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Novel Poly(imidoaryl ether ketone)s and Poly(imidoaryl ether sulfone)s Derived from Phenolphthalein

Introduction. The diarylisobenzofuran 1 was recently synthesized, and it was demonstrated that it readily undergoes a Diels–Alder reaction with maleic anhydride or N-substituted maleimides to give the adduct 2[1] (Scheme I). Much earlier Blicke[2] synthesized the unmethylated isobenzofuran 5 as shown in Scheme II. Phenolphthalein (3) is first reduced to phenolphthalin (4) with zinc dust in the presence of base, and subsequent treatment with concentrated sulfuric acid yields 5. Blicke oxidized 5 with a variety of oxidizing agents to the diketone 6. We have reacted 5 with N-substituted maleimides (Scheme III) to give the Diels–Alder adducts 7 which on treatment with acid are aromatized to give the novel imido-substituted biphenols 8–10, and from these biphenols we have prepared the corresponding poly(ether sulfone)s and poly(ether ketone)s.

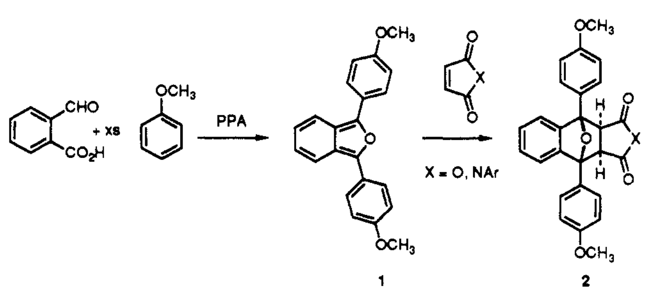
Results and Discussion. The imido-substituted biphenols **8–10** were synthesized in overall yields of 50–60%. When R is dodecyl (**9**), this bisphenol is readily soluble in NMP (20% w/v solids) at 25 °C, while when R is methyl (**8**) or phenyl (**10**), the monomers are less soluble and temperatures of 60 and 80 °C, respectively, are required to give homogeneous solutions.

The poly(arylene ether)s **12–14** were synthesized by conventional procedures[3,4] using potassium carbonate as base in *N*-methylpyrrolidone (NMP) or sulfolane as solvent as shown in Scheme IV. High molecular weight polymers with inherent viscosities above 0.5 dL/g are readily obtained. The properties of these polymers are outlined in Table I. Changing the R group has a dramatic effect on the solubility of the resulting polymer. When R is dodecyl, all of the polymers are readily soluble in chloroform and methylene chloride at room temperature. When R is phenyl or methyl, the poly(imidoaryl ether sulfone)s and poly(imidoaryl ether bisketone)s are less soluble in chloroform, and the poly(imidoaryl ether ketone)s dissolve only in selected dipolar aprotic solvents at elevated temperatures. When R is methyl, high molecular weight poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s cannot be synthesized when NMP is used as solvent, because oligomers rapidly precipitate at 140 °C during the polymerization reaction. In this case high molecular weight polymers can be synthesized if sulfolane is the solvent.

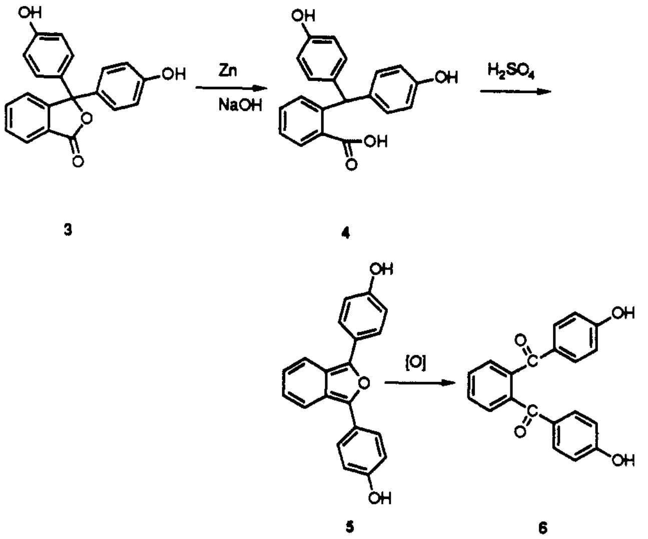
The highest glass transition temperatures were obtained for polymers where R is methyl, presumably because the chain is most rigid for these materials. When R is phenyl, T_g values are very close to those where R is methyl, but the solubility is much improved. As may be anticipated, when R is dodecyl the values for T_g are much lower, since the long alkyl chain functions as an internal plasticizer. For a given R group, the poly(imidoaryl ether sulfone)s have the highest T_g's, while the poly(imidoaryl ether bisketone)s exhibit the lowest T_g's.

All of the polymers appear to be amorphous. In an attempt to induce some degree of crystallinity the two ketone polymers (**14b** and **13b**) were held for 3 h at 300 °C and 5 h at 200 °C, respectively, and then cooled to 25 °C. Subsequent heating to 300 °C for **13b** and to 500 °C for **14b** in the DSC did not reveal a melting point for either polymer.

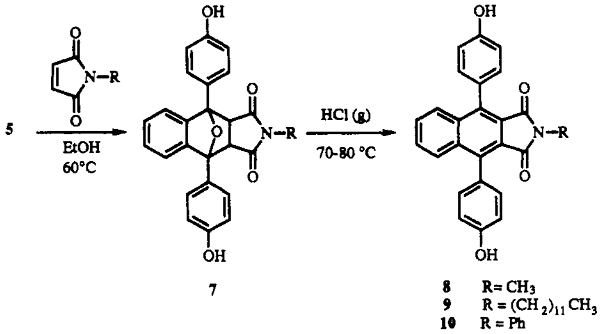
Scheme I



Scheme II



Scheme III



As would be expected, the polymers where R is a phenyl group possess the highest thermooxidative stability (Table I), while those where R is methyl and dodecyl are lower by 45–65 and 90–100 °C, respectively. The phenyl-substituted polymers are exceptionally stable by thermogravimetric analysis and show 10% weight losses in air and in nitrogen at about 550 °C. The Young's moduli of thin films (10 mm × 2.1 mm × 0.061 mm) of these polymers are in the range 2–2.7 GPa at 25 °C. When R is phenyl, the poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s maintain good mechanical properties up to 240 °C.

The glass transition temperature of the phenyl-substituted poly(ether sulfone) **14a** which contains the imide-substituted terphenyl moiety is 310 °C which is 86 °C higher than the T_g of the poly(ether sulfone) synthesized from 4,4′-biphenol (T_g = 224 °C[5]). The rigid terphenyl group, which is illustrated in a molecular model of the monomer **10** (Figure 1), increases the T_g of the polymer while the imide group introduces asymmetry into the molecule to increase the solubility of the polymer. In addition, the thermooxidative stability of the former polymer is slightly higher. All of the polymers except the methyl-substituted poly(imidoaryl ether ketone) **12b** are

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Scheme IV

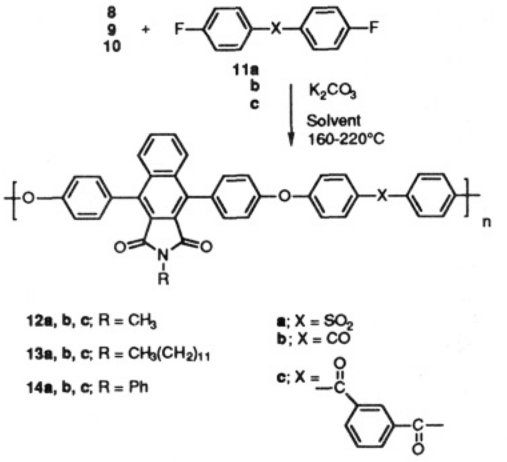

Table I
Thermal Properties of Polymers 12–14

polymer	polymerization solvent	T_g,[a] °C	TGA,[b] °C air	TGA,[b] °C N_2	solubility
12a	sulfolane	314	503	506	$CHCl_3$ and TCE
12b	sulfolane	283[c]	525	516	sulfolane
12c	NMP	251	425	515	$CHCl_3$
13a	NMP	167	471	471	$CHCl_3/CH_2Cl_2$
13b	NMP	147	482	491	$CHCl_3/CH_2Cl_2$
13c	NMP	140	489	487	$CHCl_3/CH_2Cl_2$
14a	NMP	310	556	550	$CHCl_3$ (hot)
14b	DMSO	275	551	561	$CHCl_3$
14c	NMP	245	568	566	$CHCl_3/CH_2Cl_2$

[a] DSC. Heating rate 10 °C/min. [b] TGA. Heating rate 10 °C/min. Values correspond to the temperature at which a 10% weight loss occurs. [c] Low molecular weight.

high molecular weight and can be cast from solution to give tough, flexible films which withstand at least two 180-deg folds.

In conclusion, we have synthesized a series of poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s which are amorphous from novel biphenols containing pendant imide moieties. When the substituent, R, is phenyl, the resulting polymers have very high glass transition temperatures along with exceptional thermooxidative stability while maintaining solubility in common organic solvents such as chloroform and methylene chloride.

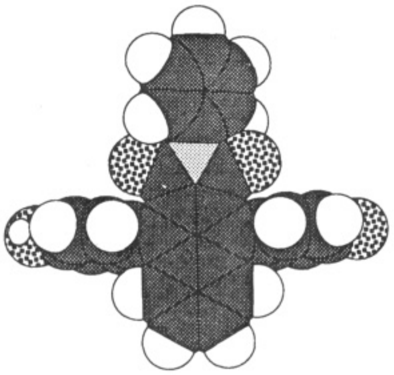

Figure 1. Molecular model of imidobiphenol **10**.

We are continuing the evaluation of the properties of these polymers and are currently exploring the effect of other R groups on the polymer properties.

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References and Notes

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