Direct C-H:C-H Arylation Polymerization of 3,4-Propylenedioxythiophene Derivatives

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Abstract

In this manuscript, we report, for the first time, a direct C-H:C-H arylation process for the polymerization of 3,4-propylenedioxythiophene derivatives. The requirement of aryl halides monomers can be completely excluded in this process, making the process atom economical and environmentally friendly. We could successfully homopolymerize Prodot-diethylhexyl using palladium acetate as catalyst. The optimized process required the stepwise ramping of the temperature from 70 °C to 140 °C. It was also observed that a direct heating of the polymerization mixture to 140 °C results in the decomposition of the catalyst leading to unsuccessful polymerization. At present, the exact mechanism of the whole process is not clear.

Introduction

The solution processible conducting polymers based on 3,4-alkylenedioxythiophenes (poly-ProDOTs) are of significant interest, both academically and industrially. Poly-ProDOTs are used in various applications such as electrochromic devices, light harvesting materials, transistors, sensors etc.[1] This is due to their superior electrical conductivity, high thermal and environmental stability, transparency, and low redox potential.[2] While the cost-effective polymerization can be performed by oxidative method,[3] the high-quality polymers suitable for electronic applications can be obtained by Grignard metathesis (GRIM) polymerization.[4] However, the former method suffers from poor yield, chain branching, and broad molecular weight distribution, whereas the latter suffers from disadvantages such as expensive organometallic reagents, stringent reaction conditions as well as loss of unreacted starting materials in the case of batch failure. Owing to these disadvantages, recent advancements in the direct C-H arylation are emerging as a promising method for polymerization because of its higher atom efficiency, fewer synthetic steps, and environmentally friendly nature.[5] As a result of this, C-H arylation is extensively investigated to prepare well-defined conjugated polymers based on various aryl building blocks, including poly-ProDOT.[6] Direct C-H arylation polymerization involves the coupling of an aryl C-H with an aryl halide. Therefore, the use of
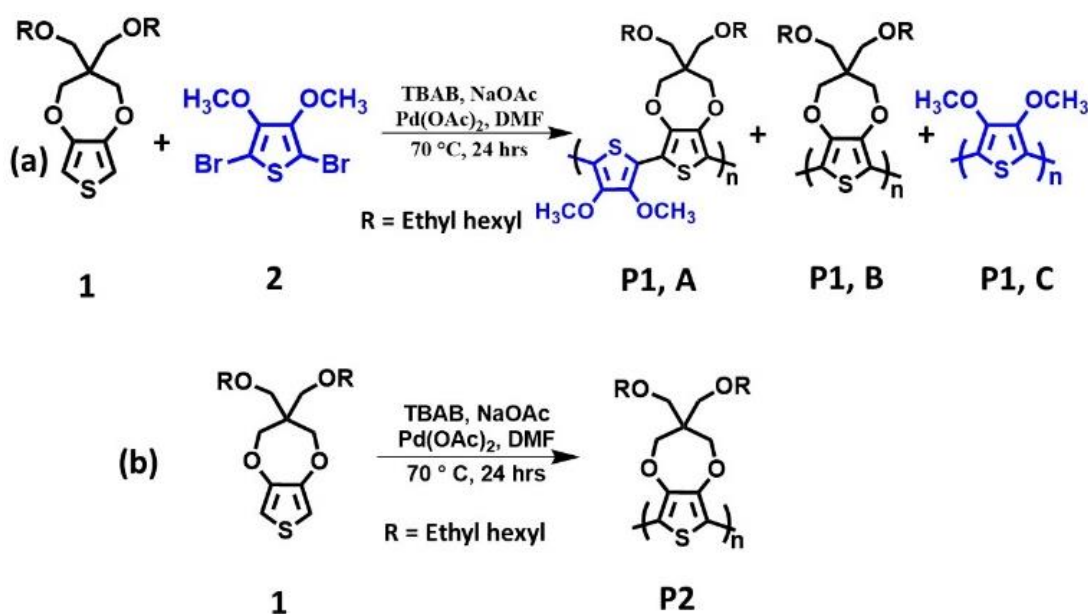
a dihalide monomer adds one more synthetic step and reduces the overall atom economy and increases the carbon footprint. It will be highly advantageous to develop a direct C-H:C-H arylation polymerization involving a homocoupling of aryl C-H moieties. In this manuscript, we report for the first time, a successful polymerization of Prodot-diethylhexyl monomer via direct C-H:C-H arylation polymerization.

Results and Discussion

In our earlier work, we have shown that by employing C-H arylation method, it is indeed possible to obtain polymers based on ProDOT derivatives at 70 °C.[7] Recently, we revisited the polymerization for process intensification. During these studies, we made an unusual observation wherein the rate of consumption of ProDOT derivatives (non-halogenated monomer) was different from that of the dihalide monomer employed. In fact, in a few trials, we found that more than 50% of one of the dihalide monomers was left behind while the non-halogenated monomer was consumed completely. The more unusual part was that the process still resulted in good quality polymers. This suggested the possibility of the direct C-H:C-H coupling during the polymerization. It was interesting to note that, Reynolds and coworkers have also observed uncontrolled incorporation of biEDOT monomer into the growing polymer chain.[8] This causes batch-to-batch variations in the desired polymer synthesis. Practically it becomes very difficult to detect this defect in the final polymer chains which can have adverse effect on device properties. There are a large number of groups who have synthesized polymers by C-H arylation method also found significant homocoupling effects in the final polymers.[9] Particularly, when synthesizing donor-acceptor type of polymers by C-H arylation method, thus limiting the generalizability of C-H arylation methods.

This intrigued us to further explore the kinetics of C-H arylation polymerization in a more systematic way. For this, we selected Prodot-diethylhexyl (**1**) and 2,5-dibromodimethoxythiophene (**2**) as model compounds aiming to obtain a copolymer (**P1**) (Scheme 1).[7] In a typical reaction, 0.2 mmol of monomer **1** was taken in DMF containing required amounts of tetrabutylammonium bromide and sodium acetate. The reaction mixture was stirred for 15 minutes at room temperature. To this reaction mixture, 0.2 mmol of monomer **2** was added followed by the addition of Pd(OAc)$_2$ and the resultant solution was heated to 70 °C. We observed the colorless reaction mixture turned into dark red within first

20 minutes and finally turned to dark maroon color in 24 hours. We monitored the rate of consumption of the two monomers via UHPLC. The reaction mixture was quenched with methanol to remove the polymer, and the methanol fraction was analyzed by UHPLC. The results are shown in Figure 1. As can be seen from Figure 1, the concentration of each of the monomers **1** and **2** decreased rapidly to 19.8 % & 56.34 %, respectively, in less than 50 minutes, suggesting that more than 80 % of monomer **1** was consumed in less than 1 hr. To our surprise, even after 24 hours, 43.76 % of monomer **2** was left behind in the reaction mixture, whereas only 3 % of monomer **1** could be detected. These UHPLC results suggest three possibilities for the progress of the reaction; a) The formed copolymer may have large blocks of monomer **1** and fewer units of monomer **2** inserted in the chain (**P1A**); b) The monomer **1** may be highly reactive towards homopolymerization under our C-H arylation conditions resulting in the formation of poly-ProDOT homopolymer (**P1B**); c) The monomer **2** may also polymerize under C-H arylation conditions resulting in the formation of another homopolymer (**P1C**).

Scheme 1: (a) The conventional C-H arylation of two different monomers (1) & (2) using Pd(OAc)$_2$ and different polymers possible. (b) The improved C-H arylation of monomer (1) using Pd(OAc)$_2$ and the polymer (P2) formed.

Intrigued by this observation, we explored the possibility of homopolymerization of monomer **1** without the dihalide monomer **2** as shown in Scheme 1b [detailed procedure is given in ESI]. To our surprise, we observed the formation of red color in the reaction mixture within 20 minutes, indicating the formation of polymer, and the observation was similar to the one we had found in our previous experiment. In the present case also, the progress of the reaction was monitored by UHPLC, and the results are shown in Figure 2. As seen from Figure 2, nearly 50 % of monomer **1** is consumed within first 30 minutes, followed by total consumption in 5 hours. To confirm that the formed material is polymer, we quenched the reaction mixture after 24 hours using methanol and the obtained dark brown solid was washed several times with methanol. The obtained solid was further purified by Soxhlet extractor using hexane, methanol and later by acetone and finally the polymer was collected in chloroform. Interestingly, we found that the acetone fraction showed light brown color in the initial few washings suggesting that the formed polymer (**P2**) had low molecular weight chains. This allowed us to fractionate and separate the low molecular weight polymer in acetone and later high molecular weight polymer in chloroform.

While the decrease in monomer concentration was monitored by UHPLC, the corresponding growth of polymer chain was monitored by UV-Vis absorption spectroscopy. The UV-Vis data of the polymer **P2** recorded with reaction time is shown in Figure 3. A progressive bathochromic shift of λ_{max} (473 nm to 530 nm) was observed which is typical of dialkyl substituted moderately high molecular weight Pro-DOT polymers. As can be seen from Figure 3, there was no significant shift of λ_{max} in first 1 hour whereas more than 80 % of monomer disappeared in less than 1 hour as observed from UHPLC data (Figure 2). This suggests that, in the first one hour the reaction mixture mainly consists of low molecular weight oligomers which later couple with each other resulting in the formation of polymers.
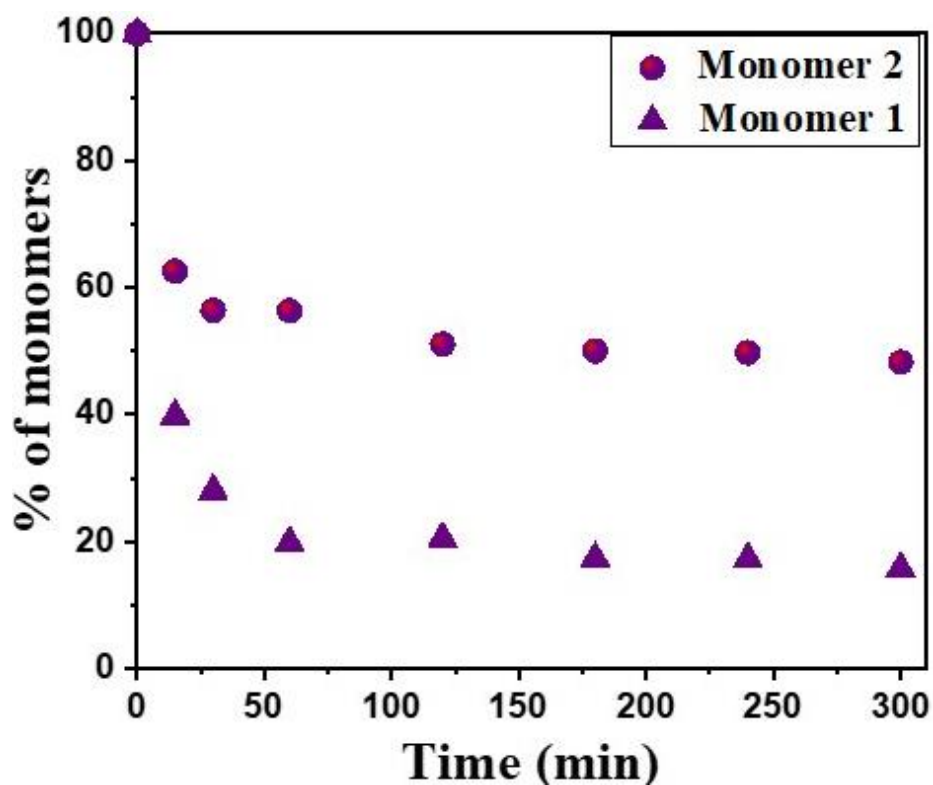
Figure 1: The UHPLC analysis for the monitoring of polymerization showing the rate of consumption of monomers (1) and (2).
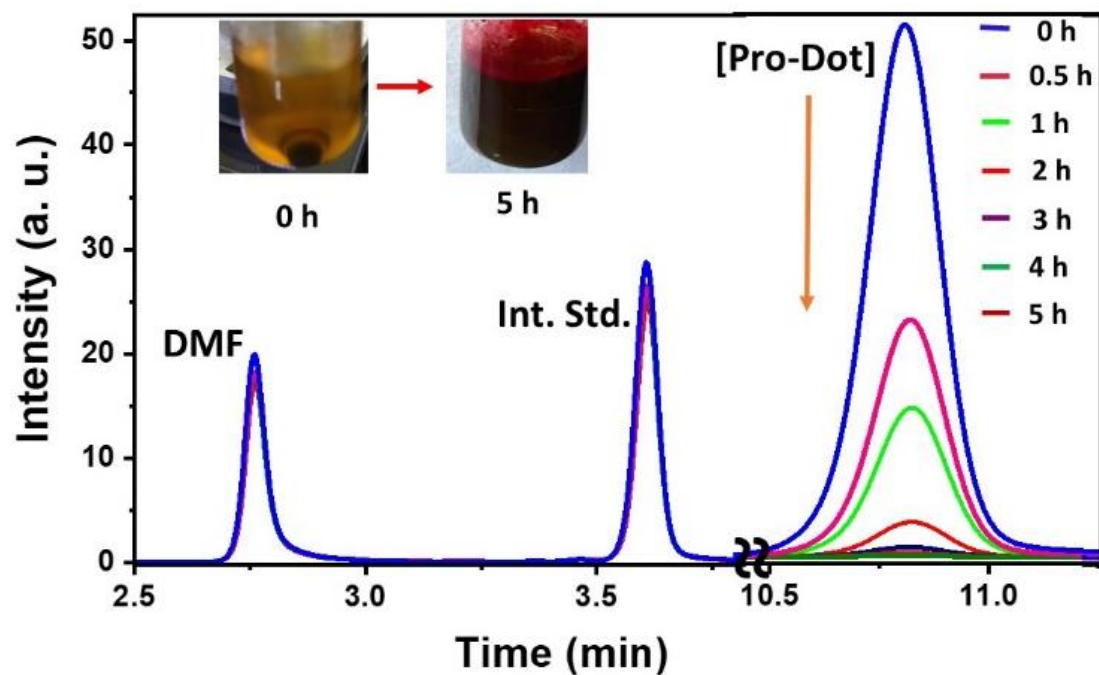

Figure 2: The monitoring of polymerization of monomer (1) by UHPLC showing the decrease in the monomer concentration with time. The inset showing the change in solution color with time.
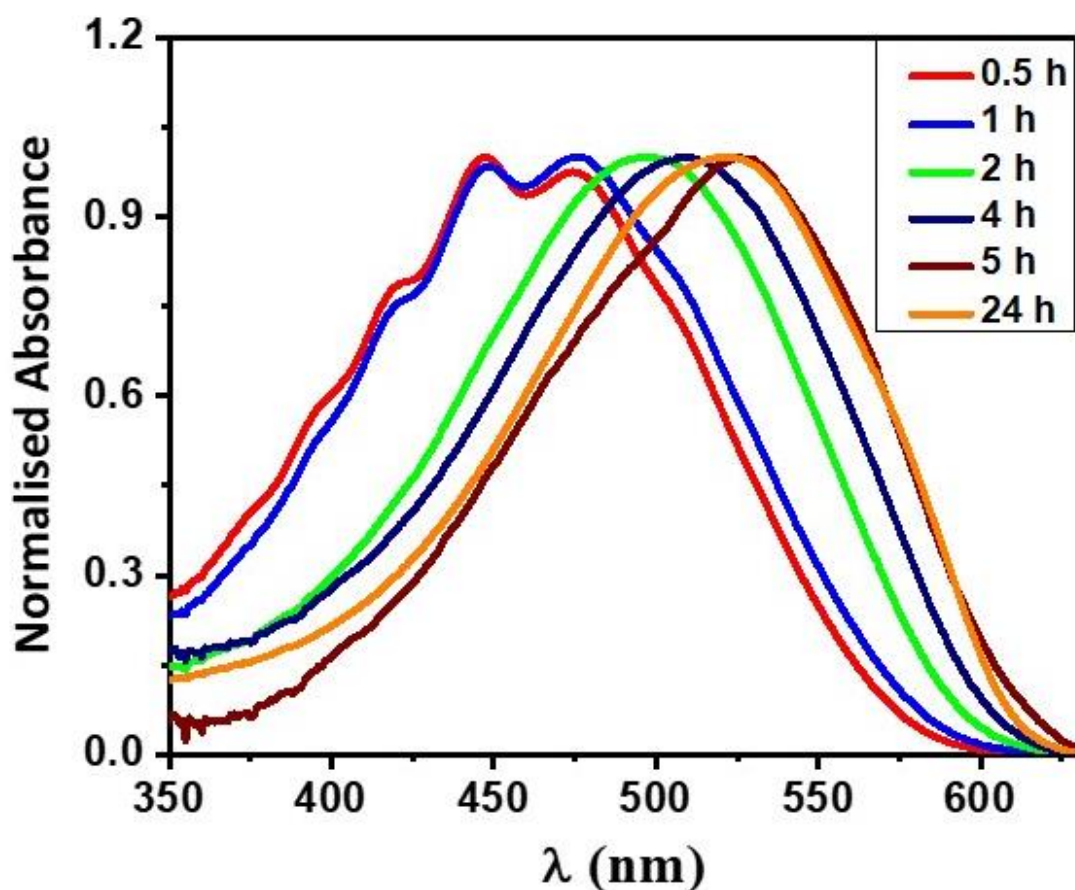
Figure 3. The UV-Vis absorbance traces of the polymer (P2) recorded as function of reaction time.

In order to get high molecular weight polymers, we decided to carry out the reaction at a higher temperature as the solubility of the polymer will be better at a high temperature. However, our attempts to polymerize monomer **1** directly at 140 °C were unsuccessful. To our surprise, when the polymerization was attempted at 100 °C, we found that characteristic brown color was imparted to the reaction mixture. This was also an unusual observation. Therefore, we decided to monitor the reaction by UHPLC as a function of reaction temperature. We monitored the reaction at two different reaction temperatures of 70 °C and 100 °C and the obtained results are summarized in Figure 4. As can be seen from Figure 4, monomer **1** was consumed completely in less than 5 hours, as observed earlier, whereas nearly 50 % of monomer **1** was left behind when the reaction was carried out at 100 °C. In order to understand this difference, we carried out a control experiment wherein DMF/Pd(OAc)$_2$ system was heated to a higher temperature. We found that the catalyst directly heated at 140 °C results in the formation of black nanoparticles of palladium whereas

the same system heated to 70 °C did not result in any particle formation even after 24 hours [Fig S7 ESI]. We have tested the catalyst efficiency of these black particles after isolating them, and found they are catalytically inactive for ProDOT polymerization. This experiment suggested that the DMF/Pd(OAc)$_2$ catalyst system may not be stable at higher temperature for longer times.[10] The catalyst decomposition rate was slower at 100 °C which suggests the slower rate of consumption of monomer **1** compared to the polymerization carried out at 70 °C which is evident from Figure 4.

As we found that the catalyst is stable at 70 °C, we decided to completely consume the monomer at this temperature leading to the formation of oligomers with active end groups consists of the catalyst. We also found, from a previous UHPLC experiment, that the time required for the complete consumption of monomer **1** is around 5 hours. This is similar to what has been reported in literature, for Stille polycondensation, C-H arylation methods. In these cases, temperature ramping is proven to be an efficient method at 70 °C, 100 °C, 120 °C and 140 °C with a time interval of 5 hours at each temperature. The monomer consumption rate during the reaction was monitored by UHPLC and the formed polymer was characterized by ^{1}H NMR as well as GPC studies. The ^{1}H NMR results are shown in Figure 5 in which the lower panel shows the ^{1}H NMR spectrum of Prodot-diethylhexyl monomer **1** and panels B-E shows the ^{1}H NMR signals of the purified polymer obtained at different temperatures. As seen from spectrum A, the aromatic peak of the monomer showed a singlet at δ 6.49 ppm with a proton integration of 2. As polymerization proceeds, this value decreased from 2 to 0.11, 0.06, 0.05 and 0.02 at temperatures 70 °C, 100 °C, 120 °C and 140 °C, respectively. The end group analysis showed that the polymer is comprised of 18, 33, 40 and 100 monomer units for the samples collected at temperatures 70 °C, 100 °C, 120 °C and at 140 °C, respectively. The molecular weight of the polymer obtained at 140 °C by end group analysis method was comparable to the one reported in the literature by conventional C-H arylation method[6d].
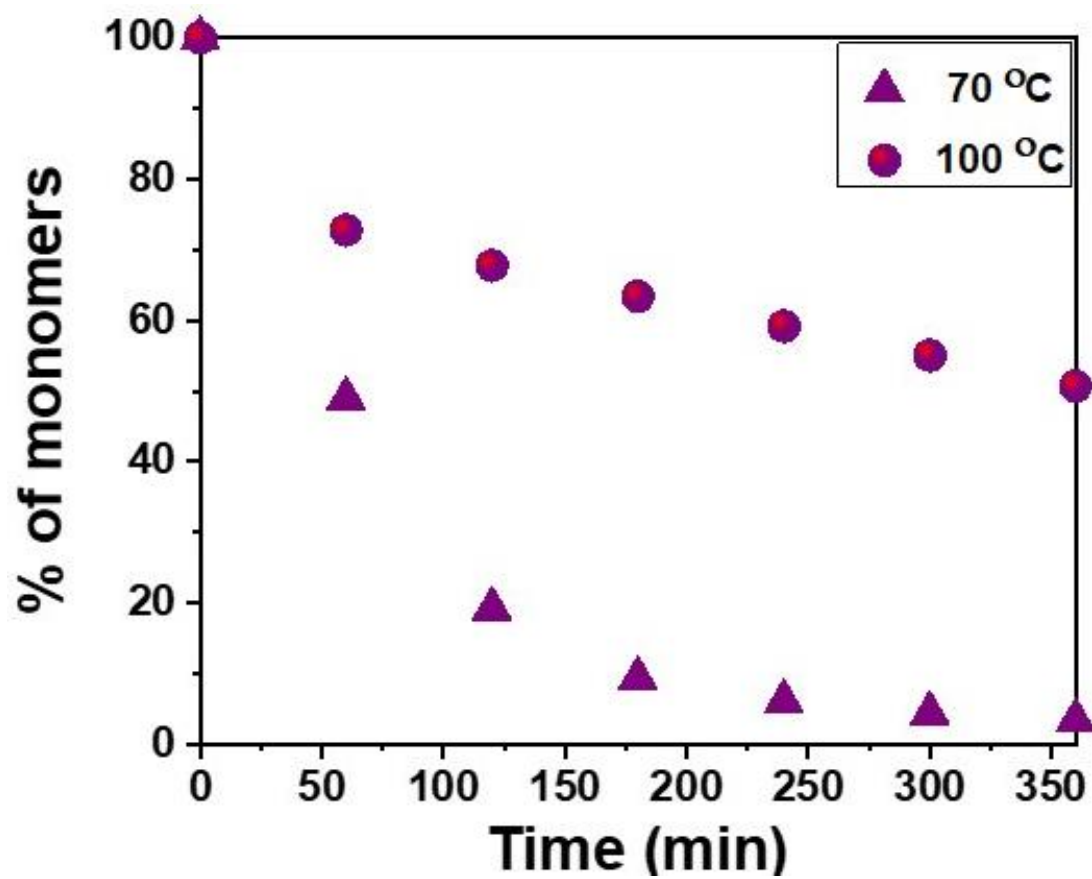
Figure 4: The UHPLC monitoring of Prodot-diethylhexyl **monomer at different polymerization temperatures.**
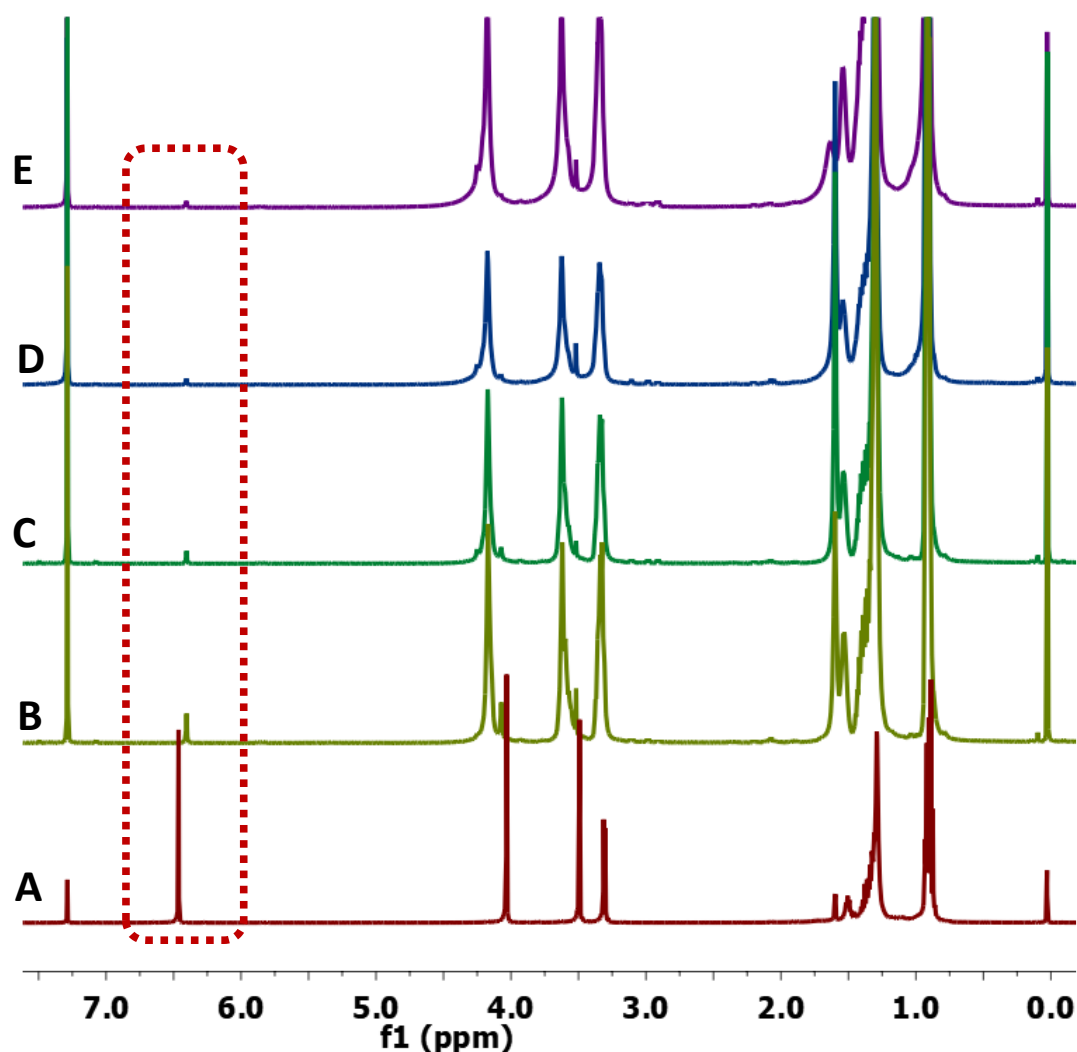
Figure 5: The ^{1}H NMR spectrum of the polymer P2 (B-E) at temperatures 70 °C, 100 °C, 120 °C, 140 °C respectively; (A) that of monomer 1.

We have attempted to monitor the polymer molecular weight growth by GPC analysis and the obtained results are summarized in Table S1, ESI. The molecular weight obtained by GPC analysis against polystyrene standards is unusually high to draw any reasonable conclusion. Though the actual reason for such high molecular weight numbers from GPC is presently unknown, we are investigating this more in detail. We have screened the effect of solvent on the polymerization reaction and found that coordinating solvents such as DMF, DMAc are preferable. On the contrary, in nonpolar solvents such as toluene and xylene, the polymerization was unsuccessful, though they are known to dissolve high molecular weight polymers. We also observed that, if either sodium acetate or TBAB is not used in the reaction (Scheme 1b), the reaction was not complete in terms of monomer consumption (Table S2,

ESI). We have also shown that the reaction proceeds as expected if we change the monomer **1** to ProDOT-didocyl suggesting that the process is capable of polymerizing other ProDOT derivatives [Figure S8]. The polymerization of monomer **2** alone under improved C-H arylation condition was unsuccessful, suggesting that polymer P1, C in Scheme 1a has not formed. Finally, we have investigated the redox property of polymer **P2** by I_2 doping and the results are shown in Figure S9, ESI. The polymer exhibited typical polaron and bi-polarons absorption peaks[11] as shown in Figure S9, further confirming the formation of poly-ProDOTs under improved C-H arylation method. At present, we don't the exact mechanism of the polymerization. However, the process has been reproduced multiple times and also with different batches of monomers and we found it to be completely reproducible.

Conclusions

In summary, we have successfully developed a direct C-H:C-H arylation polymerization of 3,4-propylenedioxythiophene derivatives. This enables the whole process to become more atom economical as well as environmentally friendly. Furthermore, elimination of the dihalide monomers leads to elimination of an additional synthetic step leading to cost savings. There are many C-H arylation polymers based on prodot's reported in literature.[1a, 6d, 7, 12] Our results indicate that the exact structure of these polymers needs to be established again. Further improvements in process intensification by continuous flow methods and to under the mechanism of the polymer is currently in progress in our lab.

Acknowledgments

Notes and references

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