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Novel Redox Polymers and Their Use as Polymeric Reagents in Organic Synthesis

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NOVEL REDOX POLYMERS AND THEIR USE AS POLYMERIC REAGENTS IN ORGANIC SYNTHESIS

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ABSTRACT

We have synthesized high molecular weight poly(aryl ether)s which contain a stable hindered biphenoxy radical in the backbone of the polymer chain. These high molecular weight biphenoxy radicals on reaction with methylene groups formed insoluble polymers which could not be characterized fully. Lower molecular weight copolymers were prepared which on reaction with molecules containing methylene groups gave soluble polymers with attached ether or acetal groups. Acid cleavage regenerated the original polymer containing hindered biphenol groups along with the corresponding alcohol or aldehyde derived from the original methylene compound.

INTRODUCTION

Polymeric supports have been used for many years in peptide synthesis [1, 2] and in other types of organic synthesis [3, 4]. Their advantages are the elimination of the rigorous purification steps generally required in organic synthesis and the need for excess amounts of one of the reagents to either accelerate the reaction or push the reaction to completion. Redox polymers such as quinone based polyfor-
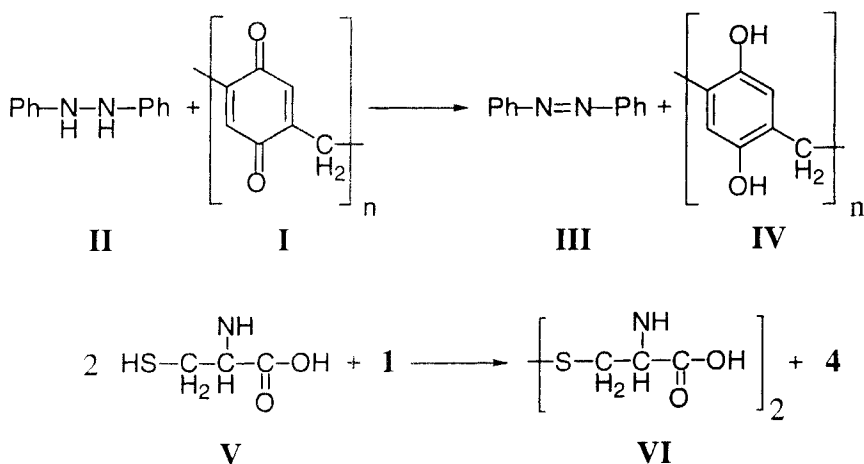
SCHEME 1

maldehyde resins **I** which are considered to be polymer reagents, have been used in the oxidative conversion of hydrazobenzene **II** to azobenzene **III** or in the oxidative coupling reaction of cysteine **V** to cysteine **VI** (Scheme 1) [5, 6] .

We previously reported the synthesis of redox polymers **VIIa, b** (Scheme 2) incorporating the hindered biphenoxy radicals [7]. Only low molecular weight polymers were obtained. In this paper we report the synthesis of a new biphenol **VIII** which led to the synthesis of high molecular weight redox polymers incorporating the biphenoxy radical. We have extended the study of radical coupling reactions previously performed with hindered biphenoxy radicals [8-10] to these redox polymers.

EXPERIMENTAL

Materials

Solvents N,N-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) were purchased from Aldrich Chemical Co. and dried over 4Å molecular sieves for 24 hours before use. Chloroform, methanol, chlorobenzene and methylene chloride were purchased from Caledon and used as received. Reagents 2-bromopropane, 1M BBr$_3$ in methylene chloride, 1M BCl$_3$ in methylene chloride, cesium carbonate, 2,4,6-collidine, and lithium iodide were purchased from Aldrich Chemical company
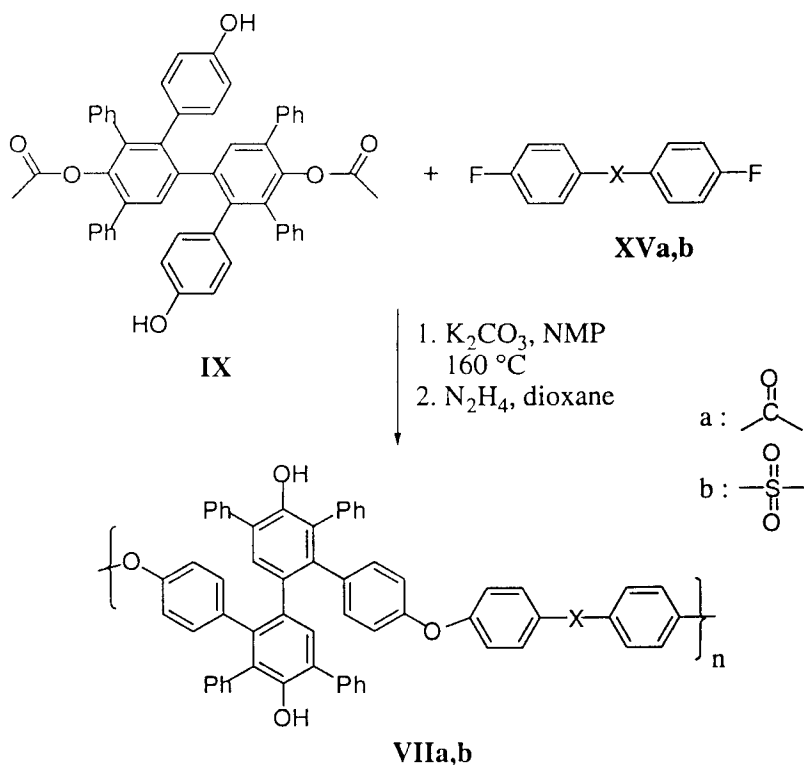
SCHEME 2

and used as received. Bis-(4-fluorophenyl)sulfone was purchased from Aldrich Chemical Co. and recrystallized from toluene. 4,4'-Difluorobenzophenone was purchased from Maybridge Chemical Co., 9,9-bis(4-hydroxyphenyl)fluorene was purchased from Kennedy & Klim Inc., and potassium carbonate was purchased from Omega and used as received.

Instrumentation

Elemental analyses were performed by Fine Analysis Laboratories Ltd., Hamilton, Ontario. All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity 500 spectrometer. GPC analyses were performed on a Waters 510 instrument equipped with a UV detector set at 254 nm and four 5 μm phenogel columns (3 x 500Å, linear) arranged in series. All molecular weights are referenced to polystyrene standards. Thermal analyses were carried out using a Seiko 220DSC and 220 TGA/DTA instrument at a heating rate of 20°C under a nitrogen

atmosphere. UV visible analyses were performed on a HP8452A diode array spectrometer. Inherent viscosity data were from chloroform solution with a concentration of 0.5 dL/g in a calibrated Ubbelohde viscometer at 25°C.

Monomer Synthesis

2,2'-Bis(4-methoxyphenyl)-3,3',5,5'-tetraphenyl-1,1'-biphenyl-4,4'-di-(1,1-(dimethyl)methyleneoxy) XIII

A three-neck 500 mL round-bottom flask equipped with a condenser and Dean-Stark trap was charged with **XI** (40.00 g, 56.96 mmol), K_2CO_3 (19.81 g, 143.33 mmol), 200 mL of DMAc, and 100 mL of benzene. The solution was refluxed for 17 hours under an atmosphere of nitrogen. Benzene was then removed from the reaction flask and the oil bath temperature was lowered to 90°C. 2-Bromopropane **XII** (57.23 g, 465.25 mmol) was added dropwise over 40 minutes and after 24 hours the reaction was complete. The solution was poured into water and the crude precipitate was dried and recrystallized from DMSO to give 36.5 g (82%) of **XIII** as tannish crystals: m.p. 265-269°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.393 (br s, 1H), 7.18 - 7.31 (m, 13H), 7.02 - 7.12 (m, 4H), 6.92 (br s, 4H), 6.79 (d, 4H, J = 8.8 Hz), 6.60 (br s, 4H), 3.71 (s, 6H, OCH_3), 3.35 (q, 2H, CH), 0.46 - 0.54 (dd, 12H, J = 5.8 & 30.8 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.55, 151.34, 140.17, 139.45, 138.46, 136.51, 135.90, 134.24, 133.56, 132.40, 131.62, 129.64, 127.57, 126.99, 126.50, 125.73, 112.49, 74.60 (CH), 55.16 (OCH_3), 21.73 (CH_3), 21.43 (CH_3); MS (FAB Matrix: NBA) m/e 787.23 (M^+, 3), 745.19 (M^+ - (C_3H_7), 2), 702.11 (M^+ - (C_6H_{14}), 4); Analysis calcd. for $C_{56}H_{50}O_4$: C, 85.46; H, 6.40. Found: C, 85.63; H, 6.54.

2,2'-Bis(4-hydroxyphenyl)-3,3',5,5'-tetraphenyl-1,1'-biphenyl-4,4'-di-(1,1-(dimethyl)methyleneoxy) VIII.

A 500 mL three-neck round-bottom flask was charged with **XIII** (25.02 g, 31.79 mmol), lithium iodide (89.16 g, 666.16 mmol), and 175 mL of 2,4,6-collidine. The solution was refluxed for 24 hours, cooled to room temperature and poured into a 5% aqueous solution of HCl. The crude product was filtered dried and recrystallized from DMSO, to give 13.80 g (58%) of **VIII** as white crystals: m.p. >295°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02-7.30 (m, 20H), 6.93 (br s, 2H), 6.67 (br s, 4H), 6.48 (br s, 4H), 4.48 (s, 2H, OH), 3.34-3.36 (q, 2H, CH), 0.47-0.53 (dd, 12H, J = 4.9 & 24.4 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.08, 151.31, 140.31, 139.50, 138.55, 136.54, 134.03, 133.61, 131.91, 131.80, 129.64, 127.64, 126.89, 126.46, 125.60, 113.92, 74.65 (CH), 21.72 (CH_3), 21.55 (CH_3);

MS (EI direct inlet at 370 °C) m/e 758.27 (M$^+$, 62), 716.25 (M$^+$-(C$_3$H$_7$), 14), 674.19 (M$^+$-(C$_6$H$_{14}$), 100); Analysis calcd. for C$_{54}$H$_{46}$O$_4$: C, 85.46; H, 6.11. Found: C, 85.99; H, 6.31.

Polymer Synthesis

Synthesis of Copolymer XXIII

A 25 mL three-neck round-bottom flask equipped with a condenser, Dean-Stark trap, and nitrogen inlet was charged with biphenol **VIII** (0.52g, 0.69 mmol), **XVb** (0.39 g, 1.55 mmol), biphenol **XVIII**, 3,5-di-t-butylphenol **XXIV** (0.06 g, 0.28 mmol), Cs$_2$CO$_3$ (0.80 g, 2.46 mmol), 5 mL of DMAc and 3 mL of toluene. The reaction mixture was dehydrated for 3 hours at 135-138°C. The reaction temperature was then increased to 142-144°C and left to react for another 7 hours. The mixture was diluted by 30% with DMAc and the polymer was precipitated out in a solution of methanol-water-acetic acid (300 mL/100 mL/1mL). Obtained was 1 g (93%) of polymer **XXIII**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.80 (br s, 37H), 7.69-7.73 (distorted t, 18H), 7.18-7.40 (m,124H), 7.12 (br s, 31H), 6.97-7.00 (br d, 37H), 6.89-6.94 (br d, 36H), 6.81-6.84 (distorted t, 26H), 6.70-6.78 (br s, 15H), 3.38-3.40 (q, 10H, CH), 1.29 (s, 36H, t-butyl methyl groups), 0.47-0.53 (dd, 60H, isopropyl methyl groups).

Polymer XXV

Boron trichloride 1M solution in methylene chloride (7.00 mL, 7.00 mmol) was added slowly with a syringe over a 20 minute period to a solution of 10 mL of methylene chloride and polymer **XXIII** (1.00 g, 0.65 mmol) at -10°C. After complete addition, the reaction mixture was left stirring at room temperature under an atmosphere of nitrogen for another 24 hours. The solution was poured into a 10% aqueous solution of NaHCO$_3$. The polymer that precipitated was redissolved in chloroform and precipitated out from methanol. There was obtained 0.79 g (84%) of **XXV**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.74-7.82 (m, 54H), 7.45 (d, 19H), 7.34-7.39 (br d, 41H), 7.21-7.30 (m, 84H), 6.98-7.12 (m, 54H), 6.90 (br s, 25H), 6.75-6.79 (t, 22H), 6.58-6.70 (br s, 25H), 5.19 (s, 10H, OH), 1.29 (s, 36H, t-butyl methyl groups).

Carbon-Oxygen Coupling Reactions

To a solution of polymer **XXV** (0.25 g, 0.17 mmol) in 10 mL of chlorobenzene was added 7 mL of a 0.77 M aqueous solution of KOH and K$_3$Fe(CN)$_6$ under an atmosphere of nitrogen. The two phase mixture was stirred at room

temperature for 20 minutes generating the biphenoxy radical which is easily detected by the appearance of the dark red color. Excess amount of compound **XXVII** (0.21 g, 1.00 mmol) was added to the mixture and than heated to 60°C for 18 hours. There was obtained 0.18 g (58%) of polymer **XXVIIa**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.76 -7.84 (m, 54H), 7.38 (br s, 57H), 7.28 (s, 28H), 6.93-7.14 (m, 116H), 6.86 (s, 56H), 6.60-6.71 (br s, 28H), 5.05-5.21 (dd, 6H, CH), 3.08-3.21 (br s, 6H, CH$_2$), 2.74-2.85 (br s, 6H, CH$_2$), 2.30- 2.43 (br d, 12H, CH$_2$), 1.29 (s, 36H, t-butyl methyl groups).

Polymer XXVIIIb

Yield 0.24g (79%) of **XXVIIIb**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.76- .82 (m, 54H), 7.65-7.71 (m, 4H), 7.39 (s, 49H), 7.26-7.34 (m, 49H), 7.20 (s, 44H), 6.74-7.14 (m, 182H), 6.62-6.65 (br s, 31H), 5.89-5.94 (m, 4H CH=CH), 5.58-5.75 (m, 5H, CH=CH), 5.32-5.49 (m, 9H, CH=CH), 4.52-4.63 (m, 9H, CH-O), 1.29 (s, 36H, t-butyl methyl groups).

Polymer XXVIIIc

Yield 0.08g (53%) of **XXVIIIc**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.78-7.85 (m, 54H), 7.38 (s, 35 H), 7.28- .30 (distorted d, 20H), 7.19 (s, 50H), 7.15 (s, 10H), 6.81-7.08 (m, 136H), 6.68 (s, 35H), 6.54-6.59 (br t, 15H), 6.41 (s, 9H), 5.15 (s, 5H, CH), 1.29 (s, 36H, t-butyl methyl groups).

Cleavage of the Carbon-Oxygen Bond

Polymer **XXVIIIa** (0.06 g, 0.03 mmol) was dissolved in 10 mL of chloroform and 0.5 mL of HCl was added. The solution was stirred for 24 hours at room temperature. Obtained was 0.04 g (83%) of polymer **XXVIIId**.

RESULTS AND DISCUSSION

Monomer Synthesis

Our original work used as the monomer the diacetate of the hindered biphenol **IX** (Scheme 2), however only low molecular weight polymers were obtained [11]. We assumed that some cleavage of the acetate groups took place under the basic reaction conditions which would upset the stoichiometry. Model reactions with 4-fluorobenzophenone **X** led to three products which confirmed that the acetate groups were being cleaved under the basic conditions. To avoid this we prepared biphenol **VIII** by reacting the potassium salt of 2,2'-di-(4-methoxyphenyl)-3,3',5,5'-tetraphenyl-(1,1'-biphenyl)-4,4'-diol **XI** with 2-bromopropane **XII** under
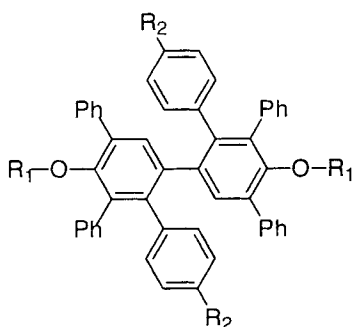
1) DMAc,toluene
   K_2CO_3, 3 h, 137°C
2) 10 eq$(CH_3)_2CHBr$
   90°C, 24 h, 82%

LiI, collidine
24h, 180°C, 58%

XI : $R_1 = H$, $R_2 = OCH_3$

XIII : $R_1 = CH(CH_3)_2$, $R_2 = OCH_3$

VIII : $R_1 = CH(CH_3)_2$, $R_2 = OH$

VIII + [X] $\xrightarrow[\substack{K_2CO_3 \\ 9 \text{ h, } 145\,°C}]{\substack{DMAc \\ toluene}}$

X

XIV

$R =$

$R_1 = CH(CH_3)_2$
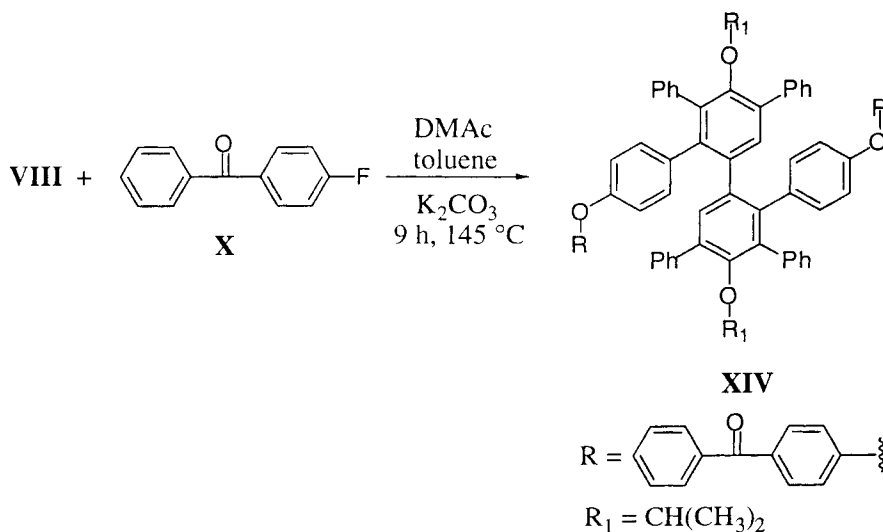
SCHEME 3

an atmosphere of nitrogen at 90°C for 14 hours affording **XIII** in 82% yield. This was followed by the selective deprotection of the methoxy group using lithium iodide in 2,4,6-collidine at 180°C for 24 hours yielding **VIII** in 58% yield (Scheme 3). In this case, only one product **XIV** was obtained when biphenol **VIII** and **X** were reacted (Scheme 3).

XVIa : G =   **XVIb** : G =

XVII : R = $(CH_3)_2CH$
XIX : R = H

XX   **XXVI**   **XXVII**
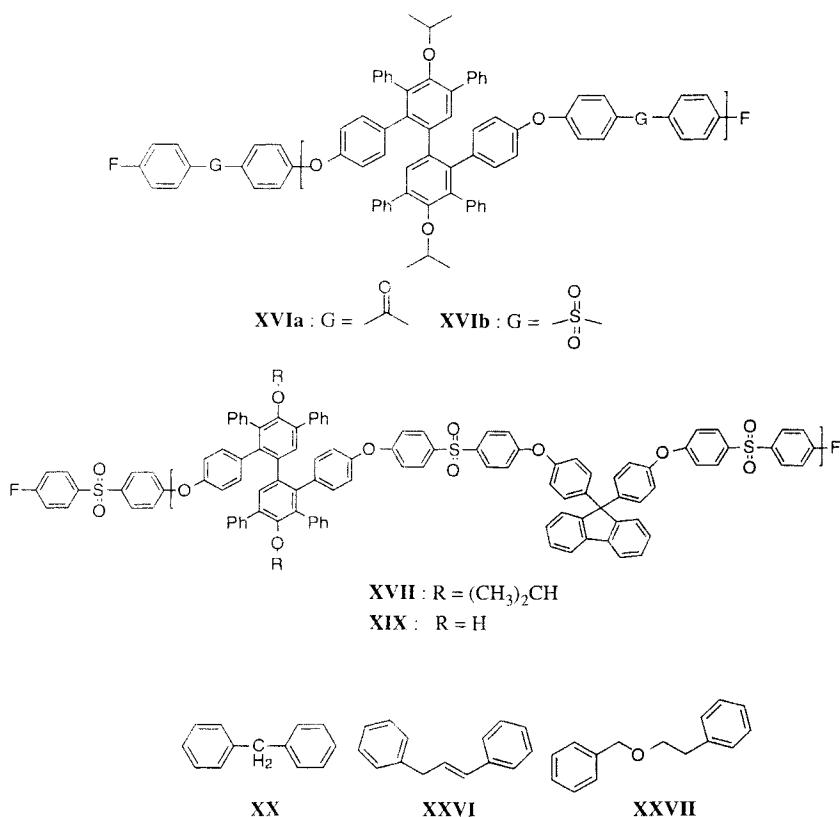
Figure 1.   High molecular weight polymers and methylene containing compounds.

Polymer Synthesis

Initial attempts at polymerization of biphenol **VIII** with 4,4'-difluoro-benzophenone **XVa** and bis(4-fluorophenyl)sulfone **XVb** yielded only low molecular weight polymers. No improvements were observed when either the temperature was increased or the solvent was changed. Only by the substitution of K_2CO_3 with Cs_2CO_3 were we able to obtain high molecular weight materials. The Cs^+ atom is larger than the K^+ atom so that the ionic bond between the Cs^+ atom and the biphenol is weaker which increases the solubility of the salt in polar solvents and the reactivity of the anion. Polymers **XVIa,b** (Figure 1) were obtained in high yields, 83% and 88%, respectively (Table 1).

All the high molecular weight polymers were designed to have 100 repeats units by using excess of the difluoro compound. ^1H, ^{31}P, and ^{19}F NMR spectra

TABLE 1. Yields and Physical Properties of the Polymers

| Entry	Isolated Yield (%)	Conv.[a] (%)	GPC			Thermal Analysis		ηinh[b] (dL/g)
			Mw (g/mol)	Mn (g/mol)	PD	T_g (°C)	5% wt. loss (°C)	
XVIa	88	--	99 000	44 000	2.3	231	411	--
XVIb	83	--	90 000	43 000	2.1	236	402	0.35
XVII	82	--	105 000	64 000	1.6	248	419	0.48
XIX	74	--	73 000	38 000	1.6	268	517	0.44
XXIII	93	--	17 000	7200	2.4	226	399	--
XXV	54	--	14 000	5400	2.6	239	500	--
XXVIIIa	58	60	127 000	6800	18.7	212	298	--
XXVIIIb	79	90	24 000	8000	3	212	341	--
XXVIIIc	53	50	153 000	9000	17.1	184	315	--

a: conversion based on ^{1}H NMR data.
b: in chlorobenzene at 25°C at a concentration of 0.5 dL/g.

confirm that the polymers are end capped with fluoro groups and have approximately 100 repeat units.

Originally, these polymers were soluble in common organic solvents, however when heated in methylene chloride or chloroform they became partially insoluble. Analysis of the insoluble fraction by DSC showed them to be crystalline with T_m's at 248°C and 268°C, respectively, for polymers **XVIa** and **XVIb**. It appears that solvents induce crystallinity in these polymers. Due to the difficulty in working with polymers **XVIa,b**, a copolymer **XVII** (Figure 1) endcapped at 100 repeat units was prepared from reaction of biphenols **VIII** and **XVIII** with **XVb** at 140-144°C in DMAc for 9 hours. Polymer **XVII** was soluble in common organic solvents and did not exhibit any changes in solubility when heated in chlorinated solvents as did the homopolymer analogs because of the random distribution of the monomers. The isopropyl groups in polymer **XVII** were quantitatively cleaved with BCl_3 in methylene chloride at -10°C to give polymer **XIX** (Figure 1).

All attempts to couple these redox polymers with activated methylene groups failed. Only the original polymer was recovered from the reaction of the pregenerated redox polymer and diphenylmethane **XX**. In the two phase oxidation system the dark red color attributed to the radical species disappeared and the

XXI   +   **XXII**

K$_3$Fe(CN)$_6$/KOH
Benzene, water 60 °C
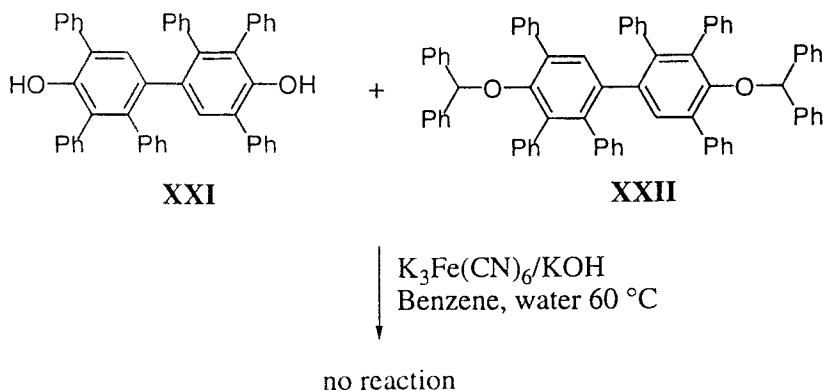
no reaction

SCHEME 4

polymer precipitated out of solution. Initially we assumed that the insoluble material is generated during the coupling reaction with the activated methylene compounds. One possibility is the abstraction of the tertiary methylene proton already attached to the polymer by the phenoxy radical followed by a coupling reaction of the carbon radical and the phenoxy radical leading to crosslinked product. However, no reaction occurred between biphenol **XXI** and diether **XXII** (Scheme 4) suggesting that the tertiary proton is unreactive toward the biphenoxy radical and that no coupling reaction would occur. That fact that the polymer still remained insoluble after being treated with a strong acid like methane sulfonic acid which is known to cleave the ether bond indicates that the carbon-oxygen coupling alone is not the cause. The change in polarity of the polymer due to the formation of the polyphenol by an oxidation reduction reaction with the methylene compound, which has been demonstrated with model compounds, may partially explain the results.

Only the low molecular weight copolymer **XXIII** (with only 6 repeat units) showed potential as a polymeric support material. Copolymer **XXIII** was prepared by a polymerization reaction in a solution of DMAc and toluene containing biphenol **VIII**, 9,9-bis-(4-hydroxyphenyl)fluorene **XVIII**, 3,5-di-t-butylphenol **XXIV**, bis-(4-fluorophenyl)sulfone **XVb** and Cs$_2$CO$_3$ at 135-138°C for 3 hours. The temperature was then increased to 140-144°C and kept at that temperature for a further 6 hours. The polymer was isolated by precipitation from methanol, yielding polymer **XXIII** in 93% yield as a white powder. The isopropyl groups were quantitatively cleaved using BCl$_3$ at -10°C for 20 minutes and at room temperature for a further 24 hours yielding **XXV** in 84% yield (Scheme 5).
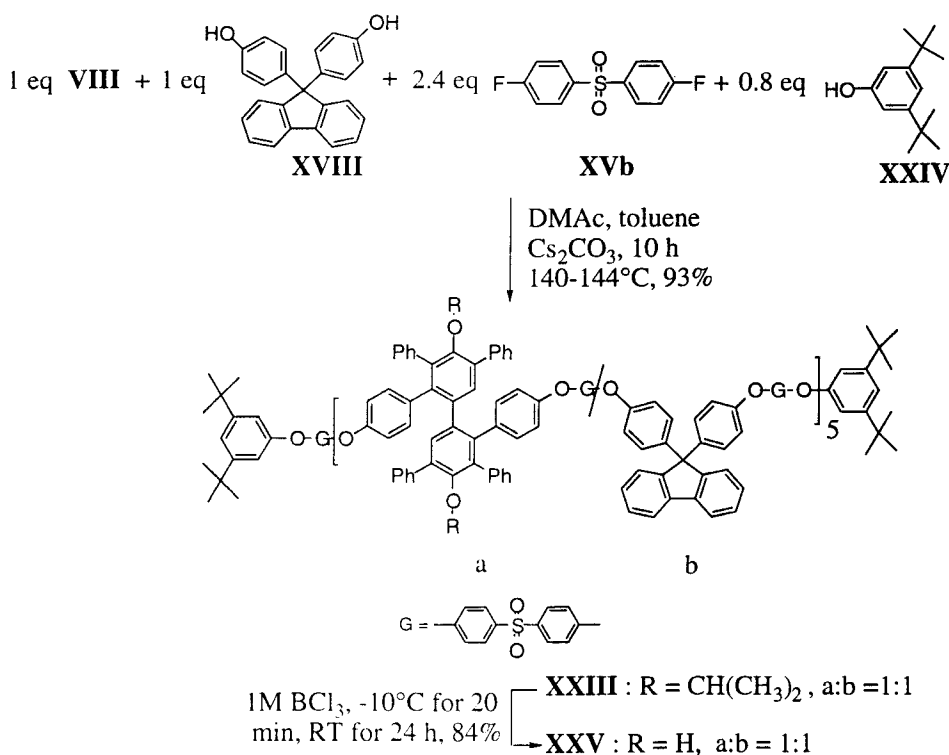
SCHEME 5

The lower glass transition temperature obtained for polymer **XXIII** (T_g = 226°C, Figure 2a) compared to polymer **XX** (T_g = 239°C, Figure 2b) can be attributed to the bulky isopropyl groups and the lack of hydrogen bonding from the phenolic hydroxy groups. The thermogravimetric analysis (TGA) trace of polymer **XXIII** (Figure 3b) showed a weight loss of 5.9% in the range of 360-450°C, which within experimental error corresponds to the theoretically expected weight loss of 5.6% due to the isopropyl groups. These results plus proton NMR data for polymer **XXIII** (Figure 4a) confirm that no cleavage of the isopropyl groups occurred during the polymerization reaction. GPC results for both polymers (Figure 5a,b) are similar with a slight shift of polymer **XXV** to lower molecular weight, due possibly to the change in polarity as well as the weight loss of the isopropyl groups. The absence of any low molecular weight fractions indicates that no cleavage of the polymer chain occurred during the removal of the isopropyl groups. A calculation of the number of repeat units from the ¹H NMR data confirmed these findings in
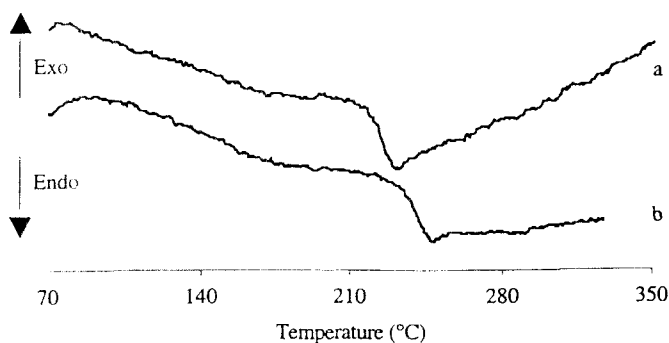
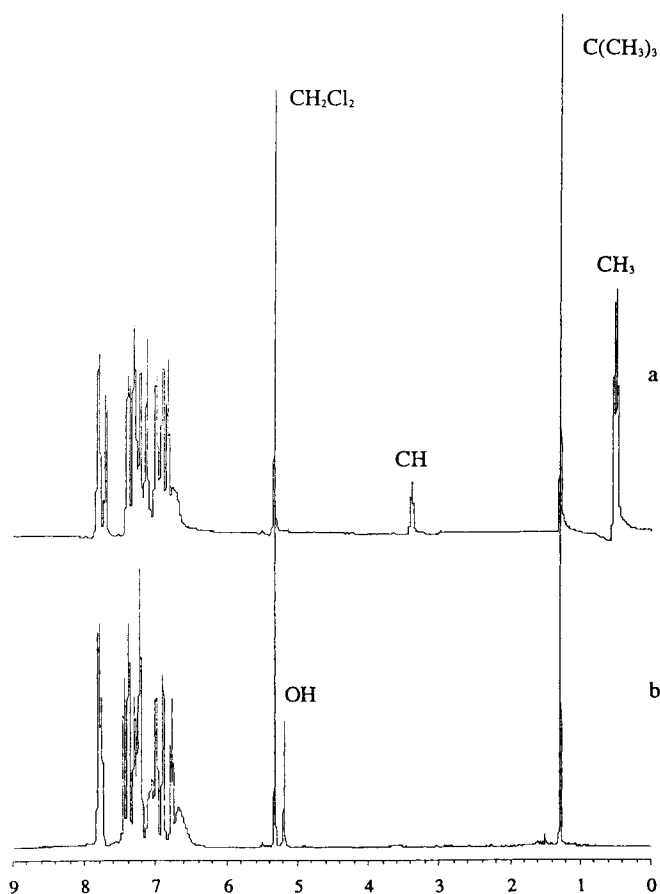**Figure 2.**   DSC traces of polymers: a) **XXIII**, b) **XXV**.
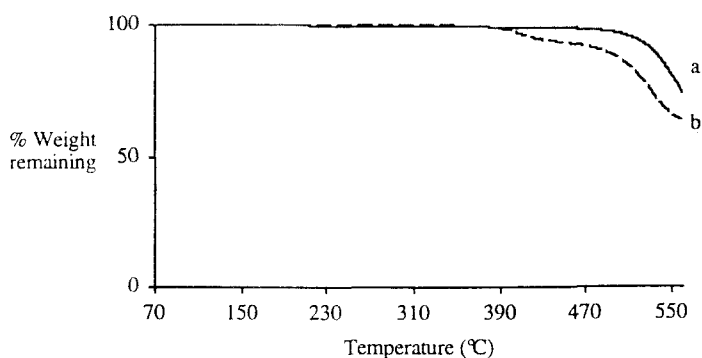
Figure 3.   TGA traces of polymers: a) **XXIII**, b) **XXV**.

that identical average numbers of repeats units were obtained for both polymers **XXIII** and **XXV** (Figure 4b).

Carbon-Oxygen Coupling in Reactions with Polymers

Two radical coupling procedures were examined. In the first procedure the redox polymer was generated by vigorously stirring polymer **XXIII** in chloro-benzene with Ag_2O at room temperature for 48 hours. An intensely red redox polymer which exhibits two bands in the UV visible spectrum at 288 nm (ε = 6.33×10^4 M^{-1} cm^{-1}) and 526 nm (ε = 2.69×10^4 M^{-1} cm^{-1}) was isolated. It was reacted with **XX** at 70°C and at a concentration of 0.04 M, which was determined to be the optimal conditions based on model reactions. After 24 hours, the dark red color associated with the radical species disappeared. Based on ^{1}H NMR only the
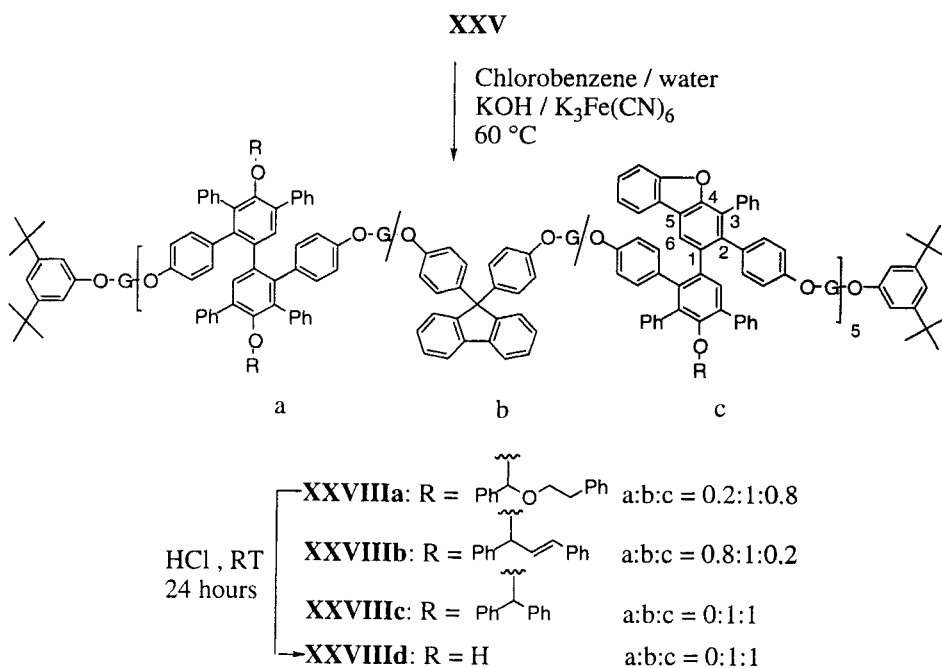
Figure 4.   ¹H NMR spectrum of polymers: a) **XXIII**, b) **XXV**.

original polymer was isolated. In an attempt to enhance the C-O coupling reaction, KOH was added to the reaction mixture. The addition of base was shown to accelerate the coupling reaction in the model reaction of **XXVI** with the biphenoxy radical **XXI**. In this case, the polymer precipitated out of solution and was insoluble in common organic solvents and acids. Since the original polymer is soluble in common organic solvents and these low molecular weight polymers are end capped with 3,5-di-t-butylphenol no reaction involving the extension of the polymer chain is possible. When this polymer was treated with a strong acid the polymer still remained insoluble, suggesting that the insolubility was not due to C-O coupling alone which leaves the formation of biphenol and dibenzofuran moieties as possibilities.
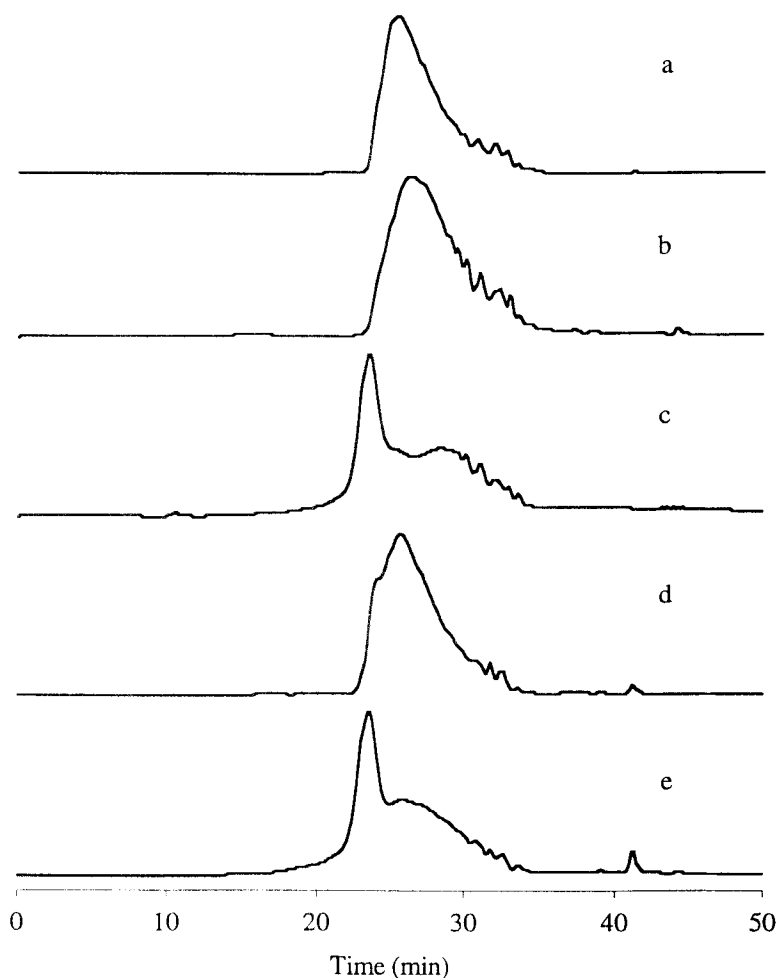
Figure 5.   GPC curves of polymers: a) **XXIII**, b) **X X V**, c) **XXVIIIa**, d) **XXVIIIb**, e) **XXVIIIc**.

Polymer **XXV** (100 mg) was dissolved in 3 ml of chlorobenzene and treated with 3 ml of a 0.75 M aqueous solution of KOH/K3Fe(CN)6, and heated to 70°C for 24 hours. the organic layer which remained dark red in color, was extracted, and treated with a few drops of hydrazine monohydrate. An insoluble suspension was observed, and 27 mg of the insoluble material was isolated. These results were further confirmed by heating the redox polymer from **XXIII** in the DSC and TGA instruments at a heating rate of 20°C per minute up to 400°C. An exothermic peak at 221°C and a shoulder at 254°C were observed in the DSC scan.

XXV

Chlorobenzene / water
KOH / K$_3$Fe(CN)$_6$
60 °C

a   b   c

HCl , RT
24 hours

XXVIIIa: R = Ph $\overset{O}{\underset{}{}}$ O Ph   a:b:c = 0.2:1:0.8

XXVIIIb: R = Ph Ph   a:b:c = 0.8:1:0.2

XXVIIIc: R = Ph Ph   a:b:c = 0:1:1

XXVIIId: R = H   a:b:c = 0:1:1

SCHEME 6

The residue in the pan was colorless as expected from previous model reactions and it was insoluble in chloroform. In model reactions with the biphenoxy radical from **XXI** three products are obtained, the biphenol, the bisdibenzofuran and the molecule with one phenolic group and one dibenzofuran group. Since this is a very high yield reaction it follows that the introduction of these groups into the polymer during the attempted C-O coupling reactions should also result in an insoluble polymer by increasing the rigidity of the polymer.

An alternative coupling reaction procedure was next studied. Polymer **XXV** was dissolved in chlorobenzene and oxidized with a 0.77M aqueous solution of KOH and K$_3$Fe(CN)$_6$ at room temperature to the corresponding redox polymer. This was followed by a coupling reaction with activated methylene groups **XX**, **XXVI, XXVII** (Figure 1) at 60°C for 18 hours. The products were isolated by precipitation in methanol to give **XXVIIIa-c** in 53% to 79% yield (Scheme 6). In the synthesis of polymers **XXVIIIa,c** insoluble products were obtained which explains the lower yields compared to polymer **XXVIIIb** which remained completely in solution. Proton NMR analysis showed that only polymer **XXVIIIb** was converted in high yield (90%), while polymers **XXVIIIa,c** were converted in
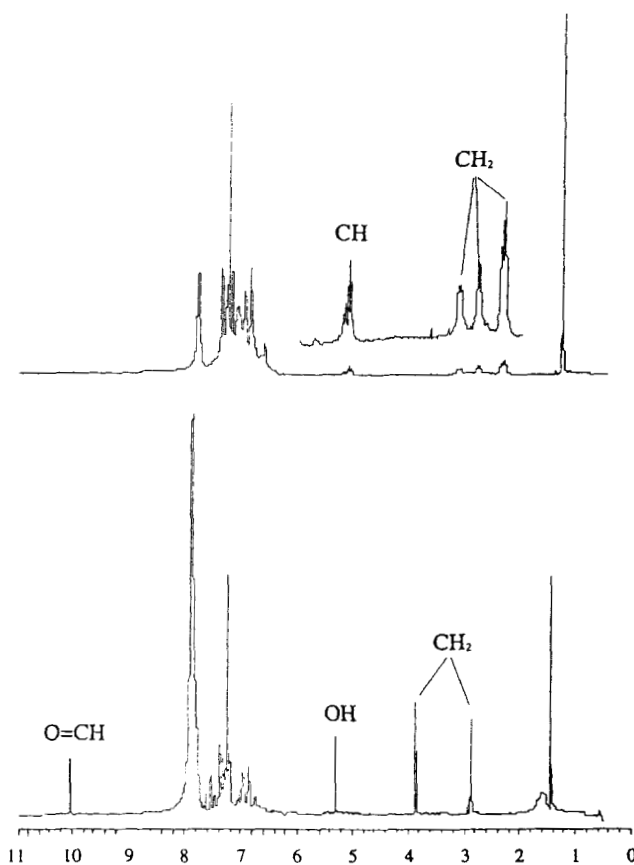
Figure 6. ^{1}H NMR spectra of a) polymer **XXVIIIa** in CDCl$_3$, b) polymer **XXVIIIa** in CDCl$_3$ treated with 1 drop of HCl.

60% (Figure 2a) and 46% yield, respectively. The lower reactivity of monomers **XX** and **XXVII** might be due to the higher energy required to abstract the methylene proton [12] and steric hindrance, respectively. This would favor the formation of the dibenzofuran derivative through an intramolecular cyclization reaction, which is known to occur with these hindered phenoxy radicals. [11] As a result, the number of reactive sites would be reduced.

Even with the low conversion due in part to the polymer coming out of solution, we were still interested in determining if these polymers were recyclable. The ^{1}H NMR spectrum (Figure 6b) of polymer **XXVIIIa** treated with 1 drop of HCl clearly shows the cleavage of the acetal functionality by the presence of the

phenolic hydroxy peak at 5.19 ppm, the aldehyde peak of benzaldehyde at 10.02 ppm and the methylene peaks of phenethyl alcohol at 2.88 and 3.85 ppm.

Polymer **XXVIIIa** was dissolved in chloroform and treated with concentrated HCl and stirred at room temperature for 24 hours. The regenerated hydroxy polymer **XXVIIId** was recovered in 84% yield, and only 57% of the phenolic hydroxy groups remained, which is consistent with the results obtained previously with the carbon-oxygen coupled polymer **XXVIIIa**. The absence of any other peaks besides the aromatic and hydroxy peaks in the ^{1}H NMR suggests that the intramolecular cyclization to the dibenzofuran derivative has occurred. Polymer **XXVIIId** was then reoxidized under similar conditions as previously described and coupled with **XXI** to give the carbon-oxygen coupled polymer in 33% yield. A 50% conversion was obtained based on the ^{1}H NMR results. In this case, a lower yield compared to the original coupling reaction was obtained because more of the polymer precipitated out of solution. This suggests that the higher concen-tration of the dibenzofuran moiety in the polymer chain might lower the solubility of the polymer and would possibily explain why in the reaction with the pregen-erated redox polymer the polymer comes out of solution and does not redissolve under acid conditions.

Theoretically, one would have expected approximately 36% conversion and not 50% based on the previous results. Since the reactivity of monomer **XXVII** remains the same, one possibility is that the oxidation potential of the phenoxy radical in polymer **XXVIIId** is lower than in the original polymer **XXV**. In polymer **XXVIIId**, the dibenzofuran groups force the pendent phenyl group at the 5 position to be planar and conjugated with the biphenyl moiety. The phenyl group becomes more electron donating than in the original polymer thus lowering the oxidation potential to a level where the rate of abstraction of the methylene protons (D°_{298} = 79 to 93 kcal/mol) [12] is faster than the abstraction of aromatic protons (D°_{298} = 111 kcal/mol) [12] .

CONCLUSION

A novel redox polymer containing hindered biphenol moieties in the back-bone has been synthesized for use as a polymeric reagent for the oxidative conversion of activated methylene groups to either their alcohol or aldehyde derivatives. Because the biphenol moiety is in the backbone of the polymer chain the side reactions which occur, which we believe is principally an intramolecular reaction to give dibenzofuran groups, result in a more rigid system which makes the

resulting polymers insoluble. Future work will concentrate on the synthesis of more stable phenoxy radicals and the incorporation of the biphenol groups in side chains rather than in the backbone to avoid the conformational changes which make the polymer insoluble.

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REFERENCES

[1]   R. B. Merrifield, *J. Am. Chem. Soc., 85*, 2149 (1963).

[2]   M. Mutter, H. Hagenmaier, and E. Bayer, *Angew. Chem. Int. Ed., 10,* 811 (1971).

[3]   N. K. Mathur and R. E. Williams, *J. Macromol. Sci.-Rev. Macromol. Chem., C15,* 117 (1976).

[4]   N. K. Mathur, C. K. Narang, and R. E. Williams, *Polymers as Aids in Organic Chemistry;* Academic Press Inc., New York, 1980.

[5]   H. G. Cassidy and K. A. Kun, *Oxidation - Reduction Polymers (Redox Polymers),* John Wiley & Sons, New York, 1965.

[6]   G. Manecke, C. Bauer, and C. Reich, *Angew. Chem., 62,* 646 (1959).

[7]   H. N. DeCarvalho, W.-G. Kim, and A. S. Hay, *J. Macromol. Sci., Pure & Appl. Chem., A30,* 385 (1993).

[8]   K. Dimroth, *Top. Curr. Chem., 129, 99* (1985).

[9]   G. Barbiero and A. S. Hay, *Tetrahedron Lett., 34,* 6199 (1994).

[10]   G. Barbiero and A. S. Hay, *Tetrahedron Lett., 35,* 5833 (1994).

[11]   W.-G. Kim, *Synthesis and Properties of Novel Thermally Stable Polymers* 1-219 (McGill University, Montreal, 1992).

[12]   R. C. Weast, *Handbook of Chemistry and Physics,* 68th Ed., CRC Press, Boca Raton, Florida, 1987-1988.