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Synthesis and characterization of hybrid organic-inorganic materials based on sulphonated polyamideimide and silica

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Abstract:

The preparation of hybrid organic-inorganic membrane materials based on a sulphonated polyamideimide resin and silica filler has been studied. The method allows the sol-gel process to proceed in the presence of a high molecular weight polyamideimide, resulting in well dispersed silica nanoparticles (<50nm) within the polymer matrix with chemical bonding between the organic and inorganic phases. Tetraethoxysilane (TEOS) was used as the silica precursor and the organosilicate networks were bonded to the polymer matrix via a coupling agent aminopropyltriethoxysilane (APTrEOS). The structure and properties of these hybrid materials were characterized via a range of techniques including FTIR, TGA, DSC, SEM and contact angle analysis. It was found that the compatibility between organic and inorganic phases has been greatly enhanced by the incorporation of APTrEOS. The thermal stability and hydrophilic properties of hybrid materials have also been significantly improved.

Keywords: sulphonated polyamideimide, silica, sol-gel process, hybrid materials

Introduction

Over recent years, the nanostructured organic-inorganic hybrid materials have received great attention as membrane materials due to the extraordinary properties of the hybrid materials. The hybrid nanostructured materials combine both the attractive properties of a mechanical and thermally stable inorganic phase and the specific chemical reactivity and flexibility of the organic phase [1-3]. The sol-gel process is one of the most efficient methods for the preparation of hybrid organic-inorganic materials by providing either specific molecular interactions or covalent linkages between phases. The advantage of the sol-gel technique for preparing hybrid materials is the low reaction temperature required (e.g. room temperature) which enables the incorporation of inorganic elements into organic materials without deterioration of their functionality [4-8]. The sol-gel method consists of an initial hydrolysis reaction and a subsequent condensation and then removal of the solvents, resulting in formation of a three-dimensional metal oxide network. These reactions are typically catalysed by an acid or a base and occur concurrently. Variables such as the alkoxide structure, the pH of the reaction medium, the type of solvent, the ratio of water and catalyst to the alkoxide, the reaction temperature and pressure, and the overall concentration of reactants all contribute to the final morphology and properties [8-11]. Under acid conditions, the hydrolysis reaction is more rapid than condensation reactions. As a result, acid-catalysted systems tend to consist of linear or random branches. On the other hand, base-catalysed systems tend to have highly branched non-interpenetrating clusters [12].

Most of the properties of hybrid materials are dependent on their structural and chemical composition as well as the dynamic properties inside the hybrid. A conglomerate of rigid oriented polyimide structures with a definite polarization, as well as the possibility of their interaction with the surrounding substrates via hydrogen bonds and other weak short-range forces, gives polyimides undisputable advantages over other polymers, and their unique chemical stability considerably extends the possibility of using these polymers for the treatment and desalination of water. However, the hydrophobicity of polyimides renders them susceptible to fouling by natural organic compounds in water treatment applications. This problem can be solved on the macromolecular level if methods are available for preparing structures with a hydrophilic component and a reliable rigid backbone segment. These provide, in turn, interchain packing with a very narrow free volume distribution [13-15].

In this study, a high molecular weight polyamideimide with a hydrophilic component ($-SO_3H$) was used as the raw polymer matrix material for the synthesis of the hybrid polyamideimide/silica materials. It was synthesized by direct polymerization using a diimide-dicarboxylic acid and sulphonated diamine monomers. There are two main reasons that we chose sulphonated polyamideimide. Firstly, aromatic polyamideimide bring together both high thermal stability and high permeability and permselectivity characteristics of polyimides and superior mechanical properties of polyamides. In particular, the polyamide unit can facilitate hydrogen bonding to other components having either a proton donor or a proton acceptor group [12, 15]. Secondly, both amide and sulphonating groups help to improve the hydrophilic properties of the hybrid materials, which is essential for this material to be used for water separation application.

One of the key issues for preparing a polymeric-inorganic hybrid material is the dispersion of the inorganic nanoparticles in the polymer matrix uniformly while aggregation is avoided. In the majority of previous studies, the inorganic phase is not covalently coupled to the polymer phase, and in many cases, aggregation of particles occurs. The influence of the interaction between the polymer and the inorganic component on the morphology of the hybrids is the primary concern. The aim of this study is to develop a highly dispersed homogeneous material of organic and inorganic phases on a nano-scale which could be potentially used for water separation membrane applications.

Experimental methods

Materials

1,3-Bis(3-aminophenoxy)benzene (TPE-R) was obtained from Chriskew Co., USA. 1,2,4-benzenetricarboxylic acid anhydride (also known as trimellitic anhydride, TMA), 2,5-diamino benzene sulfonic acid (2,5-DABS), 3-aminopropyltriethoxysilane (APTrEOS), tetraethoxysilane (TEOS), 1-methyl-2-pyrrolidinone (NMP, 99%) and dimethyl sulfoxide (DMSO, 99%), triethylamine (Et_3N), triphenylphosphite (TPP), pyridine and calcium chloride ($CaCl_2$) were obtained from Aldrich. All the chemicals were used as received and without further purification.

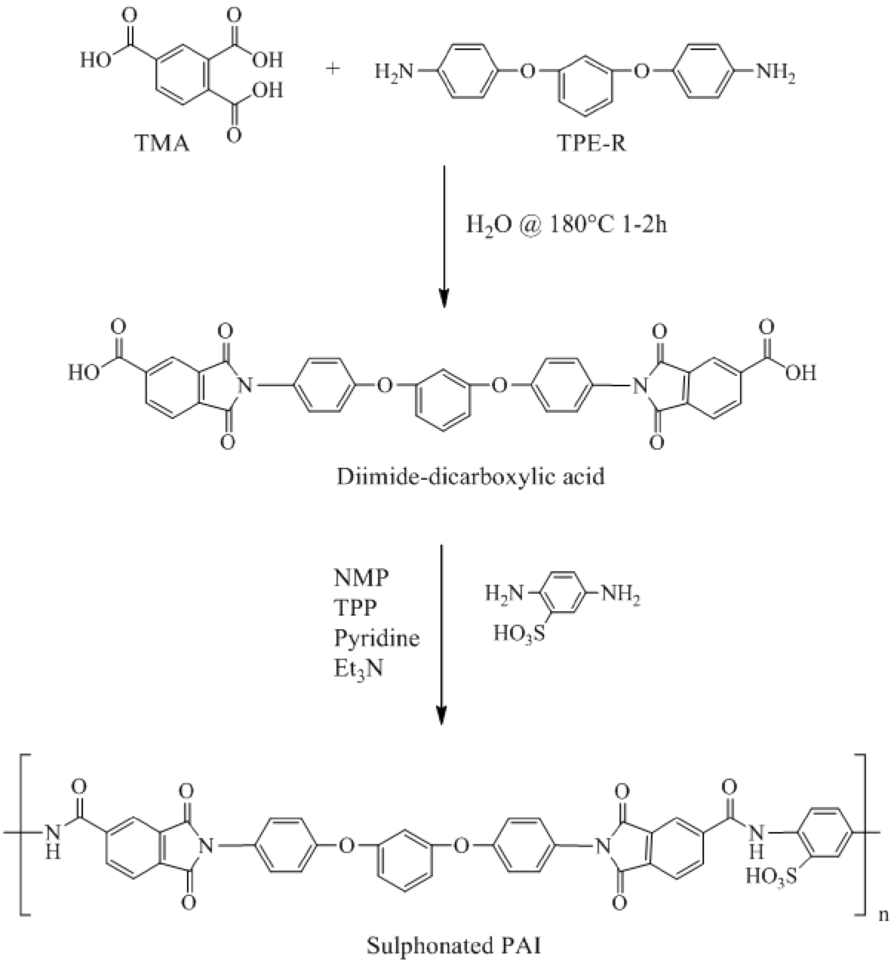

Figure 1. Synthesis scheme of sulphonated polyamideimide

Aqueous-based synthesis of the diimide dicarboxylic acid monomer using TMA and TPE-R

1,2,4- Benzenetricarboxylic acid anhydride (TMA) (11.52g, 60 mmol) was hydrolysed completely to the 1,2,4- Benzenetricarboxylic acid by stirring with degassed water (200ml) in a sealed Parr pressure vessel at 130°C for 1 hr. The vessel was allowed to cool to approximately 30-40°C before being opened. 1,3-Bis(3-aminophenoxy)benzene (TPE-R) (8.77g, 30 mmol) was slowly added to the Parr pressure vessel with rapid stirring. After several cycles of evacuation and flushing, a positive pressure of approximately 20 psi of nitrogen gas was applied to the vessel. The reaction mixture was heated to 180°C and held for 2 hr with stirring. After cooling, the off white product was removed from the reactor vessel, filtered and washed with hot water (100ml) and then methanol (100ml). The product diimide dicarboxylic acid was dried in vacuum oven at approximately 50 – 60°C overnight and collected as off white solid (18.17g, 90% yield).

δ_H (DMSO-d_6, 400 MHz) 8.40 (d, 2H, aromatic on TMA ortho to acid), 8.25 (s, 2H, aromatic on TMA ortho to acid), 8.05 (d, 2H, aromatic on TMA meta to acid), 7.45 (d and q, 4H aromatic on TPE-R ortho to imide and 1H aromatic on TPE-R middle ring meta to ether), 7.20 (d, 4H aromatic on TPE-R meta to imide), 6.85 (d, 2H, aromatic on TPE-R middle ring ortho to ether), 6.77ppm (s, 1H, aromatic on TPE-R middle ring ortho to ether). 13C (DMSO-d_6, 400 MHz) 166.3, 165.8, 157.8, 156.0, 136.5, 135.4, 134.9, 132.0, 131.4, 129.1, 127.2, 123.8, 123.3, 119.0, 114.0, 109.7ppm. FT-IR (cm^{-1}): 1782 (imide C=O sym), 1721 (imide C=O assym), 1698 (shoulder peak COOH), 1388 (C-N), 1226 (aromatic ether), 1102, 726cm^{-1} (imide ring deformation). DSC: T_m 333°C.

Synthesis of the sulphonated polyamideimide using monomers 2,5-DABS and the diimide dicarboxylic acid.

The diimide dicarboxylic acid described in Section 2.2.1 (TMA: TPE-R: TMA) (4.48g, 7.0 mmol) was dissolved in dry NMP (80ml). 2,5-DABS (90%, 1.4g, 7.7 mmole), dry triethylamine (2.0 ml), calcium chloride (3.0g, 27.0 mmol), triphenyl phosphite (7.0 ml), and dry pyridine (7.0ml) were added to the solution and refluxed over 4 h. The product was precipitated by pouring into a stirring solution of methanol (400 ml) and collected by filtration. The product was washed with hot water (2 x 200 ml), methanol (200 ml) and then stirred with 1.0N hydrochloric acid (50ml) at room temperature overnight. Finally the yellow solid product was collected by filtration and dried under vacuum at 50-60°C overnight and at 140-150°C over 12h (5.2g, 93% yield).

δ_H (DMSO-d_6, 400 MHz) 11.7 (s, N-H amide), 10.7 (s, N-H amide), 8.60-8.30 (m, 5H Ar-H), 8.25-7.90 (m, 5H Ar-H), 7.5 (d, 4H Ar-H), 7.2 (d, 4H Ar-H), 6.85-6.65 (m, 3H Ar-H). 13C (DMSO-d_6, 400 MHz) 166.5, 163.3, 162.0, 157.8, 156.0, 140.5, 136.4, 134.5, 132.8, 132.2, 131.8, 131.1, 129.6, 127.7, 124.5, 124.0, 122.7, 122.1, 120.6, 119.5, 114.3, 110.1ppm. FT-IR (cm^{-1}): 3282 (amide N-H), 1778 (imide C=O sym), 1723 (imide C=O assym), 1677 (amide C=O), 1380 (C-N), 1226 (aromatic ether), 1023 (S=O sym), 723cm^{-1} (imide ring deformation). GPC (DMF): M_n 42,000, M_w 73,000.

Synthesis of the polyamideimide/SiO_2 hybrid materials

The synthesis procedure for the polyamideimide/silica hybrid film is shown in Figure 2. At first, the sulphonated polyamideimide was dissolved in 1-methyl-2-pyrrolidinone (NMP) or dimethyl sulfoxide (DMSO) to obtain a homogeneous 7 wt% solution. Then the polyamideimide was functionalised by adding the predetermined amount of APTrEOS (Aldrich, 99%) into the solution and stirred for 2 hr. The degree of functionalisation with APTrEOS was controlled by varying the amount of APTrEOS added into the organic polyamideimide solution. Following this, the hydrolysed TEOS sol was added drop wise to the functionised solution under vigorous stirring. The reaction was kept for 2 hr at room temperature. The resulting homogeneous mixture was cast onto polypropylene dishes to the desired thickness and the solvent was removed slowly in a vacuum oven over a few days. Finally, the film sample was dried at 150°C to remove residual water and solvent. A pure sulphonated polyamideimide film sample was prepared as a control sample for comparison experiment.

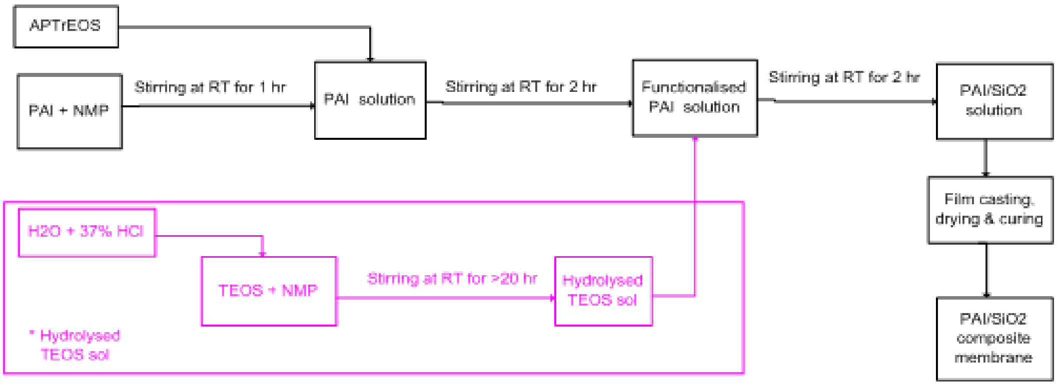

Figure 2. The preparation process of polyamideimide/SiO_2 hybrid membrane

The hydrolysed TEOS sol was obtained by the treatment of TEOS in NMP/H_2O, with a TEOS/NMP/H_2O mole ratio of 1:2.6:2.0 and a pH value of 2; similar to the conditions described by Cornelius et al. [8]. The stoichiometry of the TEOS and water was based on half the number of hydrolysable substituents in the TEOS. The pH of the solution was maintained by adding 37% HCl. The mixture was normally stirred for >20 hr at room temperature to allow the formation of a clear TEOS sol.

Material Characterisation

FTIR: Fourier transform infrared spectroscopy (FTIR) was performed on a Perkin-Elmer Spectrum 2000 FTIR instrument to assess the functional structure of sulphonated polyamideimide and hybrid film samples. FTIR spectra of thin films or KBr discs were obtained with an 8 cm^{-1} resolution, from 400 to 4000 cm^{-1} wavelength.

NMR: Nuclear magnetic resonance (NMR) was employed to confirm the molecular structure of the synthesised sulphonated polyamideimide using either a Bruker DRX 500 or a Bruker Av 400 NMR spectrometer. ^1H and ^{13}C NMR spectra were recorded in dimethyl sulfoxide (DMSO)-d_6 or deuterated chloroform ($CDCl_3$).

GPC: Molecular weights of the sulphonated polyamideimides were evaluated using a Waters 410 Gel permeation chromatography (GPC) instrument fitted with an RI detector. Tetrahydrofuran (THF) or N,N-dimethylformamide (DMF) was used as the eluent and polystyrene was used as the standard.

DSC: Differential scanning calorimetry (DSC) was conducted using a Mettler-Toledo DSC821e differential scanning calorimeter to assess the thermal properties of the sulphonated polyamideimide and hybrid film samples. The analysis was conducted under nitrogen with samples of approximately 5-10 mg at a scan rate of 10°C min^{-1} from 10 to 450°C.

TGA: Thermal stability of the hybrid film samples was assessed using a Perkin-Elmer Pyris 1 thermogravimetry analysis (TGA) instrument. Experiments were conducted on 3-5 mg thin film samples heated in flowing nitrogen at a heating rate of 20°C/min from 30 to 800°C.

Contact angle: The hydrophilic/hydrophobic properties of dried film samples were assessed by a KSV contact angle meter (CAM200) equipped with the video capturing system. Static contact angles were measured by the sessile drop method. About 8 μL of single water drop was formed on the levelled surface of the membrane for contact angle measurements.

SEM: The surface morphology of the hybrid film samples were studied by a Philips scanning electronic microscope (SEM) (ESEM Philips XL30). Energy dispersive X-ray spectrometry (EDS) was running by an EDAX detector on the SEM with a voltage of 15 kV and a working distance of 15 mm.

Results and discussion

Structure of sulphonated polyamideimide

The synthesis of the sulphonated polyamideimide is a two-step process as shown in Figure 1. The first step is the synthesis of a diimide-dicarboxylic acid monomer via an aqueous synthesis technology [16-18]. The second step in the synthesis involved the reaction of the diimide-dicarboxylic acid with 2,5-DABS using a standard polyamide synthesis technique[19].

The diimide-dicarboxylic acid monomer (TMA:TPE-R:TMA) was prepared by the condensation of an aromatic diamine (TPE-R) with two mole equivalents of benzene tricarboxylic acid (TMA) in water (Figure1). This one-step aqueous synthesis method is the most convenient method for synthesis of pure polyimides or diimide-dicarboxylic acids. The structure of the diimide-dicarboxylic acid monomer was confirmed by FTIR and NMR spectroscopy. The IR, ^{1}H and ^{13}C NMR data are listed in the synthesis of the sulphonated polyamideimide section and the NMR spectra are presented in Figure3, with peak positions assigned.

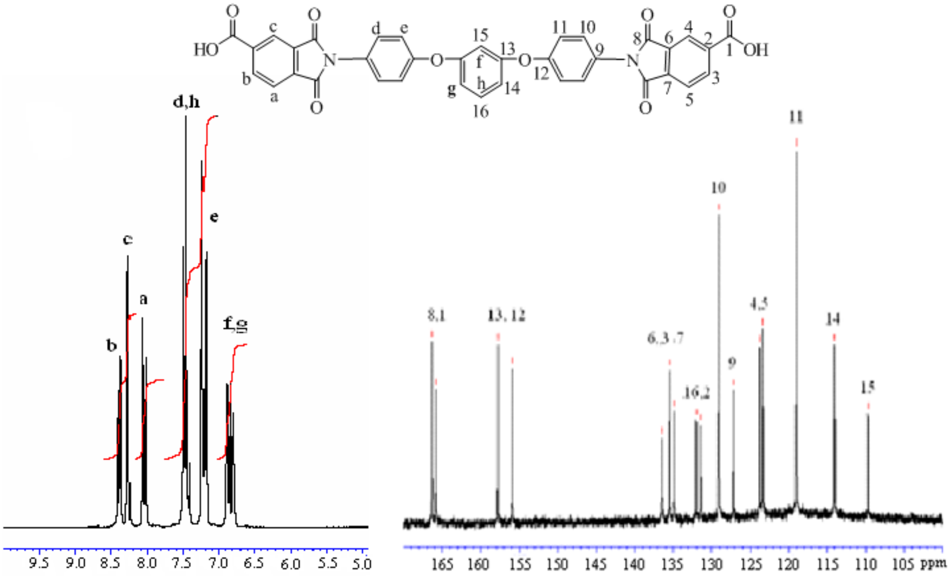

Figure 3. ^{1}H NMR and ^{13}C NMR spectra of diimide dicarboxylic acid monomer

The second step was prepared by a phosphorylation polycondensation of the diimide-dicarboxylic acid (TMA:TPE-R:TMA) with 2,5-DABS using triphenylphosphite (TPP) and pyridine as the condensing agents (Figure 1). Triethylamine (Et_3N) was used to liberate the protonated amino groups for polymerization with diimide-dicarboxylic acid [20]. The polymerization proceeded homogeneously throughout the reaction and gave a viscous polymer solution, and the product precipitated out in a powder form by pouring into methanol solution. The sulphonated polyamideimide was in the triethylammonium sulphonate form and was converted to the proton form by treating with 1.0 N hydrochloric acid at room temperature overnight. The completion of proton exchange was confirmed by the disappearance of the triethylamine peaks from the ^{1}H NMR spectrum of the sulphonated polyamideimide. The resulting sulphonated polyamideimide was obtained in high yield (93%) and high molecular weight (weight-average molecular weight of 73000 by DMF-GPC).

The structure of the polymer was identified by FTIR and NMR spectroscopy. The FTIR spectrum (Figure 4) shows a characteristic absorptions of the amide groups at 3282, 1677cm^{-1} and those of the imide absorption bands at 1778, 1723, 1380 and 723 cm^{-1} [21]. The disappearance of the carbonyl (C=O) absorption band of the carboxylic acid group at around 1698 cm^{-1} indicated that the amide formation was completed. The symmetric vibration of sulfonic acid (O=S=O) group appeared at 1023 cm^{-1} [21].

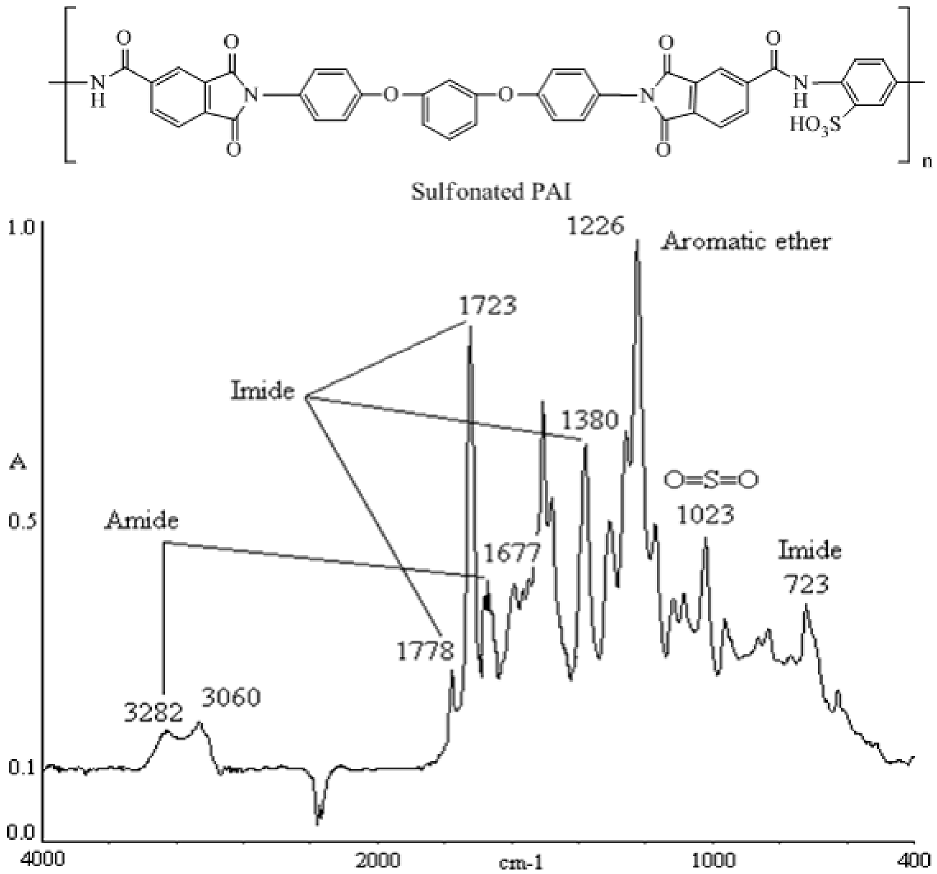

Figure 4. FTIR spectrum of sulphonated polyamideimide

The ^{1}H and ^{13}C NMR data are listed in the synthesis of the sulphonated polyamideimide section and main characteristic peaks are shown in Figure 5. Two characteristic amide (N-H) peaks at 11.7 and 10.7 ppm were assigned to N-H of amide ortho and meta to sulfonic acid group respectively. While the ^{13}C NMR shows the carbonyl of the imide groups at 166.5ppm and carbonyl of amide groups at 163.3 and 162.0 ppm, the carbonyl of carboxylic acid groups at 165.8 ppm was not observed in the spectrum. Once again this proved the completion of the amide formation and agreed well with the results provided by FTIR spectroscopy.

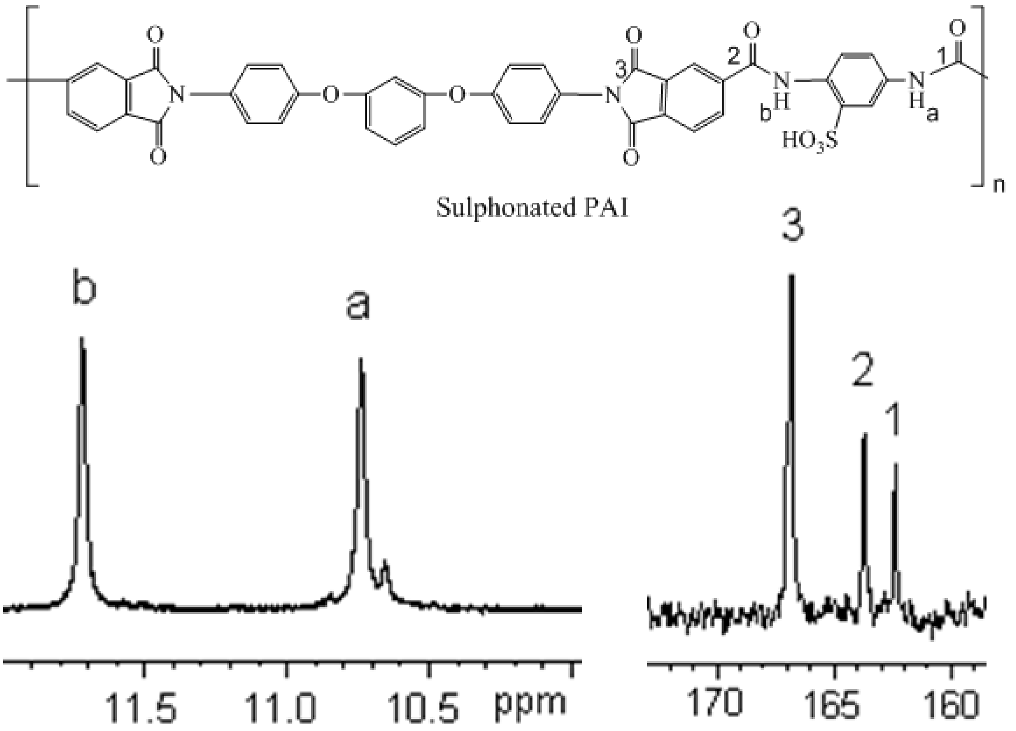

Figure 5. Main peaks of ^{1}H NMR and ^{13}C NMR spectra of sulphonated polyamideimide.

Structure of hybrid films

The proposed reaction scheme for synthesis of sulphonated polyamideimide/silica hybrid materials is shown in Figure 6. The sol-gel reaction was carried out in the NMP or DMSO solution with HCl as a catalyst. The sulphonated polyamideimide was firstly functionalised with the APTrEOS to create covalent bonds between the polyamideimide chain and the silica network. The end product consisted of organosilicate domains covalently bonded to a polyamideimide matrix, with the silane being introduced either as side groups or as part of the crosslinked structure.

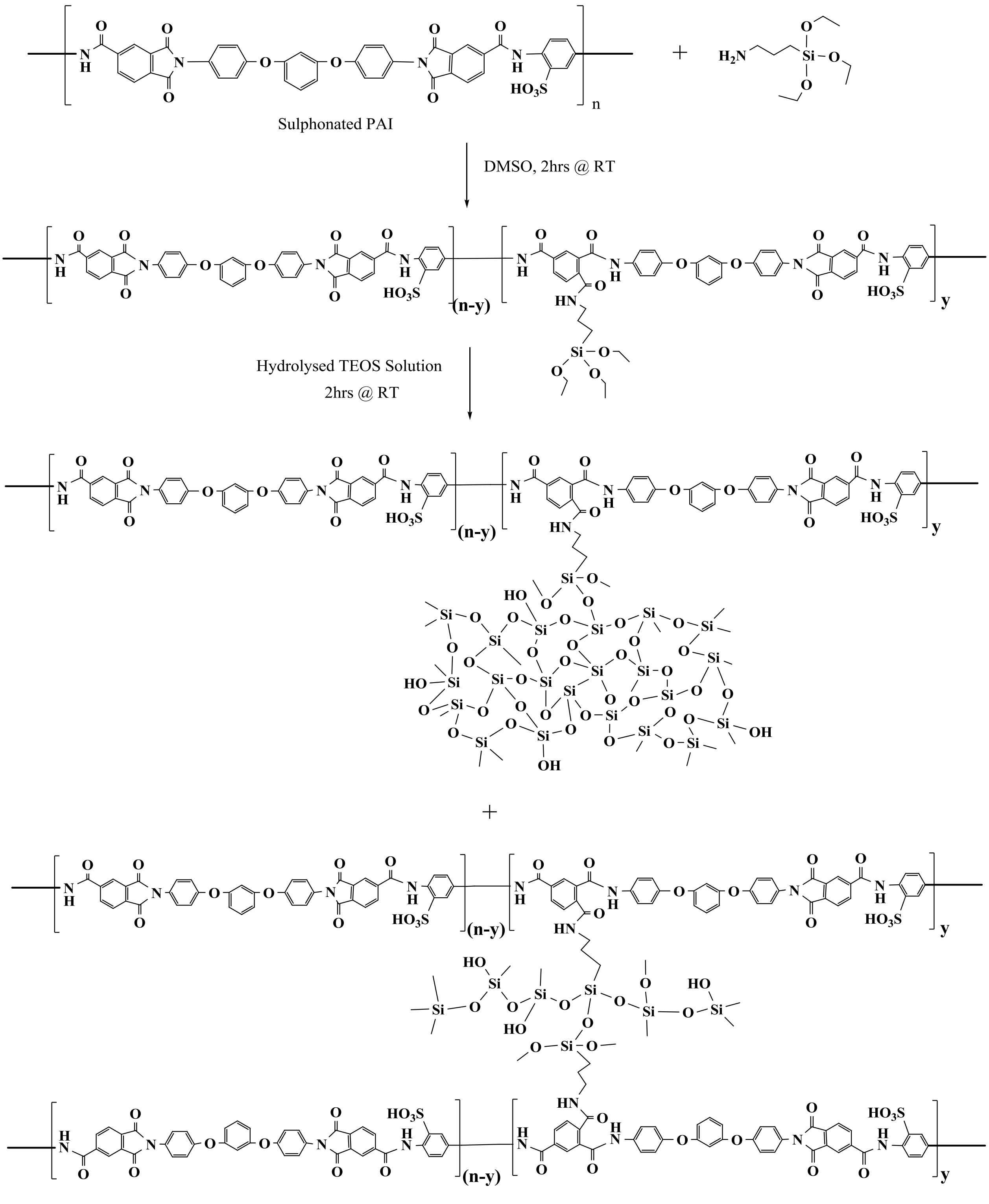

Figure 6. Reaction scheme of synthesis of sulphonated polyamideimide/silica hybrid materials.

In the reaction, APTrEOS was acting as a coupling agent. The amine group of APTrEOS opens the cyclic imide unit via nucleophilic attack on the carbonyl carbon [22]. This results in two amide bonds being formed, one to the silane moiety and one in the polymer backbone. Furthermore, the presence of the pendant APTrEOS groups on the functionalised polyamideimide facilitates chemical bonding with the hydrolysed TEOS sol via condensation reactions.

The structural feature of the hybrid films was confirmed by the FTIR spectroscopy. Figure 7 shows the typical FTIR spectra of polyamideimide and polyamideimide/silica hybrid thin film samples. The characteristic absorption bands of imide group were observed near 1778, 1723, 1380 and 723 cm^{-1}. The characteristic absorption bands of amide group were observed at 3282 and 1677 cm^{-1}. When compared with the pure polyamideimide sample (spectrum a), the polyamideimide/silica hybrid film sample (spectrum b) shows the peak intensity change for both amide and imide groups. The decreasing intensity of the imide group and the increasing intensity of the amide group indicated the decrease of the imide ring and increase of the amide unit. This clearly confirms the coupling reaction between polyamideimide and APTrEOS.

The FTIR spectrum of the polyamideimide/silica hybrid film (spectrum b) also shows the increase of the peak intensity at wavelengths 448, 960 and 1080 cm^{-1}. Peaks at 448 cm-1 (symmetric Si-O-Si stretch) and 1080 cm-1 (asymmetric Si-O-Si stretch) are attributed to the Si-O-Si inorganic networks [21]. The peak intensity at 960 cm^{-1} is attributed to the Si-OH group which was formed from the hydrolysis of TEOS. These spectral changes indicate that the chemical bonding between the organic and inorganic phases was successfully achieved by the sol-gel reaction.

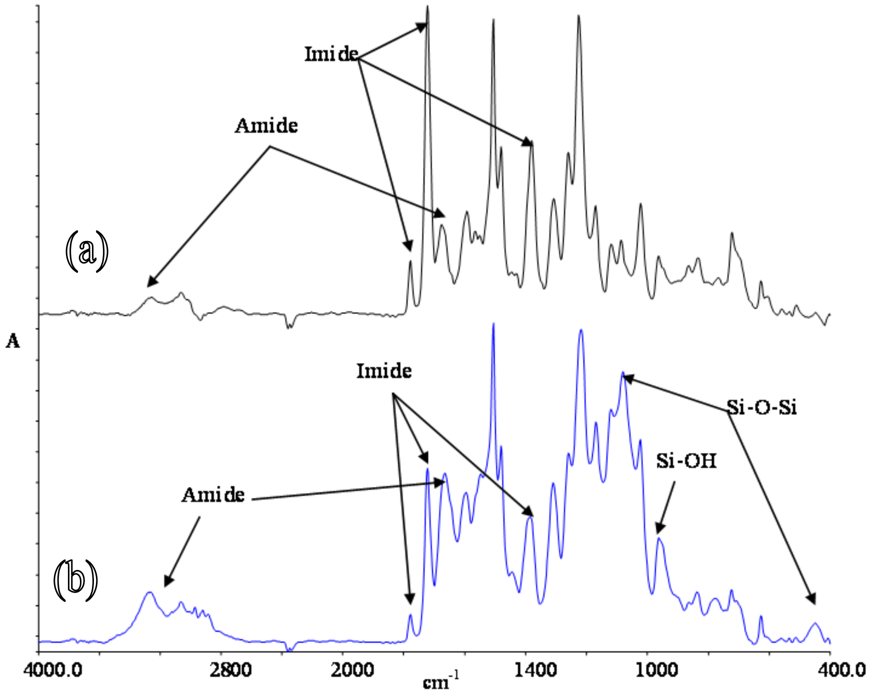

Figure 7. FTIR spectra of polyamideimide (curve a) and polyamideimide/silica hybrid (curve b) thin films.

Contact angle analysis

Hydrophilicity can be measured as the contact angle between the membrane surface and a drop of water placed on the surface of the membrane. Table 1 lists the water contact angles of hybrid polyamideimide/SiO_2 membranes. It was found the hydrophilicity of hybrid materials has been significantly improved when compared with the control sulphonated polyamideimide sample. This increase could be due to the hydrogen bonding of water to silanol groups that resulted from hydrolysis and condensation of TEOS.

Table 1: The water contact angle of hybrid films.

Samples	SiO_2 content, wt%	Contact angle
polyamideimide	0%	98°
Hybrid, 7 wt% SiO_2	7%	72°
Hybrid, 15 wt% SiO_2	15%	69°

Thermal properties

The thermal properties of the hybrid films were studied by TGA and DSC. Figure 8 shows the TGA of hybrid films with different silica contents. A pure polyamideimide was used as a control sample for comparison. Generally, there are three main decomposition stages for all samples. The first weight loss occurred around 100°C attributable to the loss of absorbed water and solvent in the materials. The second weight loss occurred at around 250°C possibly due to the loss of the sulphonated group (–SO_3H) and an aliphatic unit. In the third weight loss region (at temperatures >550°C corresponds to the thermal decomposition of the main chains of the polyamideimide.

The hybrid samples were found to have higher thermal stability than the pure polyamideimide. With the incorporation of silica particles, the decomposition temperature of main chain of the polymer increased from about 580 to 622°C and the degradation temperature for the sulphonated group from the polymer increased from 240 to 263°C. This could be explained by that the incorporation of inorganic particles made the polymer chain more rigid and tight. This reduced segmental mobility of the polymer chains and also inhibited chain packing, and hence improved the thermal stability of hybrid materials

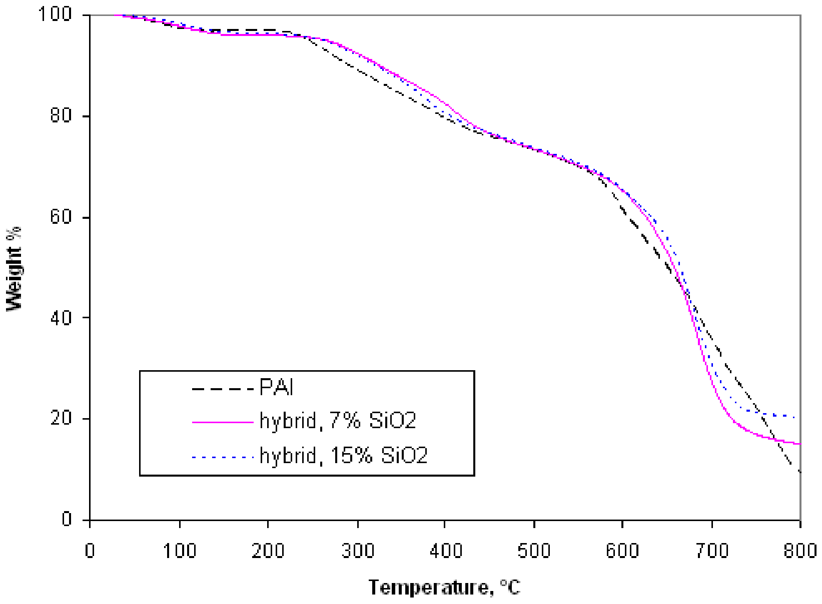

Figure 8: TGA of the hybrid films with different silica content.

Table 2 summarises the thermal properties of hybrid films including the TGA data and DSC results. All samples including the pure polyamideimide and the hybrid material revealed a good thermo-oxidative stability and a high glass transition temperature (T_g). There was no significant weight loss with the temperature up to 290°C. With incorporation of silica particles, both 5% and 10% weight loss properties were improved when compared with the pure polyamideimide sample. The residue weight increased with increasing silica content, indicating a general increase of the thermal stability. The increase in residue weight in the hybrid films was believed mainly due to the formation of silica. However, it was noted that the residue weight gain of the hybrid films from TGA analysis was lower than the theoretical silica content. This could be due to the fact that some of un-reacted TEOS were lost through vaporisation during the drying and heating stage. Similar finding was also reported by Yang et al. [23].

The enhancing effect of silica on the thermal stability of hybrid materials is also confirmed by the increase of T_g. The pure polyamideimide exhibited a T_g value of 194°C. With the introduction of silica, the T_g increased to 221°C when the silica content was 7 wt% and then to 234°C when the silica content was further increased to 15 wt% (Table 2). This could be explained by the tightness of the hybrid films. The incorporation of silica into the polymer matrix decreases the flexibility of the polymer chain and hence increases the T_gs of the hybrid.

Table 2: The thermal properties of hybrid films.

Sample	5% weight loss temperature (°C) [a]	10% weight loss temperature (°C)[a]	Residue (%)[b]	T_g (°C)[c]
Polyamideimide	244	290	9.2%	194
Hybrid, 7 wt% SiO_2	265	325	14.5%	221
Hybrid, 15 wt% SiO_2	261	323	20.4%	234

a. Temperatures at which 5% or 10% weight loss were recorded by TGA.

b. Residue weight (%) when heated to 800°C with TGA measurement.

c. Measured at a heating rate of 10°C/min with DSC measurement

Morphology

The surface morphology of the sulphonated polyamideimide/silica hybrid films was studied by SEM, with the results shown in Figure 9. It was found that the silica nanoparticles were well dispersed in the organic continuous phase. With the addition of APTrEOS (Figure 9-a), no silica particles greater than 50 nm or agglomeration could be observed in the SEM image. However, in the absence of APTrEOS (Figure 9-b), the silica particles were found in the range of 400-600 nm and spherical. This indicates that addition of APTrEOS promotes the formation of the organic-inorganic structure with the nano inorganic particles inter-perpetrating the polymer matrix.

To confirm the existence of silica in the hybrid film samples, energy dispersive X-ray spectrometry (EDS) experiments were also performed in SEM for two film samples with or without APTrEOS. For the sample with APTrEOS, EDAX analysis was conducted in a randomly selected area. In the case of the sample without APTrEOS, EDAX analysis was conducted on the observed particles. For both samples, a clear silicon signal was observed in the EDS spectra (Fig. 9), confirming the formation of silica. In addition, the Si signal does not dominate spectrum, indicating the silica has not phase separated from the surface of the film.

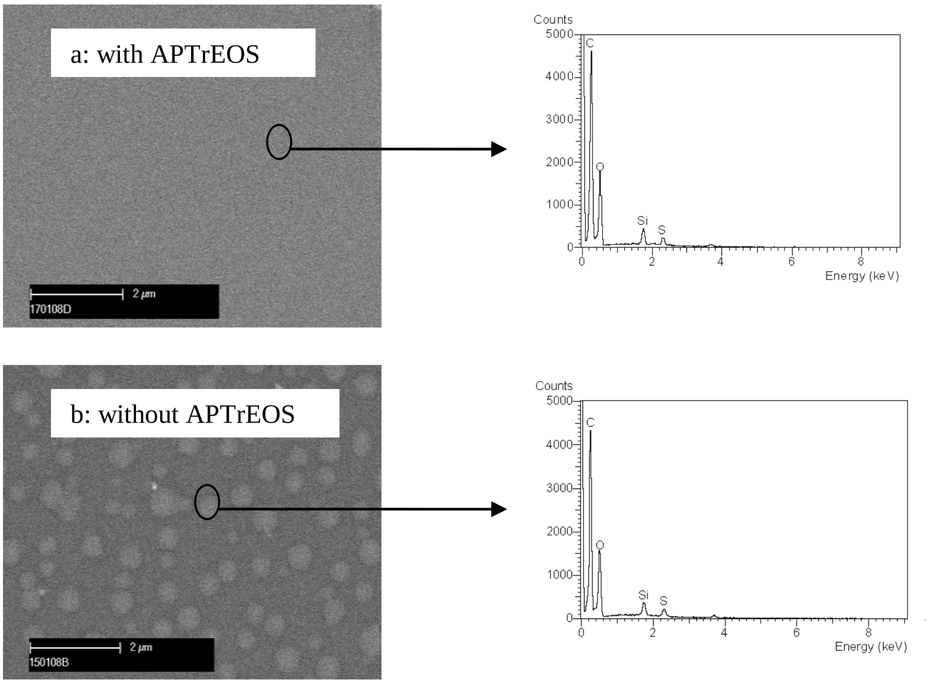

Figure 9: SEM images and EDS spectra of polyamideimide/silica hybrid film samples (all containing 7 wt% SiO2, a: with APTrEOS, b: without APTrEOS).

The optical appearance is a convenient way to judge the dispersing status of the inorganic phase in the polymer matrix for polymeric/inorganic composites. Transparency of the composite is a good indication that the inorganic phase in a polymer matrix is dispersed at the nano-scale. The introduction of chemical bonding between the polyamideimide and silica is believed to improve their compatibility and consequently the optical properties. To illustrate this, two film samples with identical silica content (15 wt% SiO_2) were prepared with or without APTrEOS bonding. It was observed the hybrid film sample with APTrEOS bonding appeared more transparent than the one without. This is because the coupling agent APTrEOS provided a link between the inorganic domains and the polymer matrix, and subsequently reduced the phase separation and led to smaller silica particles. Therefore, the sample appeared to be more transparent. The transparency feature of hybrid film sample provides additional evidence that the silica particles dispersed in the polymer matrix were at the nano-scale level.

Conclusions

In this work, a synthesis route for the fabrication of hybrid organic-inorganic materials based on sulphonated polyamideimide and silica via a sol-gel process was developed. A high molecular weight sulphonated polyamideimide synthesised via a two step process was used as the starting polymer and the silica was derived from two alkoxysilanes, APTrEOS and TEOS. The APTrEOS was found to provide bonding and improve the compatibility between the polyamideimide phase and the silica network. Highly homogeneous hybrid polyamideimide-silica films can be fabricated with well dispersed silica particles in the polymer matrix and chemical bonding between the organic and inorganic phases. The silica particles in the hybrid films were found to be less than 50 nm, resulting in improved optical properties of hybrid materials. The thermal stability and hydrophilic properties of hybrid materials were also improved with the incorporation of the silica nanoparticles.

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References

1. Ulbricht M (2006) Polymer 47(7):2217-2262.
2. Guo R, Ma X, Hu C, and Jiang Z (2007) Polymer 48(10):2939-2945.
3. Khayet M, Villaluenga JPG, Valentin JL, López-Manchado MA, Mengual JI, and Seoane B (2005) Polymer 46(23):9881-9891.
4. Schmidt H, Scholze H, and Kaiser A (1984) Journal of Non-Crystalline Solids 63(1-2):1-11.
5. Orgaz F and Rawson H (1986) Journal of Non-Crystalline Solids 82:57-62.
6. Brinker CJ and Scherer GW (1990) Sol-gel Science Harcourt Brace, Boston.
7. Keltz LW, Ejjinger NJ, and Melpolder SM (1986) Journal of Non-Crystalline Solids 83:353-360.
8. Cornelius CJ and Marand E (2002) Polymer 43(8):2385-2400.
9. Sanchez C and Ribot F (1994) New Journal of Chemistry 18:1007-1047.
10. Ying JY, Benziger JB, and Navrotsky A (1993) Journal of American Ceramic Society 76(10):2561-2570.
11. Livage J, Henry M, and Sanchez C (1988) Progress in Solid State Chemistry 18(4):259-341.
12. Hu Q, Marand E, Dhingra S, Fritsch D, Wen J, and Wilkes G (1997) Journal of Membrane Science 135(1):65-79.
13. Sazanov YN (2001) Russian Journal of Applied Chemistry 74(8):1253-1269.
14. Koros WJ (2002) Macromolecular Symposia 188(1):13-22.
15. Ohya H, Kudryavtsev VV, and Semenova SI (1996) Polyimide membranes - applications, fabrications, and properties. Kodansha Ltd., Japan.
16. Hawthorn DG, Hodgkin JH, Laycock BG, and Morton TC (2001) US Patent 6333391.
17. Chiefari J, Dao BN, Groth AM, and Hodgkin JH (2003) High performance polymer 15:269-2279.
18. Dao BN, Groth AM, and Hodgkin JH (2007) Macromolecular Rapid Communications 28(5):604-607.
19. Liaw D-J, Hsu P-N, and Liaw B-Y (2001) High Performance Polymers 13(2):S257-264.
20. Yin Y, Fang J, Watari T, Tanaka K, Kita H, and Okamoto K (2004) Journal of Materials Chemsitry 14:1062-1070.
21. Hummel DO and Scholl F (1988) Atlas of polymer plastic analysis. VCH publisher, New York.
22. Powell CE, Duthie XJ, Kentish SE, Qiao GG, and Stevens GW (2007) Journal of Membrane Science 291(1-2):199-209.
23. Yang C, Su Y, and Hsiao S (2007) Journal of Applied Polymer Science 104(6):4046-4052.