Diels−Alder Trapping of Photochemically Generated Dienes with a Bismaleimide: A New Approach to Polyimide Synthesis

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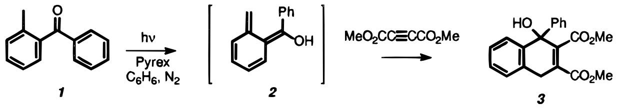
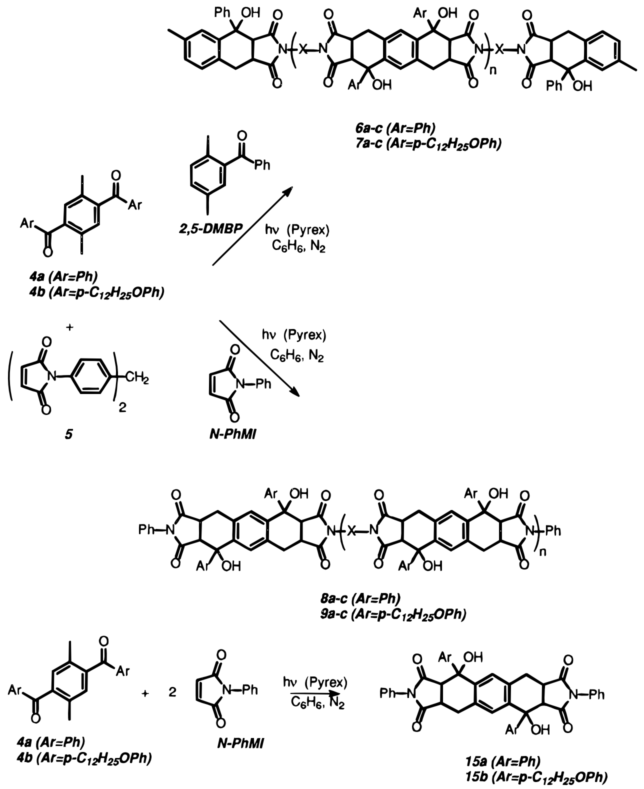
Diels−Alder cycloadditions have often been employed in polyimide synthesis as an alternative to condensation reactions.[1] Most of these Diels−Alder-based polyimide syntheses involve the reaction of a bismaleimide with a stable bisdiene such as a bisfuran[2] or a bispyrone.[3] Recently, the use of highly reactive diene intermediates, such as *o*-quinodimethanes (*o*-QDMs), has been explored.[4,5] These *o*-QDMs have typically been generated by the thermolysis of benzocyclobutene-containing monomers.

We have developed a new method for the preparation of linear aromatic polyimides which utilizes *o*-QDMs generated by a well-known photochemical reaction—the photoenolization of *o*-methylphenyl ketones. Photolysis of *o*-methylbenzophenone, **1**, produces hydroxy-*o*-quinodimethane (or photoenol) **2**, which can be trapped with dienophiles, such as dimethyl acetylenedicarboxylyate,[6] to give the corresponding cycloadduct in good yield (65%). Diels−Alder trapping of *o*-methylphenyl ketone photoenols has received considerable attention in the synthesis of fused ring systems.[7] However, the use of this chemistry in polymer synthesis has not been reported to date.

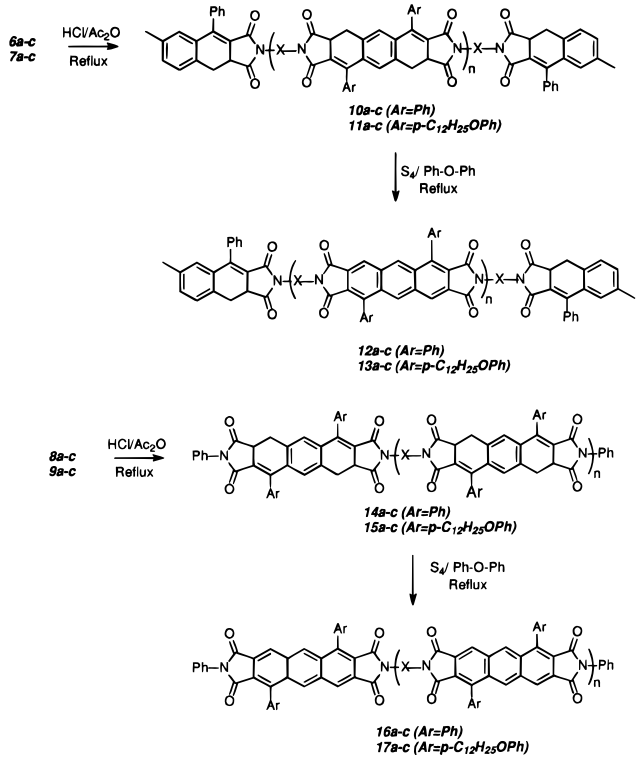


Our approach employs 2,5-dibenzoyl-*p*-xylene, **4,** which, upon photolysis, produces two photoenol moieties that can each undergo Diels−Alder cycloadditions.[8] Thus, photolysis of **4** in the presence of a stoichiometric amount of a bismaleimide should provide polyimides such as **6** (Scheme 1). These could, in subsequent steps, be converted into the corresponding anthryl system, **12** (Scheme 2). We now wish to describe the use of this chemistry in the synthesis of polyimides and bisimide model compounds.

Scheme 1. Polyimide and Bisimide Synthesis via the Diels−Alder Trapping of Photoenols



Scheme 2. Dehydration and Aromatization of 6−9



Degassed benzene or cyclohexanone solutions of **4** (**a**, Ar = Ph; **b**, Ar = *p*-$C_{12}H_{25}$OPh), 1,1-(methylenedi-4,1-phenylene)bismaleimide, **5**, and either 2,5-dimethylbenzophenone, 2,5-DMBP, or *N*-phenylmaleimide, *N*-PhMI, were irradiated under N_2 using light from a 450 W Hg lamp filtered through Pyrex. The stoichiometries of these reactants were adjusted to give polyimides with three different formulated *n* values—10, 50, and 500. Aliquots of the photolysate were withdrawn periodically during the irradiation and analyzed by HPLC for unreacted bismaleimide. When no bismaleimide could be detected, typically after photolysis overnight, the reaction was stopped and worked up by solvent evaporation under vacuum, followed by trituration with MeOH (benzene), or precipitation with hexane (cyclohexanone). Samples were then vacuum-dried overnight at 100 °C. Yields in all cases were 99% or better. Model bisimides, **18a** and **18b**, were prepared in near-quantitative yields using the same procedure in benzene solution.

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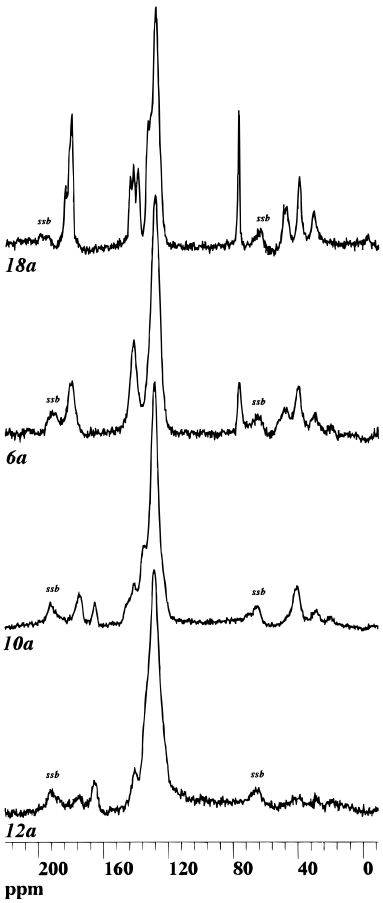

Figure 1. Comparison of ^{13}C CP-MAS spectra of bisimide **18**, polyimide **6a**, dehydrated polyimide **10a**, and anthryl polyimide **12a**. The broad peaks at ca. 65 and 190 ppm are spinning sidebands.

Spectral analysis (FTIR, ^{1}H NMR and solid-state ^{13}C NMR) of the resulting products is consistent with the formation of the desired polyimides **6**−**9**. All polymers displayed characteristic IR absorptions at ca. 1780 and 1710 cm^{-1} corresponding to the imide carbonyl and strong OH absorptions at 3500 cm^{-1}. ^{1}H NMR spectra of polyimides **6**−**9** did not show an *o*-CH$_3$ benzoyl methyl singlet at 2.3 ppm present in the spectrum of starting diketones **4a** and **4b**, indicating complete enolization and trapping of all of the *o*-methylbenzoyl moieties.

The ^{13}C CP MAS spectra of polymer **6a** and model bisimide **18a** are shown in Figure 1. There is fairly good agreement between these spectra. For example, the ^{13}C spectrum of polyimide **6a** shows a carbonyl resonance at 178 ppm, compared with 179 ppm for bisimide **18a**. Octahydroanthracene unsaturated ring carbons of bisimide **18a** appear at 80, 49, 39, and 30 ppm. Resonances for these same carbons in polyimide **6a** appear as three broad peaks at 79, 49, 39, and 27 ppm. The terminal methyl group of **6a** is found at ca. 25 ppm.

Glass transition temperatures, T_g, of these polyimides were measured by TMA in air at a heating rate of 10 °C/min. In general, polyimide T_g's showed no trend with respect to *n* values, with the exception of **6a**−**c** prepared in cyclohexanone, which decreased with increasing *n*, and **9a**−**c**, which increased with increasing *n* (Table 1). T_g's of dodecyloxy-substituted polyimides **7a**−**c** and **9a**−**c** were considerably lower than those of unsubstituted polyimides **6a**−**c** or **8a**−**c**, due to the influence of the flexible dodecyloxy substituents.

Table 1. Onsets of Decomposition (T_d) and Glass Transition Temperatures (T_g) for Polyimides Prepared from 2,5-Dibenzoyl-*p*-xylene (4a) and 2,5-Bis(4-(dodecyloxy)benzoyl)-*p*-xylene (4b)

polymer	*n*	ketone	end cap	solvent	T_d(air)[a] (°C)	T_d (N$_2$)[a] (°C)	T_g[b] (°C)
6a	10	**4a**	2,5-DMBP	B[c]	310	368	295
6b	50	**4a**	2,5-DMBP	B	338	380	300
6c	500	**4a**	2,5-DMBP	B	330	375	305
6a	10	**4a**	2,5-DMBP	C	360	378	194
6b	50	**4a**	2,5-DMBP	C[c]	313	239	170
6c	500	**4a**	2,5-DMBP	C	346	389	105
7a	10	**4b**	2,5-DMBP	B	357	380	144
7b	50	**4b**	2,5-DMBP	B	325	405	167
7c	500	**4b**	2,5-DMBP	B	327	423	189
8a	10	**4a**	*N*-PhMI	B	342	369	301
8b	50	**4a**	*N*-PhMI	B	344	387	284
8c	500	**4a**	*N*-PhMI	B	344	378	294
9a	10	**4b**	*N*-PhMI	B	338	358	121
9b	50	**4b**	*N*-PhMI	B	348	395	136
9c	500	**4b**	*N*-PhMI	B	332	449	146

[a] Onset of decomposition measured by TGA, scan rate of 10 °C/min. [b] Measured on pressed pellets by TMA in nitrogen, scan rate of 10 °C/min. [c] B = benzene, C = cyclohexanone.

Table 2. Molecular Weight Distributions Determined by GPC for Polyimides 7 and 9

polymer	end cap	*n*	MW$_{calc}$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
7a	2,5-DMBP	10	11 178	6 146	27 160	6.02
7b	2,5-DMBP	50	52 778	12 448	68 146	5.47
7c	2,5-DMBP	500	520 778	14 093	114 947	8.15
9a	*N*-PhMI	10	11 428	17 532	51 180	2.91
9b	*N*-PhMI	50	53 028	20 632	66 492	3.22
9c	*N*-PhMI	500	521 028	81 497	227 661	2.79
18b	*N*-PhMI	0	1 044	1 591	1 696	1.05

Onsets of decomposition, T_d, were measured by TGA in air and N$_2$ at a heating rate of 10 °C/min. While there was some variation in T_d's within a series of polyimides, there was no discernible trend for these T_d's with respect to polyimide *n* values. Onsets of decomposition in air were on the order of 310−360 °C for polyimides **6a**−**c** and **8a**−**c,** derived from 2,5-dibenzoyl-*p*-xylene, **4a**, and from 325 to 357 °C for **7a**−**c** and **9a**−**c** prepared from 2,5-bis(4-(dodecyloxy)benzoyl)-*p*-xylene, **4b** (Table 1). It is somewhat surprising that T_d's in air for polyimides prepared from **4a** and **4b** were roughly the same. This would suggest that oxidation of the dodecyloxy side chains of polyimides **7a**−**c** does not contribute appreciably to the initial weight losses in air.

As would be expected, T_d's in N$_2$ were statistically significantly higher than those measured in air—on the average 50 °C higher in N$_2$ than in air.[9] Onsets of decomposition in N$_2$ of dodecyloxy-substituted polyimides **7a**−**c** and **9a**−**c** were slightly higher than those of the corresponding unsubstituted systems **6a**−**c** and **8a**−**c**. During the course of irradiation, polyimide (**6a**−**c**) solutions prepared with 2,5-dibenzoyl-*p*-xylene, **4a**, became turbid, while those (**7a**−**c**) prepared with 2,5-bis(4-(dodecyloxy)benzoyl)-*p*-xylene, **4b**, remained clear. The higher T_d's in N$_2$ for polyimides **7a**−**c** may be due to a slightly higher degree of polymerization in these systems, which should lead to a lesser amount of lower molecular weight species. Further work on the decomposition of these polyimides in air and N$_2$ is in progress.

Polyimides **6a**−**c** and **8a**−**c** are nearly insoluble in solvents typically used with polyimides, e.g., NMP and DMF. This is due to extensive hydrogen bonding between pendant hydroxyl groups. When these interactions are removed by acetylation of the hydroxyl groups

Table 3. Comparison of T_d (°C) and T_g (°C) for 8 before and after Acid-Catalyzed Dehydration and after Aromatization

	n	T_d (air)[a]	T_d (N_2)[a]	T_d[b] (air) dehyd	T_d (N_2)[b] dehyd	T_d[c] (air) arom	T_d (N_2)[c] arom	T_g	T_g[b] dehyd	T_g[c] arom
8a	10	342	369	372	340	547	486	301	308	318
8b	50	344	387	391	358	414	495	284	320	331
8c	500	344	378	383	362	440	524	294	314	327

[a] T_d measured by TGA at a heating rate of 10 °C/min; T_g measured on pressed pellets by TMA at a heating rate of 10 °C/min. [b] Measured as indicated above on samples prepared by acid-catalyzed dehydration of polyimides **8**. [c] Measured as indicated above on samples prepared by treatment of dehydrated polyimides **13** with sulfur in refluxing diphenyl ether.

(treatment of the polymers with excess acetyl chloride in refluxing triethylamine/NMP), the solubility of these systems in NMP is greatly improved.

Cyclohexanone was also investigated as a reaction solvent in the synthesis of **6a**−**c** in the hope that these polyimides would remain in solution during the course of the irradiation. While the cyclohexanone reaction solutions did remain clear during photolysis, only a modest increase in N_2 T_d's was observed (Table 1). In addition, glass transition temperatures of **6a**−**c** prepared in cyclohexanone are considerably lower than T_g's of the same polymers synthesized in benzene. TGA of these polyimide samples reveals the presence of some residual cyclohexanone, despite the fact that these samples were dried overnight under vacuum at 100 °C. Because of difficulties in removing this solvent after reaction, no further work was done in cyclohexanone.

The effect of using two different chain terminating groups, 2,5-dimethylbenzophenone (2,5-DMBP) and *N*-phenylmaleimide (*N*-PhMI), was also investigated. In order for 2,5-DMBP to terminate polymerization, it must absorb a photon of light and enolize to an *o*-QDM. In high molecular weight formulations, where the concentration of 2,5-DMBP is low, this could be difficult since 2,5-DMBP would have to compete with polyimide, also a good UV chromophore, for incident UV light. On the other hand, chain termination with *N*-PhMI requires absorption of light by unreacted *o*-methylbenzoyl groups either on the polyimide or on diketone **4**. Differences in the molecular weight distributions of polyimides terminated with 2,5-DMBP and *N*-PhMI would reflect differences in the light harvesting abilities of 2,5-DMBP and polyimide as well as the Diels−Alder reactivities of these two compounds.

A comparison of the number- and weight-average molecular weights determined by GPC[10] for dodecyloxy-substituted polyimides **7a**−**c** and **9a**−**c** in NMP is given in Table 2. The GPC results for dodecyloxy-substituted bisimide **18b** are also included for reference. In general, polyimides **9a**−**c**, prepared with *N*-PhMI, had higher M_w and M_n values than did 2,5-DMBP-terminated polyimides, **7a**−**c**. Polydispersities of the *N*-PhMI-terminated polyimides were also considerably lower than those end-capped with 2,5-DMBP. Thus, *N*-PhMI appears to be more efficient at chain termination than 2,5-DMBP. Attempts to measure molecular weight distributions of unsubstituted polyimides **6a**−**c** and **8a**−**c** were not successful due to the poor solubility of these polymers in solvents typically used for GPC or viscosity measurements.

HCl-catalyzed dehydrogenation of **6**−**9** or bisimides **18a** and **18b** in refluxing acetic anhydride produced polyimides **9**, **10**, and **13** (respectively) or bisimides **19** (Scheme 2). Solid-state ^{13}C NMR spectra of dehydrated bisimides and dehydrated polyimides are in good agreement. A comparison of the ^{13}C CP-MAS NMR spectra of polyimide **6a** and the corresponding dehydrated polyimide **9a** is shown in Figure 1. The spectrum of **9a** shows a second imide carbonyl resonance at 164 ppm, due to the newly formed α,β-unsaturated carbonyl, loss of the OH, Ph-substituted ring carbon, and the formation of new unsaturated carbon peaks for the two new double bonds, as well as two saturated ring carbon resonances at 38 and 24 ppm. The ^{13}C NMR spectrum of dehydrated bisimide **16** in $CDCl_3$ has carbonyl resonances at 174 and 165 ppm, unsaturated carbon peaks from 145 to 123 ppm (vs 150−120 ppm for **9a**), and peaks at 40 and 29 ppm corresponding to the saturated ring carbons.

Dehydrated polyimides **9**, **10**, and **13** were treated with a stoichiometric excess of sulfur in refluxing diphenyl ether to afford the corresponding anthryl polyimides **11**, **12**, and **14**. Comparison of the ^{13}C CP-MAS spectrum of anthryl polyimide **11a** with that of its precursor **9a** (Figure 1) shows nearly complete loss of the carbonyl resonance at 178 ppm and tetrahydroanthracene saturated ring carbon peaks at 38 and 24 ppm. This coupled with a change in the aromatic region of the spectrum (120−160 ppm) is consistent with the proposed structure.

A comparison of the T_g's and T_d's (in air and N_2) of polyimides **8a**−**c**, dehydrated polyimides **14a**−**c**, and anthryl polyimides **16a**−**c** is given in Table 3. Dehydrated polyimides **14a**−**c** had higher T_g's than their precursors **8a**−**c**. This is a result of the increased chain stiffness brought about by the formation of more rigid tetrahydroanthracene units within the polyimide backbone. Further stiffening of the polyimide backbone in the anthryl polyimides **16a**−**c** is reflected in the still higher T_g's for systems. Higher T_d values were also observed for tetrahydroanthryl polyimides **14a**−**c** and anthryl polyimides **16a**−**c** than those of **8a**−**c.** This is consistent with the presence of more thermally and thermooxidatively stable tetrahydroanthracene and anthracene units within these polyimides.

We have described a new approach to the preparation of polyimides based upon Diels−Alder trapping of photochemically generated *o*-QDMs. Polyimides produced by this route have high T_g's and modest stability in air and N_2. Further synthetic manipulation of these polyimides using standard organic chemistry can produce polyimides with a combination of high T_g's and T_d's. Although the work described in this paper has dealt with solution photochemistry, this synthetic technique should also be viable in thin films or coatings. This would offer a photochemical alternative to more traditional thermal cures used in the preparation of polyimide thin films for electronics packaging and optical applications. This is currently under investigation. In addition, we are exploring the use of other bismaleimides and other bisdienophiles, e.g., bisacrylates, with this chemistry.

References and Notes

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(9) From a paired *t*-test analysis of T_ds. The average T_d in air was 335 °C, and the average in N_2 was 385 °C.

(10) Estimated by gel permeation chromatography in NMP containing 0.5 wt % LiBr. Polystyrene standards were used for calibration.

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