

Correlating the synthesis protocol of aromatic polyimide film with the properties of polyamic acid precursor

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Abstract. Thousands of different copolyimide combinations render it technically impossible to have a single universal synthesis method to produce aromatic polyimide film. This study aimed to outline the selection of synthesis protocol, either through the casting of chemically imidized polyimide solution or thermal imidization of polyamic acid (PAA), to produce the polyimide film. The rheological behaviour, molecular weight, and solubility of five structurally different PAA were analysed and correlated to both imidization methods. In this work, a tough polyimide film was successfully synthesized by casting the chemically imidized polyimide derived from high viscosity (> 81 cP) and high molecular weight ($\geq 1.35 \times 10^6$ g/mol) PAA. On the contrary, both low viscosity (< 13 cP) and high viscosity (> 81 cP) PAA demonstrated the possibility to produce polyimide film via thermal imidization route. The longer molecular chain of ODPA-6FpDA:DABA (3:2) polyimide produced from thermal imidization had restricted the passage of CO_2 across the polyimide film when it was applied in the gas separation application. The outcome from this work serves as a guideline for the selection of suitable polyimide film synthesis protocol, which will minimize the time and chemical consumption in future exploration of new polyimide structure.

1. Introduction

In the advent of technology advancement, global demands in searching high performance materials for industrial applications are increasing. In view of that, aromatic polyimide with attractive features such as high dimensional stability, excellent thermal and thermo-oxidative stability, good dielectric and optical properties is found to be a great potential material to apply in many fields [1-3]. At present, polyimides are extensively used as the microelectronic parts, high temperature insulator for aircraft, substrate for flexible printed circuit board, structural adhesive and gas separation membrane [4-7].

In general, polyimide can be processed into film, mold, fiber and foam. Among the polyimide forms, polyimide film constitutes the largest end user market [8]. It is evidenced by the wide application of Kapton polyimide film produced by Du Pont. Besides, Apical introduced by Kaneka as well as Upilex fabricated by Ube are among the reputable commercially available polyimide films [9]. The properties of polyimide film can be easily tailored through molecular design, in which the dianhydrides and/or diamines monomers used in polyimide synthesis are systematically selected to fulfill the specific application requirement. However, the diversity of dianhydride-diamine combinations makes it impractical to have a single universal synthesis protocol of polyimide film attributed to different processability.

Pioneering works had proposed different routes to produce polyimide film. One of the common synthesis routes is the casting of polyimide dope solution [10-13]. In this approach, polyimide powder is first obtained by performing the conventional two-step reaction, in which the polyamic acid (PAA) precursor is formed through the polycondensation of dianhydride and diamine; followed by chemical imidization of PAA to produce polyimide. Typically, chemical imidization is carried out by adding a basic catalyst (triethylamine or pyridine) and dehydrating agent (acetic anhydride) into the PAA



solution to promote the ring closure process (conversion of amide to imide functional group with the loss of water molecule). From the aspect of energy efficiency, the chemical imidization route is preferable as the ring closure process is readily achieved under ambient temperature [2].

However, owing to the insolubility of certain polyimides, the previous route is not recommended for polyimide film synthesis [14]. In this context, PAA solution is directly casted onto a substrate. Thereafter, thermal imidization is carried out by heating the thin PAA layer gradually up to 250-350 °C to convert the PAA precursor to polyimide, hence producing polyimide film [8, 15]. This method is especially useful when the final product is desirable in the form of film. However, a controlled heating protocol is needed as too rapid heating will cause the formation of bubbles in the casted PAA layer [2]. This will subsequently cause the failure in the film production. Basically, this approach is relatively simple and time saving since it omits the extra step of producing polyimide powder as compared to the previous chemical imidization route. Besides, no dangerous reagents are involved in this method.

The present study aimed to outline the selection of synthesis protocol, either through the casting of chemically imidized polyimide solution or thermal imidization of the casted PAA thin layer, to produce the polyimide film. Since PAA acts as the precursor of polyimide, its rheological behavior and molecular weight were correlated to the synthesis protocols. By taking membrane gas separation as the final application, permeation tests were performed to assess the properties of the polyimide films that were produced through the two different imidization approaches.

2. Materials and methods

2.1. Materials

Monomers comprise of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99 % purity), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA, 96 % purity), 4,4'-oxydiphthalic anhydride (ODPA, 97 % purity), pyromellitic dianhydride (PMDA, 97 % purity), 2,4,6-trimethyl-mphenylenediamine (DAM, 96 % purity), 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA, 98 % purity) and 3,5-diaminobenzoic acid (DABA, 98 % purity) were purchased from Sigma-Aldrich (USA). 1-methyl-2-pyrrolidinone (Sigma-Aldrich, USA), acetic anhydride (Acros Organics, Belgium), triethylamine (Sigma-Aldrich, USA) and methanol (Merck, Germany) were used as the solvents in polyimide synthesis. Besides, tetrahydrofuran (THF) was obtained from Fisher Scientific (UK). The gases used in permeation test were attained from Wellgas (Malaysia) with purity of > 99 %. All the chemicals were used as received without further purification.

2.2. Synthesis of PAA precursor

PAA precursor was synthesized via polycondensation of dianhydride and diamine. Owing to the water sensitive nature of reaction, all monomers were dried overnight at 40 °C. Throughout the reaction, the set-up was purged continuously with purified nitrogen to remove the trapped moisture. Two diamines (diamine₁=6FpDA or DAM and diamine₂=DABA) with molar ratio of 3:2 were first dissolved in 1-methyl-2-pyrrolidinone (NMP). Stoichiometric amount of dianhydride (6FDA, BTDA, ODPA or PMDA) was then added slowly into the diamines solution. The solution was stirred for 24 h under ambient temperature (25 °C) to yield 20 wt. % PAA solution. The PAA precursor was then converted to polyimide through either chemical or thermal imidization. A few combinations of dianhydride and diamine were studied, where the polyimide structures are displayed in figure 1. In the discussion, the polyimide was named as A-B:C where A is the dianhydride, B is diamine₁, C is diamine₂ and the ratio between B:C was 3:2.

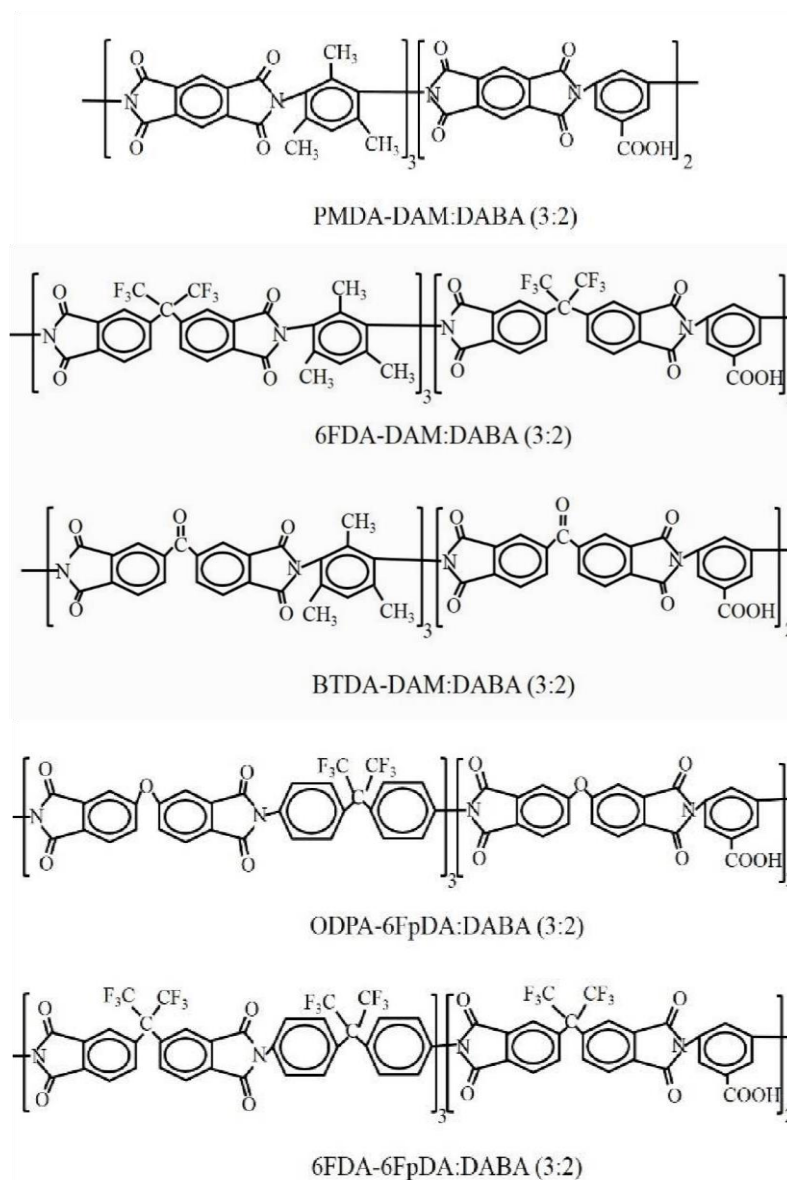


Figure 1. Polyimide structures studied in this work.

2.3. Film preparation using chemically imidized polyimide

The PAA was chemically imidized through the addition of equimolar triethylamine (catalyst) and acetic anhydride (dehydrating agent) into the PAA solution. The solution was stirred for 24 h under nitrogen purging and ambient temperature (25 °C) to produce polyimide solution. Thereafter, the polyimide was precipitated and washed for several times using methanol. The precipitated polyimide was then air-dried in fume hood for 16 h followed by drying at 200 °C for 24 h under vacuum condition.

10 wt. % dope solution was prepared by dissolving the polyimide in THF (6FDA and ODPA based polyimide) or NMP (PMDA and BTDA based polyimide). The dope solution with volume corresponding to initial film thickness of 1300 µm was poured onto a glass petri dish placed inside a glove box with controlled environment. After two days of phase inversion, the film was dried in vacuum oven at 180 °C for 24 h to eliminate the residual solvent. Afterward, the film was thermally treated in a dual zone split tube furnace (MTI- OTF-1200X-80-II, USA) under nitrogen purging to

promote decarboxylation crosslinking. The thermal treatment was performed in three steps: heating from room temperature to 330 °C at fast ramping rate of 5 °C/min, slow ramping rate of 1 °C/min to 370 °C and dwelling at 370 °C for 1 h.

2.4. Film preparation via thermal imidization of PAA precursor

20 wt. % PAA solution was diluted to concentration of 10 wt. % using NMP solvent. Specific volume of 10 wt. % PAA solution corresponding to initial film thickness of 1300 µm was poured onto a glass petri dish placed inside vacuum oven. The casted PAA thin layer was then thermally imidized to polyimide film by successive heating at 60 °C, 150 °C and 200 °C for 1 h each. The produced polyimide film was further thermally treated in a dual zone split tube furnace with similar thermal treatment protocol described in section 2.3. However, an additional 30 min heating step at 300 °C was included to ensure the complete imidization of the PAA precursor.

2.5. Characterization

The viscosity of 10 wt. % PAA solution was measured by Brookfield viscometer (model: DV2TLV, USA). The measurement was carried out under room temperature (25 °C). Multiple point averaging method was selected to obtain the average viscosity at rotation speed of 10 rpm.

Gel permeation chromatography (GPC, Agilent Technology 1260 Infinity, USA) equipped with PLgel 5 µm MIXED-C column (300 mm x 7.5 mm, 5 µm particle size) was employed to determine the average molecular weight (M_w) of PAA precursors and polyimides. Samples (PAA precursors and polyimides) were prepared in NMP or THF at 0.05 wt. % concentration. Throughout the analysis, the flow rate of mobile phase was controlled at 1 mL/min. The elution time of samples was detected using the variable wavelength detector (VWD), which was then correlated to the M_w of PAA and polyimide.

Gas separation performances of the synthesized polyimide films were analyzed using a membrane cell with effective area of 7.07 cm² at 25 °C. The whole system was thoroughly purged with purified nitrogen prior to the permeation test. After achieving steady condition, the permeate flow rate was measured by a bubble flow meter. The gas permeability was calculated based on the steady permeate flow rate according to equation (1).

$$P = \frac{\dot{V}pl}{TA \Delta p} \times 2695.93 \quad (1)$$

where P is gas permeability in Barrer (1 Barrer = 1 x 10⁻¹⁰ cm³ (STP) cm/cm²·s·cmHg), V indicates permeate flow rate (cm³/s), p refers to downstream pressure (Pa), l signifies membrane thickness (µm), T denotes operating temperature (K), A represents effective membrane area (cm²) and Δp stands for differential pressure (cmHg).

3. Results and discussion

The five PAA precursors studied in this work demonstrated two extremely different rheological behaviors which can be categorized into two groups: high viscosity (> 81 cP) and low viscosity (< 13 cP), as shown in figure 2. PAA combinations of 6FDA-DAM:DABA, 6FDA-6FpDA:DABA and ODPA-6FpDA:DABA showed significantly higher viscosity in the range of 81.65- 91.33 cP as compared to PAA combinations of BTDA-DAM:DABA and PMDA-DAM:DABA, which showed viscosity at only 5.78 cP and 12.38 cP respectively. Indeed, both categories exhibited viscosity difference of at least 560%.

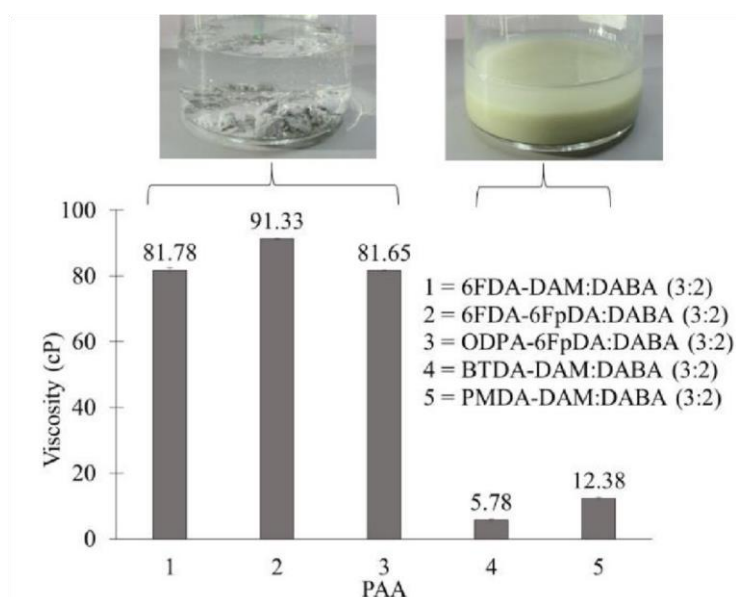


Figure 2. Viscosities of PAA precursors formed from different combinations of dianhydride and diamine.

Principally, the viscosity of PAA solution is closely related to the PAA molecular weight, which can be qualitatively interpreted from its precipitated form. Figure 2 displays the big clusters of PAA precipitant when the high viscosity PAA precursors (>81 cP) were precipitated in deionized (DI) water. On the contrary, the precipitation of low viscosity PAA precursors (<13 cP) yielded a fine, powdery deposit. By comparing both precipitated forms, it can be deduced that the bigger lump of PAA (left image in figure 2) visually indicated higher molecular weight than the powdery deposit (right image in figure 2). It is suggested that PAA of higher M_w should have more restricted molecular mobility attributed to the higher internal friction between molecules. The greater flow resistance hence increased the viscosity of the solution. The result was in well agreement to the findings by other researchers, where a more viscous polymer solution always reflected in higher molecular weight of polymer [16, 17].

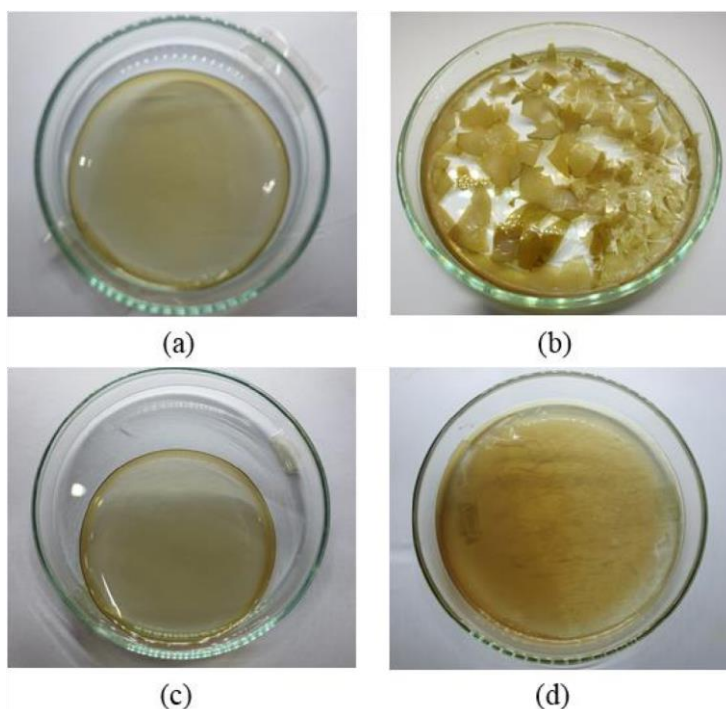
Quantitatively, the molecular weight of PAA was analyzed by GPC, as summarized in table 1. The high viscosity PAA (>81 cP) had consistently revealed higher molecular weight than that of the low viscosity PAA (<13 cP). As for the less viscous BTDA-DAM:DABA and PMDA-DAM:DABA, the molecular weight of PAA were an order of magnitude smaller than those of high viscosity PAA. Indeed, the GPC result supported well the previous discussion on figure 2, where higher molecular weight PAA was present in the more viscous solution.

Table 1. Molecular weight of PAA precursors.

PAA	M_w (g/mol)
6FDA-6FpDA:DABA	5.28×10^6
ODPA-6FpDA:DABA	2.49×10^6
6FDA-DAM:DABA	1.35×10^6
BTDA-DAM:DABA	0.54×10^6
PMDA-DAM:DABA	0.30×10^6

In this work, the solubility of PAA precipitant was tested using THF, the preferable solvent used to synthesize polyimide film due to its high volatility. It is hypothesized that if PAA is undissolved in THF, the THF will also be unable to dissolve the latter chemically imidized polyimide since their chemical properties are literally identical (same monomer combinations). In such case, the chemically imidized polyimide approach would not be feasible to produce the polyimide film. Instead, thermal imidization route is preferable. After 24 h of stirring, the PAA precipitant of 6FDA-DAM:DABA, 6FDA-6FpDA:DABA and ODPA-6FpDA:DABA were shown to be fully dissolved in THF, where clear and homogeneous solutions were observed (data not shown). Meanwhile, suspensions were observed when dissolving the PAA of BTDA-DAM:DABA and PMDA-DAM:DABA, which indicated the poor solubility of both PAA precursors in THF. Hence, it was deduced that further chemical imidization of BTDA-DAM:DABA and PMDA-DAM:DABA PAA precursors was not recommended. Both PAA precursors should proceed for membrane casting followed by thermal imidization.

For fair comparison between the different synthesis routes, all the five PAA combinations were subjected to both chemical and thermal imidization in producing polyimide film. NMP was used instead as the casting solvent for those polyimide undissolved in THF. As illustrated in figure 3, defect free polyimide thin films were obtained for the chemically imidized 6FDA-DAM:DABA, 6FDA-6FpDA:DABA and ODPA-DA:DABA polyimide (figures 3a, 3c and 3e). The successful formation of defect free polyimide films had a direct relationship to the M_w of polyimide. It is reasonable to assume that the trend of polyimide M_w behaves similarly to that of PAA M_w , as polyimide is transformed from PAA precursor with only the loss of water molecule [18]. Therefore, the high M_w of 6FDADAM:DABA, 6FDA-6FpDA:DABA and ODPA-6FpDA:DABA PAA precursors in table 1 reflected to the high M_w of the corresponding polyimides. During film formation, mass exchange occurred between the solvent (THF/NMP in casting dope solution) and non-solvent (water vapor in atmosphere), where polyimide molecules in the casting dope tended to attract to each other. The higher M_w of polyimide had promoted better interaction between the molecules, hence forming a tough and defect free polyimide thin film [19].



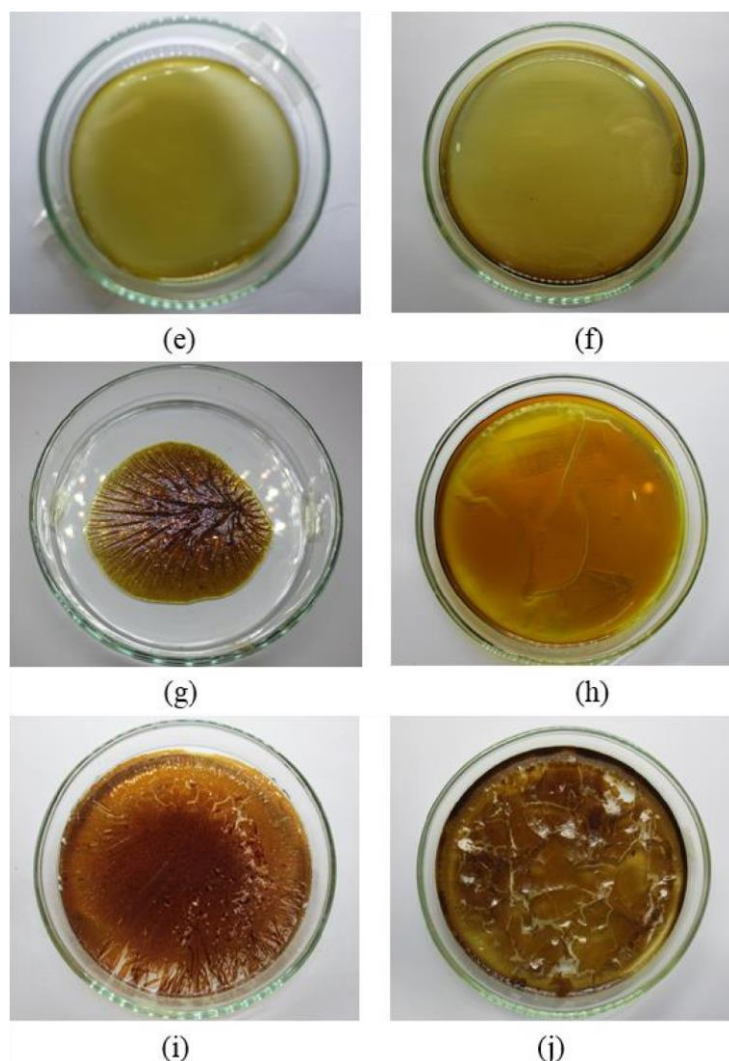


Figure 3. Polyimide film of (a-b) 6FDA-DAM:DABA, (c-d) 6FDA-6FpDA:DABA, (e-f) ODPA6FpDA:DABA, (g-h) BTDA-DAM:DABA and (i,j) PMDA-DAM:DABA synthesized by casting of chemically imidized polyimide solution (left) and thermal imidization of casted PAA precursor (right). Experiments repeated at least thrice to confirm the repeatability of film formation.

The significant contribution of polymer M_w in film-forming was further proven as the polyimide with lower M_w failed to produce a tough thin film (figures 3g and 3i). BTDA-DAM:DABA polyimide film showed serious shrinkage and cracked (figure 3g). Meanwhile, a fragile cracked film was also observed for the PMDA-DAM:DABA polyimide film (figure 3i). It was believed that the interaction between the low molecular weight polyimide was insufficient to ensure a proper film formation. Up to this point, the experimental observation stressed the necessity of high viscosity and high molecular weight of PAA precursor for successful film fabrication via chemically imidized polyimide approach.

Unfortunately, the polyimide film-forming via thermal imidization of casted PAA thin layer did not correlate well with the viscosity and/or molecular weight of PAA precursors. Either high viscosity-high molecular weight PAA (ODPA-6FpDA:DABA, figure 3f) or low viscosity-low molecular weight PAA (BTDA-DAM:DABA, figure 3h) showed the possibility to form a nice piece of polyimide film. The results hinted that another factor might be governing the film formation during thermal imidization. Thence, the stiffness of thermally imidized polyimides were tested by dissolving the thermally imidized polyimide films (figures 3b, 3d, 3f, 3h and 3j) in THF. As found, the nicely formed polyimide films in figures 3f and 3h (ODPA-6FpDA:DABA and BTDA-DAM:DABA) were insoluble

in THF while other cracked films (figures 3b, 3d and 3j) were soluble in THF. This indicated that stiffer polyimide chains were formed by the ODPA-6FpDA:DABA and BTDA-DAM:DABA PAA throughout the thermal imidization process [20]. It is well accepted that the stiffness of polyimide chain increased with the degree of imidization [2], hence it can be inferred that both ODPA6FpDA:DABA and BTDA-DAM:DABA polyimide films had achieved the sufficient imidization degree. Owing to the stronger mechanical strength, the stiffer ODPA-6FpDA:DABA and BTDA-DAM:DABA polyimide chains were thus able to produce the nice pieces of polyimide films (figures 3f and 3h).

It is of interest to analyze the properties of polyimides obtained from the two different imidization approaches. Figure 4 presents the molecular weight of polyimides synthesized from chemical imidization and thermal imidization. Generally, thermally imidized polyimides consistently demonstrated higher molecular weight than that of chemically imidized polyimides. This phenomenon can be explained from the aspect of PAA hydrolytic stability. PAA precursor is well-known to be hydrolytically unstable, in which PAA chain cleaves under humid condition hence lowers the molecular weight of the resulting polyimide [21]. In chemical imidization, the water liberated during ring closure process (imidization) was removed by acetic anhydride. However, the removal of water molecules occurred by chance based on the effective contact between acetic anhydride and water molecules during stirring. This meant the possibility of chain cleavage by water molecules during chemical imidization still existed. Thus, relatively shorter polyimide chains were observed (figure 4). Since the thermally imidized polyimides possessed the higher molecular weight, it could be postulated that thermal heating was more effective in removing the water by-product from system, hence minimized the chain scissoring that reduced the molecular weight of polyimide.

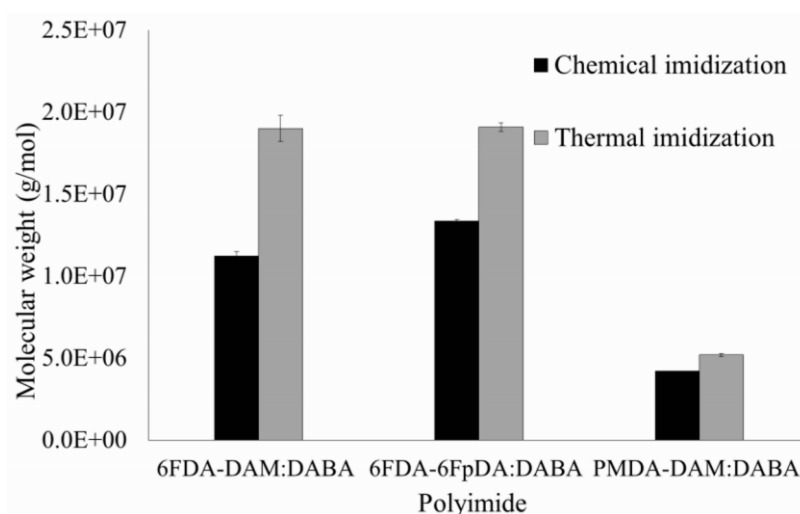


Figure 4. Molecular weight of polyimides synthesized from chemical and thermal imidization.

The molecular weight of polyimide will not only affect the film formation but also its effectiveness in gas separation. In view of the increasing interest on carbon dioxide removal, by taking ODPA6FpDA:DABA as example, the gas transport behavior of the polyimide films prepared from the two approaches was evaluated. As denoted in figure 5, the chemically imidized ODPA-6FpDA:DABA film had demonstrated higher CO₂ permeability over the tested pressure range (up to 6 bar). As discussed earlier, the chemically imidized polyimide exhibited lower molecular weight than the thermally imidized polyimide (figure 4). In regards, more polymer chain ends existed within the chemically imidized polyimide film matrix [22]. In fact, the higher number of polymer chain ends contributed towards higher free volume of the polyimide film [23]. Hence, more free spaces were available for the transport of CO₂ across the chemically imidized ODPA-6FpDA:DABA film, which subsequently increased the CO₂ permeability.

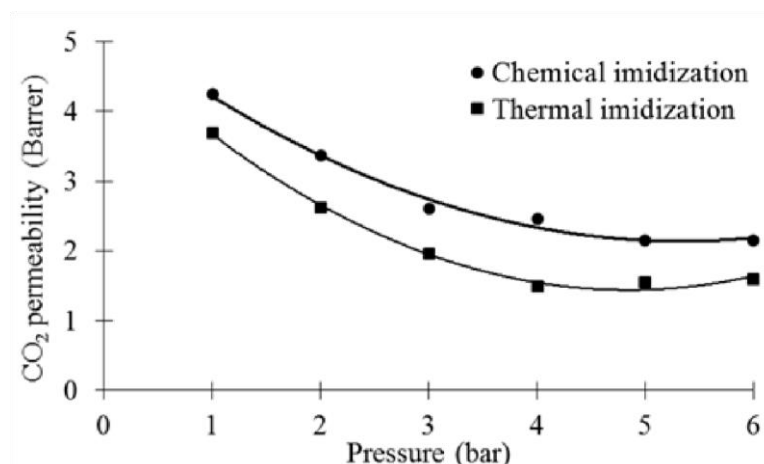


Figure 5. CO₂ permeability of ODPA-6FpDA:DABA polyimide film prepared by casting of chemically imidized polyimide solution and thermal imidization of casted PAA precursor.

4. Conclusions

The present work provided a guidance on the selection of synthesis protocol to produce polyimide film, by correlating the synthesis protocol to the molecular weight and rheological behavior of PAA precursor. A high viscosity (> 81 cP) and high molecular weight ($\geq 1.35 \times 10^6$ g/mol) of PAA precursor was necessary to ensure the formation of defect free polyimide film through the casting of chemically imidized polyimide solution. On the contrary, the production of polyimide film via thermal imidization of casted PAA layer was feasible by using both low viscosity (< 13 cP) and high viscosity (> 81 cP) PAA precursor. It was speculated that high imidization degree was the prerequisite to obtain a defect free polyimide film via the thermal imidization route. In comparison, the chemically imidized polyimide had consistently showed lower molecular weight than that of thermally imidized polyimide. The chemically imidized ODPA-6FpDA:DABA (3:2) film with shorter chain length had reflected in higher free spaces for the transport of CO₂ across the film, which subsequently increased the CO₂ permeability.

Acknowledgments

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