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Mechanistic Insights into the Kinetic and Regiochemical Control of the Thiol-Promoted Catalytic Synthesis of Diphenolic Acid

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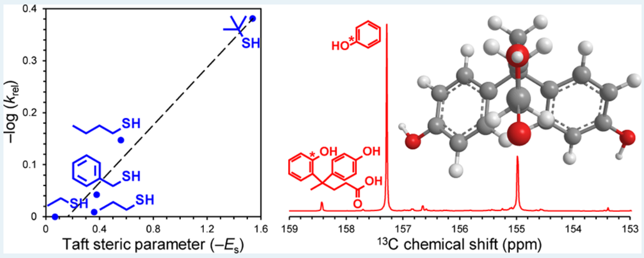
Ⓢ *Supporting Information*

ABSTRACT: The mechanism of the acid-catalyzed condensation between levulinic acid and phenol to form diphenolic acid (DPA) was investigated using a combination of sulfonated hyperbranched poly(arylene oxindole)s and thiols. Taft-type steric and electronic parameters were applied to study the correlation between the nature of the thiols and the condensation rate. The kinetic effect of thiols to tune the regiochemical control was shown to be dependent on the substituent size of the thiols. Although thiols cause an increase in the regioselectivity to the desired *p,p′*-DPA, the isomer distribution is found to converge to a thermodynamic equilibrium at high conversions of levulinic acid. The hitherto unconsidered acid-catalyzed isomerization of *p,p′*-DPA to *o,p′*-DPA was demonstrated by condensation reactions with both *m*-cresol and ^{13}C-labeled phenol supported by density functional theory (DFT) calculations.



KEYWORDS: *acid−thiol cooperative catalysis, biomass, levulinic acid, renewable bisphenols, hyperbranched polymers*

The future of biomass as an alternative resource for the polymer industry depends strongly on the incorporation of renewable platform chemicals into existing petrochemical processes and products.[1−24] A number of studies have shown that diphenolic acid (DPA), produced from cellulose-derived levulinic acid (LA),[25−33] can potentially displace bisphenol A (BPA) as a structural analogue in the preparation of polybenzoxazines,[34] aromatic polyesters[35] and polycarbonates.[36,37] In addition to its use as a coating material,[38] current estimates suggest that DPA could capture 20% of the demand for BPA, allowing a total market size of 15 million lb/year.[23,29] The condensation between LA and phenol to form DPA is an exothermic reaction ($\Delta H = -19$ kJ/mol)[39] which can be performed under mild conditions using Brønsted acid catalysts and in the absence of solvents. Although previously reported yields were fairly high (>50%),[40−44] the efficiency of this catalytic reaction is hindered by the formation of undesired *o,p′*-DPA isomers. Improving the regioselectivity of acid catalysts toward 4,4-bis(*p*-hydroxyphenyl)pentanoic acid, also referred to as *p,p′*-DPA, remains a scientific challenge of high industrial relevance. The molar ratio of both isomers plays, for instance, an important role in the synthesis of polycarbonates with improved physicochemical properties such as color stability,[45] crystallinity, and intermolecular attractive forces between the polymer chains.[46] In the case of BPA synthesis, most of the commercial applications require separation of the isomers by energy-intensive procedures involving fractional distillation coupled with crystallization.

Acid-catalyzed coupling reactions of LA with phenol proceed via protonation of the ketone which subsequently reacts with phenol to form DPA.[40−44] Of particular importance is the acid-thiol cooperative catalytic action of sulfonic acid-functionalized catalysts and thiol-containing compounds, first demonstrated for the condensation of acetone and phenol to BPA.[47−55] Recently, we reported that the combination of sulfonated hyperbranched poly(arylene oxindole)s (SHPAOs) and thiol promoters allows the catalytic synthesis of DPA in high yields (>50%).[40] The SHPAOs possess a high Brønsted acid density (4.3 mmol H^+ g^{-1}), a high solubility in polar solvents and a low solution viscosity, which explains the growing interest for their use in catalytic applications.[25,40,56] To facilitate the reuse of the catalyst, we aimed to incorporate thiol promoters into the hyperbranched polymer matrix by neutralization of the sulfonic acid groups via ionic bonding with 2-aminoethanethiol or 2-(4-pyridyl)ethanethiol.[40] Details on the synthetic procedure and characterization of the SHPAOs by acid−base titration, ^{1}H and

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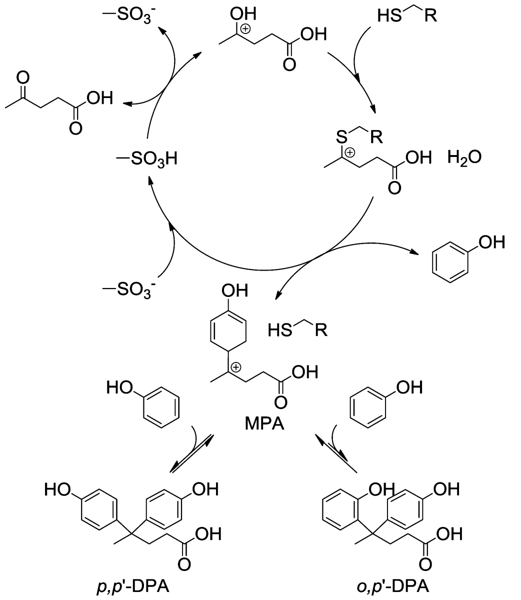
^{13}C NMR spectroscopy, gel-permeation chromatography (GPC), Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis/mass spectrometry (TGA/MS) can be found elsewhere (see also the Supporting Information).[25,40,57,58]

The proposed catalytic cycle featuring the cooperative action of sulfonic acid and thiol groups is depicted in Scheme 1.

Scheme 1. Catalytic Cycle for the Condensation between LA and Phenol to DPA Using Sulfonic Acid-Functionalized Catalysts and Thiol Promoters



Zeidan et al. have suggested that the formation of a charged sulfonium intermediate increases the electrophilicity of the ketone group, leading to increased reaction rates.[47,48] The subsequent condensation with phenol releases the product as an isomeric mixture of *p,p′*-DPA and *o,p′*-DPA and returns the SHPAOs to initiate a new catalytic cycle. Importantly, our earlier attempts to improve the yields of DPA focused on systematically investigating combinations of SHPAOs and thiols with different sizes, such as ethanethiol, 1-propanethiol, 1-butanethiol, 1,1-dimethylethanethiol, and phenylmethanethiol.[40] It was proposed that the thiol substituent sterically affects the approach of phenol and consequently alters the regioselectivity toward the desired *p,p′*-DPA isomer.[40,47,49] Thus, a higher regioselectivity toward *p,p′*-DPA was expected for reactions cocatalyzed by more hindered thiol groups. However, an anomalous result was observed: a reaction catalyzed by SHPAOs in the presence of ethanethiol (1:1 molar ratio of thiols to sulfonic acid sites) gave 52.9% yield of DPA with a *p,p′*:*o,p′* ratio of 19.5 at 69.5% conversion after 16 h at 100 °C, while 1,1-dimethylethanethiol generated a *p,p′*:*o,p′* ratio of 10.5 at 38.9% conversion under similar reaction conditions.[40] Note that a reaction without thiols under the same conditions, yielded only 34.9% yield of DPA and a *p,p′*:*o,p′* ratio of 7.6 at 40.0% conversion. The generally accepted explanation based on steric hindrance of the thiol side chains for the approach of phenol indeed fails to explain these experimental observations. Therefore, despite the availability of the empirical data, a more detailed understanding of regiochemical control is needed. In this work, we present a comprehensive mechanistic description of the effects that alkyl- and phenyl-substituted thiols have on the observed reaction rates and product regioselectivity.

Reaction rates were correlated to Taft-type steric and electronic parameters to investigate the mechanism of the catalytic reaction. Traditionally, these types of correlations have been created by evaluating the catalytic activity as a function of substrate substituents,[59,60] but have not been previously made as a function of cocatalyst substituents. However, as phenol condensation is identified to be the rate-determining step in the mechanism (vide infra), the sulfonium intermediate in Scheme 1 can be considered as the active substrate for the coupling with phenol. In analogy to Taft's original hypothesis for acid-catalyzed aliphatic ester hydrolysis, we anticipated that the overall reaction rate would be influenced by the steric repulsion of the substituent (CH_2R) of the sulfonium intermediate. In this study, Taft linear free energy relationships were determined by plotting $-\log(k_{rel})$, where k_{rel} is the pseudo-first-order rate constant for condensation reactions in the presence of SHPAOs and five different thiols measured relative to reactions performed with ethanethiol, versus the steric substitution constants E_S and polar substitution constants σ^* (see Figure 1 and the Supporting Information, Table S1). The catalytic reactions followed identical kinetics with a pseudo-first-order dependence on the concentration of LA. The condensation rate decreased in the following order: ethanethiol >1-propanethiol > phenylmethanethiol >1-butanethiol > 1,1-dimethylethanethiol. A comparison of the correlation coefficients for linear fits of $-\log(k_{rel})$ versus $-E_S$ ($R^2 = 0.96$) and $-\sigma^*$ ($R^2 = 0.39$) suggests that the reaction rate is mainly influenced by steric effects, which is in agreement with previous studies on the catalytic synthesis of BPA.[47] The sensitivity for the electron-donating ability of the thiol side chains seems to be less clear.

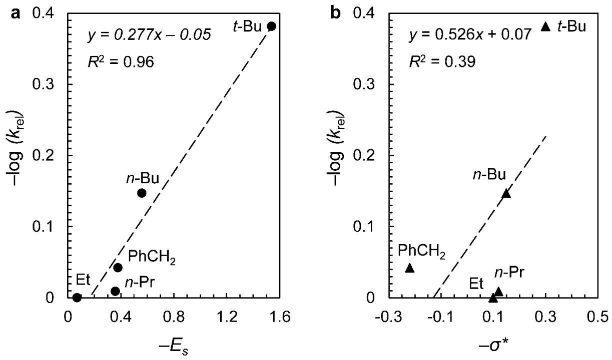


Figure 1. Plot of $-\log(k_{rel})$ versus Taft steric (a) and electronic parameters (b), respectively, in the acid-catalyzed condensation of LA and phenol in the presence of SHPAOs and thiol promoters with different substituents. Et = CH_2CH_3, *n*-Pr = $CH_2CH_2CH_3$, *n*-Bu = $CH_2CH_2CH_2CH_3$, *t*-Bu = $C(CH_3)_3$, Ph = phenyl. Reaction conditions: 3.4 mmol LA, 10.2 mmol phenol, 0.22 mmol H^+ in added catalysts, 1:1 molar ratio of thiols to acid sites, 100 °C.

Figure 2 shows the evolution of the *p,p′*:*o,p′* ratios of DPA during the condensation of LA and phenol as a function of LA conversion. Most notably, Zeidan et al. found a constant BPA selectivity at different levels of conversion for the condensation of acetone with phenol using 1-propanethiol as promoter and homogeneous and SBA-15-immobilized sulfonic acids as catalysts (100:1 molar ratio of acetone to sulfonic acid sites).[47] Other studies on the cooperative action of acid-thiols in the catalytic synthesis of BPA or DPA have focused only on a single value of the regioselectivity at the reaction end

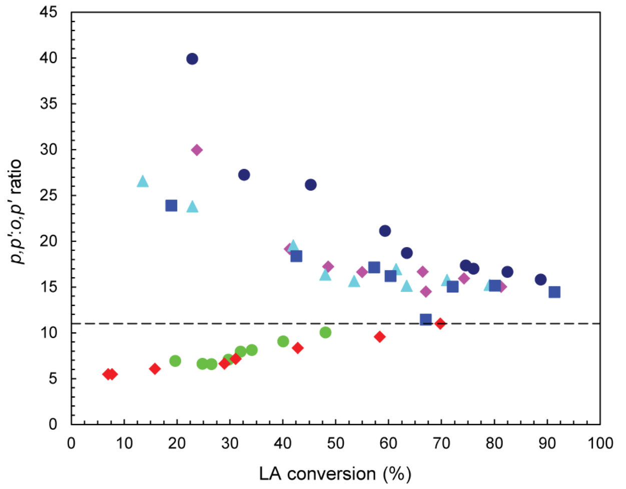


Figure 2. p,p':o,p' ratio as a function of LA conversion for the acid-catalyzed synthesis of DPA in the presence of SHPAOs and different thiols: ethanethiol (indigo circles), 1-propanethiol (violet diamonds), 1-butanethiol (turquoise triangles), phenylmethanethiol (blue squares), and 1,1-dimethylethanethiol (green circles). Data for reactions catalyzed by SHPAOs in the absence of thiols are included for comparison (red diamonds). The dashed line shows the thermodynamic equilibrium ratio at 100 °C as determined by DFT calculations at the B3LYP level. Reaction conditions: see Figure 1.

point.[40,49,54,61] We are unaware of previous studies reporting on condensations of LA and phenol where a conversion-dependent regioselectivity has been used to derive mechanistic insights. It will be shown how careful analysis of the data presented in Figure 2 indicates a complex kinetic behavior. However, to gain insight into the underlying reaction mechanism, it is critical to understand the differences between the initial regioselectivities.

For reactions in the absence of thiols, the initial p,p':o,p' ratio was 5.5 at a conversion of 7.0%. The general preference of phenol for electrophilic aromatic substitution at the *para* position is interpreted as the result of orbital-controlled rather than charge-controlled reactivity. A seemingly counterintuitive trend in Figure 2 is the increasing initial regioselectivity with decreasing sizes of the thiol substituent. Although access to ethanethiol is expected to be the least sterically hindered by its substituent and thus to exhibit the lowest regioselectivity toward p,p'-DPA, it exhibited the highest initial p,p':o,p' ratio (39.9 at a conversion of 23.0%). This is, to the best of our knowledge, the highest value reported for catalytic synthesis of DPA. For instance, Guo et al. reported p,p':o,p' ratios in the range of 1−4 for reactions catalyzed by $H_3PW_{12}O_{40}$/silica composites under similar conditions.[41−43] The observed trend in this study points out that regiochemical control in fact results from the kinetic effect of thiols on the formation rate of the sulfonium intermediate (see Scheme 1). Our kinetic analysis indicates that LA reacts approximately 2.4 times faster in the presence of ethanethiol than in the presence of 1,1-dimethylethanethiol, resulting in a significantly larger contribution of the more reactive sulfonium intermediate. Consequently, a higher regioselectivity is observed in the first condensation reaction with phenol.

A striking and unprecedented trend observed in Figure 2 is that the experimentally obtained p,p':o,p' ratios converge to an apparent equilibrium value at high conversions of LA. In view of the mechanism outlined in Scheme 1, we hypothesized that p,p'-DPA would be able to isomerize to o,p'-DPA in the presence of the acid catalyst. Indeed, upon reacting a mixture of p,p'-DPA and phenol under standard conditions in the presence of SHPAOs, o,p'-DPA was obtained in 6.5% yield, resulting in a p,p':o,p' ratio of 9.8 after 72 h (see Figure 3a). It is worthwhile mentioning that theoretical calculations, performed at the B3LYP-DFT level of theory, predict a thermodynamic equilibrium p,p':o,p' ratio of 11 at a temperature of 100 °C (see the Supporting Information).[62] Blank experiments with p,p'-DPA showed that yields of only 0.2% o,p'-DPA were obtained in the absence of SHPAOs at an equivalent reaction time. The data support the hypothesis that the isomerization of p,p'-DPA to o,p'-DPA is acid-catalyzed and initiated through a protonation of the aromatic ring that enables cleavage of the bond between the phenol group and the bridging carbon atom in the reverse direction of the electrophilic aromatic substitution shown in the bottom part of Scheme 1.[63]

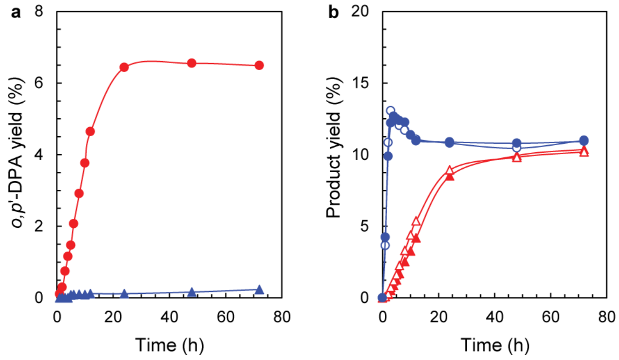


Figure 3. Acid-catalyzed isomerization of pure samples of p,p'-DPA and phenol as starting reactants: (a) Yield of o,p'-DPA against time for reactions in the presence (red circles) and absence of SHPAOs (blue triangles). (b) Yield of o,p'-DPA (red triangles) and MPA (blue circles) against time for reactions catalyzed by SHPAOs in the presence (open symbols) and absence of ethanethiol (closed symbols). Reaction conditions: 15.3 mmol phenol, 2.6 mmol p,p'-DPA, 0.32 mmol H^+, 100 °C.

To further substantiate the proposed isomerization mechanism, we reacted p,p'-DPA with *m*-cresol instead of phenol as a starting reactant and investigated the resulting product distribution. The equilibrium p,p':o,p' ratio amounted to 2.8 after 16 h, indicating a strong steric hindrance effect of the methyl group in *m*-cresol that is located in close proximity to the reactive carbon atom. The presence of phenol in the reaction medium confirmed the proposed cleavage of p,p'-DPA during isomerization. A qualitative GC/MS analysis after trimethylsilylation of the product mixture showed one main peak and several smaller peaks corresponding to intermediates with parent mass spectral signals at m/z 264 and 278 (see the Supporting Information, Figure S3). These signals are consistent with the molecular weights of trimethylsilylated species of LA bound to one molecule of phenol or *m*-cresol, respectively. Formation of the latter compound can again be explained by acid-catalyzed cleavage of DPA, followed by nucleophilic substitution of phenol with *m*-cresol. Interestingly, Hunter et al. suggested that analogous products can be formed in the acid-catalyzed synthesis of *p*-isopropenylphenol via hydrothermal cleavage of BPA.[63]

Unambiguous evidence for the incorporation of phenol during isomerization of DPA came from catalytic isomerization reactions of p,p'-DPA in the presence of ^{13}C-labeled phenol (Figure 4). A comparison of the ^{13}C NMR spectra of phenol-

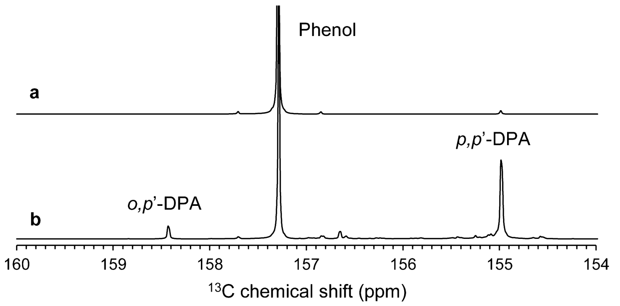


Figure 4. ^{13}C NMR spectra of (a) labeled 1-^{13}C phenol and (b) the product mixture obtained after acid-catalyzed isomerization of *p,p'*-DPA in the presence of 1-^{13}C phenol. Reaction conditions: see Figure 3.

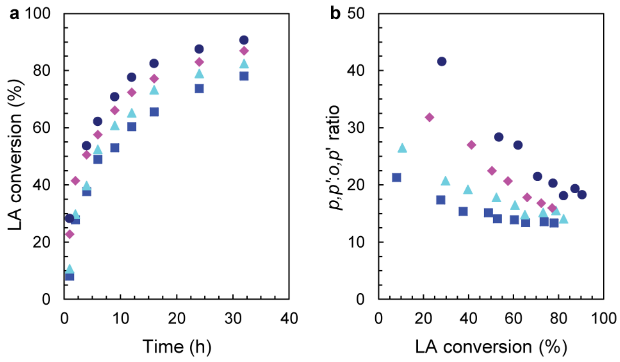


Figure 5. Effect of the proportion of acid to thiol groups: (a) LA conversion against time and (b) *p,p'*:*o,p'* ratio against LA conversion for the catalytic condensation of LA and phenol in the presence of SHPAOs and 1-butanethiol for different SO_3H:SH ratios: 1:4 (indigo circles), 1:2 (violet diamonds), 1:1 (turquoise triangles), and 2:1 (blue squares). Reaction conditions: see Figure 1.

1-^{13}C before and after reaction with *p,p'*-DPA revealed resonances at δ = 155.0 and 158.4 ppm, corresponding to phenol incorporation into *p,p'*-DPA and *o,p'*-DPA, respectively.

Finally, after demonstrating the occurrence of interconversion between *p,p'*-DPA and *o,p'*-DPA, we assessed whether this acid-catalyzed isomerization would be influenced by the presence of thiols. Figure 3b shows the evolution of the product distribution in the isomerization of *p,p'*-DPA as a function of reaction time using ethanethiol as a representative example. It was observed that the yields of both *o,p'*-DPA and the monosubstituted reaction intermediate (monophenolic acid or MPA, Scheme 1) were barely affected by the presence of ethanethiol. These results suggest that while the cocatalysts are favorable for the first acid-catalyzed condensation step in the synthesis of MPA, they do not influence the parallel isomerization reaction or the second condensation with phenol to DPA (which occurs through the same reaction intermediate). Note that there is a sharp increase in the concentration of MPA during the first 4 h of the reaction. This trend suggests that MPA is primary in origin and that phenol condensation is the rate-determining step in the acid-catalyzed isomerization.

The experimental evidence dictates that catalyst design needs to be tailored such that the reaction rate of this condensation step is enhanced while maintaining the highest possible regioselectivity to *p,p'*-DPA. We have already identified that balancing the proportion of acid to thiol groups is an effective method to meet these two objectives. Specifically, as demonstrated in Figure 5, low SO_3H:SH ratios are crucial to achieve high yields of *p,p'*-DPA, as these conditions favor the overall reaction rate as well as increased *p,p'*:*o,p'* ratios.

In conclusion, the mechanistic scenario that evolves from our experimental study provides a rationale for the role of thiols as a cocatalyst in the acid-catalyzed synthesis of DPA. The mechanism proposed in the literature attributes the preferred formation of *p,p'*-DPA to the steric hindrance of the side chains of the thiols, which would result in higher *p,p'*:*o,p'* ratios for less sterically accessible thiols. However, this hypothesis is rejected by the experimental evidence provided herein. We show, based on Taft linear free energy relationships, that steric effects play a predominant role in determining the condensation rate and formation of MPA, while the resulting kinetic effects influence the regioselectivity. These insights reveal the importance of using relatively high amounts of thiols with small substituents at low LA conversions to successfully tune the regiochemical control toward *p,p'*-DPA, which could ultimately be exploited in continuous-flow systems. Our understanding of how the acid-catalyzed isomerization reaction occurs, and what the implications for the synthesis of DPA are, could be useful for the rational development of even more efficient catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the polymer synthesis and catalytic reactions, Taft constants and pseudo-first-order rate constants, details on the DFT calculations, schematic representation and ^{1}H NMR spectra of the sulfonated hyperbranched poly(arylene oxindole)s and GC/MS data of the product mixture of the acid-catalyzed isomerization reaction of *p,p'*-DPA in the presence of *m*-cresol. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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