



# Elemental Sulfur Mediated Novel Multicomponent Redox Polycondensation for the Synthesis of Alternating Copolymers Based on 2,4-Thiophene/Arene Repeating Units

Hatice Mutlu,\* Daniel A. Döpping, Birgit Huber, and Patrick Theato\*

A sulfur-based self-condensation method is investigated as an efficient tool for the synthesis of polythiophene derivatives. The reaction proceeds through multicomponent redox polycondensation between readily available diketone compounds and elemental sulfur in the presence of a Brønsted acid/base pair. Six different diketone derivatives have been screened and the polymerization is generalized by the synthesis of so-far-unprecedented alternating copolymers based on 2,4-thiophene/arene repeating units. By exploiting microwave heating the synthetic procedure is optimized, particularly for alternating copolymers containing aryl and thiophene units, such that a copolymer can be synthesized in only 24 h compared to the conventional process taking 6 d, yielding polymers within the same apparent weight average molar mass ( $M_w$ ). All obtained copolymers are analyzed in detail using size exclusion chromatography (SEC), nuclear magnetic resonance (NMR), attenuated total reflectance infrared spectroscopy (ATR-IR), thermal gravimetric analysis and differential scanning calorimetry (DSC).

Importantly, this type of synthetic transformation facilitates the reduction of waste, and saves time and work compared to classical approaches involving a sequence of individual reactions.<sup>[2]</sup> Inevitably, MCRs were introduced into polymer science in 2011 by Meier and co-workers as the result of the increasing quest towards new functional polymeric materials.<sup>[3]</sup> Since then, benefiting from the inherent modular character, easy reaction setup, and high tolerance towards functional groups, plethora of MCRs have been implemented for synthesis of functional monomers as well as polymerization and post-polymerization modification techniques.<sup>[4]</sup> Despite the elegant achievements in MCRs, including that by our research group,<sup>[5]</sup> the scope of starting materials used for MCRs and hence the unprecedented possibilities to access diverse molecular archi-

## 1. Introduction

Multicomponent reactions (MCRs) are receiving ever-growing interest as high atom- and step-efficient processes with the idea to construct high added value molecules with functional and structural diversity from simple starting materials.<sup>[1]</sup>

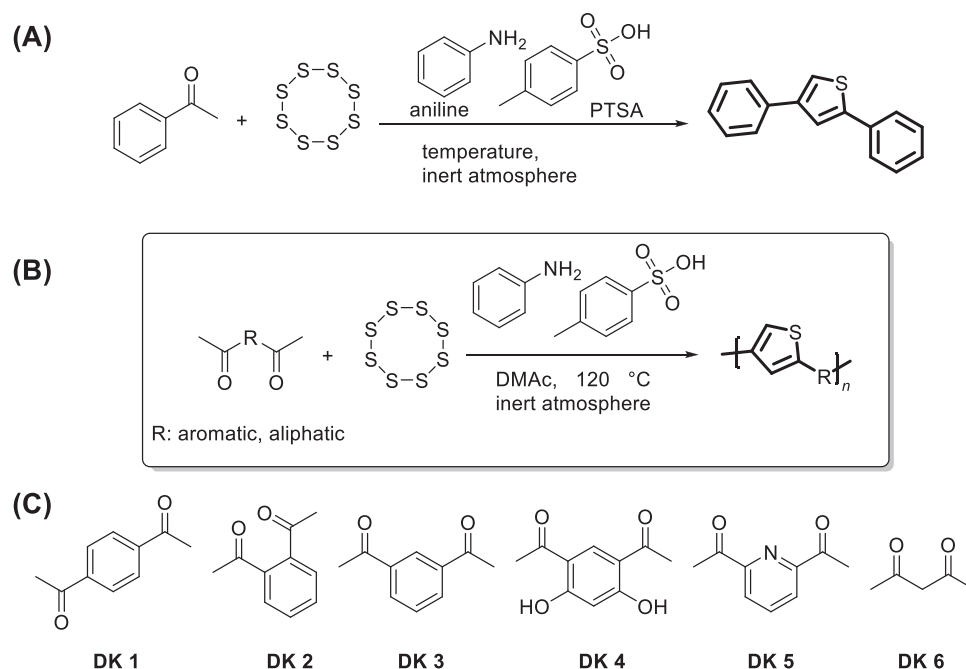
On the one hand, reactants such as aldehydes/ketones, ammonia/amines, isonitriles (isocyanides), carboxylic acids, and their derivatives are accounted as the most common reactants for MCRs. On the other hand, as a waste product of modern oil and gas refineries, elemental sulfur has appeared as an alternative and extremely cheap starting material for MCRs.<sup>[6]</sup> For instance, Nguyen and colleagues have shown that the bench-stable, environmentally benign and non-toxic elemental sulfur,  $S_8$ , reacts with ketone derivatives via a multicomponent redox condensation reaction to provide thiophene derivatives, particularly 2,4-diarylsubstituted thiophenes (Scheme 1A).<sup>[7]</sup> The reaction, which takes place in the presence of catalyst system based on aniline and a strong Brønsted acid (such as *p*-toluenesulfonic acid, PTSA), features high efficiency, broad scope of substrates, mild conditions, and releases only water as a by-product. Undoubtedly, within the last five years divers multicomponent polymerizations (MCPs) have proved to be a powerful tool to convert elemental sulfur, as user-friendly synthetic tool, into sulfur-containing polymers under mild conditions with a simple operation.<sup>[8]</sup> Thiophene-based polymers<sup>[9]</sup> linked in conjugated manner through the 2- and 5-position<sup>[10]</sup> have been investigated as organic semiconductors due to their outstanding electronic properties.<sup>[11]</sup> In contrast, the synthesis of copolymer/oligomer derivatives of 2,4-diarylthiophene, i.e.,

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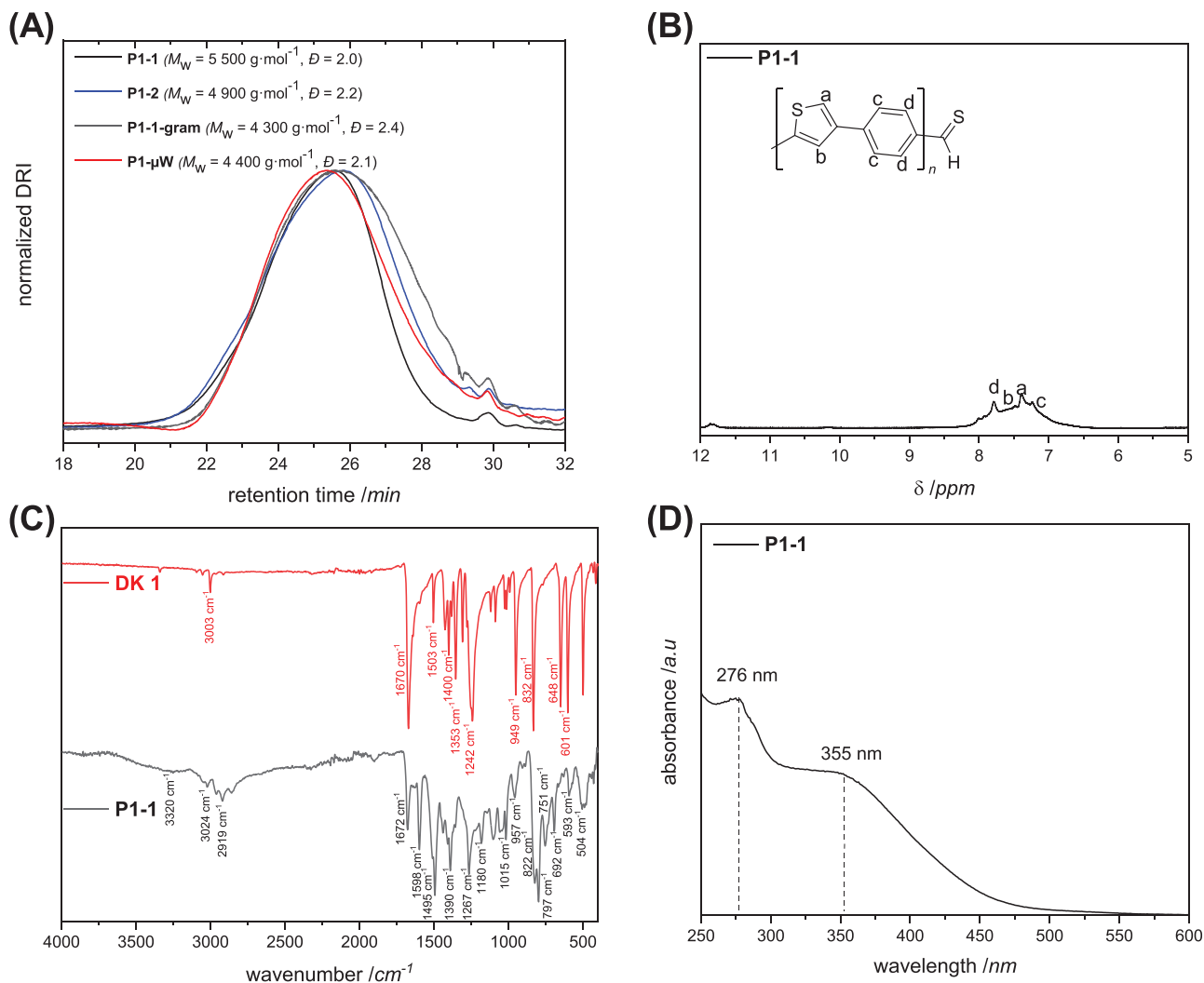
**Scheme 1.** Schematic representation of A) the multicomponent redox condensation reaction to provide 2,4-diarylsubstituted thiophene derivatives, which takes place in the presence of catalyst system based on aniline and a strong Brønsted acid (such as *p*-toluenesulfonic acid, PTSA), B) the MCP toward the synthesis 2,4-thiophene based alkyl/aryl copolymers/oligomers, and C) dicarbonyl (i.e., diketone) derivatives (**DK 1-DK 6**), respectively, utilized for the synthesis of the corresponding copolymers/oligomers.

thiophene/arene alternating copolymers/oligomers, is scarcely reported.<sup>[12]</sup> The procedures reported so far for the synthesis of thiophene/arene alternating oligomers are not practical, requiring often laborious conditions and rely on ring-closure reactions consisting of high-temperature sulfuration of appropriate olefins, known as the Baumann–Fromm thiophene synthesis.<sup>[13]</sup> Accordingly, in order to explore the general applicability of the multicomponent redox condensation of elemental sulfur as a novel polymerization approach, we have anticipated the synthesis of thiophene/arene alternating copolymer/oligomer derivatives starting from commercially available raw materials.

To develop the multicomponent redox polycondensation of elemental sulfur (Scheme 1B) with dicarbonyl (e.g., diketone) derivatives (Scheme 1C), commercially available sublimed sulfur ( $S_8$ ) and *para*-acetylacetophenone (**DK 1**) were selected as monomers to react in the presence of aniline and a strong Brønsted acid (e.g., PTSA) as catalyst system. In order to define the optimal polymerization reaction conditions, the MCP was tested by adopting a slightly modified procedure of the already reported reaction conditions.<sup>[7]</sup>

While the original procedure was performed without solvent, the aim of our study was to obtain high-molecular-weight polymers, and hence a high boiling point solvent (such as *N,N*-dimethylacetamide, DMAc) that solubilizes efficiently thiophene/arene derivatives and enables high reaction temperatures was used.<sup>[14]</sup> Accordingly a mixture of **DK 1** (1 eq.), elemental sulfur ( $S_8$ , 3 eq. of atomic sulfur/carbonyl functional group), aniline (0.5 eq.), and PTSA (5 mol%) dissolved in DMAc (2 M) was reacted at 120 °C in an inert atmosphere (Section SA.2., Supporting Information). It is crucial to emphasize

that an exact stoichiometric balance is essential to obtain a high molecular weight linear polymers, as determined by Carothers law.<sup>[15]</sup> However, several reports dealing with sulfur-based MCPs<sup>[16]</sup> reveal that an excess amount of sulfur is beneficial for the polymerization. The latter could be also rationalized mechanistically as outlined in Figure S1 (Supporting Information). Even so, in order to increase the degree of polymerization and hence obtain high molar mass polymers, the influence of the reaction time on the molar mass was subsequently followed over the time of 6 d. In fact, size exclusion chromatography (SEC) analysis of the purified (i.e., precipitated in ice-cold methanol) product **P1-1** (Figure 1A) showed an elution peak with an apparent weight average molar mass ( $M_w$ ) of 5500 g mol<sup>-1</sup> ( $\bar{D} = 2.0$ ). After monitoring the evolution of the molar mass over a period of 14 d (Figure 1A), there was a minimal decrease in the molar mass of the polymer **P1-2** ( $M_w$  of 4900 g mol<sup>-1</sup>,  $\bar{D} = 2.2$ ), though it was supposed that longer reaction time should deliver polymers with high molecular weight. This might be due to the exocyclic bond angle (i.e., core angle) for 2,4-disubstitution of 140.5° that retains the polymerization efficiency.<sup>[17]</sup> Nevertheless, in order to confirm the postulated chemical structure in Scheme 1B, **P1-1** was further analyzed via nuclear magnetic resonance (NMR) and attenuated total reflectance infrared spectroscopy (ATR-IR), respectively. As depicted in Figure 1B and Figure S3 (Supporting Information), the <sup>1</sup>H NMR spectra display broader line widths with the characteristic magnetic resonances associated with the aromatic C=C bonds (7.86 and 7.21 ppm, respectively) in addition to the characteristic olefin hydrogens of the 2,4-disubstituted thiophene repeating unit (7.45–7.32 ppm). These broad signals are due to the formation of aromatic  $\pi$ -stacks and derive from the mutual



**Figure 1.** A) Comparative SEC of P1-1 (black line, reaction time = 6 d,  $M_w = 5500 \text{ g mol}^{-1}$ ,  $\bar{D} = 2.0$ ), P1-2 (blue line, reaction time = 14 d,  $M_w = 4900 \text{ g mol}^{-1}$ ,  $\bar{D} = 2.2$ ), P1-1-gram (grey line, reaction time = 6 d,  $M_w = 4300 \text{ g mol}^{-1}$ ,  $\bar{D} = 2.4$ ), and P1- $\mu$ W (red line, reaction time = 1 d,  $M_w = 4400 \text{ g mol}^{-1}$ ,  $\bar{D} = 2.1$ ). B) Zoomed  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ) spectrum of P1-1. C) Comparative ATR-IR spectra of DK 1 and P1-1. D) UV-vis absorption spectrum of P1-1 recorded in THF at 25 °C.

shielding effect of aromatic rings placed above or below to one another in these macromolecules,<sup>[18]</sup> hence underpinning the successful polymerization. The comparative ATR-IR spectra of monomer DK1 and polymer P1-1 in Figure 1C depicted that the 1242  $\text{cm}^{-1}$  band arising from C-(C=O)-C bond of the monomer almost vanished after the polymerization, while bands at 1672 and 1495  $\text{cm}^{-1}$  appeared as the characteristic C=C asymmetric and symmetric stretching vibration modes of thiophene ring, in addition to the band at 1598  $\text{cm}^{-1}$  attributed to the aromatic ring vibrations. The bands at 1267, 1015, 797, 692, and 593  $\text{cm}^{-1}$  could be assigned to C-H bending, C-H in-plane deformation, C-H out of plane deformation (particularly for *para*-position disubstituted derivatives), C-S bending and C-S-C ring deformation, respectively, whereas, the band at 822  $\text{cm}^{-1}$  may be attributed to the C-H vibration out-of-plane of the thiophene ring for 2,4, substituted derivatives.<sup>[19]</sup> In addition, there are several low intensity peaks present in the range of 2900–3100  $\text{cm}^{-1}$ , which can be attributed to the C-H

stretching vibrations of the copolymer. To confirm the successful integration of sulfur atoms in the postulated polymer structure shown in Figure 1B (refer also to the mechanism shown in Figure S1 in the Supporting Information), elemental analysis was performed. The experimentally obtained values for P1-1 (C: 61.03, H: 4.26, S: 29.87) were in reasonable agreement to the theoretical values for the postulated repeating fragments for polymer P1-1 (Figure S2, Supporting Information). Last but not at least, the optical spectrum of the orange-brown colored solution of P1-1 in tetrahydrofuran (THF) (Figure 1D) exhibited an absorption band with two maxima at 276 and 355 nm, respectively, and with edge tailing down to 550 nm, indicating that certain thiophene/arene units were incorporated in each polymer chain. Finally, attempts to measure additionally high resolution ESI-MS of polymer P1-1 in order to determine the nature of the end-groups were not successful, and end-groups or possible repeating unit fragments could not be assigned. In order to investigate structure-property relationships as well as

explore potential applications, it is essential to scale the synthesis to a gram-scale. Thus, a gram-scale polymerization was performed (**P1-1-gram**). In an illustrative example, **DK 1** was polymerized in the same manner as it was performed for **P1-1**. SEC revealed the formation of polymer with  $M_w$  of 4300 g mol<sup>-1</sup> ( $\mathcal{D} = 2.4$ ) as shown in Figure 1A (grey line), therefore imparting the success of the gram-scale polymer synthesis.

It is well-known that polymerizations can be accelerated by microwave ( $\mu$ W) radiation heating compared to classical thermal heating.<sup>[20]</sup> For example, compared to analogous thermal polymerizations, the synthesis time of polythiophenes via Suzuki coupling by employing a  $\mu$ W-assisted process is reduced from days to minutes.<sup>[21]</sup> Accordingly, with the intention to elucidate the benefits of  $\mu$ W-promoted synthesis, the multicomponent redox polycondensation of **DK 1** was performed under  $\mu$ M-radiation in analogy to abovementioned thermal polymerization. The SEC curve of the isolated polymer after reaction time of 1 d, **P1- $\mu$ W**, exhibited an average  $M_w$  of 4400 g mol<sup>-1</sup> ( $\mathcal{D} = 2.1$ ) with almost identical intensities in the lower molar mass region, i.e., high retention time (compare Figure 1A), proving the efficiency of  $\mu$ W-assisted polymerization. Noteworthy, the scalability of  $\mu$ W-induced processes represents an important obstacle due to numerous factors, such as increased heat loss, changes in absorption, and limited penetration depth of the radiation into the reaction medium (only a few centimeters at 2.45 GHz) amongst others, and is hence not feasible under standard laboratory conditions.

Next, the scope and limitation of the unusual multicomponent redox polycondensation reaction was investigated for the aryl/alkyl diketone derivatives **DK 2 – DK 6** (Scheme 1C) by conducting all polymerizations under the same reaction conditions as for **P1-1**.

It is well known that the solubility of aromatic polymers can be tailored by incorporation of less symmetric structures such as *ortho*- or *meta*-linked aromatic units in the main chain.<sup>[22]</sup> Particularly, the incorporation of *ortho*- or *meta*-linked units into the polymer backbone may interrupt the chain packing, thus leading to improved solubility. Therefore, *ortho*- or *meta*-acetylacetophenone derivatives (**DK 2** and **DK 3**) were investigated for their applicability as monomers in the multicomponent redox polycondensation. While, the *meta*-acetylacetophenone, **DK 3**, polymerized efficiently as shown by SEC, NMR, and ATR-IR analysis (**P3** in Table 1,  $M_w = 4700$  g mol<sup>-1</sup>,  $\mathcal{D} = 2.3$ , Figures S4 and S5, Supporting Information), **DK 2** was inactive

(Table 1). These results indicated that the reaction is sensitive to steric hindrance at the enolizable carbon center of the ketone (see the mechanism shown in Figure S1 in the Supporting Information). With the attempt to broaden the scope of diketone derivatives, 4,6-diacetylresorcinol (**DK 4**) was also investigated, which is recognized as a key starting material for the synthesis of many organic heterocyclic systems.<sup>[23]</sup> The multicomponent redox polycondensation of **DK 4** produced hydroxyl functionalized thiophene/arene polymer **P4** with  $M_w = 15\,500$  g mol<sup>-1</sup>,  $\mathcal{D} = 1.8$  (Table 1; Figures S6 and S7, Supporting Information), which was slightly soluble in highly polar organic solvents such as *N,N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO), but insoluble in conventional polar solvents such as THF and chloroform.

The presence of nitrogen atom within a polymeric structure produces a polarized bond which improves the solubility of the prepared polymers due to increased dipole–dipole interactions in the polymer–solvent system.<sup>[24]</sup> Therefore, with the idea to fine-tune the solubility of the polymers while maintaining thermal stability, the multicomponent redox polycondensation of elemental sulfur was performed with pyridine derivative **DK 5** in similar manner to **P1-1**. Accordingly, **P5** was isolated with  $M_w$  of 5700 g mol<sup>-1</sup> and  $\mathcal{D} = 1.4$  (Table 1; Figures S8 and S9, Supporting Information). Interestingly, **P5** was also slightly soluble only in highly polar organic solvents (e.g., DMAc).

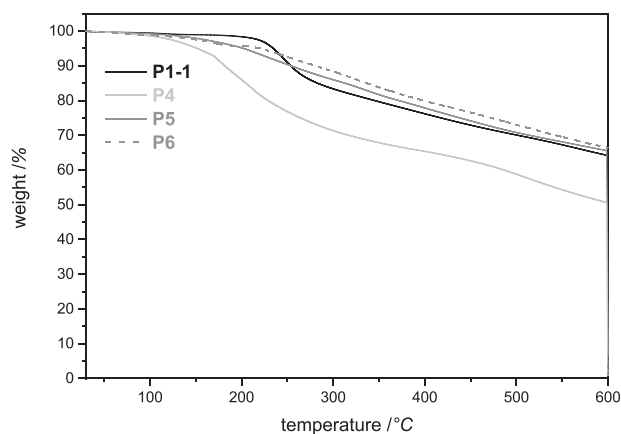
Last but not at least, the multicomponent redox polycondensation of aliphatic 1,3-diketone derivative, i.e., acetylacetone (**DK 6**), which is another important building block for the synthesis of heterocyclic compounds, was evaluated. Whereas acetylacetone was shown to be highly reactive as indicated by <sup>1</sup>H NMR and ATR-IR (Figure S11, Supporting Information), SEC analysis revealed a polymer with only  $M_w$  of 900 g mol<sup>-1</sup> ( $\mathcal{D} = 1.9$ , Figure S10, Supporting Information). The steric hindrance at the enolizable carbon center of the aliphatic ketone could be postulated as a reason either for the formation of oligomers with low molecular weight, or cyclic oligomeric structures.

Accurate thermal characterization is essential for appropriate application-oriented explorations of these novel polymers. In general, thiophene derivatives with substituents at the 2- and 4-positions are known to display lower thermal stabilities and transition temperatures than the corresponding 2,5-disubstituted thiophenes, as they deviate from linearity with core angle of 140.5°. The decomposition temperature ( $T_d$ ), defined as the temperature at 5% weight loss, was determined by TGA. As

**Table 1.** Molecular characterization and thermal analysis of polythiophene derivatives obtained via the elemental sulfur mediated novel multicomponent redox polycondensation of diketones **DK 1–DK 6**. Typical polycondensation conditions were as follows: diketone derivative (1 eq.), elemental sulfur ( $S_8$ , 3 eq. of atomic sulfur/carbonyl functional group), aniline (0.5 eq.), and PTSA (5 mol%) dissolved in DMAc (2 m) were reacted at 120 °C under inert atmosphere for 6 d.

Polymer	Dicarbonyl (diketone)	$M_w$ [g mol <sup>-1</sup> ] SEC	$\mathcal{D}$ ( $M_w/M_n$ ) SEC	$T_d$ [°C] TGA <sup>c)</sup>	Residue at 600 °C (wt.%) <sup>d)</sup>	$T_g$ (°C) DSC <sup>e)</sup>
<b>P1-1</b>	<b>DK 1</b>	5500 <sup>a)</sup>	2.0	235	64.4	129.1
<b>P3</b>	<b>DK 3</b>	4700 <sup>a)</sup>	2.3	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
<b>P4</b>	<b>DK 4</b>	15 500 <sup>b)</sup>	1.8	145	50.8	73.5
<b>P5</b>	<b>DK 5</b>	5700 <sup>b)</sup>	1.4	201	65.8	83.6
<b>P6</b>	<b>DK 6</b>	900 <sup>a)</sup>	1.9	210	66.5	83.8

<sup>a)</sup>Determined by SEC using THF as eluent; <sup>b)</sup>Determined by SEC using DMAc (+0.3% LiBr) as the eluent; <sup>c)</sup>The decomposition temperature ( $T_d$ ) defined as the temperature at 5% weight loss was detected by TGA; <sup>d)</sup>Detected by TGA; <sup>e)</sup>The glass transition temperature ( $T_g$ ) observed during the second heating measurement via DSC analysis.



**Figure 2.** Comparative TGA of P1-1 and P4 to P6.

shown in **Figure 2** and Table 1, the  $T_d$  of polymer P1-1, P4, and P5 were exemplarily measured, and were around 235, 145, and 201 °C in inert conditions (i.e., nitrogen), respectively, which are lower compared to conventional polythiophene derivatives ( $T_d$  of 296 °C).<sup>[25]</sup> The results also indicated that the thermal stability of the P4 is lower than that of P1-1 and P5, which is mainly because of the easily oxidized hydroxyl groups tethered to the aryl structure of P4. Even so, P1-1, P4 and P5 all remained around 50 wt% at 600 °C. Obviously, the thermal properties of P1-1 and P5 are still adequate for application in optoelectronic devices.<sup>[26]</sup> Interestingly, P6 showed decomposition temperature ( $T_d$ ) of 210 °C which is comparatively higher compared to P4 and P5 (compare Figure 2 and Table 1).

The thermal transitions of P1-1 and P4-P6 were also investigated by differential scanning calorimetry (DSC). It was detected that the glass transition temperature  $T_g$ , observed during the second heating measurement via DSC analysis, was in correlation with decomposition temperature ( $T_d$ ), as P1 exhibited  $T_g$  of 129.1 °C. The structure of the diketone also affected the  $T_g$  values as the polymer P5 obtained from pyridine derivative DK 5 featured a higher  $T_g$  than polymer P4 derived from 4,6-diacetylresorcinol (DK 4) (compare P4 (73.5 °C) and P5 (83.6 °C) in Table 1), although the relative molecular mass of P4 was higher than P5. Notably, no  $T_m$  values were observed within the measurement range of -20 to 250 °C.

In conclusion, we have presented the applicability of the multicomponent redox condensation of elemental sulfur as novel polymerization approach. To enrich the product structures of MCPs, the synthesis of thiophene/arene alternating copolymer/oligomer derivatives starting from commercially available raw materials was studied. The reaction was catalyzed by commercially accessible Brønsted acid/base pair and delivered polymers with  $4700 < M_w < 15\,000\text{ g mol}^{-1}$ . By exploiting  $\mu\text{W}$  radiation compared to classical thermal reaction, the synthetic regime was optimized in terms of reaction time, such as that copolymer can be made within 24 h compared to the conventional thermal heating requiring 6 d, yielding polymers within the same apparent weight average molar mass ( $M_w$ ). Importantly, detailed NMR, SEC, and ATR-IR studies confirmed the successful polymerization. Further investigation of this intriguing approach for polymer synthesis and its potential

for delivering specialty materials with potential applications in the field of energy are currently underway.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

## Keywords

alternating thiophene/arene copolymers, elemental sulfur, multicomponent reactions, multicomponent redox polycondensation

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