

AROMA-FREE POLYIMIDES

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ABSTRACT

Two kinds of tetracarboxylic dianhydrides bearing a polyalicyclic structure were synthesized and polycondensated with an polyalicyclic diamine in HMPA to give aroma-free polyimides. The resulting polyimides were soluble in polar organic solvents and formed colorless and flexible films. The 5%-weight loss temperatures (T_5 's) in N_2 were as high as 455-460°C. The T_g 's estimated from the TMA were 300-340°C. The thermal stabilities of these polyimides were sufficiently high in spite of the absence of aromatic rings. This nature may give us some suggestion that aromatic rings are not always indispensable to thermal stable polymers if they are well designed.

INTRODUCTION

Wholly aromatic polyimides are often insoluble and intractable in their fully imidized form unless carefully designed, thus presenting serious processing difficulties. The soluble precursor polymers, poly(amic acid)s, are deposited onto the substrates and thermally cyclodehydrated at elevated temperature to yield the insoluble polyimide coatings or films. One of the major drawbacks of these precursors is that they have a limited pot-life and must generally be kept refrigerated during storage. Additionally, water is given off during the imidization process, which may lead to voids, shrinkage, and stress formation in the final coating. Much endeavor has been focussed on synthesizing tractable, processable polyimides with no reasonable sacrifice of the desired properties. Meanwhile, most of the wholly aromatic polyimides intensely absorb visible light and are colored reddish yellow, or pale yellow even if well-designed. The origin of the coloration is known to be caused by their highly conjugated aromatic structures and/or the intermolecular charge-transfer(CT) complex formation. Consequently, they cannot be used in areas where colorlessness and transparency are important requirements. Recently, we have reported the preparation and characterization of soluble and colorless polyalicyclic polyimide films from bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3:5,6 dianhydrides and aromatic diamines.^{1,2} A representative example of the polyimides is shown in Figure 1. The polyimides showed excellent thermal stability with no significant weight loss up to approximately 400°C and the 5% weight loss temperatures in N_2 were over 450°C. The polyimides had glass transition temperatures over

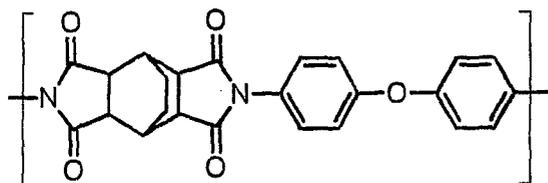


Figure 1. Representative Polyalicyclic-Aromatic Polyimide (T_5 ; 464°C, T_g ; 383°C)

380°C. These results brought us doubt "are aromatic rings really indispensable to thermally stable polymers?". In the present paper we will discuss the synthesis and the properties of non-aromatic polyimides which we call here "aroma-free polyimides" and which were prepared from polyalicyclic dianhydrides and a polyalicyclic diamine.

EXPERIMENTAL

Materials Bis(aminomethyl)bicyclo[2.2.1]heptane (**BBH**) was donated from Mitsui Chemicals, Co. Ltd., and purified by fractional distillation over CaH_2 under reduced pressure. Hexamethylphosphoramide (HMPA) was fractionally distilled over CaH_2 under reduced pressure.

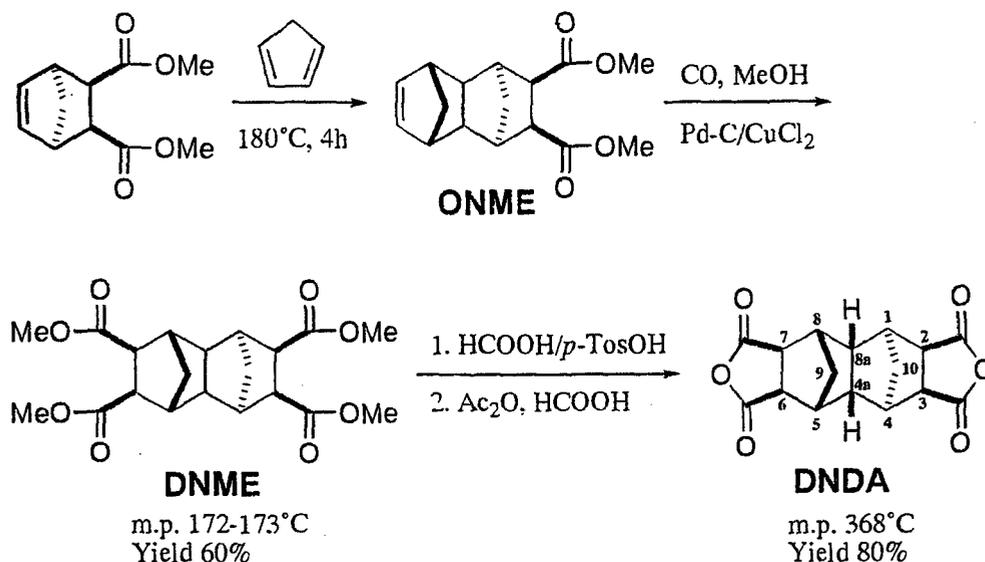
Monomer Synthesis Bicyclo[2.2.1]heptane-2-*endo*,3-*endo*,5-*exo*,6-*exo*-tetracarboxylic 2,3:5,6-dianhydride (**BHDA**) was synthesized according to the previous paper.³ (4*arH*,8*acH*)-Decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (**DNDA**) was prepared as follows. In a 200-mL autoclave were placed dimethyl bicyclo [2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylate (126 g, 0.6 mol) and dicyclopentadiene (26.4 g, 0.4 mol as cyclopentadiene), and the apparatus was heated at 180°C for 4 h. By fractional distillation of the reaction mixture a colorless fraction (22.1 g, 20% based on cyclopentadiene) boiling at 130-135 °C (4 mmHg) was collected, which was identified as dimethyl (4*arH*,8*acH*)-1,2,3,4,4*a*,5,8,8*a*-octahydro 1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*-dicarboxylate (**ONME**). In a 500-mL three necked flask were placed **ONME** (13.8 g, 0.05 mol), CuCl_2 (13.5 g, 0.10 mol), 5% Pd/C (1.6 g, 0.15 mmol as Pd) and absolute methanol (300 mL). After replacement of the air with carbon monoxide, the reaction was allowed to proceed at room temperature with magnetic stirring, carbon monoxide being sometimes introduced at normal pressure, until no more consumption of carbon monoxide was observed (about 3 h). The reaction mixture was filtered through Celite, and then evaporated to dryness. A mixture of chloroform (100 mL) and water (100 mL) was added to the residue, and the organic layer was separated and washed throughout with an aq. NaHCO_3 solution and then with water. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from ethanol and tetramethyl (4*arH*,8*acH*)-decahydro-1*t*,4*t*:5*c*,8*c* dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylate (**DNME**) was obtained as a white crystalline (11.8 g, 60%). After the ester-exchange reaction of **DNME** catalyzed by *p*-toluenesulfonic acid in formic acid (90 °C, 6 h), the resulting tetracarboxylic acid was dehydrated without isolation in acetic anhydride (90 °C, 6 h) to **DNDA** in 80% yield (based on **DNME**). **DNDA**: m.p.368 °C; ^1H NMR($\text{DMSO}-d_6$) δ 1.10(1H, $J_{9,9}=11$, H¹-9(6,7-side)), 1.34(1H, d, $J_{10,10}=12$, H¹-10(2,3-side)), 1.45(1H, d, $J_{9,9}=11$, H-9), 1.63(1H, d, $J_{10,10}=12$, H-10), 1.85(2H, s, H-4*a*,8*a*), 2.67(2H, s, H-5,8), 2.80(2H, d, $J_{1,2}=J_{4,3}=1$, H-1,4), 3.25(2H, s, H-6,7), 3.51(2H, d, $J_{2,1}=J_{3,4}=1$, H-2,3); ^{13}C NMR ($\text{DMSO}-d_6$) δ 36.7(C-9), 37.1(C-10), 39.2(C-1,4), 43.3(C-4*a*,8*a*), 43.9(C-5,8), 45.5(C-6,7), 50.6(C-2,3), 172.4(2,3 side C=O), 173.9(6,7 side C=O); IR (KBr) 3045, 2960, 2900, 1840, 1770, 1480, 1300, 1232, 1140, 1085, 920 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_6$: C, 63.58; H, 4.64. Found: C, 63.55; H, 4.80.

General Polymerization Procedure and Film Preparation of Polyimide In a 30-mL three-necked flask equipped with a mechanical stirrer were placed the dianhydride (2.0 mmol) and 3 mL of HMPA. A slow stream of nitrogen gas being maintained, the mixture was stirred until the dianhydride was entirely dissolved. **BBH** (2.0 mmol) and an additional 2 mL of HMPA were then added into the clear solution. After being

stirred at room temperature for 12 h and then at 130°C for 6h, the reaction solution was poured into 300 mL of acetone. An aliquot of the polycondensation solution containing poly(amic acid) was cast on a glass plate using a doctor blade. The polyimide film was prepared by heating the glass plate at 80°C for 3 h, at 200°C for 1 h, and then at 250°C for 1 h under vacuum.

RESULTS AND DISCUSSION

Synthesis of DNDA The synthetic route of (4*a**H*,8*a**H*)-decahydro-1*t*,4*t*:5*c*,8*c* dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (**DNDA**) is illustrated in Scheme 1. The tetramethyl ester **DNME** was synthesized by the Pd catalyzed bis-methoxycarbonylation of **ONME** which was afforded by the Diels-Alder re-



Scheme 1. Synthetic Route to **DNDA**

action of dimethyl bicyclo[2.2.1]hept-5-ene-2-endo,3-endo-dicarboxylate with dicyclopentadiene. The assignment of stereochemistry of **DNME** made by the NMR spectra was coincident with the Stille's description that in the palladium(II) catalyzed bis methoxycarbonylation of norbornene the two methoxycarbonyl groups are introduced with *exo*-configuration.⁴ After the ester-exchange reaction of **DNME** catalyzed by *p* toluenesulfonic acid in formic acid, the resulting tetracarboxylic acid was dehydrated in acetic anhydride to the anhydride **DNDA**. The ORTEP drawing of **DNDA** obtained from the X-ray crys-

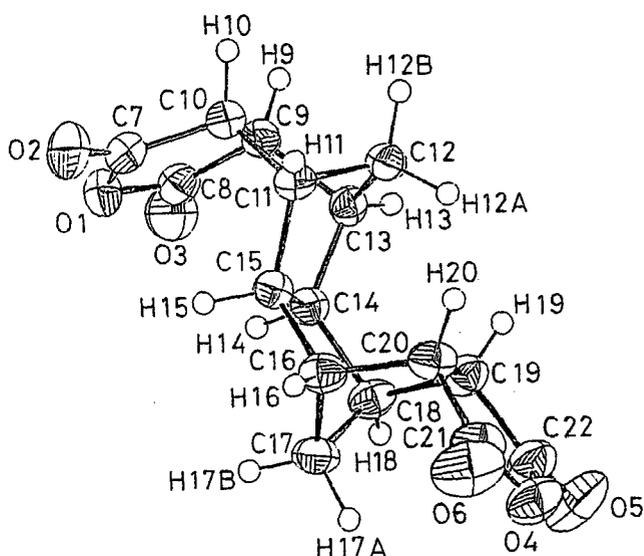


Figure 2. ORTEP drawing of **DNDA**

① ordered structure?
wide range

tallographic analysis is shown in Figure 2. The anhydride is crystallized in the space group $P2_1/a$ (No. 14) and has four formula units in the unit cell.

Synthesis and Properties of Polyimides Homogeneous poly(amic acid) solutions were obtained only when **BBH** was slowly added to the HMPA solution of the dianhydride. A precipitate developed when adding the dianhydride to the HMPA solution containing **BBH** (in the reverse order). The difference can be explained by the salt formation, that is, in the latter case, a carboxyl group of amic acid that was produced by the reaction between the diamine and the dianhydride reacts easily with an excess amount of the free diamine to form the salt. A precipitate appeared also using *N,N*-dimethylacetamide (DMAc) as a polymerization medium instead of HMPA. The structures of the polyimides are illustrated in Figure 3. The colorless and flexible polyimide films were prepared by

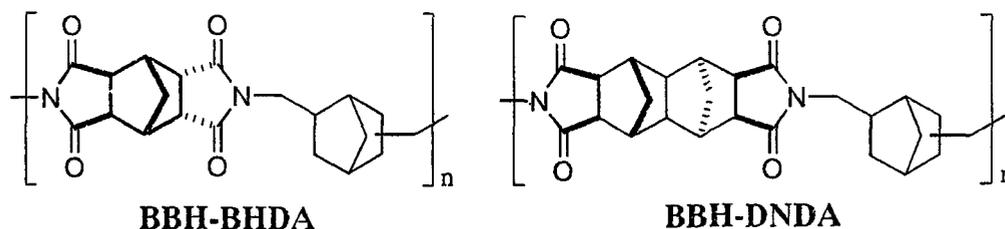


Figure 3. Structures of Aroma-Free Polyimides

vacuum-curing the glass plates on which the polymerization solutions were cast using a doctor blade. **BBH** used here is not a single compound but a mixture of at least two isomers, 2,5-bis(aminomethyl)bicyclo[2.2.1]heptane and its 2,6-isomer. In the sense, the polymers are practically co-polyimides in stereochemistry. The disorder of the polymer chain, therefore, may enhance its film-formability. It is also noteworthy that a film could be obtained from the HMPA solution in which the precipitate once formed in DMAc were dissolved. The films were soluble in common organic polar solvents such as HMPA, DMAc, *m*-cresol. The 5%-weight loss temperatures (T_5 's) of **BBH-BHDA** and **BBH-DNDA** polyimides in N_2 were as high as 455°C and 459°C, respectively. The T_g 's estimated from the TMA were 297°C for **BBH-BHDA** and 340°C for **BBH-DNDA**. In conclusion, the thermal stabilities of these aroma-free polyimides are sufficiently high in spite of the absence of aromatic rings, and the high thermal stabilities are considered to be due to the introduction of polycyclic structures into polymer chain. This nature may preliminarily give us some suggestion that aromatic rings should not be always indispensable to thermal stable polymers if they are well-designed.

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