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Effects of Thermal Treatments and Dendrimers Chemical Structures on the Properties of Highly Surface Cross-Linked Polyimide Films

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We have conducted an extensive study to investigate the effects of thermal treatments and dendrimers' structures on the chemical and physical properties of the surface-modified polyimide films. The amidation and cross-linking reaction between G0 PAMAM dendrimers and polyimide were examined by XPS (X-ray photoelectron spectrometer) and FTIR-ATR (attenuated total reflection) measurements after thermal treatments under different temperatures. Moderate thermal treatment (120 °C) is proven to be able to induce the highly amidation reaction and to increase the degree of cross-linking on the polyimide surface. The gas separation performance of modified polyimide films is significantly improved due to the enhanced "molecular sieving" ability by dendrimer modification and the stronger interactions between the polyimide chains, such as covalent cross-linking bonding and hydrogen bonding. When the temperature of treatment reaches 250 °C, ^{1}H NMR and GPC test implied that the cross-linking structure between polyimide chains is broken and that the degradation of polyimide backbone chains also occurs. Gas permeation tests also indicated that high-temperature treatment of dendrimer-modified polyimide films is not beneficial to separation. In addition, the performance comparison between different dendrimers, PAMAM- and DAB-modified films, is carried out. The chemical structural differences in PAMAM and DAB dendrimers have also been verified as one of the important factors in determining the properties of modified polyimide films. At room temperature, PAMAM dendrimers show stronger cross-linking ability.

Introduction

Polyimide films are of widespread interest in electronics and gas separation applications because of their superior thermal, electrical, and membrane properties.[1−4] To enhance the selectivity and gas permeability of polyimides for gas separation, researchers have suggested that their polymer backbone chains must be stiffened by inhibiting the intra-segmental mobility and that the inter-segmental packing of polymer chains should be simultaneously prevented.[5] The syntheses of various polyimides containing different monomers have been carried out[6,7] as a means of modifying gas transport properties through changes in polymer solid-state structure.[8,9] These attempts appear to have reached the limit of the tradeoff curve for gas permeability and selectivity.[10,11] Therefore, an alternative method, cross-linking, has been developed as a means of altering membrane structure/performance and has utilized different techniques including ultraviolet (UV) light irradiation, high-temperature thermal treatment, and chemical modification.[12−28] With an increasing degree of cross-linking, higher gas selectivity can be achieved due to reduced intra-segmental polymer chain mobility. It has also been shown that a cross-linked structure will limit material swelling in the presence of plasticizing agents as well as promoting chemical and thermal stability. A negative attribute of polymer cross-linking is a decrease in gas permeabilities due to higher chain packing.

Novel cross-linking reagents, star-like dendrimers such as polyamidoamine (PAMAM) and diaminobutane (DAB),[29,30] have been recently reported.[31−33] The high-density functional groups at the surface or in the cavities of dendrimers offer numerous potential applications based on their chemical, physical, optical, multi-redox, and catalytic properties.[34,35] The high density of terminal amine groups in dendrimers provides a large number of reactive sites for cross-linking when used as a modifier for polymides and offers the potential to improve the gas selectivity and physical properties of those polyimide films. Alternatively, the large molecular size of dendrimers may prevent polyimide chains from packing when these two materials are combined. Moreover, the steric hindrance of dendrimers may restrict cross-linking modification to the surface of films, favoring high gas permeability. Dendrimers can play three important roles in this approach: (1) they are structural building blocks that provide multiple covalent branching sites for amidation to construct the cross-linked network; (2) they act as spacers in the polymer matrix that prevents the chain from packing; and (3) they offer free amine groups with strong affinity for CO_2 and facilitate the transport of that permeant gas.[36−38] Thus, the surface modification of polyimide films by dendrimers is a potential approach to obtain materials with better gas separation performance.

The objective of this paper is to describe the effects of thermal treatment on the chemical and physical properties of dendrimer-modified polyimide films. The surface modification of the polyimide during thermal treatment was characterized by FTIR-ATR (attenuated total reflection), XPS (X-ray photoelectron spectroscopy),

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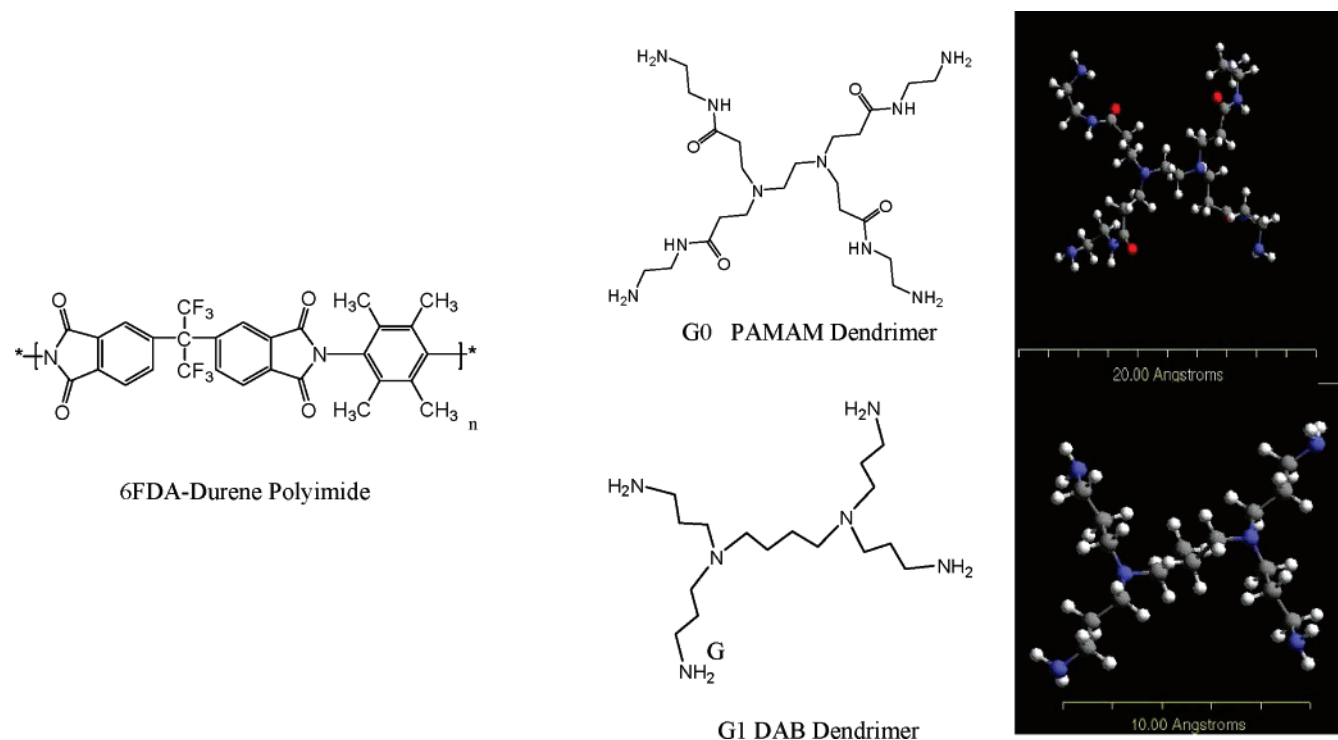† National University of Singapore.
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Figure 1. Chemical structure of polyimide and dendrimers.

¹H NMR (nuclear magnetic resonance), and GPC (gel permeation chromatography). Gas permeation measurements were used to understand the effect of dendrimers on separation properties of modified polyimide membranes. UV absorption spectroscopy was also carried out to detect the charge transfer between polyimide chains. The modification efficiencies of two different dendrimers, G0 PAMAM and G1 DAB, were compared under different treatment conditions.

Experimental Section

Materials. The polyimide material studied in this work was synthesized in our lab from 2,2′-bis(3,4′-dicarboxyphenyl)hexafluoropropane diandydride (6FDA) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine). 6FDA was sublimated before use, durene diamine was recrystallized from methanol, and NMP (*N*-methyl-pyrrolidone) was distilled at 42 °C under 1 mbar after drying with molecular sieve before use. Dichloromethane and methanol were used as received. Methanol (20 wt %) solutions of PAMAM generation 0 dendrimer and pure DAB generation 1 dendrimer were purchased from Aldrich. The chemical structure of 6FDA-durene polyimide and the planar schematic structure of these two dendrimers are shown in Figure 1. A stoichiometric 6FDA was added to a durene diamine solution of NMP with stirring under argon at room temperature. After reaction for 24 h, acetic anhydride and triethylamine (4:1 molar ratio) were slowly added to the solution to perform imidization for 24 h. After precipitation in methanol, the polymers were filtered and dried under 150 °C in a vacuum for 24 h.

Dense Membrane Preparation and Modification. Polymer dichloromethane (2% w/w) solutions were cast onto silicon wafers at ambient temperature to obtain dense films. Subsequently, the dense membranes were dried in a vacuum oven at 250 °C. Only the membranes with a thickness from 45 to 50 μm were used in the following studies. For surface modification, 5 wt % methanol solutions of dendrimers were prepared. The modification was carried out by immersing the polyimide films into above 5 wt % dendrimer solutions for a fixed period of time. After washing away the residual dendrimers on the surface with fresh methanol, the modified films were dried at ambient temperature for more than 24 h or were thermally treated in a vacuum oven at the setting temperature for 2 h.

Characterization. The weight loss of modified polyimide films during thermal treatment was characterized by a TGA 2050 thermogravimetric analyzer (TA Instruments). The analysis was carried out with a ramp of 10 °C/min at the temperature range from 100 to 800 °C. The purge gas for balance was N$_2$, and its flow rate was controlled at 50 mL/min.

The gel contents of the modified films were measured by extracting the films in dichloromethane for 24 h, after which time the insoluble fractions were dried to constant weight at 150 °C in a vacuum oven for 24 h. The weights of polymer films before and after extraction were measured. The gel contents were calculated by

$$\text{gel \%} = W_1/W_0 \times 100$$

where W_0 and W_1 are the original weight and the insoluble fraction weight of the polyimide films, respectively. The error of gel content test is around 0.5%.

The molecular weights of the modified polyimide were determined by gel permeation chromatography (GPC) measurements, which were carried out on a HP 1100 HPLC system equipped with the HP 1047A RI detector and the Agilent 79911GP-MXC columns. Tetrahydrofuran was used as the solvent, and the flow rate was controlled as 1.0 mL/min. The polymer was dissolved in tetrahydrofuran at a concentration of 0.005 wt %. The molecular weights were estimated by comparing the retention times in the column to those of standard poly(styrene).

FTIR-ATR measurements were carried out using a Perkin-Elmer FTIR microscope at 8 cm^{-1} resolution over the 500−2200 cm^{-1} range. Each sample was scanned 20 times. The XPS measurements were carried out by an AXIS HSi spectrometer (Kratos Analytical Ltd., England) using a monochromatized Al Kα X-ray source (1486.6 eV photons). All core-level spectra were obtained at a photoelectron takeoff angle of 90° with respect to the sample surface. UV absorbance spectra were obtained on a Beckman DU-65 spectrophotometer. A Bruker 400 MHz NMR spectrometer was used for recording ^{1}H NMR spectra of polyimide in the region of 0−12 ppm at room temperature using CDCl$_3$ as a solvent. Chemical shifts (δ) are given in ppm with tetramethylsilane as an internal standard.

Gas Permeation and Sorption Measurements. Gas permeabilities were obtained by a constant volume method at 35 °C and 10 atm in the sequence of CH$_4$ and CO$_2$. The pressure of CO$_2$ was varied from 2 to 30 atm for the plasticization test. A detailed description of the permeation cell design and testing conditions can be found elsewhere.[39] The modified films were mounted onto the permeation cell and vacuumed at 35 °C for more than 24 h before the gas permeation test was carried out. The permeability of each gas was obtained from the average value of at least three tests with a difference smaller than 1%, and each test was carried out at an interval of 6−8 h. The ideal selectivity is defined as follows: $\alpha_{A/B} = P_A/P_B$, where P_A and P_B are the permeabilities of pure gases A and B, respectively.

CO$_2$ and CH$_4$ sorption tests were conducted for the modified polyimide films using a Cahn D200 microbalance sorption cell at 35 °C, which is the same temperature as the gas permeation tests. The microbalance was first calibrated with gas as a function of pressure. Then approximately 200 mg of the film material was placed on the sample pan, followed by evacuation for 24 h. Pure gas was fed into the sample chamber from 0 to 25 atm and was allowed to sorb in the polymer sample until sorption equilibrium was established. From the weight gain, the amount of gas dissolved in the material was calculated after accounting for the buoyancy correction.[40] The solubility coefficients of polymers at 10 atm were calculated from

$$S = C/p = k_D + C_H'b/(1 + bp)$$

The sorption parameters in the equation, k_D (cm^3 (STP)/cm^3 atm), C_H' (cm^3 (STP)/cm^3), and b (1/atm) were obtained from the nonlinear least-squares fitting method based on pressure and fugacity, respectively. The diffusion coefficients were calculated for the pure gases using the measured values of permeabilities and solubility coefficients by $D = P/S$, where D is the diffusivity coefficient, P is the permeability, and S is the solubility coefficient.

Results and Discussion

Effects of Thermal Treatment on PAMAM Dendrimer-Modified Polyimide Films. TGA was used to investigate the thermal stability of PAMAM-modified polyimide. As shown in Figure 2, the original polyimide is thermally stable up to 500 °C, whereas the polyimide treated with dendrimer for 24 h showed the onset of degradation at approximately 200 °C. From Balogh et al.'s report,[41] we have already known that thermal degradation of pure PAMAM dendrimers starts around
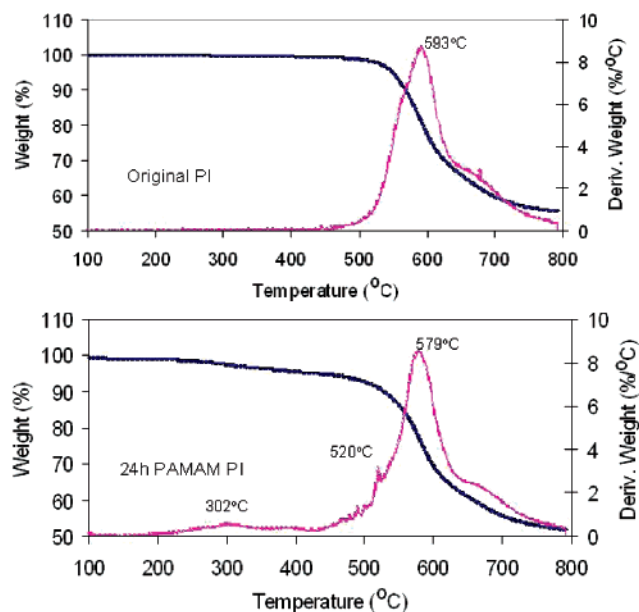

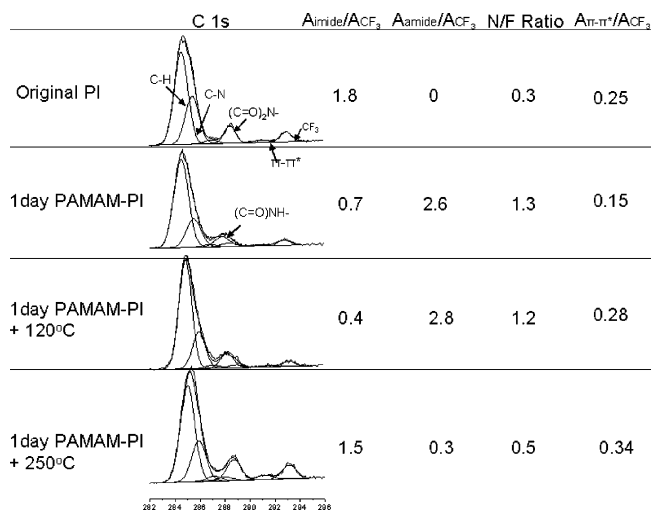**Figure 2.** TGA of PAMAM dendrimer (G0)-modified 6FDA-polyimide films.

Figure 3. XPS analysis of the original and modified polyimide films.

120 °C for retro-Michael process and transamidation. The most of weight loss of PAMAM dendrimers occurs near 300 °C for thermal decomposition. Therefore, the weight loss of PAMAM modified polyimide between 200 and 500 °C may be attributed to the decomposition of PAMAM dendrimers. Moreover, an unexpected decrease in thermal stability of the polyimide is observed after the polyimide was treated with PAMAM dendrimers. The decomposition temperature of polyimide under nitrogen has decreased from 593 to 579 °C after dendrimer treatments. Additionally, a small decomposition peak at 520 °C also appears. Therefore, the heat treatment temperatures for dendrimer-modified polyimide films were chosen at 120 and 250 °C under vacuum condition to bracket the observed TGA degradation onset.

XPS experiments that provide information about the quantity and chemical state of elements on the surface of modified films were used to verify the chemical reactions occurring on the polyimide surface. Figure 3 presents the N/F elemental ratio for the original and modified polyimide surfaces. During the modification
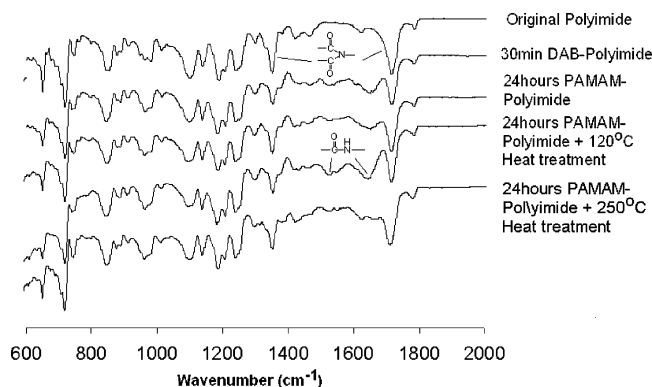
Figure 4. Comparison FTIR-ATR spectra of the original and modified polyimide films.

process, the fluorine content in polyimide samples is expected to remain constant. Hence the increased nitrogen content after 1 d of PAMAM modification indicates the loading of PAMAM on the surface of polyimide. The N/F ratio is almost the same for modified polyimide films with or without heat treatment at 120 °C. This finding implies that the PAMAM dendrimer is thermally stable at 120 °C. When cured at 250 °C, the N/F ratio decreases from 1.2 to 0.5, indicating the release of decomposed PAMAM dendrimers. Figure 3 also displays the respective C 1s core-level spectra. The C 1s core-level spectrum of the original polyimide membrane can be curve-fitted to six peak components, having bond energies at 284.6 eV for the **C**−H species, at 285.8 eV for the **C**−N and **C**−(C=O) species, at 286.8 eV for the **C**−(CF$_3$) species, at 288.4 eV for the N(C= O)$_2$ (imide) species, at 291.1 eV for the $\pi-\pi^*$ transition due to aromatic ring structure, and at 292.8 eV for the **CF$_3$** species.[42] The peak at 292.8 eV for the CF$_3$ species was selected as an internal reference since this group is not involved in the modification reaction. Therefore, for the 1 d PAMAM-modified polyimide, the intensity of the peak of imide groups (288.4 eV) decreases, indicating that the imide groups react with primary amine groups of PAMAM dendrimers to form amide groups. As a result of this reaction, the modified membranes exhibit a new peak at 287.9 eV for −NH− (C=O)− (amide) species. Thermal treatment at 120 °C further decreases the intensity of imide groups and increases the characteristic peak of amide groups, indicating additional amidization at the elevated annealing temperature. Thermal treatment of PAMAM-modified polyimide films at 250 °C, which resulted in the imidization of poly(amic amide) and the thermal decomposition of the PAMAM dendrimer, was found to increase the imide characteristic peak and decrease the amide characteristic peak.

Figure 4 gives the FTIR-ATR spectra of original and modified polyimide films. Compared with the original polyimide, the polyimide film modified by the G0 PAMAM dendrimer shows a stronger intensity of the characteristic peaks of amide group at 1656 and 1550 cm^{-1} but a weaker intensity of the characteristic peaks of imide group at 1780 and 1380 cm^{-1}. This can be explained by the amidization reaction between imide groups of polymer and free primary amine groups of dendrimers. Consistent with the XPS spectrum, after 120 °C thermal treatment, the FTIR spectra shows that the modified polyimide has stronger intensity of amide characteristic peaks, while the characteristic peaks of imide group decrease. This phenomenon indicates that

Table 1. Comparison of Gel Content and UV Absorption for Original and Modified Polyimide Films

	gel content (%)	λ (UV) (nm)
Original polyimide	0	330
G0 PAMAM-polyimide 1 d	93	327
G0 PAMAM-polyimide 1 d + 120 °C heat treatment	95	338
G0 PAMAM-polyimide 1 d + 250 °C heat treatment	0	350

more amidization reaction occurs after thermal treatment at 120 °C. However, when the heat treatment temperature is increased to 250 °C, the amide characteristic peaks almost disappear, and the intensity of imide characteristic peaks increases. Two possible explanations for the disappearance of amide characteristic peaks include (1) thermal decomposition of PAMAM dendrimers containing amide groups, which may break down the cross-linked structure, and (2) imidization of the poly(amic amide) when the treatment temperature increases to 250 °C.

Table 1 lists that the gel content increases after the polyimide is immersed into PAMAM dendrimer solution for 1 d, indicating that the cross-linking reaction between the polyimide chains and the dendrimer takes place on the outer skin layer of polyimide films, resulting in a decrease in the polyimide solubility in dichloromethane. However, we have conducted the gel content measurement with small pieces of films cut from a fully surface-modified membrane. A result of about 50% gel content was acquired. Therefore, we believed that the membranes were not fully cross-linked, as the dendrimers might not fully penetrate into the whole depth of membranes. As a consequence, solvent diffused into the polymer matrix from the cut edge and dissolved the un-cross-linked parts of membranes. After heat treatment at 120 °C, the modified polyimide films still show poor solubility in the solvent. This hints that the cross-linked structure remains intact under such temperature treatment. However, when heat treated at 250 °C, the modified polyimide films are almost totally soluble in dichloromethane, strongly supporting the hypothesis that the dendrimer−polyimide cross-linked structure is broken down by the high temperature.

Figure 5 illustrates the ^{1}H NMR spectrum of the original polyimide and 1 d PAMAM dendrimer-modified polyimide with heat treatment at 250 °C. Proton peaks of the original 6FDA-polyimide appear at 7.9−8.2 ppm attributed to the aromatic protons of 6FDA moiety and
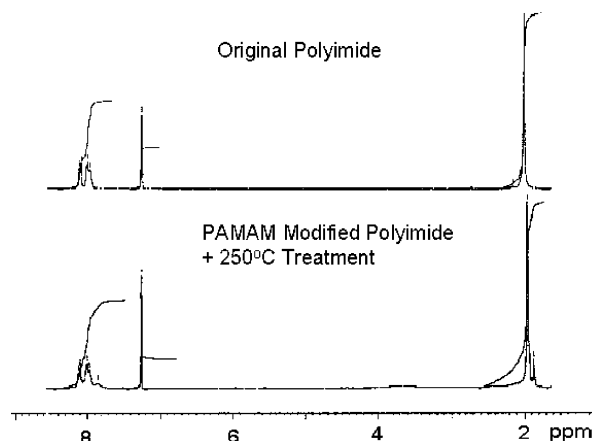

Figure 5. ^{1}H NMR spectrum of the original and modified polyimide in CDCl$_3$.
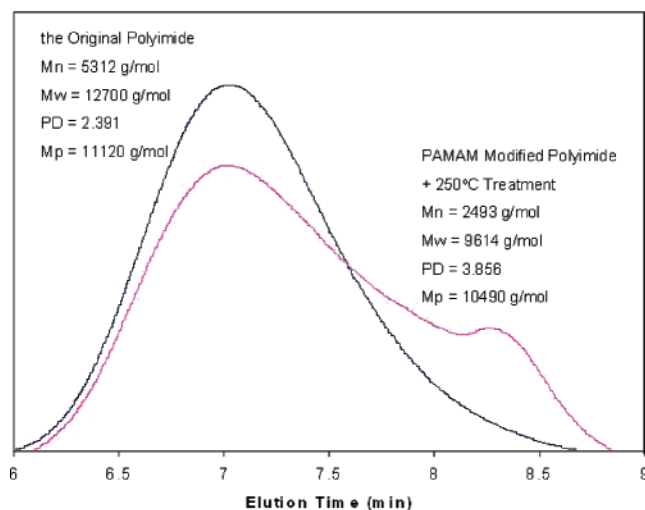
Figure 6. GPC curves for the original and modified polyimide.

1.9−2.0 ppm from the methyl proton of durene moiety. As compared with the original polyimide, the modified polyimide shows two small new peaks at 7.8 and 1.8 ppm. The chemical shift of 1.8 ppm is in the range of the characteristic peak of alkyl protons, which may be contributed by the fragments of decomposed PAMAM dendrimers. The peak at 7.8 ppm can be attributed to the protons of amide groups. This suggests that the PAMAM dendrimers may be cleaved into small molecules at 250 °C. Some small molecules evolve from the polymer matrix as gases, and others attached to the polyimide backbone chains by amide linkages. Weight (M_w) and number (M_n) average molecular weights and polydispersity (PD) of the original polyimide and 1 d PAMAM dendrimer-modified polyimide with 250 °C thermal treatment determined by GPC are given in

Figure 6. After high-temperature treatment, the molecular weight of modified polyimide decreases and the polydispersity increases as compared to that of the original polyimide. Two peaks are observed in the elution curve of the modified polyimide film. The elution time of first peak is same as that of the original polyimide, which may be contributed from unmodified polyimide layer in the middle of films. The peak of long elution time means that the low molecular weight compounds may come from the degradation of polyimide chains with the existence of PAMAM dendrimer. This observation is just consistent with the result of TGA test, which shows the decrease in the thermal stability of PAMAM-modified polyimide. During the heating process, the existence of PAMAM in polyimide may make polyimide chains degrade to low molecular weight fragments, which have lower thermally stability.

Figure 7 shows the possible chemical reactions that occurred during the whole modification process. In our previous study,[33] it was reported that there are still some free primary amine groups for the loaded PAMAM dendrimers on the surface of polyimide films if it is only dried at room temperature. Since heat treatment at moderate temperatures may increase the inter-segmental mobility, it would be expected to increase the opportunity of the free primary amine groups of PAMAM dendrimer to meet the imide groups in the backbone of polyimide. Thus, the amidization between free primary amine groups and polyimide chains is enhanced by heat treatment. More imide rings are broken to form amide groups, and the degree of cross-linking also increases on the surface of modified polyimide films. However, the high temperature treatment not only induces a significant decomposition of dendrimer at the amide linkage, which may break down the cross-linked structure, but also results in the degradation of poly-
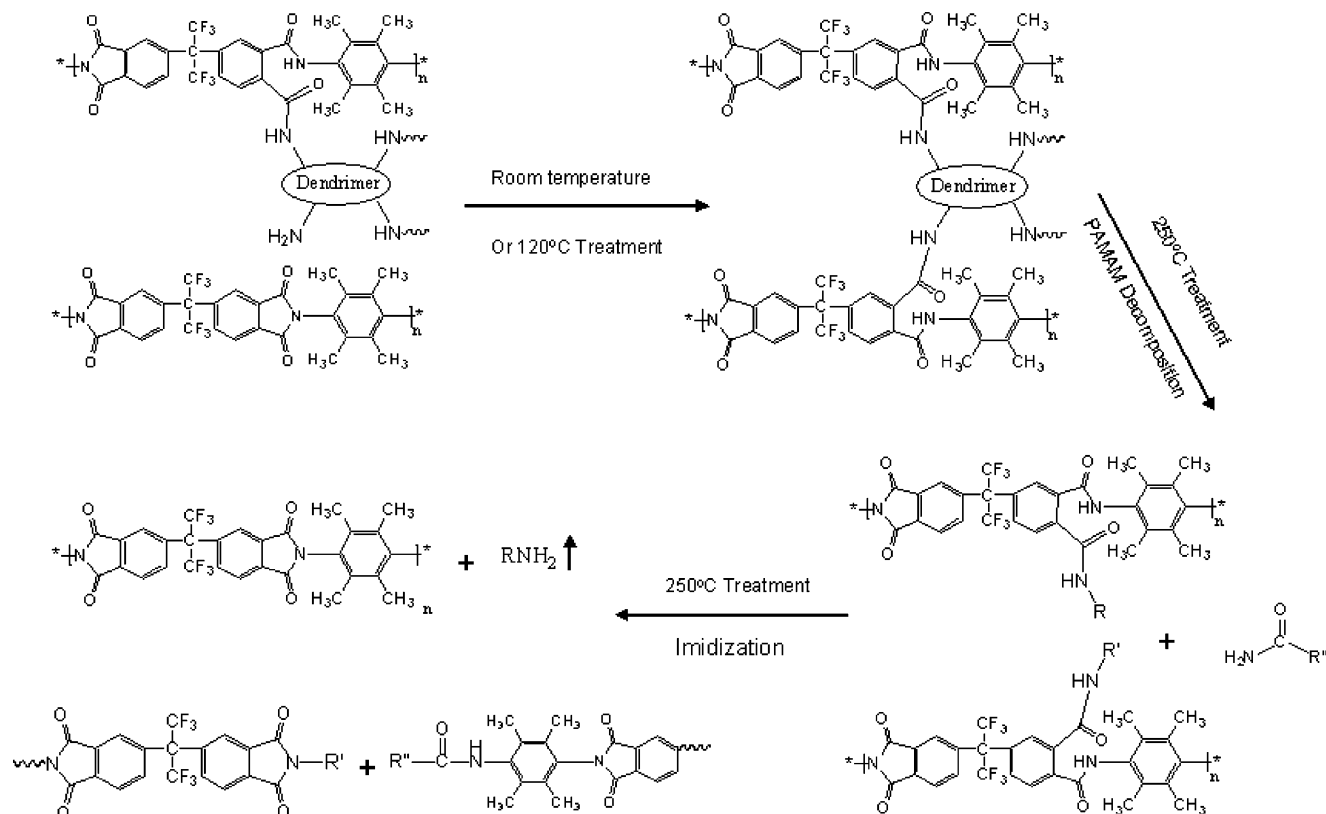

Figure 7. Possible chemical mechanisms of polyimide modification by G0 PAMAMA dendrimer.

Table 2. Gas Transport Properties for Original and Modified Polyimide Films[a]

	CO_2			CH_4			CO_2/CH_4		
	P	D	S	P	D	S	P_i/P_j	D_i/D_j	S_i/S_j
Original polyimide	520	5.0	100	33	0.91	36	16	5.5	2.9
G0 PAMAM-polyimide 1 d	160	1.5	100	4.4	0.14	33	36	11	3.2
G0 PAMAM-polyimide 1 d + 120 °C heat treatment	70	0.8	86	1.9	0.07	29	37	12	3.0
G0 PAMAM-polyimide 1 d + 250 °C heat treatment	84	1.0	80	2.8	0.10	27	30	10	3.0

[a] P (permeability): barriers (1×10^{-10} cm^3 (STP)-cm/cm^2 s cmHg). D (diffusivity): 10^{-8} cm^2/s. S (solubility): 10^{-2} cm^3 (STP)/cm^3 cmHg.

imide, which may produce a heterodispersed population of compounds with lower molecular weights.

The color of aromatic polyimide is usually attributed to the formation of charge-transfer complexes (CTCs) between polyimide chains.[43] In general, CTCs are often formed between benzene rings and the five-member imide rings when the rings are able to approach each other closely enough to allow transfer of π-electrons. The bulky CF_3 groups in the linear polyimide backbones largely eliminate the CTCs, resulting in colorless 6FDA polyimide films. The PAMAM dendrimer-modified polyimide films are also colorless. After 120 °C heat treatment, the modified polyimide films show a slightly yellow color. When treated at 250 °C, the color becomes darker. The change in color could also be detected by UV spectroscopy. The absorption maxima move to higher wavelengths with increasing heat history (Table 1). A possible explanation for the color change and the shift of UV absorption peak is the growth of CTCs within polyimide chains with heat treatment.

When 6FDA-polyimide films are immersed into dendrimer solutions, the swelling effect of methanol solvent and the opening of imide rings by amidization reactions could make CTC formation more difficult than was the case with the original 6FDA-polyimide. After heat treatment at 120 °C, the increase of cross-linking reaction would cause the polymer chains to become closer, and the CTCs could be more readily formed between neighboring polyimide chains. This chain of events would explain color generation in the modified polyimide films. After heat treatment at 250 °C, the imidization of poly(amic amide) produces more imide rings in the backbone of polymer chains, thus enhancing CTC formation. The formation of CTCs also can be verified by XPS. As discussed before, the C 1s core-level XPS spectrum of the original polyimide membrane can be curve-fitted to six peak components, which include one at 291.1 eV for the π–π* transition. The formation of CTCs will enhance the π–π* transition. Therefore, it is easy to explain why the area ratio of π–π* transition characteristic peak to the characteristic peak of the internal reference CF_3 increases with an increase in heat treatment temperature, as shown in the right-hand column of Figure 3.

The gas permeability, diffusivity, and solubility coefficients of CO_2 and CH_4 through modified polyimide films are listed in Table 2. It is clear that the gas permeabilities of both PAMAM-modified polyimides dried at room temperature and thermally treated are lower than the original polyimides. The degree of permeability reduction is comparable to those of other cross-linking polyimides.[24-28] For the modified polyimide films without heat treatment, the reduction in gas permeability is clearly due to a decrease in the gas diffusivity coefficient. The cross-linked structure results in increased inter-segmental interaction among the amide groups with the aid of hydrogen bonds and, consequentially, a reduction in free volume. With the
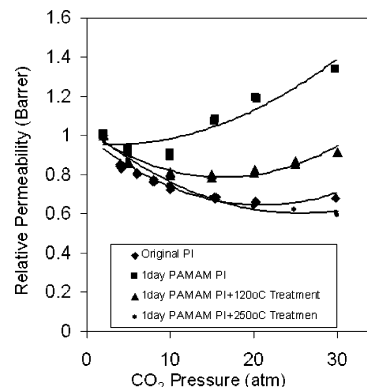
Figure 8. CO_2 permeation isotherms at 35 °C for original and modified polyimide films.

reduction in free volume, gas diffusion through the outer skin of modified films is retarded. Simultaneously, the cross-linking structure also limits the intra-segmental mobility of polyimide chains and thus results in an increase in gas diffusivity selectivity. The denser cross-linked structures exhibit reduced CH_4 solubilities. The strong interaction between CO_2 and free primary amine groups of PAMAM likely explains the more modest reduction in CO_2 solubility with cross-linking. In summary, the increase in CO_2/CH_4 selectivity is a result of combined increases in gas diffusivity selectivity and solubility selectivity.

As discussed above, heat treatment at 120 °C induces more amidization reactions and increases the degree of cross-linking of polyimide surface. Therefore, heat treatment at 120 °C leads to further increase in gas diffusivity selectivity of the modified polyimide films. It appears that the majority of the free primary amine groups within PAMAM are consumed because of the additional amidation reaction during heat treatment, reducing interactions between CO_2 and PAMAM, and therefore decreasing the solubility selectivity of CO_2/CH_4. Since heat treatment at 250 °C decomposes the PAMAM dendrimer and destroys the cross-linked structure, more free volume is created within the polymer matrix. As a consequence, gas permeability increases as compared with the films treated at 120 °C. However, films treated at 250 °C still exhibit lower gas permeabilities than that of the original polyimide films. One possible reason is that the free volume of polyimide is partly filled by the fragment of decomposed PAMAM dendrimers. Another explanation is that the formation of CTCs under high-temperature treatment constricts interstitial space between polymer chains. The third hypothesis may be that the polymer is likely to undergo some physical aging at 250 °C, which also acts to reduce gas permeability properties.

Figure 8 illustrates the effect of PAMAM modification and thermal treatment on the CO_2 permeation isotherm. In membrane separations, plasticization is generally defined as an increase in the permeability of a penetrant molecule due to increased polymer chain segmental
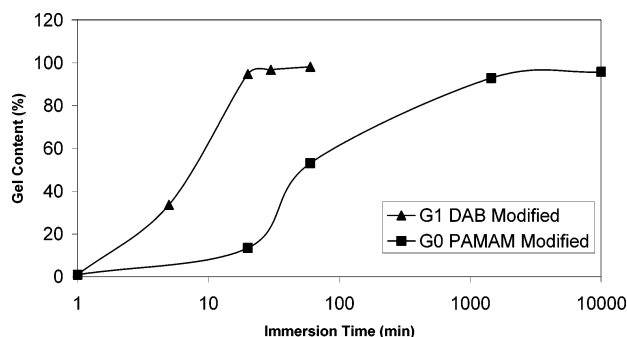
Figure 9. Gel contents of modified PI by different dendrimers.

Figure 10. "Tradeoff" line for the CO_2/CH_4 separation.

mobility.[21] For polyimide films, CO_2 is a strong plasticizer due to its high condensability. Therefore, the CO_2 plasticization phenomena can be used to monitor the change of polymer chain segmental mobility. The "plasticization pressure" is defined as the pressure at which there is a minimum in the isotherm. The immersion in PAMAM dendrimer solution for 1 d reduces the plasticization pressure. This phenomenon may arise from following factors: (1) the cleavage of imide rings in the main chains because of amidation reaction and (2) the swelling effects induced by methanol.

Thermal treatment at 120 °C offers somewhat better plasticization resistance than a simply immersion modification. This is likely due to the fact that a high-temperature treatment induces a higher degree of cross-linking, which tightens the polymer chains and limits intersegmental chains mobility. Interestingly, the modified films treated at 250 °C even exhibit better anti-plasticization than the original polyimide films. The most likely explanation is that the 250 °C treatment rebuilds the imide ring in the main backbones of polymer and enhances chain rigidity. At the same time, the formation of CTCs between neighboring polyimide chains also help to decrease CO_2 sorption, reduce chain mobility, and stablilize the structure.

Comparison of the Modified Polyimide Films by G0 PAMAM and G1 DAB. Cerius2 software was employed to simulate the molecular sizes and configuration of G0 PAMAM and G1 DAB dendrimers. As illustrated in Figure 1, both of the G0 PAMAM and G1 DAB have four branches and four free primary amine groups. However, the molecular size of G0 PAMAM is almost double that of G1 DAB. Therefore, it is expected that the DAB dendrimer should diffuse into the polyimide matrix more easily than PAMAM dendrimer and that the modification efficiency of DAB should be stronger than PAMAM dendrimer if the modification (immersion) time is the same. The gel contents of modified polyimide films were measured to testify the hypothesis. Figure 9 shows that the gel content increases with an increase in the immersion time, indicating that the reaction occurs between the polymer and the dendrimer on the surface of polyimide films. This reaction results in a decrease in the polymer solubility in the solvent. It also gives the evidence that the DAB can effectively modify the polyimide surface after a 30 min immersion time. Correspondingly, it takes about 1 d for PAMAM to completely modify the surface of polyimide films.

Figure 4 presents the FTIR-ATR analysis performed on the 30 min DAB-treated polyimide film and 1 d PAMAM-treated polyimide film. As compared with the PAMAM-modified film, the DAB-modified film shows a stronger intensity of the characteristic peaks of amide
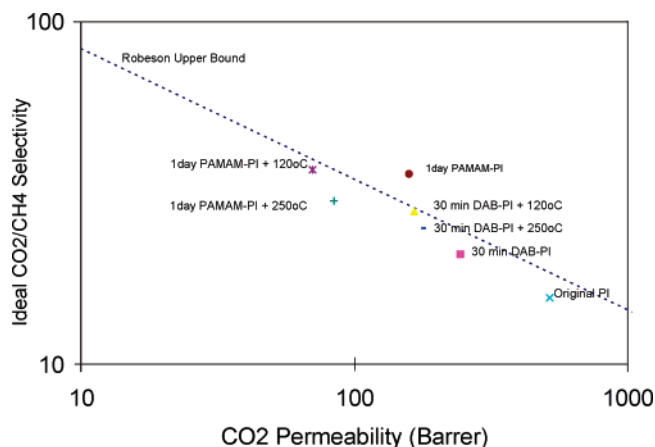
group at 1656 and 1550 cm^{-1} but a weaker intensity of the characteristic peaks of imide group at 1780 and 1380 cm^{-1}. The FTIR-ATR results substantiate a higher degree of amidization between the polyimide and the DAB dendrimer than that of polyimide and PAMAM. This may arise from the fact that the DAB dendrimer is smaller than the PAMAM dendrimer, which can penetrate deeper into the polymer matrix and thus construct a thicker cross-linking layer on the surface of polyimide films.

Figure 10 summarizes the gas permeabilities of the original 6FDA-durene polyimide film, 1 d PAMAM polyimide filmm and 30 min DAB polyimide film as compared with the Robeson upper-bond limit line of CO_2/CH_4 separation. The reduction of gas permeability for PAMAM-modified polyimide films is more significant, and the gas selectivity becomes much higher as compared with that of DAB-modified polyimide films. This suggests that the PAMAM dendrimer has greater ability to alter the gas permeation through polyimide films than the DAB dendrimer, although the DAB dendrimer has a stronger reactivity and penetration ability. This interesting phenomenon may be due to the fact that the longer branch length of the PAMAM dendrimer may be advantageous in connecting two neighboring polyimide chains. Another other possible explanation is that more hydrogen bonding between amide groups could be formed in the PAMAM dendrimer-modified polyimide films than in the DAB-modified films, as the PAMAM molecules contain additional amide groups in their own structure along with those produced by amidization reaction. The stronger cross-linking ability and more hydrogen bonding do result in the smaller gas permeabilities and higher gas selectivity of PAMAM-modified membranes than those of DAB-modified films.

After thermally treating at 120 °C, DAB G1-modified polyimide films show a similar trend as PAMAM G0-modified polyimide films, wherein the gas permeabilities keep decreasing but selectivity increases. However, the increment in gas selectivity of DAB-modified polyimide films is more pronounced than that in PAMAM-modified polyimide films (Figure 10). As mentioned previously, the heat treatment at 120 °C induces more amidization reactions and increases the degree of cross-linking on the outer layer of dendrimer-modified polyimide films. Therefore, although PAMAM dendrimers have stronger cross-linking ability than DAB dendrimers at room temperature, both PAMAM- and DAB-modified polyimide films show a highly cross-linking structure after

heat treatment. Additionally, in comparison with PAM-AM dendrimer, DAB dendrimer has shorter branches and smaller molecular size, as shown in Figure 1. Therefore, the effects of the improvement of cross-linking on gas transport properties of the DAB-modified polyimide films is more obvious than the PAMAM-modified polyimide films after 120 °C heat treatment. Selectivity is thereby enhanced since the greater chain stiffness enables the polyimide matrix to better discriminate between the permeation gases of different sizes and shapes. After 250 °C thermal treatment, DAB dendrimers are also decomposed and leave voids in the polymer matrix, resulting in increasing of the gas permeability and decreasing of selectivity.

Conclusion

The following conclusions are made from this study:

(1) The surface of 6FDA-polyimide films were modified by PAMAM G0 and DAB G1 dendrimers through simple immersion procedures. Thermal treatment at low temperatures was verified to facilitate the amidization reaction between polyimide and dendrimers as well as to enhance the degree of the cross-linking of dendrimer-modified polyimide films. FTIR-ATR, XPS, and pure gas permeation tests were employed to characterize the modified films.

(2) High-temperature treatment was found to destroy the cross-linking structure of modified polyimide by decomposing the dendrimer molecules and degrading the polyimide backbone chains. This was verified by ^{1}H NMR and the GPC test. Such high-temperature treatment is proven to be negative for gas separation performance of the modified polyimide films. Thus, treatment at an optimum temperature is required to obtain the best separation performance.

(3) G0 PAMAM and G1 DAB dendrimers showed differing abilities to modify polyimide films at varying temperatures. Immersion time of 30 min is required for DAB G1 modification at room temperature, while a longer time of 1 d immersion is needed for PAMAM G0 modification to reach the saturation of surface modification. As compared to the DAB dendrimer, the PAMAM dendrimer exhibited higher cross-linking ability than the DAB dendrimer at room temperature and induced better gas separation performance for polyimide films. After thermal treatment at 120 °C, the gas selectivity of the DAB-modified polyimide film was improved impressively due to more amidization and cross-linking.

Acknowledgment

Literature Cited

(1) Paul, D. R.; Yampol'skii, Y. P. *Polymeric Gas Separation Membranes*; CRC Press: Boca Raton, FL, 1994.

(2) Matsuura, T. *Synthetic Membranes and Membrane Separation Processes*; CRC Press: Boca Raton, FL, 1994.

(3) Ho, W. S. W.; Sirkar, K. K*.*, Eds. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992.

(4) Baer, E. An introduction to performance polymers. *High Perform. Polym.* **1990**, 11.

(5) Stern, S. A. Polymers for gas separations: the next decade. *J. Membr. Sci.* **1994***, 94,* 1.

(6) Hirayama, Y.; Yoshinaga, T.; Kusuki, Y.; Ninomiya, K.; Sakakibara, T.; Tamari, T. Relation of gas permeability with structure of aromatic polyimides I. *J. Membr. Sci.* **1996**, *111*, 169.

(7) Ayala, D.; Lozano, A. E.; Abajo, J. D.; Perez, C. G.; Campa, J. G.; Peinemann, K. V.; Freeman, B. D.; Prabhakar, R. Gas separation properties of aromatic polyimides. *J. Membr. Sci.* **2003**, *215*, 61.

(8) Baer, E.; Hu, Y. S.; Liu, R. Y. F.; Schiraldi, D. A.; Hiltner, A. Barrier properties of polyesters—relationship between diffusion and solid-state structure. *Polym. Mater. Sci. Eng.* **2003**, *89*, 19.

(9) Hu, Y. S.; Schiraldi, D. A.; Hiltner, A.; Baer, E. Structural model for oxygen permeability of a liquid crystalline polymer. *Macromolecules* **2003**, *36*, 3606.

(10) Robeson, L. M. Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.* **1991**, *62*, 165.

(11) Freeman, B. D. Basis of permeability/selectivity tradeoff relations in polymeric gas separion membranes. *Maromolecules* **1999**, *32*, 375.

(12) Kita, H.; Inada, T.; Tanaka, K.; Okamoto, K. Effect of photocrosslinking on permeability and permselectivity of gases through benzophenone-containing polyimide. *J. Membr. Sci.* **1994**, *87*, 139.

(13) Matsui, S.; Ishiguro, T.; Higuchi, A.; Nakagawa, T. Effect of ultraviolet light irradiation on gas permeability in polyimide membranes.1. Irradiation with low-pressure mercury lamp on photosensitive and nonphotosensitive membranes. *J. Polym. Sci.* **1997**, *35*, 2259.

(14) Coleman, M. R.; Xu, X.; Ilconich, J.; Hu, L. Effective hydrogen separation using ion beam modified polymeric membranes. *Polym. Prepr.* **2004**, *45*, 5.

(15) Bos, A.; Punt, I. G. M.; Wessling, M.; Strathmann, H. Suppression of CO_2-plasticization by semi-interpenetrating polymer network formation, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1547.

(16) Bos, A.; Punt, I. G. M.; Wessling, M.; Strathmann, H. Plasticization-resistant glassy polyimide membranes for CO_2/CH_4 separations, *Sep. Purif. Technol.* **1998**, *14*, 27.

(17) Kang, J. S.; Won, J.; Park, H. C.; Kim, U. Y.; Kang, Y. S.; Lee, Y. M. Morphology control of asymmetric membranes by UV irradiation on polyimide dope solution, *J. Membr. Sci.* **2000**, *169*, 229.

(18) Won, J.; Kim, M. H.; Kang, Y. S.; Park, H. C.; Kim, U. Y.; Choi, S. C.; Koh, S. K. Surface modification of polyimide and polysulfone membranes by ion beam for gas separation. *J. Appl. Polym. Sci.* **2000**, *75*, 1554.

(19) Rezac, M. E.; Sorensen, E. T.; Beckham, H. W. Transport properties of cross-linkable polyimide blends, *J. Membr. Sci.* **1997**, *136*, 249.

(20) Staudt-Bickel, C.; Koros, W. J. Improvement of CO_2/CH_4 separation characteristic of polyimides by chemical crosslinking. *J. Membr. Sci.* **1999**, *155*, 145.

(21) Wind, J. D.; Staudt-Bickel, C.; Paul, D. R.; Koros, W. J. The effect of crosslinking chemistry on CO_2 plasticization of polyimide gas separation membranes. *Ind. Eng. Chem. Res.* **2002**, *416*, 139.

(22) Hayes, R. A. Polyimide gas separation membranes. U.S. Patent No. 4,717,393, 1988.

(23) Hayes, R. A. Amine-modified polyimide membranes. U.S. Patent No. 4,981,497, 1991.

(24) Liu, Y.; Wang, R.; Chung, T. S. Chemical cross-linking modification of polyimide membranes for gas separation. *J. Membr. Sci.* **2001**, *189*, 231.

(25) Cao, C.; Chung, T. S.; Liu, Y.; Wang, R.; Pramoda, K. P. Chemical cross-linking modification of 6FDA-2,6-DAT hollow fiber membranes for natural gas separation. *J. Membr. Sci.* **2003**, *216*, 257.

(26) Liu, Y.; Chung, T. S.; Wang, R.; Li, D. F.; Chng, M. L. Chemical cross-linking modification of polyimide/poly(ether sulfone) dual-layer hollow-fiber membranes for gas separation. *Ind. Eng. Chem. Res.* **2003**, *42*, 1190.

(27) Tin, P. S.; Chung, T. S.; Wang, R.; Liu, Y.; Liu, S. L.; Pramoda, K. P. Effects of cross-linking modification on gas separation performance of Matrimid membranes. *J. Membr. Sci.* **2003**, *225*, 77.

(28) Zhou, C.; Chung, T. S.; Liu, Y.; Wang, R.; Goh, S. H. The accelerated CO_2 plasticization of ultra-thin polyimide films and the effect of surface chemical cross-linking on plasticization and physical aging. *J. Membr. Sci.* **2003**, *225*, 125.

(29) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. Dendritic macromolecules: Synthesis of starburst dendrimers. *Macromolecules* **1986**, *19*, 2466.

(30) Tomalia, D. A.; Frechet, M. J. Discovery of dendrimers and dendritic polymers: a brief historical perspective. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2719.

(31) Chung, T. S.; Chng, M. L.; Pramoda, K. P.; Xiao, Y. C. PAMAM dendrimer induced cross-linking modification of polyimide membranes. *Langmuir* **2004**, *20*, 2966.

(32) Shao, L.; Chung, T. S.; Goh, S. H.; Pramoda, K. P. Transport properties of cross-linked polyimide membranes induced by different generations of diaminobutane (DAB) dendrimers. *J. Membr. Sci.* **2004**, *238*, 153.

(33) Xiao, Y. C.; Chung, T. S.; Chng, M. L. Surface characterization, moidification chemistry and separation performance of polyimide and PAMAM dendrimer composites. *Langmuir* **2004**, *20*, 8230.

(34) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. About dendrimers: Structure, physical properties, and applications. *Chem. Rev.* **1999**, *99*, 1665.

(35) Zhuo, R. X.; Du, B.; Lu, Z. R. In vitro release of 5-fluorouacil with cyclic core dendritic polymer. *J. Controlled Release* **1999**, *57*, 249.

(36) Kovvali, A. S.; Chen, H.; Sirkar, K. K. Dendrimer membranes: A CO_2-selective molecular gate. *J. Am. Chem. Soc.* **2000**, *122*, 7549.

(37) Kovvali, A. S.; Sirkar, K. K. Dendrimer liquid membranes: CO_2 separation from gas mixtures. *Ind. Eng. Chem. Res.* **2001**, *40*, 2502.

(38) Kovvali, A. S.; Sirkar, K. K. Carbon dioxide separation with novel solvents as liquid membranes. *Ind. Eng. Chem. Res.* **2002**, *41*, 2287.

(39) Lin, W. H.; Vora, R. H.; Chung, T. S. Gas transport properties of 6FDA-durene/pPDA copolyimides. *J. Polym. Sci.: Part B: Polym. Phys.* **2000**, *38*, 2703.

(40) Chung, T. S.; Chan, S. S.; Wang, R.; Lu, Z.; He, C. Characterization of permeability and sorption in Matrimid/C_{60} mixed matrix membranes. *J. Membr. Sci.* **2003**, *211*, 91.

(41) Balogh, L.; Leuze-Jallouli, A.; Dvornic, P.; Kunugi, Y.; Blumstein, A.; Tomalia, D. A. Architectural copolymers of PAMAM dendrimers and ionic polyacetylenes. *Macromolecules* **1999**, *32*, 1036.

(42) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*: *The Scienta ES CA300 Database*; John Wiley: New York, 1992.

(43) Hasegawa, M.; Kochi, M.; Mita, I.; Yokota, R. Molecular aggregation and fluorescence spectra of aromatic polyimides. *Eur. Polym. J.* **1989**, *25*, 349.