

Linear Soluble Polybenzyls

ABHIJIT SOM, S. RAMAKRISHNAN

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 29 January 2003; accepted 10 May 2003

ABSTRACT: Linear soluble polybenzyls, although deceptively simple in structure, have been strangely elusive. We report for the first time the synthesis of perfectly linear soluble polybenzyls by the polycondensation of 1,2,4,5-tetrasubstituted benzenes with formaldehyde using CHCl_3 /trifluoroacetic acid (TFA) as the medium, wherein TFA served both as an acidic catalyst as well as a cosolvent. The number-average molecular weights (M_n 's) of the polymers, as determined by gel permeation chromatography, varied from about 1000 to 37,000, depending on the nature of the substituent on the benzene ring; M_n was highest when all four substituents were alkoxy groups and was lowest when they were all alkyl groups. This correlated well with susceptibility of the aromatic ring toward electrophilic aromatic substitution, which is the underlying polymerization mechanism. Differential scanning calorimetry of the polymers showed that most of the samples were amorphous with glass-transition temperatures ranging from about -80° to $+80^\circ \text{C}$, whereas a few that were either symmetrically substituted or possessed a long alkyl substituent were partially crystalline. Preliminary studies suggested that the methylene unit linking the phenyl rings in these polybenzyls could be readily oxidized to generate conjugated polymers that may be perceived as carbon analogues of polyaniline–poly(arylmethine)s. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 2345–2353, 2003

Keywords: conjugated polymers; Friedel–Crafts polycondensation; linear poly(benzyl)s

INTRODUCTION

Polybenzyls¹ belong to a class of polymers having an alternating sequence of phenylene and methylene units. Because of their hydrophobic and thermally stable nature, these polymers are projected as promising materials for water-resistant and heat-resistant applications such as in coatings of permanent implants, packaging applications in microelectronics,^{2–5} and as a low dielectric constant material in future generation microprocessors wherein reduction of cross-talk noise and propagation delay are of paramount impor-

tance. Despite their deceptively simple structure, attempts to prepare soluble linear, high-molecular-weight polybenzyls, which span from the mid-19th century to date, have proven to be rather elusive.⁶ Most reported synthetic strategies have used Friedel–Crafts-type polycondensation. Very often, this type of an approach leads to branching and crosslinking. To suppress chain branching, conditions such as very low temperatures and/or the use of α -methyl-substituted derivatives⁷ have been applied. A few other approaches to polybenzyls, such as reductive coupling⁸ and ring-opening polymerization,⁹ have also been explored with limited success. A method with montmorillonite K10 as the Friedel–Crafts catalyst to get polybenzyls has been reported,¹⁰ but the resulting polymers were only partially soluble in common organic solvents, although the backbone was de-

Correspondence to: S. Ramakrishnan (E-mail: raman@ipc.iisc.ernet.in)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 2345–2353 (2003)
© 2003 Wiley Periodicals, Inc.

signed to contain alternating meta-para linkages for enhanced solubility.

Chen et al.¹¹ synthesized various analogous soluble methine-substituted poly(heteroarylene methine)s by condensation of thiophene with benzaldehyde derivatives, using catalysts like POCl₃ or sulfuric acid. The high reactivity of thiophene and the very selective reaction at the 2- and 5-positions of the thiophene ring were key elements that led to the successful preparation of moderately high-molecular-weight polymers. Thiophene methanol¹² and furfuryl alcohol and their derivatives¹³ have also been polymerized by self-condensation under similar reaction conditions. Such approaches, however, fail to yield structurally well-defined polymers when attempted with benzene analogues, which typically give lower-molecular-weight polymers that are often highly branched. For instance, benzyl alcohol gives mainly trimers when treated with SnCl₄.¹⁴ This can be attributed to the lower reactivity and multiple positions of attack on the phenyl ring. Friedel-Crafts-type electrophilic aromatic substitution reactions have been used both as a polycondensation process for the synthesis of polymers, as polyketones and polysulfones,¹⁵⁻¹⁸ and as an effective method for the modification of preformed polymers, such as styrene.^{19,20}

One approach to ensure the formation of linear polybenzyls is to use tetrasubstituted benzene derivatives as monomers. Earlier attempts with Durene as one such monomer, however, have led to an insoluble polymer suggesting that the methyl groups were not adequate to induce solubility.²¹ The introduction of longer lateral substituents is expected to enhance the solubility. Recently, we prepared several 1,2,4,5-tetrasubstituted benzene derivatives that served as monomer intermediates for the preparation of polyethers via a novel melt-transesterification process developed in our laboratory.²² Attempts to condense these tetrasubstituted benzene derivatives with benzaldehyde failed to yield the desired polymers, possibly because of steric constraints. The use of a sterically less-demanding aldehyde, such as formaldehyde, it was reasoned, could lead to successful polymerization. Cyclotetrameratrylenes, which are cyclic analogues of polybenzyls, are readily prepared via the self-condensation of 3,4-dialkoxybenzyl alcohols in the presence of trifluoroacetic acid (TFA), with dichloromethane as a solvent.²³ To adapt this approach to polybenzyl preparation, a suitable medium that will retain both the monomers as well as polymers in solution

during the course of polymerization is essential, we chose a TFA/CHCl₃ mixture. With this approach, we report the synthesis and structural characterization of a variety of soluble high-molecular-weight polybenzyls on the basis of a range of tetrasubstituted benzene derivatives.

EXPERIMENTAL

Measurements

¹H and ¹³C NMR spectra were recorded on a Bruker ACF 200-MHz spectrometer. ¹H acquisitions were done in CDCl₃ with a 10-s delay. For C-H decoupled ¹³C spectra, chloroform was used as a solvent with an external D₂O lock. Thermal analyses were carried out on Rheometric Scientific DSC Plus. The instrument was calibrated with indium, tin, and lead standards. Typically, about 10 mg of the sample were taken in an aluminum pan, and the thermograms were recorded under a dry N₂ purge (at 5 mL/min). The molecular weights were measured with a gel permeation chromatography (GPC) setup consisting of a Waters inline degasser, Waters 515 pump, Rheodyne injector, 2 PL mixed-bed columns in series, and a Viscotek 150 T triple-detector array, which consisted of RALLS, a differential viscometer, and refractive-index detectors in series. The columns and the detectors were maintained at 40 °C, and toluene was used as the eluent. A 10-point Universal calibration curve was constructed with narrow polystyrene standards. TRISEC software (Viscotek) was used to calibrate and analyze the data with universal calibration. Bruker Fourier transform infrared was used for the IR data, where the sample was in the form of a KBr pellet and a background measurement was done on a pure KBr pellet. A Hitachi spectrophotometer was used to record the ultraviolet-visible (UV-vis) absorption spectra with chloroform as the solvent. Elemental analysis was done in a Heraeus CHN-O-Rapid machine.

Materials

1,2,4,5-Tetramethylbenzene, 2,5-dihydroxybenzoquinone, 2,5-dimethylphenol, TFA, and 1,2,4-trimethylbenzene were purchased from Aldrich Chemical Co. and used directly without further purification. All solvents were purified/dried by standard procedures. *Para*-formaldehyde (95%) was purchased from Sarabhai Chemicals (India)

and used as such. 1,4-Dimethoxy-2,5-dimethylbenzene,²² 2,5-dimethylhydroquinone,²² and 1,2,4,5-tetramethoxybenzene²⁴ were prepared according to the reported procedures. The latter was purified over a silica gel column with petroleum ether as the eluent, followed by recrystallization from methanol. Purity was checked by elemental analysis.

1,4-Dibutoxy-2,5-dimethylbenzene

About 0.6 g of NaOH was dissolved in 15 mL of ethanol by warming under a dry N₂ jacket. Approximately 0.95 g of 2,5-dimethyl hydroquinone was dissolved in 20 mL of ethanol and added to the NaOH solution, and the contents were refluxed for 2 h. Twenty grams of butyl bromide were then added, and refluxing was continued for an additional 48 h. Ethanol was removed with a rotary evaporator, the residue then taken up in ethyl acetate, and the resulting solution was washed with 2% NaOH solution followed by water. The crude product obtained after removal of the solvent was loaded on a silica column and eluted with pet ether. The first fraction was collected. Yield: 0.77 g (46%); mp: 42–44 °C.

¹H NMR (CDCl₃) δ (ppm): 6.54 (s, 2H), 3.84–3.88 (t, 4H), 2.14 (s, 6H), 1.69–1.78 (m, 4H), 1.46–1.56 (m, 4H), 0.95–1.0 (t, 6H). ELEM. ANAL. Calcd. C, 76.75%; H, 10.46%. Found: C, 75.98%, H, 10.83%.

1,4-Dioctyloxy-2,5-dimethylbenzene

A similar procedure as mentioned previously was followed, except that bromooctane was used instead of bromobutane. Yield: 70%; mp: 61–63 °C.

¹H NMR (CDCl₃) δ (ppm): 6.63 (s, 2H), 3.85–3.91 (t, 4H), 2.16 (s, 6H), 1.71–1.79 (m, 4H), 1.29–1.44 (m, 20H), 0.85–0.88 (t, 6H). ELEM. ANAL. Calcd. C, 79.49%; H, 11.67%. Found: C, 79.03%; H, 11.12%.

1,4-Dibutoxy-2,5-dimethyl-6-methoxymethylbenzene

About 2.9 g of 1,4-dibutoxy-2,5-dimethyl benzene were dissolved in 10 mL of dioxane and taken along with 10 mL of concentrated HCl and 10 mL of aqueous formaldehyde solution (37 wt %) in a round-bottom flask. The contents were stirred under a HCl gas purge for 12 h, with an additional charge of formaldehyde solution (10 mL) being made after 1 h. The HCl purge was then stopped, an additional 30 mL of HCl were added, and the

stirring was continued for another 12 h. The yellowish oil that separated out of the mixture was extracted with chloroform, separated, washed with water, dried over Na₂SO₄, and concentrated to yield the product oil. The oil was directly treated with excess sodium methoxide in 30 mL of methanol and refluxed overnight. The reaction mixture was poured in water, extracted in ether, and the extract was washed with water, dried over Na₂SO₄, and evaporated. The crude product was loaded on a silica gel column and eluted in a pet ether–chloroform mixture, and the pure product was collected as the second fraction in the form of a colorless oil. Yield: 1.2 g (37%).

¹H NMR (CDCl₃) δ (ppm): 6.62 (s, 1H), 4.47 (s, 2H), 3.92–3.86 (t, 2H), 3.76–3.70 (t, 2H), 3.4 (s, 3H), 2.24–2.21 (d, 6H), 1.81–1.71 (m, 4H), 1.57–1.47 (m, 4H), 1.02–0.92 (m, 6H).

3,6-Bis(hydroxymethyl)-1,2,4,5-tetramethylbenzene

About 9.75 g of 3,6-bis(chloromethyl)-1,2,4,5-tetramethylbenzene²² were reacted with 30 g of sodium acetate in 150 mL of acetic acid under reflux conditions for 36 h and then poured into water to yield a white precipitate (9 g). Approximately 4.5 g of this product were treated with 6.2 g of sodium hydroxide in 100 mL of water for 15 h. A white precipitate that comes out from the reaction mixture was collected and purified by sublimation under reduced pressure. Yield: 1.2 g.

¹H NMR (CDCl₃) δ (ppm): 4.5 (s, 4H), 2.35 (s, 12H). ELEM. ANAL. Calcd. C, 74.19%; H, 9.34%. Found: C, 74.13%; H, 9.44%.

1,4-Dibutoxy-2,5-dimethoxybenzene

2,5-Dibutoxy hydroquinone was synthesized according to a reported procedure.²⁵ About 1.8 g of it were dissolved in 50 mL of ethanol, and 10 mL of Me₂SO₄ and 50 mg Na₂S₂O₄ were added to it and the contents stirred. To the homogeneous solution, an aqueous NaOH solution (5 g in 40 mL) was added dropwise. After stirring at room temperature for 30 min, the ethanol was removed with a rotary evaporator, and the residue was extracted with ether. The ether layer was then dried over anhydrous Na₂SO₄ and concentrated to yield an oily residue, which was loaded on a basic alumina column and eluted with pet ether. The product was collected as the first fraction. Yield: 1.58 g (80%); mp: 36–38 °C.

¹H NMR (CDCl₃) δ (ppm): 6.59 (s, 2H), 3.93–4.00 (t, 4H), 3.82 (s, 6H), 1.71–1.82 (m, 4H), 1.43–

1.54 (m, 4H), 0.93–1.00 (t, 6H). ELEM. ANAL. Calcd. C, 68.05%; H, 9.28%. Found: C, 68.86%; H, 8.78%.

1,4-Didodecyloxy-2,5-dimethoxybenzene

2,5-Didodecyloxy hydroquinone was made according to a reported procedure.²⁵ About 1.4 g of this were dissolved in 100 mL of ethanol containing 2 mL of Me₂SO₄ and 50 mg of sodium dithionite. An aqueous NaOH solution (0.8 g in 10 mL) was then added dropwise, and the reaction was left stirring for 30 min. The ethanol was removed with a rotary evaporator, and the residue was extracted with ether. The ether layer was then dried over anhydrous Na₂SO₄ and concentrated to yield an oily residue, which was loaded on a basic alumina column and eluted with pet ether. The product was collected as the first fraction. Yield: 0.81 g (55%); mp: 57–58 °C.

¹H NMR (CDCl₃) δ (ppm): 6.59 (s, 2H), 3.92–3.99 (t, 4H), 3.82 (s, 6H), 1.71–1.85 (m, 4H), 1.26–1.5 (m, 36H), 0.84–0.91 (t, 6H). ELEM. ANAL. Calcd. C, 75.83%; H, 11.53%. Found: C, 75.87%; H, 12.18%.

1,2,4-Trimethyl-5-hexylbenzene

Nine grams of 1,2,4-trimethyl benzene were taken in 25 mL of cyclohexane with 15.3 g of AlCl₃ and cooled to 0 °C. Twelve grams of hexanoyl chloride were added dropwise to it, and the contents were stirred for 1 h. The reaction mixture was poured in 1:1 aqueous HCl and extracted with cyclohexane. The volatiles were first removed by distillation, and the residue was distilled under reduced pressure. The product was collected as the second fraction at 180 °C (at 10 Torr). Yield: 15 g (97%). The ketone was reduced to give the monomer in 82% yield by following the mixed hydride reduction procedure.²⁶

¹H NMR (CDCl₃) δ (ppm): 6.90 (s, 2H), 2.46–2.557 (t, 2H), 2.2–2.23 (d, 9H), 1.32–1.55 (m, 8H), 1.32 (t, 3H).

Typical Polymerization Procedure

About 0.3 g of the appropriate monomer and an equimolar amount of *para*-formaldehyde (95%) were taken in a 10-mL round-bottom flask fitted with a condenser and a gas inlet/outlet and purged with dry N₂ for 30 min. One milliliter of TFA and 1 mL of dry chloroform were added to it and set for reflux. After 36 h, the mixture was poured in methanol. The precipitate was filtered, dissolved in minimum volume chloroform, and

reprecipitated in methanol. After filtration the polymer sample was dried *in vacuo*. Typical yields ranged between 60 and 70%.

Polymerization of 1,4-Dibutoxy-2,5-dimethyl-6-methoxymethylbenzene

About 0.3 g of the monomer was taken in a polymerization tube fitted with a condenser and a gas inlet/outlet and purged with dry N₂ for 30 min. One milliliter of TFA and 1 mL of dry chloroform were added to it and set for reflux. After 36 h, the mixture was poured into methanol. The precipitate was filtered, dissolved in minimum volume chloroform, and reprecipitated in methanol. After filtration the polymer sample was dried. Yield: 100 mg (33%). The ¹H NMR spectrum of the polymer was identical to that of sample 3.

Polycondensation of 3,6-Bis(hydroxymethyl)-1,2,4,5-tetramethylbenzene with Thiophene

Approximately 0.31 g of the bis(hydroxymethyl) monomer and 0.135 g of thiophene were taken in a constricted tube, and 1 mL of dry chloroform and 1 mL TFA were added. After several freeze-pump-thaw cycles, the tube was sealed *in vacuo*. The sealed tube was kept for polymerization at 90 °C for 36 h with occasional agitation to ensure homogeneous mixing of the contents. The seal was broken, and the polymer was isolated by precipitation in methanol and further purified by an additional dissolution-precipitation process. Yield: 250 mg (60%).

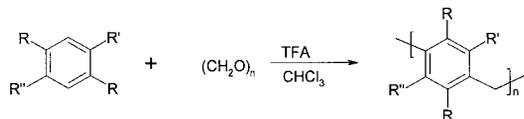
RESULTS AND DISCUSSION

As stated previously, one of the approaches to obtain well-defined linear polybenzyls would be to use 1,2,4,5-tetrasubstituted benzene derivatives. Previous efforts²¹ with Durene, the simplest of such monomers, resulted in a completely insoluble polymer. To obtain polybenzyls with improved solubility, we prepared three types of tetrasubstituted benzene monomers (see Scheme 1) having side groups of varying types and different lengths.

The first type had all four substituents as alkyl groups (**1** and **5**) yielding purely hydrocarbon polymers; the second type had two methyl groups and two alkoxy groups (**2–4**), whereas the third had four alkoxy substituents (**6–8**). Thus, the role of steric and electronic effects as well as substituent chain length on the polymerization behavior and on the properties of the resulting polymers

was probed. Condensation of the tetrasubstituted benzene monomers was carried out under dry nitrogen atmosphere, with TFA both as a catalyst and as a solvent, along with dry chloroform as a cosolvent. A ratio of 1:1 TFA:chloroform (v/v) was most suitable—at higher TFA concentrations increased discoloration of the polymers was noticed. Typically, the polymerizations were allowed to proceed for 36 h, after which the polymerization mixture was poured into methanol. In most cases, the polymers were isolated as white powdery material, except in the cases of **5** and **8**, which were obtained as sticky material. All the polymers were purified by reprecipitating from chloroform–methanol. Polymer **1** was insoluble and precipitated out of the reaction mixture within 15 min, whereas polymer **2** had poor solubility—the soluble fraction was of low molecular weight as evident from the end-group signal intensity in its NMR spectrum. All the other polymers were readily soluble in chloroform, toluene, chlorobenzene, and TFA, although their solubility in tetrahydrofuran was low.

The ^1H NMR spectra of three representative polybenzyls are displayed in Figure 1, and a complete listing of the peak positions and their assignment for all the polymers is provided in Table 1. In all cases, no significant peaks due to either of the possible end groups, namely the aromatic protons or benzylic protons, PhCH_2OH , were visible. The backbone benzylic protons that lie between two phenyl groups appeared around 4.2 ppm for tetraalkyl- and dialkoxy–dialkyl polymers (**3–5**), but they were slightly upfield shifted to 4.0 ppm for the more-electron-rich tetraalkoxy (polymers **6–8**). The integral intensities of the various peaks agreed with the expected values confirming the expected linear structures depicted in Scheme 1. These observations are further supported by their ^{13}C NMR spectra. In Table 2 all the ^{13}C NMR



Polymer	R	R'	R''
1	Me	Me	Me
2	Me	OMe	OMe
3	Me	OC4	OC4
4	Me	OC8	OC8
5	Me	Me	C6
6	OMe	OMe	OMe
7	OMe	OC4	OC4
8	OMe	OC12	OC12

Scheme 1

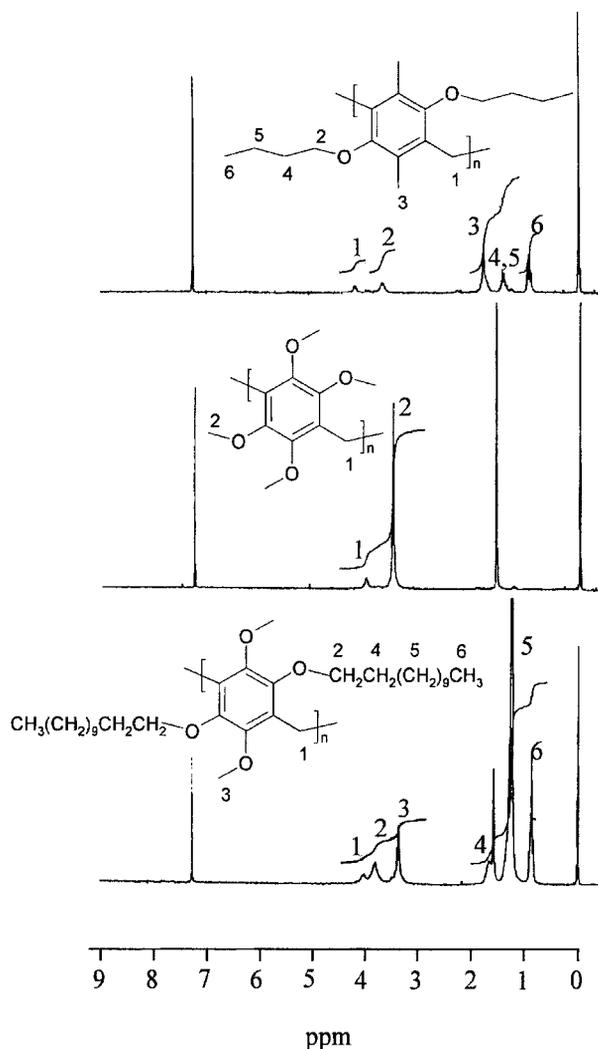


Figure 1. ^1H NMR spectra of representative polybenzyls; from top to bottom: samples **3**, **6**, and **8**, respectively.

peak positions and their assignments are provided. In all cases, the aromatic region exhibited only three signals, and these were assigned as indicated. Here again, no additional signals due to the end groups were evident.

GPC of the polymers was performed with a refractive-index and a differential viscosity detector in series, and the molecular weights were estimated with a Universal calibration curve on the basis of narrow polystyrene standards. A comparison of the molecular weights of the various polybenzyls (see Table 3) clearly brings out certain trends—one is that the tetraalkoxy derivatives yielded polymers of the highest molecular weights [with degrees of polymerization (DPs) in the range of 70]. The dialkoxy–dialkyl deriva-

Table 1. ^1H NMR Data

Polymer	Ar—CH ₂ —Ar	Ar—OCH ₂	Ar—OCH ₃	Ar—CH ₃	—(CH ₂) _n —	—CH ₃
3	4.2	3.68	—	1.79	1.79, 1.26–1.43	0.89–0.96
4	4.16	3.56	—	1.82	1.71, 1.26	0.86
5	4.16–4.23	—	—	2.56, 2.23, 2.0	1.3	0.88
6	4.0	—	3.51	—	—	—
7	4.01	3.82	3.36	—	1.62–1.66, 1.33–1.44	0.86–0.93
8	4.0	3.80	3.36	—	1.66, 1.24	0.83–0.89

tives, however, had significantly lower DP values in the range of 35–40, whereas the tetraalkyl derivatives yielded only oligomeric species. This variation in molecular weights is readily rationalized on the basis of the susceptibility of the different types of tetrasubstituted benzene monomers toward electrophilic aromatic substitution. The tetraalkoxy derivatives would be most susceptible, whereas the tetraalkyl derivatives would be the least. Any steric effect of lateral substituent chain length appears to be minimal as evident from the nearly similar values of DP when the chain length is varied within a given type of monomer. The decreased molecular weights thus reflect the slower rates of polymerization as we move from *tetra*-alkoxy to *tetra*-alkyl derivatives, under the selected polymerization conditions. Experiments were also conducted to follow the evolution of molecular weight with time, taking **6** as the representative polymer. As seen from Table 4, the optimum time for polymerization was found to be 36 h, beyond which there appears to be a slight reduction in molecular weight that is accompanied by an increase in the extent of discoloration. The polydispersity index in most cases, as expected, is around 2; a slightly lower value in some instances is possibly due to inadvertent fractionation during the purification

process. The molecular weights in most cases were significantly higher than those reported for similar systems, as well as those reported for polythiophene/bithiophene/terthiophene methines.¹¹ The high reactivity of the *tetra*-alkoxy monomers led to the formation of high-molecular-weight polymers even under relatively mild polymerization conditions. However, the use of a stronger acid catalyst may be required in the case of the *tetra*-alkyl derivative for the generation of high-molecular-weight polybenzyls. The polycondensation of the substituted aromatic monomers with formaldehyde, in the presence of TFA, would be expected to follow a mechanism similar to that proposed for phenol–formaldehyde condensation under acid-catalyzed conditions,²⁷ and the molecular weight development would follow the expected of typical step-growth polymerization processes (Carrother's equation). Decreasing molecular weights at longer polymerization times therefore suggests the occurrence of side reactions. One possible side reaction under protic acid-catalyzed conditions is the scrambling of the methyl (or benzyl) groups.^{28,29} Such a scrambling process could occur via an intermediate formed by the displacement of benzyl (or methyl) groups by the proton from the acid catalyst.³⁰ Such side reactions could lead to decreased molecular

Table 2. ^{13}C NMR Data

Polymer	C _{Ar} —O	C _{Ar} —C	C _{Ar} —CH ₂	Ar—CH ₂ —Ar	O—CH ₃	O—CH ₂	Ar—CH ₃	—(CH ₂) _n CH ₃
3	152.3	131.7	128.2	19.6	—	72.97	12.9	32, 14
4	151.8	131.2	127.6	22.2	—	72.8	12.4	25–31, 13.6
5	—	137.3, 136.1	127.9	19.5	—	—	12.8	35.3
		131.7	128.5	19.9			13.1	32.6
		130.2				—	16.2	14.1
							16.4	
6	147.7	—	127.4	19.5	59.7	—	—	—
7	147.8, 146.8		127.5	20.1	59.5	72.6	—	32, 13
8	147.8, 146.8		127.5	20.1	59.5	72.8	—	23–32, 14

Table 3. Molecular Weight Data

Polymer ^a	$M_n^b \times 10^{-3}$	$M_w \times 10^{-3}$	DP	Yield (%)
3	11.1	23.9	42	90
4	12.7	19.8	34	73
5	0.8	2.03	3	73
6	17.5	33.5	78	66
7	23.1	44.6	79	83
8	36.9	72.1	72	60

^a In all cases, the polymerization was carried out for 36 h.

^b By universal calibration.

weights as well as the formation of branched and possibly crosslinked products, especially if the extent of such processes is very high.

Thermal analyses of the polybenzyls were carried out by DSC, and the results are listed in Table 5. Polymers **3**, **4**, and **6** were crystalline as prepared and did not show any T_g , except when rapidly quenched from the melt. However, polymers **5**, **7**, and **8** were amorphous and did not exhibit a melting endotherm. Within a series, for instance, when comparing samples **6**, **7**, and **8**, the *tetra*-methoxy derivative **6** has the highest T_g and exhibits a melting transition. However, when two of the methoxy groups are replaced by longer alkoxy groups, the polymers become completely amorphous, and their T_g 's decrease with an increasing substituent chain length. Thus, it is apparent that by variation of the lateral substituent in polybenzyl derivatives, both the T_g and the crystallization propensity can be readily varied.

One other interesting aspect of polybenzyls is that they can be viewed as carbon analogues of the completely reduced form of polyaniline, the leucoemeraldine form. When viewed in this context, it becomes interesting to pose the question as to whether these polybenzyls could be readily oxidized to generate the fully oxidized pernigraniline analogue of polyaniline. As synthesized, these polybenzyls are almost white in color and have no significant absorption in the visible re-

Table 4. Molecular Evolution in Case of Polymer 6

Polymerization Time (h)	M_n
12	5,378
24	7,196
36	16,270
51	13,080

Table 5. Thermal Data

Polymer	T_g (°C)	T_m (°C)	T_d (°C) ^a
2	—	—	270
3	77	292	260
4	3	250	—
5	-6	—	—
6	150	315	315
7	53	—	250
8	-79	—	—

^a Onset of degradation.

gion confirming the absence of conjugation. Preliminary attempts to oxidize the polymer suggested that oxidation was indeed feasible. The oxidation of polymer **3** was carried out with various oxidizing agents such as DDQ, FeCl₃, and AgO. In all cases, the UV-vis spectra (Fig. 2) underwent a noticeable change, and two peaks at 811 and 911 nm reminiscent of the polaronic and bipolaronic bands in other conjugated polymers were evident.³¹ As the ambient stability of the oxidized forms may be low, further detailed investigations under stringent inert atmosphere are now underway to establish the exact nature of the oxidized species and to investigate their electronic properties.

Instead of A-A + B-B type polycondensation, we also synthesized an AB-type monomer (Scheme 2), which was polymerized by self-condensation to give **3a**. Here again, the condensa-

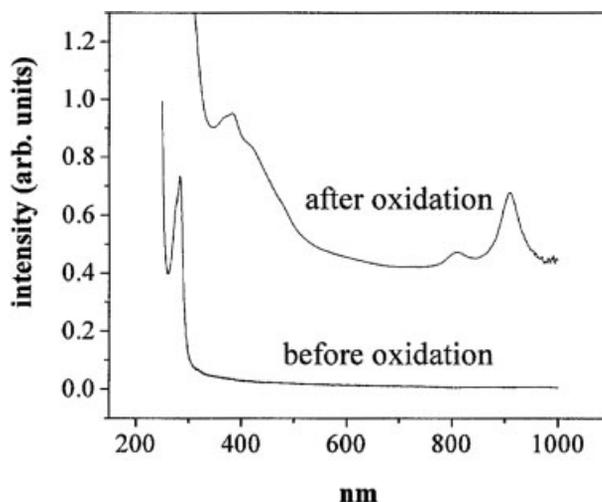
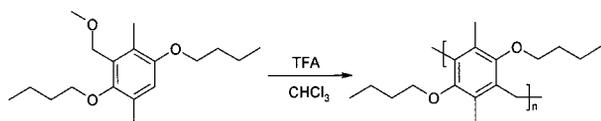


Figure 2. UV-vis spectra of polybenzyl (**3**) before and after oxidation with DDQ. The latter is the y axis shifted for clarity.



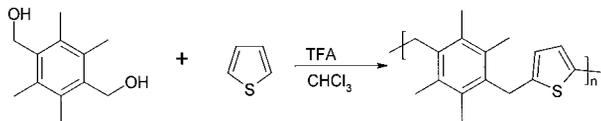
Scheme 2

tion occurred by a similar Friedel–Crafts alkylation process as before, but in this case with an exclusion of methanol.

The NMR spectra of **3a** was essentially identical to that of **3** (with no visible end-group signals) and so was its molecular weight [number-average molecular weight (M_n) = 4.5 kD, weight-average molecular weight (M_w) = 9.0 kD]. Despite the more cumbersome monomer synthesis, the self-condensation approach provided no specific advantage over the simpler direct condensation route with *para*-formaldehyde. However, this demonstration of self-condensation polymerization with a methoxymethyl derivative opens up the possibility of designing analogous AB_2 - and A_2B -type monomers for the preparation of analogous hyperbranched polybenzyls. The synthesis of such monomers and their polymerization is now in progress and will be reported elsewhere.

Copolymerization of bis(hydroxymethyl) durene with thiophene and bithiophene (Scheme 3) also leads to the generation of linear polymers of reasonable molecular weights (M_w ca. 10 kD).

These copolymers were also readily oxidized to the conjugated form by DDQ, as evident from their UV–vis spectra. The properties of the conjugated derivatives of both polybenzyls and poly(thiophene-durene methine)s are under investigation. These oxidized polymers, it may be expected, will provide access to low band-gap polymers that are similar to other systems reported previously.³²



Scheme 3

CONCLUSIONS

Soluble polybenzyls of moderately high molecular weights were readily prepared, with 1,2,4,5-tetra-

substituted benzenes as one of the monomers and *para*-formaldehyde as the other, under electrophilic aromatic substitution conditions with chloroform/TFA as the polymerization medium. The resulting polybenzyls were devoid of branching, and most of them were readily soluble in a variety of common organic solvents. The molecular weights were highest when the substituents on the phenyl ring were of an electron-donating nature, whereas only oligomers were obtained when they were simple alkyl groups, suggesting the much slower polymerization rates in the latter case. These linear soluble polybenzyls underwent oxidation readily to generate a backbone that can be perceived as a carbon analogue of the pernigraniline form of polyaniline. Studies to investigate the oxidation process and to understand the properties of these potentially low band-gap systems are now underway and will be reported.

The authors thank the Department of Science and Technology (New Delhi) and 3M India, Ltd. for the funding.

REFERENCES AND NOTES

1. Tsonis, C. P. *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., Eds.; Pergamon: 1989; Vol. 5, Chapter 26, pp 455–464.
2. Tsonis, C. P. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; pp 407–416.
3. Maier, G. *Prog Polym Sci* 2001, 26, 3–65.
4. Wang, Z.; Wang, H.; Mitra, A.; Huang, L.; Yan, Y. *Adv Mater* 2001, 13, 746–749.
5. Ito, Y. (Sumitomo Bakelite Co., Ltd., Japan). *Jpn Kokai Tokkyo Koho* 6.CAN 136:387141, 2002.
6. Kricheldorf, H. R.; Schwarz, G. In *Handbook of Polymer Synthesis*, Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Chapter 27, pp 1629–1711.
7. Chandler, J. E.; Johnson, B. H.; Lenz, R. W. *Macromolecules* 1980, 13, 377–380.
8. Klarner, C.; Greiner, A. *Macromol Rapid Commun* 1998, 19, 605–608.
9. Lim, K. T.; Choi, S. K. *J Polym Sci Part C: Polym Lett* 1986, 24, 645–647.
10. Baudry-Barbier, D.; Dormond, A.; Dumont, F.; Duriau-Montagne, F. *Chem Commun* 1998, 813.
11. Chen, W.; Jenekhe, S. A. *Macromolecules* 1995, 28, 454–464.
12. Stagnaro, P.; Costa, G.; Gandini, A. *Macromolecules* 2001, 34, 26–32.
13. Choura, M.; Belgacem, N. M.; Gandini, A. *Macromolecules* 1996, 29, 3839–3850.

14. Fournet, F.; Doucet, A.; Doucet-Baudry, G.; Janier-Dubry, J. *J Chem Res Synop* 1980, 91.
15. Udea, M.; Sato, M. *Macromolecules* 1987, 20, 2675–2678.
16. Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* 1993, 26, 6324–6329.
17. Shu, C.-F.; Leu, C.-M. *Macromolecules* 1999, 32, 100–105.
18. Parodi, F. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., Eds.; Pergamon: New York, 1989; Vol. 5, Chapter 33, pp 561–591.
19. Nasrullah, J. M.; Raja, S.; Vijayakumaran, K.; Dhamodharan, R. *J Polym Sci Part A: Polym Chem* 2000, 38, 453–461.
20. Raja, S.; Dhamodharan, R. *J Polym Sci Part A: Polym Chem* 2001, 39, 1203–1215.
21. Montaudo, G.; Bruno, G.; Maravigna, P.; Bottono, J. *J Polym Sci Polym Chem Ed* 1974, 12, 2881–2889.
22. Jayakannan, M.; Ramakrishnan, S. *Macromol Chem Phys* 2000, 201, 751–760.
23. Percec, V.; Cho, C. G.; Pugh, C. *J Mater Chem* 1991, 1, 217–222.
24. Benington, I.; Morin, R. D.; Clark, J. R. *J Org Chem* 1955, 20, 102–108.
25. Rodriguez, J. M.; Duran, R.; Wegner, G. *Macromolecules* 1989, 22, 2507–2516.
26. Nystrom, R.; Berger, C. R. *J Am Chem Soc* 1958, 80, 2896–2898.
27. Lin-Gibson, S.; Glass, T. E.; Shultz, A. R.; Riffle, J. S. *Polymer* 2002, 43, 2017–2029.
28. Brown, H.; Jungk, H. *J Am Chem Soc* 1955, 77, 5579–5584.
29. Sisido, K.; Udo, Y.; Nakamura, T.; Nozaki, H. *J Org Chem* 1961, 26, 1368–1371.
30. In a control reaction, bis(methoxymethyl)durene when treated with 25 wt % PTSA at 150 °C yielded oligobenzyl species. This process, we postulate, occurs via the displacement of the methoxymethyl group first by a proton, which further condenses to yield the oligobenzyl species.
31. Zagorska, M.; Pron, A.; Lefrant, S. *Spectroelectrochemistry and Spectroscopy of Conductive Polymers*. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, England, 1997; Vol. 4, pp 183–218.
32. Goto, H.; Akagi, K. *Synth Met* 2001, 119, 165–166.