Imide-Based Polymers of Intrinsic Microporosity: Probing the Microstructure in Relation to CO$_2$ Sorption Characteristics

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ABSTRACT: A range of microporous, imide-based polymers were newly synthesized using two-step poly-condensation reactions of bis(carboxylic anhydride) and various aromatic diamines for CO$_2$ gas capture and storage applications. In this report, we attempted to assess the relative significance of molecular structural aspects through the manipulation of the conformational characteristics of the building blocks of the polymeric structures, the spiro-containing acid anhydride and the aromatic amines, to induce greater intrinsic microporosity and higher surface areas for the resulting solids. Results obtained from this study were thus used to outline a working relationship between the structural diversity of the constructed porous solids and their performance as CO$_2$ sorbents.

INTRODUCTION

Growing modern age dependence on fossil fuel and, consequently, increased levels of CO$_2$ emissions have led to adverse global environmental impacts. As a short-term solution to mitigate CO$_2$ emissions, materials capable of capturing CO$_2$ molecules before escaping into the atmosphere could prove useful. Crystalline porous materials such as zeolites and metal–organic frameworks possess ordered molecular structures, high surface area, and, in many cases, strong affinity toward CO$_2$. However, shaping such crystalline materials into moldable forms remains challenging. On the other end of the molecular order, amorphous porous materials including polymers of intrinsic microporosity (PIMs) are of interest because of their ease of synthesis and their compatibility with casting and molding processes, which make them attractive choices in a wide range of industrial applications, including CO$_2$ capture and separation. Generally, polymers lack microporosity because they possess enough conformational and rotational freedom to pack space efficiently. However, PIMs are composed of highly rigid and contorted molecular links with restricted conformational freedom, preventing efficient space packing and consequently resulting in molecular-sized interconnected voids. The rigidity is caused by the presence of fused rings along the polymeric backbone, whereas the contorted structures arise from the incorporation of nonplanar sites of contortion. McKeown and co-workers have synthesized a networked polymer consisting of phthalocyanine rings fused together with spiro-cyclic groups to produce a highly porous material. In their synthesis, 4,5-dichlorophthalonitrile was reacted with 5,5′,6,6′-tetrahydroxy-3,3′,3′-tetramethylspiro-bisindane to give the required bis-phthalonitrile. This procedure resulted in frameworks with noteworthy microporosity as confirmed by nitrogen adsorption measurements. These frameworks were studied as potential gas storage materials and as heterogeneous catalysts. The term intrinsic microporosity was introduced by McKeown in 2001 following the synthesis of porous soluble polymers with interconnected pores designed to overcome the loss of porosity upon desolvation, known for extrinsic microporous materials. PIMs lack the rotational flexibility along the polymer backbone, which guarantees that the macromolecular components are incapable of re-adjusting their conformity upon solvent removal and that their highly contorted shape is maintained throughout the synthesis and activation processes.

PIMs’ structures have been manipulated to reach desired properties in terms of porosity, solubility, and thermal and mechanical properties. Most of the PIMs that have been synthesized are composed of either dibenzodioxin or imide repeat units. In both strategies, at least one of the monomers has a contortion site, which provokes the formation of the interconnected pores. The high solubility of PIMs in organic solvents is one of their specific desirable properties. PIMs’ rigid and contorted molecular structures reduce the intermolecular interactions through...
controlling the extent of contact among the polymer chains and thus facilitating the solubility of the chains in organic solvents. The spirobisindane unit was also found to help in improving the polymer solubility.27 Interestingly, PIMs exhibit no glass transition or other thermal transitions below their decomposition temperature at around 450 °C.24 The majority of PIMs had Young’s modulus exceeding 1 GPa24 with a deformation ability of about 1%. The reported surface areas for several PIMs fall within the range of 720–875 m²/g.14,19,21 Only few PIMs had a greater apparent surface area.18 PIMs containing more flexible structures such as those derived from the tetrahedronaphthalene unit had significantly less surface area than the equivalent spirobisindane-based polymers.28 However, for some rigid substituents such as fused fluorenes, a modest enhancement has been noted,29 as flexible side chains may fill the microcavities during the polymeric chain packing. The apparent surface area was also observed to be significantly when the nitrile groups are substituted with carboxylic, thioamide, or tetrazole groups. This was attributed to the increase in the cohesion interactions between the polymeric segments which subsequently improved the packing efficiency of the polymer and thus reducing its microporosity.22,23 PIM membranes have been designed to possess both high permeability and selectivity for use in gas separation applications.30 It was shown that PIMs are dominated by the diffusivity selectivity model as smaller gas molecules diffuse faster.18 PIMs’ gas selectivity also falls above or near the upper bound line for several commercially significant gas mixtures, including CO₂/CH₄, H₂/N₂, and H₂/CH₄. The microporosity of PIMs provides a moderate to high capacity for gas uptake, which might be the reason behind their high apparent gas solubility. It has been noticed that polymers with rigid molecular structures usually fall on or close to Robeson’s upper bound line.18

It is the purpose of the current study to synthesize novel microporous materials based on the manipulation of the conformational characteristics of the building blocks of the polymeric structures to investigate the structure–property relation through outlining the diamine rigidity effect on the overall polymeric chain rigidity and consequently its characteristics including surface area, porosity, and behavior toward CO₂ adsorption. In this regard, five novel tailored CO₂ were synthesized and tested for their ability and selectivity to capture and store carbon dioxide gas. The design of the PIMs presented here is inspired from a computational chemical investigation conducted earlier.31,32 The synthesis of different polymers is accompanied by complete characterization of their chemical structure by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and elemental analysis, with the achieved molecular weights and the degree of polymerization determined using gel permeation chromatography (GPC). Gas sorption analyses were utilized to investigate the microporosity and CO₂ gas sorption capacity and affinity for the constructed PIMs.

## RESULTS AND DISCUSSION

The current study aimed at probing the underlying structure–function relationship in a tailored family of PIMs. Toward this goal, a number of such polymers sharing the same spiro center but with several different diamine moieties, with different rigidities, were constructed. The selected diamine molecules were utilized to produce six different polymers, of which five are novel structures with one polymer previously published elsewhere33 and synthesized herewith for comparison purposes. On the basis of our previous computational investigation for a similar family of PIMs, the aromatic diamines utilized here were carefully selected to provide a wide range of conformational behaviors in the targeted PIMs. In this report, we opted to conduct a systematic, computational-guided, experimental investigation of the interplaying structure–function relationships that determine the overall gas sorption characteristics of the selected family of PIMs.

As shown in Scheme 1, PIM-AUC-1 and PIM-AUC-2 have the diamine groups separated either by oxygen or ethylene

**Scheme 1. Chemical Synthesis of PIM-AUCs. PIM-AUC-3 was Prepared as a Reference for Comparison with Previous Studies**

![Scheme 1. Chemical Synthesis of PIM-AUCs. PIM-AUC-3 was Prepared as a Reference for Comparison with Previous Studies](image-url)
dehydration of the carboxylic acids have led to the formation of 9,9′,9′′-tetramethyl-8,8′,9′-tetrahydro-7,7′-spirob[indeno-[5′,6′:5,6][1,4]dioxino[2,3-f]isobenzofuran]-1,1′,3,3′-tetraone (5), referred to shortly as bis(carboxylic anhydride), as shown in Scheme 1.33 PIM-AUC-1 was synthesized by polycondensation reaction of (5) and 4,4′-oxydianiline, a diamine with conformational flexibility around a central oxygen atom. Similarly, PIM-AUC-2 was synthesized through an imide condensation of (5) and 4,4′-ethylenediamine, a ditopic diamine with some conformational flexibility around the ethylene bridge. In contrast to the two abovementioned examples, PIM-AUC-3 and PIM-AUC-4 were prepared by the reaction of (5) and the aromatic amines 1,5-diaminonaphthalene and 1,8-diaminonaphthalene, respectively. Both of the ditopic amines utilized in the construction of PIM-AUC-3 and PIM-AUC-4 demonstrate fused aromatic rings with expected constriction in their conformational flexibility. Both aromatic amines used to prepare PIM-AUC-5 and PIM-AUC-6, namely, the 2,2′-biphenyldiamine and benzidine, respectively, exhibit a rigid biphenyl group as a spacer between the two amine moieties in both molecules. After completion of the polymerization reactions, the isolated compounds were exchanged with methanol to remove any solvent trapped within the polymeric matrices pores, prior to conducting further characterization analyses. A myriad of structural and composition analysis techniques including the FTIR, NMR, elemental analysis, GPC, and X-ray powder diffraction (XRD) techniques were utilized to probe the structure and composition of the synthesized polymers.

The FTIR spectra shown in Figure 1 of the PIMs isolated clearly indicated the formation of the imide bonds as evident from comparison of the spectra of the six PIMs with the dianhydride monomer. The absence of absorption bands characteristic of primary or secondary amines in the range of 3000–3500 cm⁻¹ accounts for the formation of the tertiary amine (R–N(CO)₂). The observed shift in the carbonyl (C=O) peaks from 1840 to 1760 cm⁻¹ in the anhydride monomer to lower wavenumbers 1780–1750 cm⁻¹ in all the synthesized polymers assures the substitution of the oxygen atom of the anhydride with the nitrogen of the diamines. PIM-AUC-3 is also in a great agreement with polyimide-based-PIMs found in the literature, especially PIM-PI-7 synthesized by Ghanem et al.,35 which is used for comparative reasons in this report. In ¹H NMR, singlets in range of δ 1.33–1.39 ppm and doublets in the range of δ 2.19–2.35 ppm in all synthesized polymers represent 12H atoms of 4 methyl groups and 4H atoms of 2 methylene groups, respectively, which indicate the presence of the spiro ring. In addition, the singlets in range of δ 6.39–6.73 ppm represent the 4H atoms in the aromatic rings of the dianhydride monomer. All the peaks ensure that the dianhydride monomer remained unchanged except through the condensation reaction with the diamine monomer which has been presented through the different multiple peaks found from the range δ 7–9 ppm and differs according to the type of the diamine used. Additionally, in ¹³C NMR, signals with chemical shifts at δ 30, 31, 43, 57, and 59 ppm represent 4CH₃, 2CH₂, 2C, and 1C, respectively. These signals are ascribed to the carbons in the spiro rings. The reactions of the dianhydride monomer with different diamines have been confirmed through the signals with a chemical shift in the range of δ 110–170 ppm that represent the aromatic and carbonyl carbons. The signal at δ 166 ppm in all the synthesized polymers indicates the presence of carbonyl groups.

All prepared polymers showed high thermal stability, as indicated by their corresponding thermogravimetric analysis (TGA). Common to all tested PIM-AUCs (1–6), there was an observed single degradation temperature (ranging from 450 to 550 °C) that can be ascribed to the presence of the highly stable imide groups; see the Supporting Information. This range agrees with the thermal degradation range reported by Ghanem et al. in the synthesis of PIM-PI.35 As mentioned formerly, the prepared samples were pretreated with methanol which ensures the removal of any trapped solvent or guest molecules; this was also confirmed by TGA thermograms, as no weight losses were observed for the majority of the compounds before their thermal degradation, indicating successful removal of guest molecules from the synthesis.

Nitrogen sorption isotherms measured at 77 K were utilized to evaluate the surface area and porosity of the synthesized polymers, as shown in Figure 2. The polymers present significant adsorption at low relative pressures, an indication of the presence of microporosity, as shown in Figure 2 with an increasing uptake with increasing relative pressures. It is also obvious from the figure that for all the polymeric structures, the desorption curve lies well above the adsorption curve, indicating significant hysteresis that was extended to the low relative pressure region. This could be explained by considering the tortuosity of the pore structures. This behavior can be ascribed to swelling of the materials due to flexibility of the polymer chains. As shown in Table 1, the apparent BET surface

**Figure 1.** FTIR analysis of the six synthesized PIM-AUCs.

**Figure 2.** N₂ gas adsorption (closed symbols) and desorption (open symbols) isotherms for PIM-AUC-1–6.
tourtousness of the spiro center by utilizing rigid diamine maintaining the intrinsic microporosity introduced by the cc/g, respectively). which were found to possess total pore volume 0.08 and 0.23 surface areas of 61 and 81 m²/g, respectively). The total pore (except for PIM-AUC-1 and PIM-AUC-2, demonstrated structures or, alternatively, rings with bulky side chains to work, Mckweon and Ghanem utilized mostly fused ring microstructure through a rigid diamine moiety. In previous containing monomer, it also needs to be translated to the polymers contain the same spiro center as other PIMs reported herein but with more flexible diamine linkers. Therefore, although intrinsic microporosity does stem from the spiro-containing monomer, it also needs to be translated to the microstructure through a rigid diamine moiety. In previous works, Mckweon and Ghanem utilized mostly fused ring structures or, alternatively, rings with bulky side chains to construct PIMs of high surface areas. As it gets more difficult for the polymer chains to swirl around during packing, as a consequence of the presence of these bulky side groups or the stiff fused ring structures, the chains are forced to form pores with greater size cavities and larger surface areas. In PIM-AUC-4 and -6, rather larger surface areas and pore volumes were observed. This is to be expected because of utilization of the rigid diamine monomers. Applying the nonlocal density functional theory model of carbon finite pore systems to the adsorption isotherms permitted calculation of the PSD histograms for the analyzed PIMs, as shown in Figure 3. The PSD histograms indicated three distinctive categories of pore systems inside the six PIMs analyzed. For PIM-AUC-1 and -2, similar PSD patterns were observed, centered around 15 Å for the most prominent pore system. This is in contrast to PIM-AUC-4 and -5, where the most significant pore systems were more dispersed and observed at 6, 14, 17, and 30–35 Å. PIM-AUC-4 and -5 demonstrated closely similar patterns for their PSD, demonstrating three size ranges for their pore systems. PIM-AUC-3 and -6 demonstrated comparable PSD patterns with most of the pores distributed between 7 and 15 Å. As PIM-AUC-3–6 were constructed with different bridging rigid diamines, the similarities and differences between the observed PSD histograms cannot be directly explained. It appeared to us that the main driving force for similarities and differences between the PSD histograms can originate from differences in the packing of the polymers’ chains, and thus, more in-depth investigation into the packing of such polymers is needed. A detailed computational analysis of the most energetically favored packing for the abovementioned polymers indicated two major packing patterns that are in agreement with the experimentally observed trends.

Moreover, the observed trends in PSD mapped well into the initial values for the isosteric heat of adsorption (Qst) of CO2 inside the PIMs, especially for PIM-AUC-3 and -6. As both compounds demonstrated a narrow pore size for relatively significant population of their pore systems, these two compounds also demonstrated the highest initial Qst for CO2. Variable temperature (0, 10, and 20 °C) carbon dioxide adsorption isotherms were collected for the PIMs reported herein Figure 4; see the Supporting Information for further data. It was observed that PIM-AUC-4 adsorbed the highest CO2 quantity through the temperature ranges compared to other PIM-AUCs, which is in agreement with being the most porous structure among the probed compounds. Additionally, PIM-AUC-1 and -2, being the least porous, demonstrated the lowest total uptake of CO2. In agreement with the abovementioned general trend, PIM-AUC-3, -5, and -6 demonstrated total CO2 uptake in between the two extremes.

The Qst plots for CO2 in the reported PIM-AUCs are shown in Figure 5. The calculated Qst reported here falls within the range of 25–33 kJ/mol. As expected, the Qst plots for PIM-AUC-3 and -6 demonstrated steeper decay as compared to the other PIMs, which could be rationalized based on quick saturation of the smaller pores, that is, those centered at 6 Å. From the above, it is concluded that to attain best performing material of this family toward CO2 capture applications, a proper tuning of the high surface area with narrow pore systems is required. The example of PIM-AUC-4, in contrast to PIM-AUC-3 and -6, demonstrated clearly that merely the high

### Table 1. Brunauer–Emmett–Teller (BET) Surface Areas and Pore Volume of PIM-AUCs

| compound   | BET surface area (m²/g) | pore volume (cm³/g) |
|------------|-------------------------|---------------------|
| PIM-AUC-1  | 61                      | 0.08                |
| PIM-AUC-2  | 81                      | 0.23                |
| PIM-AUC-3  | 362                     | 0.40                |
| PIM-AUC-4  | 508                     | 0.59                |
| PIM-AUC-5  | 506                     | 0.57                |
| PIM-AUC-6  | 450                     | 0.47                |

Figure 3. Pore size distribution (PSD) histograms for PIM-AUC-1–6.

Figure 4. CO2 gas adsorption isotherms for PIM-AUC-1–6 at 0 °C.
surface area with no control over the pore dimensions can contribute to high overall uptake of CO₂ but will inevitably affect the affinity of the solid toward CO₂.

To probe the material selectivity toward CO₂ in a CO₂/N₂ mixture, we utilized the ideal gas adsorption theory (IAST)³⁴ to calculate the CO₂/N₂ selectivity for all the PIMs reported here. The data points from the N₂ and CO₂ sorption isotherms, all measured at 273 K, were utilized into pyIAST³⁵ to calculate the selectivity in a mixture of 10% CO₂ in N₂, as shown in Figure 6.

CONCLUSIONS

We demonstrated here a family of PIMs sharing the same functionality in their backbone structures and constructed through imide condensation reactions. A clear structure—property relationship is outlined where the degree of freedom of the bridging diamine functionality transforms well into the observed gas sorption characteristics of the corresponding polymer. As this particular class of compounds demonstrated high thermal stability and appreciable solubility in many organic solvents, their utilization in casted or molded structures, as thin films and/or membranes, is facilitated. Furthermore, the systematic investigation presented here established the potential for tailoring the solid–gas interactions through controlling the overall porosity and pore dimensions, targeting applications in gas sensing and separation.

EXPERIMENTAL SECTION

Materials. All the starting materials including 4,5-dichlorophthalic acid, potassium carbonate, potassium hydroxide, and the following six diamines, namely, (i) 4,4′-oxydianiline, (ii) 4,4′-ethylenedianiline, (iii) 1,5-diaminonaphthalene, (iv) 1,8-diaminonaphthalene, (v) 2,2′-biphenyldiamine, and (vi) benzidine were all purchased from Sigma-Aldrich. 5,5′,6,6′-Tetrahydroxy-3,3′,3′-tetramethyl-1,1′-spirobisindane was purchased from Alfa Aesar, Inc., Germany. The abovementioned chemicals were used as received without further purification. All other reagents and solvents such as formamidine, 33% ammonium hydroxide, thionyl chloride, N,N-dimethylformamide (DMF), ethanol, hydrochloric acid, acetic acid, acetic anhydride, toluene, anhydrous toluene, m-cresol, quinoline, methanol, and chloroform (CH₃Cl) were purchased from various commercial sources. The DMF dried over molecular sieves (4 Å, 1–2 mm beads) was also purchased from Alfa Aesar, Germany, and stored under nitrogen.

Spectral, Elemental, and Chromatographic Analyses. FTIR spectra of all synthesized polymers were recorded on a Thermo Scientific, Nicolet iS10 FTIR spectrophotometer. ¹H NMR spectra were recorded on Genini-300BB (300 MHz) in CDCl₃ as the solvent using TMS [Si(CH₃)₄] as the internal standard, and chemical shifts were expressed as ppm. ¹³C NMR spectra were recorded in CDCl₃. Elemental analyses were performed on a Thermo Scientific, FLASH 2000 CHNS/O analyzer. Molar mass distributions were determined by GPC with THF as the solvent. Measurements were carried out using Agilent 1100 series, Germany, equipped with a refractive index detector. Each sample (0.01 g) was dissolved in 2 mL of THF and filtrated using a syringe filter of 0.45 μm before being placed in the GPC device. The samples were compared to a polystyrene standard, and the PL-gel particle size was about 5 μm. Three columns of pore types 100, 104, and 105 Å were placed on series of a length 7.5 × 300 mm. Powder X-ray
diffraction (PXRD) patterns of the samples were obtained using a D8 Bruker X-ray powder diffractometer. The PXRD patterns of the samples were obtained for a 2θ range between 5° and 80° with a step increment of 0.03 per s.

**Synthesis of the Bisphthalonitrileandianhydride Monomer.** 4,5′-Dichlorophthalonitrile was prepared as outlined elsewhere, starting from 4,5′-dichlorophthalic acid. Bisphthalonitrile was then synthesized from 5,5′-6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane according to the procedures outlined by Maffei et al. The tetracarboxylic acid and its dianhydride monomer were prepared according to procedures outlined by Ghanem et al. 33

**Typical Procedure for the Synthesis of PIM-AUCs.**  For each one of the six prepared PIMs, the following procedures were executed in a similar fashion. To a 50 mL three-neck rounded-bottom flask equipped with a Dean–Stark trap, nitrogen inlet, and reflux condenser, 1.15 g (1.83 mmol) of the dianhydride monomer and 1.83 mmol of the diamine were added, followed by 10 mL of m-cresol, 0.1 mL of quinoline, and 2 mL of anhydrous toluene. After stirring at room temperature for half an hour, the temperature of the reaction mixture was raised gradually to 200 °C and was kept at that temperature for further 5 h. Water was constantly removed from the reaction mixture by azeotropic distillation. After cooling, the resulting solution was diluted with 20 mL of chloroform. The mixture was added dropwise to a vigorously stirred 600 mL methanol. The resulting solid precipitate was then collected by filtration and dried under vacuum. Scheme 1 illustrates the general procedures for the chemical preparation of the six different PIMs used in this study. It should be mentioned that PIM-AUC-3 has the same chemical structure as that of PIM-PI-7, previously prepared by Ghanem et al. 33 Under the code name PIM-PI-7, the polymer was prepared as a reference material to facilitate the comparison with previous studies.

**PIM-AUC-1.** PIM-AUC-1 was prepared by the reaction of the anhydride monomer with the 4,4′-oxydianiline diamine monomer. Off-white; yield: 55%; FT-IR (cm⁻¹): 3030 (CH, aromatic), 2952 (CH, aliphatic), 1780 and 1750 (C═O); 1H NMR (CDCl₃, δ ppm): 1.33 (s, 6H, 2CH₃), 1.39 (s, 6H, 2CH₃), 2.19 (d, 2H, J = 13.5 Hz, CH₂), 2.35 (d, 2H, J = 13.5, CH₂), 3.69 (s, 2H, aromatic), 6.73 (s, 2H, aromatic), 7.00–7.54 (m, 12H, aromatic); ¹³C NMR (CDCl₃, δ ppm): 30.06, 31.45 (4CH₃), 43.53 (2CH₂), 57.23 (2C), 59.11 (1C), 112.02, 119.48, 119.65, 127.13, 127.73, 128.19, 140.58, 146.35, 147.40, 149.03, 156.43 (aromatic C), 166.27 (C═O); Anal. Calc'd for C₉H₁₄N₂O₈ (repeat unit): C, 75.76%; H, 4.15%; N, 3.61%. Found: C, 78.87%; H, 4.60%; N, 3.66%; GPC: Mₘ = 3490.2, Mₙ = 254, Mₘ/MD = 3.5; XRD: amorphous.

**PIM-AUC-2.** PIM-AUC-2 was prepared by the reaction of the anhydride monomer with the 4,4′-ethylenediamine diamine monomer. Pale yellow; yield: 38%; FT-IR (cm⁻¹): 3030 (CH, aromatic), 2952 (CH, aliphatic), 1780 and 1750 (C═O); 1H NMR (CDCl₃, δ ppm): 1.33 (s, 6H, 2CH₃), 1.39 (s, 6H, 2CH₃), 2.19 (d, 2H, J = 13.5 Hz, CH₂), 2.35 (d, 2H, J = 13.5, CH₂), 2.99 (s, 4H, 2CH₂), 6.39 (s, 2H, aromatic), 6.73 (s, 2H, aromatic), 7.03–7.39 (m, 12H, aromatic); ¹³C NMR (CDCl₃, δ ppm): 30.20, 31.55 (4CH₃), 37.50 (2CH₂), 43.53 (2CH₂), 57.23 (2C), 59.11 (1C), 112.03, 119.98, 126.53, 127.82, 129.18, 129.74, 133.63, 140.49, 141.66, 146.34, 147.33, 149.00 (aromatic C), 166.31 (C═O); Anal. Calc'd for C₉H₁₄N₂O₈ (repeat unit): C, 75.92%; H, 4.75%; N, 3.47%. Found: C, 75.60%; H, 4.65%; N, 4.20%; XRD: amorphous.
synthesized polymers. The samples (20–50 mg) were degassed at 120 °C with a rate of 1 °C/min and 10 μmHg pressure with a rate of 5 mmHg/s. This was followed by the analysis of the degassed samples using N2 gas at 77 K (liquid nitrogen). Carbon dioxide isotherms were also evaluated; however, in these analyses, the temperature was controlled by means of a chiller (LAUDA RA8) filled with water and the ethylene glycol mixture (10% ethylene glycol). The analysis was carried out at three different temperatures, namely 0, 10, and 20 °C.

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