Effect of block versus random copolyimide structure on hollow fiber membrane spinnability

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ABSTRACT

Soluble homopolyimides can be made into spinnable dopes; but copolyimides often present challenges. A 6FDA (4,4'-(Hexafluoroisopropylidene)diphthalic anhydride)-based copolyimide was used to illustrate these challenges when forming both defect-free and “nodular” skinned fibers. This copolyimide is soluble in strong solvents; but when combined in proportions with nonsolvents to allow forming an asymmetric structure, a gel, rather than a flowable dope solution can occur in some cases, making fiber spinning impossible. Analysis of problems and solution are presented to show how varied copolymer chemical structures affect dope formation. Studies were extended to other 6FDA-based copolyimides to show the generality of the problem and solution to the problem. We found a random copolyimide that forms a soluble spinnable dope becomes problematic when a block copolyimide with sufficient insoluble chain segments is present. Branching in copolyimide, impurity, and excessive molecular weight also affect dope formation, but to a less drastic degree.

Keywords: Polyimide membrane; Hollow fiber spinning; Dope formation; Block copolymer; Chemical structure.

1. Introduction

Membrane separation technologies offer more energy-efficient, environmentally friendly, low capital cost, and smaller footprints benefits compared to conventional gas separation technologies [1-6]. Although inorganic molecular sieve membranes and mixed matrix membranes have been investigated, glassy polymeric membranes are most commonly used for practical applications. These polymer membranes have intrinsically good separation properties, i.e., high productivity and high selectivity, which are essential to minimize capital and operating cost. Among such polymers, 6FDA-based polyimides membranes show excellent intrinsic gas separation properties, thermal and chemical stabilities, and robust mechanical properties under high-pressure natural gas feeds [7-19]. Furthermore, 6FDA-based polyimides can be dissolved in common solvents, which allows easy fabrication of the polymer into a working device. Compared with homopolyimides, the copolyimides, such as 6FDA:BPDA-DAM (1:1) copolyimide (BPDA: 3,3',4,4'-biphenyl dianhydride; and DAM: 2,4-Diaminomesitylene), are much more attractive, since their chemical structures can be tailored. As a result, the properties, especially separation properties, for different gas pairs are tunable, which broadens the applications. Meanwhile lower costs polymeric materials such as BPDA which is more than 3 times less expensive than 6FDA can be used in some applications. Therefore, copolymer such as 6FDA:BPDA-DAM is less expensive than 6FDA-based homopolymers and still shows excellent properties.

Among membrane configurations such as plate, frame, or spiral wound, etc., hollow fiber membranes provide the highest surface area to volume ratio. As a result, the maximum productivity and efficiency are easy to achieve. However, formation of a skinned asymmetric structure requires special solution compositions and processing procedures. Polymeric defect-free asymmetric hollow fiber membranes have been used in large-scale in industry [1, 2]. Defect-free polymeric hollow fibers can be used as membranes [6, 10, 20-26], or as precursors for making carbon molecular sieve

(CMS) hollow fibers [27-30], while porous hollow fibers can be used as highly efficient sorbents [31], for gas separation.

However, to spin defect-free asymmetric hollow fiber is extraordinarily challenging, even with conventional polymers, and only a few advanced polymers have been reported in defect-free asymmetric hollow fiber forms [10, 32-37]. Polyimide hollow fibers (including defect-free hollow fiber membrane, “nodular” hollow fiber, and porous hollow fiber sorbent) are usually fabricated via a dry-jet/wet-quench spinning process. Many parameters influence the success of hollow fiber spinning [6, 25, 34, 35, 38]; however forming a spinnable “dope” solution is the primary first key requirement [6, 10, 34, 39]. “Dope” solutions are composed of polymer, solvents, and non-solvents. A good “spinnable” dope is a one-phase, homogeneous solution, which can form a fiber upon exiting the spinneret without breaking, and ideally can also form a defect-free selective skin in the case of membrane.

Several defect-free hollow fiber membranes have been successfully spun using 6FDA-based polymers [6, 10, 36, 37, 39-42]. Hollow fiber with “nodular” skin morphology also has been successfully spun with Matrimid® and 6FDA:BPDA-DAM(1:1) polymers [21, 43], *but no matter which type of fiber is spun, forming a tailorable spinning dope solution is critically important.* Recently, we found that a slight variation of polymer structure influences dope formation greatly or even prevents forming a workable dope. Soluble *homopolyimides*, such as 6FDA/DAM and Matrimid®, have no problem in making workable “dope”; however, depending on synthesis “batch”, the copolyimide, 6FDA:BPDA-DAM(1:1), encounters problem in making “dope”. Surprisingly, the unworkable copolymer samples are still soluble in strong solvents; however, such samples are worthless for practical spinning when additions of non-solvents are needed.

In this paper, formation of dope solution with 6FDA:BPDA-DAM(1:1) copolymer is discussed as an important example. Studies were also extended to 6FDA:ODPA-DAM(1:1) and 6FDA:BTDA-

DAM(1:1) copolyimides (ODPA: 4,4'-Oxydiphthalic Anhydride, and BTDA: Benzophenone-3,3',4,4'-tetracarboxylic dianhydride). The structure of the resultant copolyimide is determined by synthesis methods and conditions. Solutions to achieve “spinnable” 6FDA:BPDA-DAM(1:1) copolymers, which are independent of synthesis “batch” will be reported later.

2. Background

Development of asymmetric polymeric hollow fibers includes the following sequential process steps: polymer synthesis, “dope” development, fiber spinning, dehydration, module formation, testing, and post-treatment for defective fiber containing pinholes when necessary.

Key spinning parameters are listed in Table 1, and as noted above, the “dope” composition is a primary factor relying upon proper selection of polymer, solvents and non-solvents [6, 10, 34, 39]. Optimization of dope composition is carried out using a ternary phase diagrams via the cloud point technique, and potentially spinnable dope compositions lie in the one-phase region, close to the binodal line [6, 21]. Because of the complex optimization requirements, the “solvent” and “non-solvent” may, in fact, comprise a mixture of components that allow control of evaporation rates, solvent power and other subtle properties. Therefore, in the process of spinning, when dope is extruded through the spinneret into air gap, the evaporation of volatile solvents causes the outermost region of the composition to approach the vitrified region, thereby forming a dense skin layer on the outer of fibers. When the nascent fiber enters the water quench bath, non-solvent water diffuses into the polymer solution and induces phase separation in the underlying porous support.

Table 1. Key parameters in a dry-jet/wet-quench hollow fiber spinning process

Dope composition	Air gap height	Quench bath temperature
Bore fluid composition	Take-up rate	Quench bath composition
Dope/bore fluid flow rate	Spinning temperature	Humidity

Previous research shows that polymer molecular weight and polymer concentration influence dope viscosity and the compositions to form a spinnable dope [10, 44]. Surprisingly, we recently found that a slight variation of polymer structure influences dope formation greatly. The polymer structure determines whether the polymer can be made into a workable dope. We bought custom-synthesized 6FDA:BPDA-DAM(1:1) copolymer from a custom contract synthesis company to spin hollow fiber. Unfortunately, the quality of the polymer varied between different synthesis batches, and polymers from some batches cannot make a workable dope, and they even formed gels when combined into compositions that should have formed spinnable dopes. Extensive research on polymer synthesis and dope formation, with consideration of many possible factors ultimately showed that polymer structure variation, caused by synthesis conditions, was the primary source of problems. A spinnable dope must comprise a one-phase solution containing polymer and at least one solvent (with or without non-solvents), with adequate viscosity at sufficient polymer concentration to be extruded and form fibers with adequate mechanical strength to form fibers. Although pure polymer solutions (without non-solvents) can produce fibers with appropriate fine structures, the resultant hollow fibers might have excessive substrate resistance, i.e., inadequate permeance for practical applications, because phase separation in the quench bath is too slow to form an open porous substructure. Optimization can occur by addition of non-solvent to accelerate phase separation of the polymer solution underneath the nascent skin layer.

3. Experimental

3.1. Polymer synthesis

The polyimide, 6FDA:BPDA-DAM(1:1) is usually synthesized through the condensation of the dianhydride (6FDA and BPDA) with diamine (DAM), with the mole ratio of 6FDA to BPDA is 1 to 1, as shown in Scheme 1. The synthesis is a two-step reaction in which the first step produces a high molecular weight polyamic acid, and the second step is imidization, i.e., to close the ring by releasing water and producing chemical stable polyimide.

Scheme 1 Synthesis of 6FDA:BPDA-DAM (m:n) copolyimide.

Through analysis of possible factors on “dope” formation, we synthesized 6FDA:BPDA-DAM(1:1) copolymers using a conventional method (through a contract synthesis company used previously), as well as a modified method, to get copolymers with different structures. Furthermore, homopolyimide 6FDA/DAM and BPDA/DAM, as well as copolyimides of 6FDA:BPDA-DAM(m:n)

with a mole ratio of 6FDA:BPDA, i.e., m:n as 2:1, 1:2; 1:3; 1:5; and 1:10 were synthesized, too. The details of polymer synthesis process will be discussed later.

3.2. Dope preparation and hollow fiber spinning

A ternary phase diagram of 6FDA:BPDA-DAM (1:1) copolymer was developed by using spinnable polymers, as shown in Fig. 1. The solid point refers to a typical spinning composition, and the solid line indicates the approximate composition of the two-phase boundary at 35 °C.

Both in-lab synthesized and commercial polymers were used to prepare dopes with various compositions, to study factors that determine “dope” formation,

Fig. 1. Ternary phase diagram of spinnable 6FDA:BPDA-DAM(1:1) copolymer

especially the role of polymer structure. Our standard dope solution is composed of: (1) 6FDA:BPDA-DAM(1:1) copolymer, (2) solvents (NMP (1-Methyl-2-pyrrolidinone), and THF (Tetrahydrofuran), with varied ratios), and (3) non-solvent (Ethanol and Lithium nitrate with varied ratios). The concentration of each component is optimized using the ternary phase diagram as shown

in Fig. 1. Defect-free hollow fibers were spun successfully, using the compositions showed at or near the solid point in Fig. 1. The details of hollow fiber spinning is described elsewhere [21].

The dope solution for spinning “nodular” fiber is also composed of polymer, solvent, and non-solvent. However, unlike spinning defect-free hollow fiber, no THF was used in that case.

4. Results and discussion

Because of its good combination of permeance and selectivity, as well as good processability in hollow fiber spinning, the ideally random copolyimide, 6FDA:BPDA-DAM(1:1) is attractive to form polymer membranes as well as being a precursor for making carbon molecular sieve (CMS) membranes in gas separations and purifications [29, 45]. The structure of 6FDA:BPDA-DAM(1:1) is illustrated in Scheme 1, where m:n is 1:1. We used this 6FDA:BPDA-DAM(1:1) copolymer to spin hollow fiber membranes.

To spin defect-free hollow fiber, the polymer must, of course, be dissolved in a mixture of solvents (NMP and volatile THF) and non-solvents to form a homogeneous solution with a satisfactory viscosity to allow successful fiber formation, i.e., so-called “dope” solution. A workable dope is photographed as shown in Fig. 2. Phase separation and/or gel in polymer in the dope prior to spinning makes the hollow fiber spinning unfeasible. Such cases were encountered with commercial 6FDA:BPDA-DAM(1:1) copolymers we bought before, as well as polymers synthesized under conventional method in our lab.

Fig. 2. Workable dopes made from 6FDA:BPDA-DAM (1:1).

4.1. Non workable copolymers

We bought 6FDA:BPDA-DAM(1:1) copolymer from a contract synthesis company for spinning hollow fiber. We found that, some batches of the polymers were good for making dope solution and spinning hollow fibers (Fig. 2), while some batches of the polymer were “bad”, which could not make workable dopes. The “bad” polymers were hard to dissolve, obviously phase separated, or formed gels, as shown in Fig. 3. All of those “bad” polymers can be dissolved into dilute solutions in pure

Fig. 3. Non-workable “dope” from bad 6FDA:BPDA-DAM (1:1) polymers.

NMP or THF solvents, which means the “bad” polymers have no problem in casting a dense film membrane using dilute solution or in making polymeric composite materials. The key fact is that at higher concentration, such as 25wt%, the spinnable 6FDA:BPDA-DAM(1:1) copolymer is easily dissolved in organic solvent and forms a homogenous solution, while the non-spinnable “bad” copolymer is hard to be dissolved, or form gel (Fig. S1 in the Electronic Supplementary Material). These facts show that it is not surprising that the complex solvent-nonsolvent mixture needed to spin useful fiber may not be achievable with subtly different copolymer compositions or block structures, and that in some cases, an actual insoluble gel is formed, thereby making fiber spinning unfeasible.

The question to answer is of course, why do the “bad” polymers reveal such kind of “dope” formation problem? While definitive proof is difficult to provide, we pursued a series of systematic studies to assess whether the problem might relate primarily to impurity, molecular weight, and/or chemical structure of the polymers. All of these issues might, of course, result from polymer synthesis methods/conditions and procedures.

4.2. Impurities in polymer

Impurities, such as ions, might crosslink polymer due to the presence of residual unreacted carboxylic groups, thereby makes the polymer hard to be dissolved. Industrial recycled methanol (some of the methanol contained ions) was used to synthesize commercial polymers provided to our lab in the past years. Moreover, if a polymer sample was not well purified, impurities such as Acetic anhydride, will change dope composition, and move binodal line. This might also change polymer's solubility in a dope composition and make polymer difficult to be dissolved.

A commercial “bad” polymeric thick fiber (the contract company provided samples which were quenched from industrial recycled methanol) was tried to make dope, however it formed gel, as shown in Fig. 4 (a). The thick fiber was then purified by chopping into powder in methanol, soaked in methanol, filtered, and dried. However this purified polymer still could not make workable dope, even though the color was lighter, as can be seen in Fig. 4 (b). This indicates that at least one impurity in as-received polymer is soluble in methanol. The methanol purified polymer powder

Fig. 4. Non-workable “dope” from bad 6FDA:BPDA-DAM (1:1) : (a) as received, and (b) purified polymer.

was dissolved in dichloromethane (DCM), quenched into methanol, soaked in methanol, filtered, and dried. However, this polymer powder still could not make workable dope and again formed gel but with lighter color. This result means at least one contaminate is soluble in DCM, but no difference was seen on FTIR from the as received polymer and purified polymers. (Fig. S2 in the Electronic Supplementary Material)

In fact, some polymer synthesized in small batch (100 gram or less) in our lab, also could not make workable dope if using the conventional synthesis method, even though all chemicals and solvents were in high purity, and polymer was carefully purified.

These results indicate that the commercial polymer was slightly contaminated, but the impurity was a *secondary issue* that caused the polymer unable to make workable dope.

4.3. *Excessive molecular weight*

Excessive molecular weight may make polymer difficult to be dissolved. The real molecular weight might be much higher than reported by polymer provider because “filtration” removed high molecular weight units before GPC (Gel permeation chromatography) measurement, thereby underestimating the true sample molecular weight. We made a dilute THF solution (3 wt.%) with a “bad” batch polymer, filtered the solution using a Millex[®]-FG syringe-driven filter (0.20μm PTFE membrane). We found the filter was blocked after a certain amount of solution passed through, indicating excessive molecular weight polymer might exist. The polymer in the filtered solution was precipitated into methanol and dried under vacuum. Despite the removal of high molecular weight fraction, our effort in making dope with the resulting polymer failed and gel existed. *This means the excessive molecular weight is not the primary issue.*

4.4. *Chemical structure of the polymer*

Like other polyimides, 6FDA:BPDA-DAM(1:1) was also synthesized using a two-step method, as shown in scheme 1. The chemical structure, molecular weight, and polydispersity are influenced by factors including: monomer purity, stoichiometric mass of monomer, moisture in reaction system, polymer concentration in solution, solvents, monomer loading method, reaction time, reaction temperature, and so on. In this research, polymers were synthesized using the conventional method

and the modified method to control polymer structures. These polymers were used to make “dope” solutions using our standard dope recipe, to investigate the relationship between dope formation and the polymer structures.

We expected random copolymer 6FDA:BPDA-DAM(1:1) to be used to spin hollow fiber. Because the difference of solubility and reactivity of 6FDA and BPDA, as well as the local temperature and monomer concentration effects, branch copolymer and block copolymer might occur in polyamic acid synthesis process using the conventional method. The existing of block or branch copolymer may appear as a gelled structure in a low power solvent such as that used to form a spinning dope with composition close to the binodal line, as illustrated in Fig. 1. In such a case the highly branched or blocked copolymer will cause effective insolubility of the polymer in the conventional dope composition. We found that 6FDA:BPDA-DAM structure even influences its solubility in pure NMP or THF solvents greatly. Essentially, block and/or branch copolymer makes the dope formation unfeasible, as will be discussed below.

4.4.1. Copolymer containing block segments

We found 6FDA was easily dissolved in NMP or DMAc (*N,N*-Dimethylacetamide) at room temperature while BPDA is very difficult; however, BPDA can be slowly dissolved in NMP or DMAc in dilute solution (< 3%) above 40 °C; 6FDA/BPDA mixture can be dissolved in NMP in dilute solution above 40 °C very slowly, while 6FDA/BPDA mixture was difficult to be dissolved in DMAc in dilute solution even at 50 °C after 3 days ([Fig. S3 and Fig. S4 in the Electronic Supplementary Material](#)). This monomer solubility difference might result in a formation of block and branch copolymer during polymer synthesis.

In the polyamic acid synthesis step, 6FDA/BPDA mixed powder is usually loaded into the DAM solution in a reactor. Due to the solubility difference, an effective block copolymer may be resulted.

In such a hypothetical case, if 6FDA dissolves and reacts easily with DAM, after some of the 6FDA has been consumed with temperature quickly increasing (the formation of polyamic acid is a strongly exothermic reaction), BPDA can react with the DAM and form a block structure, although diamine DAM is beneficial to dissolve both 6FDA and BPDA in the solution. This effect also can cause local monomer concentration inhomogeneity as well as local elevated temperature, which benefits formation of block and branch structures, too. If a block copolymer, i.e., a relatively longer BPDA/DAM structure in the copolymer is formed, the copolymer might not be dissolved in dope solution, in which NMP and THF are used as solvents, since we found both BPDA/DAM oligomer and BPDA/DAM polymer are insoluble in either NMP or THF, although they can be dissolved in dilute DCM.

6FDA/DAM homopolyimide is soluble in many solvent and was found can be easily made into a workable dope, which is independent of synthesis batch. To see if BPDA/DAM moieties influence polymer solubility in NMP and THF, BPDA/DAM polyimide and oligomer, as well as copolyimides of 6FDA:BPDA-DAM(m:n) with a mole ratio of 6FDA:BPDA, i.e., m:n as 2:1, 1:1, 1:2; 1:3; 1:5; 1:10 were synthesized. We found that with increasing BPDA content, the polymer becomes more difficult to be dissolved in NMP or in THF. When the 6FDA:BPDA ratio (m:n) is less than 1:2, the copolyimides *could not be dissolved in NMP or THF* at room temperature, but can be dissolved in dilute DCM. And BPDA/DAM polyimide or oligomer only dissolved in DCM. Unfortunately, DCM can cause spinneret corrosion, so using DCM to make dope is not a good option, especially in industry. In fact, like BPDA/DAM polyimide and oligomer behaved, the copolymers also formed gel and precipitated in the imidization step at higher BPDA content during synthesis when NMP was a solvent.

Therefore, if a high molecular weight copolymer contains insoluble blocks, i.e., a relatively longer BPDA/DAM imide segment structure (like oligomer) in copolymer, the copolymer might not

be dissolved in NMP or THF and would form an effective gel in dope. Furthermore, we also found that the “bad dope” (gel) can be dissolved in dilute DCM, which indirectly proved the existence of block structure in the “bad” polymers and lack of covalent crosslinking.

A real block copolymer sample let us study directly whether it can make a workable dope. Therefore, we intentionally synthesized a block copolyimide of 6FDA:BPDA-DAM(1:1), which is composed of 6FDA/DAM segments and BPDA/DAM segments. Low molecular weight 6FDA/DAM polyamic acid solution as well as low molecular weight BPDA/DAM polyamic acid solution was synthesized separately in NMP under modified method to minimize branching structure, then the two polyamic acids solutions were mixed for further polymerization to get block copolymer with a high molecular weight. As expected, block copolymer of 6FDA:BPDA-DAM(1:1) polyamic acid solution with high viscosity which can form strong fiber, was obtained. The block copolyamic acid solution was then chemically imidized. Like above mentioned BPDA/DAM polymer and oligomer, as well as 6FDA:BPDA-DAM(m:n) copolyimides with high BPDA contents, this block copolymer also formed gel and precipitated from NMP during the imidization process. [The imidized block copolymer was confirmed as polyimide using FTIR and TGA \(Fig. S5 and Fig. S6 in the Electronic Supplementary Material\)](#). The resulting block copolyimide was swelling in NMP, can be dissolved in much diluted DCM, indicating no possibility to make a dope. The result directly proved that 6FDA:BPDA-DAM(1:1) copolyimide could not make a workable dope, if it forms a block copolyimide that contains long BPDA/DAM imide segments.

4.4.2. Copolymer containing branches

The contract company synthesized polymers in large batch for our lab using conventional method. This method may produce by-products which could be branch copolymers and block copolymers, even in a small batch synthesis. Experiments showed that in the process of polyimide

synthesis, a rapid locally violent polymerization of a polyamic acid might occur. This rapid polymerization could cause a very high viscosity and molecular weight of polymer, with branch and/or crosslinked structures, especially in the synthesis of a large amount of polymer in a big batch.

As illustrated in scheme 2,

under such conditions, the carboxylic acid groups formed may react with diamines (which was dissolved and has much higher concentration in the reacting solution, compared to dianhydrides), producing branch polyamic acid. As a result, the subsequent polyimide may contain branch structures.

Scheme 2. Proposed mechanism of branching in polyimide synthesis.

On the other hand, carboxylic acid groups may exist in hydrolyzed dianhydride, and can be activated at high temperature in the process of polymerization, and react with highly concentrated DAM in the solution,

thereby possibly forming a branching structure, as shown in scheme 3. Therefore,

Scheme 3. Proposed mechanism of hydrolyzed dianhydride induced branching.

it is good practice to thoroughly dry the

monomers, remove any moisture from solvents, and remove moisture in the reactor thoroughly.

It was reported that branched polymer showed higher value of M_z/M_w than linear polymer [46]. A “good” polymer and a “bad” polymer were measured using GPC and light scattering detector, to get M_z/M_w values, and THF was used as solvent. A M_z/M_w value ~ 1.8 was obtained for the “bad” polymer while ~ 1.4 was found for the “good” polymer. Typically, step-growth polymerization yields a molecular weight distribution of polymer as $M_n : M_w : M_z = 1:2:3$, i.e., $M_z/M_w = 1.5$, which is in agreement with the value of our “good” polymer of ~ 1.4 . The result also indicated that there might have been a branched structure in the “bad” polymer. On the other hand, no branched structure was detected from ^{13}C -NMR analysis, which means branched structure is very little in this “bad” sample, although it showed higher M_z/M_w value. Due to the lower reactivity of carboxylic acid groups than anhydride groups as well as steric hindrance, it is reasonable to assume that the formation of block structure is dominant as by-products; and branched structure might also have a less serious solubility effect than for an actual block structure on the final polymer. *Therefore, formation of block structure appears to be the primary issue that affects dope formation.*

4.4.3. Structure analysis of the polyimides

Solution ^{13}C -NMR was measured under 800 MHz spectra in deuterated DCM, to compare the structure difference between “good” and “bad” 6FDA:BPDA-DAM(1:1) polymers. Homopolymers 6FDA/DAM, and BPDA/DAM, and an intentionally synthesized block copolyimide of 6FDA:BPDA-DAM(1:1) was also measured as model samples to identify characteristic peaks.

As shown in Fig. 5, there are differences between ^{13}C -NMR spectra for 6FDA/DAM (Fig.5a) and BPDA/DAM (Fig. 5b); and Fig. 5c showed that the block copolyimide of 6FDA:BPDA-DAM(1:1) may be modeled as a clean sum of the spectra from the two individual components, i.e. there is individual segments, which are electronically identical to the segments of the two homopolymers. The peaks between 165.75 to 165.95 ppm may be assigned to carbonyl carbon atoms

in 6FDA moieties (C1 in scheme 4), while 166.54 to 166.56 ppm may be assigned to carbonyl carbon atoms in BPDA moieties (C2 in scheme 4). 6FDA/DAM spectrum shows two major carbonyl peaks, and this might result from a steric effect caused by the fluorines, i.e., the two C1 carbon atoms in scheme 4 are not identical. The two carbonyl peaks in BPDA/DAM spectrum is overlapped due to the two C2 carbon atoms are not identical as well; however, the difference is less than in 6FDA/DAM. If there is a certain amount of branching exists, distinguishable ^{13}C chemical shifts should be visible from the carbonyl peaks, therefore, the two carbonyl peaks in ^{13}C -NMR spectra of 6FDA/DAM and BPDA/DAM are not due to ring-opening/branching. In Fig. 5d and Fig. 5e, both the “good” and “bad” 6FDA:BPDA-DAM(1:1) copolyimides showed splittings and new peaks appeared, which are indicated by arrows in Fig. 5. These new peaks might be assigned as carbonyl carbon atoms in the random copolymer structures, while the peaks that are similar to Fig. 5c can be assigned as carbonyl carbon atoms in block structures. The relativity intensity of random carbonyl carbon spectra is higher in Fig.5e than in Fig. 5d.

Scheme 4. 6FDA:BPDA-DAM structure for ^{13}C -NMR analysis.

Fig. 5. ^{13}C -NMR spectra of polyimide samples: (a) 6FDA/DAM, (b) BPDA/DAM, (c) Block 6FDA:BPDA-DAM(1:1), (d) “bad” 6FDA:BPDA-DAM(1:1), and (e) “good” 6FDA:BPDA-DAM(1:1).

Peaks around 139 ppm in Fig.6 might be assigned to carbon atoms in DAM moieties (C3 and C4 in scheme 4). The 6FDA/DAM polymer showed two peaks at 138.99 and 139.15 ppm in Fig. 6a (C3 in scheme 4, characteristic of -6FDA-DAM-6FDA-), and BPDA/DAM with one peak at 138.85 ppm in Fig. 6b (The C4 in scheme 4, has a structure of -BPDA-DAM-BPDA-), and the block copolyimide of 6FDA:BPDA-DAM(1:1) showed a sum of the spectra from that of 6FDA/DAM and BPDA/DAM in Fig. 6c. Similar to spectra of carbonyl carbon atoms in Fig. 5, splittings and resulting new peaks appeared at 139.03 ppm and 138.81 ppm for the other two 6FDA:BPDA-DAM(1:1) copolymer in Fig. 6d and Fig. 6e (indicated by arrows). These results can be explained as DAM-rich moieties, which are between 6FDA and BPDA. The 139.03 ppm peak is assigned to C3, while the 138.81 ppm peak is assigned to C4 in scheme 4, i.e., a -6FDA-DAM-BPDA- structure,

which represents a true random copolyimide structure. The relative intensity of random structure is higher in Fig. 6e than that in Fig. 6d.

The ^{13}C -NMR results were also measured quantitatively for the “good” and “bad” 6FDA:BPDA-DAM(1:1) samples. The peak at 139 ppm was deconvoluted, and the ratio of relative intensity of block structure (-6FDA-DAM-6FDA- and -BPDA-DAM-BPDA-) to random structure (-6FDA-DAM-BPDA-) was computed as 0.90 for “bad” copolymer, and 0.47 for the “good” copolymer sample. This indicates that block structure in “bad” copolymer is about 2 times as that in “good” copolymer. The higher block structure in the “bad” copolymer makes it impossible to develop a workable dope solution as shown in Fig. 3 vs Fig. 2 when a good dope can be formed.

Fig. 6. ^{13}C -NMR spectra of polyimide samples: (a) 6FDA/DAM, (b) BPDA/DAM, (c) Block 6FDA:BPDA-DAM(1:1), (d) “bad” 6FDA:BPDA-DAM(1:1), and (e) “good” 6FDA:BPDA-DAM(1:1).

4.5. Other copolyimides

The findings in dope formation with 6FDA:BPDA-DAM(1:1) copolyimide was extended to 6FDA:ODPA-DAM(1:1) and 6FDA:BTDA-DAM(1:1) copolyimides. A 10wt% NMP solution was used to compare solubility of dianhydrides, and results showed that at room temperature the dianhydrides dissolved in NMP in the order of 6FDA > ODPA > BTDA >> BPDA. This indicates that formation of block copolymer is also possible for 6FDA:ODPA-DAM(1:1) and 6FDA:BTDA-DAM(1:1) if using the conventional synthesis method, although the extent of formation of block/branch structure might not be as severe as in 6FDA:BPDA-DAM(1:1). Similarly, whether a dope formation is successful for the copolymer depends primarily upon the solubility of the resulting ODPA/DAM or BTDA/DAM segments.

Both ODPA/DAM and BTDA/DAM polyimides were synthesized. It was found that ODPA/DAM was soluble and could make a workable dope. However, BTDA/DAM formed gel during the imidization step in synthesis with NMP as solvent. The BTDA/DAM polyimide could not make a dope, and it was even insoluble in pure THF, formed a gel in pure NMP, and swelled in pure DCM. The corresponding copolyimides 6FDA:ODPA-DAM(1:1) and 6FDA:BTDA-DAM(1:1) showed different behaviors. 6FDA:ODPA-DAM(1:1) can make a workable dope, even it was synthesized using the conventional method. But 6FDA:BTDA-DAM(1:1) made from the conventional method in a larger batch (100 gram) cannot make a workable dope, although a smaller batch (50 gram) works acceptably. However, different from 6FDA:BPDA-DAM(1:1), under the same polymer concentration in a dope recipe, the “bad” 6FDA:BPDA-DAM(1:1) formed gel, while the “bad” 6FDA:BTDA-DAM(1:1) only formed flowable gel-like solution. This might be due to the much higher solubility of BTDA than BPDA in NMP, making the BTDA/DAM chain segment shorter and less than the BPDA/DAM chain segment in the corresponding copolyimides.

Scheme 5. Linkage flexibility in polymer backbones.

Chemical structure determines the solubility of the 6FDA-based copolyimides, which influences the formation of a “dope” solution. A random copolyimide is soluble in NMP and can make a spinnable dope; a block copolyimide is complex, may or may not form a dope, depending on the length of corresponding block chain segment (other than 6FDA/DAM) and whether the block segment is soluble. It seems that with the decrease of flexibility of linkage from ODPA and BTDA to BPDA, i.e., from flexible segment to rigid segment in polymer, as shown in Scheme 5, the corresponding chain segment becomes more difficult to be dissolved. The polyimide showed solubility in NMP in the order of ODPA/DAM > BTDA/DAM >> BPDA/DAM. Therefore, if a block copolyimide is formed, in which the insoluble chain segment is long enough, it will result in lower solubility of the corresponding copolyimide and cause problems in dope formation. And one can estimate the possibility of dope formation of a 6FDA-based copolymer based on the linkage flexibility of the monomers. The copolyimide chemical structure was found to be determined by polymer synthesis method/conditions. The details of polymer synthesis optimization work will be discussed systemically in another paper later.

4.6. Defect-free hollow fiber spinning with the 6FDA:BPDA-DAM(1:1) copolymer synthesized using new method

Based on experiments including polymer synthesis optimizations and corresponding polymer's dope formation trials, we found that the copolymer structure is uncontrollable under the conventional synthesis method, while the new modified method is controllable to minimize block/branch structure in the product. 6FDA:BPDA-DAM(1:1) copolymer synthesis was scaled up to 3.5 kg batch under modified method; this random copolymer is still easy to make a workable dope solution, indicating negligible block/branch structure in the copolymer. Fig. 7 shows a dope made with polymer that was synthesized using modified method in a large batch; the dope is clear, transparent, and homogeneous, with proper viscosity for spinning.

Fig.7. Dope made from new method synthesized 6FDA:BPDA-DAM (1:1).

Defect-free hollow fibers were successfully spun with the dope. Dope compositions and spinning conditions are same as previous work using a “good” polymer [21]. Typical morphologies of hollow fibers are shown in Fig. 8 (a) and (b). The fiber has porous support layer with an outer selective dense skin layer. The thickness of skin layer is ~ 500 nm to $2\text{ }\mu\text{m}$ depending on spinning conditions. Selectivity of O_2/N_2 is 3.9, with O_2 permeance of ~ 40 to 80 GPU. The intrinsic O_2/N_2 selectivity of the polymer was measured as 3.8 using a dense film membrane.

Fig. 8. SEM photographs of 6FDA:BPDA-DAM (1:1) derived defect-free hollow fiber (a) cross-section and (b) selectivity skin layer.

4.7. Dope formation for spinning “nodular” hollow fiber with 6FDA:BPDA-DAM(1:1) copolymer

The above discussions were focused on dope formation for the spinning of defect-free hollow fibers, in which the solvents were composed of NMP and volatile THF. However, in the formation of dope solution for spinning of “nodular” fiber, only NMP was used as the solvent, and volatile THF was removed [43]. Both “good” and “bad” 6FDA:BPDA-DAM(1:1) copolyimides were used to make dopes with the same

Fig. 9. Dope for spinning “nodular” fibers made from (a) “good”, and (b) “bad” copolyimides of 6FDA:BPDA-DAM (1:1).

recipe for spinning of “nodular” fiber. As expected, only “good” copolymer could form spinnable dope solution (Fig. 9a), which is flowable, transparent, and homogeneous solution; all of the “bad” copolymers formed “gels” (Fig. 9b). Furthermore, the intentionally synthesized block copolyimide of 6FDA:BPDA-DAM(1:1) only got swelled in the mixture of solvent (NMP) and non-solvents (Ethanol and Lithium nitrate). Similarly, in the efforts of making “nodular” dopes with

6FDA:ODPA-DAM(1:1) and 6FDA:BTDA-DAM(1:1) copolymers, similar behaviours were observed as they did in forming defect-free dopes, as noted above.

Fig.10. SEM images of nodular 6FDA/BPDA-DAM hollow fiber membranes. (a) Overview of the cross-section, (b) Skin layer.

The dope solution without THF which formed a “good” batch of 6FDA:BPDA-DAM(1:1) copolyimide was used to spin nodular 6FDA:BPDA-DAM hollow fiber [43]. The SEM images of the resultant fiber’s cross section and skin layer are shown in Fig. 10. Nodules are clearly seen in the skin layer, suggesting “nodular” 6FDA:BPDA-DAM(1:1) hollow fibers were successfully formed. After PDMS treatment, the nodular fibers showed good gas separation performance.

5. Conclusions

6FDA-based copolyimides, including 6FDA:BPDA-DAM(1:1) copolymer, when properly synthesized, has excellent intrinsic gas separation properties and good hollow fiber fabrication characteristics. Hollow fiber for gas separation or as a precursor for making CMS fiber can only be obtained using a “spinnable” dope solution that includes both solvents and non-solvents. Polymer synthesis methods influence the polymer structure, and as a result, determine whether the polymer

can form a workable dope solution for spinning or not; either for a defect-free hollow fiber membrane or for a “nodular” hollow fiber. Random copolymer containing minimal block/branch structure is the key to obtain “spinnable” dope, although several other issues should be considered, too. Block copolyimide that contains long enough insoluble block chain segments cause problems in dope formation.

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Figure List

Fig. 1. Ternary phase diagram of spinnable 6FDA:BPDA-DAM(1:1) copolymer

Fig. 2. Workable dopes made from 6FDA:BPDA-DAM (1:1).

Fig. 3. Non-workable “dope” from bad 6FDA:BPDA-DAM (1:1) polymers.

Fig. 4. Non-workable “dope” from bad 6FDA:BPDA-DAM (1:1) : (a) as received, and (b) purified polymer.

Fig. 5. ^{13}C -NMR spectra of polyimide samples: (a) 6FDA/DAM, (b) BPDA/DAM, (c) Block 6FDA:BPDA-DAM(1:1), (d) “bad” 6FDA:BPDA-DAM(1:1), and (e) “good” 6FDA:BPDA-DAM(1:1).

Fig. 6. ^{13}C -NMR spectra of polyimide samples: (a) 6FDA/DAM, (b) BPDA/DAM, (c) Block 6FDA:BPDA-DAM(1:1), (d) “bad” 6FDA:BPDA-DAM(1:1), and (e) “good” 6FDA:BPDA-DAM(1:1).

Fig.7. Dope made from new method synthesized 6FDA:BPDA-DAM (1:1).

Fig. 8. SEM photographs of 6FDA:BPDA-DAM (1:1) derived defect-free hollow fiber (a) cross-section and (b) selectivity skin layer.

Fig. 9. Dope for spinning “nodular” fibers made from (a) “good”, and (b) “bad” copolyimides of 6FDA:BPDA-DAM (1:1).

Fig.10. SEM images of nodular 6FDA/BPDA-DAM hollow fiber membranes. (a) Overview of the cross-section, (b) Skin layer.

Scheme 1. Synthesis of 6FDA:BPDA-DAM copolymer.

Scheme 2. Proposed mechanism of branching in polyimide synthesis.

Scheme 3. Proposed mechanism of hydrolyzed dianhydride induced branching.

Scheme 4. 6FDA:BPDA-DAM structure for ^{13}C -NMR analysis.

Scheme 5. Linkage flexibility in polymer backbones.

Table 1. Key parameters in a dry-jet/wet-quench hollow fiber spinning process

Dope composition	Air gap height	Quench bath temperature
Bore fluid composition	Take-up rate	Quench bath composition
Dope/bore fluid flow rate	Spinning temperature	Humidity