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Synthesis of reactive and functional alkoxybenzene polymers

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Novolacs are prepared via acid-catalyzed addition–condensation of phenols with formaldehyde. This class of polymers is industrially important for use as curing agents, epoxy resins, and adhesives. Reactive novolacs are particularly valuable as they contain functional substituents, and can be expected to exhibit additional properties by undergoing modification to produce a variety of other polymers. In addition, they have the potential to be used as cross-linking reagents and resist materials. Therefore, these polymers have been attracting continuous attention since their initial discovery.

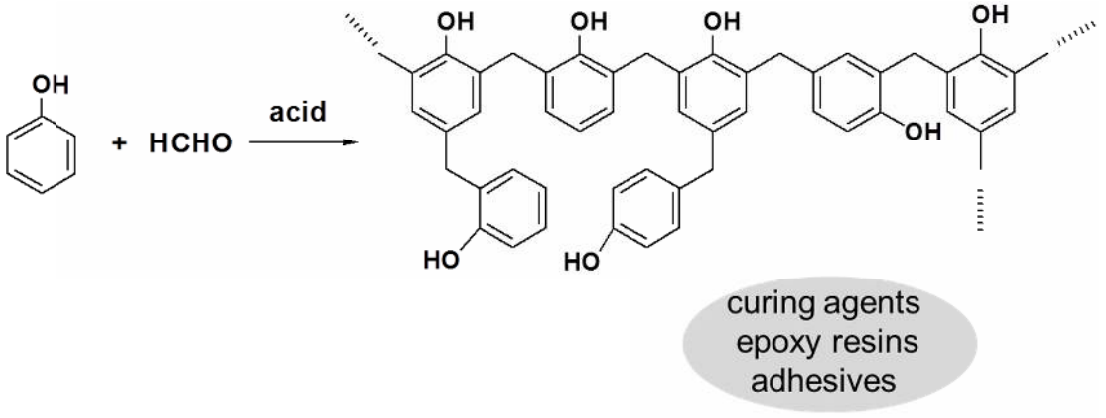

Figure 1. Structure of Novolacs and their applications.

In this thesis, novel reactive and functional polymers were synthesized using a similar acid-catalyzed phenol–formaldehyde condensation reaction. New, functional novolacs with allyl ether or bromoalkyl groups in the side chain were synthesized directly. In this process, benzene–formaldehyde condensation proceeded under specific conditions such that the functional group was not affected. Furthermore, a structure-controlled (regioregular) polymer could be synthesized via acid-catalyzed self-condensation of 4-methoxybenzyl chloride, containing only the ortho–para methylene linkage.

In addition, to achieve successful application of these functional polymers, organic and inorganic hybrids were prepared using these new alkoxybenzene materials. The hybrids were produced via an acid-catalyzed sol–gel reaction of

phenyltrimethoxysilane in the presence of novolac derivatives. The synthesized composite materials exhibited beneficial characteristics of both organic and inorganic polymers. The driving force for the dispersion of the two components was speculated to be the aromatic CH/π hydrogen bond interactions between the phenyl ring of the silica matrix and that of the novolac. This provided the possibility to prepare a hybrid glass with a high novolac derivative content.

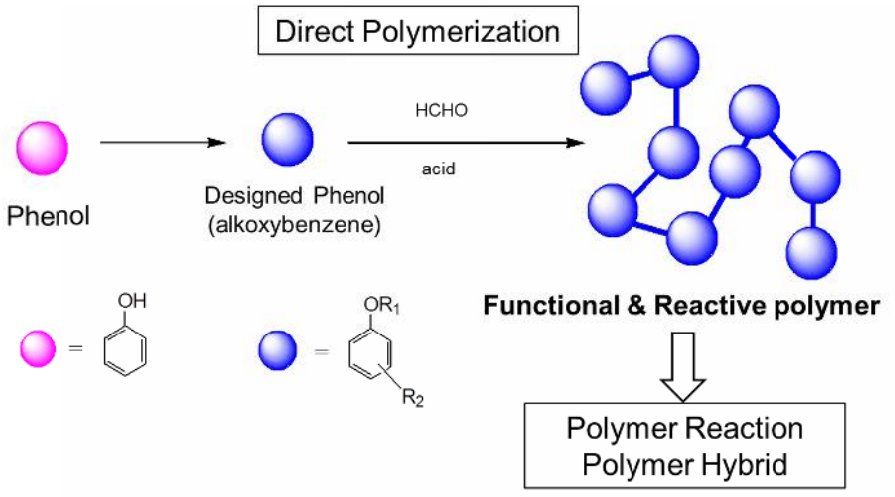

Figure 2. Direct Synthesis of reactive and functional polymers and their derivatives.

Another aspect to this study was the preparation of a new processable poly(phenylene sulfide)s (PPSs) from electron-rich benzenes and sulfur dichloride. Further, we applied this method for the preparation of the common PPS. The obtained polymers were soluble in common organic solvents including chloroform and THF. From the GPC and Mass spectra, both linear polymer and cyclic oligomer were obtained. As shown in **Figure 3**, new cyclic oligomers exhibiting interesting host-guest chemistry and a new processable PPS can be designed. These could not be achieved by using the commercially available PPS. Moreover, this synthetic method can realize the atom-economical process.

These findings confirm that this method can be applied not only in the preparation of polymer materials but also in the development of a new preparation process for PPS.

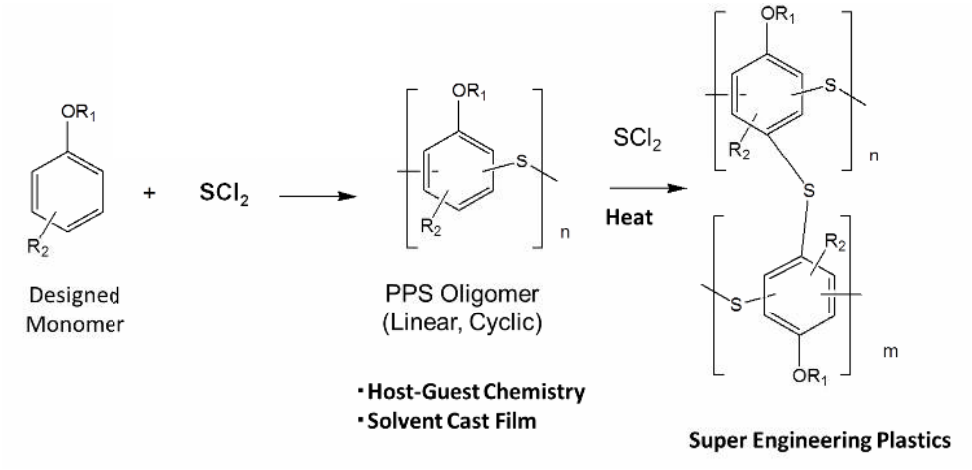

Figure 3. The Future prospects of polyphenylenesulfide (PPS) derivatives.