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Synthesis of high molecular weight polyimide consisting hexafluoroisopropylidene moiety for gas separation

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ABSTRACT

In this work, high molecular weight of heterocyclic aromatic polyimide consisting hexafluoroisopropylidene moiety in both diamine and dianhydride fragments was synthesised. The synthesis was performed via a two-step polycondensation route, which involved polyamic acid formation and chemical imidization. Subsequently, physical purification technique was conducted by microfiltration and re-crystallisation to obtain oligomers-free high molecular weight polymer. Selections of high purity and suitable solvent, type of amine catalyst, precipitation medium and reaction temperature were considered to favour the formation of high molecular weight polyimide. The synthesised polyimide was characterised by ATR-FTIR, which confirmed the presence of significant imide bands denoting the formation of imide linkage. Further confirmation of polyimide molecular structure was accomplished using ^{13}C and ^{1}H NMR. It was found that polyimide with high molecular weight (4500 KDa) was obtained with a polydispersity index of 1.48. Therefore, this polymer has favourable properties for gas separation membrane application.

Keywords: Fluorinated polyimide; chemical imidization; hexafluoroisopropylidene; gas separation.

INTRODUCTION

Nowadays, a wide range of glassy polymeric materials especially polyimides (PIs) are extensively explored in multifarious applications including gas separation for acid gas removal, hydrogen recovery and biogas applications. Fluorinated polyimide (FPI) i.e 6FDA-6FpDA is a type of heterocyclic aromatic polyimides which contains bulky fluorine fragments $(-CF_3)_2$, serving as a non-planar, twisted structure in the main branch of polymer [1-3]. Among the aromatic polyimide class, fluorine-containing polyimide seems very popular among scientists because of its superior characteristics such as thermo-oxidative capability [4], high chemical resistance [5], low refractive index [6, 7], low water absorption [6, 8], soluble in a range of organic solvents [9], high permselectivity [10-12] and fair resistance to plasticization [13, 14]. These aforementioned characteristics explained why this class of polymer is a promising candidate for gas separation application. This synthetic polymer is a more suitable material for chemical transport as compared to the naturally occurring polymer due to its hydrophobicity and inertness to chemical reaction [6, 15, 16]. Additionally, the increase in permselectivity was clearly explained from atomistic studies done by Pandiyan and his

co-workers [12, 14, 17-20]. It has been shown that the repeat fragment of hexafluoroisopropylidene group R–C(CF_3)$_2$-R, can increase both permeability and selectivity. The properties of bulky fluorine fragments in dianhydride and diamine brought significant changes to permselectivity as the substituent, R–C(CF_3)$_2$-R existed in the polymer's segmental backbone. The effects on bulk properties can be observed in dianhydride in terms of permeability and solubility while it causes material improvement when incorporated into diamine. In fact, the fluorine linkages (6F) are responsible for changes in effective packing as well as accessible free volume (FFV). The change in effective packing is associated with reduction in polymer segmental mobility, interchain interaction and an increase in FFV (0.175–0.190) as reported in literatures [10-12, 17, 19, 21, 22]. Due to the presence of 1,3-trifluoromethyl side groups in diamine and dianhydride segmental chains, it has led to restricted torsional motion of neighbouring phenyl rings and introduction of small free-volume holes. Therefore, 6FDA consisting 2-bis (4-aminophenyl) hexafluoropropane diamine (6FpDA) will give some advantages i.e., chemical affinity and polarisability towards polar gases like CO_2, O_2 and N_2. The affinity of gas molecules will form polar-polar interaction with the delocalised character of the bulky group, thereby increasing the percentage of gas retention. Thus, this will result in excellent gas permeability. Additionally, the presence of this fluorine linkage in the hexafluoroisopropylidene moiety will also increase the processability of polymer due to its solubility in various polar organic solvents.

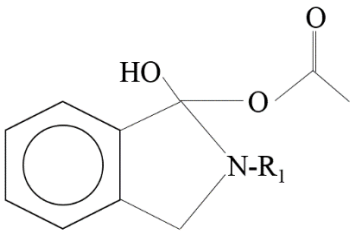

Figure 1. Isoimide (i.e., iminolactone structure).

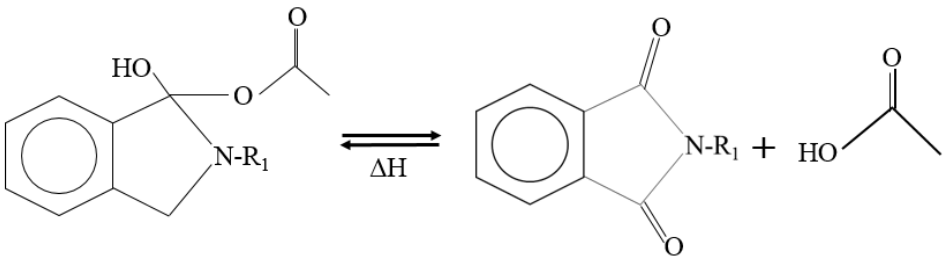

Figure 2. Isoimide conversion to imide after heat treatment.

High molecular weight FPIs basically reflect the degree of imidization (closed-ring structure of imide repeating unit) after polycondensation reaction is completed. Higher imidization degree of FPIs is needed to form polymeric membrane with the desired permeation properties and mechanical strength. Thus far, polycondensation reaction via catalytic conversion using chemical reagents (chemical imidization) was reported to yield lower molecular weight of PIs as compared to thermal conversion [23, 24]. In the chemical imidization stage where polycondensation of polyamic acid (PAA) to polyimide (PI) occurs, there is a possibility of incomplete cyclisation and also isoimide

formation (Figure 1). Therefore, thermal treatment at high temperature below the T_g of FPI will direct the rearrangement of isoimide to imide and also thermally cyclise the amide unit (Figure 2). Hence, high molecular weight of FPIs will be achieved as the degree of imidization also increases. In this work, high M_w FPIs were synthesised by a classical two-step polycondensation via chemical imidization. Chemical conversion of polyamic acid to polyimide repeating unit is favoured under the right composition of imidising mixture. It is hypothesised that the degree of imidization can further be improved with post-thermal treatment of polymer precipitates. Therefore, the as-synthesised FPIs has experienced a sufficient thermal treatment to fully convert isoimides to imides. It is also suggested that further polymer purification is crucial to remove undesired components such as excess reactants as this can affect the polymer M_w distribution. Therefore, 6FDA-6FpDA-FPIs has been successfully synthesised using the chemical imidization route.

METHODS AND MATERIALS

Experimental Setup

N-Methyl-2-pyrrolidone (NMP), calcium hydride, methanol and acetic anhydride were supplied by Merck, 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (assay: 99.9%) and β-picoline (assay: 99%) were purchased from Aldrich, 4,4′ (hexafluoroisopropylidene) dianiline (6FpDA) (assay: 98%) was supplied by Acros Organic and tetrahydrofuran (THF) was purchased from Fisher Scientific. The polymer synthesis was conducted in an inert atmosphere under nitrogen at room temperature. The route of polyimide synthesis is clearly shown in a mechanistic pathway (Figure 3). In the two-step polycondensation, formation of polyamic acid was developed by the addition of monomer into anhydrous NMP. The pre-dried diamine monomer (6FpDA) was added into the reaction solvent until complete dissolution. After that, the pre-dried dianhydride monomer (6FDA) was added in 5 aliquots as 6FDA slowly dissolved in NMP due to nucleophilic attack for the ring opening of diamine (Figure 4). This step is the most crucial step for propagation of polyamic acids. About 0.2 g of dianhydride monomer was added in excess to result in dianhydride end-capping PI. During 24 h of PAAs formation, extremely dry and high concentration mixture needed to be ensured so that the de-propagation step or reversible reaction can be minimised. The formation of polyamic amic (PAA) was conducted for 24 (h) as it will give the highest molecular weight (M_w) as reported in literature [17]. Cyclisation of PAAs was conducted via chemical imidization using a pyridine-based dehydrating catalyst (β-picoline, pKa 5.68 at 20^{o}C) and dehydrating agent i.e., acetic anhydride. This combination will give a complex counter ion which will naturally attack the poor electron deficient group in a mechanistic way (i.e., tautomerization, A and B).

After 12 h of chemical reaction, the polymer solution was poured into methanol in a beaker and precipitates were recovered from the methanol solution via filtration. The off-white coloured precipitates were obtained and dried overnight in a vacuum oven prior to thermal treatment at an elevated temperature of 150^{o}C for 12 h. Purification technique via re-crystallisation was conducted to remove impurities by re-dissolving the solid polymer in tetrahydrofuran and filtering using 1µm nylon membrane filter. A thick, viscous yellow coloured polymer gel was obtained and left for 24 h at ambient condition to remove the solvent. The polymer was further dried at 60^{o}C prior to storage.

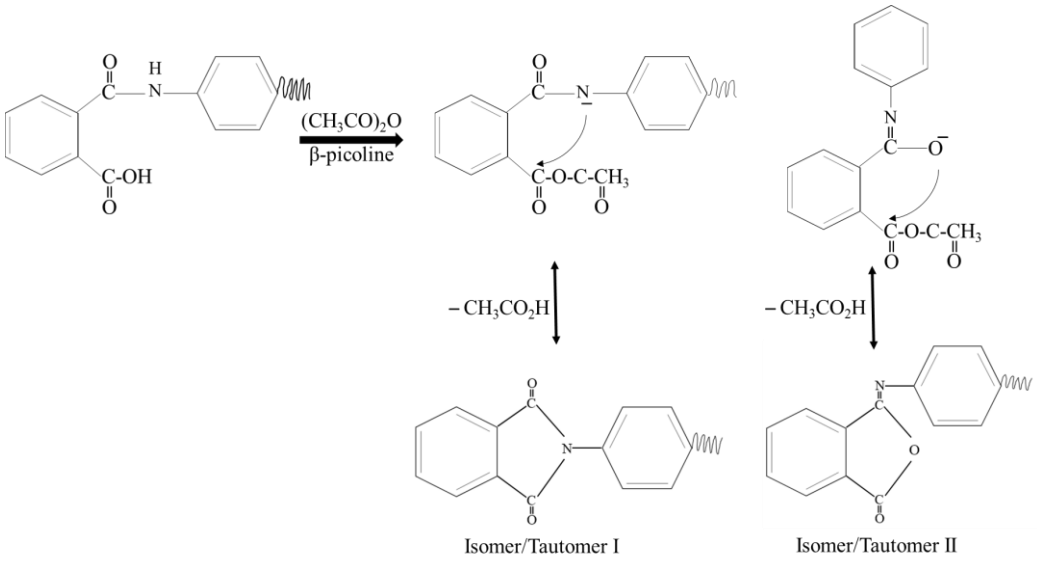

Figure 3. Possible structure of polyimide formation via tautomerization[1].

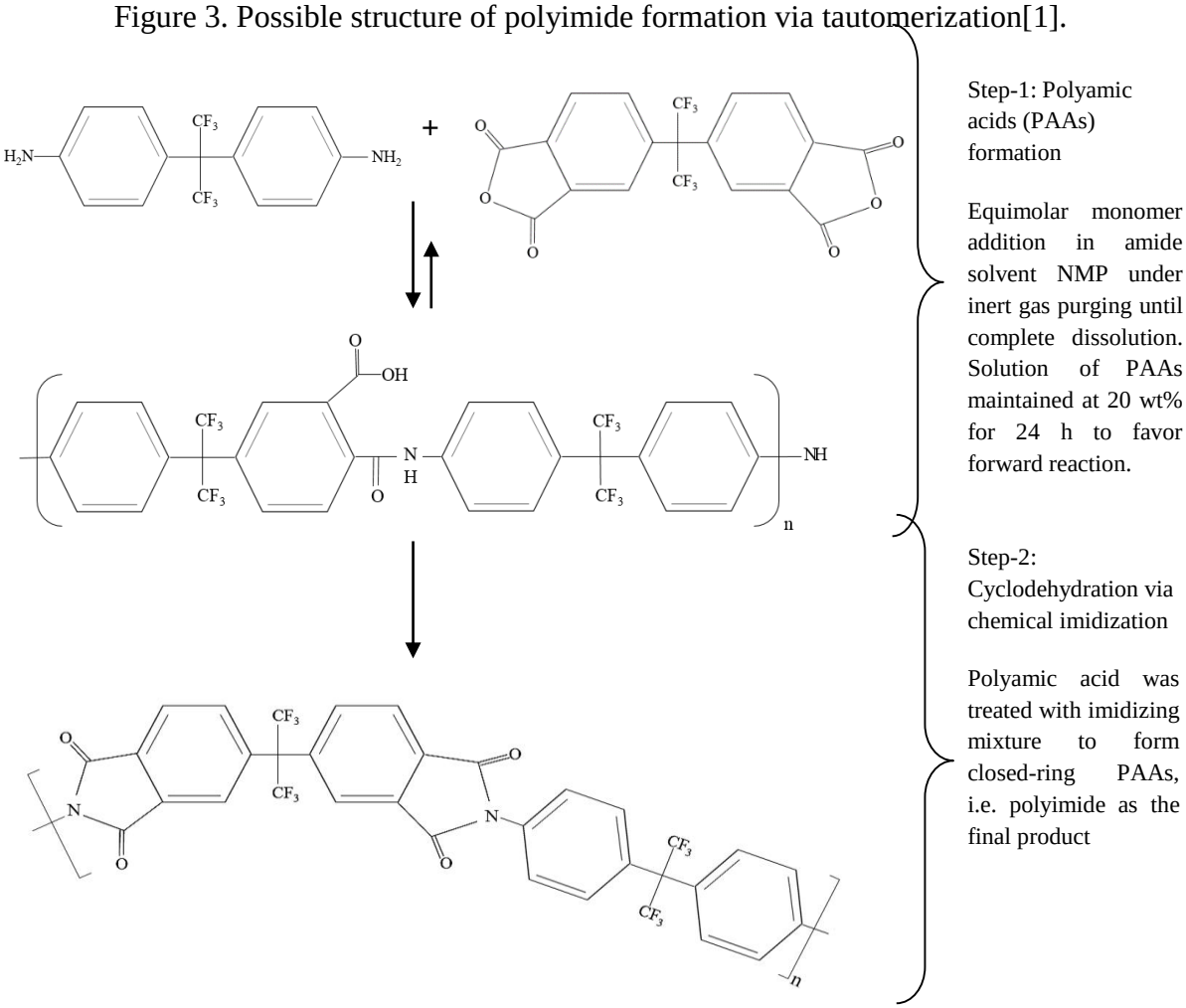

Figure 4. 6FDA-6FpDA polyimide formation [17, 25].

Polymer Molecular Weight Study Using Gel Permeation Chromatography
Five mg of sample was prepared by dissolving in THF and diluted to 5µL/mol prior to sample injection to GPC (Agilent Technologies 1260 Infinity, PLgel 5µm MIXED-C, Serial No. 0001022974-47) equipped with a light scattering detector. Polystyrene with Mw 100,000 g/mol was used as the standard.

Formation of Dense Polymeric Membrane for Gas Separation
Solvent-induced casting was employed. The 20 wt% polymer dope was dissolved until homogeneous for 12 h and degassed for 2 hr. The glass plate was immersed in chloroform overnight prior to casting. The solvent evaporation was controlled in a glove box. Flat sheet membrane was fully formed after 48 h.

RESULTS AND DISCUSSION

Polymer Molecular Weight Revealed by Gel Permeation Chromatography
The polymer molecular weight revealed by GPC is 4500 kDa with polydispersity index of 1.48. This shows that a narrow distribution of PI was formed via chemical imidization. High molecular weight polyimide revealed by GPC showed that high degree imidization can be achieved via the chemical imidization route after post-synthesis treatment and physical purification.

Imidization Degree of 6FDA-6FpDA Revealed by ^{13}C NMR and ^{1}H NMR
^{1}H and ^{13}C NMR spectra were recorded with ECA JEOL Delta NMR (400 MHz), using tetramethylsilane (TMS) as an internal reference. $CDCl_3$ was used as eluent to prepare the samples. Three samples consisted of monomers and a synthesised polymer were characterised and the results are shown below, which were in accordance with the previous literature [18-20]. Table 1 summarises the molecular arrangement of the desired functional moieties in the polyimide chain backbone. The formation of imide linkage (C-N) was detected at ^{13}C NMR, δ (ppm): 165.8(s) and 131.9 (s). While for ^{1}H-NMR, the degree of imide conversion was calculated from the signal intensities of amic acid protons i.e., –NH and –COOH δ(ppm): 10.9-10.8. However, those peaks were undetected.

Table 1. Chemical shift for ^{1}H-NMR and ^{13}C-NMR for 6FDA-6FpDA polymer.

Type of substance	Chemical shift(δ)
Polyimide: 6FDA-6FpDA polymer	^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.21, 8.05, 7.91(t), 3.715, 2.5, 1.8 (s) ^{13}C NMR (400 MHz, $CDCl_3$): **i. 140 ppm to 117ppm (upper band):** 138, 136.67 (s), 133.56, 133.25 (d),132.8, 131.9, 130.3 (s) 128, 128.5 (d) 127.2 (s) 125.2, 124.5, 123.9, 122.8 (m), 120, 19.45 (d) **ii. 71 ppm to 61 ppm (lower band):** 165.8 (s), 67.4 (s), 65.6, 65.4, 65.1, 64.8, 64.58, 64.3, 64.1, 63.8 (m)

Determination of Imide Bands via ATR-FTIR
The FTIR spectra of the conversion of polyamic acid to polyimide are shown in Figure 5 from PerkinElmer Frontier™ in a spectrum range of 4000−450 cm^{-1}.

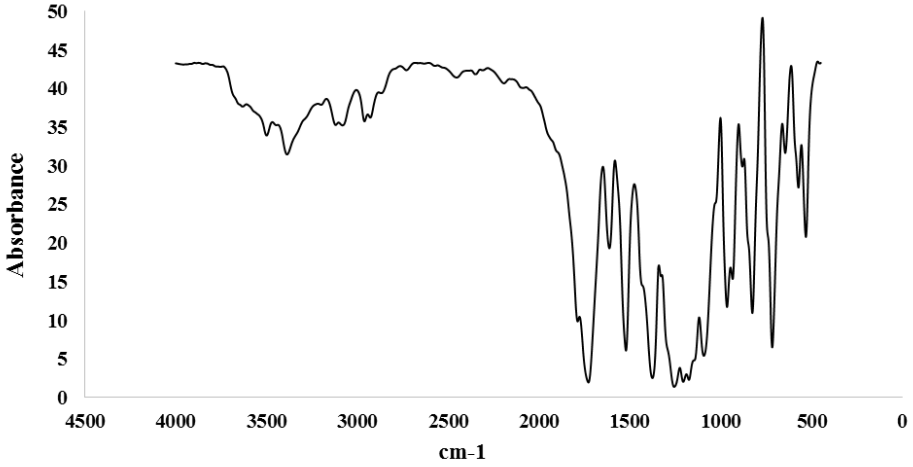

Figure 5. FTIR spectra of polyimide (6FDA-6FpDA).

The semi quantitative analysis by ATR-FTIR for as-synthesised 6FDA-6FpDA was performed to detect the degree of polyamic acid conversion to polyimide. The IR spectra revealed a small shoulder at 1788.37 cm-1, denoting the formation of imide linkage (C-N-C). The presence of amines absorption at 1728.58 cm-1 (symmetric, C=O) and 1613.28 cm-1 (C=O) likely shows an indication of amic acids [26, 27]. These bands are generally observed in most PIs synthesised via chemical imidization even at a low intensity. After physical purification, the final product studied by NMR showed a certain degree of imidization. Through 13C NMR analysis, multiple splitting of carbon peak observed two sets of quartets at δ (ppm) 125.75, 125.2, 124.5, and 123.9 (m) portraying the attached fluorine groups in both 6FDA and 6FpDA fragments [17, 28]. Imide linkage formation was detected at 165.8 (s) and 131.9 (s). The Mw of 6FDA-6FpDA synthesised via chemical imidization was determined via GPC analysis after purification of polymer was conducted. It was revealed that polyimide with a molecular weight (Mw) of 4500 kDa and the polydispersity index of 1.48 was achieved.

CONCLUSIONS

Fluorinated polyimide (FPIs) i.e., 6FDA-6FpDA was successfully synthesised via a two-step polycondensation reaction employing catalytic cyclodehydration such as chemical imidization. Based on the degree of imidization studies via ATR-FTIR, ^{1}H and ^{13}C NMR showed a formation of imide linkages after thermal treatment during post-synthesis, while GPC analysis confirmed that FPIs having the molecular weight and dispersity index of 4500 kDa and 1.48, respectively, were obtained. Hence, the results from IR spectra, proton and carbon shift of NMR along with GPC showed that sufficient conversion degree of polyamic acid to polyimide had been achieved. Based on the polyimide precipitates recovered after microfiltration and recrystallisation, about 85% yield of FPIs was successfully produced. Furthermore, the intrinsic solubility of FPI produced was extraordinary, showing the existence of $–CF_3$ in the polymer repeating unit. Due to this property, fabrication of flat sheet membrane can be easily made in a wide range of solvents. Based on the polymer's ease of processability and material properties, this polymer has a great prospect for gas separation application, especially to produce small

footprint technology with superior separation performance of membrane from a lab to industrial scale.

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