Ultra-low-\(\kappa\) materials based on nanoporous fluorinated polyimide with well-defined pores via the RAFT-moderated graft polymerization process


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Thermally-initiated living radical graft polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) with ozone-pretreated fluorinated polyimide (FPI) via the reversible addition–fragmentation chain transfer (RAFT)-moderated process was carried out. The chemical composition and structure of the copolymers were characterized by nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and molecular weight measurements. The “living” character of the grafted PEGMA side chains was ascertained in the subsequent extension of the PEGMA side chains. Nanoporous ultra-low dielectric constant (\(\kappa\)) fluorinated polyimide films were prepared by solution casting of the graft copolymers, followed by thermal decomposition of the labile PEGMA side chains in air. The nanoporous FPI films obtained from the RAFT-moderated graft copolymers had well-preserved FPI backbones, porosity in the range of 2–10\% and pore size in the range of 20–50 nm. These films also had more well-defined pores, more uniform pore size distribution, and better-retained mechanical properties than those of the corresponding nanoporous FPI films obtained from the graft copolymers prepared by the conventional free-radical process. Dielectric constants approaching 2.0 were obtained for the nanoporous FPI films prepared from the RAFT-moderated graft copolymers.

1. Introduction

The demand for low dielectric constant (low-\(\kappa\)) materials in the microelectronics industry has recently led to considerable interest in porous materials, in particular, nanoporous materials. \(^{1–5}\) Polyimides (PI’s) have been widely used as dielectric and packaging materials in the microelectronics industry because of their good mechanical, thermal and dielectric properties. \(^{6–12}\) However, with dielectric constants in the range of 3.1–3.5, conventional polyimides are insufficient to meet the requirement of \(\kappa < 2.5\) for the dielectrics of the near future, and the ultra-low-\(\kappa\) of less than 2.2 for technology nodes below 130 nm. \(^{13}\) Low-\(\kappa\) materials can be prepared by introducing voids into the bulk material to take advantage of the low dielectric constant of air (\(\kappa \sim 1\)). Alternatively, the incorporation of a silicate component into PI’s in the form of hybrids is expected to lower the dielectric constants. \(^{14,15}\) Homogeneous and closed pores with sizes in the nanometer range are preferred from the point of view of preserving the electric and mechanical properties of the material. The introduction of air gaps into interconnecting structures and nanopores into polymers to reduce their dielectric constants have become an attractive approach. \(^{16–20}\)

Approaches to the preparation of porous PI films have included microwave processing, \(^{21}\) and incorporation of foaming agents \(^{22,23}\) and hollow microspheres. \(^{23,24}\) An alternative approach to the preparation of porous, low-\(\kappa\) PI’s is through the creation of voids by thermal degradation of the poly(propylene oxide) block of a phase-separated polyimide-poly(propylene oxide) block copolymer. \(^{25,26}\) Yet another approach to the preparation of nanoporous PI films with low dielectric constants was via thermally-induced graft copolymerization of poly(amic acid) with a vinyl monomer, followed by side chain decomposition after thermal imidization. \(^{27,28}\)

The synthesis of graft copolymers from commercial polymers is most commonly accomplished via the free-radical process. \(^{29}\) Free-radicals are produced on the parent polymer chains by exposure to ionizing radiation, and/or a free-radical initiator. \(^{29,30}\) Alternatively, peroxide groups are introduced onto the parent polymer by ozone pretreatment to serve as the initiation sites for the free-radical polymerization of a monomer. \(^{31–33}\) Graft copolymerization via the conventional free-radical process usually leads to less well-defined graft chains. Recent progress in polymer synthesis techniques has made it possible to produce well-defined graft polymer chains (polymer brushes) with controlled length and specific chain architecture. Various, stable living free-radical polymerization (LFRP) processes, including the nitroxide-mediated processes (NMP), have been developed. \(^{34}\) Atom transfer radical polymerization (ATRP) has been used to prepare graft copolymers from polymeric macroinitiators - polymer chains with regularly spaced pendant chemical groups containing radically transferable halogen atoms. \(^{35}\) Reversible addition–fragmentation chain transfer (RAFT)-moderated polymerization is an alternative method for achieving controlled free radical polymerization in solution. \(^{36–44}\) It involves a reversible addition–fragmentation cycle, in which transfer of a dithioester moiety between the active and dormant species maintains the controlled character of the polymerization process. Graft copolymerization by the RAFT-moderated process, thus, can be expected to produce...
well-defined side chains, which, in turn, can be expected to improve the uniformity in pore size of the nanoporous polymer films during side chain decomposition. The well-defined side chains refer to side chains with controlled length and chain architecture, and narrow molecular weight distribution.

In this work, a living radical approach to the preparation of nanoporous fluorinated polyimide (FPI) films with uniform pore size distribution and ultra-low dielectric constant is demonstrated. Initially, FPI with grafted poly(ethylene glycol) methyl ether methacrylate (PEGMA) side chains (FPI-g-PEGMA) was prepared via the thermally-induced graft copolymerization of PEGMA with the ozone-pretreated FPI in the RAFT-moderated process. Nanoporous FPI films with uniform pore size distribution were obtained by decomposition of the thermally labile, but well-structured, PEGMA polymer side chains in air.

2. Experimental section

2.1. Materials

The fluorinated polyimide (FPI) used in this study was prepared from step polymerization of 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 4,4'-bis(4-aminophenoxy) diphenyl sulfone (BADS) according to the method reported previously. The chemical structure of the FPI is shown in Scheme 1. The macromonomer, poly(ethylene glycol) methyl ether methacrylate (Mn~300 g mol⁻¹), was purchased from Aldrich Chemical Co., and was used after removal of the inhibitor in an Al₂O₃ column. The solvent, N,N-dimethylformamide (DMF), was purchased from Fisher Scientific Co., Leics, UK, and was used as received. The chain transfer agent (CTA), 1-phenylethyl dithiobenzoate (PDB), was prepared according to the published procedures.

2.2. RAFT-moderated graft copolymerization of PEGMA with the fluorinated polyimide (FPI-g-PEGMA copolymer)

The FPI powders were dissolved in DMF to a concentration of 75 g L⁻¹. A continuous stream of O₃/O₂ mixture was bubbled through 14 ml of the solution at 25 °C. The O₃/O₂ mixture was generated from an Azcozon RMU 16-04EM ozone generator. The gas flow rate was adjusted to 300 L h⁻¹ to give rise to an ozone concentration of about 0.027 g L⁻¹ of the gaseous mixture. A typical treatment time of about 5 min was used. This pretreatment time gave rise to a peroxide content of about 1.3 × 10⁻⁵ mol g⁻¹ of the polymer. The dependence of peroxide concentration and molecular weight of FPI on the ozone treatment time under similar experimental conditions had been reported earlier. The number average molecular weight of FPI decreased, while the polydispersity increased, with the ozone treatment time. The degradation of the FPI chains had probably also resulted in the formation of active sites on the chains for the subsequent reaction with oxygen to form the peroxides and the oxidized species. The ozone-pretreated FPI solution (containing about 1 g of FPI) and 1 mL of the DMF solution of PDB (1.46 × 10⁻¹ mol/L) were transferred to an ampule. DMF solution of PEGMA was then introduced into the ampule to give a final volume of 20 mL and a PEGMA concentration ranging from 0.11 to 0.26 g mL⁻¹. The ampules were degassed with three freeze-evacuate-thaw cycles. They were then sealed and heated at 60 °C for 6 h. After the desired reaction time, the reactor flasks were cooled in an ice bath. Each FPI-g-PEGMA copolymer sample was precipitated in an excess amount of ethanol, and recovered by filtration. The copolymer sample was purified thrice by redissolving in DMF and reprecipitating in ethanol. It was further purified by washing in excess ethanol for another 48 h. Since ethanol is a good solvent for the PEGMA homopolymer, the homopolymer of PEGMA generated during the RAFT-moderated graft copolymerization process should have been extracted out completely. Finally, the copolymer samples were dried by pumping under reduced pressure overnight at room temperature.

2.3. Preparation of the nanoporous FPI films

Nanoporous FPI films were prepared by a two-step process, involving (i) solution casting of the copolymer film and (ii) thermal decomposition of the grafted side chains. The process is shown in Scheme 1. Initially, the graft copolymer was dissolved in DMF to a concentration of 20 wt%. The film was
obtained by casting the solution of the copolymer on a polished silicon substrate (Si(100) wafer). The film was heated initially in a vacuum oven at 90 °C for 1 h under atmospheric pressure. It was then heated at 150 °C for 1 h, at 200 °C for 1 h and finally at 220 °C for 2 h in a vacuum oven pre-purged with argon. The film was then cooled gradually to room temperature. The nanoporous FPI film was formed subsequently by thermolysis and removal of the grafted side chains. Thus, the nanoporous FPI film was obtained by heating the FPI-g-PEGMA copolymer film at 250 °C for 12 h in air. The resulting nanoporous FPI film had a thickness of about 200 μm.

2.4. Characterization of the graft copolymers

Proton nuclear magnetic resonance (1H NMR) was performed on a Bruker ARX 300 instrument with deuterated DMF as the solvent. Gel permeation chromatography (GPC) was performed using DMF as the eluent and polystyrene standards as the references. The thermal properties of the copolymers were measured by thermogravimetric analyses (TGA). The samples were heated to 900 °C at a heating rate of 10 °C min⁻¹ under dry nitrogen or air in a Du Pont Thermal Analyst 2100 system, equipped with a TA2050 thermogravimetric thermal analyzer. Differential scanning calorimetry (DSC) studies were conducted on a DSC 822e (Mettler Toledo Co., Switzerland) apparatus at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

2.5. Characterization of the nanoporous films

The morphology of the nanoporous FPI films was studied by field emission scanning electron microscopy (FESEM) on a JEOl JSM-6700F FESEM at an accelerating voltage of 5 kV. The nanoporous film was fractured under liquid nitrogen and mounted on the sample stub by means of double-sided adhesive tape for the cross-sectional view. A thin layer of platinum was deposited on the sample stud by means of double-sided adhesive tape for the cross-sectional view. A thin layer of platinum was sputtered onto the cross-sectional surface prior to the FESEM measurement. Film density was measured on a RF impedance/capacitance material analyzer (Hewlett Packard model 4291B) in the frequency range 1 MHz to 1.8 GHz and at 50% relative humidity (25 °C) under the ambient atmosphere.

Table 1

| Graft concentration | GPC molar mass | Est. | Graft chain
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<tr>
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<tr>
<td>FPI-g-PEGMA</td>
<td>([-PEGMA]-)[-FPI-]bulk or [PEGMA][-FPI-]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Feed molar ratio | Mole ratio | Wt. fraction | Weight loss/°C | T/°C | Mw/g mol⁻¹ | Mz/g mol⁻¹ | Mn/g mol⁻¹ | Mz/Mn | Mw/Mn | Density/g cm⁻³ | Porosity/°C
| FPI | 0 | 0 | 0 | — | 293 | 194300 | 118500 | 1.64 | 118500 | — | 1.50 | 3.1
| Conv | 14.5 | 0.44 | 0.138 | 11.2 | 273 | 284300 | 159700 | 1.78 | 137400 | 12300 | 1.35 | 10.1 | 2.0
| a | 5.80 | 0.15 | 0.052 | 5.6 | 289 | 204800 | 126400 | 1.62 | 124900 | 42000 | 1.47 | 2.0 | 2.9
| b | 8.69 | 0.22 | 0.073 | 7.8 | 285 | 224700 | 142200 | 1.58 | 127900 | 6100 | 1.45 | 3.3 | 2.7
| c | 11.6 | 0.29 | 0.096 | 9.3 | 282 | 232000 | 149700 | 1.55 | 130900 | 8100 | 1.39 | 7.3 | 2.4
| d | 14.5 | 0.37 | 0.118 | 10.8 | 278 | 244300 | 158600 | 1.54 | 134400 | 10300 | 1.36 | 9.3 | 2.0

* From conventional free radical-initiated graft copolymerization in the absence of the chain transfer agent, and prepared from the 5-min ozone-pretreated FPI, with a molar feed ratio of 14.5, at 60 °C in DMF for 6 h. The extent of the first major loss in TGA under a nitrogen atmosphere.

* From GPC measurements, based on polystyrene standards. From the 1H NMR-derived composition. Averaged molecular weight of grafted chains was calculated from the peroxide concentration of the ozone-pretreated FPI and the graft concentration. The dielectric constant was obtained at 1 MHz and 50% relative humidity under the ambient atmosphere.

Fig. 1 300 MHz ¹H NMR spectra of the FPI-g-PEGMA copolymer with a bulk graft concentration of 0.37. Resonances labeled s₁, s₂ are solvent peaks associated with the deuterated DMF.

on an Instron model 3345 universal testing system at room temperature.

3. Results and discussion

3.1. Chemical structure of the graft copolymers

The chemical structure of the FPI-g-PEGMA copolymer was first characterized by ¹H NMR spectroscopy. The chemical shifts in the range of 7.2–8.3 ppm are attributable to the aromatic protons of FPI. Grafting of the PEGMA polymer to FPI resulted in the appearance of chemical shifts at 3.7 ppm, 4.2 ppm, 3.3 ppm and in the region of 1.1–2.2 ppm, attributable, respectively, to the OCH₃ group, COOCH₂ group, OCH₃ group and the hydrogen species associated with the backbone of the grafted PEGMA chain. The signal of the dithiobenzoate end group of the side chain in the region of 7.5 to 8 ppm, which was associated with the chain transfer agent of the RAFT-moderated process, was obscured by the aromatic protons of FPI. The molar ratio of the PEGMA units in the graft chains (PEGMA) per repeat unit of FPI (FPI-) in the copolymer, or the ([PEGMA]-)[FPI-]bulk ratio, was then calculated based on the ratio of the integrals of the resonance at 4.2 ppm to that of the combined resonances at 7.2–8.3 ppm. The copolymer composition so calculated is shown in Table 1. The ¹H NMR spectrum of the FPI-g-PEGMA copolymer with a ([PEGMA]-)[FPI-]bulk ratio of 0.37 is shown in Fig. 1. The solvent peaks s₁ and s₂ were subtracted from the spectrum using their known intensities relative to that of the solvent peak s₃, obtained from the analysis of pure deuterated DMF.
Fig. 2 GPC traces of (a) the pristine FPI, and the FPI-g-PEGMA copolymer via the RAFT-moderated process (b) with a bulk graft concentration of 0.37 and (c) after subsequent block copolymerization with PEGMA from the “living” end groups of the grafted PEGMA chains. The molecular weight scale was calibrated using polystyrene standards.

The molecular weight and polydispersity of the graft copolymers, obtained from the GPC measurements, are presented in Table 1. The GPC traces for the pristine FPI (curve a) and the FPI-g-PEGMA copolymer with a bulk graft concentration of 0.37 (curve b, sample d in Table 1) are shown in Fig. 2. Graft copolymerization of FPI with PEGMA has resulted in a significant increase in molecular weight relative to the FPI parent polymer. The molecular weight distribution (MWD) of the FPI-g-PEGMA copolymers was approximately unimodal. The GPC trace was virtually unchanged after 48 h of extraction of the copolymer in a large volume of ethanol, a good solvent for poly(PEGMA), indicating that the minor shoulder at the lower mass was not due to the homopolymer of PEGMA. The lower mass shoulder was also observed in the GPC trace of the FPI parent polymer. The MWD’s of the graft copolymers appear to be narrower than that of the FPI base polymer. The observed decrease in polydispersity of the graft copolymer is most likely to have resulted from preferential removal of the low molecular weight fraction of the copolymer during the repeated precipitation and extraction process employed to purify the copolymer after the RAFT-moderated graft copolymerization. In comparison with the FPI-g-PEGMA copolymer prepared from conventional radical copolymerization in the absence of the chain transfer agent, the MWD’s of the graft copolymers prepared by the RAFT-moderated process are also significantly narrower.

The number-averaged molecular weights were also obtained from the NMR results using the relationship,\[ M_{n,\text{graft}} = M_{n,\text{FPI}} \left(1 + x \frac{M_{g,\text{PEGMA}}}{M_{0,\text{FPI}}} \right) \], where \( M_{n,\text{FPI}} \) is the number-averaged molecular weight of the parent FPI obtained from GPC measurement, \( x \) is the molar ratio of the PEGMA units per FPI repeat unit in the copolymer as measured by NMR, and \( M_{0,\text{FPI}} \) and \( M_{g,\text{PEGMA}} \) are the molar masses of the FPI repeat unit and of PEGMA, respectively. The \( M_{n} \)’s of the graft copolymers so calculated are also shown in Table 1 for comparison purposes. The averaged molecular weight of the graft chains was estimated from the peroxide concentration of the ozone-pretreated FPI and the graft concentration. The \( M_{n} \) of the graft chains is in the range from 4200 to 12300 (Table 1). Ideally, the molecular weight characteristics of the PEGMA graft chains in the RAFT-moderated process should resemble that of the corresponding PEGMA homopolymer in the reaction mixture. Attempts to recover the PEGMA homopolymer from the reaction mixture were not successful because of the good solubility of PEGMA polymer in the organic and aqueous solvents, as well as the presence of unreacted PEGMA monomer in the reaction mixture.

3.2. Side chain extension of the FPI-g-PEGMA copolymer

In order to further ascertain the presence of a RAFT-moderated process during graft copolymerization, and thus the “living” character of the PEGMA side chains, the FPI-g-PEGMA copolymer was subjected to another round of graft copolymerization with PEGMA. The FPI-g-PEGMA copolymer with an initial graft concentration of 0.37 (0.4 g, \( M_{n} = 158600, M_{w}/M_{n} = 1.54 \), prepared via the RAFT-moderated process), PEGMA (5 mL), 2,2-azobisisobutyronitrile (AIBN, 0.8 mg), PDB (0.7 mg), and DMF (10 mL) were transferred into an ampule. The resulting mixture was degassed, sealed and heated at 60 °C for 20 h. The resulting copolymer was precipitated in ethanol, and extracted vigorously with ethanol to remove the PEGMA homopolymer. The volatiles were removed in vacuo to give rise to a FPI-g-PEGMA copolymer of \( M_{n} = 165700 \) and \( M_{w}/M_{n} = 1.50 \). The GPC traces of the FPI-g-PEGMA copolymer before and after the side chain extension reaction are shown in Fig. 2. The \( M_{w}/M_{n} \) ratio and the increase in \( M_{n} \), after the side chain extension are readily reproducible in repeated experiments. The molecular weight only increases slightly and slowly for a prolonged reaction time above 20 h. Block copolymerization with another monomer (styrene) using the grafted PEGMA as the macro-chain transfer agent has been demonstrated in an earlier study.47

Since the free radicals for graft copolymerization are generated on the FPI chains, some of the chains initiated from these radicals will probably undergo the traditional free-radical graft copolymerization. These graft chains will not have a controlled molecular weight mediated by RAFT, and the actual ‘RAFT chains’ will be present within the reaction mixture. Under these circumstances, the chain transfer agent does not act as a ‘RAFT agent’ to control the molecular weight of the graft chains. It only acts as a traditional chain transfer agent to limit the molecular weight of the graft chains. On the other hand, the presence of the ‘RAFT agent’ on some of the graft chains is indicated by the ability of the graft chains to subsequently undergo side chain extension, as well as block copolymerization with a second monomer.47

3.3. Thermal analysis of the graft copolymers

The thermal properties of the graft copolymers were studied by thermogravimetric analysis (TGA) in air and in nitrogen (Fig. 3), as well as by differential scanning calorimetry (DSC) in nitrogen (Table 1). In comparison with the pristine PEGMA...
homopolymer, which has an onset decomposition temperature of about 300 °C in nitrogen (curve a) and about 200 °C in air (curve b), the copolymer samples exhibit an intermediate weight loss behavior and undergo a two-step degradation process. The onset of the first major weight loss (sample b, Table 1), which occurs at about 250 °C in air (curve c) and at about 300 °C in nitrogen (curve d), corresponds to the onset of decomposition of the PEGMA side chains in the copolymer. The second major weight loss begins at about 510 °C, which coincides with the decomposition temperature of the FPI main chain. The TGA results, thus, suggest that thermal treatment of FPI-g-PEGMA at 250 °C in air for 12 h during the formation of the nanoporous structure should be sufficient to decompose the thermally labile side chains, while leaving the FPI main chain intact. There are almost no remaining side chains after such thermal treatment, as indicated by the weight loss curve of the corresponding nanoporous FPI film (curve e). At the same time, the thermal treatment temperature of 250 °C in air for the generation of the nanoporous structure is above the decomposition temperature of the PEGMA homopolymer in air, and yet below the glass transition temperature (T_g) of the FPI backbone (293 °C, Table 1), or T_g of the copolymer (285 °C, sample b, Table 1), to avoid the collapse of the porous structure. The weight fraction of the graft chains in each copolymer coincided approximately with the fraction of weight loss during thermal decomposition, suggesting that nearly 100% decomposition efficiency of the side chains was achieved during thermal treatment at 250 °C in air. The collapse of pores was observed when the thermal treatment temperature was above the T_g of the copolymer. The migration of the degraded side chain fragments in the FPI matrix is probably facilitated by the fact that glassy polyimides are known for their good gas permeability. For all copolymer samples, the extent of the first major weight loss in nitrogen is approximately equal to the bulk PEGMA content in the respective graft copolymer, as derived from the NMR data and converted to the mass basis (Table 1). The pristine (ungrafted) FPI has a T_g of about 293 °C. The T_g of the graft copolymer decreases with the increase in graft concentration, as shown in Table 1. Graft copolymerization with PEGMA reduces the structural rigidity of the FPI backbone and increases the molar free volume of the polymer, resulting in the lowering of T_g.

3.4. Morphology of the nanoporous FPI films

The pore size and pore size distribution are of great importance to the mechanical and dielectric properties of the nanoporous materials. In this study, the structure of the nanoporous FPI films was revealed by cross-sectional FESEM images. Figs. 4(a) and 4(b) show the respective FESEM images (cross-sectional view) of the FPI-g-PEGMA film (sample d in Table 1, graft concentration = 0.37) and the corresponding nanoporous FPI film. The FPI-g-PEGMA film has a dense (non-porous) morphology prior to thermal decomposition of the grafted side chains. The nanoporous structure is discernible in the FESEM cross-sectional image of the corresponding FPI films after thermal decomposition of the side chains at 250 °C for 12 h in air. The dark areas are the voids left behind by the degraded PEGMA phase (part b)). The pore size of the nanoporous FPI film prepared from the RAFT-moderated FPI-g-PEGMA copolymer is in the range of 20–50 nm. The pores are fairly uniform in size and have few interconnections. On the other hand, the pore size of the nanoporous FPI film prepared from the FPI-g-PEGMA copolymer, obtained via the conventional free-radical process in the absence of the chain transfer agent, is poorly defined (Fig. 4(c)). The pores are irregular in shape and show a certain degree of interconnectivity.

3.5. Physical properties and dielectric constant of the nanoporous FPI films

Density measurements were used to characterize the porosity of the nanoporous FPI films. As shown in Table 1, the density of the nanoporous FPI films prepared from the FPI-g-PEGMA copolymers decreases with the increase in graft concentration. The dielectric constant (κ) of the resulting nanoporous FPI film is of primary concern. For the nanoporous FPI film, the ultimate κ value is governed by the intrinsic κ value of the FPI matrix, and the morphology and porosity of the porous structure. Table 1 gives the dielectric constant (measured at 1 MHz) of the pristine FPI film and the nanoporous FPI films, prepared from the FPI-g-PEGMA copolymers, as a function of the porosity of the films. The dielectric constant of the pristine FPI film is 3.1 under ambient conditions. As anticipated, all the nanoporous FPI films exhibit considerably lower dielectric constants. The dielectric constant decreases with increasing porosity. A dielectric constant of about 2.0 is obtained for the nanoporous FPI films prepared from the RAFT-moderated FPI-g-PEGMA copolymer with an initial weight fraction of the grafted side chains of about 0.118 and a final porosity of about...
9.3%. This dielectric constant is comparable or lower than that of the poly(tetrafluoroethylene) (PTFE) film (κ ~ 2.1).15 Graft copolymerization with PEGMA reduces the structural rigidity and the intermolecular packing density of the FPI chains and, thus, increases the molar free volume of the polymer. As a result, the dielectric constant decreases significantly, especially after the decomposition of the grafted PEGMA side chains to form the nano-voids. Apparently, the effects of the increase in molar free volume and the concentration of the nano-voids on the dielectric constant are not additive. The changes in conformation of the FPI chains after graft copolymerization and after decomposition of the graft chains will have further effects on the dielectric constant of the polymer. Thus, the observed dependence of the dielectric constant of the polymer on porosity probably cannot be explained by the simple additive rule. The nanoporous FPI film, prepared from the conventional FPI-g-PEGMA copolymer with an initial weight fraction of the side chains of about 0.138 and a final porosity of about 10.1%, exhibits an analogous dielectric constant of about 2.0. Nevertheless, the contribution and benefits of the RAFT-moderated process over the conventional free-radical process in the preparation of nanoporous materials are obvious from the well-defined nanostructure of the dielectric films.

The effect of porosity on the mechanical property of the FPI films was evaluated from the stress–strain relations. The pristine FPI film has a nominal tensile strength (σ) of about 67 MPa. The σ value decreases to about 62 MPa for the nanoporous FPI film (sample d, porosity = 9.3%, Table 1), prepared from the RAFT-moderated FPI-g-PEGMA copolymer. For the conventional nanoporous FPI film of comparable porosity (sample Conv, porosity = 10.1%, Table 1), a σ value of only about 55 MPa was obtained. The higher tensile strength of the RAFT-moderated nanoporous FPI film, in comparison to that of the conventional nanoporous FPI film of comparable porosity, can probably be attributed to the more well-defined and less interconnected pores in the RAFT-moderated nanoporous film.

4. Conclusions
Fluorinated polyimides with grafted PEGMA side chains have been successfully prepared via the RAFT-moderated process. Nanoporous ultra-low-k FPI films with 2.9 < κ < 2.0) were obtained by thermal decomposition of the grafted PEGMA side chains on the FPI backbones in air. The dielectric constant of the nanoporous FPI film can be varied by varying the graft concentration of the labile side chains. The more well-defined graft chain from the RAFT-moderated process, in comparison with those from the conventional free-radical process, allowed the preparation of nanoporous low-k FPI films with refined film morphology, preserved FPI backbone, more well-defined pores, and more uniform pore size distribution. The synergistic effect arising from the refinement in film morphology and in the structure of the nano-voids associated with the RAFT-moderated process has given rise to better retention of the mechanical properties of the FPI film.

References


