

INHERENT CONJUGATION ASSISTED MICROPOROUS POLYMERS FOR ORGANIC SOLVENT NANOFILTRATION

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Abstract: The recent ages have seen an embarking trend in the technology revolving around the Organic Solvent Nanofiltration (OSN) that employs pressure gradient to separate molecules in the range of (200-1000) g/mole. Considering a mild operation scenario, the OSN technique generally provides better energy efficiency as compared to conventional practices such as chromatography or solvent extraction. This one of the prime reasons the OSN technique is used in commercially viable sectors such as fuel industries and chemical plants. Amidst these advantages, the methodology is still in its evolutionary phase since the fabrication of a material which may be stable in various kinds of solvents is an arduous task for the researchers. To add more, a bolstered reproducible result is not obtained from this technique creating several loopholes while considering this operation. This short review refers to the recent works reported by Liang et al using conjugated microporous polymer membrane fabricated by surface-initiated polymerization. The membranes not only exhibited a much-reinforced resistance to the organic solvents but also exhibited an enhanced efficacy when contrasted to hexane and methanol.

Keywords: Organic Solvent Nanofiltration, Conjugation, Microporous Polymers, Surface Initiated Polymerization, Membranes

1. INTRODUCTION

A general strategy to fabricate the commercial membranes lied in the fact of polymers having moderate rigid chains aiming to develop minute intermolecular voids. Often the interactions between the polymer chains and the solvent molecules cause these chain networks to swell up decreasing the overall selectivity of the membrane [1-2]. Scientists have found that the polymers having the intrinsic property of microporosity (PIMs) are considered to be one of the competing materials in the search for the synthesis of OSN membranes. The increase in the rigidity of the monomers along with the crystal structure leads to the packing of the polymers which in turn, leaves interconnected voids within the system whose size ranges between (1.80-2) nm. As far as the PIMs are concerned, the enhanced chain rigidity causes a detrimental effect on the one-dimensional chain alignment coupled with the increased solubility [3-4]. Thus to incorporate a shape dedicated property in the membranes, new materials have been developed with elevated microporosity blended with non-discrete channels and lofted overall material stability.

2. REVIEWING THE TRENDS IN THE MEMBRANES FACILITATING ORGANIC SOLVENT NANOFILTRATION (OSN)

Materials having the traits of reticular organic porosity (ROM) such as the organic covalent frameworks (COFs) and polymers with conjugated microporosity (CMPs) with rigid backbone aided with tight pores are proved to be the ideal materials for developing the OSN membranes [4]. The bolstered backbones provided with the rigid polymer structures helps to elevate the solvent stability of the membrane, while the porous structure helps in the diffusion of the solvent molecules [5].

Even though these materials have shown several areas to promote the efficiency of solvent facilitation, there are a still lot of areas that need improvisations especially in the scopes of processibility and escalating it to the industrial level.

The increased percentage of the crystallinity induced owing to the organic frameworks networks often creates a problem while processing the material [6-8]. To undermine this disadvantage, scientists have come up with the idea of conjugated microporous polymers (CMPs) are specially selected to have the π -conjugation amongst them. The rotation which is aided by the π -conjugated bonds leads to amorphous three-dimensional crystal networks possessing a few local molecular order [9]. This, in turn, assists in eliminating the crystal edges producing perfect defect-free conjugated microporous polymer membranes [9].

3. FOCUSING ON THE DEVELOPMENT OF CMP MEMBRANES VIA SURFACE-INITIATED POLYMERIZATION

The CMPs even after proving to be a superior model fails with the effect of solubility comes into the play. The low solubility of these materials fails in the preparation of these membranes via the solvent casting method. A novel method recently reported in *Nature Chemistry* employs a newly adopted technology of surface-initiated polymerization to fabricate a centimeter-scale minute defect void CMPs [10]. The CMPs are based on the all-rigid porous backbones fabricated with the C-C and C-H bonds only proving the system to be completely inert as compared to the previously discussed structures frame-worked upon PIM membranes.

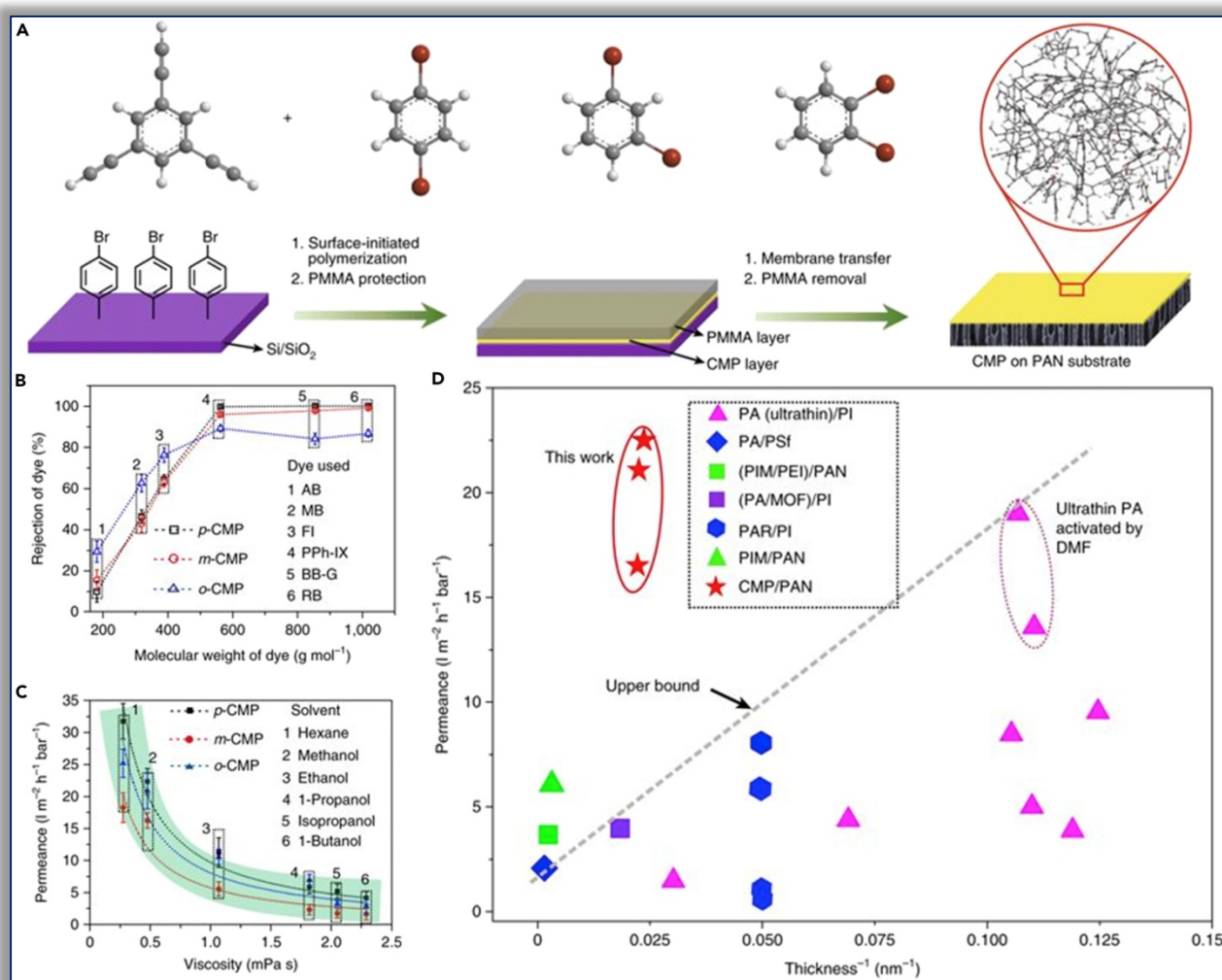


Figure 1: To illustrate the synthesis of the CMP membranes and the OSN properties (Abbreviations of the selected dyes: rose bengal (RB; 1,017 g mol⁻¹), brilliant blue G (BB-G; 854 g mol⁻¹), PPh-IX (562 g mol⁻¹), fluorescein-4-isothiocyanate (FI; 389 g mol⁻¹), methylene blue (MB; 320 g mol⁻¹), and azobenzene (AB; 188 g mol⁻¹) [10].

The CMP membranes were developed on a silica wafer functionalized with bromobenzene. The surface-initiated chemistry was followed very similar to the Sonogashira-Hagihara polymerization of 1, 3,5-triethynylbenzene with dibromobenzene, aided by 1,4-dibromobenzene, 1,3-dibromobenzene, and 1,2-dibromobenzene [10]. The membranes, thus formed were labeled as the *p*-CMP, *m*-CMP, and *o*-CMP following the position and the thickness of these membranes ranged in a bracketed value between 42 nm to 45 nm. The tensile test of samples fetched a value of Young's

modulus in the range of 4-6 GPa which is indeed higher than that of the conventional Polyamide membrane which normally shows a value of 0.36 GPa [11]. The high mechanical properties enhance the surface area of the membrane and the pore size proving to be an important improved feature while considering the purification process. The authors had also tried to prove their results by carrying out the Nitrogen adsorption isotherms at 77K. From the recorded graphs, the -Emmett-Teller surface areas were concluded as 513, 383, and 593 $\text{m}^2 \text{g}^{-1}$ for *p*-CMP, *m*-CMP, and *o*-CMP, respectively. The pore sizes of the *p*-CMP, *m*-CMP, and *o*-CMP membranes were reported to be 1.5 nm, 1.5nm, and 2.2 nm respectively defining a supplementary conclusion that the sizes of the pres still can be fine-tuned by modulating the surface behavior of the monomer.

The prepared CMP membranes were conveyed on the surface of the porous polyacrylonitrile (PIM) framework to develop into a composite material for the subjected OSN application. While the *p*-CMP and *m*-CMP membranes exhibited a molecular cutoff of ca. 560 g/mole with a similar trajectory in the dye rejection traits, the dye rejection behavior of *o*-CMP was below 90%, perhaps because of the larger pore size due to the positioning of the functional group in the benzene ring. A constant pressure of 1 bar was employed to observe the permeation and the interaction behavior of various solvents with the membrane as reported in Figure 1C. The solvent permeation showed the trend which is inversely proportional to the viscosity concluding that there was no significant interactive behavior between the hydrophobic pores in the membranes and the externally added solvents. The *p*-CMP membrane, when exposed to hexane and methanol, exhibited a permeation value of 32 and 22 $\text{L m}^{-2} \text{hr}^{-1} \text{bar}^{-1}$, respectively. As compared to the traditional 8 mm Polyamide membrane cast on the XP84 support, these values were way higher as compared to 19 $\text{L m}^{-2} \text{hr}^{-1} \text{bar}^{-1}$ [11]. The adaptive filtration behavior makes this CMP membrane a unique material to be developed for OSN applications.

The developed CMP membranes showed the highest methanol permeability when compared with the Polyarylate, PIM, and metal-organic frameworks [12]. The reason may be attributed to the fact that the CMP has the highest structural rigidity and a much higher number of developed micropores. As far as the PIM membranes are concerned, the solvent poses a low-efficiency solution and diffusion process when traversing through a relatively dense polymer membrane, attributed due to the absence of permanent pores. This eventually results in the process's structure framework stability to go down hence affecting the permeance.

On an additional note, several molecular simulations have been performed to get an overall idea of the style when exposed to a more realistic case. The molecular dynamics showed that the CMP membrane matrix was filled with numerous numbers of porous networks and continuous voids inferring the results on the evolved microporosity and interconnected networks derived from the surface-initiated polymerization which originated the continuous solvent flow.

Several allied tests led to the conclusion that these membranes do possess brilliant permeance stability of more than 100 hours apart from having a solvent tolerance resistance for more than 7 days [10]. Furthermore, all conjugation skeleton rigidity catalyzed the highly resistive behaviors of these membranes when exposed to a mechanical, thermal, and chemical stimulus.

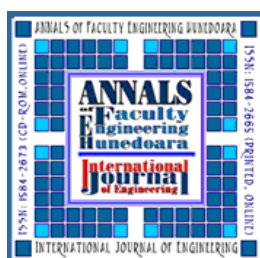
4. CONCLUSIONS

The work looks like a very prosperous technique for the fabrication of a highly robust membrane model using the aid of the surface to initiate polymerization. The material not only does exhibit an enhanced permeability for a varied range of organic solvents but also a wide range of polarity. The next-generation advanced membranes based on conjugated network polymers shall be an ocean of opportunities for the researchers to dive into in the current years.

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ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN 1584 - 2665 (printed version); ISSN 2601 - 2332 (online); ISSN-L 1584 - 2665
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