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Preparation and characterization of sulfone-based polyimide nanofoams grafted with poly(propylene glycol)

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***Abstract*:** A route to thermally stable polyimide nanofoams was developed. Nanofoams were prepared from graft copolymers consisting of thermally stable and thermally labile blocks as continuous and disperse phase, respectively. The copolymers were synthesized via reaction of sulfone-based diamines with aromatic dianhydrides through the poly (amic acid) precursor, followed by thermal imidization. Foam formation was achieved by thermolysis of thermally labile block, leaving pores of the size and shape corresponding to the initial copolymer morphology. Polyimide precursors and nanofoams were subjected to a variety of characterization including FT-IR, thermal gravimetric analysis (TGA), dielectric constant, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The nanofoams showed good processability, high thermal stability, and low dielectric constant which are prerequisites for application in electronic industry.

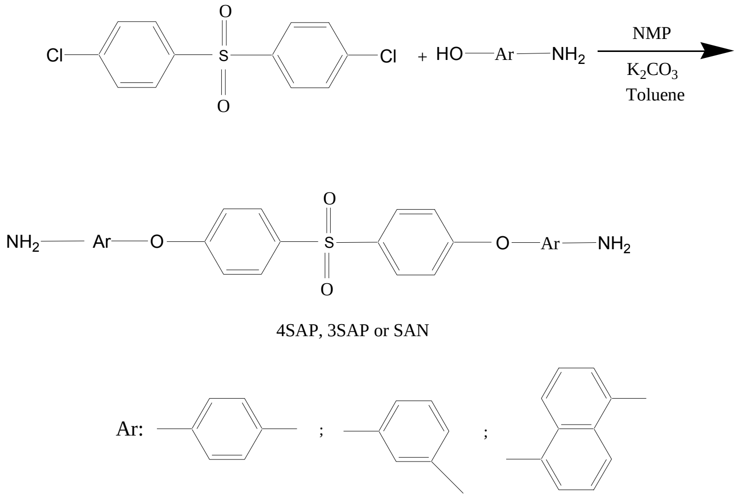
Keywords: polyimide; nanofoam; dielectric constant; thermally stable.

Introduction

Aromatic polyimides are well accepted as high performance polymers as well as high temperature resistant materials [1-8]. They exhibit favorable balance of physical and chemical properties and show excellent thermal, mechanical and electrical properties; so they are the prime candidates polymeric insulator in microelectronic industrials. Although polyimides meet many of the material requirements, future advances in high performance computing will require improved dielectric insulators with substantially lower dielectric constants. In recent years, several studies have been contributed to the preparation of the low dielectric constant polyimides. The most common approach was via the incorporation of fluorinated substituents which resulted in polyimides with dielectric constant below 3 [9-11]. However, fluoro-polyimides possessed low glass transition temperature, low mechanical strength and they were expensive. Additionally, the methodology for developing highly fluorinated polyimides can be limited to a certain extent by synthetic difficulties associated with the fluorine-containing comonomers. In an effort to circumvent these problems, an alternative approach has been developed to reduce the dielectric constant while maintaining the thermal and mechanical properties. The reduction in dielectric constant is achieved by introducing voids into polyimide thin films, by replacing the polymer having a dielectric constant ~3.0 with air which has a dielectric constant of 1. Accordingly, various processing routes have been investigated based on solution casting of block or graft copolymers containing a thermally stable and a thermally labile block and the thermal decomposition of labile group to produce nanofoams [12-16]. In this article, the preparation of new nanoporous thin films of sulfone-based polyimides was described. These polyimides were prepared from graft copolymers consisting of a polyimide block as continuous phase and poly (propylene glycol) as disperse phase.

Result and discussion

Three diamines were synthesized in one step via nucleophilic substitution reactions. Bis(4-chlorophenyl) sulfone was reacted with 4-aminophenol, 3-aminophenol, and 5-amino-1-naphthol in the presence of potassium carbonate to produce 4SAP, 3SAP, and SAN, respectively (Scheme 1). FT-IR, H-NMR and elemental analysis were used to confirm the structures of diamines and the results are collected in Table 1.



Scheme 1. Preparation of diamines.

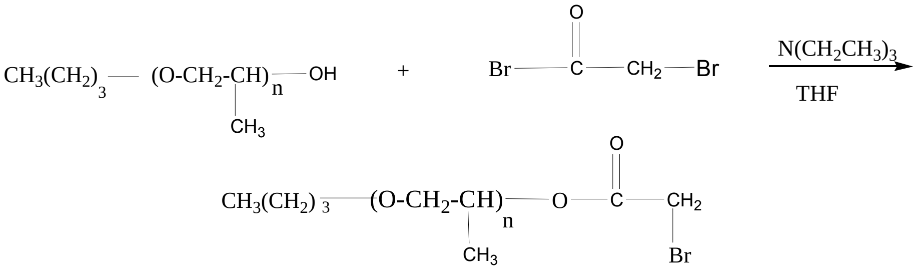
Prepared diamines with structural features including flexible ether and sulfone groups would induce solubility and proccesability to the final polyimide films. Also presence of aromatic groups and avoidance of any weak linkages in the structure of diamines would maintain thermal stability of the polymers. The prepared diamines were used for polyimides formation. The graft copolymers consisting of a thermally stable polyimide block and a thermally labile polymer block, were prepared by two stage process, which include the poly(amic acid) formation followed by esterification. One of the most important requirements of the thermally labile block is the availability of proper synthetic route to well-defined functional oligomers suitable for incorporation into polyimides. In this work the functionalized PPG (M_w of 1000 and 2500 g/mol) as a labile oligomer was prepared via reaction of poly(propylene glycol) monobutyl ether with 2-bromoacetyl bromide in the presence of triethylamine [17] (Scheme 2).

Synthesis of graft copolymers (PAAE-g-PPG) were done by the reaction of the diamines (4SAP,3SAP,SAN) with pyromellitic dianhydride and then addition of bromo-terminated PPG to it as shown in Scheme 3.

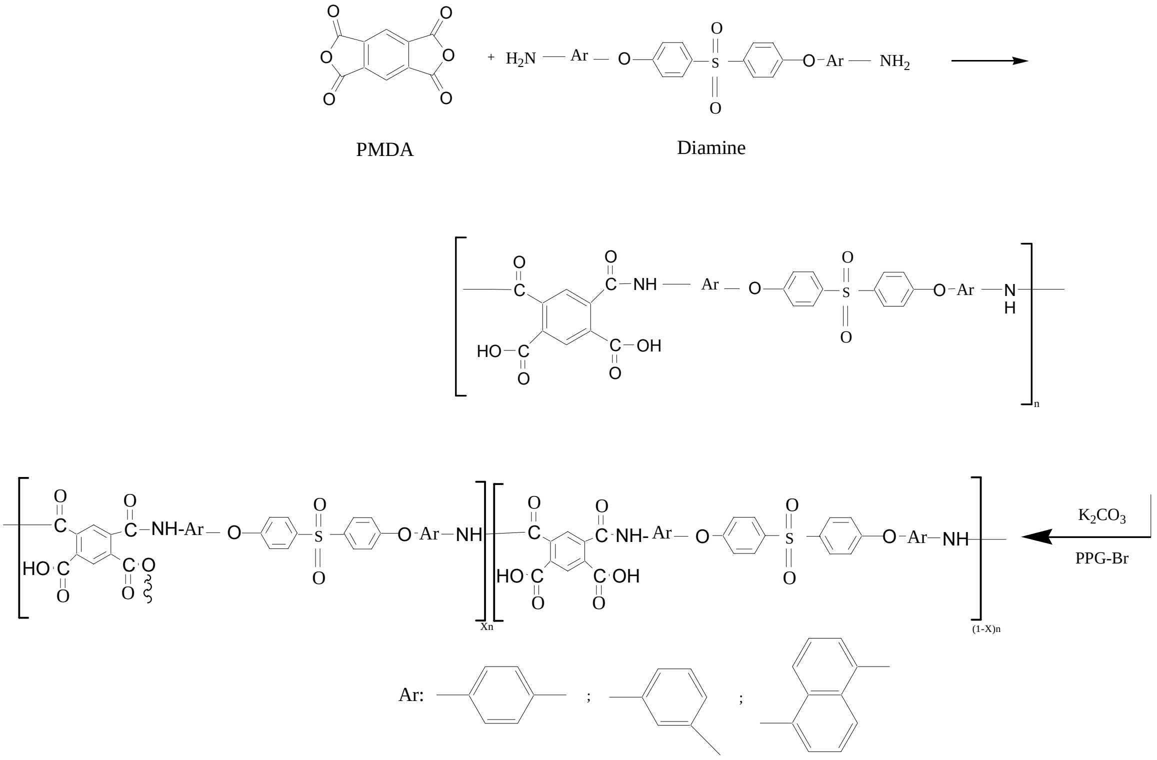
FT-IR and TGA were used to characterize the poly (amic acid)s and the results are tabulated in Table 2. In the FTIR spectra the peaks correspond to aliphatic and ester groups were seen at about 2924-2928 and 1715-1720 cm^{-1}, respectively representing the formation of PAAE-g-PPG (Fig 1).

Tab.1. Characterization of diamines.

No.	Diamine Structure	IR(KBr) cm^{-1}	NMR(DMSO-d_6,δ)	Elemental Analysis					
				Calc.			Found.		
				C	H	N	C	H	N
1	4 SAP	3365-3456 (NH_2) 3056 (CH, Aromatic) 1584 (C-N, N-H) 1234 (C-O) 1141 (S=O, Sulfone)	5.07 (s, 4H, NH) 6.57 (d, 4H, Phenyl) 6.75 (d, 4H, Phenyl) 7.80 (d, 4H, Phenyl)	65.55	6.61	2.47	65.18	6.40	2.69
2	3 SAP	3375- 3475 (NH_2) 3068 (CH, Aromatic) 1579 (C-N, N-H) 1236 (C-O) 1146 (S=O, Sulfone)	5.30 (s, 4H, NH) 6.16 (s, 2H, Phenyl) 6.22 (d, 2H, Phenyl) 6.38 (d, 2H, Phenyl) 7.02 (dd, 2H, Phenyl) 7.05 (d, 4H, Phenyl) 7.88 (d, 4H, Phenyl)	65.55 2.29	6.61	2.47	65.15	6.82	
3	SAN	3367-3460 (NH_2) 3058 (CH, Aromatic) 1589 (C-N, N-H) 1243 (C-O) 1148 (S=O, Sulfone)	5.88 (s, 4H, NH) 6.67 (d, 2H, Naphthyl) 6.92 (d, 2H, Naphthyl) 7.01 (d, 4H, Phenyl) 7.14(dd,2H, Naphthyl) 7.17(dd,2H, Naphthyl) 7.35 (d, 2H, Naphthyl) 7.85 (d, 4H, Phenyl) 7.98 (d, 2H, Naphthyl)	72.18 6.05	4.51	5.26	70.24	4.24	



Scheme 2. Structure of PPG-Br.



Scheme 3. Preparation of poly (amic acid-co-amic ester) grafted PPG.

TGA thermographs of the poly(amic acid)s showed three-step decomposition at about 100, 300, and 500 °C which were related to thermal imidization of the amic acids due to H_2O elimination, degradation of PPG units, and decomposition of the matrix of the polyimides, respectively (Fig 2). Also, the PPG content of the polymers was obtained from TGA method and the results are collected in Table 2.

The decomposition temperature of labile block must be sufficiently high to permit standard film preparation and solvent removal yet well below the glass transition temperature (T_g) of the polyimide block to avoid foam collapse. Therefore, in order to obtain an optimized temperature for polyimide and subsequently nanofoam formation, the glass transition temperature of the pure polyimides was studied using DSC technique. The glass transition temperature of the polyimides was higher than 320 °C and therefore it was concluded that the imide and foam processes should be achieved below this temperature. Since the decomposition temperature of PPG began at about 230 °C and completed at about 300 °C, so this oligomer was selected as the labile block for the nanofoam preparation.

Tab. 2. Characterization of PAAE-g-PPGs by FT-IR and TGA.

No.	Polymer[a] Structure	IR(KBr) cm^{-1}	PPG content[b] (wt%)	TGA analysis		
				1st weight loss (°C)	2nd weight loss (°C)	3rd weight loss (°C)
1	4SAP-1000	3253-3436,2925 1725,1719,1653 1504,1243	11	100	305	520
2	3SAP-1000	3252-3431,2928 1722,1720,1655 1500,1243	15	101	309	507
3	SAN-1000	3252-3438,2926 1724,1715,1663 1501,1242	18	103	314	498
4	4SAP-2500	3256-3438,2927 1724,1718,1655 1506,1241	9	99	310	530
5	3SAP-2500	3251-3429,2925 1723,1718,1654 1502,1242	13	101	314	510
6	SAN-2500	3248-3432,2924 1722,1716,1666 1498,1240	16	104	320	500

[a] Number 1000 and 2500 represent the Mw of 1000 and 2500 g/mol for PPG
[b] Estimated from TGA method

For imidization of copolymers, thin films were made by solution casting of the poly (amic acid)s using NMP or DMAc as solvent. After solution casting, the samples were subjected to a heating cycle for effective solvent removal and subsequent imidization. Typically, the samples were heated from 50 °C to 180 °C under nitrogen atmosphere and held at this temperature for 1 h to complete the imidization. The structures of polyimides were confirmed by FT-IR spectra and a representative spectrum was shown in Fig 3. Peaks at about 1778 (imide ─C═O asymmetrical stretching), 1726 (imide ─C═O symmetrical stretching), 1373 (imide C─N stretching), and 725 cm^{-1}(─C═O out of plane deformation) approved the imide bonds formation and also bands at about 2931 cm^{-1} confirmed the presence of PPG moieties in the structures.

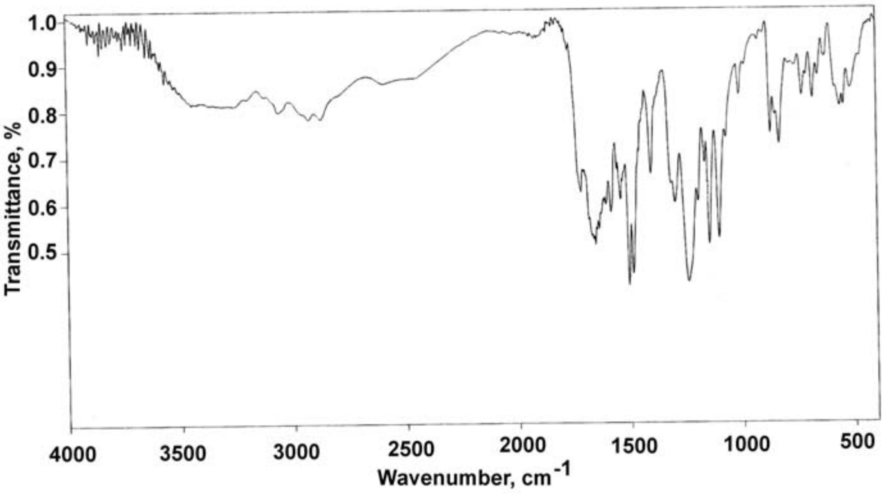


Fig. 1. FT-IR spectrum of 4SAP based PAAE-g-PPG-2500.

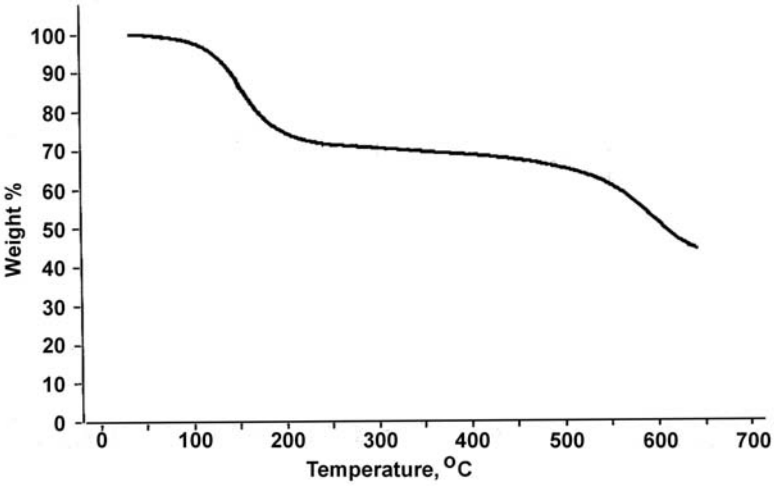


Fig. 2. TGA thermogram of 4SAP based PAAE-g-PPG-2500.

The generation of the foam structures was accomplished through decomposition of the PPG by subjecting the copolymer films to the thermal treatment in air. Nanofoams were formed by heating the copolymers at 300 °C in air for 9 h (Scheme 4). A typical FT-IR spectrum of the polyimide and its nanofoam is shown in Fig 3. Residue of PPG byproducts were not observed in the resulting polyimide nanofoams due to absence of aliphatic bands at about 2924-2928 cm^{-1} in the IR spectra. Also no detectable weight losses at about 300 °C related to PPG labile block were observed in TGA thermograms of the nanofoams.

The molecular weights of the copolymers were determined using GPC method in DMF over polystyrene standards. Table 3 shows the data obtained from chromatography method and accordingly, the copolymers showed reasonable molecular weights. Since the symmetry of the structures had a direct effect on the growth of molecular weights and therefore improvement of physical properties of the polymers, 4-SAP derived polyimides showed higher thermal stability than 3-SAP derived polyimides and they were in turn more thermally stable than SAN derived polyimides. On the other hand, increasing the molecular weights of polyols (thermally weak linkages) had an inverse effect on the thermal stability of the polyimides with the same diamine structure.

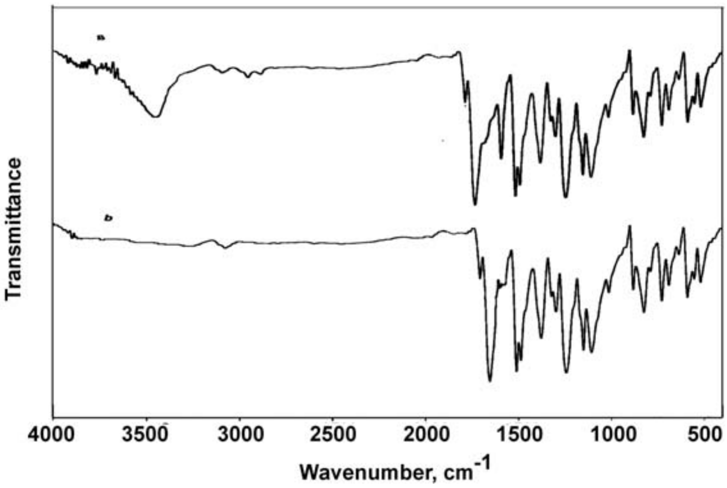
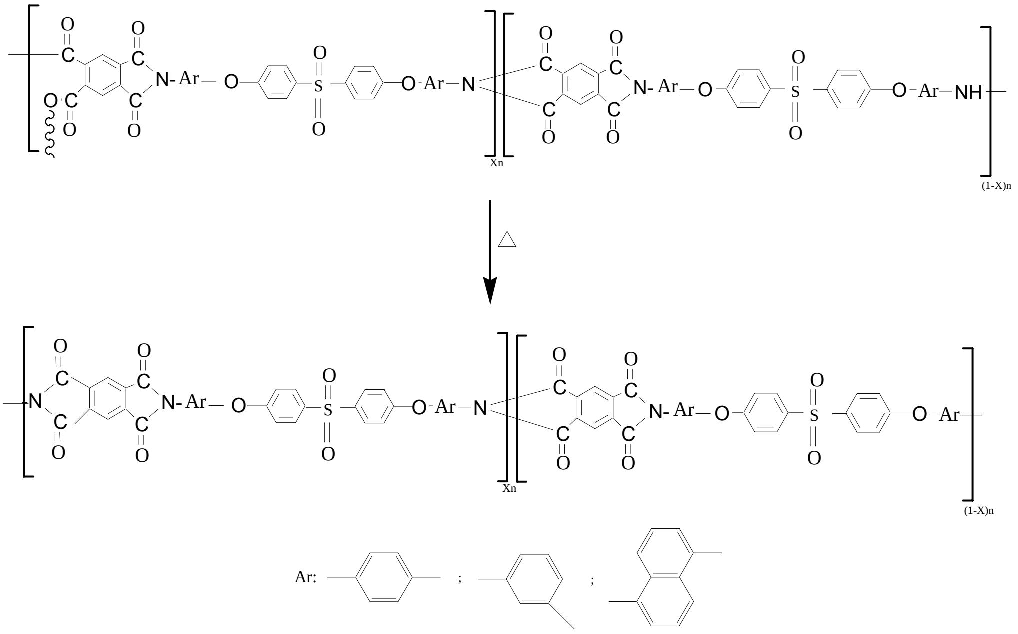


Fig. 3. FT-IR spectra of 4SAP-2500 based a) polyimide and b) nanofoam.



Scheme 4. Preparation of polyimide nanofoams

To obtain an estimation about the dielectric properties of the thin films, the refractive indices of thin films of foamed samples were measured and based on the Maxwell equation ($\varepsilon = \eta^2$, $\Delta\ \varepsilon = +\ 0.3$) [18], the dielectric constants of nanofoams were obtained (Table 4). The smaller dielectric constants of nanofoams in comparison with the related polyimides were mainly due to the incorporation of pores into the final structures.

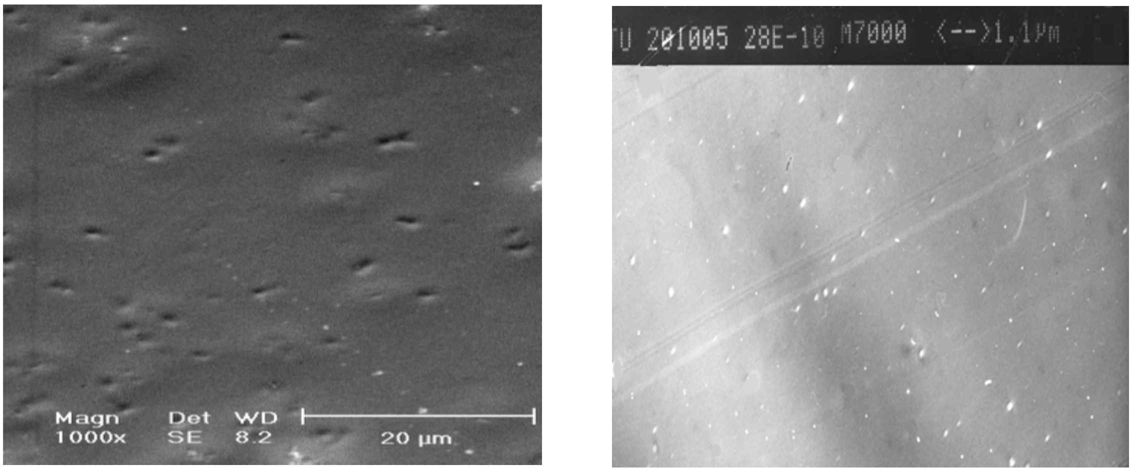
Tab. 3. Molecular weights of polyimides based on GPC data.

Polymer	M_w	M_n	M_w/M_n
4SAP-1000	75500	50300	1.5
3SAP-1000	73300	45800	1.6
SAN-1000	72500	45300	1.6
4SAP-2500	88300	55200	1.6
3SAP-2500	87500	46100	1.9
SAN-2500	86400	48000	1.8

Tab. 4. Refractive indices and dielectric constants of polyimides and their nanofoams.

Polymer[1]	η_i[2]	η_o[3]	$\Delta\eta$	ε_o[4]
4SAP (h)	1.72	1.68	0.04	3.12
4SAP-1000 (n)	1.54	1.50	0.04	2.55
4SAP-2500 (n)	1.58	1.53	0.05	2.64
3SAP (h)	1.70	1.65	0.05	3.02
3SAP-1000 (n)	1.51	1.47	0.04	2.46
3SAP-2500 (n)	1.56	1.50	0.06	2.55
SAN (h)	1.68	1.64	0.04	2.99
SAN-1000 (n)	1.48	1.43	0.05	2.34
SAN-2500 (n)	1.54	1.49	0.05	2.52

[1] h: homopolymer; n: nanopolymer; [2] η_i: in-plane refractive index
[3] η_o: out-of-plane refractive index; [4] ε_o: out-of-plane dielectric constant



(a) (b)

Fig. 4. (a) SEM and (b)TEM micrographs of SAN-2500 based foam.

Also, BAN-based foams showed lower dielectric constants than 3BAP-based corresponding foams and they in turn showed lower dielectric constants than 4BAP-based corresponding foams. This may well be related to free volume in the polymer since the naphthyl substituted systems should have a higher degree of entropy with respect to meta and para linkages [19].

The morphology of the prepared nanofoams was studied using SEM and TEM techniques. According to the micrographs the size of the spherical particles was found to be in the nanometer scale (10-40 nm) with a uniform distribution of nanopores and also little interconnectivity between the pores (Fig 4).

Conclusions

A means of preparing six different polyimide nanofoams with pore sizes in the nanometer regime was demonstrated. Microphase separated graft copolymers comprising of a polyimide as the thermally stable matrix and the dominant phase with a thermally labile material, PPG, were prepared. Resulted nanofoams of the polyimides showed high thermal stability and low dielectric constant; prerequisites for application in electronic and microelectronic devices as insulating materials.

Experimental

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. Pyromellitic dianhydride (PMDA) was dried in a vacuum oven at 110 ˚C overnight. Bis(4-chlorophenyl) sulfone was recrystallized from aqueous ethanol. N-Methyl-2-pyrrolidone (NMP) and toluene were distilled under reduced pressure over CaH_2 and sodium wire, respectively. 4-Amino phenol, 3-amino phenol, and 5-amino-1-naphthol were sublimed under reduced pressure.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in DMSO-d_6 solution using a Bruker Avance DPX 250 MHz (GmbH, Germany). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Refractive index of polyimide thin films was measured with a Metricon Prism Coupler PC-2000 (Pennington, NJ) for determination of in-plane and out-of-plane refractive indices. The molecular weights (M_w and M_n) were determined by gel permeation chromatography (GPC). It was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent.

Monomer synthesis

Synthesis of bis-[4-(4-amino-phenylene-1-yloxy)-phenyl]-sulphone (4SAP), bis-[4-(3-amino-phenylene-1-yloxy)-phenyl]-sulphone (3SAP), and bis-[4-(5-amino-naphthalene-1-yloxy)-phenyl]- sulphone (SAN) diamines

Into a 100-mL, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was placed 0.01 mol of bis(4-chlorophenyl) sulfone, 25 mL of dry N-methyl-2-pyrrolidone (NMP), and 15 mL of dry toluene and 0.021 mol of 4-amino phenol (for 4SAP diamine). Then 0.0315 mol of K_2CO_3 was added to the mixture and the reaction mixture was heated to 140 ˚C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165 ˚C by removing more toluene, and kept at the same temperature for 20 h. The resulting reaction mixture was cooled and poured into water. Then 100 mL of 5% NaOH was added to the mixture and the mixture was washed repeatedly with a 5% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 60 ˚C (Yield 94 %). The 3SAP and SAN diamines were prepared similarly in 88 and 92 % yields, using 3-amino phenol and 5-amino-1-naphthol instead of 4-amino phenol, respectively.

Synthesis of poly (propylene glycol) 2-bromoacetate (PPG-Br)

The preparation of poly(propylene glycol) 2-bromoacetate (PPG-Br), having a number- average molecular weights of ca. 2500 and 1000 g mol^{-1} (PPGBr-1,2), was as follows: A 100-mL flask was charged with 5 mmol of poly(propylene glycol) monobutyl ether (PPGOH), 5.5 mmol of triethylamine (TEA), and 50 mmol of 2-bromoacetyl bromide. The mixture was stirred overnight and then diluted with 100 mL of tetrahydrofuran (THF). The suspension was filtered to remove the precipitated triethylamine hydrobromide salt, and the solvent was evaporated. The residue was then dissolved in 100 mL of chloroform and washed with 5% $NaHCO_3$ several times. The mixture was dried with anhydrous $MgSO_4$ and then the solvent was evaporated, and the resulting bromide derivative was dried under vacuum for 24 h, yielding a viscous liquid. The yield of the reactions was about 86 and 80 % for PPG-OH=2500 and 1000, respectively.

Synthesis of graft copolymers

The graft copolymers were prepared in one-pot process. A 100-mL two-necked flask, fitted with a nitrogen inlet was charged with 5 mmol of 4SAP (or 3SAP or SAN) and 20 mL of NMP. After complete dissolving of the diamine, the flask was cooled to 5 °C and then 5 mmol of PMDA was added to it. The solution was warmed to room temperature and stirred for 24 h. To this mixture, 0.1 mmol of K_2CO_3 and 0.1 mmol of PPGBr were added. The solution was stirred for 48 h at room temperature. The resulting solution was precipitated into methanol/water (1:1 v/v) and methanol several times. The resulted poly(amic acid-co-amic ester) grafted PPG (PAAE-g-PPG) was dried under vacuum for 24 h at 40 °C (yields about 85 %).

Preparation of polyimide and porous polyimide films

A copolymer solution was prepared by dissolution of the copolymer (1g) in 8.74 mL of NMP or dimethylacetamide (DMAc) followed by casting solution on a glass substrate by doctor blading. The removal of solvent and subsequent imidization was accomplished by heating the polymer incrementally to 200 °C for 7 h under a nitrogen atmosphere (polyimide formation). Then it was heated at 300 °C for 9 h in the presence of oxygen to get nanoporous polyimide (foam formation).

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