



166166

16th April 2004

- 1 -

A CHEMICAL CURING PROCESS FOR POLYIMIDE FORMATION

Background of the Invention

Field of the Invention

The present invention relates to a method of carrying out chemical curing of polymer precursors – in particular, curing of polyimide precursors by chemical imidization. Further, the invention relates to the use of a solvent in the supercritical state as a means of conveying the requisite dehydrating agents, catalysts, and other necessary chemicals to the precursor matrix. Further, it relates to a method of chemical imidization that is much faster than by conventional means. Still further, the disclosure relates to a method of effective removal of residual chemicals and solvents from the cured matrix. Even further, it relates to a method of sequestering and protecting thermally sensitive molecular species and materials that are soluble in common organic and aromatic solvents in mechanically and thermally robust polymer matrices.

Description of the Related Art

Thermally stable polymers such as polyimides find a variety of engineering and electronic applications. Most of these polymers possess extended rigid planar aromatic and hetero-aromatic structures and are infusible and insoluble. The conventional method of overcoming this processing problem is to prepare the final product by a two-step synthesis (C.E. Sroog, A.L. Endrey, S.V. Abramo, C.E. Berr, W.M. Edwards, and K.L. Olivier, J. Polym. Sci. A3 (1965) 1373).

The first step consists of obtaining a soluble polymer precursor, namely, a polyamic acid, ester or salt. Typically, this is prepared in one of a variety of dipolar amide solvents. After forming as desired, the polyamic precursor is converted to the final polyimide by thermal or chemical treatment.

The thermal method of imidization (i.e., converting the polyamic precursor to polyimide) is carried out by heating the precursor to temperatures in the range of 250-400° C. At these conditions, the open polyamide structure in the polyamic acid is converted to a closed imide form with the accompaniment of loss of a water molecule. The heating rate influences the final product: a gradual increase in temperature is a popular heating cycle (V.L. Bell, B.L. Stump, and H. Gager, J. Polym. Sci., Polym. Chem. Ed., 14 (1976) 2275); however, since the presence of solvent increases the plasticity and thus the mobility of the reacting functional groups, a rapid heating that allows higher (temporary) solvent



G00002

concentrations is considered to yield polyimides with higher degrees of imidization (A.I. Baise, J. Appl. Polym. Sci. 23 (1986) 4043). Similarly, thicker films cure to a higher degree than do thinner films because of the retention of larger proportions of solvents (R. Ginsberg and J.R. Susko, in 'Polyimides: Synthesis and Characterisation', Vol. 1, (ed. K.L. Mittal), Plenum, New York (1984) p. 237).

Polyamic acids can be converted to the corresponding polyimides at ambient temperature by treatment with mixtures of aliphatic carboxylic acid anhydrides that act as dehydrating agents and tertiary amines that catalyze cyclodehydration (M.I. Bessonov, M.M. Koton, V.V. Kudryavtsev and L.A. Laius, 'Polyimides: Thermally Stable Polymers', New York, Plenum (1987)) Solvents typically employed are aromatic in nature, such as benzene.

While either of these methods is suitable for conventional curing operations, each method has its drawbacks when dealing with advanced, heterogeneous and composite structures. First, as seen above, the degree of imidization is dependent on the solvent content in the matrix during the curing state. While a high rate of heating is suitable for increasing the degree of imidization, loss of solvent from the matrix at an excessive rate will result in bubble formation and lack of homogeneity (T. Takekoshi in 'Polyimides: Fundamentals and Applications' (eds. M. K. Ghosh, K.L. Mittal), New York, Marcel Dekker (1996)). Second, thermal imidization limits the applicability of polyimides to situations that can tolerate high temperature. Thus, the thermal treatment process is unsuitable for composite structures that contain thermally sensitive materials that either decompose or evaporate at elevated temperatures. Though high temperatures can be avoided in chemical imidization, this method still has to deal with long imidization times (K.F. Schoch, W.A. Su, and M.G. Burke, 'Deposition and Characterisation of Polyimide Langmuir-Blodgett Films', Langmuir 9 (1993) 278), dissolution of low molecular weight materials, low diffusivities, and solvent disposal and environmental problems. Also, chemically imidized materials will still have to undergo a heat treatment process to ensure complete removal of solvent (P.M. Cotts, in 'Polyimides: Synthesis, Characterisation and Properties', Vol. 1, ed. K.L. Mittal, Plenum, New York (1984)). Still further, chemical imidization in its present form, though not energy intensive, does not find favor for commercial applications because of problems associated with handling of the reagents (F.W. Harris, in 'Polyimides' (eds. D. Wilson, H.D. Stenzenberger and P.M. Hergenrother), New York, Chapman and Hall (1990)).

The supercritical state, often called the fourth state of matter, refers to matter whose temperature and pressure are both above the critical values. At these conditions, the material occupies a state intermediate between that of a gas and a liquid and has properties representative of a combination of both these states. For instance, the density of matter in the supercritical state is close to that of the liquid; however, the transport properties (diffusivity, viscosity) are more representative of the gaseous state. The enhanced solubility of many organic (and even inorganic) substances in the fluid is an attractive feature of material in the supercritical state. Coupled with the gas-like transport properties, this characteristic makes supercritical fluids (and dense gases in general) suitable as solvent vehicles for extractions/impregnations from/to solid matrices. The published literature provides numerous instances of specific organic and inorganic species that are soluble in supercritical fluids (for example, A.W. Francis, J. Phys. Chem., 58 (1954) 1099).

Formation of polyimide by chemical imidization is a well-established method. Fujisaki et al. (K. Fujisaki, T. Ikeda, T. Miwa, S. Numata and H. Shimanoki (European Patent 389,195 (1992))) teach a method of using chemical imidization to obtain patterned polyimide films by selectively reacting the polyimide precursor through a mask. Kamikita and Awaji (Japanese Patent 63,069,567 (1988)) describe a method of using chemical imidization to obtain ultrathin polyimide films for membrane and insulation applications formed by the Langmuir-Blodgett method. Kajitani (Japanese Patent 3,177,407 (1991)) discusses the use of a supercritical fluid as a solvent conveying polymerizable compounds to a polymer molding matrix. A polyimide was impregnated with maleic anhydride by means of supercritical carbon dioxide. Fu et al. demonstrate a method of replacing conventional organic solvents in the preparation of a conductive polypyrrole-polyurethane foam (Y. Fu, D.R. Palo, C. Erkey and R.A. Weiss, Macromolecules 30 (1997) 7611). Polyurethane is impregnated with an oxidant by using supercritical carbon dioxide. Subsequently, pyrrole vapour is introduced into the oxidant-containing matrix resulting in polymerization of pyrrole to form polypyrrole.

The above references discuss the applications of chemical imidization and use of supercritical media in polymeric matrices that have been fully formed. These methods of imidization still have to contend with long exposure times, and use and disposal of chemicals. Further, the references pertaining to the use of supercritical fluids discuss processing techniques subsequent to formation of the matrix polymer and do not discuss

performing part of the two-step polyimide synthesis in a supercritical medium. The latter technique, described in detail later, possesses attendant benefits in terms of speed of reaction, impregnation and retention of thermally sensitive compounds, low reagent consumption and removal of solvent under mild conditions.

5 This disclosure is concerned with a method of chemical curing that replaces the aromatic solvent environment with a material, typically carbon dioxide, in the supercritical state. This technique accomplishes a number of things not possible in conventional imidization processes. It allows for retention of functional, thermally sensitive compounds in the cured polymer matrix; it facilitates provision of a controlled environment of specific
10 solvent and chemicals to the desired extent for the desired duration, and it facilitates rapid transport of species to and from the matrix. Furthermore, it allows for controlled use of chemicals with minimal excess and affords recovery of the desired compounds.

Summary of the Invention

The invention relates a chemical imidization technique for curing polymers such as
15 polyimides. A suitable solvent (typically, carbon dioxide) is compressed and its temperature controlled to form a supercritical state in a high-pressure vessel that contains the polymer precursor in its formed state (for example, as a thin film). Metered amounts of dehydrating agents (typically, acetic anhydride) and catalysts (typically, pyridine or triethyl amine) that are soluble in the supercritical fluid are fed into the vessel as solutes.
20 The polymer precursor is thus exposed to the dense gas environment together with the chemical agents. After a suitable period of exposure at these conditions, the dense gas mixture containing the unused chemicals is displaced by the pure solvent. This ensures complete removal of the chemical agents and residual organic solvents. Finally, the vessel is de-pressurized. This process results in a cured polymer that performs as well as
25 conventionally imidized polymers. Furthermore, it allows for incorporation of functional, low molecular weight materials that are thermally sensitive, and also allows the plasticizing effect of the solvent to be retained to the extent and for the time desired.

Brief Description of the Drawings

FIG. 1 is a schematic drawing of the experimental apparatus for chemical
30 imidization in the supercritical phase;

FIG. 2 is a series of infrared spectra of polyimides made by various methods;

FIG. 3 is a series of graphs of thermogravimetric analyses of polyimides imidized

by different methods;

FIG. 4 is a series of graphs of thermogravimetric analyses of imidization reactions at supercritical conditions;

5 FIG. 5 is the visible absorption spectrum of polyimide-Cu octabutoxy phthalocyanine LB film before and after imidization in the supercritical medium;

FIG. 6 is the visible absorption spectrum of polyimide-Cu octabutoxy phthalocyanine LB film before and after chemical imidization in benzene;

FIG. 7 is the visible absorption spectrum of polyimide-poly (3-n-dodecyl thiophene) LB film before and after imidization; and

10 FIG. 8 is a graph of thermogravimetric analyses of polyimide films chemically imidized for the same duration in different media.

Detailed Description of the Preferred Embodiment

A chemical imidization technique for converting polyimide precursor to polyimide is disclosed. The polyimide precursor can exist in the form of a polyamic acid or polyamic
15 acid-alkyl amine salt. Further, the precursor can be configured as a thin film or as a Langmuir-Blodgett multilayer. The precursor is held in a high-pressure vessel together with a dehydrating agent (typically, acetic anhydride) and catalyst (typically, pyridine). Carbon dioxide is compressed to a pressure not less than 7.3 MPa, heated to a temperature not less than 35° C so that it attains the supercritical state, and is conveyed to the high-
20 pressure vessel. The precursor is exposed to the dehydrating agent and catalyst for a pre-determined period of time in the supercritical medium, at the specified pressure and temperature which is held constant (the static stage).

Controlled amounts of a solvent for the precursor (for example, an amide solvent such as dimethyl acetamide) can be introduced together with the dehydrating agent and
25 catalyst to provide an additional variable for optimization of the process.

At the end of the static stage, fresh carbon dioxide is introduced into the high-pressure column in order to flush the unreacted chemicals and reaction products in the so-called dynamic phase. The dynamic stage is continued to the extent required for removing the residual material. The experimental conditions under which the dynamic flush is
30 performed can be the same as that employed for the static stage, or can be optimized independently of the static stage.

Unreacted chemicals and reaction products can be recovered from the effluent during the dynamic flush by use of a cold trap with a suitable solvent.

- 6 -

The dynamic flush is followed by de-pressurization to ambient conditions and subsequently, the imidized precursor is removed from the high-pressure column.

This method eliminates the need for an aromatic solvent such as benzene or toluene as a vehicle for conveying reactants and products to and from the precursor matrix.

5 Further, this method obviates the need for a thermal treatment subsequent to the curing step.

Chemical curing in the supercritical medium requires smaller amounts of the dehydrating agent and catalyst compared to that required for conventional chemical imidization.

10 The use of a solvent in a supercritical state facilitates rapid, facile transport of chemical agents and products to and from the precursor matrix. Further, the method allows for rapid and effective diffusion of species in solid precursor matrices, such as thin films. Even further, the use of a supercritical medium results in a much shorter duration of exposure to chemical agents than that required in conventional chemical curing treatment.

15 Use of a supercritical medium allows formation of polyimide composites containing thermally sensitive compounds or chemicals that are soluble in common organic or aromatic solvents. The guest species are introduced as dopants into the precursor matrix (the host) or are incorporated as mixed Langmuir films in Langmuir-Blodgett multilayers. The performance of the guest moieties is unaffected by the
20 described imidization process.

1. Experimental Methods

Example 1: Polyimide from Polyamic Acid

Pyromellitic dianhydride (obtained from TCI) was purified by recrystallization from acetic anhydride followed by vacuum drying at 150-180° C for 4 hr. 4,4'-
25 diaminodiphenyl ether (TCI) was purified by recrystallization from ethanol followed by vacuum drying at 60° C for 4 hrs. N, N'-dimethyl acetamide (Merck) was distilled at atmospheric pressure. Pyridine (Fluka), acetic anhydride (Merck), and benzene (Fluka) were used without further treatment.

30 The polymerization reaction to obtain polyamic acid was carried out in a 50 ml flask fitted with a magnetic stirrer, nitrogen inlet and outlet, drying tube and stopper. 0.5 g of diamino diphenyl ether (0.0025 mol) was added to the flask through a dry powder funnel and the residue flushed into the flask with 8 ml of dry dimethyl acetamide. 0.545 g

of pyromellitic anhydride (0.0025 mol) was then added through a second dry powder funnel and the residue flushed into the flask with 2 ml of dimethyl acetamide. The contents of the flask were vigorously stirred and the system subjected to a vacuum environment. Then, the system was maintained under slight positive nitrogen pressure and the mixture stirred for 4 hr at room temperature. Subsequently, the solution was spin-coated onto glass slides at 600 rpm for 1 minute and dried under vacuum for an hour at 85 °C.

The films were imidized thermally and chemically. Thermally imidized films were prepared by heating the dried film at 300 °C for 1 hr. Heating beyond this time did not result in any further change in the infrared absorption spectrum. Chemical imidization was performed by immersing the dried film in a mixture of acetic anhydride and pyridine in benzene (volumetric ratio 1.4:1:10) for 12 hr. Subsequently, the film was rinsed copiously with benzene and dried at 80 °C under vacuum.

Chemical imidization in a supercritical medium was performed in the experimental apparatus shown in Figure 1. The dried film was placed in a high- pressure column together with an adsorbent holding about 3 ml each of acetic anhydride and pyridine. The column was held at a constant temperature in the range of 35 °C to 50 °C in a heated water bath. After an initial flush with carbon dioxide to displace ambient air, the column was filled with carbon dioxide after the latter had passed through a pre-heating coil and was pressurized to a constant, operating pressure in the range 7.5 MPa to 15 MPa. The entrance and exit to the column were sealed, and the column was maintained at these conditions for a time that ranged from 15 minutes to 1 hour; subsequently, a stream of carbon dioxide at the system pressure or at a pressure different from the system pressure was introduced into the column, and a flow was set in motion to replace the environment around the sample with pure carbon dioxide. The preferred conditions for the static stage were 13 MPa for pressure, 40 °C for temperature, and 1 hr for the duration. The preferred duration for the dynamic flush stage was 1 hour at a flow rate of 200 ml/min (measured at STP conditions).

After the displacement, the column was gradually de-pressurized to one atmosphere. The imidized samples were characterized by infrared spectroscopy and thermogravimetry. The latter was performed at a heating rate of 3° C/min in a nitrogen atmosphere.

The peak at 1780 cm⁻¹ in the IR spectra (Figure 2) confirmed the presence of imide.

Figure 2 also shows that the IR scans for samples treated thermally, chemically and in the supercritical medium are similar to each other. The TG (thermogravimetric) curves for the three samples show that they decompose at about the same temperature (Figure 3).

Example 2: Polyimide Langmuir-Blodgett Films

5 Polyamic acid prepared in N, N'-dimethyl formamide or N, N'-dimethyl acetamide as in Example 1 was mixed with n-octadecyl amine in a 1:2 mole ratio and dissolved in a benzene-dimethyl formamide solvent mixture (1:1 by volume). This solution was spread on an aqueous surface contained in a NIMA Langmuir-Blodgett deposition instrument. The aqueous medium was purified by distillation followed by de-ionisation. A Langmuir
10 film was formed at the air-water interface by compression and the film was sequentially transferred to a silicon wafer, glass slide or calcium fluoride plate. Prior to the deposition, the substrates had been made hydrophobic by treatment with ferric stearate. 20 or more molecular layers were deposited at a surface pressure of 20 mN/m. The film was subjected to chemical curing in supercritical carbon dioxide as described according to the preferred
15 conditions described in Example 1. IR characterisation before and after imidization revealed the presence of the imide absorption at 1780 cm⁻¹ and a greatly diminished alkyl absorption peak at 2900 cm⁻¹, indicating successful completion of the imidization reaction.

Example 3: Employment of triethyl amine as catalyst

Film preparation and chemical imidization in the supercritical medium was carried
20 out according to the preferred conditions described in Example 1, with pyridine replaced by triethyl amine. No significant difference was observed in the spectroscopic and thermogravimetric characterisation relative to using pyridine as the catalyst.

Example 4: Employment of varying conditions in the dense gas state

Chemical imidization was carried out in the dense gas environment at varying
25 temperatures and pressures. Subsequently, the imidized samples were characterised by thermogravimetry. Figure 4 illustrates the effect of the conditions on weight loss. In general, the supercritical state facilitates completion of the imidization reaction, as indicated by the absence of weight loss of the polyimide until higher temperatures are attained. On the other hand, sub-critical conditions (viz., carbon dioxide in the liquid
30 state) are not conducive for completion of the reaction. Further, the reaction is incomplete at the lowest density employed in the supercritical state.

Example 5: Recovery of unreacted chemicals

Film preparation and chemical imidization in the supercritical medium was carried out as in the preferred conditions described in Example 1. During the dynamic flush stage, the effluent from the high-pressure column was decompressed through a metering valve kept at elevated temperatures. The decompressed gas was bubbled through a flask containing benzene that was maintained at about 5° C. The presence of unreacted pyridine and acetic anhydride in the aromatic solvent was confirmed by infrared spectroscopy.

Example 6: Incorporation of thermally sensitive materials: composite Langmuir-Blodgett films

Spreading solutions containing polyamic acid, octadecyl amine and copper octabutoxy phthalocyanine (about 50% chromophore content, mol basis) were dissolved in a solvent vehicle consisting of benzene and dimethyl acetamide (1:1 by volume). Langmuir-Blodgett films were deposited on calcium fluoride plates as described in Example 2. One set of such films was imidized chemically in the presence of supercritical carbon dioxide according to the preferred conditions as described in Example 1. Ultraviolet-visible spectroscopy before and after the imidization process showed that the phthalocyanine was retained in the film (Figure 5).

Another set of films was imidized chemically by the conventional method (immersion in a mixture of acetic anhydride and pyridine in benzene (volumetric ratio 1.4:1:10) for 12 hr) as described in Example 1. The resulting films showed complete loss of copper octabutoxy phthalocyanine when examined by UV-visible spectroscopy (Figure 6).

Spreading solutions containing polyamic acid, octadecyl amine and poly (3-n-dodecyl thiophene) (about 50% chromophore content, mol basis) were dissolved in a solvent vehicle consisting of benzene and dimethyl acetamide (1:1 by volume). Langmuir-Blodgett films were deposited on calcium fluoride plates as described in Example 4. One set of such films were imidized chemically in supercritical carbon dioxide according to the preferred conditions as described in Example 1. The films were characterised by ultraviolet-visible spectroscopy subsequent to doping by iodine (Figure 7). Imidization in the supercritical medium did not compromise the functional properties of the thiophene; however, thermal imidization did result in loss of activity of the thiophene group.

Surface resistivity of the composite Langmuir-Blodgett films was measured to

ascertain the electrical activity of the films. The composite film containing copper octabutoxy phthalocyanine displayed a surface resistivity of 10^5 ohms/square; this value is comparable to that obtained from Langmuir-Blodgett films of pure copper octabutoxy phthalocyanine. The surface resistance of the poly (3-n-dodecyl thiophene)-containing composite Langmuir-Blodgett films were above 10^{11} ohms/square when measured after the imidization process as performed according to the preferred conditions described in Example 1. When the films were exposed to iodine vapour, the values obtained were less than 10^5 ohms/square. This is comparable to the surface resistivity of a pure Langmuir-Blodgett film of poly (3-n-dodecyl thiophene).

10 **Example 7: Duration of the imidization reaction**

Films of polyamic acid were spin-coated on silicon wafers as described in Example 1. One sample was imidized chemically by conventional means as described in Example 1, but with an immersion time of 1.5 hrs. Another sample was imidized chemically in the supercritical environment at the preferred conditions of temperature and pressure described in Example 1. The static stage was performed for 0.5 hr and the dynamic flushing was carried out for 1 hr. Thermogravimetry shows that an exposure of 1.5 hr is insufficient to complete the imidization in the case of the conventional method using benzene (Figure 8).

CLAIMS

1. A method of chemical curing or chemical imidization of a polyimide precursor in the form of a polyamic acid or polyamic acid-alkyl amide salt and configured as a thin film or as a Langmuir-Blodgett multilayer to form an aromatic polyimide comprising the steps of:
 - a) reacting the polyimide precursor with a dehydrating agent and a catalyst in the presence of a solvent in a supercritical fluid to form an aromatic polyimide and further reaction products:
 - b) flowing supercritical fluid through said aromatic polyimide for a time sufficient to rinse out said dehydrating agent, said catalyst, and said further reaction products, wherein the said flowing is subsequent to said reacting; and
 - c) removing said supercritical fluid from said aromatic polyimide to obtain the cured polyimide.
2. The method of claim 1, wherein the dehydrating agent or the catalyst is incorporated in controlled amounts in said supercritical fluid.
3. The method of claim 1, wherein the curing reaction is carried out at pressures greater than 7.3 MPa.
4. The method of claim 1, wherein said reacting is carried out at temperatures greater than 35°C.
5. The method of claim 1, further comprising recovering unused dehydrating agent, catalyst, or supercritical fluid.
6. The method of claim 1, wherein said aromatic polyimide contains phthalocyanine compounds, or poly-thiophene.

7. The method of claims 1 or 6, wherein said aromatic polyimide is soluble in aromatic solvents.
8. The method of claim 1, wherein said supercritical fluid comprises carbon dioxide.
9. The method of claim 1, wherein said dehydrating agent comprises acetic anhydride.
10. The method of claim 1, wherein said catalyst comprises pyridine or triethylamine.
11. An aromatic polyimide prepared by the method of claim 1.
12. The aromatic polyimide of claim 11, wherein said aromatic polyimide is cured.
13. The aromatic polyimide of claim 11, wherein said aromatic polyimide contains phthalocyanine compounds or poly-thiophene.
14. The aromatic polyimide of claim 13, wherein said aromatic polyimide is prepared by reacting a polyimide precursor with a dehydrating agent and a catalyst in a supercritical fluid.
15. The aromatic polyimide of claims 11, wherein the aromatic polyimide is soluble in aromatic solvents.

16. The aromatic polyimide of claim 15, wherein said aromatic polyimide is prepared by reacting a polyimide precursor with a dehydrating agent and a catalyst in a supercritical fluid.