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# Effects of acyl chloride monomer functionality on the properties of polyamide reverse osmosis (RO) membrane

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ABSTRACT

In this work, three novel polyacyl chloride monomers: 2,4,4′,6-biphenyl tetraacyl chloride (BTAC), 2,3′,4,5′,6-biphenyl pentaacyl chloride (BPAC) and 2,2′,4,4′,6,6′-biphenyl hexaacyl chloride (BHAC) have been successfully synthesized. For the purpose of investigating the effects of the polyacyl chloride functionality on the reverse osmosis (RO) membrane properties, the thin film composite (TFC) RO membranes were prepared through interfacial polymerization of trimesoyl chloride (TMC), BTAC, BPAC, and BHAC with *m*-phenylenediamine (MPDA) respectively. The membrane properties including physicochemical properties and separation performances were evaluated by a combination of attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle (CA), streaming potential measurements as well as cross-flow reverse osmosis tests. The results reveal that the functionality of the acid chloride monomer strongly influences the properties of the RO membrane. As the functionality of the acid chloride monomer increased, the resulting membrane skin layer became more negatively charged, thinner and smoother. However, the change of hydrophilicity did not seem to follow any rule or trend, which could be ascribed to the cooperative effects of surface roughness and the carboxylic acid group content. In addition, all the four membranes exhibited close salt rejection rates according to the RO separation performance tests. However, with the increase of acid chloride functionality the permeate flux of the resulting RO membrane became lower, due to a combination of the increase in the carboxylic acid groups on the membrane surface, lower surface roughness, and lower mobility of the crosslinked polyamide chains.

## 1. Introduction

Reverse osmosis (RO) separation is an effective technology, and has been used extensively in many fields such as for the desalination of seawater and brackish water, ultrapure water production and wastewater treatment [1–3]. Nowadays, the RO membrane market is mainly dominated by thin-film-composite (TFC) polyamide membranes containing three layers: a polyester web serving as the structural support (120–150 μm thick), a microporous polysulfone film acting as the supporting mid-layer (about 40 μm), and a selective ultra-thin barrier layer on the upper surface (about 0.2 μm) [4]. The topmost ultra-thin polyamide layer is generally fabricated through interfacial polymerization (IP) of polyfunctional amine and acid chloride monomers at the interface of two immiscible solvents.

The most important properties of the TFC membranes are permeability and selectivity, which are basically determined by the physicochemical properties of the upper polyamide layer such as surface roughness, hydrophilicity, charge performance as well as skin layer thickness. Factors affecting these physicochemical properties include: support membrane structure and chemistry [5,6], monomer structures and concentration [7–16], catalysts and other additives in the aqueous solution and/or in the organic solution during the interfacial polymerization [17–22], reaction and curing conditions [23–25], and other post-treatments [26–28]. Among all these factors, the inherent chemistry of the monomers employed in the polymerization has been proven to play a major role as confirmed from various studies over the past decades. Roh and Khare [12] for example, found that the network polyamide synthesized from MPDA and TMC shows higher water flux as well as salt rejection compared to the linear polyamide made from MPDA and isophthloyl chloride. The higher water flux was attributed mainly to the increased hydrophilicity of the network polyamide due to the presence of the pendant carboxylic acid groups. In addition, the influence of the isomeric diamine

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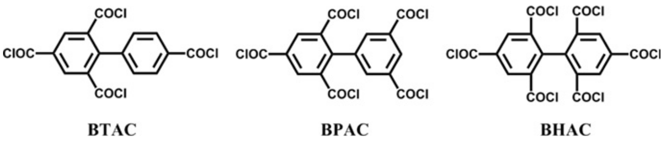
monomers on membrane performances were also studied [14]. It was revealed that the meta-positioned polyamide (TMC/MPDA) had higher hydrophilicity and greater polymer chain mobility compared with the para-positioned polyamide (TMC/PPDA), hence resulting in higher water flux. Moreover, Zhou et al. found that the incorporation of *m*-phenylenediamine-5-sulfonic acid (SMPD) into the amine solution of MPDA during the IP process could increase the membrane flux at the same time reducing the surface roughness, due to the lower reactivity of SMPD with TMC arising from the electron withdrawing nature of the sulfonic acid group [15].

Since the interfacial polymerization process is diffusion controlled in the organic layer, developing a new type of organic phase monomer can be seen as an effective strategy towards improving the RO performance [29]. However, as is widely known, a comprehensive and profound understanding of the structure–property relationship of the RO membrane is definitely necessary which will enable the rational design of new membrane materials at the molecular level. In our previous report, RO membranes based on a series of isomeric tetra-functional biphenyl acid chloride monomers (*mm*-Biphenyl tetraacyl chloride, *om*-Biphenyl tetraacyl chloride, and *op*-Biphenyl tetraacyl chloride) were prepared for the first time [8]. Our research showed the obvious differences in separation performance, chemical composition, hydrophilicity and surface morphology among the three RO membranes, which resulted from the different reactivity of the three isomeric acid chlorides with MPDA during the interfacial reaction.

Driven by our continuing interests towards the investigation of structure–property relationship between the acid chloride monomer structure and RO membrane properties [7–10], three novel polyacyl chloride monomers: 2,4,4′,6-biphenyl tetraacyl chloride (BTAC), 2,3′,4,5′,6-biphenyl pentaacyl chloride (BPAC) and 2,2′,4,4′,6,6′-biphenyl hexaacyl chloride (BHAC) were designed and successfully synthesized in this work (Scheme 1). The significant distinction in the functionality of the active acid chloride group among the four monomers of TMC, BTAC, BPAC and BHAC could be observed, which increases in the order of TMC < BTAC < BPAC < BHAC, from trifunctional to hexafunctional. Nevertheless, unlike our previous research in which we mainly focused on addressing the correlation between the position of substitution of the acyl chloride group and the corresponding membrane performance [8], the objective of the current study was to investigate the impacts of the polyacyl chloride functionality on the separation performance and physicochemical properties of the resulting RO membranes. Our consequential insights of the specific role of monomer functionality on the RO membrane properties would deepen the understanding of the structure–property relationship between the monomer structure and membrane properties. Furthermore, to the best of our knowledge, there have been no reports of the RO membranes derived from the penta and hexa-functional acid chloride monomers. However, as a complementary data towards the full understanding of the properties of interfacially polymerized TFC membranes based on a series of organic phase reactants, the information about such highly-functional acid chloride based RO membranes can greatly enrich the knowledge for designing new membrane materials with improved performance [30]. Herein, we report the preparation of the RO membranes based on these new polyacyl chlorides. The membrane properties including physicochemical properties and separation performances were characterized by attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle (CA), streaming potential measurements and cross-flow reverse osmosis tests. The influences of the acid chloride monomer functionality on the RO membrane properties were evaluated from the comparative studies of their separation property, chemical composition of the skin layer, surface hydrophilicity, morphology, charge performance and skin layer thickness of the membranes based on the above mentioned four monomers.



**Scheme 1.** Structures of the novel polyacyl chloride monomers.

## 2. experimental

### 2.1. Synthesis of monomers

#### 2.1.1. Materials

*N*,*N*-dimethylformamide (DMF) was stirred with calcium hydride for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. Copper bronze was dried at 100 °C under vacuum for 3 h before use. Isopa G (Isoparaffin type hydrocarbon oil) was purchased from Guangdong Jesan Chemical Ltd. TMC (purity > 98%) was purchased from Qingdao Ocean Chemical Company. MPDA (purity > 99%) was purchased from TianJin Guangfu Fine Chemical Research Institute. Other reagents and solvents were obtained commercially and used without further purification.

#### 2.1.2. Synthesis of 2,4,4′,6-tetramethylbiphenyl

A 500 ml three-necked round-bottomed flask equipped with mechanical stirring, nitrogen inlet and outlet was placed with 2-bromo-1,3,5-trimethylbenzene (7.6 ml, 50 mmol), $Pd(PPh_3)_4$ (2.9 g, 2.5 mmol), $Cs_2CO_3$ (18 g, 55 mmol), dimethoxyethane (200 ml) and water (0.1 ml). The flask was evacuated and filled with nitrogen for three times. The mixture was stirred and gradually warmed to 80 °C. Then, a solution of 4-methylphenylboronic acid (6.8 g, 50.3 mmol) in 50 ml ethanol was added dropwise and the resulting reaction mixture was refluxed for 5 h. After cooling to room temperature, the solution was diluted with ethyl ether, washed with $H_2O$ and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The concentrate was purified by silica gel column chromatography to give 2,4,4′,6-tetramethylbiphenyl as a waxy white solid. Yield: 65%. $^1$H NMR (300 MHz, $CDCl_3$): 7.23 (d, 2 H, $J$=7.9 Hz), 7.03 (d, 2 H, $J$=7.9 Hz), 6.91 (s, 2 H), 2.40 (s, 3 H), 2.33 (s, 3 H), 2.01 (s, 6 H).

#### 2.1.3. Synthesis of 2,4,4′,6-biphenyl tetracarboxylic acid

To a stirred mixture of 2,4,4′,6-tetramethylbiphenyl (6.5 g, 31 mmol), aqueous NaOH (10 g, 248 mmol, 300 ml $H_2O$) and 100 ml pyridine under reflux solid $KMnO_4$ (78 g, 500 mmol) was added portionswise during 4 h. After additional 4 h heating, the excess of $KMnO_4$ was removed by several drops of formaline, the mixture was filtered and the separated $MnO_2$ was washed with hot water. The filtrate and washings were combined, concentrated to 100 ml and acidified to pH 1 with concentrated HCl. The deposited tetra-acid was isolated by filtration, washed with cold water and dried. Yield: 85%. $^1$H NMR (300 MHz, DMSO-$d_6$): 8.35 (s, 2 H), 7.93 (d, 2 H, $J$=9.0 Hz), 7.32 (d, 2 H, $J$=9.0 Hz).

#### 2.1.4. Synthesis of 2,4,4′,6-biphenyl tetraacyl chloride (BTAC)

The method for the preparation of BTAC was similar to our previous report [7]. Yield > 95%. $^1$H NMR (300 MHz, $CDCl_3$): 8.89 (s, 2 H), 8.23 (d, 2 H, $J$=8 Hz), 7.40 (d, 2 H, $J$=8 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$): 167.69, 165.80, 165.70, 144.45, 141.34, 137.85,