# 7-Hydroxynadic Acid: A New End Cap for Improved Oxidation Resistance in Addition Polyimides

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We consider possible replacements for the norbornenyl end cap in addition polyimides that should favor bridge degradation and lead to lower weight loss in the resin system. Our preliminary evaluation demonstrates that molding powder made with 7-hydroxynorbornene-2,3-dicarboxylic acid, **17**, as the end cap can be fully imidized at 200 °C. By differential scanning calorimetry (DSC), onset of cross-linking occurs approximately 50 °C lower than that for the unsubstituted end cap. The hydroxy-bearing carbon on **17** is more easily oxidized to carbonyl on aging in the polymer than the parent end cap. Therefore, the new end cap more highly favors bridge degradation. However, processing studies, long-term weight loss, and careful evaluation of degradation mechanisms must be carried out to fully assess **17** as a more thermo-oxidatively stable replacement for the parent norbornenyl end cap.

## Introduction

Over the past several decades, high-performance, low-density polymers and polymer matrix composites (PMCs) have found increasing application in the aerospace industry as metal replacements.[1,2,3] The PMCs are generally composed of graphite fibers saturated with a polymer resin. However, it is the resin that dominates the thermal-oxidative stability (TOS) of a given high-temperature PMC. The best polymers to date for these high-temperature applications, combining TOS, processability, and good mechanical properties, are the norbornenyl-end-capped PMR (polymerization of monomer reactants) polyimides.[3,4]

The PMR resins are prepared by the initial formation of oligomeric prepolymers capped at both ends by a reactive end group. The end cap undergoes cross-linking during processing, producing the desired low-density, high-specific-strength materials. For example, the classic preparation of PMR-15 involves the initial formation of a polyimide prepolymer via the 120−230 °C condensation of three monomer reactants: the *end cap* 2-carbomethoxy-3-carboxy-5-norbornene (the monomethyl ester of nadic diacid, NE), the *diamine* 4,4′-methylenedianiline (MDA), and the *diacid diester* of benzophenone-3,4,3′,4′-tetracarboxylic 3,4,3′,4′-dianhydride (BTDE). The resulting low-molecular-weight polyimide oligomer undergoes cross-linking through the nadic end cap at 275−325 °C to produce a void-free network structure (Figure 1).[5] There is also a final post-cure which generally raises the glass transition temperature ($T_g$) of the resin.

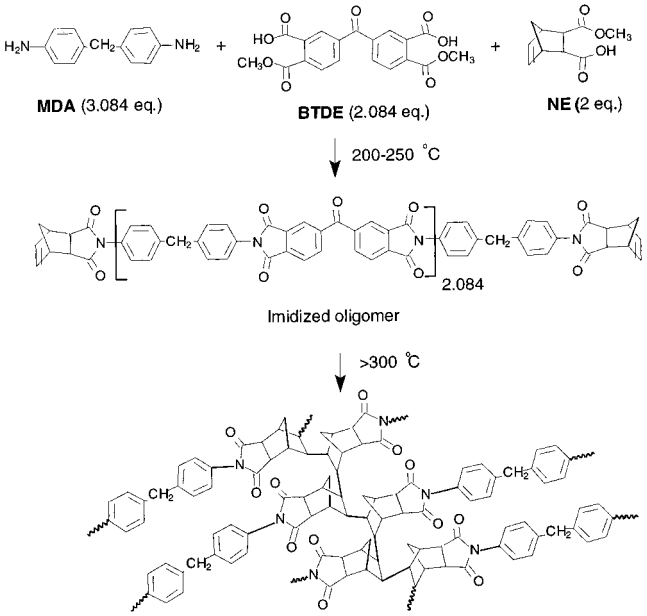


**Figure 1.** Reaction scheme for the preparation of PMR-15.

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(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(2) See the collection of papers in *Resins for Aerospace*; ACS Symposium Series No. 132; American Chemical Society: Washington, DC, 1980.

(3) For a review of norbornenyl-end-capped materials as well as other latent addition end-capped systems, see: Meador, M. A. *Annu. Rev. Mater. Sci.* **1998**, *28*, 599−630.

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(5) Meador, M. A. B.; Johnston, J. C.; Cavano, P. J. *Macromolecules* **1997**, *30*, 515−19. We note that other end caps undoubtedly undergo degradation as well. However, to the best of our knowledge, no systematic study has been carried out in these other systems to determine the end cap contribution to the overall weight loss. Further discussion of their degradation, cross-linking temperature, and processability is beyond the scope of this paper.

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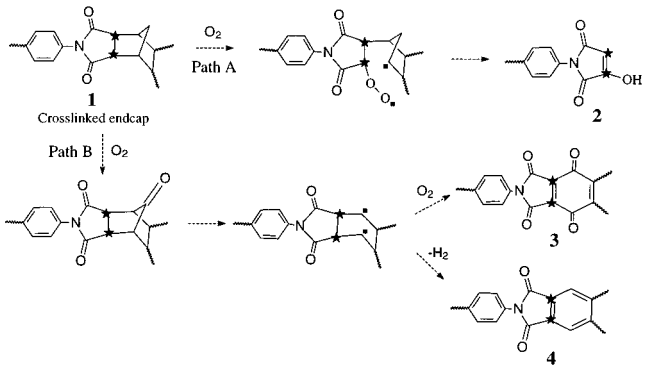



**Figure 2.** End cap degradation pathways (★ = labeled carbons).

The end cap facilitates processing by controlling the molecular weight of the oligomer and allowing flow before it cross-links. However, this very end cap, after cross-linking, accounts for much of the weight loss in the polymer on aging in air at elevated temperatures.[6] Understanding this degradation provides clues for designing new end caps to slow degradation and, thereby, prolong the lifetime of the material.

Previously,[6] we reported studies on the thermo-oxidative aging of a modification of PMR-15, in which we $^{13}$C-labeled the nadic end cap at the methyne carbon α to the carbonyl groups (see **1** in Figure 2). This labeled carbon in the as-processed polymer has an enhanced $^{13}$C NMR peak at 48 ppm. The solid NMR difference spectrum of the $^{13}$C labeled PMR-15 aged as a powder for up to 64 h indicates that, upon oxidation, nearly all of this nadic peak at 48 ppm is consumed. In its place, three broad peaks for $^{13}$C labeled carbons grew in at 105−120, 125−140, and 150−165 ppm.

On the basis of these chemical shifts, results from delayed decoupling NMR experiments, and comparison to model compounds,[7] we can conclude that the major nonvolatile products of oxidation are **2**, **3**, and **4**, as shown in Figure 2, and that this oxidation proceeds through two primary pathways. Path A or "ring" degradation is proposed to proceed through initial thermal opening of the norbornyl ring to form a biradical which undergoes attack by oxygen to form 2-hydroxymaleimide (**2**). Structures such as the latter can account for the olefinic peaks at 105−120 and 150−165 formed on oxidation of labeled polymer. Path B or "bridge" degradation proceeds through oxidation of the bridging methylene of the norbornene moieties followed by carbon monoxide extrusion. Aromatization of the resulting biradical ultimately leads to substituted phthalimide **4** or quinone **3** and related secondary degradation products. Structures such as these account for the large peak at 125−140 ppm, which grows in the spectrum of the labeled polymer after oxidation.

"Ring" oxidation products such as **2** are cleavage products that are most likely formed concomitant with large amounts of weight loss in the polymer system. In contrast, structures such as **3** and **4** resulting from "bridge" oxidative degradation are formed with very little weight loss. Therefore, new end cap structures that more strongly favor bridge degradation should lead to lower weight loss in "addition polyimides" and result in less shrinkage and cracking in the oxidation layer.[8]

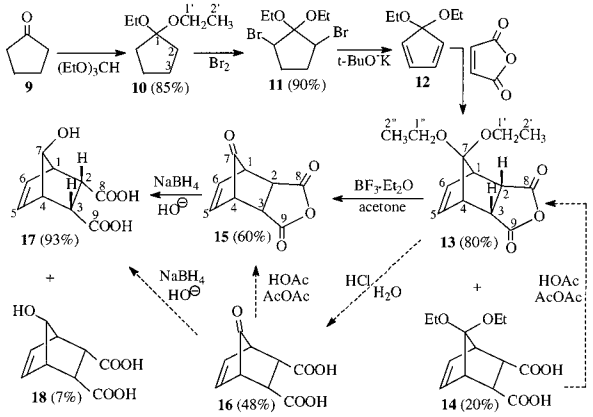
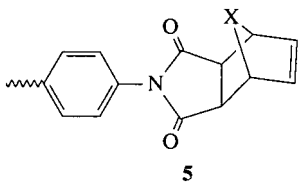



**Figure 3.** Synthetic scheme for the preparation of 7-hydroxy-nadic acid (**17**).

In this paper, we wish to explore the design of new end caps that might favor Path B bridge degradation. We propose the utilization of structures such as **5** (below), where X is more labile than the methylene of




the parent norbornenyl end cap or is readily oxidized under the aging conditions to a more labile group. Such structures should oxidize and/or aromatize to stable structures such as **3** and **4**. It is important at the same time, however, to preserve the desirable processing properties of the norbornene end cap. Hence, X must also be stable enough to survive imidization (200 °C) and cross-linking (315 °C). In addition, cross-linking must occur in the same way as for the parent norbornene structures (mostly through the double bond and not mostly through retro-Diels−Alder reaction), lest oxidation proceed in a different fashion.

Herein, we focus on the synthesis of one such derivative of **5**, compound **18**, where X is a hydroxymethylene group. We also describe the cure of polymers using **18** as an end cap. In addition, we compare the isothermal aging, monitored by CP-MAS NMR, of polymer using **18** with that of polymer using the parent norbornenyl end cap.

## Experimental Section

Solution NMR spectra were obtained on 600, 400, and 200 MHz Fourier transform spectrometers, using TMS as the internal standard. Assignments were facilitated by COSY and NOESY experiments. The carbon numbering of the various compounds used in the spectral assignments is shown in Figure 3. Solid polymer samples were run on the Bruker AM 300 MHz FT spectrometer fitted with a high-power solids attachment, utilizing cross-polarization and magic angle spinning at 5 kHz (CPMAS). The acquisition also employed

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spinning sideband suppression using a TOSS sequence. The spectra were externally referenced to the carbonyl of glycine (196.1 ppm relative to TMS). Delayed decoupling experiments were carried out with the same TOSS sequence, but with an additional delay of 40 $\mu$s included after the CP contact time but before acquisition. High-resolution mass spectra (HRMS) were run on a VG-Fison AutoSpecE high-resolution spectrometer. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel microcards.

Compounds **10**,[9,10] **11**,[9,11−13] **12**,[9,11−13] **13**,[9,13] **15**,[9,13,14] and **23**[15] are known in the literature. Nevertheless, the $^{13}$C spectral data are lacking, while the $^{1}$H NMR data are of relatively low resolution; hence, these are cited below where appropriate.

**1,1-Diethoxycyclopentane (10).** A three-necked 500 mL round-bottom flask fitted with a magnetic stirrer, a drying tube, and a pressure-equalizing addition funnel was charged with cyclopentanone (**9**, 44 mL, 42 g, 0.5 mol). The addition funnel was charged with triethylorthoformate (83 mL, 74 g, 0.5 mol), tosic acid (4.75 g, 0.025 mol), and absolute ethanol (46 g, 1 mol), and the latter solution was rapidly added dropwise over 20 min. During the addition, the reaction mixture warmed slightly and gradually turned yellow. Following addition, the reaction mixture was stirred for another 20 min (it turned golden brown), neutralized with sodium methoxide (1.62 g, 0.03 mol), and stirred for 15 min more. The resulting precipitate was gravity-filtered, and the filtrate was concentrated by rotary evaporation and refiltered washing with $CH_2Cl_2$ (rotary evaporation gave essentially pure product (67 g, 0.42 mol, 85% yield). Vacuum distillation (79−80 °C/38 Torr) afforded the desired pure ketal **10** (63.2 g, 0.40 mol, 80% yield).

**10:** $^{1}$H NMR ($CDCl_3$) $\delta$ 3.44 (q, $J$ = 7 Hz, 4H, $H_{1'}$), 1.80−1.67 (m, 4H, $H_2$), 1.67−150 (m, 4H, $H_3$), 1.14 (t, $J$ = 7 Hz, 6H, $H_{2'}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 111.51 ($C_1$), 56.84 ($C_{1'}$), 34.81 ($C_2$), 22.92 ($C_3$), 15.48 ($C_{2'}$).

**2,5-Dibromocyclopentanone (11).** A three-necked 1 L round-bottom flask fitted with a magnetic stirrer, a thermometer, a drying tube, and a pressure-equalizing addition funnel containing bromine (10.2 mL, 31.8 g, 0.2 mol) was charged with diethoxycyclopentane (**10**, 15.8 g, 0.1 mol) dissolved in 250 mL of absolute ethanol. The reaction mixture was cooled to 5 °C. Bromine (3 drops) was added, and it took ~7 min until the solution turned colorless. The dropwise addition of $Br_2$ was continued over the next 3 h, maintaining a light brown color and a reaction temperature below 10 °C. Following addition, the reaction was stirred for 10 min at 5 °C, $K_2CO_3$ (70 g, 0.5 mol) was added, and the reaction mixture was stirred for 10 min more at 5 °C. Ice-bath-chilled pentane (170 mL) was added to the reaction vessel, and the contents of the latter were emptied into a 1 L flask containing 130 mL of ice−water. The reaction mixture, which had turned yellow, was immediately poured into a separatory funnel, and the upper organic layer was separated, dried over $MgSO_4$, and rotary evaporated using a water bath maintained at <15 °C. The viscous product (24 g, 0.09 mole, 90% yield) was essentially clear and light tan in color. The product was relatively labile; hence, it was stored in the freezer (−10 °C) until it was used within an hour in the next step. The NMR spectral data (in particular the overlapping triplets of equal height at 1.21 and 1.28 ppm) suggested that the product was composed of a 1:1 mixture of both the *cis*- and *trans*-dibromo isomers.

**11:** $^{1}$H NMR ($CDCl_3$) $\delta$ 4.8 and 4.2 (m, 2H, $H_2$), 3.78 (bq, $J$ = 6 Hz, 4H, $H_{1'}$), 2.5 (m, 4H, $H_3$), 1.205 and 1.275 (overlapping t, $J$ = 6 Hz, 6H, $H_{2'}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.11 ($C_1$), 73.51 ($C_2$), 59.28 ($C_{1'}$), 27.98 ($C_3$), 16.34 ($C_{2'}$).

**5,5-Diethoxycyclopenta-1,3-diene (12), 7,7-Diethoxynadic Anhydride (13), and 7,7-Diethoxynadic Acid (14).** A three-necked 1 L round-bottom flask fitted with a magnetic stirrer, a thermometer, a drying tube, and a pressure-equalizing addition funnel containing dibromoketal **11** (24 g, 0.09 mol) dissolved in 50 mL of dry DMSO was charged with potassium *tert*-butoxide (42 g, 0.37 mol) dissolved in 400 mL of dry DMSO. The temperature in the reaction vessel was brought to 18 °C with an ice bath. The dibromoketal solution was added rapidly over 10 min while maintaining the temperature in the reaction vessel below 22 °C. During the addition, the reaction mixture was manually and vigorously agitated, and cooled when necessary in a dry ice−acetone bath. The reaction mixture darkened and a white precipitate formed during the course of the dibromide addition. Upon completion of the addition, 200 mL of cold (ice-bath-chilled) pentane was added to the reaction vessel, and the contents of the latter were poured into a cooled (ice bath) 1 L Erlenmeyer flask, containing 200 mL of cracked ice, water, and NaCl. The upper pentane layer was decanted into a stoppered 1 L Erlenmeyer, which was cooled in a dry ice−acetone bath. The aqueous phase was washed four more times with 150 mL portions of cold pentane, with the pentane extracts decanted as before into the dry ice−acetone-bath-cooled Erlenmeyer. These extracts contain the desired 5,5-diethoxycyclopenta-1,3-diene (**12**).

Following the last washing, a stirring bar and finely ground maleic anhydride (8.8 g, 0.09 mol) were added to the pentane extracts, and the pentane solution was vigorously stirred and allowed to come to room temperature overnight. Any solid formed was filtered (identified as primarily **13**), and the pentane was removed by rotary evaporation to give a solid suspension in viscous oil. The crude product (both solid and oil) was a mixture of variable amounts of anhydride **13** (70−80%), diacid **14** (20−30%), and unreacted maleic anhydride (<5%). The diacid was insoluble in $CHCl_3$ or ethyl acetate; hence, taking up the crude product in either solvent separated **13** from **14**. Anhydride **13** was recrystallized from boiling cyclohexane, which was allowed to cool and then stand overnight in the freezer.

The diacid **14** can be cyclized to anhydride **13** as follows. Crude diacid (4 g, 0.015 mol) was refluxed for 1 h in a solution composed of 8 mL of acetic acid and 5 mL of acetic anhydride. The solvent was removed, the resulting colored solid was dissolved in methylene chloride, and the solution was swirled with silica. Filtration and evaporation of the solvent gave anhydride **3** (3 g, 0.12 mol, 75% yield). The latter was vacuum-dried to remove any remaining acetic acid.

The various compounds were characterized by their spectral data. With regard to the spectral data of anhydride **13**, we note that the protons within the pairs $H_1 + H_4$, $H_2 + H_3$, and $H_5 + H_6$ are magnetically nonequivalent. COSY and double-resonance experiments reveal that the peaks at 6.285 ($H_5 + H_6$) and at 3.660 ($H_2 + H_3$) are coupled with those at 3.430 ($H_1 + H_4$) but not with each other. Proton assignments are based on double-resonance (including integration), NOE, 2D-NOE, and HETCOR experiments. The $^{13}$C assignments were confirmed by INADEQUATE experiments. For spectral evidence that the anhydride moiety lies *endo* to the norbornene ring, see the Results and Discussion section on the synthesis of hydroxydiacid **17**.

**13:** $^{1}$H NMR ($CDCl_3$) $\delta$ 6.285 (t, $J_{1,5} = J_{4,5}$ = 2.4 Hz, 2H, $H_5 + H_6$), 3.660 (dd, $J_{3,4}$ = 3.2 Hz, $J_{1,3}$ = 1.6 Hz, 2H, $H_2 + H_3$), 3.472 (q, $J_{1',2'}$ = 7.2 Hz, 2H, $H_{1'}$), 3.430 (m, 2H, $H_1 + H_4$), 3.389 (q, $J_{1'',2''}$ = 7.2 Hz, 2H, $H_{1''}$), 1.128 (t, $J_{1'',2''}$ = 7.2, 3H, $H_{2''}$), 1.182 (t, $J_{1',2'}$ = 7.2, 3H, $H_{2'}$); $^{1}$H NMR (acetone-$d_6$) $\delta$ 6.25 (t), 3.765 (dd), 3.535 (q), 3.41 (q), 3.41 (m), 1.17 (t), 1.08 (t); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.23 ($C_8 + C_9$), 132.96 ($C_5 + C_6$), 120.58 ($C_7$), 60.80 ($C_{1''}$), 58.45 ($C_{1'}$), 48.45 ($C_1 + C_4$), 44.84 ($C_2 + C_3$), 15.24 ($C_{2'}$), 14.93 ($C_{2''}$); $^{13}$C NMR (acetone-$d_6$) $\delta$ 172.65, 133.79, 120.65, 61.19, 58.97, 49.03, 46.00, 15.63, 15.35.

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**14:** $^1$H NMR (DMSO-$d_6$) $\delta$ 6.04 (t, $J$ = 2 Hz, 2H, $H_5 + H_6$), 3.39 (q, $J$ = 7 Hz, 2H, $H_{1'}$), 3.28 (q, $J$ = 7 Hz, 2H, $H_{1''}$), 3.27 (m, 2H, $H_1 + H_4$), 3.01 (bs, 2H, $H_2 + H_3$), 1.11 (t, $J$ = 7, 3H, $H_{2''}$), 1.00 (t, $J$ = 7, 3H, $H_{2'}$); $^1$H NMR (acetone-$d_6$) $\delta$ 6.25 (t), 3.635 (dd), 3.44 (q), 3.39 (m), 3.36 (q), 1.15 (t), 1.09 (t); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 172.59 ($C_8 + C_9$), 131.56 ($C_5 + C_6$), 116.15 ($C_7$), 59.40 ($C_{1''}$), 57.32 ($C_{1'}$), 48.45 ($C_1 + C_4$), 45.88 ($C_2 + C_3$), 15.28 ($C_{2'}$), 14.98 ($C_{2''}$); $^{13}$C NMR (acetone-$d_6$) $\delta$ 171.33, 132.93, 120.55, 60.76, 58.42, 48.39, 44.84, 15.25, 14.93; FTIR (KBr) 2969 (vbr s, OH), 1721 (s, C=O), 1705.97 (s, C=O), 1621 (w, C=C) cm$^{-1}$; MS (CI, 70 eV), 271 ($MH^+$, 3.39%), 253 ($MH^+ - H_2O$, 44.75%), 225 ($MH^+ - C_2H_5OH$, 13.40%), 207 ($MH^+ - H_2O - C_2H_5OH$, 100%), 179 ($MH^+ - 2C_2H_5OH$, 43.76%). Anal. HRMS: Calcd ($C_{13}H_{19}O_6$, $MH^+$) 271.1182, obsd 271.1150; calcd ($C_{13}H_{17}O_5$, $MH^+-H_2O$) 253.1076, obsd 253.1098.

**7-Oxonadic Anhydride (15).** A 250 mL round-bottom flask, fitted with a magnetic stirrer and reflux condenser topped with a drying tube, was charged with ketal **13** (4.36 g, 0.017 mol) dissolved in 150 mL of dry acetone. Boron trifluoride diethyl etherate (1.5 mL, Aldrich) was added, and the reaction solution was gently refluxed for 3 h. The acetone was then rotary evaporated through a trap filled with Drierite in order to maintain dryness throughout the removal of the solvent. An auburn viscous liquid (6.88 g) was obtained which was composed of the desired keto-anhydride **15** (~90%) contaminated with diacid and etherate derivatives. The crude product was dissolved in dry ether and allowed to recrystallize in the freezer overnight to give 1.79 g (0.01 mol, 60% yield). Anhydride **15** can also be obtained in poor yield from the corresponding diacid **16,** by refluxing the latter in an acetic acid/acetic anhydride solution for 1 h, as outlined above for the conversion of diacid **14** to anhydride **13**.

**15:** $^1$H NMR (acetone-$d_6$) $\delta$ 6.77 (t, $J$ = 2 Hz, 2H, $H_5 + H_6$), 4.055 (dd, $J$ = 4 Hz, $J$ = 2 Hz, 2H, $H_2 + H_3$), 3.58 (m, 2H, $H_1 + H_4$); $^1$H NMR ($CDCl_3$) $\delta$ 6.71 (t), 3.755 (dd), 3.63 (m); $^{13}$C NMR (acetone-$d_6$) $\delta$ 195.64 ($C_7$), 170.98 ($C_8 + C_9$), 133.29 ($C_5 + C_6$), 48.63 ($C_1 + C_4$), 42.48 ($C_2 + C_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 194.85, 179.01, 132.37, 48.05, 41.44.

**7-Oxonadic Acid (16).** Ketal **13** (7 g, 0.027 mol) was suspended in 20 mL of distilled water containing 5 mL of concentrated HCl and refluxed for 0.5 h, heating in a oil bath set for a maximal temperature of 120 °C. The solid dissolved. The water was concentrated, and the desired keto-diacid **16** (2.5 g, 0.013 mol, 48% yield) precipitated.

**16:** $^1$H NMR (acetone-$d_6$) $\delta$ 6.60 (t, $J$ = 2 Hz, 2H, $H_5 + H_6$), 3.59 (t, $J$ = 2 Hz, 2H, $H_2 + H_3$), 3.20 (m, 2H, $H_1 + H_4$); NMR (acetone-$d_6$) $\delta$ 199.24 ($C_7$), 171.84 ($C_8 + C_9$), 132.07 ($C_5 + C_6$), 50.66 ($C_1 + C_4$), 44.15 ($C_2 + C_3$); FTIR (KBr) 3416 (vbr s, OH), 1792 (s, C=O), 1730 (s, C=O), 1715 (s, C=O), 1629 (w, C=C) cm$^{-1}$; MS (CI, 70 eV), 197 ($MH^+$, 3.13%), 179 ($MH^+ - H_2O$, 48.36%). Anal. HRMS: Calcd ($C_9H_9O_5$, $MH^+$) 197.0450, obsd 197.0433; calcd ($C_9H_7O_4$, $MH^+ - H_2O$) 179.0344, obsd 179.0326.

***anti*- and *syn*-7-Hydroxynadic Acid (17 and 18).** A 50 mL round-bottom flask, fitted with a magnetic stirrer, was charged with keto-anhydride **15** (1.79 g, 0.01 mol) suspended in 25 mL of distilled water containing NaOH (0.8 g, 0.02 mol). The reaction mixture was stirred for 15 min until all of the substrate dissolved. $NaBH_4$ (190 mg, 0.05 mol) was added, and the reaction was stirred for 5 h at room temperature. Two workup procedures were developed: (1) In the first, most of the water was removed by lyophilization, concentrated HCl was carefully added to the resulting suspension until the liquid phase turned acidic, and the mixture was gently heated until all the precipitate dissolved; precipitation of hydroxydiacid occurred upon cooling. (2) In the second method, the reaction was carefully acidified with dilute HCl and the diacid product was continuously extracted with ether; the latter is dried over $MgSO_4$ and evaporated to give the desired hydroxyacid product. The yield in the first mode was somewhat higher (1.6 g, 0.008 mol, 80% yield), though the product from the second mode seemed cleaner. Spectral analysis of the product indicated the presence of two isomers, *anti*- and *syn*-7-hydroxynadic acid (**17** and **18**, respectively) in a ratio of 10:1.

**17** and **18:** mp 175.5−176.5 °C; FTIR (KBr) 3275 (vbr s, OH), 1724 (s, C=O), 1699 (s) cm$^{-1}$; MS (CI, 70 eV), 199 ($MH^+$, 1.01%), 181 ($MH^+ - H_2O$, 100%), 163 ($MH^+ - 2H_2O$, 9.50%). Anal. HRMS: Calcd ($C_9H_{11}O_5$, $MH^+$) 199.0606, obsd 199.0597; calcd ($C_9H_9O_4$, $MH^+ - H_2O$) 181.0501, obsd 181.0500.

**17:** $^1$H NMR (DMSO-$d_6$) $\delta$ 11.76 (bs, 2H, COOH), 6.01 (t, $J$ = 2 Hz, 2H, $H_5 + H_6$), 5.44 (bs, 1H, OH), 3.39 (t, $J$ = 2.1 Hz, 1H, $H_7$), 3.31 (dd, 2H, $J$ = 1.8 Hz, $J$ = 1.6 Hz, $H_2 + H_3$), 2.71 (m, 2H, $H_1 + H_4$); $^1$H NMR (acetone-$d_6$) $\delta$ 6.05 (t, $J$ = 2 Hz, 2H, $H_5 + H_6$), 3.58 (m, $H_7$), 3.49 (m, 2H, $H_2 + H_3$), 2.82 (m, 2H, $H_1 + H_4$); $^{13}$C NMR (DMSO-$d_6$) 173.85 ($C_8 + C_9$), 133.13 ($C_5 + C_6$), 82.08 ($C_7$), 50.15 ($C_1 + C_4$), 45.56 ($C_2 + C_3$); $^{13}$C NMR (acetone-$d_6$) $\delta$ 174.19, 133.72, 82.80, 50.97, 45.91.

**18:** $^1$H NMR (DMSO-$d_6$) $\delta$ 11.76 (bs, 2H, COOH), 5.99 (td, $J$ = 2 Hz, $J$ = 1 Hz, 2H, $H_5 + H_6$), 5.44 (bs, 1H, OH), 3.79 (tt, $J$ = 1.6 Hz, $J$ = 1 Hz, 1H, $H_7$), 3.18 (dd, 2H, $J$ = 1.8 Hz, $J$ = 1.6 Hz, $H_2 + H_3$), 2.86 (m, 2H, $H_1 + H_4$); $^{13}$C NMR (DMSO-$d_6$) 172.93 ($C_8 + C_9$), 130.77 ($C_5 + C_6$), 84.76 ($C_7$), 51.36 ($C_1 + C_4$), 45.41 ($C_2 + C_3$).

**Preparation of 1500 Molecular Weight Molding Powders and a Cross-Linked Network Made from the Nadic End Cap (PMR-15).** NE (392 mg, 2 mmol), BTDA (671 mg, 2.08 mmol), and MDA (611 mg, 3.08 mmol) were ground together with a mortar and pestle. The intimate mixture was heated for 1 h at 204 °C followed by a 0.5 h at 218 °C to give 1.42 g of yellow solid. $^{13}$C CP-MAS NMR $\delta$ 41.5, 45.9, 124.6, 130.0, 140.9, 165.9, 176.6, 192.3; FT-IR (KBr) 1780 (w), 1708 (s), 1512 (s), 1372 (s) cm$^{-1}$.

The yellow molding powder (500 mg) was ground and placed in a $^1/_2$ inch mold and heated in a 12 ton hydraulic press to 272 °C. Pressure (90 psig) was applied and heating was continued until the mold temperature reached 315 °C. The mold was held for 60 min at this temperature, after which it was cooled in press until the temperature reached 200 °C. Pressure was released and the part was removed from the mold. $^{13}$C CP-MAS NMR $\delta$ 31.7, 41.8, 48.0, 126.4, 130.3, 140.7, 166.8, 176.4, 193.2; FT-IR (KBr) 1779 (w), 1711 (s), 1512 (s), 1372 (s) cm$^{-1}$

**Preparation of 1500 Molecular Weight Molding Powders and Cross-Linked Network Made from 17.** 7-Hydroxynadic acid, **17**, (396 mg, 2 mmol), BTDA (650 mg, 2.02 mmol) and MDA (598 mg, 3.02 mmol) were ground together with a mortar and pestle. The intimate mixture was heated for 1 h at 204 °C followed by 0.5 h at 218 °C to give 1.41 g of brown solid. $^{13}$C CP-MAS NMR $\delta$ 43.6, 48.8, 87.6, 125.4, 130.0, 141.2, 166.5, 177.4, 193.2; FTIR (KBr) 1779 (w), 1718 (s), 1511 (s), 1375 (s) cm$^{-1}$.

The molding powder (500 mg) was ground and placed in a $^1/_2$ inch mold and heated in a 12 ton hydraulic press to 250 °C. Pressure (90 psig) was applied and heating was continued until the mold temperature reached 280 °C. The mold was held for 60 min at this temperature, after which it was cooled in press until the temperature reached 200 °C. Pressure was released and the part was removed from the mold. $^{13}$C CP-MAS NMR $\delta$ 41.2 (broad), 127.7, 131.9, 142.1, 168.3, 178.1, 195.5; FT-IR (KBr) 1780 (w), 1719 (s), 1512 (s), 1372 (s) cm$^{-1}$

**Preparation of 2:1 Adduct of 17 and MDA (22).** 7-Hydroxynadic acid, **17**, (595 mg, 3 mmol) and MDA (297 mg, 1.5 mmol) were ground together with a mortar and pestle. The intimate mixture was heated for 1 h at 204 °C followed by a 0.5 h at 218 °C.

**22:** $^{13}$C CP-MAS NMR $\delta$ 41.0, 45.7, 50.6, 88.4, 131.6, 143.7, 178.7; FTIR (KBr) 1776 (w), 1715 (s), 1515 (s), 1387 (s), 1185 (s) cm$^{-1}$.

**22** was heated at 288 °C for 1 h to effect cross-linking: $^{13}$C CP-MAS NMR $\delta$ 42.0, 131.1, 142.2, 176.6, 213.4; FTIR (KBr) 1782 (w), 1721 (s), 1508 (s), 1368 (s), 1185 (s) cm$^{-1}$

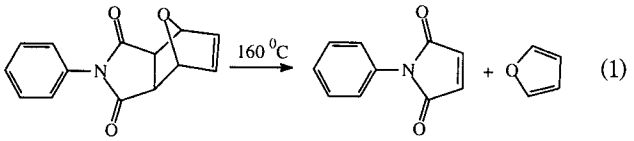
**Preparation of 2:1 Adduct of NE and MDA (23).** NE (1.96 g, 10 mmol) and MDA (991 mg, 5 mmol) were ground together with a mortar and pestle. The intimate mixture was heated for 1 h at 204 °C followed by 0.5 h at 232 °C.

**23:** $^{13}$C CP-MAS NMR $\delta$ 41.0, 46.9, 52.6, 130.8, 137.5, 144.5, 178.9; FTIR (KBr) 1776 (w), 1710 (s), 1515 (s), 1387 (s), 1185 (s) cm$^{-1}$.

**23** was heated at 315 °C for 1 h to effect cross-linking: $^{13}$C CP-MAS NMR $\delta$ 34.7, 42.0, 131.6, 143.5, 177.9; FTIR (KBr) 1783 (w), 1716 (s), 1514 (m), 1374 (s), 1185 (s) cm$^{-1}$.

## Results and Discussion

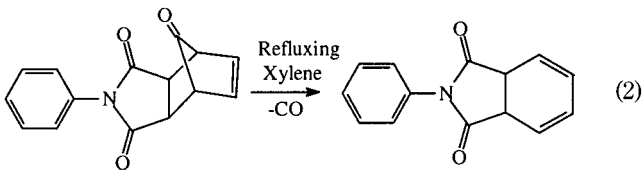
As noted in the Introduction, we were interested in preparing end caps of structure **5** (above), where X is more labile than the methylene of the parent norbornenyl end cap or is readily oxidized under the aging conditions to a more labile group. Surveying the literature, we found that the oxygen-,[16] nitrogen-,[16b] and sulfur-bridged[17] analogues of the norbornenyl end cap (**5**, X = O, N, and S, respectively) are not suitable candidates. Since furan, pyrrole, and thiophene are aromatic,[18] these structures favor facile retro-Diels–Alder reaction[19] over cross-linking through the double bond (eq 1). The carbonyl-,[20] carboxyl-,[21] and sulfoxide-




(1)

**6**

bridged[22] analogues (**5,** X = CO, $CO_2$, or $SO_2$) are also inappropriate. They each undergo extrusions of the bridge at temperatures substantially below 200 °C, as outlined below for 7-ketonadimide **7** (eq 2).




(2)

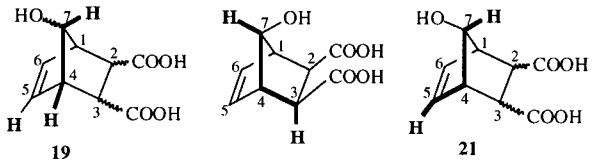
**7** **8**

We note, however, that while the carbonyl analogue is itself unsuitable, it does allow us entrée into a host of other substituted norbornenyl end caps which could potentially prove to be good candidates. In particular, we were interested in exploring the suitability of using the 7-hydroxymethylene [**5**, X = C(OH)H] analogue. During thermal-oxidative aging, we would expect the hydroxy-bearing C-7 carbon of this structure to more easily oxidize to carbonyl than the corresponding 7-methylene in the parent norbornenyl end cap. This is because substitution of one of the latter's C-7 methylene hydrogens with a hydroxyl group lowers the bond dissociation energy of the remaining C-7 hydrogen by 11 kcal/mol—and concomitantly raises its susceptibility to autoxidation.[23] As a 7-oxonadic precursor, the 7-hydroxymethylene end cap should more highly favor bridge degradation (carbonyl extrusion).

The desired 7-oxonadic anhydride (norbornen-7-one-2,3-dicarboxylic acid anhydride, **15**) was synthesized by a modification of the method of Fuchs and Scharf[9,14] (Figure 3). Thus, the bromination[11] of cyclopentanone diethyl ketal **10** and subsequent dehydrobromination[9,11] yielded 5,5-diethoxycyclopentadiene **12**. Cycloaddition[13] of the latter with maleic anhydride yields nadic ketal **13** (70%), accompanied by varying yields (15–30%) of the corresponding diacid **14**. (The latter can be recyclized back to the anhydride **13** by refluxing in acetic acid/acetic anhydride.)

Hydrolysis of ketal **13** to keto-anhydride **15** can be effected with boron trifluoride etherate in acetone.[20b,c] The $NaBH_4$ reduction of cyclic anhydrides is reported to produce lactones.[24] Thus, anhydride **15** was hydrolyzed with aqueous NaOH to the diacid prior to treatment with $NaBH_4$, which provided a good yield of the 7-hydroxydiacid analogue, **17**. (The hydrolysis of ketal **13** can also be carried out under aqueous acid conditions, giving a poor yield of keto-diacid **16.** The latter can be reduced directly to alcohol-diacid **17** or cyclized first to the corresponding anhydride **15** by refluxing in acetic acid/acetic anhydride.)

Careful spectral analysis of the hydroxydiacid (including COSY experiments) reveals the presence of two isomers, *anti*- and *syn*-7-hydroxynadic acid **17** and **18**, respectively, in a ratio of 10:1. The major product is identified as the anti isomer on the basis of the following considerations: The C-7 carbinolic peak in the major isomer is a triplet ($J$ = 2 Hz) resulting from coupling with the bridgehead hydrogens, $H_1$ and $H_4$ (structure **19**).[25] Additional long-range couplings might have been expected, namely a "W" type $^4J_{HH}$ between a syn $H_7$ and $H_2/H_3$—provided the latter are endo (structure **20**)[25b]—or between an anti $H_7$ and the olefinic $H_5/H_6$ (structure **21**).[12,25,26] The fact that in the major isomer there are




**19** **20** **21**

*no* such additional long-range couplings indicates that (a) the C-7 hydroxyl group is anti to the double bond and (b) the carboxyl groups are endo to the ring, hence structure **17** (Figure 3). Interestingly, in the minor isomer, both the carbinolic $H_7$ and the olefinic $H_5/H_6$ do

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(20) Prof. Benzion Fuchs (personal communication, 1999) has informed us that both the 7-ketonadic anhydride (158 °C) and the corresponding *N*-phenylimide (164 °C) decompose via decarbonylation at their melting points. See also ref 14, *supra*.

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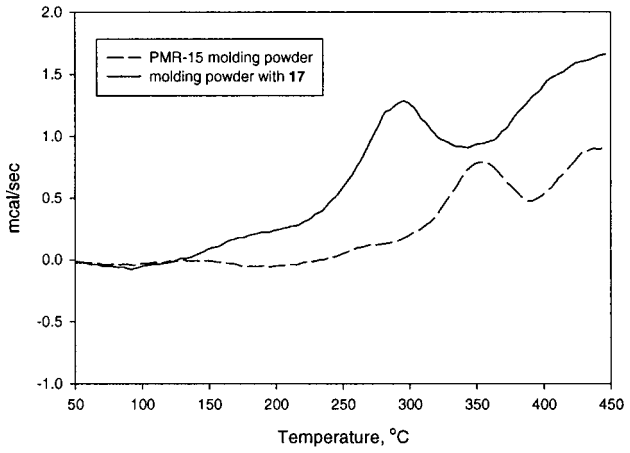


**Figure 4.** Comparison of DSC of molding powders of PMR-15 and the corresponding polyimide end-capped with **17**.

indeed show an extra 1 Hz splitting, presumably $^4J_{HH}$, while $H_2/H_3$ remains unchanged. This clearly suggests that $H_7$ is aligned syn, as shown in structure **21**, hence structure **18** (Figure 3). Given, then, that the carboxylic groups of diacid **17** are endo to the norbornene ring, we can assume that the anhydride moiety or carboxylic groups of its precursors **13**−**16** also lie endo, as drawn in Figure 3.

The 7-hydroxydiacid **17** was used in place of the norbornenyl end cap to synthesize polyimide molding powder. Analogous to the case shown in Figure 1, the molding powders were synthesized with a formulated molecular weight of 1500 from benzophenone-3,4,3′,4′-tetracarboxylic dianhydride (BTDA) and 4,4′-methylenedianiline. The three monomers were combined by grinding the solids together and heating the mixture for 1.5 h at 200 °C.

Solid CP-MAS NMR of molding powder made from **13** has nine peaks: $\delta$ 43.6, 48.8, 87.6, 125.4, 130.0, 141.2, 166.5, 177.4, 193.2. The peak at 87.6 is assigned to the carbon bearing the hydroxy group. All other peaks correspond to those of PMR-15 molding powder.

Differential scanning calorimetry (DSC) of molding powders made from both the parent end cap (PMR-15) and **17** shows the broad exotherm with an onset of approximately 300 °C and a maximum of 350 °C usually associated with the cross-linking (Figure 4) in the norbornenyl system. However, the exotherm for the molding powder made with **17** occurs with an onset of 250 °C and a maximum of approximately 300 °C, approximately 50 °C lower than that for PMR-15, not unlike the cases of other substituted end caps previously studied.[27] Nevertheless, the exotherm is high enough for the new end cap to survive intact through imidization without cross-linking.

After molding at 315 °C, the CP-MAS NMR of the cross-linked polymer has only seven peaks: $\delta$ 41.2 (broad), 127.7, 131.9, 142.1, 168.3, 178.1, 195.5. These changes are consistent with cross-linking, with one exception. The peak at 87.6 assigned to the carbon bearing the hydroxy group has disappeared. However, there is also a small, very broad peak centered at 212 ppm, which may be the ketone corresponding to oxidation of that hydroxy bearing carbon.

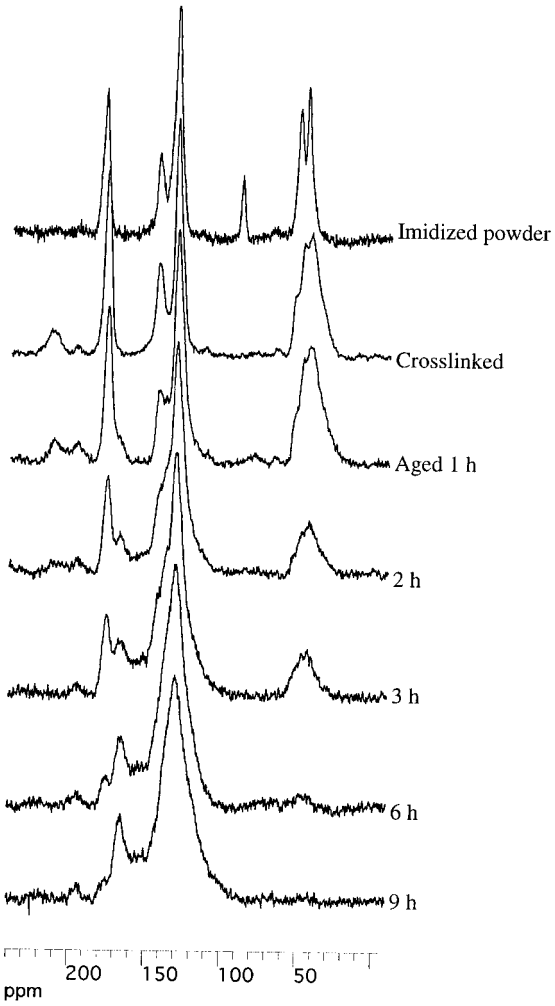


**Figure 5.** Adduct (2:1) of **17** and MDA (**22**) imidized molding powder, cured at 315 °C and aged as a powder at 315 °C for up to 9 h.

To follow changes in the end cap on curing and oxidation more clearly, 2:1 adducts of **17** and MDA (**22**), and of the parent nadic and MDA (**23**) were synthesized and cross-linked at 288 and 315 °C, respectively. The CPMAS NMR spectra for these model compounds are shown in Figure 5 for **22** and Figure 6 for **23.** Assignments are summarized in Table 1.

The only dramatic changes in the spectrum (Figure 6b) on curing for model compound **23** are the broadening of the aliphatic peaks (C-7 and C-8) of the end cap and the disappearance of the double bond (C-9 at 137.5 ppm). In the spectrum of cured model compound **22** (Figure 5b), we cannot observe the disappearance of the double bond (C-9) because it overlaps with some of the aromatic carbons (C-3 and C-4) on MDA. The peak at 131 ppm simply narrows slightly on curing. The most dramatic change in the spectrum is the disappearance of the aliphatic bridge carbon (C-10) at 88.4 ppm and the concomitant emergence of a peak at 213.4 ppm, which we have assigned to carbonyl formation (C-10).

On aging cured **22** in air at 315 °C for 1−9 h, dramatic changes begin to take place (Figure 5c-g) in the cross-link. After just 1 h (Figure 5c), the carbonyl peak at 213.4 ppm begins to disappear. After 3 h (Figure 5e), it

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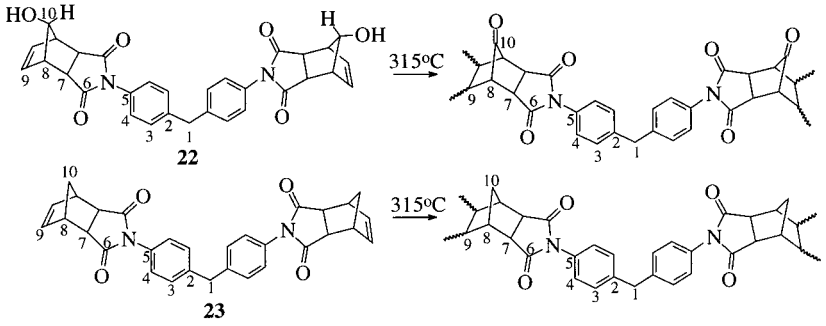
**Table 1**




**22**

**23**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **22** | 41 | 143.7 | 131.6 | 131.6 | 143.7 | 178.7 | 50.6 | 45.7 | 131.6 | 88.4 |
| after cure | * | 142.2 | 131.1 | 131.1 | 142.2 | 176.6 | | *broad peak at 42 ppm | | 213.4 |
| **23** | 41 | 144.5 | 130.8 | 130.8 | 144.5 | 178.9 | 46.9 | 46.9 | 137.5 | 52.6 |
| after cure | * | 143.5 | 131.6 | 131.6 | 143.5 | 177.9 | | *broad peak at 42 ppm | | 34.7 |

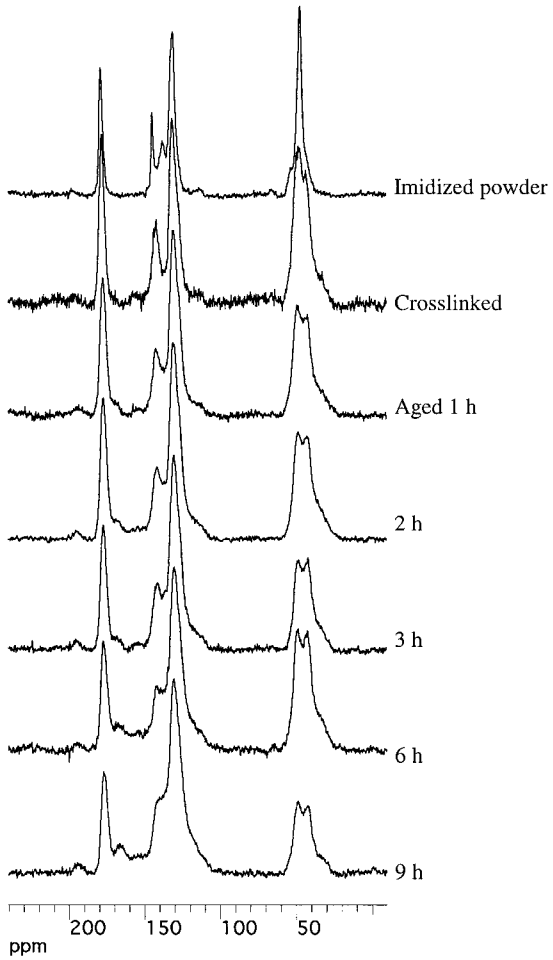



**Figure 6.** Adduct (2:1) of nadic end cap and MDA (**23**) imidized molding powder, cured at 315 °C and aged as a powder at 315 °C for up to 9 h.

has completely disappeared. In addition, there is a small shoulder evident on the imide carbonyl (176.6 ppm). After 2 h, this shoulder has clearly turned into a peak at 165.7 ppm, and the imide carbonyl at 176.6 is clearly diminishing. After 9 h (Figure 5g), the original aliphatic imide carbonyl is all but gone, replaced by the peak at 166 ppm, consistent with formation of an aromatic imide. At the same time, all of the other aliphatic peaks are disappearing and the aromatic region is broadening. These changes are all consistent with rapid conversion of the aliphatic cross-link to an aromatic one via path B or bridge degradation.

In contrast, there is much less happening in the series of spectra for the aging of adduct **23** (Figure 6c−g). A small shoulder forms on the aliphatic imide peak, indicating some conversion to aromatic imide after 1 h. However, after 9 h, it is only about 20% converted.

## Conclusions

We have considered possible replacement end caps that should favor bridge degradation and lead to lower weight loss in the resin system. Our preliminary evaluation demonstrates that molding powder made with 7-hydroxynorbornene-2,3-dicarboxylic acid (**17**) as the end cap can be fully imidized at 200 °C. By DSC, onset of cross-linking occurs approximately 50 °C lower than that for the unsubstituted end cap.

The hydroxy-bearing carbon on **17** is more easily oxidized to carbonyl on aging in the polymer than the parent end cap. Therefore, the new end cap more highly favors bridge degradation. However, processing studies, long term weight loss, and careful evaluation of degradation mechanisms must be conducted to fully assess **17** as a more thermo-oxidatively stable replacement for the parent norbornenyl end cap.

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