

Synthesis of New Alicyclic Polyimides by Diels-Alder Polymerization

Jun Ho Chi,¹ Gyo Jic Shin,¹ Yong Seok Kim,² Jin Chul Jung¹

¹Department of Materials Science and Engineering, Polymer Research Institute, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-dong, Pohang 790-784, Korea

²Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), 100, Jang-dong, Yuseong-gu, Daejeon 306-600, Korea

Received 15 December 2006; accepted 26 December 2006

DOI 10.1002/app.26169

Published online 4 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Four new alicyclic poly[arylene-9,10-di[4-(methoxy)phenoxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxdiimide)s (APIs) were prepared at 80°C in the presence of NaI in DMSO by the *in situ* Diels-Alder polymerization of 1,4-bis[4-(methoxy)phenoxy]-2,3,6,7-tetrakis(bromomethyl)benzene (MPBB) with four arylenebismaleimides (AMIs). The stereochemical isomerisms measured for the model compound DPAI and MDA-PI by HETCOR spectroscopy and ¹H-NMR spectroscopy, respectively, revealed that DPAI and APIs presumably have only one *trans-bis-endo*-configuration. Inherent viscosities of APIs varied in the 0.20–0.41 dL/g range. Solubility tests revealed that in spite of the alicyclic units incorporated the APIs were

only marginally soluble in polar organic solvents. In TGA in N₂ the APIs began to decompose at temperatures higher than 380°C, revealing two-step pyrolysis behavior. 4-(Methoxy)phenoxy side groups were believed to degrade in the lower temperature range. In DSC and wide-angle X-ray diffractometry APIs all appeared completely amorphous and in UV-Vis spectroscopy both DPAI and APIs were transparent at wavelengths longer than 375 nm. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3823–3832, 2007

Key words: polyimides; alicyclic polyimides; poly(octahydroanthracenediimide)s; *in situ* Diels-Alder polymerization; ring-forming polymerization

INTRODUCTION

Aromatic polyimides are widely applied in advanced technologies owing to their many advantageous properties.^{1,2} However, wholly aromatic polyimides are always colored ranging from slightly yellowish to dark brown, depending on degree of intermolecular and intramolecular charge transfer complex formation between electron-accepting dianhydride units and electron-donating diamine units.³ The color can severely hamper the polyimides from being applied as optical materials for photovoltaic cells or liquid crystal display films requiring transparency to visible lights. In addition the polyimides are usually so intractable that they should be processed in two-steps via precursor poly(amic acid)s.⁴

Alicyclic dianhydride units introduced in the polyimide backbone greatly reduce the charge transfer interaction of polyimide molecules to make them less colored⁵ since unlike aromatic dianhydride units with rigid disc-like structure they do not function as a strong π acceptor. The decrease in charge transfer

interaction brings an additional advantage in lowering the dielectric constant of polyimides,⁶ which is an important factor in the application as interlayer coatings to passivate the surfaces of high-integration semiconductors.

To improve processability of aromatic polyimides several structure modifications have been attempted such as incorporating flexible or nonsymmetrical linkages to the backbone, attaching bulky substituents, or copolymerizing to disrupt symmetry and regularity of repeat unit structure.^{7–9} Incorporation of a flexible alicyclic unit onto polyimide backbone is a promising route to enhance solubility without considerably lowering thermal stability because its double-strand structure is highly resistant against thermal degradation.^{10,11}

As well known, the Diels-Alder reaction is a thermally driven [4 + 2] cycloaddition reaction between a dienophile and a conjugated 1,3-diene.¹² When a substituted reactant is used, the reaction naturally provides its product with some asymmetric carbon atoms that cause various stereoisomerisms. Number of the stereoisomers to be formed depends on the number of the asymmetric carbon atoms, and sometimes isolation of a specific isomer from mixture of many isomers can become seriously difficult if the product contains many chiral centers. Therefore, if the Diels-Alder reaction is applied to polymerization

Correspondence to: J. C. Jung (jcjung@postech.ac.kr).

Contract grant sponsor: Korea Research Foundation; contract grant number: KRF-2006-005-J01301.

of a 2,3-disubstituted di(1,3-diene) with an unsubstituted di(dienophile), each repeat unit of the product polymer chains contains four asymmetric carbon atoms that should give, in principle, 16 stereoisomers, unless the polymerization reaction is highly stereoselective. This fact indicates that the polymerization usually gives rise to the polymer like a 16-component stereorandom copolymer, which is due to its structural irregularity reveals much enhanced tractability. This polymerization has been applied to prepare many ladder polymers with enhanced organosolubilities.^{13–17} In these syntheses an accurate stereochemical analysis of the stereoisomers was not dealt with.

In the present study an attempt was made to prepare alicyclic rings-containing poly{arylene-9,10-di[4-(methoxy)phenoxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxdiimide}s (APIs) by means of the Diels-Alder polymerization of 1,4-bis[4-(methoxy)phenoxy]-2,3,5,6-tetramethylenecyclohexane with various arylene bismaleimides (AMIs), but the bis(1,3-diene) monomer was too unstable to prepare in high purity for polymerization. However, in the literatures it was reported that 1,2-di(bromomethyl)-benzene produces *in situ* 1,2-dimethylene-3,5-cyclohexadiene by the Diels-Alder reaction with an *N*-alkylmaleimide in the presence of excess NaI^{10,11,18,19} and the [4 + 2] cycloadduct having two asymmetric carbon atoms gives only one single stereoisomer with *endo*-configuration.¹⁸ To make our attempt successful this reaction was applied to synthesize the APIs.

For this 1,4-bis[4-(methoxy)phenoxy]-2,3,5,6-tetrakis(bromomethyl)benzene (MPBB) was prepared as monomer by the Ullmann etherification of 1,4-dibromo-2,3,5,6-tetramethylbenzene with 4-(methoxy)phenol using CuCl as activator to obtain 1,4-di[4-(methoxy)phenoxy]-2,3,5,6-tetramethylbenzene (MPD), followed by monobromination of the four methyl groups of MPD's central benzene ring using *N*-bromosuccinimide (NBS). Before polymerization *N*, *N'*-diphenyl-9,10-di[(4-methoxy)phenoxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxdiimide (DPAI) was prepared as model compound by the *in situ* Diels-Alder reaction of MPBB with *N*-phenylmaleimide and chemical and stereochemical structures of DPAI were accurately determined by means of HETCOR spectroscopy. Then APIs were prepared by the same reaction with four AMIs that had been obtained by imidization of maleic anhydride (MA) with oxy-4,4'-dianiline (ODA), methylene-4,4'-dianiline (MDA), carbonyl-4,4'-dianiline (CDA) and hexafluoroisopropylidene-4,4'-dianiline (6FDA). After structural characterization of the APIs by EA and FTIR spectroscopy their solution, thermal, and optical properties were measured and discussed in respect with their chain structures.

EXPERIMENTAL

Materials

1,2,4,5-tetramethylbenzene, NBS, benzoyl peroxide (BPO), *N*-phenylmaleimide, MA, ODA, MDA, CDA, and 6FDA were purchased from Aldrich and used as received. 4-(Methoxy)phenol (Aldrich) was purified by recrystallization from ethanol. Dimethylformamide (DMF, Aldrich), *N*-methyl-2-pyrrolidone (NMP, Acros), dimethylacetamide (DMAc, Aldrich), and dimethylsulfoxide (DMSO, Kanto) were purified by vacuum distillation over CaH₂ and kept over MgSO₄. Pure CCl₄ was obtained by simple distillation. CuCl was made pure by precipitating in aqueous 10% HCl solution and subsequent washing with diethyl ether. 1,4-Dibromo-2,3,5,6-tetramethylbenzene was prepared by brominating 1,2,4,5-tetramethylbenzene in CCl₄ at ice temperature.¹⁰ Other inorganic reagents and organic solvents of chemical grade were used as received unless otherwise stated.

Measurements

¹H- and ¹³C-NMR spectra were recorded on 300-MHz Bruker AM 300 spectroscope using tetramethylsilane as internal standard and heteronuclear ¹H-¹³C-correlation (HETCOR) spectrum was recorded in DMSO-*d*₆ at 60°C. Chemical shifts are given in ppm unit and coupling constants *J* in Hz. FTIR spectra were measured using Infinite Gold Mattson Spectroscopy in KBr pellet or solution-cast film. Melting points were determined using Haake-Büchler melting point apparatus. Elemental analyses (EA) were performed using Elemental Vario EL microanalyzer (The Korea Basic Science Institute, Daegu, Korea) and phase transitions of the APIs were determined by DSC using Perkin-Elmer PC series DSC 7 thermal analyzer at 20°C/min scan rate in nitrogen atmosphere. Inherent viscosities were determined using an Ubbelohde-type viscometer from 0.2 g/dL DMSO solutions at 25°C. UV-visible spectra were recorded on Scinco UV S-2100 spectrometer in DMSO solution. TGA was carried out under nitrogen at 20°C/min heating rate. Wide-angle X-Ray diffractograms were obtained in transmission mode with Ni-filtered CuKα radiation on a Rigaku Geiger Flex Dmax 2500 X-ray diffractometer.

Synthesis

1,4-bis[4-(methoxy)phenoxy]-2,3,5,6-tetramethylbenzene

In a 500 mL three-necked round-bottom flask equipped with a condenser and a thermometer were placed 1,4-dibromo-2,3,5,6-tetramethylbenzene (8.76 g, 30 mmol), 4-(methoxy)phenol (4.96 g, 40 mmol),

dry DMF (120 mL), CuCl (4 g, 40 mmol) and K₂CO₃ (5.52 g, 40 mmol). The mixture was stirred under N₂ at room temperature for 30 min and then heated at 150°C for 20 h. Then additional CuCl (2.6 g, 26 mmol), 4-(methoxy)phenol (3.22 g, 26 mmol), and K₂CO₃ (5.52 g, 40 mmol) were added at that temperature and stirred further for 15 h. The mixture was filtered hot to remove excess CuCl and the filtrate was cooled and dropped into excess methanol/water mixture (5/5 v/v) to obtain ivory precipitates. The precipitates were collected by filtration and dried under vacuum at room temperature. Recrystallization of the crude products from 95% ethanol afforded a yellowish powder.

Yield: 55%. m.p.: 201°C. IR (KBr pellet, cm⁻¹): 2956(CH₃), 1207(aryl-aryl ether). ¹H-NMR (CDCl₃, ppm): 2.05(s, 12H, CH₃), 3.76(s, 6H, OCH₃), 6.76(d, 4H, ArH meta to OCH₃, J = 9Hz), 6.79(d, 4H, ArH ortho to OCH₃, J = 9Hz). ¹³C-NMR (CDCl₃, ppm): 13.6(CH₃), 56.4(OCH₃), 115.4(ArC ortho to OCH₃), 115.9(ArC meta to OCH₃), 129.5(ArC attached to CH₃), 148.8(ArC para to OCH₃), 153.1[ArC attached to 4-(methoxy)phenyloxy], 154.7(ArC attached to OCH₃).

1,4-bis[4-(methoxy)phenyloxy]-2,3,5,6-tetrakis(bromomethyl)benzene

In a 500 mL three-necked round-bottom flask equipped with a condenser and a thermometer NBS (13.8 g, 78 mmol) was dissolved in CCl₄ (150 mL) and then MPD (4.3 g, 11.4 mmol) and BPO (several crystals) were added to the stirred solution. The mixture was reacted under CCl₄ reflux for 20 h until no HBr gas evolved. Then the mixture was filtered to remove the remaining NBS and the filtrate was evaporated to obtain red oil. On treating with methanol the oil solidified. The solids were collected by filtration, washed twice with hot water and dried in vacuum at 30°C. They were purified by recrystallization from 95% ethanol/ethyl acetate mixture (9/1 v/v).

Yield: 65%. m.p.: 112°C. IR (KBr pellet, cm⁻¹): 2989 (aliphatic CH), 1629(aromatic ring), 1195(aryl-aryl ether), 571 and 516(C-Br). ¹H-NMR (CDCl₃, ppm, Fig. 1): 3.79(s, 6H, H-1), 4.58(s, 8H, H4), 6.83(d, 4H, H-3), 6.86(d, 4H, H-2). ¹³C-NMR (CDCl₃, ppm, Fig. 1): 23(C-h), 56.4(C-a), 115.7(C-c), 116.7(C-d), 134.6(C-g), 150.1(C-e), 152.3(C-f), 156(C-b).

Arylenebismaleimides

Three AMIs were prepared in high purity from the two-step condensation of MA with ODA, CDA, and 6FDA and characterized according to the procedure described in the literature.²⁰ Maleimide of MDA (Aldrich, m.p. 157°C) was purified by recrystallization from DMAc/methanol mixture (3/7 v/v).

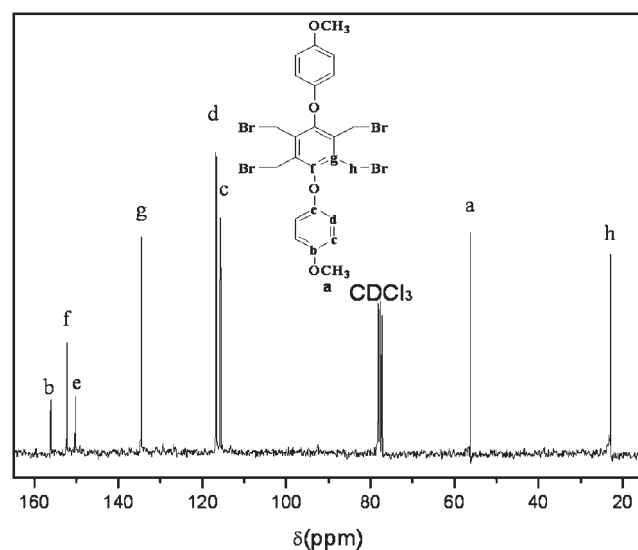
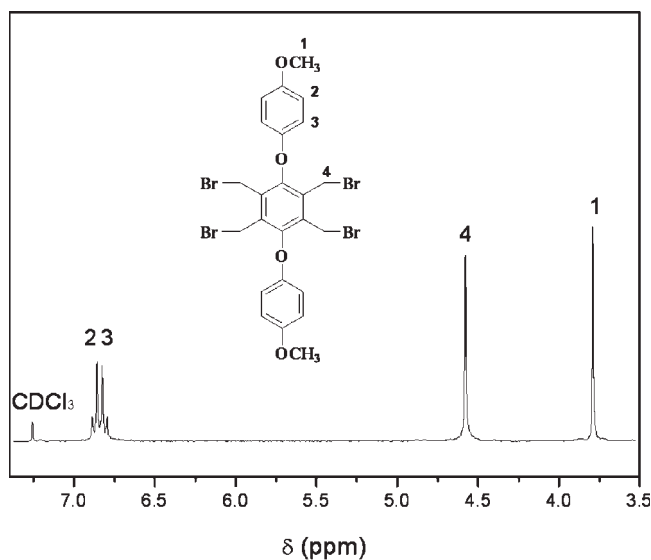


Figure 1 ¹H- (upper) and ¹³C-NMR spectrum (lower) of monomer MPBB (CDCl₃, 25°C).

ODA-MI: yield 57%, m.p. 118°C, CDA-MI: yield 69%, m.p. 190°C, 6FDA-MI: yield 67%, m.p. 243°C.

N,N'-diphenyl-9,10-di[(4-methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxydiimide as model compound

In a 500 mL three-necked round-bottom flask equipped with a condenser, a thermometer and a nitrogen gas inlet tube NaI (2.12 g, 14 mmol), MPBB (1.0 g, 1.4 mmol) and *N*-phenylmaleimide (0.87 g, 5 mmol) were suspended in dry DMSO (12 mL). The suspension was made homogeneous by heating upto 80°C and reacted in N₂ atmosphere for 36 h at that temperature. This solution was cooled and dropped

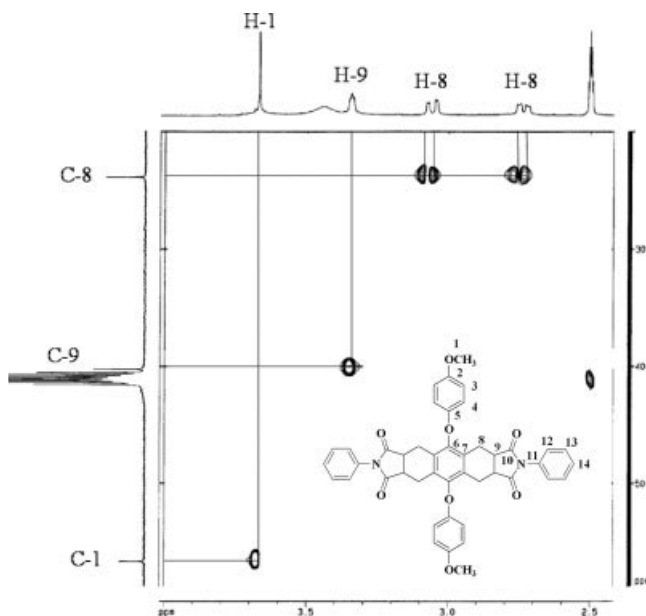


Figure 2 HETCOR NMR spectra of model compound DPAI (DMSO- d_6 , 60°C).

under vigorous stirring into 10% aqueous NaHSO₃ solution (120 mL) for precipitation. The precipitates were washed twice with water and diethyl ether and then dried. Recrystallization from CH₂Cl₂/petroleum ether (2/1 v/v) afforded a beige powder.

Yield: 48%. m.p: 335.6°C (DSC). IR (KBr pellet, cm⁻¹): 2835 and 2948(aliphatic CH), 1782 & 1715 (C=O, imide I), 1452(CH₂), 1380(C—N—C, imide II). ¹H-NMR (DMSO- d_6 , ppm, 60°C, Fig. 2): 2.72(d, 4H, H_{equatorial}-8, $J_{geminal}$ = 12 Hz), 3.05(d, 4H, H_{axial}-8, $J_{geminal}$ = 12 Hz), 3.32(m, 4H, H-9), 3.65(s, 6H, H-1), 6.64(d, 4H, H-4), 6.72(d, 4H, H-3), 6.99(d, 4H, H-12), 7.44(m, 6H, H-13, 14), ¹³C-NMR (DMSO- d_6 , ppm, 60°C, Fig. 2): 23.9(C-8), 40.3(C-9), 56.7(C-1), 116.2 (C-4), 116.6(C-3), 127.7(C-12), 129.2(C-7), 129.8(C-13), 130.1(C-14), 133.6(C-11), 146.7(C-5), 153.6(C-6), 155.4 (C-2), 178.9(C-10). EA[wt %, repeat unit = C₄₄H₃₆N₂O₉ (720.77)]: Calc.; C 73.32, H 5.03, N 3.89, O 17.76 and Found; C 73.18, H 4.99, N 3.93 O 17.90.

APIs

In a 25 mL three-necked round-bottom flask equipped with a condenser, a gas inlet tube, and a thermometer NaI (1.05 g, 7 mmol), MPBB (0.486 g, 0.7 mmol) and an AMI (0.7 mmol) were suspended in dry DMSO (7 mL). The suspension was made homogeneous by raising the temperature to 80°C and reacted for 36 h under N₂ flow at that temperature. This hot solution was cooled, diluted with dry DMSO (3 mL) and then slowly dropped under

vigorous stirring into excess 10% aqueous NaHSO₃ solution (70 mL) for precipitation. The precipitates were isolated by filtration and washed thoroughly with water, methanol, and acetone in sequence and dried in vacuum at 50°C to constant weights.

Poly[1,4-phenyleneoxy-1,4-phenylene-9,10-bis[4-(methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxdiimide]

Yield: 78%. FTIR (KBr pellet, cm⁻¹, Fig. 4): 3066(aromatic CH), 2943 and 2834(aliphatic CH), 1779 and 1715(C=O, imide I), 1380(C—N—C, imide II), 1200 (aryl-aryl ether). EA[wt %, repeat unit = C₄₅H₃₆N₂O₉ (748.78)]: Calc.; C 72.18, H 4.85, N 3.74, O 19.23 and Found; C 71.58, H 4.91, N 3.79, O 19.48.

Poly[1,4-phenylenemethylene-1,4-phenylene-9,10-bis[4-(methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxdiimide]

Yield: 76%. ¹H-NMR (DMSO- d_6 , ppm, 100°C, Fig. 3): 6.99–7.26(2d, 8H, H-3 and H-4), 6.64–6.81(m, 8H, H-12 and H-13), 4.03(s, 2H, H-15), 3.71(s, 6H, H-1), 3.32(m, 4H, H-9), 3.01(d, 4H_{axial}, H-8), 2.73(d, 4H_{equatorial}, H-8). FT-IR (KBr pellet, cm⁻¹, Fig. 4): 3055(aromatic CH), 2906 and 2834(aliphatic CH), 1778 & 1715(C=O, imide I), 1378(C—N—C, imide II), 1200(aryl-aryl ether). EA[wt %, repeat unit = C₄₆H₃₈N₂O₈ (746.80)]: Calc.; C 73.98, H 5.13, N 3.75, O 17.14 and Found; C 73.47, H 5.07, N 3.81, O 17.38.

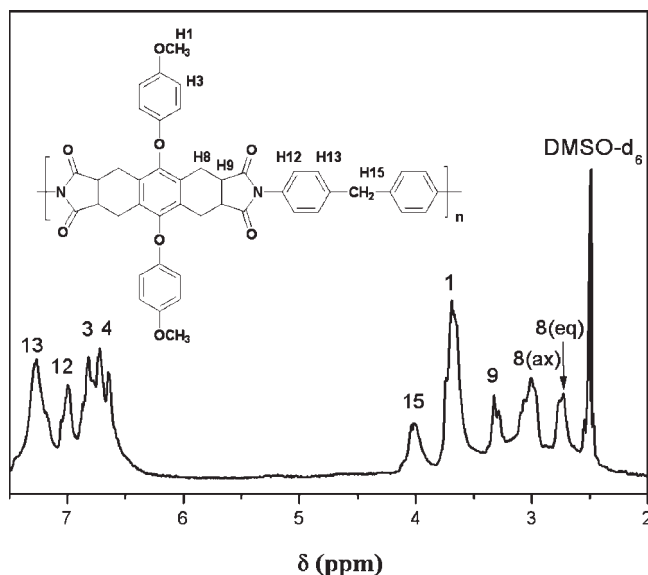


Figure 3 ¹H-NMR spectrum of MDA-PI (DMSO- d_6 , 100°C).

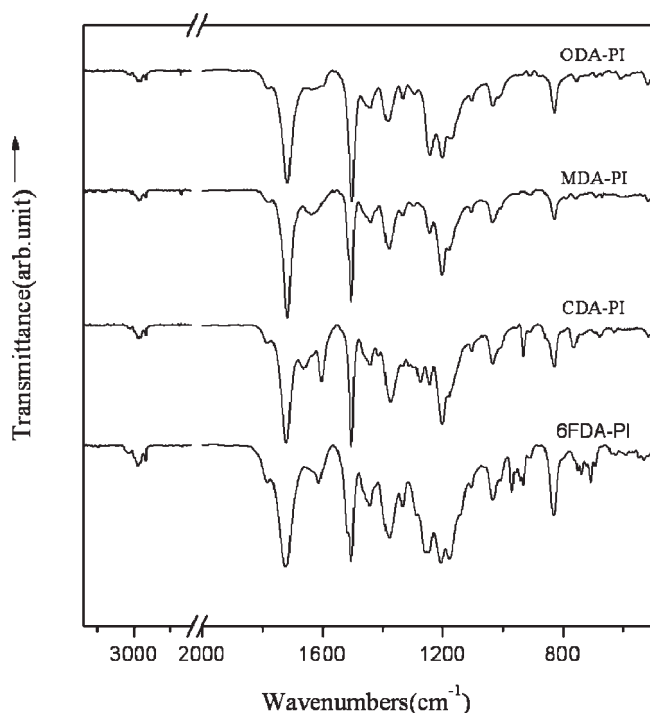


Figure 4 FT-IR spectra of polyimides.

Poly{1,4-phenylenecarbonyl-1,4-phenylene-9,10-bis[4-(methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxydiimide}

Yield: 85%. FT-IR (KBr pellet, cm^{-1} , Fig. 4): 3066(aromatic CH), 2930 and 2834(aliphatic CH), 1783 and 1719($\text{C}=\text{O}$, imide I), 1661($\text{C}=\text{O}$, ketone), 1373($\text{C}-\text{N}-\text{C}$, imide II), 1200(aryl-aryl ether). EA[wt %, repeat unit = $\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_9$ (760.79)]: Calc.; C 72.62,

H 4.77, N 3.68, O 18.93 and Found; C 72.15, H 4.83, N 3.74, O 19.15.

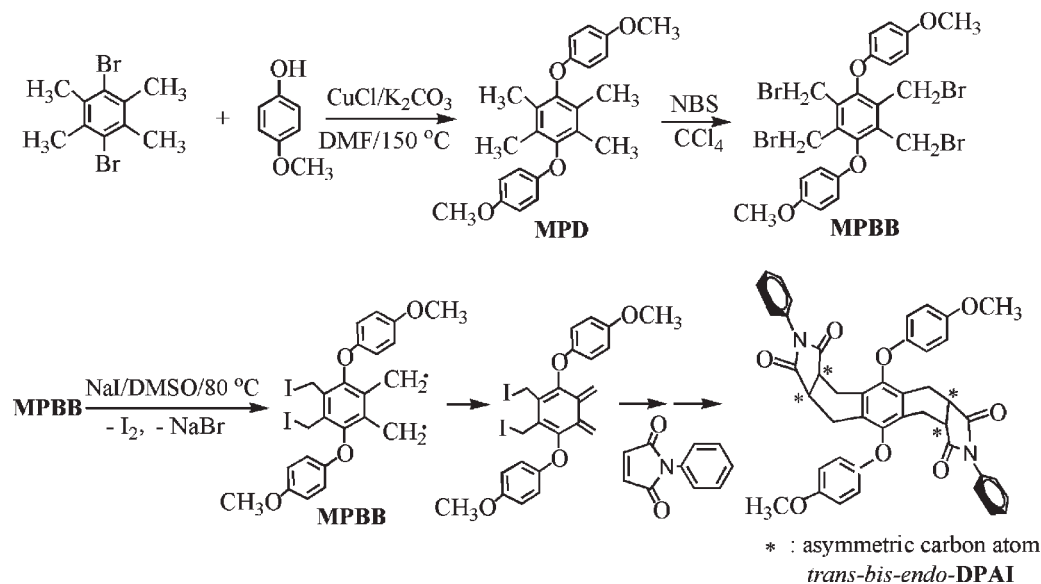
Poly{1,4-phenylene(hexafluoro)isopropylidene-1,4-phenylene-9,10-bis[4-(methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxydiimide}

Yield: 75%. FTIR (KBr pellet, cm^{-1} , Fig. 4): 3073(aromatic CH), 2949 and 2837(aliphatic CH), 1781 and 1716($\text{C}=\text{O}$, imide I), 1377($\text{C}-\text{N}-\text{C}$, imide II), 1197(aryl-aryl ether). EA[wt %, repeat unit = $\text{C}_{47}\text{H}_{34}\text{N}_2\text{O}_8\text{F}_6$ (868.77)]: Calc.; C 64.98, H 3.94, N 3.22, O 14.73 and Found; C 64.44, H 3.87, N 3.31, O 15.03.

RESULTS AND DISCUSSION

Monomer synthesis

The path for synthesis of monomer MPBB is illustrated in Scheme 1. First 1,4-di(4-methoxy)phenyloxy-2,3,5,6-tetramethylbenzene (MPD) was prepared in DMF by the Ullmann nucleophilic substitution reaction of 1,4-dibromo-2,3,5,6-tetramethylbenzene with 4-(methoxy)phenol using CuCl as activator²¹ and K_2CO_3 as HBr absorber and then the four methyl groups of MPD's central benzene ring was monobrominated under CCl_4 reflux with excess NBS in the presence of catalytic amount of BPO as free radical initiator.²² Even though the Ullmann reaction is long known,²¹ we achieved only 55% yield and we found that the addition of CuCl and K_2CO_3 in two portions is critical in achieving the 55% yield. Otherwise it sank drastically to 20% or lower.



Scheme 1 Synthesis of monomer MPBB and model compound DPAI.

When the CCl_4 solution was cooled to ambient temperature at the end of the monobromination of MPD, most NBS remaining unreacted precipitated out in CCl_4 and it was removed by filtration. Small amount of the NBS still remaining mixed in crude MPBB after CCl_4 evaporation was completely removed by washing with hot water. Bromomethyl groups were sufficiently resistant to the hot water treatment without hydrolysis to hydroxymethyl groups.

MPBB monomer thus prepared was characterized by ^1H - and ^{13}C -NMR and FTIR spectroscopy. In experimental section the spectral data are summarized and in Figure 1 ^1H - and ^{13}C -NMR spectra are reproduced together with all the peaks assignment. The ^1H -NMR spectrum in Figure 1 shows clearly that OCH_3 protons and benzylic CH_2 protons are to identify at 3.79 and 4.58 ppm, respectively. This result signifies that all the four CH_3 groups of MPD's central benzene ring were monobrominated to CH_2Br groups by NBS and the two OCH_3 groups remained intact in the bromination.

AMIs to use as dienophile monomers were prepared from MA and conventional aromatic diamines in accordance with the literature procedure²⁰ in 57–69% yields.

Model compound

To understand the stereochemical configuration of polymer backbone, *N,N'*-diphenyl-9,10-di(4-methoxy)phenyloxy-1,2,3,4,5,6,7,8-octahydroanthracene (DPAI) was synthesized as model compound in DMSO by the equimolar *in situ* Diels-Alder reaction of MPBB with *N*-phenylmaleimide at 80°C in the presence of excess NaI as activator,¹⁹ as shown in Scheme 1. In this reaction I_2 and NaBr are inevitably by-produced, and they were completely removed by dropping the DMSO solutions into large excess of aqueous 10% NaHSO_3 solution to reduce I_2 to NaI and subsequent washing of the precipitated DPAI thoroughly with distilled water. DPAI was further purified by washing with diethyl ether to remove the reactants remaining unreacted. Pure DPAI thus obtained was characterized by elemental analysis (EA), FTIR and heteronuclear ^1H - ^{13}C -correlation (HETCOR) spectroscopy.

The EA data are summarized in the experimental section. From there it is to see that the measured data are well coincident with the theoretical data calculated from the chemical structure of DPAI shown in Scheme 1. In FTIR spectrum the imide moiety of DPAI was confirmed by the characteristic imide bands at 1782 and 1715 cm^{-1} (imide I) and 1380 cm^{-1} (imide II).

Aliphatic parts of ^1H - and ^{13}C -NMR spectra of DPAI were completely interpreted with aid of

^1H - ^{13}C -HETCOR spectrum reproduced in Figure 2. It shows that the absorptions of C-8 carbon atom at 23.9 ppm, C-9 carbon atom at 40.2 ppm and C-1 carbon atom at 56.7 ppm of ^{13}C -NMR spectrum correlate well with two doublets of H-8 CH_2 protons at 2.72 and 3.05 ppm, a broad multiplet of H-9 CH protons at 3.32 ppm and a very sharp singlet of H-1 OCH_3 protons at 3.65 ppm of ^1H -NMR spectrum, respectively. Although area integration curve of the three aliphatic proton peaks is not shown in Figure 2, the peak area ratio of CH_2 : CH : OCH_3 protons could be determined roughly to be 4 : 2 : 3, which is well coincident with the theoretical protons ratio to read from the chemical structure of Scheme 1.

The two H-8 CH_2 protons bound geminal in a cyclohexane ring are not identical with each other in their chemical environment, and the equatorial protons were identified at 2.32 ppm whereas the axial protons were observed at 3.05 ppm, each absorption being split by the geminal coupling ($J_{\text{geminal}} = 12$ Hz). Each peak of H-8 CH_2 protons was observed as a small doublet that was split by an H-9 proton in their α -position ($J_{\text{H-8/H-9}} = 1.1$ Hz). Likewise the H-9 protons showed a multiplet that was split by two H-8 protons and one H-9 protons both in their α -positions, but their coupling constants were hardly identifiable because of the complex overlap of the peaks.

It is to note that in the HETCOR spectrum of Figure 2 no other aliphatic proton peaks than H-1 OCH_3 , H-8 CH_2 , and H-9 CH protons are observable. This result signifies that the 1,4-di[4-(methoxy)phenyloxy-2,3-dimethylene-cyclohexa-4,6-diene units generated *in situ* as intermediates did not undergo any side reactions such as dimerization with themselves to give 1,2,5,6-dibenzocyclooctane unit,²³ but reacted exclusively with the dienophilic $\text{C}=\text{C}$ bonds of *N*-phenylmaleimide. The absence of by-products may be attributed for the far much higher reactivity of the electrophilic dienophiles toward the nucleophilic dienes than that of the nucleophilic dienes toward themselves.

In a DPAI molecule four asymmetric carbon atoms are contained, as designated with an asterisk in its structure shown in Scheme 1 and 2, and a DPAI molecule should have, in principle, 16 stereoisomers. However, according to the literatures^{12,18} the *in situ* Diels-Alder reaction of 1,2-di(bromomethyl)benzene with *N*-alkylmaleimides, which generates two asymmetric carbon atoms and hence should inherently have four stereoisomers, produces in real *N*-alkyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboximide with only one *endo*-configuration. This experimental result had been theoretically proven later by suprafacial overlap of frontier molecular orbitals and secondary orbital interaction²⁴ and attributed for molecular symmetry of both the dienes and dienophiles. In

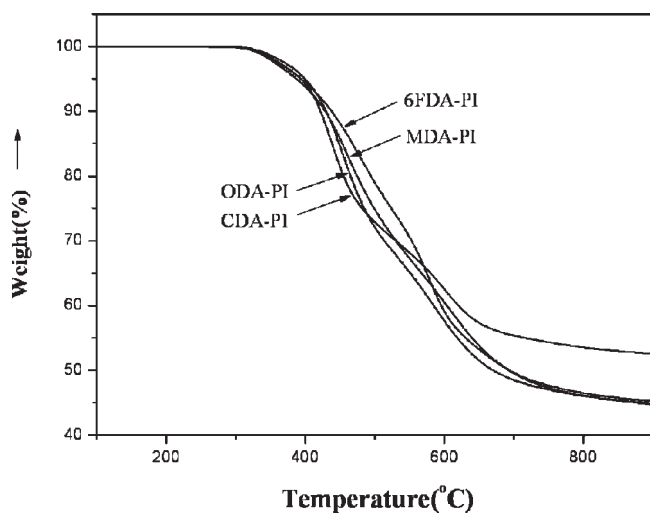


Figure 6 TGA curves of polyimides.

same procedure as that for DPAI synthesis, as shown in Scheme 2, except that crude APIs were further purified by washing with methanol and acetone to remove reactants remaining unreacted. The polymerizations gave yields higher than 75%.

The APIs thus prepared were characterized by EA and FTIR spectroscopy and chemical structure of MDA-PI was confirmed also by $^1\text{H-NMR}$ spectroscopy. The EA data of APIs are summarized in the experimental section and the $^1\text{H-NMR}$ spectrum of MDA-PI and FTIR spectra of APIs are reproduced in Figures 3 and 4, respectively. From the EA data it is to see that in all of the four APIs the measured EA values are coincident within experimental error with the theoretical values calculated from chemical structures of APIs shown in Scheme 2. In aliphatic part of $^1\text{H-NMR}$ spectrum of MDA-PI taken at 100°C in $\text{DMSO-}d_6$, equatorial CH_2 protons, axial CH_2 protons, CH protons, and OCH_3 protons were observed almost at the same positions as those of DPAI at 2.73 ppm as a doublet, 3.01 ppm as a doublet,

3.32 ppm as a multiplet and 3.71 ppm as a singlet, respectively. This result means that MDA-PI has exactly the same stereochemical structure as the model compound DPAI. In FTIR spectra of APIs the characteristic imide bands were observed at 1780 and 1715 cm^{-1} (imide I) and at 1380 cm^{-1} (imide II), but the $\text{C}=\text{C}$ absorption to be originally observable in AMIs at 3090 cm^{-1} could not be detected at all.

To roughly estimate molecular weights of APIs inherent viscosities were determined in DMSO at 25°C for their powder samples and their values are summarized in Table I together with their solubilities. As Table 1 shows, the inherent viscosities are in the $0.20\text{--}0.41\text{ dL/g}$ range, indicating that the APIs are not very high in molecular weight. Table 1 shows also that in spite of the alicyclic units incorporated onto backbone the APIs are only marginally soluble in polar organic solvents at ambient temperature and practically little effect of AMI structure on solubility is operative. This result leads to the deduction that solubility of APIs in organic solvents is governed more by their structure of diimide unit comprising four alicyclic rings and one aromatic ring fused with each other than by structure of AMI or 4-(methoxy)phenoxy side groups. As depicted in Scheme 2, the API's diimide unit has only one nearly linear chair-like structure, and it should be fairly rigid. This rigidity seems to play the role in determining solubility of APIs.

Transparency of APIs was examined by UV-Vis spectroscopy. Their UV-Vis spectra and that of DPAI are reproduced in Figure 5. It shows that $\pi\rightarrow\pi^*$ transitions of DPAI, ODA-PI, MDA-PI, and 6FDA-PI appear in the $250\text{--}322\text{ nm}$ range, while those of CDA-PI extend to 363 nm . In *p*-phenylenecarbonyl-*p*-phenylene unit of CDA-PI the π -electrons residing in the two *p*-phenylene rings are more or less delocalized over the $\text{C}=\text{O}$ group, and it should absorb UV-Vis lights at distinctively longer wavelengths than DPAI and other APIs, which do not possess such delocalization. Actually, powders of DPAI,

TABLE II
Thermal Stability of Polyimides

| API | Thermal stability in N_2 | | | | | Side group degradation (%) | |
|---------|-----------------------------------|----------------------------------|-------------------------------|-------------------------------|------------------|----------------------------|----------|
| | T_0 ($^\circ\text{C}$) | T_{10} ($^\circ\text{C}$) | T_1 ($^\circ\text{C}$) | T_2 ($^\circ\text{C}$) | R_{900} (%) | Calc. ^a | Observed |
| ODA-PI | 396 | 431 | 453 | 584 | 44.9 | 67 | 68 |
| MDA-PI | 386 | 428 | 460 | 604 | 45.2 | 66 | 66 |
| CDA-PI | 388 | 422 | 438 | 598 | 52.6 | 67 | 70 |
| 6FDA-PI | 381 | 438 | 478 | 576 | 44.7 | 72 | 74 |

^a Calculated content of 4-(methoxy)phenoxy groups. T_0 : Onset temperature of degradation, T_{10} : Temperature at 10% weight loss. T_1 : 1st maximum decomposition temperature, T_2 : 2nd maximum decomposition temperature. R_{900} : Residue at 900°C .

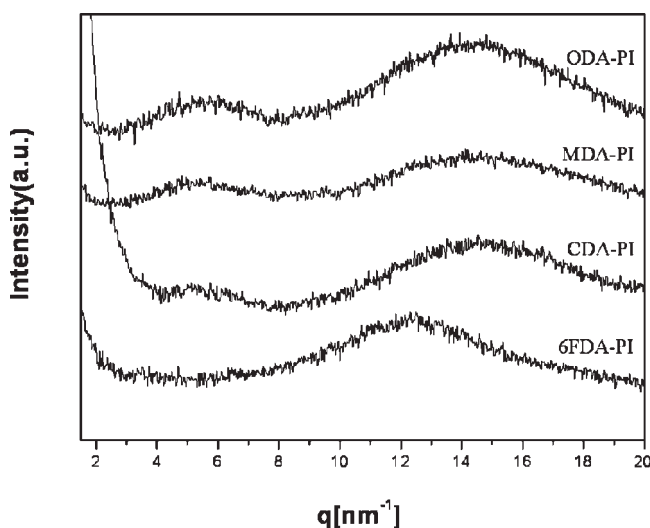


Figure 7 Wide-angle X-ray diffractograms of polyimides.

ODA-PI, MDA-PI, and 6FDA-PI are white, while CDA-PI looks slightly yellowish in color. However, all the APIs are much superior in transparency to UV-Vis lights to the fully aromatic poly(anthracenediimide)s, which have many absorption maxima up to 385 nm.¹⁸

Thermal properties of APIs were evaluated by TGA and DSC. Although the APIs are all amorphous in morphology, as to confirm from wide-angle X-ray diffractometric study to be discussed later, in the temperature range covered no phase transitions could be detected by DSC from any APIs in spite of annealing over an extended period of time. This behavior might be explained based on the fact that due to the fairly linear chair-like configuration of the alicyclic units the API chains are so high in their backbone rigidity that their chains cannot move freely in the measured temperature range to pack to each other to form a crystal domain.

Thermal resistances of APIs were examined by TGA, and their thermograms are reproduced in Figure 6 and their numerical values are summarized in Table II. Figure 6 shows that APIs begin to degrade in the 381–396°C range all with a two-step pyrolysis pattern. To know which parts of APIs cleave off in the lower-temperature range, we calculated 4-(methoxy)phenyloxy side group contents and compared them with percentage weight losses measured in the range, as shown in Table II. As to see from Table II, both data are surprisingly well coincident with each other, and we may presume that in APIs the 4-(methoxy)phenyloxy side groups are thermally more unstable than the alicyclic ring-containing backbone.

Crystalline structure of APIs was examined by wide-angle X-ray diffractometry and their diffracto-

grams are reproduced in Figure 7. It shows that all the polymers reveal no noticeable peak but only broad halos in the whole q (nm^{-1}) range, indicating that they are all amorphous in their morphology. The amorphous structure of APIs seems to arise from the fact that their diimide unit is not strictly linear and their diamine units possess the linking groups -A- (Scheme 2) all with bent or kinked structure hindering APIs chains from packing to each other.

CONCLUSIONS

Four new alicyclic polyimides (APIs) were successfully synthesized at 80°C in the presence of excess NaI by the *in situ* Diels-Alder polymerization of MPBB monomer with four AMIs derived from MA and ODA, MDA, CDA, and 6FDA. To study stereochemical structure of API chains *N,N'*-diphenyl-9,10-di[4-(methoxy)phenyloxy]-1,2,3,4,5,6,7,8-octahydroanthracene-2,3,6,7-tetracarboxydiimide (DPAI) was employed as model compound and the investigation using heteronuclear ^1H - ^{13}C -correlation NMR (HETCOR) spectroscopy revealed that among 16 possible isomers DPAI presumably consists of only one *trans-bis-endo*-configuration. Using ^1H -NMR spectrum MDA-PI was confirmed to have exactly the same *trans-bis-endo*-configuration as DPAI. After structural characterization of APIs their solution, thermal, and optical properties were measured and discussed in respect to their chain structures. Inherent viscosities of APIs varied in the 0.20–0.41 dL/g range. In spite of incorporation of the alicyclic units onto backbone APIs did not show substantial enhancement in solubility and the solubility seemed to be affected more by the fused imide-containing rings than by the arylene moiety. In TGA APIs began to degrade in the 381–396°C range with two-step pyrolysis patterns and in the lower temperature step the 4-(methoxy)phenyloxy side groups were presumed to degrade away. In DSC no phase transitions were noticed and in wide-angle X-ray diffractometry the APIs appeared all amorphous. In UV-Vis spectroscopy CDA-PI had absorption up to 363 nm while the others were transparent to the visible lights with the wavelength longer than 322 nm.

References

1. Kricheldorf, H. R. *Advances in Polymer Science: Progress in Polyimide Chemistry*, Vols. I and II; Springer-Verlag: Berlin, 1998.
2. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamental and Applications*; Marcel Dekker: New York, 1996.
3. Havva, Y.; Mathias, L. J. *Polymer* 1998, 39, 3779.
4. Spiniopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* 1998, 31, 522.

5. Liaw, D. J.; Huang, C. C.; Chen, W. H. *Macromol Chem Phys* 2006, 207, 434.
6. Matsumoto, T. *J Photopolym Sci Technol* 2001, 14, 725.
7. Li, J.; Kato, J.; Kudo, K.; Shiraishi, S. *Macromol Chem Phys* 2000, 201, 2289.
8. Lee, K.-H.; Jung, J. C. *Polym Bull* 1998, 40, 407.
9. Lee, S. J.; Jung, J. C.; Lee, S. W.; Ree, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 3130.
10. Kim, Y. S.; Jung, J. C. *Polym Bull* 2001, 46, 263.
11. Kudo, K.; Nonokawa, D.; Li, J.; Shiraishi, S. *J Polym Sci Part A: Polym Chem* 2002, 40, 4038.
12. Bennet, J. F.; Zahler, R. E. *Chem Rev* 1965, 19, 95.
13. Pollmann, M.; Wohlfarth, W.; Müllen, K. *Tetrahedron Lett* 1990, 31, 2701.
14. Vogel, T.; Blatter, K.; Schlüter, A.-D. *Makromol Chem Rapid Commun* 1989, 10, 427.
15. Blatter, K.; Schlüter, A.-D. *Macromolecules* 1989, 22, 3506.
16. Godt, A.; Enkelmann, V.; Schlüter, A.-D. *Angew Chem Int Ed Engl* 1989, 26, 1680.
17. Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew Chem Int Ed Engl* 1987, 28, 892.
18. Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J Org Chem* 1990, 55, 4794.
19. Thomas, A. D.; Miller, L. L. *J Org Chem* 1986, 51, 4160.
20. Leslie, R. D.; John, R. E.; Nicholas, J. F.; Richard, O. *Eur Polym J* 1995, 31, 647.
21. Moroz, A. A.; Shvartsberg, M. S. *Russ Chem Rev* 1974, 43, 679.
22. Kim, Y. S.; Jung, J. C. *J Polym Sci Part A: Polym Chem* 2002, 40, 1764.
23. Kircheldorf, R. A. U.S. Pat. 4,540,763 (1985).
24. Sodupe, M.; Rios, R.; Brnachadell, V.; Nicholas, T.; Oliva, A.; Dannenberg, J. J. *J Am Chem Soc* 1997, 119, 4232.
25. Laguitton, B.; Lison, P.; Pascal, T.; Sillion, B. *Polym Bull* 1995, 34, 425.