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Optimization of foaming process using triblock polyimides with thermally labile blocks

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Abstract

Triblock polyamic acid was synthesized from the reaction of amine-terminated polystyrene with 4,4′-oxydianiline and pyromellitic dianhydride in *N*-methyl-2-pyrrolidone. IR and TGA were used to determine optimum curing conditions, in which imidization was completed and the thermally labile polystyrene block was intact. From the thermomechanical analysis (TMA), it was identified that the resulting triblock polyimide film showed contraction at several points over the temperature range of 50–400°C. The first contraction at 75°C and the second at 275°C were due to the residual stresses associated with the polystyrene and polyimide blocks, respectively. The third at 330°C was probably attributed to foam collapse. The structural instability in polyimide matrix induced by the residual stresses was believed to be the reason causing the foam collapse. To overcome such a problem, an annealing process was carried out. The annealed film showed no contraction and, moreover, no foam collapse was observed in the thermomechanical analysis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Triblock polyimide; Thermomechanical analysis; Foam collapse

1. Introduction

Polyimides have been introduced into electronic packages since the early 1980s, primarily because they possess higher thermal stability, good mechanical properties, low thermal expansion coefficient, and comparatively low dielectric constant [1–5]. Currently polyimides are being evaluated as dielectrics for advanced logic chips for the same reason they were introduced into electronic packaging. Although polyimides meet many of the material requirements, future advances in high performance computing will require improved dielectric insulators with substantially low dielectric constants. Many researchers have attempted to lower the dielectric constant of polyimides [6–13]. One of the most promising approaches is to incorporate air foams into the polyimide matrix resulting in a foamed structure [14–16]. In this method, the dielectric constant can be lowered by the air foams, which have the dielectric constant of 1.

Incorporation of the air foams into the polyimide matrix can be effectively achieved from block copolymers comprising thermally stable and thermally labile materials, where the latter constitutes the dispersed phase [17–23]. The thermally labile block is decomposed by high thermal treatment resulting in the air foams. During the process it is critical that foam collapse should be avoided so that the foam size may become much smaller than the microelectronic feature sizes, and the closed-cell is produced. Polyimides have excellent thermal stability and rigidity, and so are expected to maintain dimension stability during the foaming process.

Conversion of polyamic acid to polyimide involves several specific changes in the chemical structure and morphology. Appearance of the new aromatic imide ring is concurrent with the disappearance of the carboxylic acid and amide groups. In addition, a quantitative amount of water is generated during the cyclization reaction [24]. Infrared spectroscopy (IR) provides useful information on the extent of imidization by detecting these chemical changes. Thermal gravimetric analysis (TGA) is also used to determine the degree of imidization from the weight changes due to the evaporation of water. But, these instruments can detect only the chemical changes. Researches have recently reported on the morphological changes occurring during the imidization and their impact on the properties of the resulting film [25–36]. The evaporation of solvent during the drying and imidization steps leads to the shrinkage of the film preferentially in the thickness direction, while the polymer chains parallel to the film

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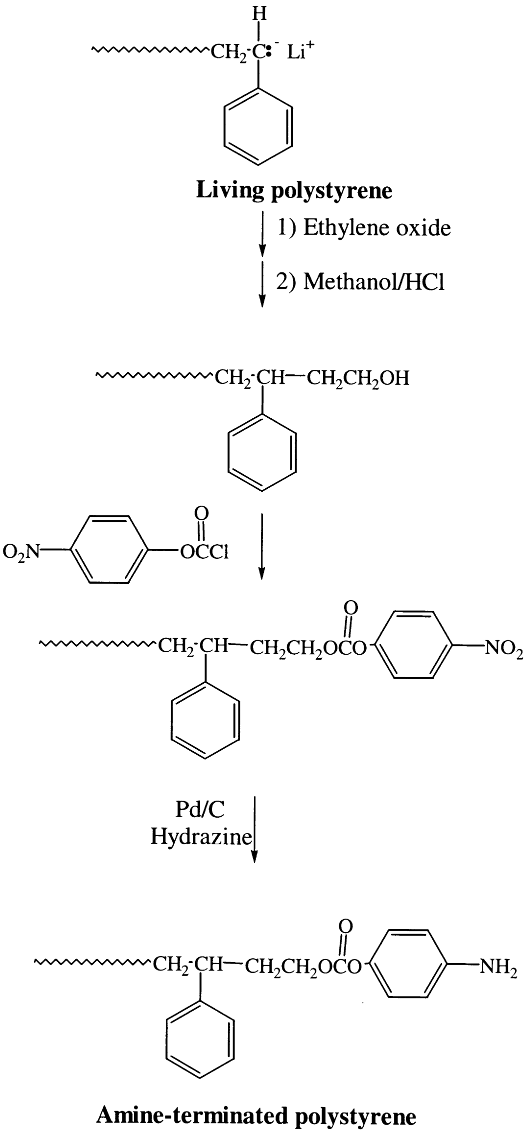


Scheme 1.

surface are constrained on the glass substrate. This causes the polymer chains to be stretched or oriented. Consequently the polymer chains are forced to return to the original state by the residual stresses.

In order to prevent the foam collapse, the triblock polyimide should be optimized. The structural instability due to the residual stresses may lead to the expansion or collapse of the foam. In this respect, an annealing process to relax the residual stresses is required for the triblock polyimide film before the foaming process. Although optimizing the triblock polyimides is an important matter to prepare the nanofoamed structure, there have been little studies about it.

In this article, we prepared triblock polyamic acid, in which polystyrene was used as a thermally labile block. IR and TGA were used to determine the extent of imidization by measuring chemical changes associated with the curing reaction. It was identified by thermomechanical analysis (TMA) that the cured triblock polyimide showed contraction at several points in the temperature range of 50–400°C. To optimize the triblock polyimide, the annealing treatment to relax the residual stresses was carried out and the result was confirmed by TMA.

2. Experimental

2.1. Materials

For anionic polymerization, styrene and benzene were purified according to the literature [37]. *sec*-Butyllithium (Aldrich Chem. Co., 1.7 M in pentane) was used as the initiator without further purification. Ethylene oxide (Aldrich Chem. Co., 99.5%) was stirred over calcium hydride. After degassing, several times in the high vacuum line, and distillation into the flask containing dibutyl magnesium, it was distilled into ampoules followed by dilution with benzene. 4-Nitrophenylchloroformate (Aldrich Chem, Co.) and pyromellitic dianhydride (Acros) were recrystallized from petroleum ether and 2-butanone, respectively. 4,4-Oxydianilline was purified by vacuum sublimation before use. Palladium on activated carbon (10% Pd) (Acros) and hydrazine monohydrate (Aldrich Chem. Co.) were used as received.

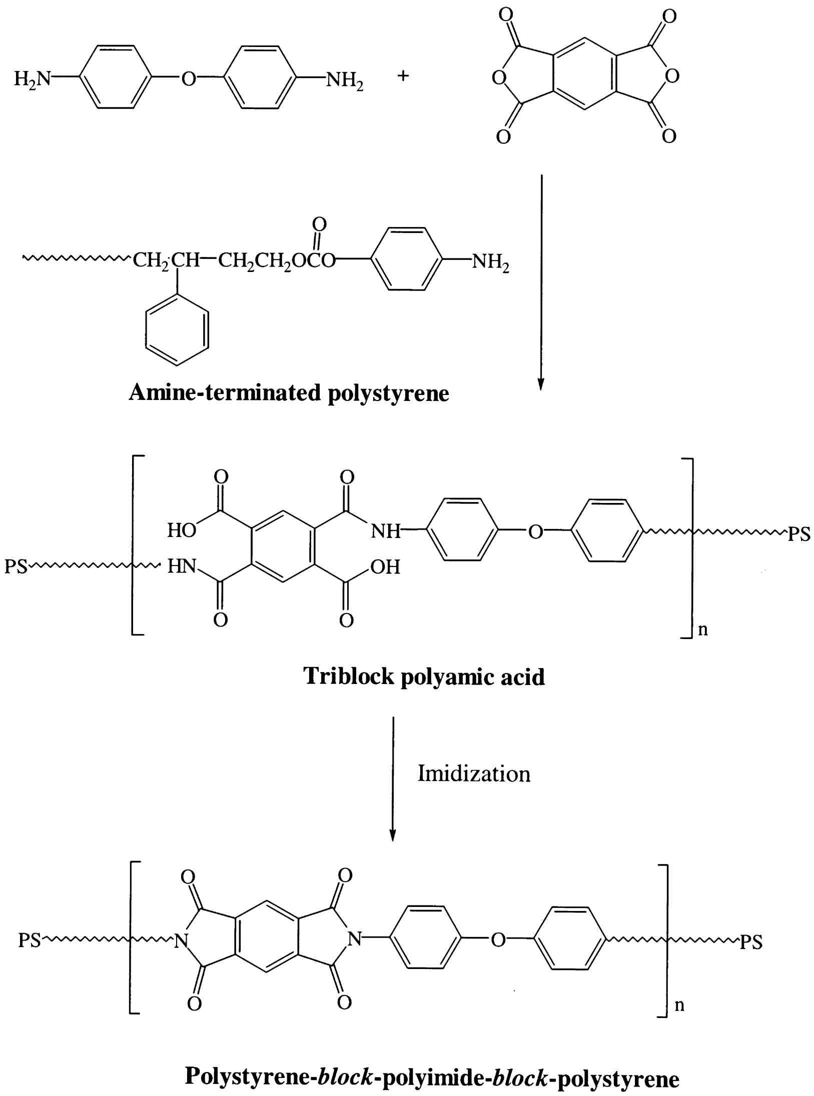
2.2. Synthesis of amine-terminated polystyrene

Amine-terminated polystyrene was prepared by anionic polymerization of hydroxyl-functionalized polystyrene followed by nitration and then reduction using palladium and hydrazine as shown in Scheme 1.

Anionic polymerization was carried out in a sealed reactor using breakseals and standard high vacuum technique. The formation of polymeric organolithium compounds could be readily identified by the specific orange-red color. After allowing the reaction to proceed overnight, ethylene oxide in the ampoules was added through the breakseal. The solution was hydrolyzed and precipitated in methanol containing a small amount of aqueous HCl. Hydroxyl-functionalized polystyrene was obtained after drying at 80°C in a vacuum oven. ^{1}H NMR ($CDCl_3$); δ (ppm) = 7.6–6.2 (aromatic protons), 3.3 (–CH_2O–), 2.6–0.8 (polymer backbone protons). IR (NaCl window, cm^{-1}); 3600 (hydroxyl group).

5.0 g of hydroxyl-functionalized polystyrene, 1 ml of pyridine, and 1.0 g of 4-nitrophenylchloroformate were dissolved in freshly distilled chloroform (50 ml) under nitrogen atmosphere, and then refluxed for 24 h. After completing the reaction, the solution was filtered and precipitated in excess methanol. The resulting solid was thoroughly washed by several reprecipitations in methanol from the chloroform solution. White powder was obtained after drying in the vacuum oven. ^{1}H NMR ($CDCl_3$); δ (ppm) = 7.6–6.2 (aromatic protons), 3.9 (–CH_2O–), 2.6–0.8 (polymer backbone protons). IR (NaCl window, cm^{-1}); 1760 (carbonyl group), 1535 and 1358 (nitro group).

2.6 g of the above product was dissolved in purified



Scheme 2.

tetrahydrofuran and 0.1 g of palladium was added into the solution. When the solution temperature reached 60°C by heating, 15 ml of hydrazine monohydrate was slowly added. The resulting solution was refluxed for 16 h. After the reaction, palladium was filtered off and the solution was poured into vigorously agitated methanol, resulting in white precipitates. Amine-terminated polystyrene was obtained after washed and vacuum dried. ^1H NMR ($CDCl_3$); δ (ppm) = 7.6–6.2 (aromatic protons), 5.6 (amine protons), 3.7 (–CH_2O–), 2.6–0.8 (polymer backbone protons). IR (NaCl window, cm^{-1}); 3448 and 3328 (amine group). GPC; M_n = 6700, $M_w/M_n = 1.09$.

2.3. Synthesis of triblock polyamic acid

Triblock polyamic acid with polystyrene as a thermally labile block was prepared as shown in Scheme 2. 4,4′-Oxydianiline (1.4928 g, 7.455 mmol) and amine-functionalized polystyrene ($M_n = 6700$, 0.603 g, 0.09 mmol) were dissolved in 30 ml of *N*-methyl-2-pyrrolidone and the solution cooled down to 0°C in an ice-water bath. Under the nitrogen atmosphere, pyromellitic dianhydride (1.6358 g, 7.50 mmol) was added into the solution and vigorously agitated by a mechanical stirrer. When the viscosity of the solution increased and stirring was not allowed any more, the reaction was stopped resulting in a yellow viscous triblock polyamic acid solution. For characterization, the polyamic acid solution was put slowly into the vigorously stirred methanol to precipitate the polymer solid, which was dried and dissolved in DMF (0.2 g dl^{-1}). Inherent viscosity (η_{Inh}) was measured with an Ubelohde viscometer at 30°C and the value was 0.49 dl g^{-1}.

2.4. Film preparation

The triblock polyamic acid solution was filtered through a

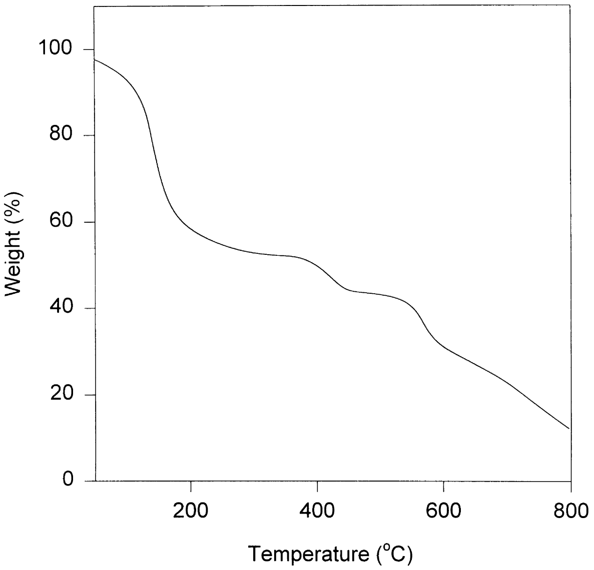


Fig. 1. TGA thermograms for the cast triblock polyamic acid film at the heating rate of 10°C min^{-1} in a nitrogen atmosphere.

Millipore Teflon filter (0.2 μm) and coated on a glass substrate with a doctor-blade. The thickness of the cast film was 0.04 mm. To remove excess solvent the film was dried in a vacuum oven at 100°C for 2 h. Then the film on a glass substrate was cured in a furnace under a nitrogen atmosphere. In this process it is important that the imidization should be carried out below the decomposition temperature of the thermally labile block.

2.5. Measurement

The molecular weight and molecular weight distribution of the synthesized polystyrene were determined by Waters GPC 410 system equipped with five Ultra-μ-styragel columns performed at a flow rate of 1.0 ml min^{-1} in THF. The values of M_n, M_w, and M_w/M_n were calculated by a calibration curve of the standard polystyrene samples. ^{1}H NMR spectra were recorded with a Varian Gemini-200 spectrometer. IR absorption spectra were measured on a Matson series 5000. Isothermal and variable temperature thermal gravimetric analyses (TGA) were performed on a Du Pont TA-2010 in a nitrogen flow. Thermomechanical analysis was carried out by Du Pont 2190 Thermomechanical Analyzer using tensile mode with a load of 0.06 N in the temperature range from 50 to 400°C at a heating rate of 5°C min^{-1}.

Atomic force micrographs (AFM) were recorded with Multimode Scanning Probe Microscope (Digital Instruments, Inc.). Tapping-mode was used to obtain height imaging data with 125 μm-long cantilevers. Cantilever has a very small tip radius of 5–10 nm. The lateral scan frequency was about 1.0 Hz. The sample moved in the *x*–*y* plane and a voltage was applied, which moved the piezo driver over the *z*-axis, in order to keep the probing force constant, resulting in a three-dimensional height image of the sample surface.

3. Results and discussion

3.1. Preparation of amine-terminated polystyrene

The block copolymer approach to polyimide nanofoams consists of a thermally stable matrix and a thermally labile material, which are chemically bonded as a triblock-type. This approach requires amine-terminated labile polymer with predictable molecular weight and narrow molecular weight distributions so as to react stoichiometrically with diamine and dianhydride leading to block polyamic acid. Alkyllithium-initiated anionic polymerization is the most effective method to make such polymers.

We prepared the living polystyrene by anionic polymerization and then incorporated amine group into the polystyrene in the chain end as shown in Scheme 1. Polstyryllithium compound was synthesized in a sealed reactor and then it reacted with ethylene oxide resulting in end-functional polystyrene. Hydroxyl-terminated polystyrene was identified by thin layer chromatography (TLC), ^{1}H NMR, FT-IR, and GPC. From the GPC chromatogram, a single narrow peak is apparent, which means that there are no coupling by-products. Polystyryllithium was perfectly converted to hydroxyl-functionalized polystyrene, which could be revealed by TLC, IR, and ^{1}H NMR. From the TLC test no evidence for unfunctionalized polymer was found. In the ^{1}H NMR spectrum, a little broad single peak at 3.3 ppm must be assigned to the methylene hydrogens bonded to the carbon, which is adjacent to the terminal hydroxyl. When the ratio of the area of this peak to the area of the aromatic hydrogen was calculated, the molecular weight calculated from the value was in accord with the GPC data.

Hydroxyl in the chain end was changed to nitro through the reaction of 4-nitrophenylchloroformate with hydroxyl-functionalized polystyrene. In the IR spectrum, the strong absorption peak of carbonyl was observed at 1760 cm^{-1} and the symmetric and asymmetric absorption bands of nitro were clearly identified at 1535 and 1358 cm^{-1}, together with the disappearance of hydroxyl. Amine-functionalized polystyrene was prepared from the reduction of nitro using palladium catalyst and hydrazine. In the IR spectrum, the two absorption peaks typical for primary amine at 3448 and 3328 cm^{-1} were apparent concurrently with the disappearance of the absorption bands of nitro. From the GPC chromatogram, the polydispersity index was found to be nearly unity.

3.2. Preparation of triblock polyamic acid

Triblock polyamic acid was prepared from the reaction of the amine-terminated polystyrene with 4,4′-oxydianiline and pyromellitic dianhydride. As the amine-terminated polystyrene has one functional group per polymer chain in

Table 1
Decomposition rates at several temperatures for amine-terminated polystyrene. These results were obtained from TGA thermograms measured under a nitrogen atmosphere

Temperature (°C)	Decomposition rate (%/min)
220	0.009
240	0.022
260	0.073
280	0.203
300	0.434

the end, the resulting polymer would be of the triblock-type with polystyrene being the terminal and polyamic acid unit being the center. The IR spectrum of the polyamic acid apparently shows the broad absorption bands of hydroxyl at 3500–2500 cm^{-1}, the strong peak of carbonyl in carboxylic acid at 1717 cm^{-1}, the peak of carbonyl in amide at 1683 cm^{-1}, and the peak associated with N–H bending vibration at 1543 cm^{-1}.

The precursor solution was filtered and coated on a glass substrate. The thickness of the cast film was 0.04 mm. To remove excessive solvent, the film was dried in a vacuum oven at 100°C for 2 h. Fig. 1 shows the TGA thermogram for the resulting film. The weight changes were recorded in the temperature range of 50–800°C under a nitrogen atmosphere. The thermograms clearly show three transitions in the weight loss (Table 1). The first transition between 100 and 200°C is attributed to the evaporation of residual solvent and the loss of water generated from the imidization reaction. The second weight loss that begins at around 350°C is due to the decomposition of the thermally labile polystyrene block (compare with Fig. 2) and the third at 550°C to thermal degradation of the polyimide block. So TGA thermograms may give very useful information when we determine the imidization condition. For example, if the cured triblock polyimide film shows no weight loss at around 200°C, this means that imidization is complete and no residual solvent remains.

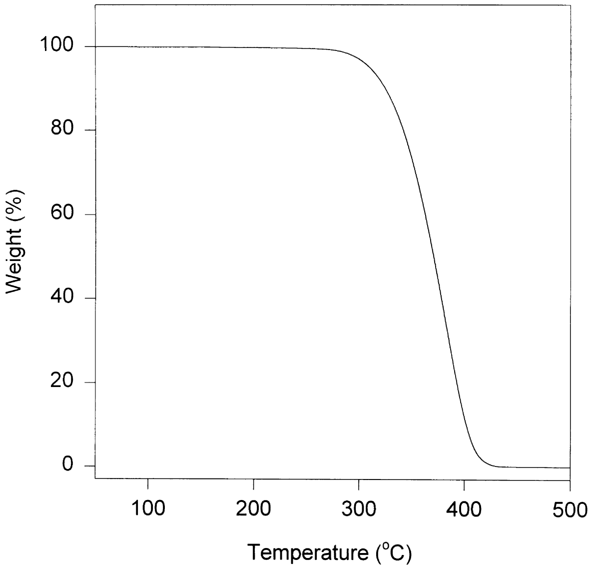


Fig. 2. TGA thermograms for polystyrene at the heating rate of 10°C min^{-1} in a nitrogen atmosphere.

3.3. Imidization

The block copolymer approach to polyimide nanofoams requires the preparation of films followed by curing to remove solvent, effect crosslinking, and imidize the triblock polyamic acid. It is essential to achieve the curing process without degrading the labile materials. Fig. 2 shows the TGA curve for polystyrene. The labile polymer was decomposed rapidly and completely in the temperature range of 300–400°C. This thermogram recommends that the curing process should be done below 300°C to avoid the thermal degradation of the polystyrene block.

To set up imidization conditions, IR measurements and TGA were used. For IR measurement the precursor solution was filtered through a Millipore Teflon filter (0.2 μm) and spin-coated onto a NaCl disk. To determine the curing temperature, each film was heated to 100, 150, 200, 250, and 300°C, respectively, at a heating rate of 5°C min^{-1} and cooled down to room temperature, then the IR spectra were measured. The results are shown in Fig. 3. As the curing temperature is increased, some absorption peaks associated with aromatic imide appeared gradually, together with those due to the disappearance of polyamic acid. The broad absorption bands of hydroxyl at 3500–2500 cm^{-1}, the strong peak of carbonyl in carboxylic acid at 1717 cm^{-1}, the peak of carbonyl in amide at 1683 cm^{-1}, and the peak of N–H bending vibration at 1543 cm^{-1} were gradually weakened. At the same time, the symmetric and asymmetric stretching vibration absorptions of aromatic imide became evident at 1780 and 1720 cm^{-1}, respectively. The IR spectra suggest that imidization was almost completed at 300°C. But we could not obtain complete imidization because it was difficult to get quantitative data from IR. Moreover, it was not certain whether NMP remained or not. Since the residual solvent affects the foaming process, it should be removed.

From the TGA thermograms, we can easily obtain quantitative proofs of complete imidization by detecting the weight loss of water due to imidization. In addition, we can make sure whether NMP remains or not. For the TGA measurement, the precursor solution was cast on a glass substrate and dried. The resulting films were heated to 100, 150, 200, 250, and 300°C, respectively, and then TGA was carried out without further annealing treatment. The results are shown in Fig. 4. As the curing temperature is increased, the amount of the first transition at around 200°C became lower. However, even the 300°C-cured sample still showed some weight loss. As the first transition was from both NMP and the water due to imidization, the amount of imidization that occurred at 300°C could not be determined

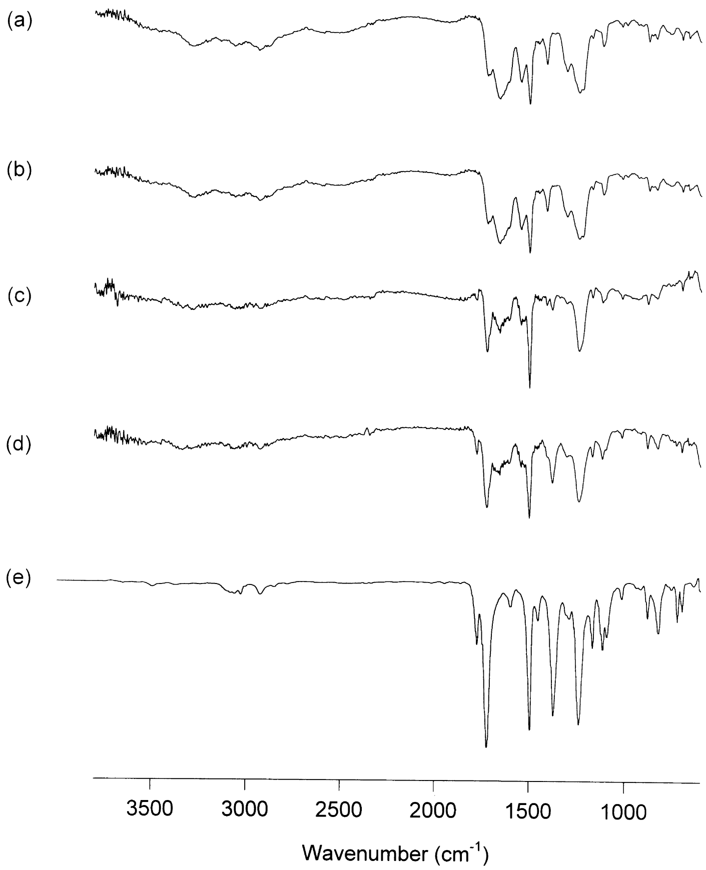


Fig. 3. IR spectra for the triblock polyimide film cured at: (a) 100°C; (b) 150°C; (c) 200°C; (d) 250°C; and (e) 300°C, respectively. All samples were heated to the curing temperature at the heating rate of 5°C min^{-1} and then, IR measured without additional annealing treatment.

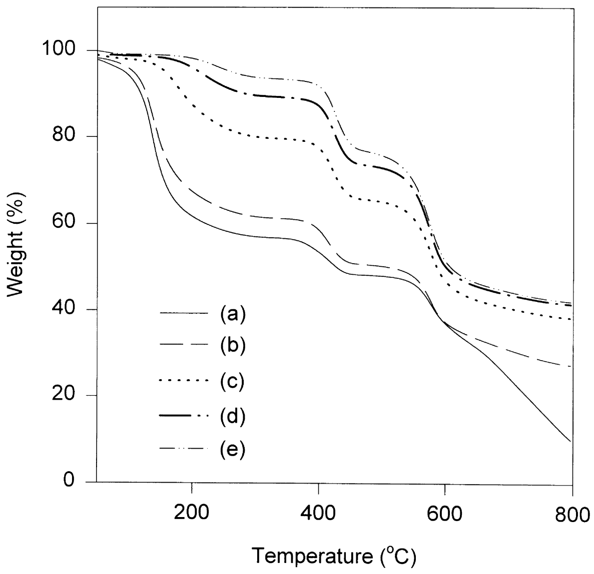


Fig. 4. TGA thermograms for the triblock polyimide cured at: (a) 100°C; (b) 150°C; (c) 200°C; (d) 250°C; and (e) 300°C, respectively. All samples were heated to the curing temperature at the heating rate of 5°C min^{-1} and then, TGA measured without additional annealing treatment.

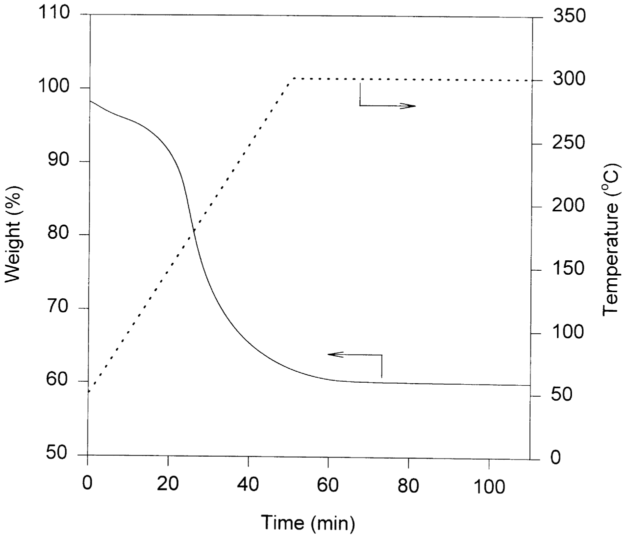


Fig. 5. Isothermal TGA test for the triblock polyamic acid to determine optimum curing condition. The dotted line is the heating profile and the solid line is the TGA thermogram.

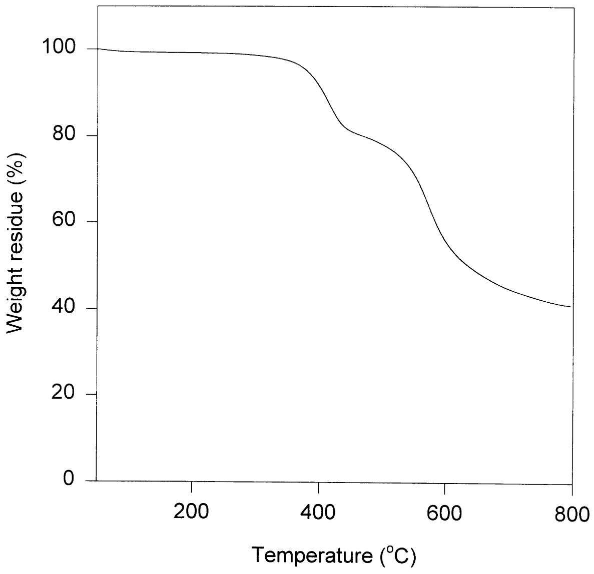


Fig. 6. TGA thermogram for the triblock polyimide cured on the condition shown in Fig. 5.

accurately. But, it was obvious that more thermal treatment was required. As can be seen in Fig. 2, thermal treatment over 300°C has a chance to decompose the thermally labile polystyrene block. So, it is better to lengthen the curing time at 300°C.

Fig. 5 shows the isothermal TGA test at 300°C to determine the curing time. The data showed that thermal treatment at 300°C for 1 h was enough to complete the curing step. Moreover, no appreciable weight loss from the labile polystyrene block was observed. Fig. 6 shows the TGA thermogram of the sample treated with this condition. The first transition thoroughly disappeared. This result provides clear evidence for the complete imidization and no residual solvent. In addition, the amount of residual labile block calculated from the thermogram is the same as the theoretical value within the error limit, indicating that the labile block is intact. Consequently, this is believed to be the optimum imidization condition.

AFM was used to investigate the triblock copolymer morphology. The precursor solution was spin-coated on a freshly cleaned slide glass after filtering the solution through a Millipore Teflon filter (0.2 μm). Then the films ware dried and cured according to the above optimum imidization condition. Fig. 7 shows the AFM image of the triblock polyimide film. The spherical phase was distributed regularly in the continuous matrix. The discrete one must be from the labile polystyrene block because it is a minor component. The sizes are ranged from 20 to 50 nm. The result indicates the triblock polyimides formed microphase-separated morphology. This is highly desirable to prepare the nanofoamed structure because according to the literature the size and its distribution of the air foams are analogous with the triblock polyimide morphology [17–21].

3.4. Thermomechanical analysis

To avoid the foam collapse, the matrix is required to have structural integrity during the foaming process. The polyimides used as the matrix material are known to have excellent thermal stability and rigidity. However, it has been reported from many studies that polyimides cured on a substrate have residual stresses developed during the solvent evaporation and curing [25–36]. According to the reports, the residual stresses cause contraction in the polyimide film. This structural instability may result in serious problems during the foaming process, such as foam collapse or blowing.

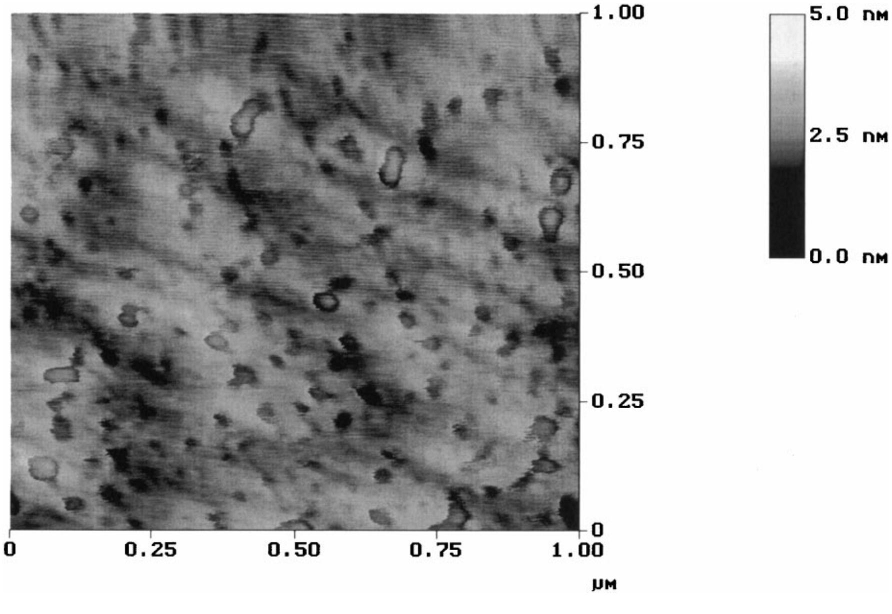


Fig. 7. AFM image for the triblock polyimide.

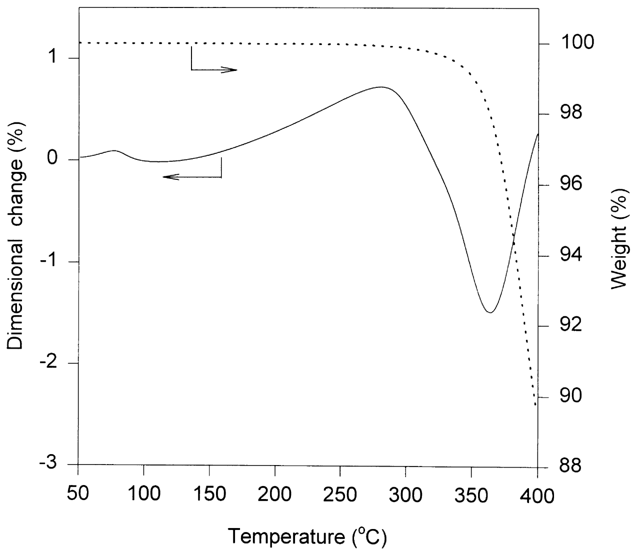


Fig. 8. TMA data (—) and TGA thermogram (–––) for the triblock polyimide. Both were measured at the heating rate of 5°C min^{-1} in a nitrogen atmosphere. TMA data was obtained by measuring the dimension changes in the plane of the film using tensile mode.

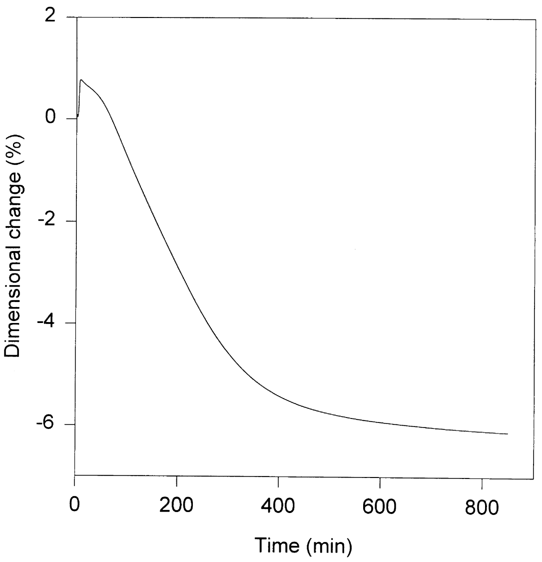


Fig. 10. Isothermal TMA test for the triblock polyimide at 270°C to determine the annealing condition to relax the residual stresses.

To identify whether contraction occurred in our sample, TMA was carried out for the triblock polyimide film. The specimen dimension was $12.79 \times 3.00 \times 0.04$ (length × width × thickness, mm) and the load was 0.06 N. The TMA data are shown in Fig. 8. As expected, contraction occurred at several points over the temperature range of 50–400°C, but it was not easy to explain the data. Comparing with the TMA data for homo polyimide without a labile block, it would be simple to interpret the data. For this end, homo polyamic acid was synthesized from the reaction between 4,4′-oxydianiline and pyromellitic dianhydride in the NMP solvent. After the cast precursor film on a glass substrate was dried and cured in the same condition with the block polyimide, thermomechanical behavior of the film was measured by TMA with the same method. The data in Fig. 9 showed that contraction occurred at around 300°C. As studied by many researchers, this is due to the residual stress formed during the drying and curing processes. According to the reports, the shrinkage associated with the solvent loss in the drying and curing steps occurs preferentially in the thickness direction, while the precursor chains parallel to the surface of the substrate (i.e. in the plane of the coating) are constrained on the glass substrate. This causes stress. When the film gets heated and the mobility of polymer chains become higher, the stretched chains would return to the original state. This explains the contraction in the TMA graph.

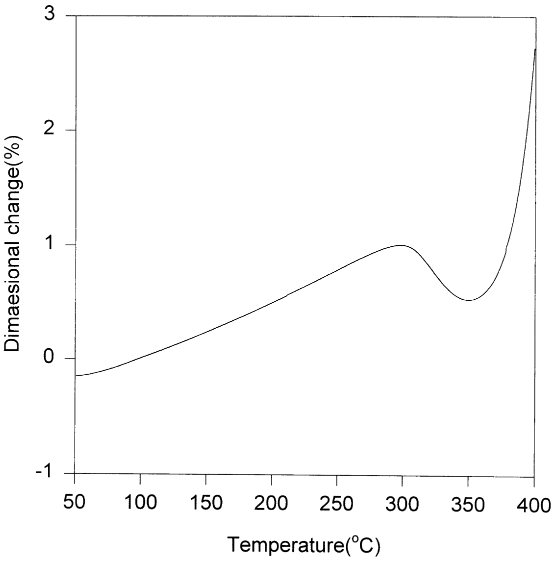


Fig. 9. TMA data for poly(4,4′-oxydiphenylene pyromellitimide) at the heating rate of 5°C min^{-1} in a nitrogen atmosphere.

Based on the above result, the TMA data for the block polyimide shown in Fig. 8 could be interpreted. The first contraction that begins at 75°C is attributed to the residual stresses associated with polystyrene blocks. The amount of this shrinkage is relatively small, because the content of polystyrene is only 16 wt% and, in addition, the polystyrene chains are chemically bonded with the rigid polyimide blocks and thus the mobility of the polymer chains is confined. The second contraction in the range of 275–360°C is probably due to the residual stresses associated with the polyimide blocks. The triblock polymer film contracted at a little lower temperature than homo polyimide, due to the already softened polystyrene blocks. Above the temperature, the shrinkage proceeds rapidly and constantly. However, as the temperature passes over around 330°C, the shrinkage rate becomes a little higher. As can be seen from the TGA thermogram (dotted line) in Fig. 8, the decomposition of labile blocks begins at this

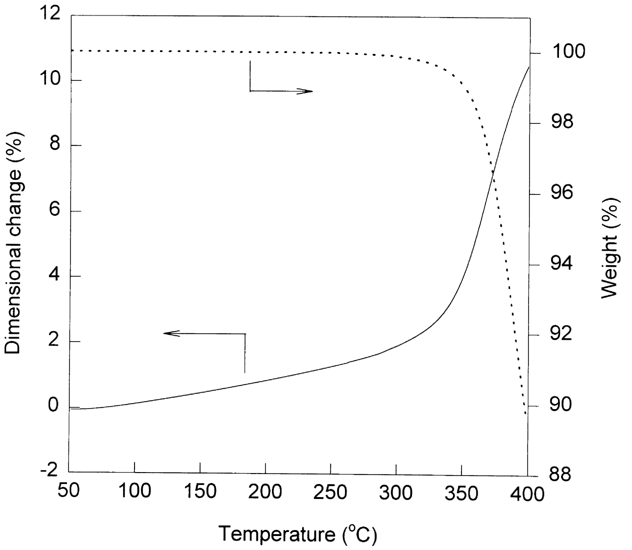


Fig. 11. TMA data (—) and TGA thermogram (---) for the triblock polyimide treated by the annealing process shown in Fig. 10. Both were measured at the heating rate of 5°C min^{-1} in a nitrogen atmosphere.

point. Namely, air foams begin to form. Contrary to our expectation, however, shrinkage rate became higher, indicating collapse of the foams.

The polyimide matrix is required to be rigid and stable lest foams should be collapsed or expanded. For this end, annealing treatment to relax the residual stresses is necessary to optimize the triblock polyimide before the foaming process. It is important that the annealing process be done so that the labile block should be intact and the residual stresses relaxed. To achieve such a condition, isothermal TMA test was carried out. The specimen dimension and the analysis method were identical to the above TMA test. The dimension changes were recorded for the triblock polyimide film at 270°C. The film shrunk rapidly and constantly for the first 6 h and then the rate was retarded. Fig. 10 shows that thermal treatment at 270°C for 14 h is enough to relax the residual stress. The TGA test confirmed that there was no decomposition of the polystyrene blocks in this condition. In Fig. 11, thermomechanical behavior was described for the triblock polyimide film treated by this annealing process. Over the temperature range of 50–300°C, no contraction was observed. Moreover, even in the range of 300–370°C, where polystyrene blocks decomposed and air foams formed, no appreciable contraction occurred. This means that there was no foam collapse. From the results, annealing is believed to be a very essential process to prepare the optimized foamed structure of the triblock polyimide. When the temperature approached around 370°C, the thermal expansion rate was retarded a little. This is probably because the polyimide matrix was so softened that foams collapsed and thus some contraction occurred.

Morphological variations with processing conditions will be discussed in the next paper.

4. Conclusion

To obtain the foamed structure from the block polyimide approaches, the polyimide matrix should have adequate structural integrity to prevent foam collapse. However, the cured triblock polyimide films have the residual stresses developed during the drying and curing steps. These residual stresses cause the film to contract in the foaming process, resulting in foam collapse. To overcome this problem, the triblock polyimides should be optimized by the annealing treatment to relax the residual stresses. From the thermomechanical analysis, the annealed triblock polyimides showed no appreciable contraction and, moreover, no foam collapse. From the results, the annealing treatment is assumed to be very essential to prepare the optimized triblock polyimide for the foamed structure.

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