Lower Temperature Curing Thermoset Polyimides Utilizing a Substituted Norbornene Endcap

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ABSTRACT: Methoxycarbonyl bridgehead substituted nadic diacid monomethyl ester, when used as an endcapping monomer, lowered the cure temperature of thermoset PMR polyimides without seriously affecting other desirable properties, such as glass transition temperature and thermal oxidative stability. The ^{13}C CP/MAS NMR of model compounds was used to follow the cure of resin systems using both the unmodified nadic endcap and the methoxycarbonyl-substituted endcap. Rheological analysis and differential scanning calorimetry (DSC) also provided evidence for the lower curing nature of the substituted endcap. Two regioisomers of the bridgehead-substituted endcap were isolated, and their chemical structures were elucidated by X-ray crystallography. The model compound and molecular modeling studies conducted ruled out the possibility of regioisomeric imide formation in the substituted endcaps.

Introduction

Interest in thermoset polyimides has been increasing recently because of their ability to withstand high temperatures for extended periods of time and their ease in processing compared with thermoplastic polyimides. The incorporation of these resins into low-density composites for aircraft structural components has resulted in both weight reduction and cost saving over the corresponding metallic parts. One of the most commercially successful thermoset polyimides is PMR-15 (Scheme I). In the PMR (*P*olymerization of *M*onomer *R*eactants) approach, the monomers are combined in a methanol solution, the solvent is evaporated, and imidization is conducted by heating at 200 °C for 1–2 h to form the endcapped oligomer 4. The polyimide oligomer is then cross-linked through the reactive endcap to form the polymer network. PMR-15/graphite fiber composites are used commercially to replace metal components in aircraft engines where temperatures reach 300 °C.

Despite the widespread application of PMR-15, thermocycling during long-term use causes microcracking, which leads to a loss of mechanical properties. However, microcracking in these composites could be reduced by the use of a lower temperature cure cycle.[2] Unfortunately, simply lowering the cure temperature for a thermoset will not minimize microcracking because there is a temperature limit below which the endcap will not polymerize. Therefore, one approach to reduce the microcracking is to use a lower temperature curing endcap. Early work[3] used methyl substitution in model norbornene imides to enhance the retro Diels–Alder reaction, which has been shown to be a dominant mode of polymerization in PMR systems.[4] However, these substituted norbornene polyimides were less thermally stable than the unsubstituted norbornene polyimides (PMR-15). Model compound studies have shown that the rate of polymerization of norbornene-endcapped polyimides can be increased through the use of electron-withdrawing substituents, e.g., methoxycarbonyl.[5,6] Use of these substituted endcaps holds the potential for lower curing temperatures.

Our approach toward lowering the cure temperature of PMR-15 was to replace the endcap, *endo,endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, monomethyl ester (1; referred to as nadic acid ester), with nadic acid ester having a methoxycarbonyl group substituted at the bridgehead position, *endo,endo*-1-(methoxycarbonyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, monomethyl esters 6 and 7 (Scheme II). Although the presence of electron-withdrawing substituents on the diene has been shown to retard the rate of retro Diels–Alder reactions[7] in model compounds, methoxycarbonyl-substituted nadimides nevertheless show increased rates of polymerization. This effect has been attributed to an initial rearrangement of the ester group from the bridgehead to the vinyl position[5] (Scheme III). This rearrangement enhances the rate of a vinyl polymerization of the nadic system through the resonance stabilization of the transition state by the methoxycarbonyl group.

In this paper we investigate the effects of the methoxycarbonyl bridgehead substitution on the chemistry of the nadic anhydride. We also demonstrate the lower temperature cure of a methoxycarbonyl model compound and show that methoxycarbonyl-modified resins are nearly identical to PMR-15 in thermal–oxidative stability.

Experimental Section

All NMR spectra were recorded with a Bruker AM-300 spectrometer. Solution chemical shifts are reported with respect to tetramethylsilane as the internal standard. The ^{13}C solid NMR spectra were run with a high power solid attachment, using cross-polarization/magic angle spinning (CP/MAS), at spinning rates up to 5 kHz. Infrared spectra were recorded on a Perkin-Elmer 1750 Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) analyses were carried out on a Waters

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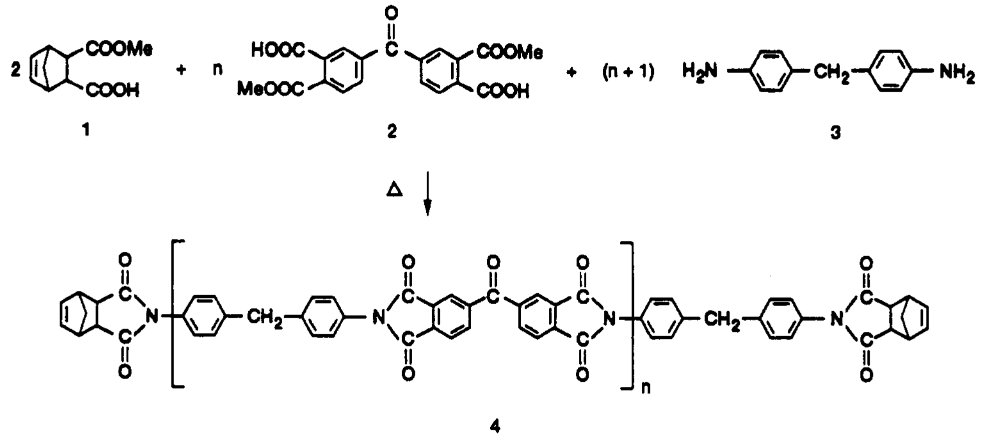
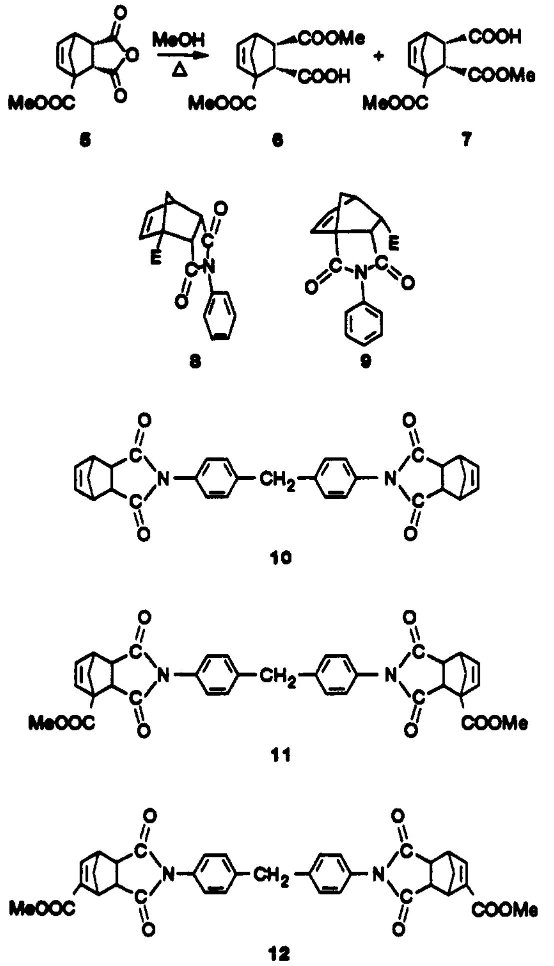
Scheme I



Scheme II



Associates system using Ultrastyragel columns, 100, 1000, and 500 Å, connected in series. Rheological measurements were performed on a Rheometrics, Inc., RMS 800 mechanical spectrometer. Thermogravimetric analyses were carried out in air on a Perkin-Elmer TGS-2 at a scan rate of 10 °C/min. Thermomechanical analyses were conducted on a Du Pont instruments 943 TMA at a scan rate of 10 °C/min. All thermomechanical analyses and thermogravimetric analyses were recorded on an Omnitherm data station. Differential scanning calorimetry was performed in air on a Perkin-Elmer DSC 7 calorimeter at a scan rate of 10 °C/min and recorded on a Perkin-Elmer Series 7 thermal analysis system. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

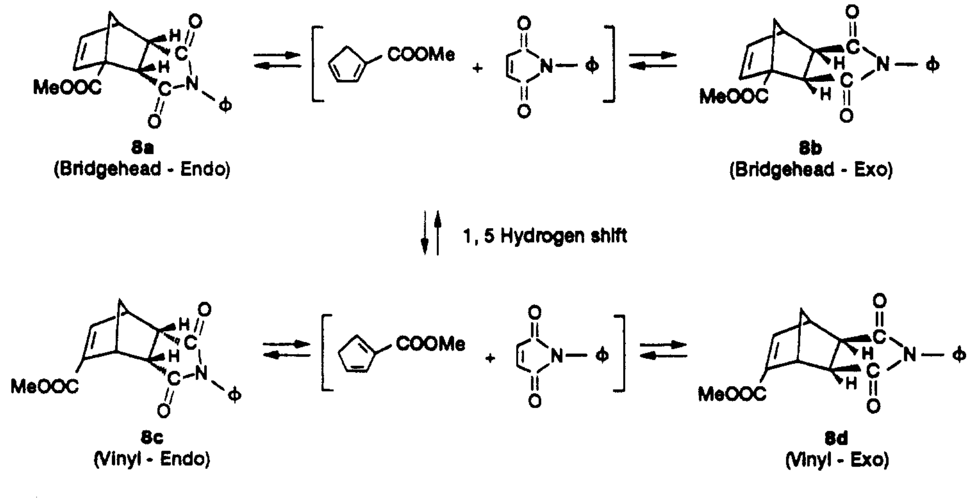
X-ray Analysis. Crystals of compound 6 were grown from an acetone solution via evaporation of the solvent. The structure was solved by direct methods. SHELXTL sotware was used for all calculations.[8] The final R value was 3.59%, and the final R_w was 4.38% for the observed data. The highest peak on the difference Fourier map was 1.31 Å from carbon atom 12. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized locations. The hydrogen atom bonded to oxygen atom 6 was calculated according to the SHELXTL programs as an OH trans to the longest bond to the adjacent atom, with the possibility of hydrogen bonding being ignored. A summary of the parameters and the final solution data are given in Tables I–III of the supplementary material.

Materials. 1-(Methoxycarbonyl)bicyclo[2.2.1]hept-5-ene-*endo,endo*-2,3-dicarboxylic anhydride (**5**; carbo anhydride) was synthesized by the method of Grunewald and Davis.[9] 1-(Methoxycarbonyl)cyclopenta-1,3-diene was prepared by lithiation of cyclopentadiene with *n*-butyllithium at low temperature, followed by acylation with methyl chloroformate. Cracking the resulting dimer under vacuum gave the methoxycarbonyl-substituted cyclopentadiene in 30% yield. Further reaction of methoxycarbonyl-substituted cyclopentadiene with maleic anhydride in diethyl ether at room temperature provided the Diels–Alder adduct in 37% yield (11% overall; mp 149–151 °C). No attempt was made to optimize the yield of **5**. 4,4′-Methylenedianiline (MDA) was purchased from Fluka Chemika and was used as received. Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, methyl ester (nadic ester) was purchased from Alfa Chemicals and used as received. All solvents were HPLC grade and were used without further purification. 3,3′,4,4′-Benzophenonetetracarboxylic acid dianhydride (BTDA) was purchased from Aldrich Chemical Co. and was used without further purification.

1-*endo*-3-(Dimethoxycarbonyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic Acid (6) and 1-*endo*-2-(Dimethoxycarbonyl)bicyclo[2.2.1]hept-5-ene-*endo*-3-carboxylic Acid (7). A typical methanolysis of the anhydride monomers used is as follows: Anhydride **5**, (10.0 g, 45.0 mmol) was placed in methanol (20 mL) under nitrogen atmosphere and refluxed for 2 h. After cooling, excess methanol was rotary evaporated to give diesters **6** and **7** in approximately a 40:60 ratio. Isomer **6** was separated from the reaction mixture by successive recrystallizations from acetone/ether to yield 3.9 g. Isomer **7** was recovered from the filtrate by rotary evaporation. The solid was washed with cold hexane and air-dried to yield 6.4 g of the diester. The recovered product yield was 10.3 g (91%). Isomer **6**: mp 196–198 °C; ^{1}H NMR ($CDCl_3$) δ 1.70 (d, 1 H, J = 8.4 Hz), 1.79 (dd, 1 H, J = 1.8, 8.4 Hz), 3.30 (br, 1 H), 3.53 (dd, 1 H, J = 3.2, 10.3 Hz), 3.62 (s, 3 H), 3.75 (d, 1 H, J = 10.3 Hz), 3.78 (s, 3 H), 6.32 (dd, 1 H, J = 2.9, 5.6 Hz), 6.43 (d, 1 H, J = 5.6 Hz); ^{13}C NMR ($CDCl_3$) δ 47.01, 49.64, 50.73, 51.77, 52.36, 53.21, 61.51, 134.23, 135.47, 171.80, 172.73, 174.62; FTIR (KBr) 3005, 3000 (br, OH), 2958, 1735, 1705, 1438, 1310, 1260, 1201 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.71; H, 5.53. Isomer **7**: mp 99–102 °C; ^{1}H NMR ($CDCl_3$) δ 1.71 (d, 1 H, J = 9.6 Hz), 1.79 (dd, 1 H, J = 1.7, 9.6, Hz), 3.30 (br, 1 H), 3.56 (dd, 1 H, J = 3.4, 10.3 Hz), 3.60 (s, 3 H), 3.72 (d, 1 H, J = 10.3 Hz), 3.77 (s, 3 H), 6.23 (dd, 1 H, J = 2.9, 5.5 Hz), 6.52 (d, 1 H, J = 5.5 Hz); ^{13}C NMR ($CDCl_3$) δ 47.36, 49.55, 51.06, 51.66, 52.22, 53.21, 61.20, 134.35, 135.26, 171.36, 172.53, 177.15; FTIR (KBr) 3000 (br, OH) 2971, 2955, 1735, 1724, 1719, 1711, 1315, 1274, 1224 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 56.83; H, 5.63.

1-(Methoxycarbonyl)-*endo,endo*-2,3-(*N*-phenyldicarboximido)bicyclo[2.2.1]hept-5-ene (8a). **6** or **7** (0.20 g, 0.78 mmol) and aniline (0.10 g, 1.1 mmol) were combined in 10

Scheme III



mL of acetic acid and refluxed for 16 h. Acetic anhydride (0.5 g, 4.9 mmol) was added to the reaction, and refluxing was continued for an additional 2 h. The solution was cooled and poured into 15 mL of cold water. The precipitate was filtered, washed twice with water, and vacuum-dried overnight at 100 °C. Chromatographic separation on silica gel (ethyl acetate/hexane 80:20, $R_f = 0.50$) yielded 0.19 g (81%) of imide: mp 173–174 °C; ^{1}H NMR (CDCl$_3$) δ 2.02 (m, 2 H), 3.57 (m, 1 H), 3.61 (d, 1 H, J = 7.6 Hz), 3.85 (s, 3 H), 3.90 (d, J = 7.6 Hz), 6.32 (dd, 1 H, J = 2.9, 5.6 Hz), 6.45 (d, 1 H, J = 5.6 Hz) 7.14 (dd, 2 H, J = 6.7, 1.5 Hz), 7.39 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 46.16, 47.02, 48.91, 52.56, 56.79, 61.06, 126.50, 128.65, 129.06, 131.69, 134.03, 134.95, 171.45, 174.67, 175.70; FTIR (KBr) 1735, 1713, 1273, 1224 cm^{-1}.

Bis[4-(norborn-5-enyl-2,3-dicarboximido)phenyl]methane (10). A typical imidization procedure is as follows: 4,4′-Methylenedianiline (**3**; 1.96 g, 9.90 mmol) and **1** (3.88 g, 19.8 mmol) were combined in 30 mL of glacial acetic acid under nitrogen and refluxed for 16 h. Acetic anhydride (3 mL) was then added, and the reaction was refluxed for an additional 3 h. The solution was cooled and poured into 50 mL of cold water. The precipitate was filtered, washed twice with water, and vacuum-dried overnight at 100 °C to yield 5.39 g of bisimide in 92% yield: mp 249–254 °C; ^{1}H NMR (CDCl$_3$) δ 1.59 (d, 2 H, J = 8.8 Hz), 1.78 (dd, 2 H, J = 1.4, 8.8 Hz), 3.41 (dd, 4 H, J = 1.5, 2.8 Hz), 3.49 (d, 4 H, J = 1.4 Hz), 4.12 (s, 2 H), 6.24 (s, 2 H), 7.05 (d, 4 H, J = 8.3 Hz), 7.21 (d, 4 H, J = 8.3 Hz); ^{13}C NMR (CDCl$_3$) δ 41.14, 45.52, 45.79, 52.23, 126.68, 129.65, 130.09, 134.61, 140.86, 176.81; FTIR (KBr) 2988, 2948, 1774, 1708, 1513, 1381, 1316, 1182 cm^{-1}. Anal. Calcd for $C_{31}H_{26}O_4N_2$: C, 75.9; H, 5.34; N, 5.71. Found: C, 76.0; H, 5.43; N, 5.83.

Bis[4-[1-(methoxycarbonyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboximido]phenyl]methane (Carbo Bisimide) (11). The bisnadimide **11** of 4,4′-methylenedianiline was synthesized from **3** and **5** as above in 90% yield, mp 165–190 °C (with visible boiling in the melting point capillary tube and observed by DSC, vide infra): ^{1}H NMR (CDCl$_3$) δ 2.01 (m, 4 H), 3.57 (m, 4 H), 3.85 (s, 6 H), 3.88 (d, 2 H, J = 7.6 Hz), 3.98 (s, 2 H), 6.30 (dd, 2 H, J = 2.8, 5.7 Hz), 6.43 (d, 2 H, J = 5.7 Hz), 7.18 (d, 4 H, J = 8.4 Hz), 7.21 (d, 4 H, J = 8.4 Hz); ^{13}C NMR (CDCl$_3$) δ 41.11, 45.60, 46.97, 48.87, 51.93, 56.75, 61.03, 126.51, 129.68, 129.83, 133.94, 134.94, 140.94, 171.48, 174.73, 175.77; FTIR (KBr) 2994, 2953, 1777, 1734 (ester carbonyl), 1713 (imide carbonyl), 1514, 1382, 1316, 1135 cm^{-1}. Anal. Calcd for $C_{35}H_{30}O_8N_2$: C, 69.30; H, 4.98; N, 4.62. Found: 69.03; H, 4.22; N, 4.62.

Bis[4-[5-(methoxycarbonyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboximido]phenyl]methane (Thermally Rearranged Vinyl Carbo Bisimide) (12). The rearranged bisimide was prepared by a thermal imidization as follows: **7** (0.838 g, 3.30 mmol) and **3** (0.327 g, 1.65 mmol) were combined in a methanol solution and heated until a viscous solution resulted. The mixture was then placed in an oven and heated at 200 °C for 1 h to give a quantitative yield of **12**. The product was determined to be fully imidized by IR. Integration of the vinyl protons by NMR proved that the rearranged vinyl-substituted methoxycarbonyl compound formed in 90% yield: mp 149–152 °C; ^{1}H NMR (CDCl$_3$) δ 1.70 (d, 2 H, J = 9.1 Hz), 1.94 (d, 2 H, J = 9.1 Hz), 3.48 (m, 2 H), 3.62 (m, 4 H), 3.73 (s, 6 H), 3.85 (m, 2 H), 3.99 (s, 2 H), 6.94 (d, 4 H, J = 8.25 Hz), 7.09 (d, 2 H, J = 2.68 Hz) 7.19 (d, 4 H, J = 8.25 Hz); FTIR (KBr) 2996, 2951, 1776, 1713, 1514, 1381, 1274, 1184 cm^{-1}. Anal. Calcd for $C_{35}H_{30}O_8N_2$: C, 69.30; H, 4.98; N, 4.62. Found: C, 68.77; H, 4.53; N, 4.75.

Preparation of Prepolymer 4. Prepolymers were prepared from the methanol solution of monomers via thermal imidization as shown in Scheme I. The number of moles of monomeric reactants is governed by the ratio $n:(n + 1):2$, where n, $n + 1$, and 2 are the number of moles of the aromatic diester (BTDE), of diamine, and of the endcap in the acid–ester form, respectively. PMR-15 molding powders were formulated for an n value of 2 by combination of the proper stoichiometric amounts of 3,3′,4,4′-benzophenonetetracarboxylic acid, dimethyl ester (BTDE) (**2**), 4,4′-methylenedianiline (**3**), and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, methyl ester (NE) (**1**) in methanol. Thermal treatment of the resultant methanol solutions as above yielded a molding powder which was determined to be fully imidized by FTIR.

Preparation of Methoxycarbonyl-Modified Prepolymer. Prepolymers containing the substituted nadic esters **6** and **7** were prepared identically to **4** in three different formulations. C-1 contains BTDE, MDA, and **6**. C-2 contains BTDE, MDA, and **7**. C-mix contains BTDE, MDA, and a 2:3 mixture of **6** and **7** obtained by esterification of **5** (Scheme II).

Neat Resin Processing. Compression molding (2000 psi) was carried out in a circular, hardened steel die with brass plungers. The charged die was placed in a press preheated to the process temperature, and the ramp rate of the die was approximately 20 °C/min. All polymerized specimens were cooled to room temperature under pressure. Isothermal weight loss studies were conducted in triplicate on neat resin samples, all cut to the same size (5.1 × 5.1 × 1.8 mm), at 316 °C in a forced hot air oven under 1 atom flowing air.

Results and Discussion

Separation and Structures of 6 and 7. Isomers **6** and **7** were easily separated by virtue of their solubility differences. One is only very slightly soluble in a range of solvents, including methanol, acetone, and chloroform and has a higher melting point. The other isomer is highly soluble in the same media. Once imidized, the resins prepared from either isomer, BTDE, and MDA behave identically. However, before imidization at 204 °C, their tack and drape properties are very different. The low solubility of one isomer could hamper its use in prepreg solutions for composite applications. For this reason, we determined the chemical structures of these isomers.

Despite a difference in the NMR spectra, structural assignments for the two isomers could not be made by NMR. Instead, X-ray crystallography of the less soluble isomer was performed. The solved structure of **6** is shown in Figure 1. The ball and stick packing diagram is shown in Figure 2. The atomic coordinates, bond angles, and bond lengths are given in Tables II and III of the

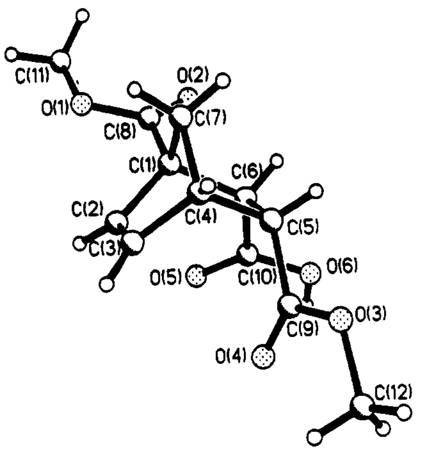


Figure 1. Ball and stick projection for 1-*endo*-3-(dimethoxycarbonyl)bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (**6**).

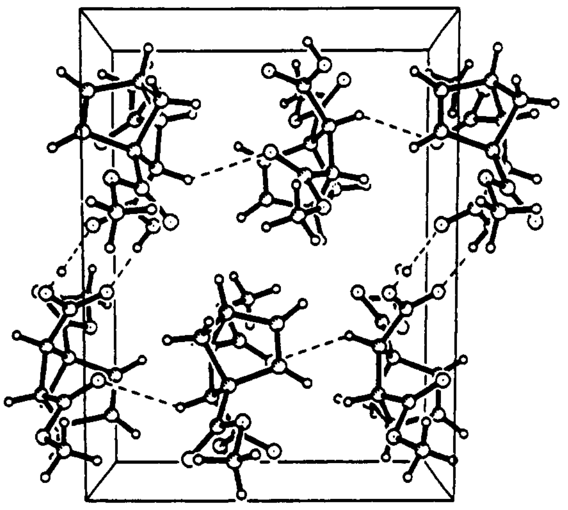


Figure 2. Packing diagram for 1-*endo*-3-(dimethoxycarbonyl)-bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid (**6**).

supplementary material. Isomer **6** occupies a monoclinic system with a unit cell volume of 1223.7 Å^3.

Analysis of Polyimide Model Compounds. Some consideration was given to the formation of **9** through imidization across the 1,2-positions of isomer **6**. It is possible to form imide **9** from **6**; the same is not true for **7** because of the 1,2-diester functionality of this isomer. Imide formation is difficult in these cases.[10] In fact, imidization of both **6** and **7** with aniline in refluxing acetic acid gave mostly 1-(methoxycarbonyl)-*endo*-2,3-(*N*-phenyldicarboximido)bicyclo[2.2.1]hept-5-ene (**8a**). Trace amounts of the 2,3-exo norbornyl imide, **8b**, were detected by NMR, which is consistent with earlier findings[5] that exo/endo isomerism occurs in substituted norbornenes (Scheme III). The melting point, ^{13}C NMR, and ^{1}H NMR matched the literature values for the same compound independently synthesized via a Diels–Alder cycloaddition of 1-(methoxycarbonyl)cyclopentadiene with *N*-phenylmaleimide.[6] No formation of 3-*endo*-(methoxycarbonyl)-1,2-(*N*-phenyldicarboximido)bicyclo[2.2.1]hept-5-ene (**9**) was observed by NMR.

MNDO-AM1[11] calculations were performed on the 1,-endo-2 imide **9** in order to assess the possibility of its formation during imidization. The results show that the heat of formation of the 1,endo-2 isomer **9** is ~20 kcal/mol higher than that of the 2,endo-3 isomer **8a**. This difference can be attributed to the increased ring strain in the 1,2-imide. Although the heats of formation are a thermodynamic parameter and the imidization is probably kinetically controlled, the increased ring strain in the formation of the 1,2-imide is probably present to a large extent in the transition state, giving a much higher barrier to its formation than in the 2,3-imide.

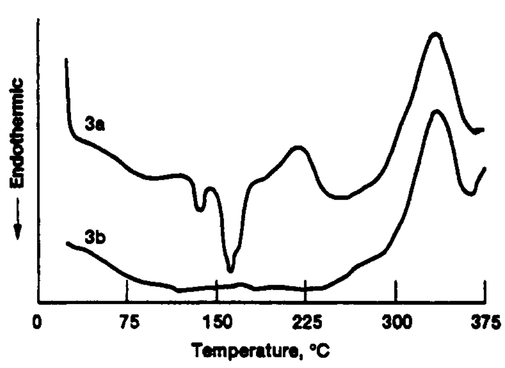


Figure 3. Differential scanning calorimetry trace of methoxycarbonyl-substituted bisimide model compounds (a) **11** and (b) **12**.

Rearrangement of the methoxycarbonyl substitution on the bicyclo[2.2.1] skeleton from the bridgehead to the vinyl position occurs for the bisimide **11** when the imidization was conducted at 204 °C. This was observed by NMR as well as FTIR. The ^{1}H NMR spectra of the vinylic protons changed from two resonances at 6.30 and 6.43 ppm in **11** to only one, shifted downfield to 7.09 ppm, in **12**. The IR spectrum shows a change in the absorption of the ester carbonyl from 1734 to 1713 cm^{-1}, this shift is characteristic of the α,β-unsaturated ester of the rearranged product. The results of differential scanning calorimetry of the unrearranged methoxycarbonyl-substituted bisimide **11** are shown in Figure 3a. An initial exotherm begins at 215 °C. We believe this corresponds to the rearrangement of the methoxycarbonyl moiety to the vinyl position. This rearrangement in substituted *N*-phenylnadimide model compounds has been demonstated by Sukenik.[5] The DSC of the thermally rearranged bisimide **12** is shown in Figure 3b. The exotherm for the unrearranged bisimide **11** beginning at 215 °C is not apparent in the rearranged bisimide **12**. Instead, the onset of exothermic activity for bisimide **12** is 254 °C.

Carbon-13 cross-polarization/magic angle spinning NMR of the model bisimides **10** and **11** was undertaken to observe the chemical changes occurring during the cure process (Figure 4). The model bisimides were processed at 260, 288, and 316 °C (500, 550, and 600 °F). Pressure was applied to the mold once the viscosity of the resin had increased enough to prevent the resin from squeezing out of the mold. For the resins cured at 316 °C, the pressure was applied when the mold temperature reached 306 °C. When the resins were cured at 288 °C, the pressure was applied 30 min aftr the mold reached the 288 °C cure temperature. For the 260 °C cure, pressure was applied for bisimide **11** after 30 min at temperature. For the unsubstituted nadic bisimide **10**, however, no pressure was applied when cured at 260 °C; after 2 h the resin was not solidified enough to prevent squeeze out from the mold. The samples were then cooled under pressure (except for **10**, which was cured at 260 °C), and the resulting resin disks were ground for NMR studies. The ^{13}C CP/MAS NMR spectra and ^{13}C solution spectra of the uncured model compounds are shown in Figure 4.

Peak assignments for the ^{13}C CP/MAS specta can be made based upon the corresponding solution spectra in Figure 4a. In both bisimides **10** and **11**, the peaks centered at 126 ppm correspond to the eight protonated aromatic carbons and the two quaternary aromatic carbons attached to the methylene linking group. The peak at 147 ppm corresponds to the quaternary nitrogen-substituted aromatic carbon. In the solution spectrum of nadic bisimide **10**, the identities of the two aromatic and one vinylic

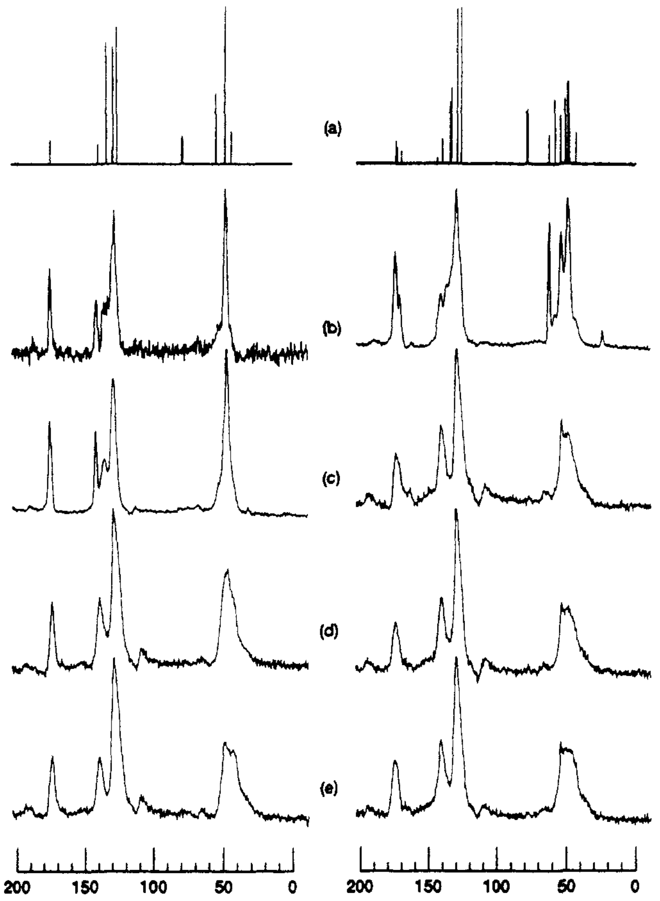


Figure 4. ^{13}C NMR spectra of unsubstituted nadic/MDA bisimide **10** (left) and methoxycarbonyl-substituted bisimide **11** (right): (a) solution spectra, (b) solids spectra of uncured imide, (c) cured for 2 h at 260 °C, (d) cured for 2 h at 288 °C, and (e) cured for 2 h at 316 °C.

resonance are ambiguous. However, the bridgehead substitution in **11** splits the vinylic peaks into two resonances, thereby identifying the peak at 134.6 ppm as the vinylic carbon in bisimide **10**. Therefore, the shoulder at 135 ppm in the ^{13}C CP/MAS spectrum of both **10** and **11** can be identified as the vinyl carbons of the [2.2.1]-hept-5-ene system. The imide carbonyl peaks are observed downfield at 175 ppm. The ester carbonyl of **11** occurs at 171 ppm. The upfield peaks correspond to the aliphatic carbons in both model compounds.

The curing process for both **10** and **11** produces several changes in the NMR spectra. These include the loss of the shoulder corresponding to the vinylic carbons at 135 ppm, a shift of the carbonyl peak to lower field, and a broadening and downfield shift of the aliphatic carbon peaks. The methoxycarbonyl-modified resin is completely cured after 2 h at 260 °C; there are no differences in the ^{13}C CP/MAS spectra of **11** cured at 260 °C and of **11** cured at higher temperatures. The unmodified model compound **10** shows only slight changes after a 2-h cure at 260 °C, indicating no appreciable reaction. Curing is still incomplete after 2 h at 288 °C, as evidenced by comparing spectra c–e. Further broadening occurs after 2 h at 316 °C. Despite the differences in cure temperatures, the two fully cured systems exhibit nearly identical ^{13}C CP/MAS NMR spectra (Figure 4e).

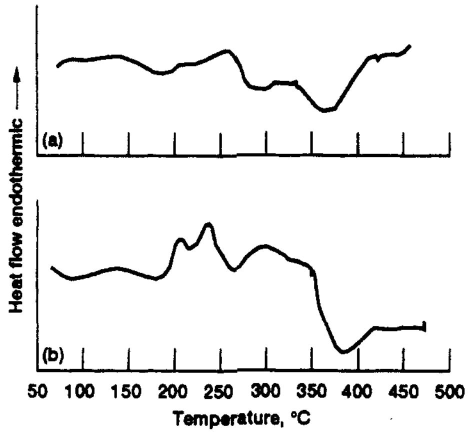


Figure 5. Differential scanning calorimetry traces of (a) methoxycarbonyl-modified PMR molding powder (C-mix) and (b) PMR-15 imidized molding powder.

Table I
Gel Permeation Chromatography Results on Methoxycarbonyl-Modified C-Mix Molding Powders

n value	formulated mol wt	M_n	M_w	polydispersity
2	1574	2386	4300	1.80
4	2542	2698	5455	2.02
6	3510	3005	5166	1.72

Characterization and Polymerization of Molding Powders From 6 and 7. Molding powders formulated from BTDE, MDA, and the 2:3 isomeric mixture of **6** and **7** resulting from ring-opening methanolysis of **5** are referred to as C-mix. Methoxycarbonyl resins composed of BTDE, MDA, and **6** are referred to as C-1, and resins formulated from BTDE, MDA, and **7** are referred to as C-2. Gel permeation chromatography was conducted on imidized molding powders of several molecular weights, using polystyrene standards for relative molecular weight characterization. The molding powders were soluble in DMF, DMAC, and NMP. DMAC was used to dissolve the polymers for GPC analysis. The results are summarized in Table I. A good correlation between formulated molecular weight and M_n is observed.

The cure characteristics of molding powders formulated from methoxycarbonyl-substituted norbornenes were investigated by DSC and rheological analysis. The DSCs of PMR-15 and C-mix of the same *n* value (*n* denotes the number of repeat units in the oligomer) are shown in Figure 5. Both polymers show melt endotherms beginning at ~200 °C, followed by an exothermic polymerization at higher temperatures. Consistent with the ^{13}C CP/MAS NMR study above, the onset for polymerization in methoxycarbonyl-modified resins is ~25 °C lower than that of PMR-15. The DSCs of both the PMR-15 and the C-mix appear very similar except for the temperature at which the substituted and unsubstituted endcaps polymerize.

The melt rheology of C-mix and PMR-15 molding powders was investigated on a parallel plate rheometer. The complex viscosity η^* vs temperature profiles are shown in Figure 6. Both resins show an initial increase in complex viscosity, presumably due to further imidization, and then a melt between 200 and 230 °C. An increase in viscosity is then observed due to cross-linking of the endcap. The two resins appear to behave very similarly, except that C-mix molding powders reach a higher complex viscosity earlier than the PMR-15 molding powder, corresponding to the earlier curing characteristics of this endcap.

Neat Resin Fabrication and Testing. Neat resin specimens were fabricated from molding powders after imidization at 204 °C. All the resin samples were formulated for an *n* value of 2. All PMR-15 resins were compression molded at 2000 psi and processed for 2 h at 316 °C. Pressure was applied when the mold temperature reached 304 °C. The methoxycarbonyl-substituted resins were staged at 260 °C for 15 min before 2000-psi pressure was applied and were then processed for 2 h at 288 °C. All samples were postcured for 16 h in air at 316 °C.

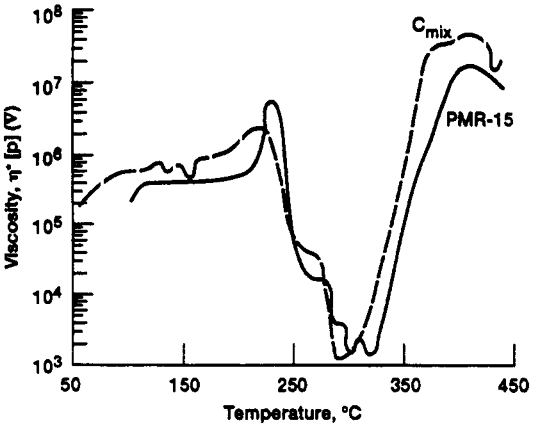


Figure 6. Viscosity vs temperature profile for PMR-15 imidized molding powder and C-mix methoxycarbonyl-modified imidized molding powder.

Table II
Properties of Cured Resins

resin	T_g,[a] °C	T_g,[b] °C	T_d,[b] °C
PMR-15	332	346	605
C-mix	304	340	609
C-1	315	329	589
C-2	310	330	608

[a] Nonpostcured resin. [b] Resin postcured in air at 316 °C for 16 h.

Table III
316 °C Isothermal Weight Loss of Methoxycarbonyl-Modified and Unmodified PMR Resins

resin[a]	1000-h wt loss,[b] %	wt loss surface area, mg/cm^2
PMR-15	15.1 (±0.5)	0.84
C-1	16.9 (±0.4)	0.87
C-2	19.8 (±0.4)	0.86
C-mix	20.5 (±0.6)	0.85

[a] All resins are cut to the same size and tested in 1 atm flowing air. [b] Values in parentheses are for one standard deviation unit.

The glass transition temperatures (T_g) and decomposition temperatures (T_d) of the resins studied are given in Table II. The nonpostcured resins show a broader glass transition when compared with that of the postcured resins. PMR-15 has a T_g of 332 °C while the T_g of the C-mix resin is 304 °C. Yet, the difference in T_g's of these two resins decreases to only 6 °C after the resins are postcured. Resin C-2 shows a similar trend. Decomposition temperatures in air are very similar for all the resin systems (~600 °C) except C-1, which has a T_d about 15–20 °C lower than the other resins (C-2, C-mix, and PMR-15).

Isothermal weight loss was conducted on neat resin specimens at 316 °C under 1 atm circulating air. The weight losses of PMR-15 and the methoxycarbonyl-modified systems ($n = 2$) after 1000 h are given in Table III. The surface area was determined by measuring the dimensions of the cut specimens. Although PMR-15 shows superior thermal oxidative stability over all three methoxycarbonyl systems, the difference is not large, and an optimization of the processing conditions of the modified resins could possibly bring the two systems within experimental error (±0.5%). After 1000 h at 316 °C, PMR-15 resin lost 15% of its weight, C-1 lost 17%, while C-2 and C-mix lost 20%.

Summary and Conclusions

Methoxycarbonyl-modified PMR-15 systems were investigated in an effort to decrease the cure temperature of polyimides. The lower temperature cure of methoxycarbonyl-substituted norbornene-capped polyimides was demonstrated by DSC and rheological analysis. Differences in the cure mechanism of the methoxycarbonyl-modified PMR resins were observed. These include a previously demonstrated[6] rearrangement of the methyl ester group attached to the bridgehead position to the norbornyl vinyl position during the imidization process. Apart from this rearrangement, other differences in the cure mechanism have not been demonstrated conclusively. Carbon 13 CP/MAS NMR was used to identify the temperature at which the methoxycarbonyl-substituted nadimide undergoes polymerization. This technique demonstrated that the methoxycarbonyl nadimides cure approximately 25 °C earlier than the unsubstituted nadimides. Although fully cured, bisimide model compounds from unsubstituted nadic anhydride and bisimides from the methoxycarbonyl-substituted nadic anhydride display virtually indistinguishable ^{13}C CP/MAS NMR spectra when completely polymerized. The glass transition temperatures T_g of modified resins are slightly lower than those of PMR-15, and decomposition temperatures T_d of the modified and unmodified resins are very close. All resins show similar thermal oxidative stabilities under long-term isothermal aging at 316 °C.

Use of the methoxycarbonyl-substituted nadic end-capped polyimides can lower the cure temperatue of PMR systems. These polymers have the potential to produce composite materials that are not as susceptible to microcracking as PMR-15. Further work is underway to evaluate these methoxycarbonyl-modified PMR resins for improved resistance to microcracking and loss of mechanical properties under thermal cycling.

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Supplementary Material Available: Crystal structure data, atomic coordinates and isotropic displacement coefficients, and bond lengths and angles (Tables I–III) for **6** (3 pages). Ordering information is given on any current masthead page.

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