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Poly(arylene ether)s via Cu(II)-Catalysis

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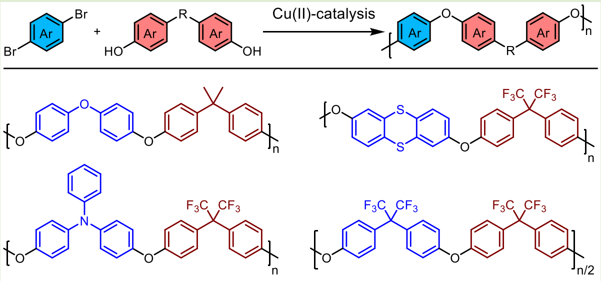
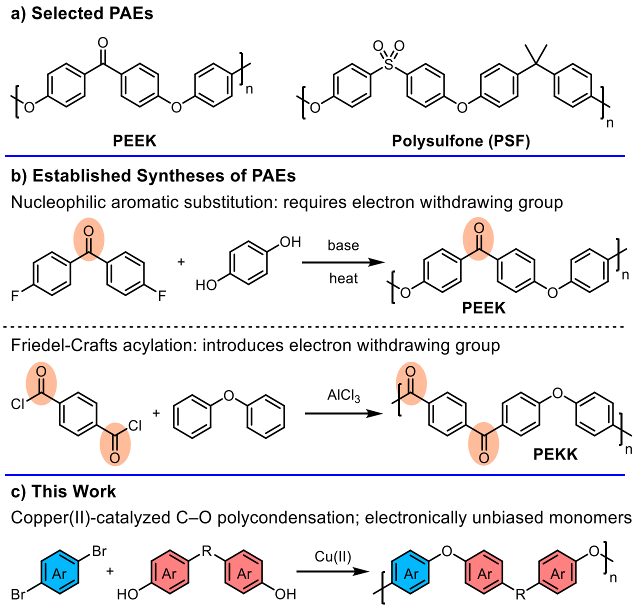
ABSTRACT: Poly(arylene ether)s (PAEs) are a versatile class of thermoplastic materials with commercial importance. Currently their synthesis relies predominantly on either nucleophilic or electrophilic aromatic substitution reactions, severely limiting the scope of available PAEs. Herein, we report the copper(II)-catalyzed polycondensation of electronically unactivated aryl bromides with bisphenols to afford a wide range of new PAEs. These PAEs are characterized by their thermal and mechanical properties. Functional PAEs were produced that have reversible acid- and redox-triggered chromophores incorporated into the backbone, which illustrates the utility of these methods.



Poly(arylene ether)s (PAEs) are versatile, high-performance thermoplastic materials defined by an ether linkage between two neighboring arene units in the polymer backbone. Examples with significant commercial importance include poly(arylene ether ketone)s (PAEKs) and polysulfones (Scheme 1a). Polyether ether ketone (PEEK) and Polyetherketoneketone (PEKK) are high-performance thermoplastics with exceptional chemical and mechanical stability, suitable for demanding applications in aerospace engineering and the oil and gas industry, as well as medical implants.[1] Polysulfone is another high-performance thermoplastic, with additional applications for micro- and nanofiltration membranes, as well as hydrogen and nitrogen purification membranes.[2,3]

Scheme 1. (a) Examples of Commercially Important PAEs; (b) Selected Syntheses of PAEs; (c) Cu(II)-Catalyzed C−O Polycondensation



PAEs are typically prepared through either nucleophilic (S_NAr) or electrophilic (S_EAr) aromatic substitution reactions (Scheme 1b).[4−6] However, S_NAr reactions most often require specialized monomers, such as aryl fluorides activated by electron-withdrawing groups, which limits structural diversity. Although S_EAr reactions are not restricted by these requirements, the electrophiles commonly employed in PAE synthesis (e.g., acyl chlorides and sulfonyl chlorides) introduce the electron-withdrawing functional groups into the polymer backbone. Therefore, a complementary method enabling the synthesis of diverse PAEs from electronically unbiased monomers is highly desirable.

A promising but underexplored approach is the synthesis of PAEs through cross-coupling of bifunctional aryl halides and bisphenols catalyzed by transition metals. For a successful step-growth polymerization, the catalyst needs to achieve very high reaction conversion and selectivity (>98%) while maintaining a precise 1:1 stoichiometric ratio of monomers.[7] This is in stark contrast to a small molecule synthesis, where an excess of one coupling partner is typically employed to boost conversion. The combination of Pd and dialkylbiaryl phosphine ligands

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was shown to overcome these challenges,[8] enabling the synthesis of select PAEs for applications such as heavy-metal remediation,[9] heterogeneous catalysis,[10,11] and gas separation.[12,13] However, widespread adoption is hampered by the high cost of catalyst and ligands as well as limited monomer scope. As a cost-effective alternative the copper catalyzed C−O coupling of aryl halides and phenols has been explored.[14−22]

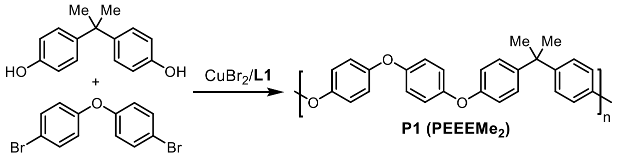
However, these methods rely on traditional Ullmann condensation conditions using catalytic Cu(I) with simple ligands such as pyridine, quinoline, or picolinic acid, and either the reported molecular weights were low or no molecular weights were reported. Moreover, most reports include only one or two examples, leaving questions about the generality of the methods unaddressed. In a recent study, Tanaka and Maeyama report the use of $Cu(PPh_3)_3Br$ as catalyst, using the coupling of bisphenol A and 4-bromophenyl ether as a model system for reaction optimization.[22] Although molecular weights of M_n = 9.3 kDa (corresponding to a number average degree of polymerization of almost 50) were obtained, the resulting molecular weight was still insufficient, giving rise to "brittle films with many cracks".

Recent advancements in ligands facilitating small molecule synthesis provide a general and efficient copper-catalyzed C−O polyetherification reaction. Dianionic ligands, such as tetrabutylphosphonium malonate,[23,24] pyrrol-ols,[25] and N^1,N^2-diarylbenzene-1,2-diamines,[26−28] have emerged as frontrunners for Cu(I)-catalyzed carbon−heteroatom bond formation. For the synthesis of biaryl ethers, dianionic oxalamide ligands, initially introduced by Ma[29,30] and further studied by Hartwig,[31] show exceptional turnover numbers and selectivities. Hartwig reported a highly efficient and mechanistically distinct C−O coupling reaction operating through a noncanonical Cu(II)/Cu(III) redox cycle in the presence of a redox noninnocent oxalamide ligand.[32] Herein, we report the synthesis of high molecular weight PAEs by C−O polycondensation of dibromoarenes and bisphenols through Cu(II)-catalyzed cross coupling (Scheme 1c).

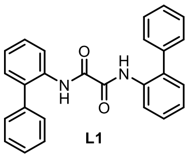
We set out to identify suitable reaction conditions using bisphenol A and 4-bromophenyl ether as model substrates (Table 1). Subjecting equimolar amounts of the monomers to catalytic $CuBr_2$ (2 mol %), *N*,*N*′-bis(2-phenylphenyl)oxamide **L1** (4 mol %), and potassium phosphate (3.0 equiv) in dimethyl sulfoxide (DMSO, monomer concentration 1.0 M) at 140 °C affords **P1**. We refer to this as $PEEEMe_2$ in analogy to PEEK, and it is obtained with a number average molecular weight (M_n) of 31.7 kDa and a dispersity ($Đ$) of 2.2 (Table 1, entry 1). High molecular weight **P1** is insoluble in DMSO even at elevated temperatures and precipitates from the reaction mixture. Although **P1** is well soluble in *N*,*N*-dimethylformamide (DMF), switching to this solvent leads to lower molecular weights, with a 1:1 DMF/DMSO mixture giving the best result without leading to precipitation (Table 1, entry 2). This stands in contrast to the Cu(II)-catalyzed C−O coupling of small molecules reported by Hartwig, where DMF was identified as optimal solvent.[32]

The combination of CuBr and oxalamide ligand **L2**[31] affords high molecular weight **P1** (Table 1, entry 3), demonstrating that a traditional Cu(I)/Cu(III) cross-coupling mechanism may also deliver high molecular weight PAEs. However, similar to the report by Tanaka and Maeyama for the synthesis of low molecular weight **P1**,[22] the resulting material had a dark brown color. This stands in contrast to that of the Cu(II)/Cu(III) catalytic system, which delivers an almost colorless reaction product. An attempt to synthesize **P1** through Pd-catalysis[12] only affords low molecular weight product (Table 1, entry 4), consistent with previous observations in our laboratory. Control experiments revealed that the copper catalyst is essential for reaction success, and exclusion of air is required to obtain high molecular weights (Table 1, entries 5 and 6). The use of the corresponding aryl iodide or aryl chloride leads to low molecular weight oligomers (Table 1, entries 7 and 8).

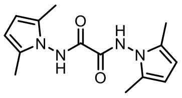
Table 1. Selected Optimization Results[a]



entry	variation from "standard conditions"[b]	yield	M_n (kDa)	$Đ$
1	none	71%	31.7	2.2
2	DMSO/DMF 1:1 as solvent	62%	22.8	1.7
3	CuBr (2%) + **L2** (4%)	75%	24.8	2.3
4	Pd conditions[c]	73%	6.5	2.5
5	no Cu	0[d]		
6	reaction under air	85%	9.2	2.2
7	aryl iodide	66%	4.9	1.6
8	aryl chloride	oligomers[e]		



L1



L2

[a] Isolated yields after precipitation from methanol. M_n and $Đ$ were measured by THF GPC vs polystyrene standards. [b] Bisphenol A (1.0 equiv), 4-bromophenyl ether (1.0 equiv), $CuBr_2$ (0.02 equiv), **L1** (0.04 equiv), K_3PO_4 (3.0 equiv), DMSO (1.0 M), 140 °C, 20 h. [c] Bisphenol A (1.0 equiv), 4-bromophenyl ether (1.0 equiv), $[Pd(cinnamyl)Cl]_2$ (0.01 equiv), *t*BuBrettPhos (0.04 equiv), K_3PO_4 (3.0 equiv), *o*-xylene (0.5 M), 140 °C, 48 h. [d] No precipitate observed. [e] Milky precipitate observed.

Having developed a protocol to access high molecular weight **P1** (Table 1, entry 1, M_n = 31.7 kDa), we moved on to study its mechanical properties. **P1** forms optically clear, flexible, and robust films by solution casting from tetrahydrofuran (Figure 1). Tensile stress−strain testing revealed a Young's modulus of 1.68 ± 0.08 GPa by tensile testing, which is lower than that of poly(ether sulfone)[3] (2.3 GPA) and PEEK[1] (3.5 GPa).

With suitable conditions for the Cu(II)-catalyzed C−O polycondensation in hand, we moved on to explore the scope of the reaction (Scheme 2). C−O coupling of inexpensive 1,4-dibromobenzene and bisphenol A affords **P2** in good yield and molecular weight. Due to the low solubility in DMSO, a switch to DMSO/DMF 1:1 as a solvent mixture was required. The combination of bisphenol C and 4-bromophenly ether furnishes **P3**, demonstrating that that substituents ortho to the reactive hydroxy-group are tolerated. The use of fluorinated bisphenol AF delivered **P4−P6** in high yield. Notably, Schönberger et al. previously attempted to synthesize **P6** through S_NAr reaction of bisphenol AF and the corresponding aryl fluoride.[33] However, in spite of the

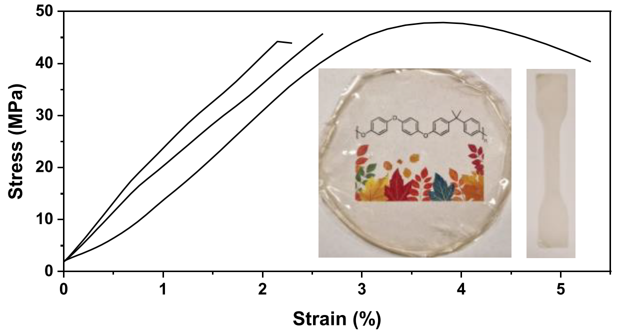


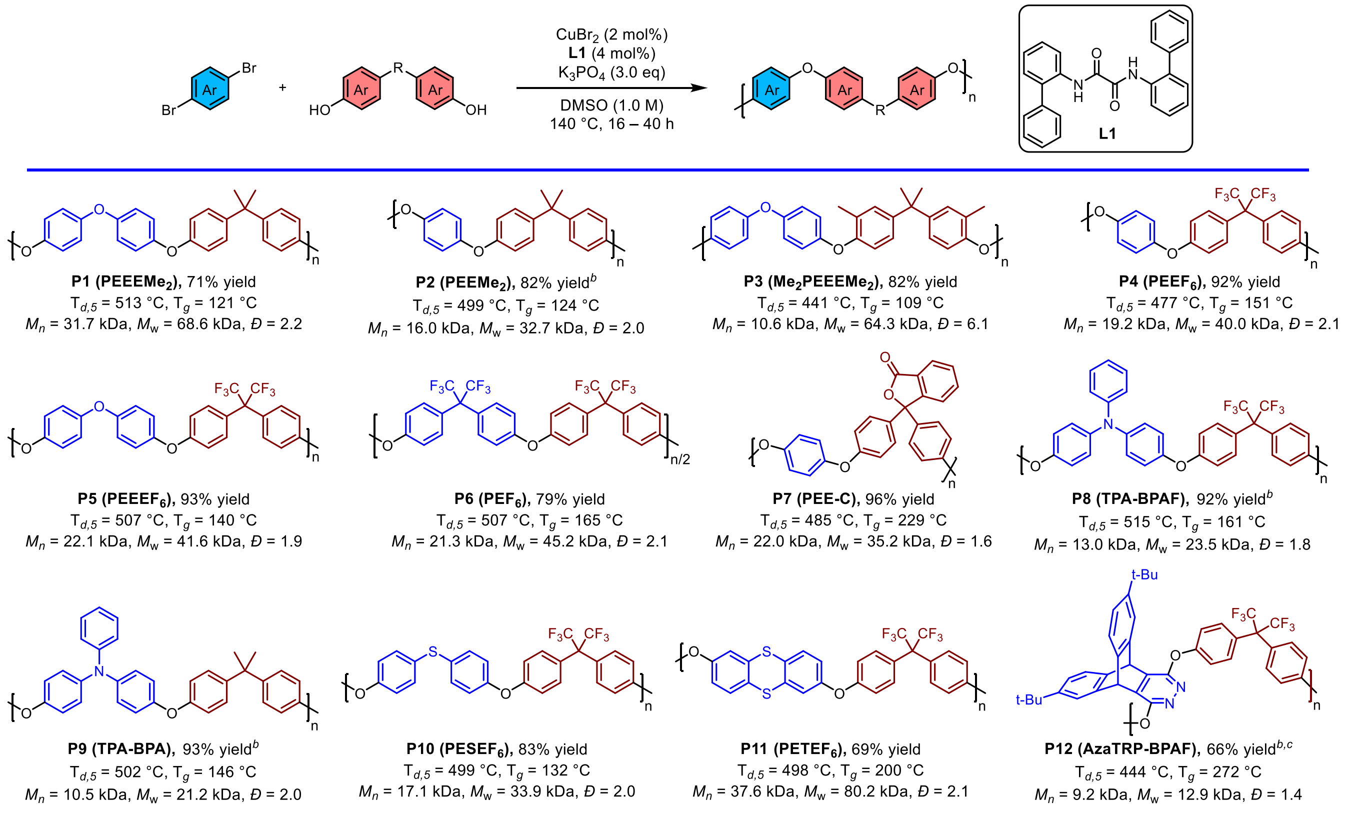
Figure 1. Tensile stress−strain curves of **P1** at room temperature. Each line represents a different sample specimen cut from the same film. Young's modulus was determined in the linear region from 1.0 to 1.5% strain (1.68 ± 0.08 GPa). Inlets: Photograph of a film of **P1** obtained by solution casting from tetrahydrofuran (thickness = 80 μm) and a dogbone specimen used for mechanical testing.

electron-withdrawing hexafluoroisopropylidene substituent, only a low molecular weight polymer (M_n ca. 5 kDa) was reported, showcasing the need for alternative synthetic approaches. The copper catalyst demonstrated good tolerance to polar functional groups, successfully delivering **P7** bearing a γ-lactone. Phenolphthalein and related structures can undergo a ring-opening reaction in highly acidic conditions, leading to a strongly colored trityl cation.[34] Indeed, a colorless solution of **P7** in dichloromethane instantly turns deep purple when treated with small amounts of triflic acid (Figure S4). Polymers containing triarylamine groups are well-known to be potential electrochromic materials.[35] Therefore, we targeted 4,4′-dibromotriphenylamine as a monomer, successfully synthesizing amine-containing polymers **P8** and **P9**. Thioether-containing polymer **P10** and thianthrene-derived polymer **P11** were synthesized with M_n = 17.1 and M_n = 37.6 kDa, respectively. Both **P10** and **P11** have previously been prepared by S_NAr reaction of the corresponding aryl fluorides, with molecular weights of M_n = 11.6 kDa and M_n = 34.3 kDa, respectively.[36] However, we have not been able to reproduce these prior results, and the Cu-catalyzed method provides a more robust synthesis. Moreover, bis(4-bromophenyl)sulfane is commercially available, unlike the corresponding aryl fluoride. Finally, a heterotriptycene[37] was shown to be a competent monomer, affording **P12** in modest molecular weight and yield.

All polymers featured in Scheme 2 show high thermal stability under a nitrogen atmosphere, with 5% weight loss ($T_{d,5}$) occurring at around 500 °C. The two exceptions are **P12** with a $T_{d,5}$ of 444 °C, presumably due to loss of N_2, and **P3** with a $T_{d,5}$ of 441 °C, which we attribute to a thermal Fries-type rearrangement involving the *ortho*-methyl group, followed by C−C bond scission.[38]

The relatively high glass transition temperatures (T_gs) of **P1**−**P12** can be tuned by choice of monomers. Polymers carrying gem-dimethyl groups have lower T_gs than their corresponding gem-bistrifluoromethyl analogues, as demonstrated by **P1** with at T_g of 121 °C compared to **P5** with a T_g of 140 °C. The number of phenylene ethers in the repeat unit

Scheme 2. Polymers Prepared by Cu(II)-Catalyzed Polycondensation[a]



[a] All yields refer to the isolated polymers after precipitation. M_n, M_w, and $Đ$ were measured by THF GPC vs polystyrene standards. [b] DMSO/DMF 1:1 was used as solvent. [c] Aryl chloride was used instead of aryl bromide.

only shows a minor impact on T_g, as seen by **P1** and **P2** having T_gs of 121 and 124 °C, respectively. Introduction of a spirocycle fused to the polymer backbone significantly increases the glass transition temperature, with **P7** having a T_g of 229 °C.

Intrigued by the potential of triarylamine-containing polymers to display electrochromism[35] we set out to study the properties of 4,4′-dibromotriphenylamine derived polymer **P8**. To this end, we elected to employ a solution phase *in situ* spectroelectrochemistry approach.[39] Placing an electrochemical cell directly in the beam path of a UV−vis spectrometer allows one to directly study various redox states of the analyte without requiring chemical oxidants and with minimal temporal delay between the redox event and the measurement. The use of a "honeycomb" working electrode ensures that light can pass through the electrochemical cell.[40] Applying a cell potential of 0.9 V to an initially colorless solution of **P8** in 0.1 M ^{n}Bu$_4$N$^+$ PF$_6^-$/CH$_2$Cl$_2$ quickly gives rise to broad absorption peaks through the entire visible spectrum, with a distinct maximum at 748 nm (Figure 2). To study the electrochromic properties of **P8** in the solid state, we prepared a thin-film electrode by drop-casting a tetrahydrofuran solution of the polymer onto ITO-coated glass slides. In agreement with the solution-state results, the colorless film turns deep blue when applying a cell potential of 1.0 V (Figure 2, inlet). These results demonstrate the potential of **P8** as an electrochromic or a robust hole transport material in organic optical devices.

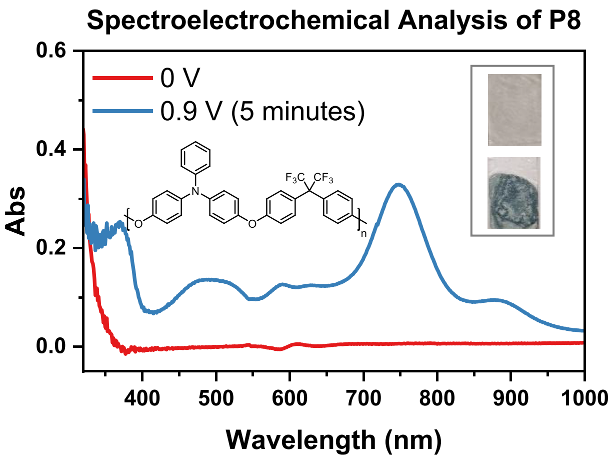


Figure 2. Spectroelectrochemical analysis of **P8** in 0.1 M ^{n}Bu$_4$N$^+$ PF$_6^-$/CH$_2$Cl$_2$ before and after applying a potential of 0.9 V for 5 min. The inlet shows photographs of a thin film on ITO glass before (top) and after (bottom) applying a potential of 1.0 V for 5 min.

In summary, we report a Cu(II)-catalyzed C−O polycondensation reaction of aryl bromides and bisphenols. This robust and operationally simple method allows the use of inexpensive and electronically unbiased monomers to synthesize structurally diverse poly(arylene ether)s that are inaccessible through an S$_N$Ar-polycondensation approach. As such, we expect our work to enable the discovery of novel PAEs for applications in the fields of chemistry, engineering, and materials science. Moreover, we demonstrate that the newly emerging noncanonical Cu(II)/Cu(III) cross-coupling manifold shows exceptional performance for highly demanding applications, such as polycondensation reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00703.

Experimental procedures and characterization data, cyclic voltammetry data, UV−vis absorption spectra, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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