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Exceptional organic solvent uptake by disulfide-linked polymeric networks†

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Disulfide-linked covalent organic polymers (COPs) were prepared through catalyst-free oxidative coupling polymerization. Owing to the excellent swelling behavior, low cost, and efficient synthesis, these materials can be promising materials for removal of organics in concentrated streams. COPs show 1,4-dioxane uptake up to 1.8 g g^{-1}.

Polymers containing disulfide repeating linkages are of great concern due to the dynamic covalent bonds which could break and form again at will.[1–3] The applications of poly(disulfide)s include engineering plastics,[4] medicinal use,[5,6] and catalysis.[7] Organic solvents are often used for the production of fine chemicals, petroleum products, and pharmaceuticals. The concentrations of water miscible organic solvents are usually extremely high when they are discharged from the reaction vessels to wastewater streams. Thus, developing effective and inexpensive materials to remove harmful solvents from wastewater is technologically and environmentally a significant issue. The removal of organic contaminants from wastewater *via* physicochemical and biological techniques has been extensively studied.[8–10] Several materials, such as activated carbons,[8] mesoporous silica and zeolites,[11] organoclays,[12] metal–organic frameworks,[13] membrane,[14] and porous polymers[15–17] are reported for the removal of hazardous organics from wastewater. Biodegradation of organic pollutants in water is also one of the promising ways for a sustainable and environmentally friendly industry.[18]

In recent years, development of polymeric materials with tuned functionalities and controllable pore geometries have been gaining enormous importance since their wide range of applicability.[19,20] Polymers and their derivatives – poly(acrylic acid),[21] cellulose,[22] carbonaceous materials,[23,24] poly(orthocarbonate),[25] microporous polymers,[26] poly(lactic acid)[27] – as superabsorbents have been studied to remove oils and organic solvents from water. These materials were synthesized using expensive catalysts, monomers or high temperature conditions and none of the reports studied separation of solvents from water at high concentrations.

This study focuses on the synthesis of novel disulfide-linked covalent organic polymers (COPs) containing disulfide linkages (–S–S–) by oxidative coupling under catalyst-free mild conditions. These COPs show water stability and thermal stability up to 310 °C in air. The solvent uptake efficiency of the wide range of solvents by COPs was demonstrated. Furthermore, the separation of water miscible solvents, 1,4-dioxane was studied to elaborate potential application of COPs.

Inherent advantages of "thiol–ene" click chemistry[3] for the efficient polymerization of thiol functionalized monomers offer easy route for the synthesis of disulfide-linked polymeric networks. Tetravalent and trivalent aliphatic monomers are polymerized in dimethyl sulfoxide (DMSO) to afford highly swellable disulfide-linked COPs (Fig. 1).

Typically, trimethylolpropane tris(3-mercaptopropionate) or pentaerythritol tetrakis(3-mercaptopropionate) is added into DMSO, and the solution is heated at 80 °C for 24 h with vigorous stirring. The reaction mixture is cooled down to room temperature and excess of methanol was added to facilitate precipitates. The precipitates were centrifuged and soaked in tetrahydrofuran for 12 h. This procedure was repeated four times. Finally, gel-like material was dried under vacuum to obtain COP-65 and COP-66 (Fig. 1) (for detailed experimental procedures, see ESI†). CP/MAS ^{13}C-NMR spectra of COP-65 and COP-66 (Fig. 2a) confirmed the formation of disulfide polymeric networks as evidenced by characteristic chemical shifts at 171.5, 64.2, 41.6, 34.1, 23.5 and 7.6 for COP-65, and 171.5, 63.4, 42.5, 34.4 and 20.3 for COP-66.[28] FT-IR spectroscopy could also confirm the formation of disulfide linkages in COP-65 and COP-66 network (Fig. 2b).

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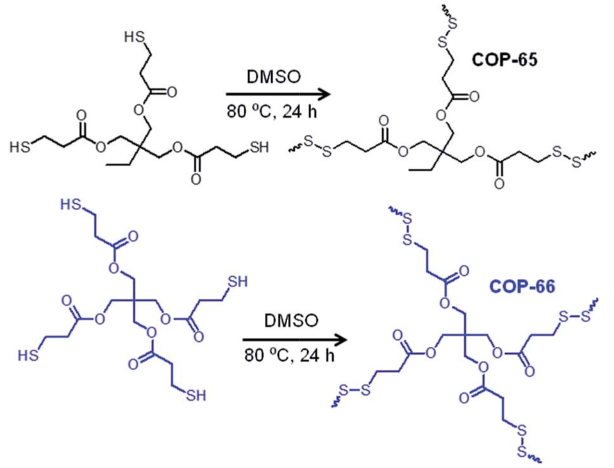

Fig. 1 Oxidative coupling of trimethylolpropane tris(3-mercaptopropionate) and pentaerythritol tetrakis(3-mercaptopropionate) in DMSO under mild conditions to form covalent organic polymers (COPs).

The characteristic vibration peaks for –C═O, –C–O, –C–S and –S–S– are visible at 1733, 1041, 667 and 468 cm^{-1}, respectively.[2] There is also terminal –S–H group present in both the networks as indicated with a minor peak at 2557 cm^{-1}. Intense stretching signals at 2800–3000 cm^{-1} correspond to –C–H groups. The experimental elemental analysis of the COP-65 and COP-66 is also in well accordance with the theoretical content, which further supports the formation of desired polymeric networks (Table S1†). Thermal stability of the COPs up to 800 °C in oxidative and inert conditions is measured by thermogravimetric analysis (Fig. 2c). They undergo single step decomposition which arises due to decomposition of aliphatic chains of COPs. The residual mass left after heating up to 800 °C is 0.98 and 1.39% for COP-65 and COP-66, respectively, in inert atmosphere, while the complete decomposition of COPs is observed in oxidative condition. COP-65 and COP-66 are stable up to 310 °C in inert as well as oxidative environment. As anticipated, largely because of the aliphatic nature of the networks and the absence of rigid building blocks, COP-65 and COP-66 are nonporous with negligible Brunauer–Emmett–Teller (BET) surface area (Fig. S1†). The XRD pattern shows (Fig. S2†) only one broadened Bragg diffraction peak at around 20°, proving the resulting polymeric networks are indeed amorphous materials.

Several organic solvents which have been employed for synthetic organic chemistry in industries – namely, hexane, benzene, toluene, diethyl ether (DEE), chloroform, dioxane, ethyl acetate (EA), tetrahydrofuran (THF), dichloromethane (DCM), 1,1,2,2-tetrachloroethane (TeCE), tetrachloroethylene (TeCEy), 1,1,2-trichloroethane (TrCE), 1,2-dichloroethane (DCE), 1,2-dichlorobenzene (DCB), acetone, acetonitrile (AcCN), dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetic acid (AA), *n*-butanol, isopropyl alcohol (IPA), ethanol, methanol and water – were treated with COP-65 and COP-66 (Fig. 3). The chlorinated solvents, TeCE and TrCE demonstrated the highest swelling of COP-65 up to 5.3 and 4.7 g g^{-1}, respectively. The separation of TrCE and DCE during vinyl chloride synthesis (feed stock for polyvinyl chloride) is a challenging problem since small amount of TrCE results fouling in the reactor and hampers production. COPs showed higher swelling capacity for TrCE (4.67 and 2.54 g g^{-1} for COP-65 and COP-66, respectively) when compared to DCE (2.02 and 1.39 g g^{-1} for COP-65 and COP-66, respectively), which indicate the use of these COPs

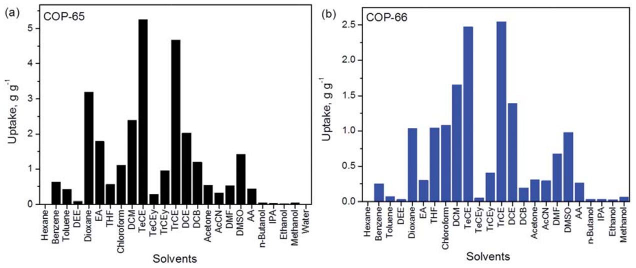

Fig. 3 Solvents uptake by (a) COP-65 and (b) COP-66 at ambient condition. DEE: diethyl ether, EA: ethyl acetate, THF: tetrahydrofuran, DCM: dichloromethane, TeCE: 1,1,2,2-tetrachloroethane, TeCEy: tetrachloroethylene, TrCE: 1,1,2-trichloroethane, DCE: 1,2-dichloroethane, DCB: 1,2-dichlorobenzene, AcCN: acetonitrile, DMF: dimethylformamide, DMSO: dimethylsulfoxide, AA: acetic acid and IPA: isopropyl alcohol (numerical values reported in Table S2†).

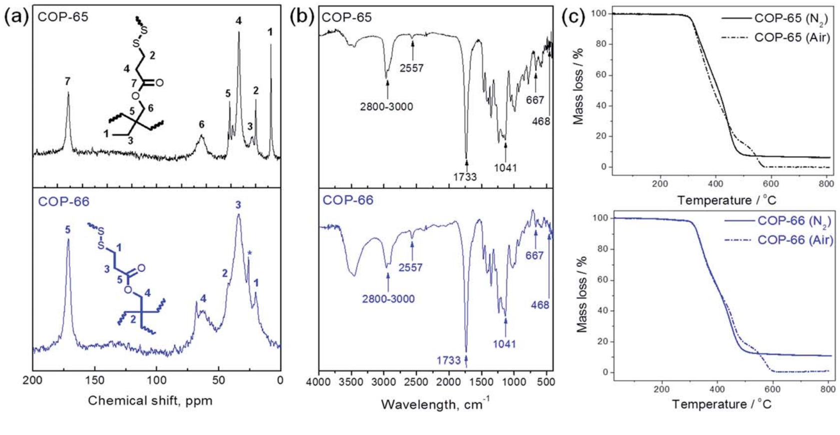

Fig. 2 (a) CP/MAS ^{13}C-NMR spectroscopy (b) FT-IR spectrums, and (c) thermogravimetric curves of COPs.

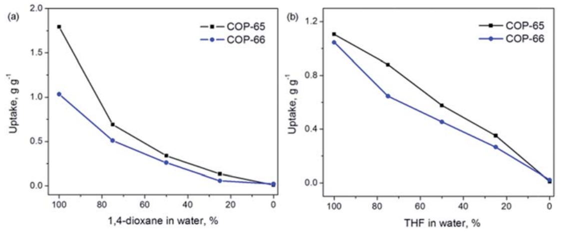

Fig. 4 (a) 1,4-Dioxane and (b) THF uptake from the mixtures of water–dioxane/THF.

other than just water treatment. The changes in the volume of the COPs with respect to swelling of solvents were also monitored (Fig. S3a and b†). The increase in the volume of COPs granules is distinctively visible after soaking for 12 h in various organic solvents. Cyclic ethers, *i.e.* dioxane and THF also showed excellent swelling with uptake capacity of 1.8 and 1 g g^{-1} and 1.1 and 1 g g^{-1} in COP-65 and COP-66, respectively.

Aromatic nonpolar solvents as well as aliphatic ether and hydroxyl containing polar solvents demonstrated moderate to negligible swelling in COPs. COP-65 performed better swelling characteristics than COP-66 owing to more flexible framework, which features from trivalent aliphatic building blocks instead of a tetravalent geometry. These polymeric networks did not decompose in a wide variety of organic solvents and also stable in oxidative conditions up to 310 °C. The regeneration of COP-65 and COP-66 were simply done by raising temperature close to the boiling points of the solvents. The repeated swelling cycles (10 cycles) didn't affect THF and dioxane uptake capacities of COPs (Fig. S4†), one of the most desired properties of materials that are designed for wastewater treatments.

Because of the negligible water uptake by COPs (0.01 and 0.02 g g^{-1} for COP-65 and COP-66), water miscible hazardous solvents that are present in high concentration in wastewater streams can be removed efficiently. 1,4-Dioxane is a cyclic ether, $C_4H_8O_2$, a widespread industrial contaminant in environmental waters and is designated as a human carcinogen by the US Environmental Protection Agency (EPA/635/R-09/005-F, 2010).[18,29,30] Dioxane is mainly utilized as a solvent stabilizer in the manufacture and processing of paper, textile products, automotive coolants, electronics, pesticides and cosmetics, as well as a stabilizer in 1,1,1-trichloroethane.[31] The dioxane removal is particularly very important as both water (100 °C) and dioxane (101 °C) have almost similar boiling point. THF is also one of the key solvents used industrially for synthetic chemistry. It is not as toxic as dioxane, however, prolonged exposure of THF may cause serious damage to kidney, liver and respiratory track (EPA/635/R-11/006F, 2012).

The synthetic mixtures of water and dioxane/THF in the ratio of 0 to 100% (v/v) were used to study uptake performance of COPs on batch scale experiments (Fig. 4). The uptake of dioxane and THF from the mixtures goes down with respect to increasing concentration of water in both COPs. However, it is interesting to note that the removal efficiency of COP-65 and COP-66 at 50 : 50 ratios for dioxane is 0.34 and 0.26 g g^{-1} while THF is 0.57 and 0.45 g g^{-1}, respectively. These values clearly suggest the exceptional efficiency of COPs for uptakes of hazardous solvents from water miscible solvents. Furthermore, the stability and regeneration of COPs ability is an added advantage of these types of polymeric frameworks.

Conclusions

To conclude, we have demonstrated catalyst-free oxidative coupling polymerization of tetravalent and trivalent aliphatic thiols to form extended covalent organic polymers. COPs can be obtained from commercially available cost effective monomers, and the resultant swellable frameworks exhibited unique uptake behavior for various solvents. From a practical viewpoint, COPs are proved to be excellent materials for removal of dioxane and THF from the water–dioxane/THF mixtures. At 50 : 50 ratios of dioxane/THF and water, COP-65 uptake 34 and 57% of dioxane and THF, respectively while the swelling capacity of COP-65 for dioxane is 180%. The swelling capacity of TeCE is 525 and 247% for COP-65 and COP-66, respectively. Higher swelling efficiency of COPs for TrCE over DCE demonstrates potential use of COPs in purifying monomer feedstocks for vinyl chloride production. These COPs are reusable, not decomposed in various solvents and thermally stable in oxidative environment.

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