienting groups or steric protection on the β-positions of 2,2'-bithiophene, which leads to insoluble materials being obtained presumably due to significant amounts of embedded β-defects.[34,35] As reported by Kanbara et al. and Leclerc et al, both the polar solvent DMA (after 3 hours of reaction time) and the non-polar solvent toluene (after 210 minutes of reaction time) afford insoluble cross-linked materials with a M_n of P3 not exceeding 28 kg/mol.[34,35] Using the optimized DArP condition developed in this report for P1 and P2 (entry 3 and entry 6), P3 was afforded with a high M_n of 42.0 kg/mol and a yield of 89.2% (entry 8). Importantly, even after 24 hours of reaction time, no insoluble material was obtained after Soxhlet extraction. Polymer P3 was found to be completely $CHCl_3$-soluble, which along with evidence from ^{1}H NMR spectroscopy (discussed below), suggests a defect-free synthesis of P3 using p-cymene. Notably, the M_n of P3 provided by using p-cymene as the solvent (42.0 kg/mol) surpassed those prepared using toluene as the solvent via DArP (28 kg/mol) or Suzuki (19 kg/mol) polymerization methods.[35] However, premature precipitation of P3 was observed in p-cymene during the reaction, which is likely due to the limited solubility of P3, as evidenced by a large polydispersity (Đ = 5.21).[35]



Scheme 2. Synthesis of PCDTBT using p-cymene as the solvent.

To further expand the scope of p-cymene as a new green solvent for DArP, we investigated the compatibility of this newly developed DArP condition in the synthesis of poly[(9-(heptadecane-9-yl)-9H-carbazole)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)] (PCDTBT), a perfectly alternating copolymer widely explored in OPVs due to its high-efficiency in organic solar cells.[36] Conventionally, PCDTBT is prepared using the Suzuki polymerization method, however, only moderate M_n (ranging from 5.1 kg/mol to 11.1 kg/mol) of this material is obtained by utilizing different DArP conditions, potentially due to its limited solubility in traditional hazardous solvents such as DMA, THF and toluene.[37] Therefore, we envisioned that p-cymene with a high solubilizing property for conjugated polymers may allow an improvement in M_n for the synthesis of PCDTBT via DArP. Using p-cymene as the solvent, PCDTBT was afforded with M_n = 23.4 kg/mol using p-cymene as the solvent (Scheme 2), which is much higher than those previously prepared via DArP (5.1-11.1 kg/mol).[37,38] A small amount of premature precipitation was observed during this reaction, likely due to the fact that PCDTBT is more inclined to aggregation as reported in the literature.[35-38] Suggested by literature reports, a dichloromethane Soxhlet extraction has been added to the purification of PCDTBT.[35,36] A slightly lower yield (55.8%) and a relatively lower polydispersity (Đ = 1.75) were obtained for this reaction, which can be attributed to a fraction of material being removed in the dichloromethane fraction of the Soxhlet extraction.

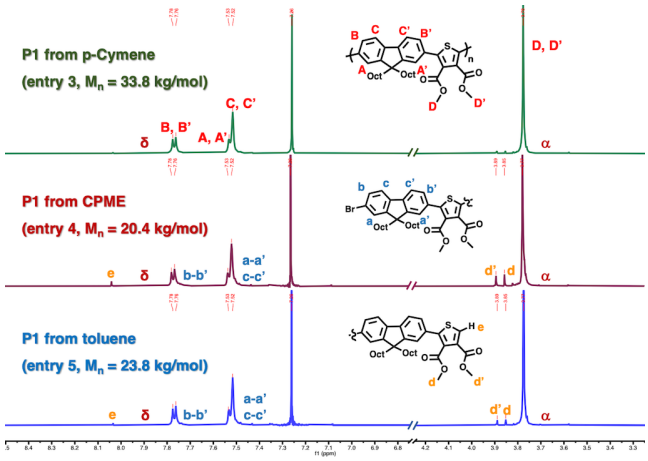


Figure 2. ^{1}H NMR analyses of P1 synthesized using p-cymene (Table 1, entry 3), CPME (Table 1, entry 4), and toluene (Table 1, entry 5) as the solvent. Major resonances (A-D') and potential resonances for end groups (a-e) and defects (δ, α) are denoted. Collected in $CDCl_3$ at 25 °C and 600 MHz.

Polymer structural characterization was performed by using ^{1}H NMR spectroscopy and UV-vis absorbance spectroscopy (^{1}H NMR and UV-vis spectra are included in the SI). Major resonances in the ^{1}H NMR spectra collected for P1-P3, and PCDTBT, were referenced and compared to those previously reported.[17,30,32,35,37,38] As shown in Figure 2, for P1 prepared using p-cymene, CPME, and toluene (Table 1, entry 3-5), major resonances (A-D') in the ^{1}H NMR spectra were identical without any defects such as donor-donor (δ) or acceptor-acceptor (α) homocoupling being detected. End-group assignments were performed based on literature reports, and the intensities of end-groups were minimized when p-cymene was used as the solvent to afford the highest M_n for P1 (33.8 kg/mol, entry 3).[17,30,32] UV-vis spectra of P1 from entry 3-5 were

also identical with λ_{max} = 389 nm (Figure S17). Similarly, major resonances of P2 (see Figure S14) synthesized from p-cymene and toluene (entry 6-7) matched without any δ or α homocoupling defect. For the UV-vis spectra of P2, polymers obtained by using p-cymene as the solvent (entry 6) with a higher M_n (51.3 kg/mol) displays a slight bathochromic shift (λ_{max} = 450 nm) compared to that by using toluene as the solvent (λ_{max} = 445 nm) (Figure S18), which is consistent with the observation by Leclerc et al.[35] The ^{1}H NMR spectrum of P3 was collected in $C_2D_2Cl_4$ at 100 °C to be consistent with literature reports on the same polymer and to allow better comparisons to be drawn.[9,35] For the ^{1}H NMR of P3, the signals corresponding to the β-protons of the 2,2'-bithiophene (D, D') were present and integrated to the correct value (Figure S12 and Figure S15). This likely indicates the exclusion of β-defects embedded in the polymer structure, which is also suggested by the absence of insoluble materials as mentioned above. End-group assignments for P3 were performed on the basis of the report by Leclerc et al., in which the same chemical shifts (at 7.25 ppm and 7.12 ppm) corresponding to the end-groups were depicted (See Figure S15 for details).[35] Additionally, no δ or α homocoupling defect was identified for P3 (Figure S15). UV-vis spectroscopy shows a similar absorption profile for P3 (Figure S19) compared to that reported by Leclerc et al. with a similar λ_{max} of 451 nm, which is found to be the saturation of the absorption maximum with the increase of M_n (from 0.8 kg/mol to 28.0 kg/mol) for P3.[35]

As reported by Sommer et al., β-branching and δ homocoupling for the synthesis of PCDTBT via DArP could be major sources of defects, however, no evidence of these defects could be observed for PCDTBT provided using the conditions described in Scheme 2 (Figure S16).[38] The UV-vis spectrum of PCDTBT is in agreement with previous report with no deviation (Figure S20).[37] Importantly, Sommer et al. reported that aromatic solvents such as toluene exhibit high C-H reactivity, leading to end-capping events of naphthalene diimide (NDI)-Br chain ends under DArP conditions.[26,39] However, all minor resonances in the ^{1}H NMR spectra of the polymers synthesized by using p-cymene or toluene as the solvent (P1-P3, PCDTBT) in this report can be adequately attributed to potential end-groups from the monomers (see analysis above). Therefore, no end-groups corresponding to potential solvent end-capping defects were identified for p-cymene or toluene. This might be due to the use of different types of monomers (fluorene-based or carbazole-based monomers, as opposed to NDI-based monomers) in this report. Consistent with our findings, literature reports on DArP protocols using these type of monomers did not show evidence any end-capping defects with the use of aromatic solvents.[30,35]

In conclusion, a novel, sustainable aromatic solvent for DArP has been presented to replace traditional hazardous solvents such as DMA, THF, and toluene. As a constituent of naturally-occurring essential oils produced from citrus fruit processing, p-cymene is advantageous as a new green solvent for DArP relative to ethereal solvents such as CPME because of its high boiling point and exceptional solubilizing property for conjugated polymers. By comparing with CPME and toluene, we found that p-cymene provided the best results for the synthesis of P1 and P2 using two different electron-deficient thiophene substrates, affording polymers with M_n up to 51.3 kg/mol and yields up to 96.2%. P3, a polymer previously found to crosslink due to significant β-defects when using DMA and toluene, was synthesized using p-cymene as the solvent without forming any insoluble materials, affording a high M_n of 42.0 kg/mol. Application of p-cymene towards the synthesis of PCDTBT afforded a good M_n of 23.4 kg/mol and a yield of 55.8%, which is significantly higher than the values previously reported via DArP (5.1-11.1 kg/mol) when more hazardous solvents were employed. ^{1}H NMR spectroscopy confirmed the structures of these polymers to be free of defects. Overall, this work reveals the significant potential of p-cymene in DArP towards the synthesis of high-M_n, defect-free alternating copolymers while aligning with the important principles of green chemistry.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures including the synthesis and characterization for all monomers and polymers are included in the supporting information (SI). This material is available free of charge via the internet at http://pubs.acs.org.

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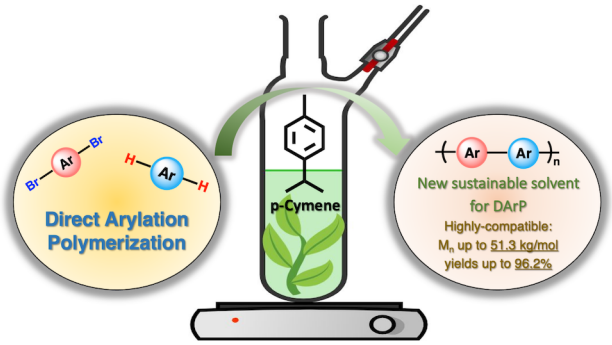
Direct Arylation
Polymerization
p-Cymene
New sustainable solvent
for DArP
Highly-compatible:
M_n up to 51.3 kg/mol
yields up to 96.2%