Dielectric and Gas Transport Properties of the Films of Thermally Stable Poly(arylene ether ketone)s Containing Content-Tunable Benzimidazole Moiety

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ABSTRACT: A series of thermally stable poly(arylene ether ketone)s (PAEKs) bearing benzimidazole structure in the main chains, named poly(arylene ether ketone-benzimidazole)s (PAEK-BIs), were directly synthesized by polycondensation of dimethyl bisphenol, dibenzimidazole bisphenol, and difluorobenzophenones. By systematically varying the amount ratio of two kind of bisphenols, the content of benzimidazole moiety in the backbone was controlled straightforwardly. The prepared amorphous polymers were characterized in terms of Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, thermal, dielectric, and gas transport properties. Evaluation of solubility reveals that PAEK-BIs with >60% content of benzimidazole units could be soluble in commonly used organic solvents. Also polymers containing content-tunable benzimidazole show high glass-transition temperatures (T_g's, 157–319°C) and excellent thermal stability (e.g., temperature of 5% weight loss, above 438°C in air). Dielectric constants of PAEK-BIs measured at 25°C are all less than 2.66 in the frequency range of 0.1–50 kHz. For dense films, the ideal gas selectivity and permeability coefficients could be compared with that of commercial Ultem 1000 membrane, which indicate that the PAEK-BIs are potential to be used for gas separation membrane material. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41289.

INTRODUCTION

Semicrystalline poly(arylene ether ketone)s (PAEKs) have been widely used as high-performance engineering thermoplastics for the high melting point ranging from 180 to 400°C.[1] The unique combination of excellent chemical resistivity, thermal stability, mechanical/electrical/insulating, and antiultraviolet properties, permit PAEKs to be applied in aerospace, electronics, nuclear industries,[2–8] etc. However, nonsubstituted PAEKs generally show very low solubility toward common used organic solvents for the relatively high crystallinity. At ambient temperature, these materials are only soluble in concentrated sulfuric acid and some other strong acid solvents.[1,9,10] An example of commercial poly(ether ether ketone) (PEEK) shows that it is insoluble in all common organic solvents at room temperature. On the other hand, the PEEK possesses the glass-transition temperature (T_g) of around 143°C.[7,11] Also it was reported that PAEKs containing nonlinear bisphenol units exhibit the T_g's ranging of 153–217°C, when systematically varying the bisphenol ratio.[1,12]

The relatively low T_g's typically mentioned might somewhat limit the applications of this category at elevated temperature. Therefore, in order to improve the solubility and simultaneously enhance the T_g's, and endow the PAEKs with some special properties for applications, numerous improvements were performed. Benzoxazole-containing PAEKs were reported that the introduction of aromatic bulk groups improved the solubility and T_g's (173–245°C).[13] Many other structure modified polymers, for example, copolymer PEEKs with pendant phenyl groups, PEEK-co-PEEKK, PEEK/poly(aryl ether sulfone) containing biphenylene moiety block copolymer, and PEEK/polyethersulfone block copolymer[14–17] were also reported to increase the T_g's, by incorporation of bulky pendant groups or some special linkages. In view of the above, soluble PAEKs with high T_g's could be particularly interesting.

It is known that processable polymers with high T_g's are potential candidate materials for various applications, specially, in microelectronic devices and gas separation.[18,19] Reportedly, low
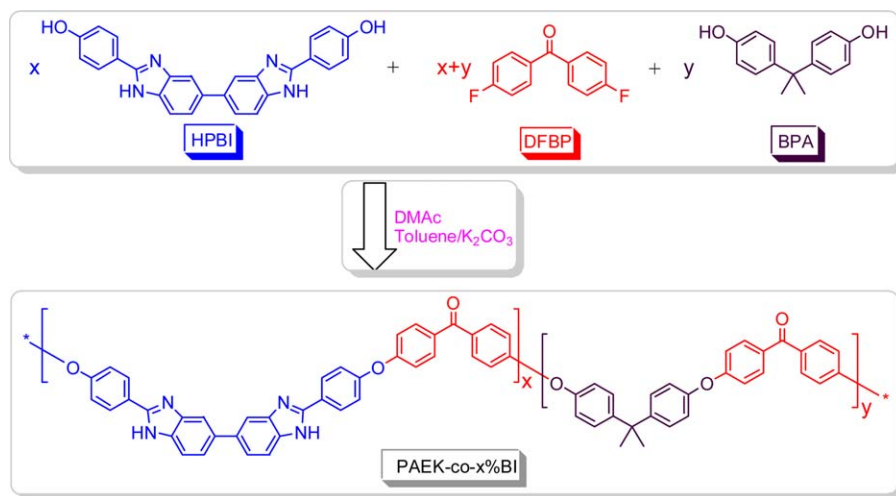
Scheme 1. Synthesis of poly(arylene ether ketone-co-x%benzimidazole). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dielectric constant polymer materials have been promisingly developing, mainly including aromatic (heteroaromatic) polymers, silicon-containing polymers, fluorinated polymers, porous polymers, etc. As for aromatic polymers, polyimides, polynitriles, SiLK resin, benzocyclobutene resins, poly(binaphthylene ether), polydiphenyl, and polyquinolines have been widely investigated.[20,21] Expectedly, PAEKs could fall into this category, however, the reported PAEKs for dielectric materials, such as PEEK, PEEKK, and PEEKDK are suffering from undesirable solubility.[22] Herein, soluble PAEK with low dielectric constant as well as thermal stability might further expand the diversity of materials for microelectronic devices. In addition, aromatic polymers such as polysulfones, polycarbonates, polyarylates, poly(aryl ketone), poly(arylene ether)s, and polyimides as gas separation materials have been widely studied for applications.[23,24] However, investigation on gas permeation properties of PAEKs as a family of polymers is almost unexplored. Only few reports available on gas permeability of PAEK based on bulky side group indicated that it is suitable to candidate for gas separation application.[25] According to generally accepted model[26,27] for the gas permeation, the present of bulky groups in the backbone or as substituents tend to induce high free volume and therefore result in high permeability. Meanwhile, rigid polymer backbone with restricted segmental mobility tends to high selectivity.[28] Aromatic polybenzimidazoles (PBIs), a class of excellent high-performance linear thermoplastic polymers with T_g's of 425–435°C, have been evaluated for their potential usage for dielectric capacitors, gas separation, and fuel cell polyelectrolyte in high temperature.[29–31] Along this line, possibly, by introducing of benzimidazole moiety into PAEKs, it might help to fabricate a high-performance polymer material.

Based on the above strategy, novel PAEKs were fabricated by combining the arylene–ether–ketone and benzimidazole moieties together in one main chain, to develop a novel soluble and thermally stable polymer. Effects of benzimidazole moieties on inherent viscosities, solubility, and thermal stability were discussed. Simultaneously, dielectric and gas permeation properties were evaluated for applications.

EXPERIMENTAL

Materials
4,4′-Difluorobenzophenone (DFBP) was purchased from Songsheng Chemical Company and recrystallized from absolute ethanol before used. 2,2′-bis(4-hydroxy-phenyl)propane (BPA) was used as received from Sinopharm Chemical Reagent Co. The synthesis of 5,5-bis[2–4(-hydroxyphenyl)benzimidazole] (HPBI) was synthesized according to the literature.[32] Potassium carbonate, toluene, N,N-dimethyl acetamide (DMAc), N,N-dimethylformamide (DMF), and methanol were obtained from commercial sources, and were used as received.

Polymer Synthesis (in Case of PAEK-co-20%BI)
The synthetic scheme of poly(arylene ether ketone-co-x%benzimidazole) (PAEK-co-x%BI) is illustrated in Scheme 1. A series of polymers having different HPBI content was synthesized by varying the mole ratio of two diphenol aromatic monomers. In this article, notation PAEK-co-x%BI will be used, where x% (20, 40, 60, and 80%) denotes the mole percent of HPBI with respect to the total amount of diphenol aromatic monomers in the feed. In a typical polycondensation procedure (in case of PAEK-co-20%BI), into a three-neck flask charged with a mixture of 2.1820 g of DFBP (10 mmol), 1.8263 g of BPA (8 mmol), 0.8369 g of HPBI (2 mmol) in 70 mL DMAc using 11.5 mmol of K_2CO_3 as catalyst, and 35 mL toluene as an azeotropic agent to remove produced water during the reaction. The reaction mixture was heated to 140°C for 4 h under nitrogen atmosphere. After dehydration and removal of toluene, the reaction mixture was heated to about 160°C. After 3 h, when the solution viscosity increased apparently, proper amount of DMAc was added to dilute the solution, and the reaction mixture was heated to 160°C for 16 h. The resulting viscous solution was then cooled down to room temperature, and precipitated in an excess of methanol. The precipitation was filtered, washed with hot deionized water and hot ethanol

Table I. Physicochemical Properties of PAEK-co-x%BI Copolymers

Polymer	DMAc [a]	DMF [b]	NMP [c]	DMSO [d]	CHCl$_3$ [e]	THF [f]	C$_6$H$_6$ [g]	H$_2$O	η_{inh} (dL g^{-1})	Yield (%)
PAEK	+ [h]	S [i]	+	− [j]	+	+	+	−	0.57	90.5
PAEK-co-20%BI	+	+	+	−	S	+	−	−	0.57	91.7
PAEK-co-40%BI	+	+	+	S	−	S	−	−	0.58	90.2
PAEK-co-60%BI	+	+	+	+	−	S	−	−	1.32	92.8
PAEK-co-80%BI	+	+	+	+	−	−	−	−	1.01	91.7
PAEK-alt-BI	+	+	+	+	−	−	−	−	0.74	89.1

Tests were carried out in 0.5 g dL^{-1} solution in DMF at 25°C.
[a] N,N-Dimethylacetamide.
[b] N,N-Dimethyl-form-amide.
[c] N-Methyl-2-pyrrolidone.
[d] Dimethyl sulfoxide.
[e] Trichloromethane.
[f] Tetra-hydrofuran.
[g] Benzene.
[h] Soluble.
[i] Swollen.
[j] Insoluble.

alternately to remove residual solvent and salt, and finally dried under vacuum at 80°C for 24 h.

Membrane Preparation

5% (W/V) polymer solutions were prepared by dissolving PAEK-co-x%BI in DMAc, respectively. The polymer solutions were filtered through 0.45 μm Teflon microporous membranes to remove undissolved materials or dust particles, and casted on glass plates at ambient temperature. After slow solvent evaporation at 60°C for 12 h, films were elevated to 90°C and kept for 6 h. To get rid of the residual solvent completely, the films were further vacuum-dried at 110°C for 12 h, then peeled off. Membrane samples are of 40–50 μm in thickness.

Instruments

Proton nuclear magnetic resonance (^{1}H-NMR) spectra was recorded on a Bruker Avance III 500MHz spectrometer using DMSO-d_6 as a solvent. IR spectra of copolymer samples were recorded by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using Nicolet 6700 FTIR-spectrometer. Thermogravimetric analysis (TGA) was performed on a TGA Q50 V6.7 instrument with a heating rate of 20°C min^{-1} in N$_2$ and air. Each sample was preheated from room temperature to 180°C, and held for 30 min to remove the absorbed moisture, followed by cooling to 100°C. Differential scanning calorimetry (DSC) was measured on a TA DSCQ200 instrument (heating rate of 10°C·min^{-1} in N$_2$). First-order transition temperatures were reported as the minima of their endothermic peaks during second heating. Dynamic mechanical analysis (DMA) was performed on a TA Instrument DMA 2980. The analyzer was run in tensile mode at a frequency of 1 Hz and a heating rate of 5°C min^{-1} from 25 to 280°C with a helium purge. The tests of dielectric constant were carried out on a DS6000 DETA Tesla machine at a frequency spectrum of 0.1–50 kHz at 25°C.

Measurements

An Ubbelohde viscometer (capillary diameter is 0.6–0.8 mm) was employed to determine the inherent viscosity. A 0.5 g dL^{-1}

solution was obtained by dissolving the copolymer in DMF, of which the inherent viscosity was measured at 25°C (the temperature of solution). The inherent viscosities were calculated by using the following equation:

$$\eta_{inh} = \frac{\ln (t/t0)}{C} \tag{1}$$

where η_{inh} is the inherent viscosity, C is the concentration of polymer solution, and t, t_0 are the time of polymer solution and pure solvent flowing through the capillary of the Ubbelohde viscometer, respectively.

The gas transport properties were measured by using variable pressure (constant volume) method. Permeation properties of H$_2$, O$_2$, N$_2$, and CO$_2$ were measured. Ultrahigh-purity gases (99.99%) were employed for the experiments. The details of measurement were followed our previous work.[33,34] One approach used to estimate the permeability coefficients of polymers was illustrated as follows[12]:

$$\ln P = \varphi_1 \ln P_1 + \varphi_2 P_2 \tag{2}$$

where P is the permeability coefficient, φ is the mole fraction and subscripts 1 and 2 refer to the two homopolymers, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of PAEK-co-x%BI

Polymers of PAEK-co-x%BI were synthesized according to Scheme 1 described in Polymer synthesis (in case of PAEK-co-20%BI) section, respectively. Yields, listed in Table I, of all copolymers are higher than 89%.

Typically, PAEK, PAEK-co-40%BI, PAEK-co-60%BI, and PAEK-alt-BI were characterized by ATR-FTIR, respectively. As it shown in Figure 1, absorption bands 1642 cm^{-1} are assigned to stretching vibration of C=O groups, while bands at 1625, 1591, and 803 cm^{-1} are assigned to the characteristic peaks of benzimidazole rings. Also, it could be seen that the intensities of the two bands at 1625 and 803 cm^{-1} increase for the increased
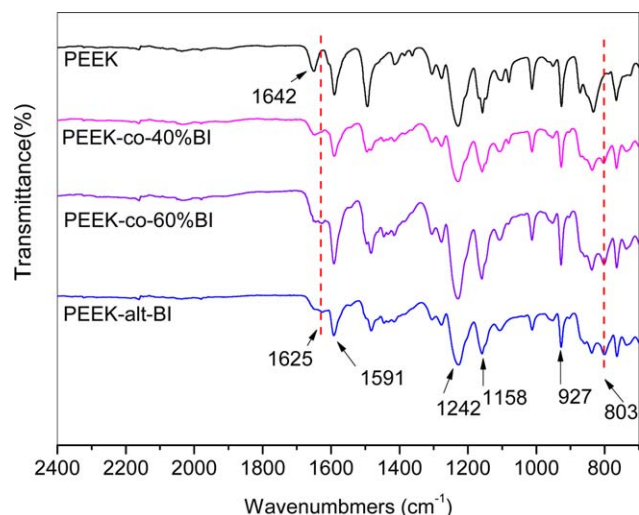
Figure 1. FTIR spectra of PAEK, PAEK-co-40%BI, PAEK-co-60%BI, and PAEK-alt-BI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content of benzimidazole moiety, the results are consistent with the proposed structure in our previous reports.[35,36] Absorption bands at 1242, 1158, and 927 cm^{-1} are attributed to the vibration of C–O–C groups, and vibration of aromatic rings in Ar–O–Ar and Ar–CO–Ar, respectively.

Chemical structure of polymer was further confirmed by ^{1}H-NMR in DMSO-d_6. Figure 2 shows the signal assignments in the field region of 1.5–14.0 ppm for PAEK, PAEK-co-80%BI, and PAEK-alt-BI, respectively. A peak at 13.0 ppm corresponding to N-H proton (denoted as H3) indicates the presence of imidazole ring in both PAEK-co-80%BI [Figure 2(b)] and PAEK-alt-BI [Figure 2(c)], which is in line with literature reported.[37] For PAEK-co-80%BI and PAEK-alt-BI, as increasing the content of benzimidazole moiety in the main chain, intensities of peaks at 7.23 (H1), 8.28 (H2), 7.95 (H4), 7.76 (H5), and 7.59 (H6) ppm increased, respectively. In addition, peaks at 1.71 (H10) ppm [Figure 2(c)] corresponding to C–H proton of methyl groups in PAEK-co-80%BI was observed while disappearing in PAEK-alt-BI, further verifying the chemical structure of PAEK-co-x%BI. Specially, integration of ^{1}H-NMR signals was used to evaluate the actual bi-benzimidazole (monomer of HPBI) content (BBC) in copolymers. The integration values of two types of peaks (H3 and H10) were calculated by using the following equation:
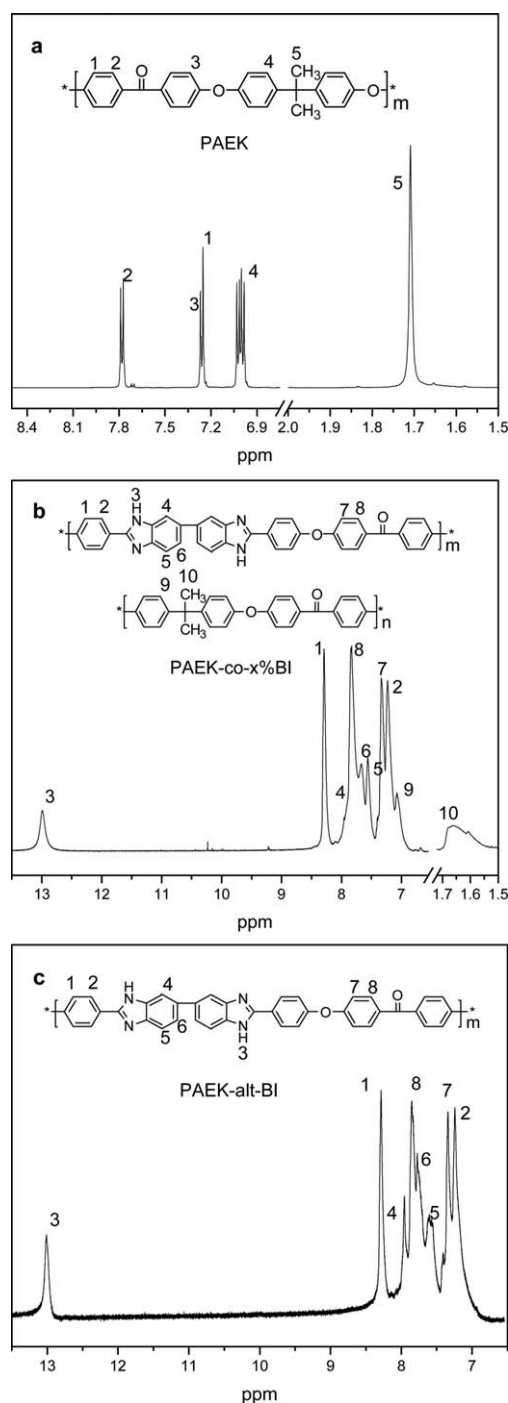
$$BBC = \left[\frac{3 \times H_3}{3 \times H_3 + H_{10}} \right] \times 100\% \qquad (3)$$

For example, the BBC of PAEK-co-80%BI was calculated as the value of around 74%, the calculated value agreed well with the theoretical one. Overall, the two methods used for structure characterization demonstrate that the target product was obtained.
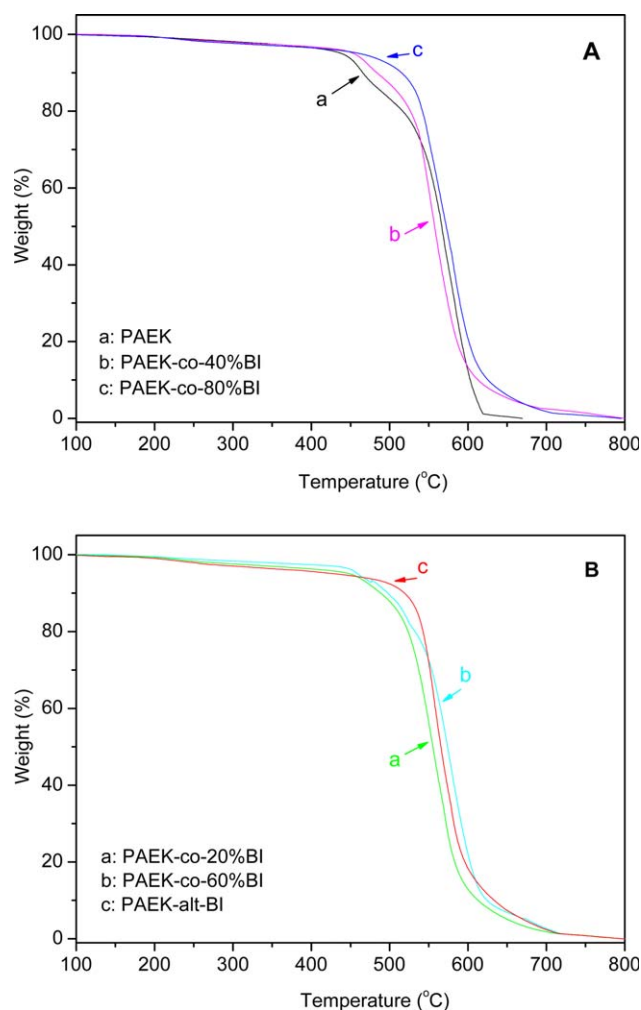
Solubility and Intrinsic Viscosity

The solubility of PAEK-co-x%BI was investigated in various solvents at 25°C. Reportedly, the introduction of methyl groups in PAEK could improve the solubility, especially in the case of all-

aromatic polymer.[38] As it shown in Table I, PAEK without modification, could be dissolved in some polar aprotic solvents and all other organic less polar ones. As expected, benzimidazole-containing polymers (BBC > 40%) are quite soluble in DMAc, DMF, and NMP, this trend is similar to those copolymers bearing benzoxazole from Lee's group.[39] Interestingly, in DMSO, the solubility of the PAEK-co-x%BI gradually enhances as the raise of benzimidazole content, whereas it becomes insoluble in less polar solvents such as THF, chloroform, and benzene. As it reported that the interchain hydrogen bonding and the strong

Figure 2. ^{1}H-NMR spectra of PAEK, PAEK-co-80%BI, and PAEK-alt-BI.

Figure 3. TGA curves (A and B) of PAEK-co-x%BI in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

main aspects: (1) the instinctive DFBP or BPA moieties dilute the concentration of benzimidazole units in the main chain, meanwhile, the methyl groups are beneficial for solubility; (2) the benzimidazole moieties possess both proton-donor (–NH–) and proton-acceptor (–N=) hydrogen bonding sites and exhibit specific interactions with polar solvents, making it readily dissolved in polar aprotic solvents for the solvation effect.

Intrinsic viscosities (η_{inh}) were detected to evaluate the molecule weight of polymers. From Table I, it is found that the η_{inh} attains its maximum at the content of 60%, then slightly decreases as increasing benzimidazole moiety. The crystallization effect of polymer segments leads to the precipitation of polymers from DMAc (as solve) prior to the formation of high molecule weight products, therefore, the further increased rigid-rod units might block this rising trend. This similar tendency was reported by Jian's and Hay's groups.[41,42] As for PAEK-co-x%BI membranes, all of them are transparent and tough, indicating that high molecule weight copolymers are obtained.

Thermal Stabilities

Thermal stabilities of PAEK-co-x%BI were determined by TGA under the air and nitrogen atmosphere, respectively. Typically, TGA curves in Figure 3 reveal that the weight loss onset of polymers in air is at around 480°C, it is most likely attributed to the decomposition of backbones. By incorporation of benzimidazole moiety, thermal stabilities of copolymers increase gradually. For example, in air, as benzimidazole content increased from 0 to 100%, the T_{max} increased from 559 to 574°C (see Table II). The elevated decomposition temperature could be ascribed to the incorporated thermostable heterocyclic architecture, which restricts the segmental mobility and hinders the chain rotation of polymer chains.[30] Similarly, Temperatures for 5% weight loss ($T_{5\%}$) of copolymers in N_2, are estimated to be a range of 459–521°C, which are accordance with our prior report (around 470°C).[35] The results could be compared with the phthalazinone-containing PAEKs of 431–508°C in N_2 from Cheng's group.[43] Obviously, all polymers in air show almost completed decomposition with the char yields of near 0 underwent from 553 to 576°C, while in N_2 estimated to be the char yields of 31.4–60.4%. The increased char yield in N_2, is due to the bigger mole percent of benzimidazole moiety, suggesting that the target polymers have been smoothly created also.

polarity of imidazole ring fatigue the dissolution of PBI in organic solvents.[31,37] Jana's group[40] reported that the initial monomer concentration in polymerization mixture played an important role in controlling the performance of PBI. In this case, the good solubility of PAEK-co-x%BI may account for two

Table II. Weight Loss Temperature and Char Yield of PAEK-co-x%BI Copolymers

Polymer	$T_{5\%}$ [a] (°C)		T_{max} [b] (°C)		C_y [c] (%)	
	In air	In N_2	In air	In N_2	In air	In N_2
PAEK	438	459	559	553	0	31.4
PAEK-co-20%BI	445	464	563	557	0	31.3
PAEK-co-40%BI	451	485	567	564	0	42.3
PAEK-co-60%BI	458	497	568	568	0	50.9
PAEK-co-80%BI	462	517	570	574	0	60.4
PAEK-alt-BI	487	521	574	576	0	59.9

[a] Temperature for 5% weight loss, heating rate of 20°C min $^{-1}$.
[b] Temperature for the maximum weight loss rate, heating rate of 20°C min $^{-1}$.
[c] Char yield calculated as the percentage of solid residue after heating from 90 to 800°C.
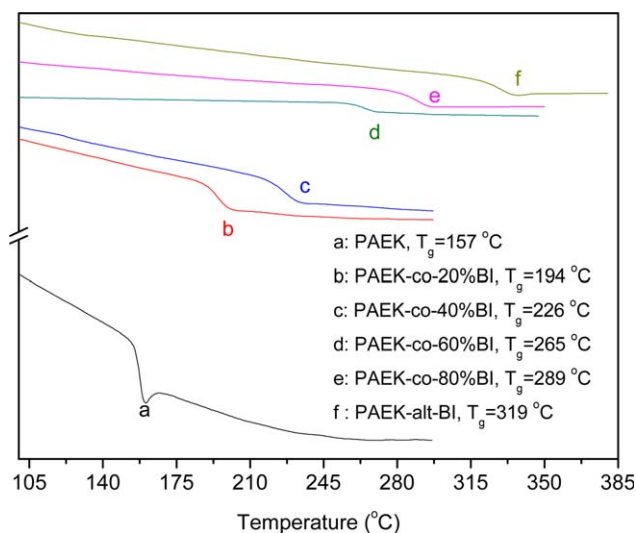
Figure 4. Glass-transition temperature curves for PAEK-co-x%BI copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DSC and DMA Investigations

T_g was measured by DSC. From Figure 4, one can see that the T_g's of polymers widely rise from 157 to 319°C, depending on the benzimidazole content, which are obviously higher than commercial PEEK of 143°C,[11] and simultaneously could be compared to the phthalazinone-containing PAEKs of 162–245°C,[41] amino-functionalized PAEKs of 190–197°C.[44] The high T_g's might be associated with two factors. One is that the introduced rigid-rod benzimidazole units lead to the decreased torsional mobility of backbones, because the additional repeat moieties improve the energy barrier of segmental mobility. Another one is due to the molecular packing structure governed by both hydrogen bonds and π–π interactions inter- and intramolecularly.[45,46] Besides, the unique T_g of each copolymer demonstrates that polymers are amorphous.

The expected T_g's of the random polymers were estimated by the Fox eq. (4) as follows:

$$\frac{1}{Tg} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \qquad (4)$$

Table III. T_g's of PAEK-co-x%BI Copolymers Tested by DSC and DMA

| Polymer	T_g's (°C)		
	By DSC		By DMA
	Measured	Calculated	
PAEK	157	–	150
PAEK-co-20%BI	194	178	187
PAEK-co-40%BI	226	206	226
PAEK-co-60%BI	265	238	264
PAEK-co-80%BI	289	275	ND
PAEK-alt-BI	319	–	ND

ND: not detected.

where W_1 and W_2 are weight fractions, T_{g1} and T_{g2} are the T_g's of two homopolymers, respectively. Surprisingly, as it illustrated in Table III (T_g by DSC), the measured T_g's are almost in line with the calculated values by the Fox equation. However, the calculated results from the Fox equation are slightly lower than that of measured results. The deviation of T_g from the theoretical predictions in copolymers might be accounted for that the hydrogen bondings between the N–H group of imidazole and C=O of arylene ether ketone structure, providing the specific interaction for intermolecular packing.[45–47] On the other hand, the difference of conformation between PAEK and PAEK-alt-BI homopolymers may not be negligible.[12,45,46]

Dynamic mechanical properties were investigated by dynamic mechanical analysis (DMA) from 25 to 280°C (due to the temperature limitations of DMA equipment), to further confirm the T_g's of PAEK-co-x%BI. Figure 5 shows the curves of storage modulus vs. temperature for PAEK, PAEK-co-20%BI, PAEK-co-40%BI, and PAEK-co-60%BI. Four similar storage modulus drops over the temperature range of 100–150°C are observed, but there are different reasons for them. For PAEK, the storage modulus drop was accelerated by the segment mobility of polymer matrix when the testing temperature (around 150°C) got close to the T_g (157°C, by DSC). As the temperature further evaluated, storage modulus dropped dramatically at around 200°C again, indicating the viscoelastic state achieved. Similarly, fall of storage modulus of benzimidazole-containing PAEK occurred at around 150°C. However, unlike PAEK, the T_g's (194–265°C by DSC) of benzimidazole-containing PAEK are much higher than 150°C (see Table III), it is concluded that the rigid-rod backbones contribute less to the fall of storage modulus at around 150°C, whereas, the drops possibly are due to the damage of interactions (e.g., hydrogen bonds) in polymer matrix. As increasing the temperature further, slight drops are observed at around 190, 220, and 260°C, which are due to the segment mobilities of PAEK-co-20%BI, PAEK-co-40%BI, and PAEK-co-60%BI matrix, respectively. The results will be further confirmed by T_g testing by DMA. T_g's by DMA in Table III
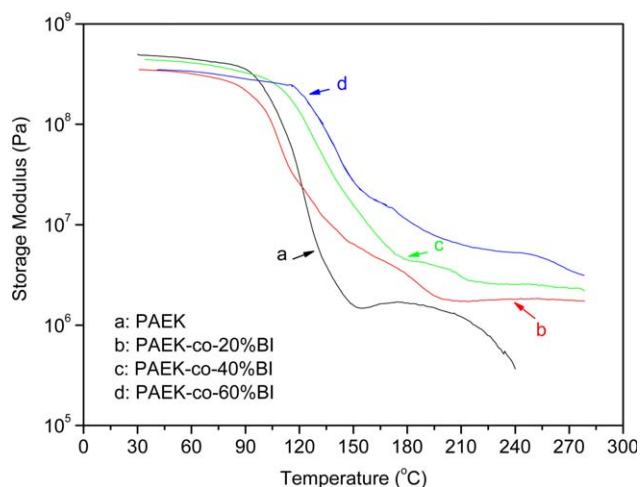
Figure 5. Storage modulus dependence of temperature curves for PAEK-co-x%BI membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
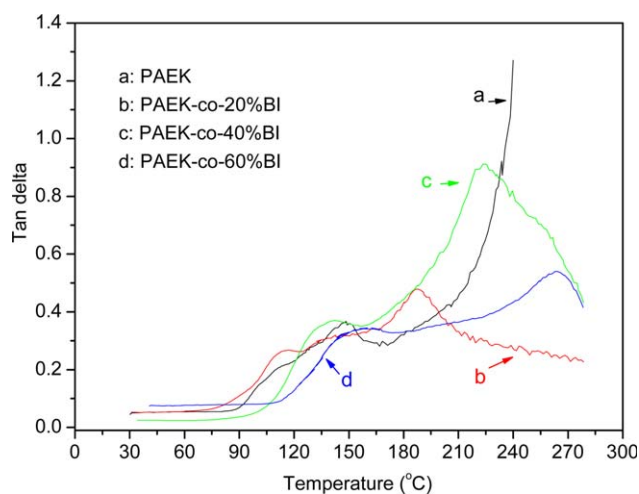
Figure 6. Tan delta dependence of temperature curves for PAEK-co-x%BI membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were obtained from tan δ versus temperature plots (see Figure 6). One can see that the secondary relaxation peaks (around 120–150°C) appear and become more distinguishable as the addition of the benzimidazole moiety, which are possibly related to the specific interactions that have been discussed above from Figure 5. Besides, the T_g's detected by both the DMA and DSC in Table III are tallying each other quite well. As expected, the T_g's are high enough to allow for high performance thermoplastic processing treatment.

Dielectric Properties

Dielectric analysis (DEA) was performed as a function of frequency ranging from 0.1 to 50 kHz at 25°C. As it shown in Table IV, dielectric constants of PAEK-co-x%BI show a weak frequency dependence, and tend to decrease slightly or stay almost constant as the increased frequency over the setting range. Reportedly, when a group of atoms with a permanent dipole align are responding to an electric field, dipole polarization will lead to the redistribution of charges. In particular, alignment of permanent dipoles in solid state, requires reasonably more time than that electronic or atomic polarization at frequency of 10^9 Hz or even lower frequencies.[48] In this

case, dielectric constants of PAEK-co-x%BI were tested far below 10^9 Hz, therefore, the polarizable units of polymers could orient fast enough to keep up with the oscillations in the alternating electric field.[49] Besides, alignment of polar groups in electric field is generally varied with the changed conformation of polymers. However, the T_g's (157–319°C) of heterocyclic architecture of PAEK-co-x%BI are much higher than the testing temperature (25°C), these "frozen structures" greatly restrict the segmental mobility and the chain rotation in polymer matrix. It could be concluded that the limited polar groups and their disturbed orientation (carboxyl and imidazole groups), contribute greatly to the stable dielectric constants.

No strongly polar groups or substituents contained in polymers might be related to the considerably stable dielectric characteristics.[2,50] For PAEK-co-x%BI, there are both the polar carboxyl and imidazole groups in the main chains, therefore, effects of polar moiety on dielectric constants should be considered. As it shown in Table IV, bisphenol-based PAEK shows relatively low dielectric constants, it may result from the completely symmetrical structure of BPA moieties and the nonpolar methyl groups as well as the free volume caused by the space-occupying methyls in polymer matrix.[20] Interestingly, for all polymers at the same frequency, dielectric constants of PAEK-co-20%BI firstly decrease, it might be due to that the rigid-rod benzimidazole structure firstly disorganized the arrangement of PAEK-co-20%BI matrix and led to the increased free volume, when compared to PAEK. However, as the benzimidazole moieties further increasing from 40 to 100%, for example, the values gradually increased from 2.32 to 2.66 at 0.1 MHz. This may be explained by two aspects: (1) the polarity, where there are increased benzimidazole moieties with polar groups, would contribute to the higher dielectric constants and (2) the interactions, for example, hydrogen bonds help to compact the polymer matrix and reduce the free volume.[51] Thus, dielectric constant increases. Dielectric constants (2.25–2.66) of PAEK-co-x%BI are lower than that of commercial Ultem1000 (3.15, 1 kHz),[52] and some fluorinated PAEKs (2.70–8.82, 1 MHz,[20] 2.81–3.08, 1 MHz[53]), suggesting that these polymers with high T_g's might be potential to many applications, such as in electronic packaging and circuit board.

Table IV. Dielectric Constant (ε) of PAEK-co-x%BI Membranes at Different Frequency

Membrane	Dielectric constant					
	0.1 kHz	0.5 kHz	1 kHz	5 kHz	25 kHz	50 kHz
PAEK	2.41	2.37	2.35	2.31	2.28	2.27
PAEK-co-20%BI	2.32	2.30	2.29	2.28	2.27	2.25
PAEK-co-40%BI	2.46	2.44	2.43	2.42	2.40	2.40
PAEK-co-60%BI	2.54	2.52	2.51	2.50	2.48	2.48
PAEK-co-80%BI	2.57	2.54	2.53	2.51	2.49	2.49
PAEK-alt-BI	2.66	2.61	2.60	2.57	2.55	2.54
Ultem 1000	–	–	3.15 [a]	–	–	–

[a] Tested at 25°C. The data were obtained from literature.[52]

Table V. The Gas Separation Performance of PAEK-co-x%BI and Ultem 1000 Membranes

Membrane	Permeability (Barrer) [a]				Selectivity (α)		
	H_2	N_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
PAEK	6.13	0.052	0.382	1.59	118	7.35	30.6
PAEK-co-20%BI	5.84	0.053	0.396	1.61	110	7.47	30.4
PAEK-co-40%BI	5.47	0.048	0.340	1.47	114	7.08	30.6
PAEK-co-60%BI	6.01	0.062	0.390	1.63	97	6.29	26.3
PAEK-co-80%BI	5.83	0.044	0.344	1.72	132	7.81	39.1
PAEK-alt-BI	5.84	0.038	0.315	1.50	154	8.28	39.5
Ultem 1000	6.04 [b]	0.052 [c]	0.380 [c]	1.45 [c]	163 [b]	7.31 [c]	27.8 [c]

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cm Hg) [55].
[b] Tested at 25°C.
[c] Pure gas permeation measurements with 50 psia upstream for CO_2, CH_4, O_2, and N_2. Temperature: 35°C. [56]

Gas Transport Properties

Amorphous polymers with high T_g's are usually considered as good materials for gas separation membranes.[19] In this article, intrinsic gas transport properties of PAEK-co-x%BI membranes with high T_g's were discussed. Table V summarized the permeability coefficients and perm-selectivities (the ratio of pure gas permeabilities) of PAEK-co-x%BI membranes. The testing temperature was maintained at 35°C and the feed pressure was 0.2 MPa. One could see that the gas permeabilities tend to decrease slightly or stay almost constant as the raise of benzimidazole moieties, however, the selectivites of the gas pairs such as H_2/N_2, O_2/N_2, and CO_2/N_2 are increasing, this might result from those two methyl substitutions in PAEK that prevent the chain packing and lead to a relatively larger free volume. As it reported,[30] PBI is considered to be a base polymer for existing four nitrogen atoms per repeat unit, two of which has hydrogen atom bonded to them, forming hydrogen bonding (N–H group). In this case, the increased density of intermolecular hydrogen bonds enhanced the molecular packing of polymer matrix but reduced the openness and the free volume. As a result, the inhibited segment mobility increased the selectivity. It is also noted that the gas permeability coefficients decrease in the following order: $P(H_2) > P(CO_2) > P(O_2) > P(N_2)$, which agrees well with the increasing sequence of kinetic diameters of the gas molecules at critical temperature.[54] It demonstrates that these amorphous polymers are dominant of diffusion mechanism when gas permeating. In addition, permeabilities by calculation (the black) based on eq. (2) and experiment (the red) were described in Figure 7. It can be found that the experimental results of both plots are almost in agreement with the predicted values, indicating that chain-packing efficiency has a prominent effect on the gas permeation properties.

Commercial Ultem1000 is amorphous thermoplastic aromatic polyimide with a T_g of 217°C, containing ether (–O–) and isopropylidene [–C(CH$_3$)$_2$–] groups, which has been widely used as gas separation membranes due to its superior strength and chemical resistance.[55–58] Obviously, the PAEK-co-x%BI polymers have the similar groups and T_g's to that Ultem1000, therefore, it would be worth to compare the permeability and selectivity of PAEK-co-x%BI membranes with this commercial one. From Table V, one can see that permeabilities of H_2, N_2, O_2, and CO_2 from the two categories, are of the same order of magnitude, while, selectivities of O_2/N_2, CO_2/N_2 are slightly higher than that of Ultem1000. The results demonstrate that this type of PAEK-co-x%BI polymers is potential material for gas separation membrane.
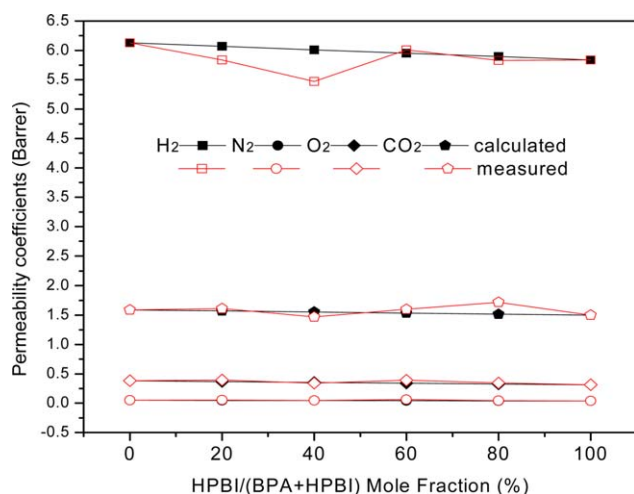
Figure 7. Permeability dependence of mole fraction of HPBI curves based on calculated and measured values for PAEK-co-x%BI membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

A series of novel thermally stable PAEK-BIs with content-tunable benzimidazole moiety were synthesized. All polymers synthesized are amorphous in nature. High molecular weight polymers could be readily achieved. These copolymers show good solubility and high T_g's ranging from 157 to 319°C. Meanwhile, the onset degradation temperatures (5% weight loss temperature) are above 438°C in air and above 459°C in nitrogen. The results demonstrate that the incorporation of benzimidazole moiety into these polymers helps to develop a novel high

performance polymers for low dielectric constant (2.25–2.66) and gas separation materials at high temperature.

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REFERENCES

1. Walker, K. A.; Markoski, L. J.; Moore, J. S. *Macromolecules* **1993**, *26*, 3713.

2. Ozden, S.; Charayev, A. M.; Shaov, A. H. *J. Mater. Sci.* **1999**, *34*, 2741.

3. Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, M.; Pakula, T. *Polym. Bull.* **2001**, *47*, 1.

4. Wang, F.; Chen, T.; Xu, J.; Liu, T.; Jiang, H.; Qi, Y.; Liu, S.; Li, X. *Polymer* **2006**, *47*, 4148.

5. Ohno, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3447.

6. Johnson, R. N.; Karnham, A. G.; Clendinning, F. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci. Polym. Chem.* **1967**, *5*, 2375.

7. Meng, Y.; Hlil, A. R.; Hay, A. S. *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 1781.

8. Meng, Y. Z.; Tjong, S. C. *J. Polym. Sci.* **2001**, *81*, 2687.

9. Bishop, M. T.; Karasz, F. E.; Russe, P. S.; Langley, K. H. *Macromolecules* **1985**, *18*, 86.

10. Xie, J.; Peng, W.; Li, G.; Jiang, J. *J. Fiber. Bioeng. Inform.* **2010**, *3*, 3.

11. Thomas, S.; Viskash, P. M. In Handbook of Engineering and Speciality Thermoplastics: Polyether Ether Ketones; Wang, J. W., Eds.; John Wiley & Sons, Inc., Hoboken, NJ, USA, **2011**, Vol. 3, Chapter 3, pp 61.

12. Chng, M. L.; Xiao, Y.; Chung, T. S.; Toriida, M.; Tamai, S. *Polymer* **2007**, *48*, 311.

13. Wang, S.; Meng, Y.; Hlil, A. R.; Hay, A. S. *Macromolecules* **2004**, *37*, 60.

14. Wu, T.; Liu, P. Q.; Shi, M. W.; Lu, J.; Yea, G. D.; Xua, J. *J. Polym. Int.* **2011**, *60*, 1318.

15. Zhang, Y. H.; Liu, Q. H.; Niu, Y.; Zhang, S. L.; Wang, D.; Jiang, Z. H. *J. Appl. Polym. Sci.* **2005**, *97*, 1652.

16. Shibata, M.; Cao, J. K.; Yosomiya, R. *Polymer* **1997**, *38*, 12, 3103.

17. Cao, J. K.; Su, W. C.; Wu, Z. W. *Polymer* **1996**, *37*, 20, 4579.

18. Robeson, L. M. *Solid State Mater. Sci.* **1999**, *4*, 549.

19. Khan, A. L.; Li, X.; Vankelecom, I. F. *J. Membr. Sci.* **2011**, *372*, 87.

20. Zhao, X. Y.; Liu. H. *J. Polym. Int.* **2010**, *59*, 597.

21. Volksen, W.; Miller, R. D.; Dubois, G. *Chem. Rev.* **2010**, *110*, 56.

22. Liu, B. J.; Wang, G. B.; Wei, H.; Jin, Y. H.; Chen, C. H.; Jiang, Z. H.; Zhang, W. J.; Wu, Z. W.; Yen, W. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 3392.

23. McHattie, J. J.; Koros, W. J.; Paul, D. R. *Polymer* **1992**, *33*, 1701.

24. Hellum, M. W.; Koros, W. J.; Husk, G. R.; Paul, D. R. *J. Appl. Polym. Sci.* **1991**, *43*, 1977.

25. Wang, Z. G.; Chen, T. L.; Xu, J. P. *Macromolecules* **2007**, *40*, 3238.

26. Wang, Z. G.; Chen, T. L.; Xu, J. P. *Macromolecules* **2000**, *33*, 5672.

27. Tocci, E.; Hofmann, D.; Paul, D.; Russo, N.; Drioli, E. *Polymer* **2001**, *42*, 521.

28. Ahn, T. K.; Kim, M.; Choe, S. *Macromolecules* **1997**, *30*, 3369.

29. Kim, T. H.; Kim, S. K.; Lim, T. W.; Lee, J. C. *J. Membr. Sci.* **2008**, *323*, 362.

30. Kumbharkar, S. C.; Karadkar, P. B.; Kharul, U. K. *J. Membr. Sci.* **2006**, *286*, 161.

31. Kumbharkar, S. C.; Kharul, U. K. *Eur. Polym. J.* **2009**, *45*, 3363.

32. Wang, F.; Chen, T.; Xu, J. *J. Macromol. Chem. Phys.* **1998**, *199*, 1421.

33. Wang, L. N.; Cao, Y. M.; Zhou, M. Q.; Liu, Q. H.; Ding, X. L.; Yuan, Q. *Eur. Polym. J.* **2008**, *44*, 225.

34. Wang, L. N.; Cao, Y. M.; Zhou, M. Q.; Zhou, S. J.; Yuan, Q. *J. Membr. Sci.* **2007**, *305*, 338.

35. Wang, J. L.; Yu, H. F.; Lee, M. H.; Zhang, S. G.; Wang, D. H. *J. Appl. Polym. Sci.* **2012** *124*, 3175.

36. Wang, J. L.; Song, Y. L.; Zhang, C.; Ye, Z. B.; Liu, H.; Lee, M.; Wang, D. H.; Ji, J. B. *Macromol. Chem. Phys.* **2008**, *209*, 1495.

37. Liu, Y.; Shi, Z. X.; Xu, H. J.; Fang, J. H.; Ma, X. D.; Yin, J. *Macromolecules* **2010**, *43*, 6731.

38. Ohno, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3447.

39. Li, J.; Lee, Y. M.; *Macromol. Chem. Phys.* **2006**, *207*, 1880.

40. Sannigrahi, A.; Ghosh, S.; Lalnuntluanga, J.; Jana T. *J. Appl. Polym. Sci.* **2009**, *111*, 2194.

41. Sun, Q.; Wang, J.; He, L.; Song, Y.; Jian, X. *J. Appl. Polym. Sci.* **2007**, *104*, 1744.

42. Meng, Y.; Hlil, A. R.; Hay, A. S.; *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1781.

43. Cheng, L.; Ying, L.; Feng, J.; Wang, C. Y.; Li, J. L.; Xu, Z. *J. Polym. Sci. Part A: Polym. chem.* **2007**, *45*, 1525.

44. Parthiban, A.; Le Guen, A.; Yansheng, Y.; Hoffmann, U.; Klapper, M.; Mullen K. *Macromolecules* **1997**, *30*, 2238.

45. Totsatitpaisan, P.; Nunes, S. P.; Tashiro, K.; Chirachanchai, Su. *Solid State Ionics* **2009**, *180*, 738.

46. Totsatitpaisan, P.; Tashiro, K.; Chirachanchai, S. *J. Phys. Chem. A* **2008**, *112*, 10348.

47. Hosseini, S. S.; Teoh, M. M.; Chung, T. S. *Polymer* **2008**, *49*, 1594.

48. Simpson, J. O.; St Clair, A. K. *Thin Solid Films* **1997**, *308*, 480.

49. Tang, H. L.; Yang, J.; Zhang, J. C.; Zhao, R.; Liu, X. B. *Mater. Lett.* **2011**, *65*, 2758.

50. Chen, B. K.; Du. J. U.; Hou, C. W. *IEEE Trans. Dielec. Electri. Insul.* **2008**, *15*, 127.

51. Chu, H. J.; Zhu, B. K.; Xu, Y. Y. *Polym. Adv. Technol.* **2006**, *17*, 366.

52. Vora, R, H.; Krishnan, P. S.; Goh, S. H.; Chung, T. S. *Adv. Funct. Mater.* **2001**, *11*, 361.

53. Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, M.; Pakula, T. *Polym. Bull.* **2001**, *47*, 1.

54. Pesiri, D. R.; Jorgensen, B.; Dye, R. C. *J. Membr. Sci.* **2003**, *218*, 11.

55. Monson, L.; Moon, S. I.; Extrand, C. W. *J. Appl. Polym. Sci.* **2013**, DOI: 10.1002/APP.37517.

56. Vu, D. Q.; Koros, W. J.; Miller, S. J. *J. Membr. Sci.* **2003**, *211*, 311.

57. Yen, H. J.; Wu, J. H.; Huang, Y. H.; Wang, W. C.; Lee, K. R.; Liou, G. S. *Polym. Chem.* **2014**, DOI: 10.1039/c4py00449c.

58. Saufi, S. M.; Ismail, A. F. *Carbon* **2004**, *42*, 241.