Notes

Soluble Polyimides with Polyalicyclic Structure. 2.[1] Polyimides from Bicyclo[2.2.1]heptane-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-Dianhydride

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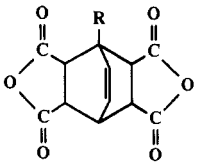
Introduction

Although polyimides synthesized from aromatic tetracarboxylic dianhydrides and aromatic diamines such as Kapton exhibit high-temperature stability, the application of the aromatic polyimides is restricted due to their poor solubility in organic solvents and their high glass transition or softening temperatures[2] that cause difficulty in fabrication. Thus, many attempts have been made to improve their fabricability. Among them, aromatic polyimides have been presented utilizing aromatic dianhydrides and/or aromatic diamines which were polyphenylated[3-6] or contained fluorine, chlorine, phosphorus, etc.[7-12] On the other hand, another approach to attain an enhanced solubility was utilization of alicyclic dianhydrides such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride[13] and cyclobutane-1,2,3,4-tetracarboxylic dianhydride,[14,15] though the thermal stability was anticipated to be compromised. On the basis of the results, adoption of a polyalicyclic dianhydride has been undertaken toward the improvement of their fabrication without sacrificing thermal stability. The introduction of a polyalicyclic structure into the polymer backbone would facilitate less polymer–polymer interaction and increased main chain rigidity and, additionally, possibly less probability of main chain scission because of having multibonds.

In our first study,[16] polyalicyclic dianhydrides such as bicyclo[2.2.2]oct-7-ene-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (1) and its homologue were



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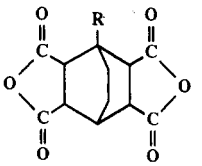

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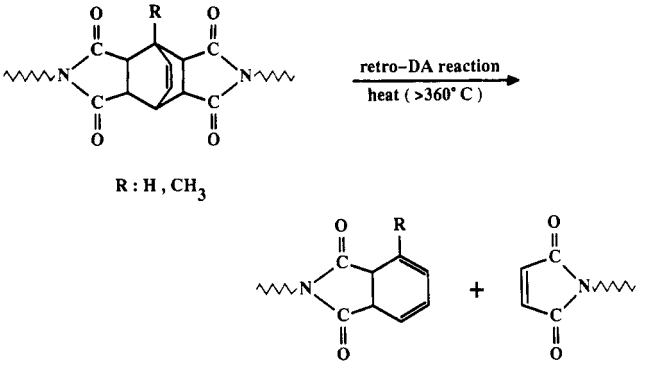
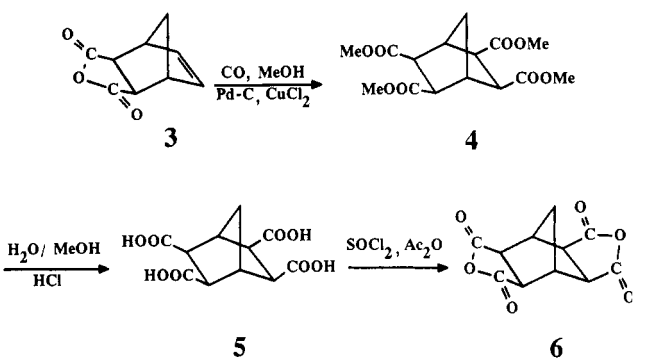
synthesized and used for polycondensation with aromatic diamines to produce polyimides with better solubility and thermal stability. From the GC–MS analysis of the pyrolyzed products of the prototype of the polyimides and the thermogravimetric analysis of the polymers, it was proposed that the decomposition that commenced around 360 °C in nitrogen was a consequence of the retro-Diels–Alder (DA) reaction of the retrodegradative bicyclo[2.2.2]-oct-7-ene structure (Scheme I). Keeping in mind these

Scheme I



Scheme II



facts, it was postulated that if bicyclo[2.2.2]octane-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-dianhydrides (2) were polymerized with an aromatic diamine, the resultant polyimide would be more thermally stable because the retro-DA reaction no longer seems to take place at the polyalicyclic unit. Compound 2 was thought to be easily prepared by reduction of 1. A variety of reductive procedures were applied to 1; however, these efforts to produce 1 were unsuccessful, probably due to a steric hindrance toward hydrogenation. Hence, Pd-catalyzed bismethoxycarbonylation on 5-norbornene-2-*exo*-3-*exo*-dicarboxylic anhydride (3) was attempted to produce a novel dianhydride with a bialicyclic structure, bicyclo-[2.2.1]heptane-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (6), which would not be retrodegradative and to then obtain from it the soluble and thermally stable polyimides. Most recently, the dianhydride 6 was reported to be prepared from 3 by Pd-catalyzed bismethoxycarbonylation in the presence of CO, $CuCl_2$, and methanol under atmospheric pressure, together with the compound's configuration.[17] We wish to report here the synthesis and the characterization of soluble polyimides from the novel dianhydride 6.

Results and Discussion

The dianhydride 6 was prepared according to a previously reported procedure (Scheme II).[17] The synthetic route of the polyimides from 6 and the various diamines employed is depicted in Scheme III. Poly(amic acid)s were produced by reacting 6 with 4,4′-diaminodiphenyl ether (DDE), (4,4′-diaminodiphenyl)methane (DDM), 4,4′-di-

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Scheme III

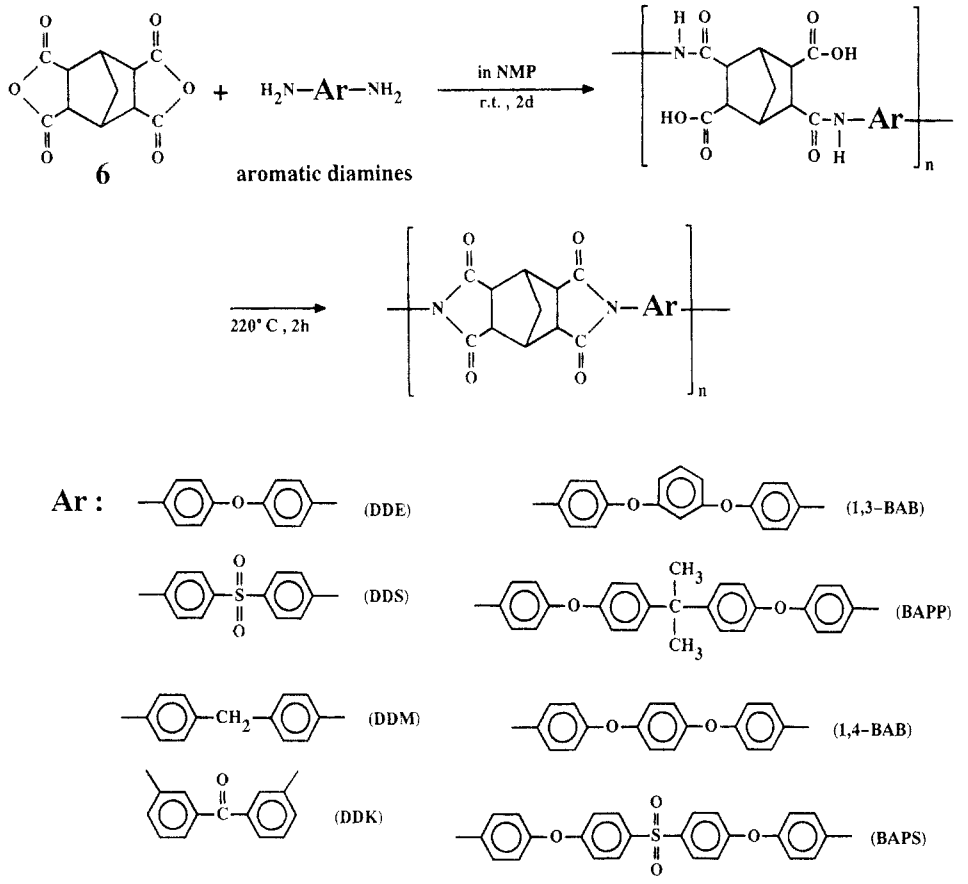

Table I. Polyimides from 6 and Diamines[a]

diamine	$\bar{M}_n$[b] × 10^{-4}	$\bar{M}_w$[b] × 10^{-4}	film quality	T_5[c] (°C) in air	T_5[c] (°C) in N_2	T_{dec}[c] (°C) in air	T_{dec}[c] (°C) in N_2	T_g[d] (°C)
DDE	13.1	15.7	flexible	438	475	456	477	292
DDM	9.8	12.7	flexible	415	463	398	496	200
DDS	3.2	3.5	brittle	412	463	440	481	178
1,4-BAB	9.5	20.9	flexible	423	463			
1,3-BAB	5.4	5.9	flexible	426	479	438	441	210
BAPS	2.3	4.6	brittle	455	485			
BAPP	9.6	13.4	flexible	440	478	459	473	252
DDK	3.3	9.7	flexible	396	420	438	441	261

[a] Polymerization: dianhydride, 2.1 mmol; diamine, 2.1 mmol; pyridine, 1.0 mL; solvent (NMP), 10 mL; room temperature; 2 days. Imidization: 220 °C, 2 h. [b] GPC (0.05 M DMF solution of LiBr), polystyrene standards. [c] Sample form, film; 5% weight loss and decomposition temperatures measured by TGA with a heating rate of 5 °C/min. [d] Glass transition temperature measured by TMA with a constant load of 10 g (stress; 0.125 MPa) at a heating rate of 10 °C/min.

aminodiphenyl sulfone (DDS), 3,3′-diaminodiphenyl ketone (DDK), 1,3-bis(4-aminophenoxy)benzene (1,3-BAB), 1,4-bis(4-aminophenoxy)benzene (1,4-BAB), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), and bis[4-(4-aminophenoxy)phenyl] sulfone (BAPS) in *N,N*-dimethylacetamide (DMAc) in the presence of pyridine at room temperature for 2 days under a nitrogen atmosphere. The resultant viscous poly(amic acid) solutions were cast on glass plates and dried under vacuum. By curing at 220 °C for 1 h in a preheated oven, the poly(amic acid)s were transformed into the polyimides. Polyimides were also prepared by a thermal solution imidization technique (heating at 200 °C for 2 h). These polyimides are soluble in organic solvents; therefore, their good solubilities made it possible to produce each polyimide film even by the latter procedure.

The molecular weights of the soluble polyimides were measured by GPC (0.05 M *N,N*-dimethylformamide (DMF) solution of LiBr as an eluent) after calibration with the standard polystyrenes. The results along with film quality are summarized in Table I. These polymers had molecular weights in the range from 2.3×10^4 to 13.1×10^4 as $\bar{M}_n$ and formed tough and flexible films except for the polyimides from DDS and BAPS. Polyimide films from DDS and BAPS were somewhat brittle probably due to their lower molecular weights. All of the obtained films were transparent and almost colorless. These polymers were very soluble in *N*-methylpyrrolidone (NMP), DMAc, and concentrated sulfuric acid while moderately soluble in 1,3-dimethyl-2-imidazolinone and pyridine. These excellent solubility properties may be considered expectedly to be attributed to the incorporation of the bialicyclic unit into these polymer's main chains.

The thermal properties of the polyimide films were evaluated by measuring the 5% weight loss and decomposition temperatures (T_5 and T_{dec}) using thermogravimetric analysis (TGA) and the glass transition temperature (T_g) using thermomechanical analysis (TMA). As a representative example, the TGA curves of the polyimide obtained from the dianhydride and DDE are shown in Figure 1. In the TGA profile, T_{dec} is noted as the point where the TGA curve intersects the bisected line drawn

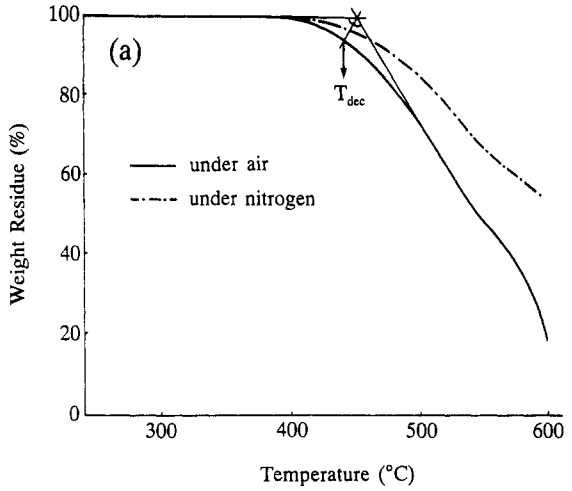

Figure 1. TGA curves of polyimide from 6 and DDE under air and nitrogen with a heating rate of 5 °C/min.

through the intersection of the extrapolations of the two slopes in the TGA curve. TGA was carried out in air or nitrogen with a heating rate of 5 °C/min. Thermogravimetric curves of the poly(amic acid)s showed that the imidization commenced around 110 °C and was complete at 210 °C. Followed by IR spectroscopy of the above results, the absorptions at *ca.* 3300 and 1550–1650 cm^{-1} due to the carboxylic and carbonyl groups of poly(amic acid) that were initially observed disappeared entirely after heating over 200 °C and, at the same time, new strong absorptions at 1765–1775 and 1710–1720 cm^{-1} due to the imide carbonyl appeared. TMA was carried out using a penetration probe of 1.0-mm diameter and an applied a constant load of 10 g (stress; 0.125 MPa) with a heating rate of 10 °C/min in order to estimate the T_g's of the polymers.[18] The sample size was less than 0.125 mm thick. The thermal properties of these polyimides are listed in Table I. These results showed that all the polyimides had good thermal stability with no significant weight loss up to 400 °C and the T_5 in a nitrogen atmosphere was over 420 °C in each case. The T_5's of the polyimides from 6 are 50–100 °C higher than those from 1 which decomposed around 360 °C due to the retro-DA reaction. The introduction of a structure that undergoes no retro-DA reaction was able to produce the polyimides with higher thermal stability, as previously mentioned. These polymers have T_g's over 200 °C except for the polyimide obtained from DDS. The lower T_g of polymers from DDS may be a reflection of the lower molecular weight.

The mechanical properties were investigated using a thermomechanical analyzer with a drawing rate of 10 mm/min (sample size (film); 10-mm length, 3-mm width, about 20-μm thickness) at room temperature. The polyimide films prepared from 6 and DDE, DDM, and BAPP showed 1.25, 1.67, and 1.05 GPa in tensile modulus, 145, 91, and 96 MPa in tensile strength, and 15, 12, and 9% in elongation at break, respectively.

We could successfully synthesize the soluble and thermally stable polyimides by using a bialicyclic dianhydride that would not undergo the retro-DA reaction and aromatic diamines.

Experimental Section

Materials. The solvents were purified in the usual way prior to use. Pyridine was refluxed with CaH_2 and fractionally distilled. DDE, DDS, 1,3-BAB, and 1,4-BAB were purified by recrystallization from methanol. BAPP, BAPS, DDK, and DDM were recrystallized from ethanol, acetonitrile, ethyl acetate, and benzene–hexane (1:1), respectively.

Monomer Synthesis. The dianhydride 6 was synthesized according to a previously reported procedure.[17] The bismethoxycarbonylation of 3, which was obtained from the *endo* isomer by thermal isomerization,[19] with carbon monoxide in methanol afforded 2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylate 4 in the presence of catalytic amounts of 5% Pd–C and stoichiometric amounts of $CuCl_2$. The tetracarboxylic acid 5 was prepared by the acid-catalyzed hydrolysis of 4. The dianhydride 6 was synthesized by the dehydration reaction of 5 with thionyl chloride. It was also prepared by the thermal dehydration reaction of 5.

Polymerization. In a 30-mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet was placed a mixture of a diamine (2.1 mmol) and pyridine (1 mL) in 10 mL of dry NMP (distilled over CaH_2) and then 6 (0.5 g; 2.1 mmol) was added in one-fifth portions over a period of 5 h at room temperature. The resulting mixture was stirred under a nitrogen atmosphere for 2 days at room temperature. The resultant viscous poly(amic acid) solution was cast on a glass plate, dried under vacuum for 12 h at room temperature, and then transformed into the polyimide by heating for 1 h at 220 °C. After curing, the glass plate was immersed in boiling water to facilitate removal of the polyimide film.

Measurements. Infrared spectra were recorded using a JASCO A-102 infrared spectrometer. Molecular weight and molecular weight distribution were determined using a JASCO 800 gel permeation chromatograph equipped with an RI detector and two Shodex KD-80M columns connected in series in 0.05 M DMF solution at 50 °C; molecular weight calculations were made on the basis of polystyrene standards. Thermogravimetric analyses were performed using a Shimadzu DT-30 thermal analyzer at a scan rate of 5 °C/min in air or in a N_2 atmosphere. Thermomechanical analysis was performed using a Seiko Instruments TMA/SS with a constant load of 10 g (stress; 0.125 MPa) at a heating rate of 10 °C/min. Mechanical properties were examined at room temperature using a Seiko Instruments TMA/SS at a drawing rate of 10 mm/min; the sample size was 10 mm in length, 3 mm in width, and about 20 μm thick.

References and Notes

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