On the Oxidative Degradation of Nadic End-Capped Polyimides. 3. Synthesis and Characterization of Model Compounds for End-Cap Degradation Products

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ABSTRACT: The oxidative degradation of PMR (for *p*olymerization of *m*onomeric *r*eactants) polyimides at elevated temperatures was followed by cross-polarized magic angle spinning (CP-MAS) NMR. Labeling of selected sites in the polymers with ^{13}C allowed for direct observation of the transformations arising from oxidation processes. The formation of several degradation products has been proposed to be occurring in the cross-links derived from the nadic end caps on oxidation. Model compounds have been synthesized and characterized by CPMAS NMR with both normal and delayed decoupling to distinguish between protonated and unprotonated carbons. Comparison of these spectra to predicted chemical shifts of proposed products for the aged polymer provides further insight to degradation occurring in the cross-linked moieties.

Introduction

High-temperature polyimides, like norbornene end-capped PMR (for *p*olymerization of *m*onomeric *r*eactants) polyimide resins[1] are widely used as polymer matrix composite materials for aircraft engine applications,[2] since they combine ease of processing with good oxidative stability up to 300 °C. These PMR resins are prepared by a two-step approach involving the initial formation of oligomeric prepolymers capped at both ends by a reactive end cap. 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 (Scheme 1) involves the initial formation of a polyimide prepolymer via the 200−250 °C condensation of three monomer reactants: 4,4′-methylenedianiline (MDA, **1**), the dimethyl ester of benzophenone-3,4,3′,4′-tetracarboxylic-3,4:3′4′-dianhydride (BTDE, **2**), and 2-carbomethoxy-3-carboxy-5-norbornene (the monomethyl ester of nadic diacid, NE, **3**).[2] This results in a polyimide oligomer with a formulated molecular weight of approximately 1500− hence, the acronym PMR-15. This oligomer has a low enough melt viscosity to allow the volatile byproducts of the condensation reaction to escape before it undergoes cross-linking primarily through the vinyl group of the nadic end cap at 275−325 °C, producing a void-free network structure.[3]

It is the end cap that facilitates processing by controlling the molecular weight of the oligomer and allowing flow before cross-linking at elevated temperatures. However, it is the resulting cross-link that accounts for much of the weight loss in the polymer on aging in air at elevated temperatures.[4] Understanding this degradation may provide clues for designing new end caps to slow degradation and to prolong the lifetime of the material.

Previously,[4] we reported studies on the thermooxidative aging of a ^{13}C-enriched modification of PMR-15, in which we labeled the nadic end cap at the methyne carbon α to the carbonyl groups. This labeled carbon in the as-processed polymer, shown in **5** below, has a ^{13}C NMR chemical shift of 48 ppm. The solid NMR difference spectrum of a sample of the nadic labeled PMR-15 aged as a powder at 300 °C for up to 64 h indicates that, upon oxidation, nearly all of this ^{13}C-labeled peak at 48 ppm is consumed. In its place, three new broad peaks for labeled carbons grew in at 105−120, 125−140 and 150−165 ppm (see Figure 1). On the basis of the chemical shifts, we suggested several possible degradation pathways and structures formed.

In this paper, to test the correctness of these various oxidative pathways in our system, we searched the literature for various model compounds corresponding to some of the products suggested by the ^{13}C labeling studies. We also synthesized several previously unknown compounds. Solid NMR was run on nearly all the model compounds and assignments made for the carbons corresponding to those labeled in the polymer. In addition, we have attempted to glean more information about the possible degradation products from NMR by utilizing delayed decoupling experiments on the ^{13}C labeled polymers and the model compounds. From these various pieces of the puzzle, a clearer picture of cross-link degradation is emerging.

Experimental Section

General Data. Isopropylmalic acid, 2-methyl-*N*-phenylmaleimide, *N*-phenylphthalimide, salicylamide salicylanilide, 5-chlorosalicylanilide, 3,6-dihydroxyphthalonitrile, and oxalacetic acid were purchased from Aldrich Chemical Co. and used without further purification. High-resolution mass spectra (HRMS) were performed on a VG-Fison AutoSpecE high-

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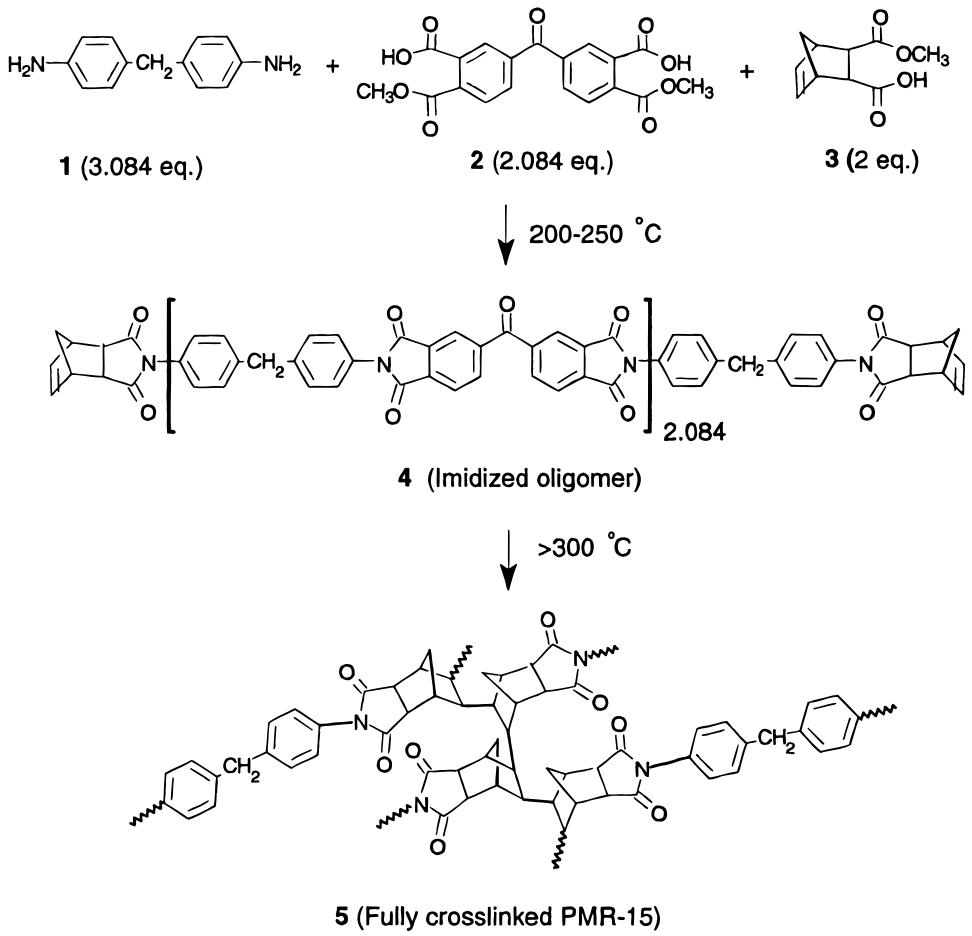
Scheme 1. Formation of PMR-15



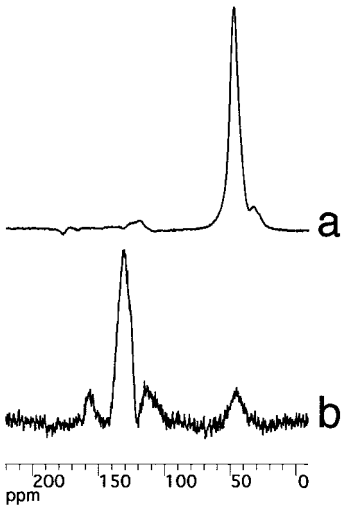


Figure 1. CPMAS NMR difference spectra of PMR 15 labeled on the nadic end cap (a) as cured and (b) after aging as a powder for 64 h at 315 °C in air.

resolution spectrometer. Thin-layer chromatography (TLC) was carried out on silica gel using Riedel-De Haen microcards. ^{13}C-labeled PMR-15 was made as previously described.[4] The labeled polymer samples were aged as powders alongside of natural-abundance samples in a flowing air oven at 315 °C for 64 h,

NMR. ^{1}H and ^{13}C NMR spectra were obtained either on a Bruker AM 300 spectrometer controlled by a TECMAG data system, running MACNMR 5.3, or on a Bruker AM 600 Fourier transform spectrometer. Assignments were facilitated by COSY and NOESY experiments and by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra. For solution NMR, tetramethylsilane (TMS) served as the internal standard.

Solid polymer samples were run on the Bruker AM 300 fitted with a high power solids attachment, utilizing cross-polarization and magic angle spinning at 5 kHz (CPMAS). The acquisition also employed 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 μs included after CP contact time but before acquisition. Isotope-enriched spectra are shown as difference spectra obtained by subtracting the corresponding natural-abundance spectra, prepared and aged in the same way. Acquisition conditions were carefully matched between enriched and natural abundance samples. Consequently, the difference spectra contain only isotope-labeled resonance peaks.

Preparation of 2-Isopropylmaleic Anhydride (21). A round-bottom flask fitted with a reflux condenser topped by a drying tube was charged with 3 mL of distilled acetic anhydride, sodium acetate (dry and shiny, 0.1 g, 1.21 mmol), and 2-isopropylmalic acid, **29** (0.09 g, 0.51 mmol; eq 1). The flask was heated in an oil bath at 80 °C and the formation of **21** along with isopropylidenesuccinic anhydride, **32**, was followed by TLC (25% hexane in ethyl acetate). It should be noted that the starting diacid is not fluorescent. However, during the course of the reaction, a fluorescent band is observed near the bottom of the TLC plate, which presumably corresponds to isomeric acids, **30** and **31**. After 3.5 h this fluorescent band disappears, and the heating was stopped. The acetic anhydride was rotary evaporated and the resulting residue (ca. 50 mg) partially dissolved in chloroform. Evaporation of the $CHCl_3$ solution yielded a 1:2 (via NMR) mixture of **21** and **32** (30 mg,

19.0 mmol, 37% yield). The chloroform-insoluble fraction was taken up in acetone and DMSO and proved to be a mixture of assorted acids and sodium acetate. Heating the reaction mixture beyond 3.5 h resulted in reduced yield. Attempts to dehydrate **29** by azeotroping off the water proved unsuccessful. The numbering of the carbons in compounds **21** and **32** are as shown in eq 1.

21: ^{1}H NMR ($CDCl_3$) δ 6.56 (d, $J_{4,1'} = 1.6$, 1H, H_4), 2.90 (septd, $J_{1'2'} = 6.9$, $J_{4,1'} = 1.6$, 1H, $H_{1'}$), 1.28 (d, $J_{1'2'} = 6.9$, 3H, $H_{2'}$); ^{13}C NMR ($CDCl_3$) δ 165.21 (C_2), 163.95 (C_5), 159.21 (C_3), 126.97 (C_4), 26.56 ($C_{1'}$), 20.41 ($C_{2'}$).

32: ^{1}H NMR ($CDCl_3$) δ 3.50 (qq, $J_{4,2''} = 2.0$, $J_{4,2'} = 1.5$, 2H, H_4), 2.36 (t, $J_{4,2''} = 2.0$, 3H, $H_{2''}$), 1.97 (t, $J_{4,2'} = 1.5$, 3H, $H_{2'}$); ^{13}C NMR ($CDCl_3$) δ 168.71 (C_5), 163.79 (C_2), 157.36 ($C_{1'}$), 116.09 (C_3), 33.86 (C_4), 24.85 ($C_{2'}$), 21.39 ($C_{2''}$).

21 and **32**: HRMS calcd ($C_7H_9O_3$, M^+) 141.0552, obsd 141.0571.

2-Acetoxymaleic anhydride (22): Following the procedure of Fenton and Wilks,[7] oxalacetic acid (**33**) (13.2 g, 0.1 mol) was dissolved in 50 mL of hot glacial acetic acid. Upon dissolution, the solution was allowed to cool slightly, and 30 mL (0.3 mol) of acetyl chloride was added and the solution refluxed for 20 min. Rotary evaporation gave 14.35 g of crude solid, which upon recrystallization from ether furnished 9.2 g (58% yield) of the desired product as a yellowish solid.

22: mp 88−89 °C; ^{1}H NMR ($CDCl_3$) δ 2.44 (s), 6.86 (s); ^{13}C NMR ($CDCl_3$) δ 165.35, 162.53, 160.29, 150.17, 112.05, 20.92; HRMS calcd ($C_6H_5O_5$, MH^+) 157.0137, obsd 157.0140;

2-Acetoxybenzanilide (26). The title compound was prepared in 73% yield from acetylsalicoyl chloride (Aldrich) and aniline according to the procedure described by Lenz[6] for *N*-methyl-2,4,5-trimethoxybenzanilide. The crude product was recrystallized from methanol/water (mp 138 °C; lit.[7] 136−7 °C). The numbering of the carbons are as shown in eq 3.

26: ^{1}H NMR ($CDCl_3$) δ 8.14 (bs, 1H, H-8, N−H), 7.80 (d, $J_{5,6} = 8$ Hz, $J_{4,6} = 2$ Hz, 1H, H-6), 7.58 (m, 1H, H-10), 7.49 (td, $J_{4,3+5} = 8$ Hz, $J_{4,6} = 2$ Hz, 1H, H-4), 7.34 (m, 1H, H-11), 7.30 (td, $J_{5,4+6} = 8$ Hz, $J_{4,5} = 1.5$ Hz, 1H, H-5), 7.14 (m, 1H, H-11), 7.13 (d, $J_{3,4} = 8$ Hz, $J_{3,5} = 1.5$ Hz, 1H, H-3), 2.30 (s, 3H, H-15); ^{13}C NMR ($CDCl_3$) δ 169.27 (C-14), 163.80 (C-7), 147.80 (C-2), 137.85 (C-9), 131.98 (C-4), 129.69 (C-6), 129.02 (C-11), 128.69 (C-1), 126.33 (C-5), 124.55 (C-12), 123.22 (C-3), 120.02 (C-10), 20.91 (C-15); HRMS (CI, 55 eV) calcd ($C_{15}H_{14}NO_3$, MH^+) 256.0974, obsd 256.0940; HRMS (CI, 55 eV) calcd ($C_{13}H_{12}NO_2$, $MH^+ - CH_2CO$) 214.0840, obsd 214.0868; MS (CI, 55 ev) *m/z* 256 (MH^+, 35.90%); 214 ($MH^+ - CH_2CO$, 100%), 163 ($M^+ - C_6H_5NH$, 7.60%), 121 ($M^+ - CH_2CO - C_6H_5NH$, 8.89%).

Solid CPMAS NMR. Samples of the model compounds were run with both normal TOSS and delayed decoupling pulse sequences. The peaks unchanged after delay decoupling are listed in bold italics.

N*-Phenyl-2-methylmaleimide, 20:** ***δ 171.45, ***146.35***, ***133.41***, 130.30, 14.103.

2-Acetoxymaleic Anhydride, 22: *δ* ***166.27***, ***164.21***, ***160.84***, ***152.04***, 112.97, 23.16

N*-Phenyl-3,6-Dihydroxyphthalimide, 23:** ***δ 168.58, ***149.81***, ***148.19***,[10] ***131.37,*** 130.40, 128.14, ***113.26***.

N*-Phenylbenzoquinone-2,3-dicarboxylic Imide, 24:** ***δ 185.72, ***165.99***, 138.81, ***136.87***, 134.28, 127.82, 124.58.

N*-Phenylphthalimide, 25:** *δ* ***169.03, 135.88, ***133.16***, 131.37, 128.81, 125.91.

2-Acetoxybenzanilide, 26: *δ* ***170.92***, ***164.97***, ***150.22***, ***139.09***, ***130.81***, 127.45, 124.08, 21.34

Salicylamide, 27: *δ* ***176.27***, ***162.32***, 136.06, 129.35, 121.38, 118.48, ***117.04***.

Salicylanilide, 28: *δ* ***168.12***, ***158.70***, ***141.49***, 132.43, 129.89, 125.00, 122.11, ***120.93***.

Results

Possible pathways for degradation of cross-links derived from nadic end cap based on previous isotope labeling studies are outlined in Scheme 2. Path A proposes initial opening of the norbornyl ring to form biradical **6.** Subsequent rearrangement could give the alkyl-substituted maleimide **7** with chemical shifts of the labeled carbons predicted[9] to be 154 and 128 ppm (see Table 1). Biradical **6** might also undergo attack of oxygen to form a 2-hydroxy-substituted maleimide **9** with the oxygen-bearing carbon predicted to be as high as 164 ppm and the adjacent carbon next to it shifted upfield (101 ppm). Degradation could also proceed through path B. Oxidation of the bridging methylene followed by carbon monoxide extrusion and oxidative aromatization might ultimately lead to substituted phthalimides **15** in which the labeled carbon is predicted to appear at 130 ppm. The presence of phthalimides is proposed in another study following heat treatment of norbornene end capped polyimides at 371 °C for up to 100 h.[10] Alternatively, this same oxidative cleavage of the methylene could lead to either quinone **13** with a predicted chemical shift of 156 ppm or hydroquinone **14** with a predicted chemical shift of the labeled carbon of 118 ppm.

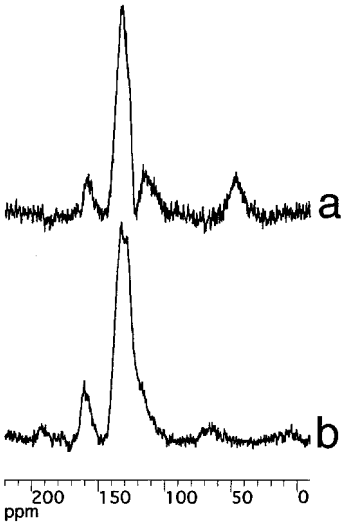


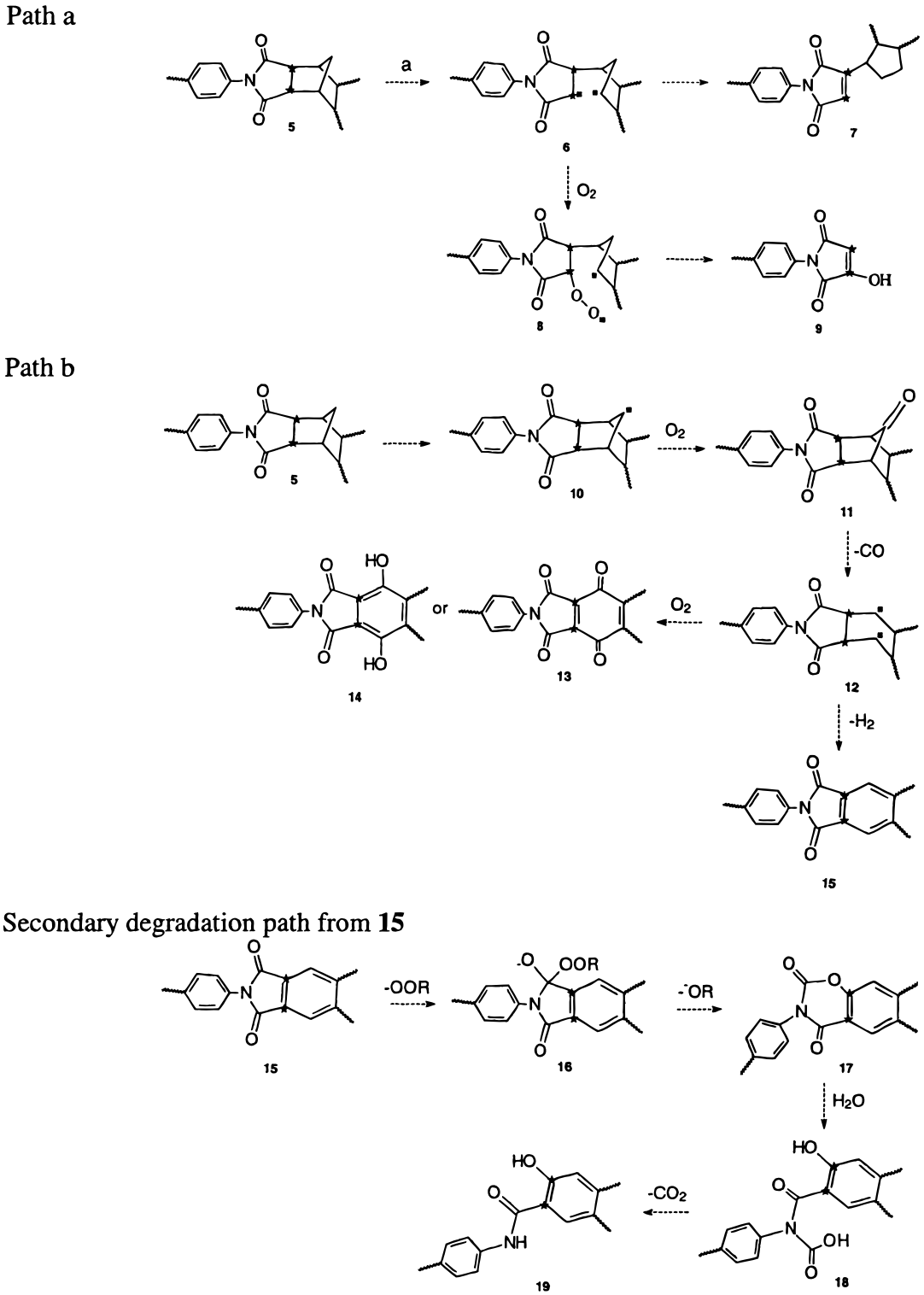
Figure 2. Aromatic region of CP-MAS NMR difference spectra of aged PMR-15 labeled on the nadic end cap: (a) with normal TOSS; (b) with delayed decoupling.

The initial degradation products themselves can undergo further oxidation. For example, Baeyer−Villager type oxidation of **15** might lead to oxidative cleavage of the imide bond. This would ultimately give rise to structures such as phenylsalicylamide **19**, in which the labeled carbon directly attached to the oxygen is predicted to appear downfield (153 ppm), while the other labeled carbon attached to the carbonyl would appear upfield (118 ppm). This could also be the mechanism of degradation of main chain imide rings in the BTDE portion of PMR-15.

In general, based only on the predicted chemical shifts, any of these possible oxidation products could fit the previously reported NMR spectra of the aged nadic-labeled PMR-15 (also shown in Figure 2a). Indeed, the line widths in the spectra of the aged polymer are so broad that it seems rather likely that various different oxidation products are present. However, synthesis of model compounds is necessary to refine chemical shifts for the predicted products. In addition, supplemental NMR experiments may serve to eliminate some of the suggested pathways and products.

NMR. Previously reported solid NMR of ^{13}C isotope labeled PMR-15 gave the spectra shown in Figure 2a after aging. Since these are difference spectra obtained by subtracting the spectra of the natural-abundance

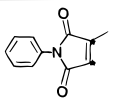
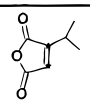
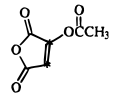
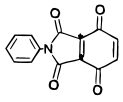
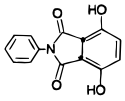
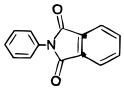
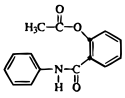
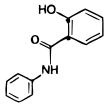
Scheme 2. Proposed Degradation Paths.



aged polymer from that of the labeled polymer, all of the peaks in the spectrum arise from the labeled carbons. Further information on the nature of the labeled carbons can be gathered by using a delayed decoupling or dipolar-dephasing experiment (Figure 2b). In this type of NMR experiment, an extra delay (40 μs) is added to the normal TOSS sequence after CP contact time but before the acquisition. This extra delay allows those carbons that have strong coupling to hydrogen to dephase, resulting in reduction or disappearance of the peak for that carbon. Unprotonated carbons are unaffected. In the spectra of the aged PMR-15 labeled on the end cap, the only peak in the aromatic region affected by delayed decoupling was that residing in the 105−120 ppm region. This peak is considerably reduced in size, suggesting that most of the carbon(s) absorbing in this region are attached to hydrogen. Since the peaks at 125−140 and 150−165 ppm are largely unaffected by the delayed decoupling, it must be that these other labeled carbons in the aged polymer have no hydrogens attached.

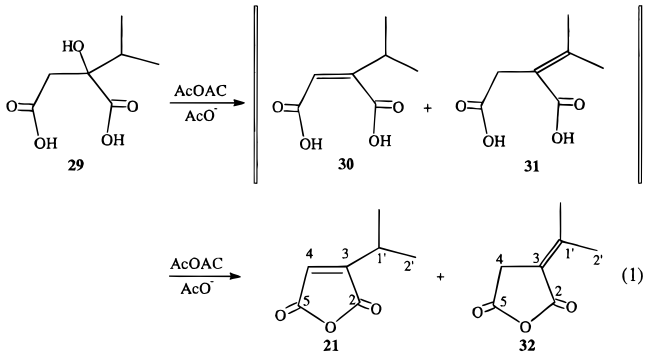
Model Compounds. All of the possible oxidation products and predicted chemical shifts of carbons corresponding to those ^{13}C labeled in the polymer are

Table 1. Predicted and Actual Chemical Shifts for Model Compounds

Structure from Schemes 2	Calculated[8] chemical shift of labeled carbons	Attached hydrogens?	Proposed model compound	Observed Chemical shift of labeled carbons
7	154 128	no yes	 **20**	146.35 130.30
7	154 128	no yes	 **21**	159.21 126.97
9	164 101	no yes	 **22**	150.17 112.05
13	156	no	 **24**	136.87
14	118	no no	 **23**	113.26
15	130	no	 **25**	133.16
17/18	149 124	no no	 **26**	150.22 130.81
19	152 119	no no	 **27**	162.32 117.04
19	153 118	no no	 **28**	158.70 120.93

summarized in Table 1. It is also identified whether these carbons have attached hydrogens. Model compounds corresponding to the possible oxidation products from Scheme 2 were either commercially available or synthesized. Solid ^{13}C NMR of most of these compounds were run using both normal TOSS and delayed decoupling to simplify assignment of the chemical shifts for the carbons corresponding to those labeled in the oxidized PMR-15. These assignments are also summarized in Table 1.

As a model for the proposed oxidation product **7,** the commercially available 2-methyl-*N*-phenylmaleimide, **20**, should provide a fairly good match. It was thought, however, that a closer match to **7** could be obtained with the 2-isopropylmaleic anhydride **21** (and the corresponding maleimide). Since **7** is expected to have a cyclopentene ring in the 2-position, the 2-isopropyl group should predict a more accurate value for the chemical shift of that carbon. Anhydride **21** was synthesized in low yield as a 1:2 mixture with isopropylidene−succinic anhydride, **32**, by heating 2-isopropylmalic acid, **29**, in acetic anhydride in the presence of sodium acetate (eq 1). Presumably, the reaction proceeds through the isomeric acids, **30** and **31**.

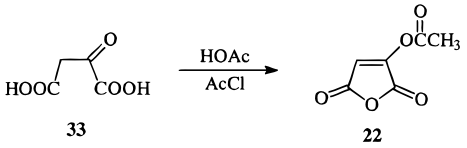


(1)

The chemical shifts of carbons of interest in model **21** are in good agreement with the those predicted for

oxidation product **7**. It is unlikely, however, that structures such as **7** are present in the oxidized polymer to any great degree. For one thing, the chemical shift of 146.35 ppm falls between two of the peaks in the NMR spectrum of the aged labeled cross-link. In addition, the carbon at 133.30 ppm in the model structure has an attached hydrogen and, thus, does not match up with the delayed decoupling NMR of the isotope-labeled oxidized polymer. There is no change in the labeled peak in the range of 125−140 ppm in the delayed decoupling spectrum of the oxidized polymer.

As a model for oxidation product **9**, 2-acetoxymaleic anhydride, **22**, was synthesized from oxalacetic acid, **33** (Aldrich), and acetyl chloride in acetic acid.[5]



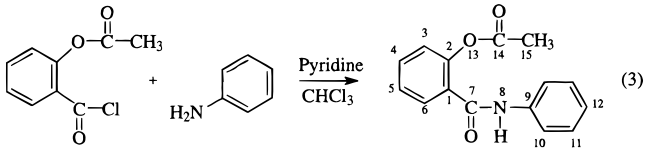
33 **22** (2)

The chemical shifts of the carbons of interest for **22** occur at 112.05 and 150.17 ppm, somewhat shifted from those predicted for the isotope-labeled carbons of the proposed oxidation product **9**. However, these peaks correspond quite well with the normal TOSS and delayed decoupled spectra of the labeled and aged PMR-15, since the carbon assigned to the 112.05 ppm peak bears a proton and the carbon occurring at 150.17 does not. It is also of interest to note that the peaks at 105−120 and 150−165 ppm in the NMR spectra of the end-cap-labeled PMR-15 do appear to grow in size at the same rate as aging progresses,[4] suggesting that the two peaks may arise from the same structure. In any case, structures such as **9** could account for these peaks in the NMR spectra of the aged PMR-15.

N-Phenyl-3,6-dihydroxyphthalimide, **23**, was synthesized as a model for structure **14** in three steps from the analogous phthalonitrile.[11,12] The actual chemical shift of the carbon in **23** corresponding to the labeled carbon was 113.26 ppm. Since this carbon is quaternary, however, this cannot account for the resonance in the labeled and aged PMR-15. Structures such as **14,** therefore, are not likely present as an oxidation product of PMR-15.

As a model compound for **13**, quinone **24** was synthesized by treatment of **23** with phenyliodine difluoroacetate.[9] Quinone **24** and *N*-phenylphthalimide **25**, which is a model compound for **15**, have chemical shifts for the carbon of interest of 136.87 and 133.16 ppm, respectively. The chemical shifts of these carbons in both of the models fall in the region of 125−140 ppm, corresponding to the largest peak in the spectrum of the isotope-labeled aged PMR-15. In addition, both carbons in the models are quaternary, consistent with the delay decoupled spectrum of the aged polymer. Hence, structures such as **13** and **15** can be present as major oxidation products of PMR-15.

2-Acetoxybenzanilide, **26**, a model for **17**, was prepared in 73% yield from acetylsalicoyl chloride (Aldrich) and aniline (eq 3). The carbons of interest, both quaternary, occur at 150.22 and 130.81 ppm. Since these peaks fall under the broad resonances at 125−140 and 150−165 ppm in the spectrum of labeled and aged PMR-15, structures such as **17** can also be present in the oxidized polymer.



26 (3)

Salicylamide, **27**, and salicylanilide, **28**, were both examined as models for a structure such as **19**. The chemical shifts of the carbons of interest, all quaternary, occur at 162.50 and 117.04 ppm in **27** and at 158.70 and 120.93 ppm in **28**. This type of structure can account for some of the oxidized product present in the polymer. There is a small shoulder at approximately 117 ppm in the delayed decoupling spectrum of the aged labeled PMR-15, indicating that there is some quaternary carbon present in that region.

Conclusions

We may thus conclude that the major nonvolatile products of oxidation of the cross-link derived from the norbornene end cap of PMR polyimides are most likely *N*-phenylphthalimides such as **15**, and other substituted aromatic structures like **13**, **17**, and **19**. The chemical shifts of the quaternary carbons of interest in this type of structure fall within the largest peak (125−140 ppm) evident in the aged, end-cap-labeled difference spectra. These structures are most likely present to a significant extent in the oxidation layer of aged PMR polyimides, and can be accounted for by the proposed oxidation mechanism shown in path b. Path b is initiated by oxygen attack and subsequent decarbonylation of the norbornenyl bridgehead carbon.

The carbons in structures **7** and **14** corresponding to labeled carbons in the norbornene cross-link do not agree with the delayed decoupled spectra of the aged PMR-15. Therefore, it can be concluded that structures such as these are not present in the oxidation layer of aged PMR-15.

Structure **9**, a 2-hydroxymaleimide, from path a is the only structure studied which can account for the protonated carbon peak at 105−120 ppm present in the end-cap-labeled and aged PMR-15. Structures such as these are likely present as a minor product in the oxidation layer of PMR polyimides.

Nonvolatile oxidation products such as **9** are cleavage products that are most likely formed concomitant with large amounts of weight loss in the polymer system. In contrast, structures such as **15** from path b can be formed with very little weight loss. Therefore, new end cap structures which more strongly favor path b degradation should lead to lower weight loss in addition polyimides.

References and Notes

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(8) Curiously, the carbons bearing the hydroxy groups in compound **23** show up as a single peak at 150.52 ppm in the solution ^{13}C NMR spectrum, but in the solid NMR spectra they are split into two peaks at 149.81 and 148.19 ppm. This is perhaps due to intra- or intermolecular hydrogen bonding in the crystalline solid.
(9) From ChemWindows ^{13}C NMR Module available from Softshell, Inc.
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