at 60 °C. At specified intervals, one of the test tubes was taken out and cooled. The aqueous solution was separated from the insoluble material by decantation. The carboxylic acid content of the aqueous solution $[COOH]_{aq}$ was measured by UV spectroscopy using the absorption at 210 nm (ϵ = 71). The water-insoluble material was washed with water, dried under vacuum, and weighed. The number-average molecular weight was determined by gel permeation chromatography. The carboxylic group content of the water-insoluble material $[COOH]_{insol}$ was estimated from its weight and molecular weight assuming that an ester bond cleavage in the main chain produced one carboxylic group. The degree of hydrolysis (in percent) was represented as the percentage of the total moles of the liberated carboxylic groups ($[COOH]_{aq}$ + $[COOH]_{insol}$) to the moles of the monomeric unit in feed.

Acknowledgment. This research is one of a series of works of the U.S.-Japan Cooperative Science Program supported by the National Science Foundation, Division of Material Research, and the Japan Society for the Promotion of Science.

Registry No. 1, 100190-12-3; 1 (homopolymer), 100190-22-5; (1) (5) (copolymer), 107711-19-3; 3, 100762-90-1; 5, 107711-15-9; 5 (homopolymer), 107711-18-2; 6, 107711-21-7; 9, 100190-14-5; 10, 107711-16-0; *p*-TSA, 104-15-4; PF_5, 7647-19-0; BF_3OEt_2, 109-63-7.

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"Defect-Free", Crystalline Aromatic Poly(ether ketones): A Synthetic Strategy Based on Acetal Monomers

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ABSTRACT: A novel synthesis of high molecular weight, crystalline aromatic poly(ether ketone) 1 [poly(oxybenzophenone), mp 370 °C] has been developed which minimizes the introduction of chemical defects into the polymer backbone. Consequently, poly(ether ketone) **1K** exhibited higher crystallinity, as evidenced by modulus and thermal characteristics, than poly(ether ketones) prepared by direct methods. Solution and solid-state ^{13}C NMR spectra are consistent with a highly uniform para-oriented backbone and with the observed crystallinity. The synthetic strategy involved the preparation of an amorphous precursor poly(ketal ketone) (**3b**) under mild reaction conditions by nucleophilic displacement polycondensation of acetal monomer **2b** [2,2-bis(4-hydroxyphenyl)-1,3-dioxolane] with 4,4'-difluorobenzophenone at 150–220 °C in a dipolar aprotic solvent. Amorphous polymer **3b** was then quantitatively converted to high molecular weight, crystalline, insoluble poly(ether ketone) **1K** by acid-catalyzed hydrolysis under heterogeneous conditions. Reaction temperatures above the polymer T_g were required, which is consistent with a diffusion-limited reaction. Homogeneous hydrolysis in concentrated sulfuric acid (25 °C) was also effective. An improved synthesis of the novel cyclic acetals of 4,4'-dihydroxybenzophenone is also reported which employs a combination of glycol, trialkyl orthoformate, and montmorillonite clay catalyst. The acyclic dimethyl acetal monomer **2a** was found to be unsuitable for the polycondensation because it undergoes an unusual degradation under basic reaction conditions to a postulated quinone methide.

Introduction

The crystallinity of aromatic poly(ether ketones) imparts valuable characteristics, including excellent resistance to solvents, high melting points, and useful properties at temperatures exceeding 250 °C. However, because of their crystallinity and the resultant insolubility, these polymers are also difficult to prepare with sufficiently high molecular weights unless extreme conditions are used.

Friedel–Crafts polycondensations of carboxylic acids or acid chlorides in organic solvents or in polyphosphoric acid

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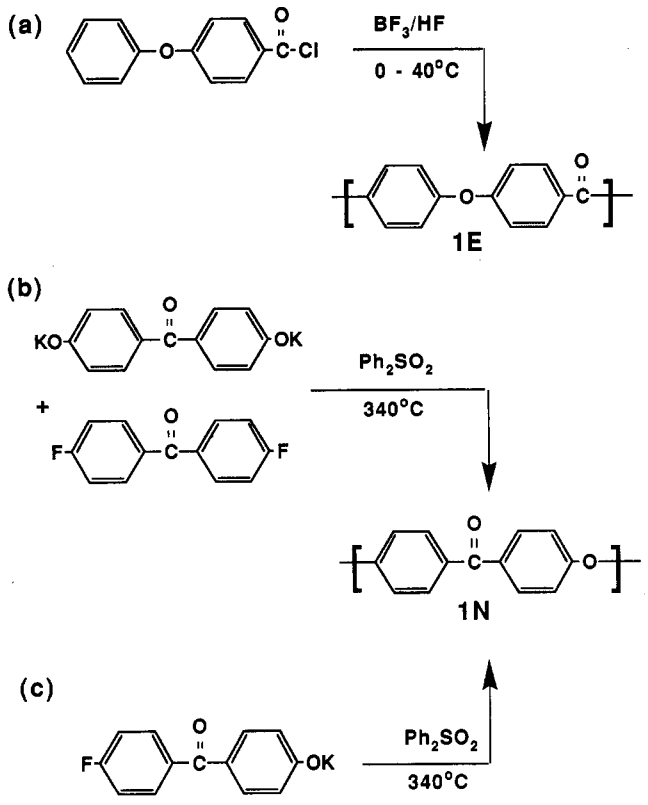
Scheme I



generally have produced low molecular weight aromatic poly(ether ketones).[1-3] Even in those instances where high molecular weights have been achieved,[4,5] the propensity for alkylation by the solvent[5] and the difficulty in removing the catalyst (e.g., $AlCl_3$)[4] would preclude isolation of pure aromatic polymer.

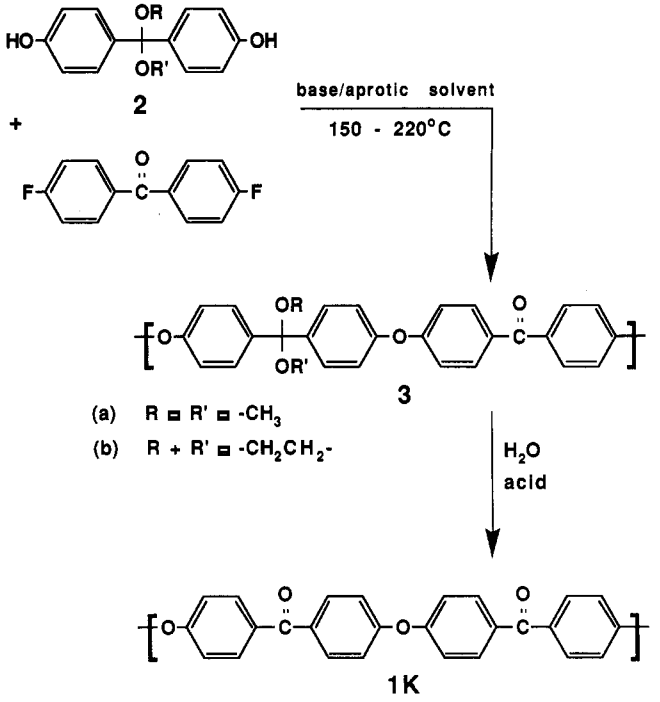
Marks[6] and Dahl[7] were able to prepare high molecular weight poly(oxybenzophenone) [poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene)] **1E** by using boron trifluoride catalyst and anhydrous hydrogen fluoride, one of the few room-temperature solvents for this polymer (Scheme Ia). Aside from the obvious practical limitations inherent with this process, it is doubtful that exclusive para substitution could occur. Some ortho substitution would be expected[8] and has been reported[9] to lead to 9-phenylxanthydrol end groups in similar systems.

Nucleophilic displacement polycondensations[10] in aprotic dipolar organic solvents can result in premature crystallization of high-melting poly(aryl ethers) when relatively low reaction temperatures, e.g., <250 °C, are used. Higher boiling solvents, such as diphenyl sulfone,[10a] can be used to prepare high molecular weight **1N** (parts b and c of Scheme I) under rather severe conditions (>330 °C).[11] Because the reaction mass may solidify at about 300 °C, isolation of the polymer involves tedious extractions of the ground reaction mixture to remove solvent and salt byproducts.

Such high reaction temperatures could be expected to lead to detrimental side reactions. Indeed, branching reactions were postulated[11] to account for gels, high UV absorbance, and lower toughness of **1N** prepared from fluorohydroxy monomer (Scheme Ic).

Korshak[12] has proposed that, with rare exceptions, most polymers contain some anomalous units or chemical "defects" which can alter or mask the true properties of the nominal polymer structure. Consequently, our understanding of the relationship between polymer structure and the properties of these structures may be inaccurate.

Scheme II



In the case of poly(ether ketone) **1**, it is doubtful that high molecular weight polymer consisting totally and entirely of para repeat units, as shown, and uncontaminated by branch points or other defects has been prepared by direct synthesis by either the electrophilic[1-9] (**1E**) or the high-temperature nucleophilic displacement[10,11] (**1N**) processes.

We report a novel strategy (Scheme II) for the synthesis of poly(oxybenzophenone) (**1**) in which a high molecular weight poly(ketal ketone)[13] (**3**) is prepared by nucleophilic displacement under moderate conditions from novel acetal monomers (**2**) and then converted quantitatively to crystalline poly(ether ketone) **1K**.[14] This strategy not only avoids many of the practical drawbacks of the prior direct processes[1-11] but also produces a polymer which exhibits enhanced properties indicative of a structure containing few, if any, isomeric or defect units.

Results and Discussion

The Ketal Strategy. Acetals are commonly used in chemical syntheses to protect or distinguish carbonyl groups.[15] For our purposes, the anticipated function of the acetal group was to disrupt the regularity of the polymer backbone to prevent crystallization.[16] The intermediate poly(ketal ketone) should be amorphous and, therefore, should exhibit enhanced solubility in organic solvents. Our strategy was to build in defects purposely to facilitate the backbone synthesis and then to remove them to obtain the desired properties (Scheme II).

The anticipated synthetic and practical advantages of this strategy were as follows: (a) common aprotic reaction solvents,[10] such as dimethylacetamide (DMAc), could be used because of the enhanced solubility of poly(ketal ketone) **3**; (b) modest reaction temperatures (150–220 °C) would minimize side reactions; (c) pure para-substituted monomers would virtually assure a linear para backbone structure under these milder conditions; (d) the reactivity of dihydroxybenzophenone acetal (**2**) should be enhanced compared to 4,4'-dihydroxybenzophenone because of the electron-donating ability of the acetal group in contrast to the electron-withdrawing carbonyl of DHBP, which reduces the nucleophilicity of the corresponding phenate

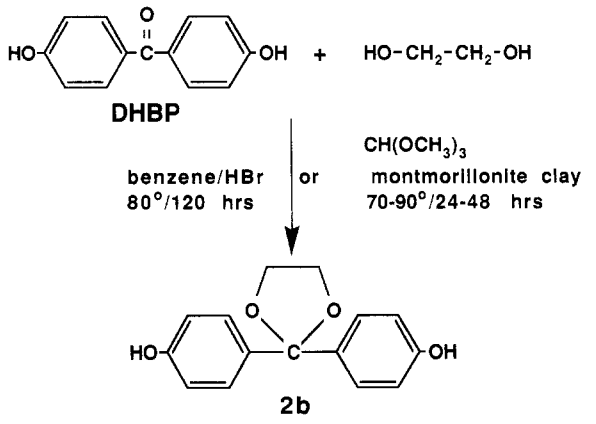
anion;[11] and (e) recovery and purification of soluble poly(ketal ketone) **3** should be relatively facile compared to the previous direct syntheses.[1-11] All of these advantages have been realized.

However, the success of this strategy depended on three key conditions: (1) synthesis of the acetals of 4,4′-dihydroxybenzophenone (DHBP), (2) stability of these acetal monomers under the polymerization conditions, and (3) *quantitative* conversion of the ketal groups to carbonyls in the final polymer.

Monomer Synthesis. 4,4′-Dihydroxybenzophenone (DHBP) proved to be a particularly recalcitrant substrate for formation of its acetal derivatives, which perhaps explains the absence of any prior literature references to these compounds. The electron-releasing para hydroxyls obviously aggravate the inherently low reactivity[15] of the diaryl ketone.

The dimethyl acetal of DHBP (**2a**) was prepared in modest yields by the classical method[15] with methanol, HBr catalyst, and excess trimethyl orthoformate. Conversion to >50% required over 24 h (as conveniently followed by the shifted A^2B^2 aromatic protons by NMR). The deactivating influence of the hydroxyl groups was reduced somewhat by first converting DHBP to its acetate diester, preparing the dimethyl ketal under similar conditions, and then removing the acetate groups by transesterification; yields up to 70% were obtained. Acetal **2a** was rather sensitive to hydrolysis during work up; repeated purifications gave ca. 90% pure acetal contaminated with DHBP.

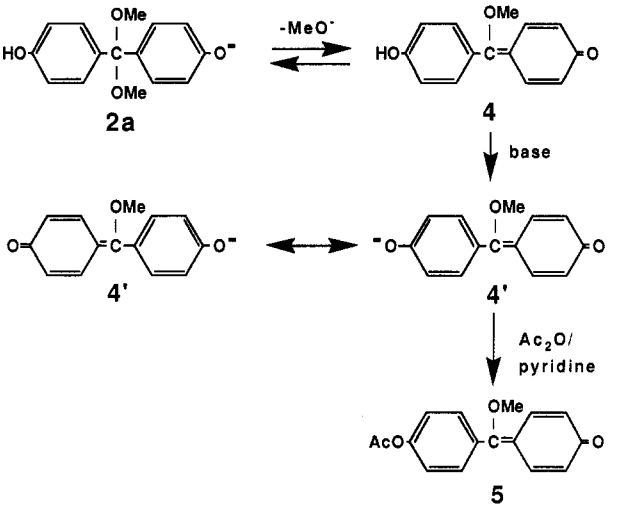
The cyclic acetals of DHBP proved to be even less amenable to the classical synthetic procedures. Whereas benzophenone is converted in 80% yield in 5 h to its ethylene acetal [dioxolane] by ethylene glycol, acid catalyst, and benzene azeotrope at 80 °C,[17] only 5% conversion of DHBP was detected under these conditions. Inconveniently long reaction times, at least 17 days, were required to achieve 50–60% conversion. The yield of **2b** was improved subsequently to 80% (after 5 days) by using a large excess of glycol (>15/1 mole ratio glycol/DHBP) and a relatively high level of HBr catalyst (5 mol %). An 85%



yield of the corresponding acetal was obtained with 1,2-propanediol and toluene azeotrope at 115 °C in 48 h.[14] The cyclic acetal **2b** was stable during purification. Essentially pure acetal, containing only small amounts of unreacted DHBP, could be isolated (see Experimental Section).

Because of the inefficiency of the classical methods and of a number of variations not discussed here, we explored an alternative synthesis[14] based on acidic montmorillonite clay catalyst.[18] The unique combination of glycol, trialkyl orthoformate, and clay afforded >70% conversion of DHBP to **2b** within 24 h at 70–90 °C; up to 95% conversion was achieved in a reasonable reaction time. A

Scheme III



number of control experiments and variations[14] established that the orthoformate and clay are both required to achieve high yields. Large excesses of glycol and orthoformate are not necessary, but the amount of clay directly influenced the conversion to acetal. Besides providing a more efficient conversion to acetal, an advantage of this method was that tedious purification was unnecessary, even when unrecrystallized DHBP starting material was used. Filtration to remove clay, extraction to remove glycol, evaporation of the solvent, and trituration with dichloromethane to remove impurities afforded polymerization quality monomer (**2b**) without recrystallization.

Synthesis of Poly(ketal ketone). Attempts to prepare poly(ketal ketone) **3a** from dimethyl acetal **2a** and 4,4′-difluorobenzophenone using the carbonate method[10b] in DMAc were unsuccessful. Two low molecular weight fractions ($\eta_{red} \approx 0.1$) were isolated. One fraction was insoluble in DMAc and other organic solvents, but the other fraction was soluble in DMAc and *N*-methylpyrrolidinone. Infrared analysis showed that the soluble fraction contained acetal groups.

The most startling feature of this polymerization was the formation of a brilliant red reaction solution at 150 °C, a unique and unusual color for this type of polymerization. We postulated that 4,4-dihydroxybenzophenone dimethyl acetal (**2a**) was unstable under the reaction conditions, as shown in Scheme III. After formation of the phenate anion by reaction with carbonate, expulsion of methoxide anion would lead to the quinone methide structure (**4** or **4′**). This rearrangement is unprecedented, especially when one considers the usual stability of acetals under basic conditions.[15] However, this reaction would explain the color (e.g., **4′**) and also the formation of low molecular weight product. Chain termination by the monofunctional quinone would occur, and backbone cleavage by methoxide, analogous to known cleavage reactions of poly(aryl ethers), would also be likely. When acetal **2a** was reacted in the absence of 4,4′-difluorobenzophenone with K_2CO_3 in dried DMAc at 125–165 °C, an intense scarlet red solution formed. GC analysis (samples quenched with acetic anhydride/pyridine) indicated the complete disappearance of **2a** and the formation of some DHBP along with a new peak, believed to be **5**,[19] at a retention time shorter than that of the acetal diacetate. The scarlet red solution exhibited a UV absorption maximum at 375 nm (in CH_3CN) with an apparent molar extinction coefficient of about 35 000 (based on GC yield). The red solution is quite stable in air and upon addition of pyridine but is rapidly de-

Table I
Effect of Reaction Parameters on the Heterogeneous Hydrolysis of Poly(ketal ketone) 3b

				recovered polymer		
expt	T,[a] °C	time,[a] h	acid,[b] M	T_m,[c] °C	wt. loss,[d] %	conversion,[e] %
1	200	20	0.02	361	0.20	>98
2	200	10	0.02	340[f]	5.5	46
3	200	4	0.10		3.4	66
4	175	20	0.02	360	0.24	98
5	175	10	0.02	348	1.7	83
6	160	20	0.02	351	1.5	85
7	150	40	0.01		5.6	45
8	100	24	0.05		9.0	9

[a] Preceded by pretreatment at 150 °C for 4 h, except for experiment 8. [b] HCl for experiments 1–6, H_2SO_4 for experiments 7 and 8; experiments established the equivalence of the acids. [c] By differential scanning calorimetry (DSC) on recovered (unannealed) polymer. [d] By thermogravimetric analysis (TGA) at 425 °C/20 min and rounded to nearest 0.1% for values >1%; at for values <1%, high sensitivity operation allowed estimates to ±0.02%. [e] Minimum estimate; based on the theoretical weight loss of the poly(ketal ketone) samples [10.1% for experiments 1–7 (found for **3b** 10.3–10.5%) and 9.87% for experiment 8 (found for **3b** 9.5%)]. [f] Weak transition.

colorized upon the addition of acetic anhydride.

We postulated that loss of methoxide ion or methanol is a driving force for the decomposition of the acyclic acetal. Therefore, the corresponding cyclic acetals should be less prone to this rearrangement. In fact, polymerizations with 2,2-bis(4-hydroxyphenyl)-1,3-dioxolane monomer (**2b**) gave no indication of quinone formation, and high molecular weight polymers were formed easily under standard polymerization conditions[10] in DMAc at 150 °C and in sulfolane at 220 °C.

The poly(ketal ketone) **3b** [poly(1,3-dioxolan-2-ylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene)] was soluble in DMAc, as expected. It was also soluble in chloroform, although insoluble polymer slowly separated from solution after several hours, possibly due to partial hydrolysis of the polymer by absorbed ambient moisture. The reduced viscosities, both in concentrated sulfuric acid and in chloroform, clearly indicated high molecular weight was obtained. Figure 1 illustrates the effect of the proportion of ketal monomer on the polymer molecular weight (reduced viscosity) achieved after up to 8-h reaction time. The lower molecular weight obtained with higher proportions of DHBP probably reflects the relatively slow reaction rate of DHBP (see above). Decreased polymer solubility is not a plausible explanation for this trend because the poly(ketal ketones) were soluble in DMAc at acetal to DHBP monomer ratios >3:1. Because of their solubility, the poly(ketal ketones) were isolated easily by normal methods, e.g., coagulation in isopropyl alcohol (see Experimental Section). A control experiment confirmed that DHBP itself in place of the acetal monomer gave only low molecular weight polymer (η_{red} = 0.12) under these conditions.

Compression molded plaques of poly(ketal ketone) were transparent and exhibited properties typical of amorphous poly(aryl ethers) (Table II); the impact strength was exceptionally good.

Conversion to Poly(ether ketone) 1K. Hydrolysis of the ketal groups was accomplished by heating a slurry of polymer fluff in water containing acid catalyst, e.g. HCl or H_2SO_4. This procedure was remarkably effective in spite of the heterogeneous conditions. Conversion to poly(ether ketone) **1K** was conveniently estimated by thermogravimetric analysis, which showed essentially quantitative degradation of the ketal groups at 425 °C within 20–30 min (Figure 2). Pyrolysis GC/MS showed that the volatile byproduct is acetaldehyde.

We examined several reaction variables, but temperature was the critical factor for efficient hydrolysis of **3b** (Table I). Virtually no hydrolysis occurred at 100 °C after 24 h, which conflicts with the reaction requirements previously

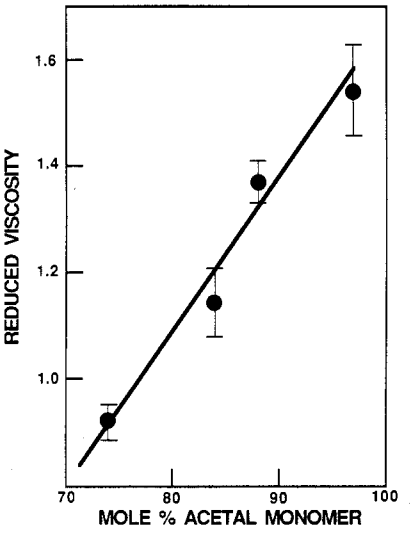


Figure 1. Effect of the proportion of acetal monomer **2b** on the molecular weight of poly(ketal ketone) **3b** obtained in DMAc at 150 °C [η_{red} in concentrated H_2SO_4]; the stoichiometric balance of bisphenol monomer was 4,4′-dihydroxybenzophenone.

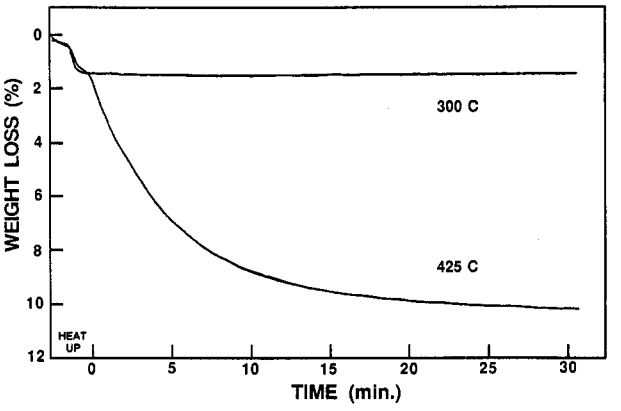


Figure 2. Thermal weight loss of poly(ketal ketone) **3b** at 300 and 425 °C (under N_2).

suggested[16] for hydrolysis of poly(ketal ketones). Even at 150–160 °C, conversion was very slow and incomplete. Complete reaction was achieved at temperatures above 160 °C.

Our results are consistent with a diffusion-limited reaction. Because the polymer chain mobility is restricted at temperatures below the glass transition temperature (145 °C for poly(ketal ketone) and 155 °C for poly(oxybenzophenone)), the reaction was extremely slow at these temperatures. Above the T_g, the enhanced mobility of the

Table II
Polymer Physical Properties

	poly(ketal ketone) **3b**	poly(oxybenzophenone)			
		1K[a]	**1K**[b]	**1E**	**1N**[c]
reduced viscosity (η_{red})[d]	1.64[e]	1.96	1.49	1.90	2.56
tensile modulus, MPa	1930	2760	2910	2570	2720
tensile strength, MPa	66	94	100	83	95
elongation at break, %	115	31	6.3	31	14
pendulum impact strength, MJ/m^3	>20.7	16.9	10.2	10.2	12.2

[a] Ketal route—heterogeneous hydrolysis. [b] Ketal route—homogeneous hydrolysis. [c] See Scheme Ic. [d] 1 g of polymer/100 mL of concentrated H_2SO_4 solution, 25 °C. [e] η_{red} = 0.80 in $CHCl_3$ (0.2 g/100 mL, 25 °C). [To convert MPa to psi, multiply by 147.]

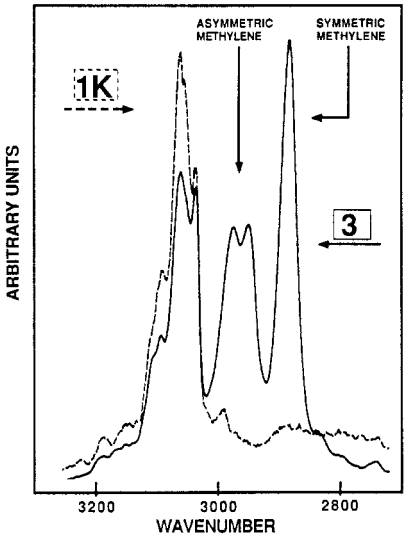


Figure 3. Alkyl region of the diffuse reflectance FT infrared spectra of poly(ketal ketone) **3b** and poly(oxybenzophenone) **1K** obtained from heterogeneous hydrolysis of **3b**.

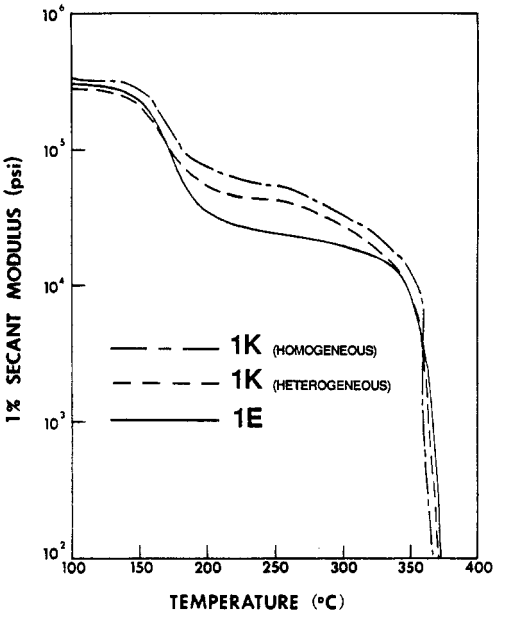


Figure 4. Modulus-temperature characteristics of poly(oxybenzophenones) **1K** and **1E**.

polymer chains allows complete reaction to occur. Temperatures significantly above the T_g and higher acid concentrations did not accelerate the hydrolysis significantly (Table I), which is also consistent with a heterogeneous, diffusion-limited process.

Under optimum conditions, the conversion to crystalline poly(ether ketone) was quantitative, as indicated by the very low thermal weight loss (Table I). Because other very slow degradations could well account for the residual values at 425 °C, e.g., <0.6%, the calculated >98% conversions are believed to be a lower limit. Quantitative conversion was substantiated by the lack of detectable alkyl absorptions by diffuse-reflectance infrared analysis (Figure 3) and by the excellent properties of the poly(ether ketones) (see below).

Quantitative hydrolysis was also achieved under homogeneous conditions when the poly(ketal ketone) **3b** was dissolved in 85–98% sulfuric acid at room temperature. This reaction is probably almost instantaneous. Exhaustive washing of the poly(ether ketone) was required, however, to remove trace levels of acid.

Poly(ether ketone) Properties. The mechanical properties of polymer **1K** prepared by the ketal route were generally similar to those of polymers **1E** prepared by the Friedel–Crafts electrophilic route and **1N** by the high-temperature nucleophilic route (Table II). The solvent resistance of polymer **1K** was also exceptional, as expected (see Experimental Section). The thermal properties of **1K** were particularly distinguishable, however, as shown by the higher modulus plateau exhibited by **1K** between the T_g and T_m (Figure 4). The tensile moduli were about twice as great compared to **1E** or **1N** (Table III). The heats of fusion (ΔH_f) and crystallization (ΔH_c) were also significantly higher for polymer prepared by the ketal route. The

Table III
Poly(oxybenzophenone) (1) Thermal Properties

	ketal route		electrophilic route, **1E**	nucleophilic route, **1N**[c]
	1K[a]	**1K**[b]		
T_m,[d] °C	366	372	370	372
ΔH_f,[d] (cal/g)	8.3	9.5	5.5	8.3
ΔH_c,[d] (cal/g)	10.6	12.3	6.3	9.1
tensile modulus, MPa				
at 200 °C	434	531	234	262
at 250 °C	303	386	159	172
at 300 °C	172	221	103	114

[a] From heterogeneous hydrolysis. [b] From homogeneous hydrolysis in concentrated H_2SO_4. [c] By single monomer route (see Scheme Ic). [d] By differential scanning calorimetry; samples were heated first to 400 °C, cooled at 10 °C/min to measure ΔH_c, and then reheated at 10 °C/min to measure ΔH_f and T_m.

moduli measurements and the heats of fusion and crystallization are mutually consistent with, and qualitatively substantiate, a higher level of crystallinity for **1K**.

Dynamic mechanical properties were also determined on poly(ketal ketone) **3b**, polyketone **1K**, and polyketone prepared via the electrophilic route (**1E**) using a free vibration torsion pendulum. The results are shown in Figure 5. This poly(ketal ketone) sample **3b** exhibited a T_g at 144 °C and a rapid drop in modulus indicative of an amorphous material. Poly(ether ketone) **1E** exhibited a T_g at 155 °C with a modulus plateau at higher temperatures. Poly(ether ketone) **1K** exhibited a T_g of 156 °C with a modulus plateau higher than that of **1E**, which is indicative of a higher level of crystallinity. The peak height

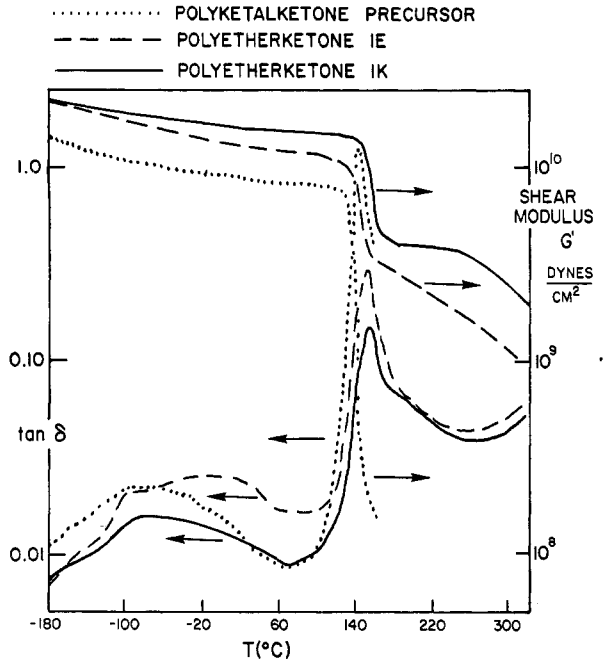


Figure 5. Dynamic mechanical properties of poly(ketal ketone) **3b** and poly(ether ketones) **1K** and **1E** in the temperature range from −180 to 330 °C.

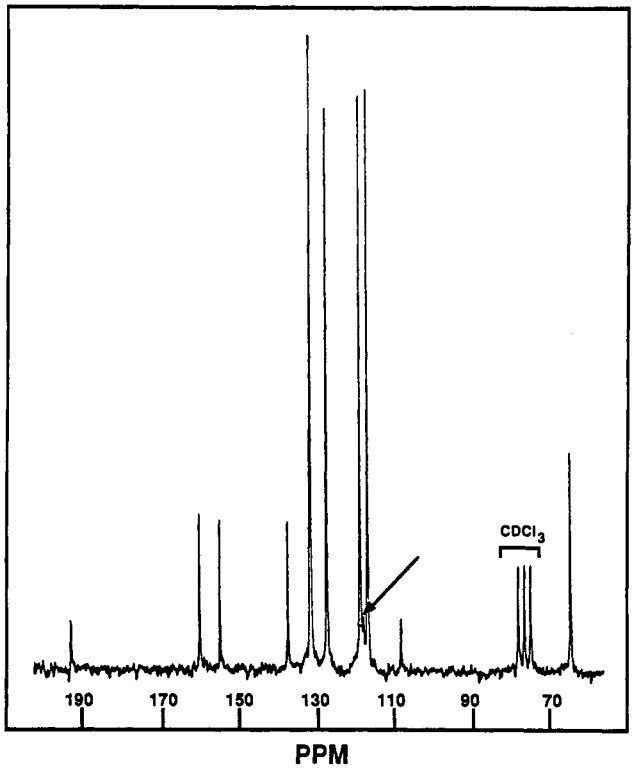


Figure 6. ^{13}C NMR spectrum of poly(ketal ketone) **3b** in $CDCl_3$ (relative to internal Me_4Si). Peak assignments are given in the Experimental Section. The small peak at 118.64 ppm (arrow) is due to para ketone–ether–ketone linkages (see text).

of tan δ is qualitatively *inversely* related to the degree of crystallinity. Polymer **1K** exhibited a lower value for tan δ than **1E** which is additional evidence for the higher crystallinity of **1K**. The secondary loss transition at −100 °C is believed to be due to a rotational mode involving the aryl ether group.[20] The samples were thoroughly dried so that the contribution of water, which is known to influence the magnitude of the −100 °C transition, is believed to be negligible.

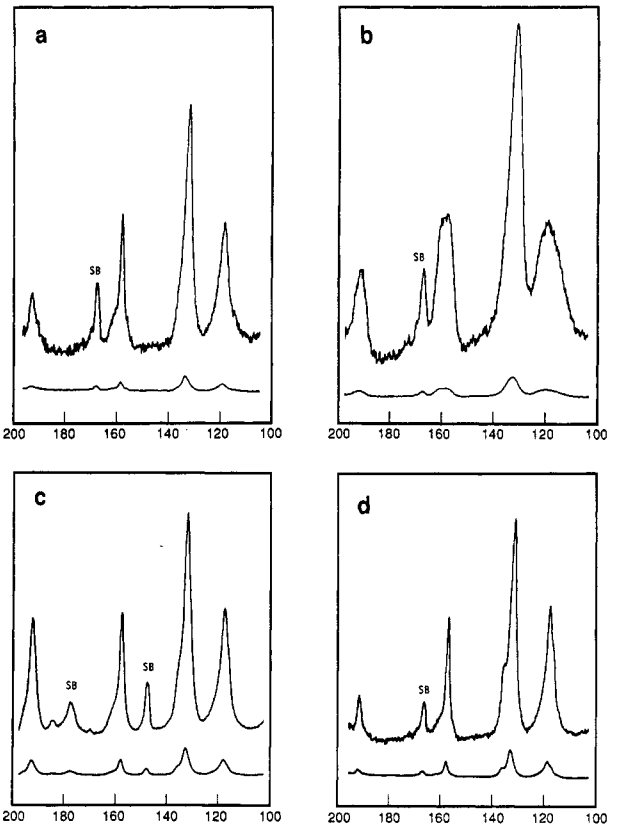


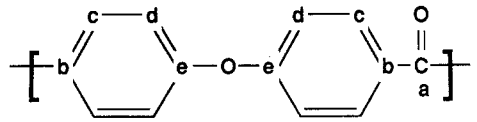
Figure 7. Solid-state ^{13}C CP-MAS nuclear magnetic resonance spectra of poly(oxybenzophenones): (a) ketal route **1K** [Scheme II], (b) electrophilic route **1E** [Scheme Ia], (c) high-temperature nucleophilic displacement route **1N** [Scheme Ib, dual monomers], (d) nucleophilic route **1N** [Scheme Ic, single monomer]; SB = spinning side band.

These observations indicate a highly crystalline, uniform structure for **1K**. Because of the specific para backbone structure dictated by the monomers and the relatively low reaction temperatures feasible with the ketal strategy, which should minimize side reactions, the poly(oxybenzophenone) structure (**1K**) should be essentially linear and "defect-free". In contrast, the lower crystallinities of the polymers prepared by electrophilic polyacylation (**1E**) or by high-temperature nucleophilic displacement (**1N**) are likely a logical consequence of the formation of anomalous units, such as ortho substitution[9] or branching.[11]

Direct evidence for the relative degree of perfection of these polymers is difficult to obtain. Because of the insolubility of **1K** in acceptable solvents, solution NMR of **1K** to detect isomeric structures was not feasible. However, ^{13}C NMR spectra (Figures 6 and 7) support the superior uniformity of the poly(oxybenzophenone) prepared by the ketal route.

The solution spectrum of the precursor poly(ketal ketone) **3b** (Figure 6) was extremely clean. One small peak (arrow) at 118.64 ppm which does not fit the poly(ketal ketone) substructure is assigned to the aromatic carbon ortho to the ether oxygen in the para ketone–ether–ketone [CO–C_6H_4–O–C_6H_4–CO] linkages in this polymer. These originate from the 2% 4,4′-dihydroxybenzophenone impurity in the acetal monomer. Within the detection limits of the NMR experiment (<1%), the precursor poly(ketal ketone) backbone consisted entirely of para linkages.

The solid-state, magic-angle spectrum of poly(ether ketone) **1K** (Figure 7a) revealed sharp, symmetrical absorptions which are consistent with the para unit structure (calculated shifts are shown in parentheses):



a	193.2		b	132.8	(132.9)	c	132.8 (132.2)
d	118.3	(119.3)	e	158.9	(161.1)		

The absorption bands for the electrophilic-route polymer (**1E**, Figure 7b) were also rather symmetrical but, in comparison, considerably broader; the peak width at half-height was twice as wide. We also examined the polymers (**1N**) prepared by high-temperature, nucleophilic displacement (parts b and c of Scheme I). The NMR absorption bands were fairly sharp but noticeably less symmetrical; e.g., shoulders were detectable for the 132, 158, and 193 ppm peaks in Figure 7c and readily apparent for the 132 ppm absorption in Figure 7d.

The broader spectrum of the electrophilic-route polymer (**1E**, Figure 7b) is consistent with its lower inherent crystallinity (Table III). The broad 132 ppm band, in particular, suggests some degree of ortho substitution. Our calculations on model compounds predict resonances at 132.2 and 132.9 ppm for the para structure, which agree well with the observed band at 132.8 ppm. Ortho substitution is predicted to exhibit resonances at 123.3, 128.9, 132.2, and 134.1 ppm. Combined with the predominant para resonances, these additional bands would account for the broader 132.8 and 118.3 ppm absorptions.

The shoulders observed in parts c and d of Figure 7 are most probably related to defect structures. This interpretation is consistent with the prior evidence[11] that nucleophilic substitution polycondensations at elevated reaction temperatures can lead to side reactions, particularly in the case of the single monomer route (Scheme Ic).

Conclusions

We have demonstrated that high molecular weight, amorphous poly(ketal ketone) **3b** can be prepared from the cyclic acetals of 4,4′-dihydroxybenzophenone under mild conditions. The cyclic acetal monomers are required because the acyclic analogues undergo an unusual postulated rearrangement under basic conditions to quinone methides (**4** and **4′**). The amorphous poly(ketal ketones) were converted quantitatively to crystalline poly(oxybenzophenone) **1K** by hydrolysis under heterogeneous or homogeneous conditions. The entire reaction sequence can be carried out at temperatures below 175 °C, which minimizes side reactions.

The excellent physical properties of poly(oxybenzophenone) obtained by this route, especially the high degree of crystallinity, indicate a uniform, linear backbone structure. Solid-state NMR spectra are consistent with this interpretation and suggest less than uniform structures for polymers prepared by direct methods. Within the available limits of detection, the polymer prepared by our process is essentially free of chemical structural defects.

The ketal strategy also provides several practical advantages over previous syntheses,[1-11] including the use of common aprotic organic reaction solvents, moderate reaction temperatures (150–220 °C), and convenient polymer isolation techniques. Our results demonstrate that linear, crystalline aromatic polymers can be prepared cleanly from amorphous, high molecular weight precursor polymers.[21]

Experimental Section

General. Except as noted, compounds and solvents were commercial reagents. 4,4′-Dihydroxybenzophenone [DHBP] was recrystallized from 40:60 methanol:water and/or sublimed. 4,4′-Difluorobenzophenone was recrystallized from absolute ethanol and dried thoroughly under vacuum; purity was >99.9% by GC analysis. Potassium carbonate was ground in a Waring blender to a fine powder, dried under vacuum at 120 °C, and stored in a desiccator. Ethylene glycol was dried by multiple treatment with molecular sieves. Gas chromatographic [GC] analyses were performed on a HP 5880 with a thermal conductivity detector using a 6 ft × $^1/_8$-in. 3% OV-1 stainless steel column at 190–200 °C or programmed oven temperatures from 130 to 270 °C. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed on Perkin-Elmer TGS-2 and Du Pont 990 or 1090 instruments, respectively. Routine ^{1}H NMR spectra (60 MHz) were obtained on a Varian EM-360 spectrometer with tetramethylsilane standard; routine solution ^{13}C spectra were obtained on a Varian CFT-20. Routine infrared spectra were obtained by using a P-E 299B instrument. Diffuse reflectance FT-IR on polymer powders were run on a Digilab FTS-15 with a liquid nitrogen cooled Hg–Cd–Te detector and a Harick diffuse reflectance accessory. Reduced viscosities [$\eta_{red} = (t - t_0)/t_0c$] were measured at 25 °C by using a Cannon-Fenske viscometer with either chloroform or concentrated sulfuric acid as solvent; the polymer concentration was 0.2 g/100 mL and 1.0 g/100 mL, respectively.

Solid-State NMR. Cross-polarization–magic angle spinning (CP-MAS) NMR spectra were obtained by using a Bruker CXP-200 instrument at 50.31 MHz and an Andrew-Beams MAS Delrin rotor. The {^{1}H–^{13}C} Hartmann–Hahn condition was matched for a 5-μs 90° pulse on ^{1}H and ^{13}C using adamantane. The spectra were calibrated against external Me_4Si; the precision of our system was better than 0.1 ppm. The magnetic field was shimmed to 6-Hz fwhh for ^{1}H on benzene, which is more than adequate for the polymer samples. Typically 720 scans with 3-ms single contacts, 50-ms acquisition time, sweep width 13158 Hz, and 4K data table were used to acquire the spectra. The data were zero-filled to 8192 data points and transformed by using 4-Hz exponential line broadening. The carrier was set to the resonance of the Delrin rotor to remove its quadrature image. Each sample was run at two or more spinning rates to identify spinning sidebands; typical spin rates were about 4000 and 3000–3500 Hz.

Bis(4-hydroxyphenyl)dimethoxymethane (2a). DHBP (11.0 g, 50 mmol), trimethyl orthoformate (6.5 g, 60 mmol), and 1 drop of concentrated HBr in 75 mL of methanol were heated to gentle reflux and slowly distilled (partial take-off distillation head). Over the next 48 h, additional orthoformate (12 g, 111 mmol), methanol (90 mL), and HBr (2 drops) were added in portions to the reaction. The methanol was then distilled over and the reaction cooled and neutralized with excess sodium acetate. The remaining methanol was removed by vacuum distillation, and the residue was slurred twice in 200 mL of dichloromethane with 0.1 g of sodium carbonate and filtered. The solution was stripped on the rotary evaporator to give 6.1 g of ketal (47% yield corrected for purity). NMR (ppm, $CDCl_3$): 7.35, aromatic A^2B^2, 8 H; 3.20, s, CH_3O, 6 H. NMR (ppm, $CDCl_3$) of the diacetate derivative (Ac_2O/pyridine): 7.23, aromatic A^2B^2, 8 H; 3.07, s, CH_3O, 6 H; 2.20, s, CH_3CO, 6 H.

Somewhat higher overall yields (ca. 70%) were obtained by treating the diacetate of DHBP with orthoformate in methanol essentially as described above. The acetate groups were then removed by transesterification in dry ethanol with a catalytic amount of sodium ethoxide at room temperature.

Due to hydrolysis to ketone during the workup, even after multiple triturations with dichloromethane, the maximum ketal purity was ca. 90%.

2,2-Bis(4-hydroxyphenyl)-1,3-dioxolane (2b). Azeotrope Method. A 250-mL flask fitted with a Dean-Stark trap, condenser, $CaSO_4$ drying tube, and magnetic stir bar was charged with 4.5 g (25 mmol) of DHBP, 38.8 g (625 mmol) of ethylene glycol, 0.2 g (2.5 mmol) of HBr, and 100 mL of benzene; the mixture was heated to reflux at 80 °C. After 5 days, NMR analysis showed 80% conversion to ketal. When lower glycol/DHBP ratio was used, e.g., 5/1, approximately 17 days was required to achieve >50% conversion. The benzene was then distilled off, the residue was dissolved in EtOAc, and the solution was extracted 4 times with 5% $NaHCO_3$ solution and once with saturated NaCl solution and dried over Na_2SO_4. The solvent was evaporated, the residue slurried in dichloromethane, and the solution evaporated to give

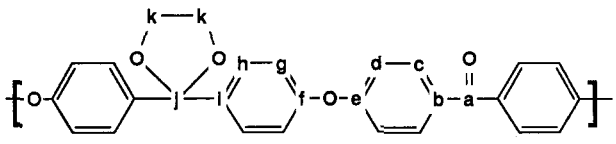
essentially pure ketal (31% isolated yield). NMR (ppm, $CDCl_3$): 7.45, aromatic A^2B^2, 8 H; 4.07, s, CH_2O, 4 H. Elemental analysis: 69.83% C, 5.59% H, 24.69% O (found); 69.76% C, 5.46% H, 24.78% O (calcd). The NMR (ppm, $CDCl_3$) of the diacetate derivative (pyridine/Ac_2O) was also consistent with the structure: 7.42, A^2B^2, 8 H; 3.88, s, CH_2O, 4 H; 2.17, s, CH_3CO, 6 H. Mp of diacetate 118–121 °C.

2,2-Bis(4-hydroxyphenyl)-1,3-dioxolane (2b). Clay/Orthoformate Method. A 1-L, three-neck flask fitted with a mechanical stirrer, thermometer, and variable take-off distillation head was charged with 99 g (0.448 mol) of DHBP (Aldrich, 97% unrecrystallized), 269 g (4.3 mol) of ethylene glycol, 96 g (0.91 mol) of trimethyl orthoformate, and 150 g of montmorillonite clay (K-10, United Catalysts, Louisville, KY) and heated to 70–90 °C to give slow distillation of reaction byproducts. After 18 h, 66 g of distillate had been collected and 64 g (0.6 mol) of orthoformate was added. NMR analyses of reaction samples showed 69% and 95% conversion to acetal after 24 and 48 h reaction time, respectively. The cooled reaction mixture was diluted with ethyl acetate and filtered on a Büchner funnel and the clay washed with ethyl acetate. The combined solution was extracted 4 times with 2% sodium bicarbonate solution and with saturated NaCl solution and dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product (115 g) was ground in a mortar, slurried twice in a minimum of dichloromethane, and filtered, and the creamy white solid was dried under vacuum (99.9 g). GC analysis of the diacetate (Ac_2O/pyridine) showed 95.4% acetal and 4.6% ketone. The isolated yield was 82.5% (87% including recovered ketone). HPLC analysis (1:1 CH_2Cl_2:EtOAc, 254 nm, Partisil PAC column) of the acetal confirmed the purity and showed no detectable impurities other than DHBP.

When azeotropic distillation with benzene was used in place of orthoformate, the conversion to acetal was <20% after 47 h; when the clay was replaced by HBr catalyst, the conversion to acetal was <20% after 120 h.

Poly(ketal ketone) 3b. A 500-mL four-neck flask fitted with a mechanical stainless steel stirrer, thermometer, argon inlet, Vigreaux column, Dean-Stark trap, and condenser was charged with 23.16 g (90.03 mmol) of 2,2-bis(4-hydroxyphenyl)-1,3-dioxolane (97.95 % acetal and 2.05% DHBP by GC analysis of the diacetate derivatives), 19.64 g (90.03 mmol) of 4,4′-difluorobenzophenone, 13.68 g (99 mmol) of potassium carbonate, 160 mL of dried *N,N*-dimethylacetamide, and 115 mL of toluene. The stirred reaction mixture was purged with argon for 1 h at room temperature and heated to reflux in an oil bath, and the reflux temperature was gradually increased to 150 °C by removing distillate from the trap. After 5.5 h, 0.02 g of 4,4′-difluorobenzophenone (in 2 mL of DMAc) was added to the viscous polymer solution to assure stoichiometry. After 30 min, 135 mL of DMAc was added and the reaction temperature adjusted to 110 °C. Methyl chloride was sparged for 1 h into the polymer solution to end-cap the polymer. The solution was then heated to 150 °C, filtered through a heated sintered glass funnel, and coagulated into excess isopropyl alcohol in a Waring blender. The solid polymer was washed with isopropyl alcohol, distilled water, and methanol in the blender and dried under vacuum at 100 °C to give 35.5 g of **3b** (90% isolated yield). The reduced viscosity in chloroform was 0.80; the η_{red} in concentrated sulfuric acid was 1.64 dL/g. The polymer was compression molded at 250 °C to give a clear, tough, almost colorless plaque.

The ^{13}C NMR spectrum of the poly(ketal ketone) (in $CDCl_3$/Me_4Si) was exceptionally clean and gave the absorptions shown (assignments based on spectra of acetal monomer, dihydroxybenzophenone, and benzophenone):



a	194.07 ppm	e	161.00	i	138.18
b	132.48	f	155.69	j	108.97
c	132.20	g	117.53	k	65.03
d	119.48	h	128.08		

One additional small peak at 118.64 ppm was found (see Figure 6 and text), which is assigned to the ketone–ether–ketone substructure from the 2% dihydroxybenzophenone in the starting monomer.

Heterogeneous Hydrolysis. General Procedure. The glass liner of a Parr rocker bomb was charged with poly(ketal ketone) fluff and dilute aqueous acid (10–100 mL/g of polymer), capped with the ground glass stopper (with pinhole to allow pressure equalization), and sealed in the bomb. The bomb was placed in the heater jacket and adjusted to rock gently in an almost vertical position. The temperature of the bomb (thermocouples) was initially adjusted to 150 °C; higher reaction temperatures were then usually used (see Table I). The polymer was recovered by filtration and the polymer washed with water, stirred twice with boiling water, washed with methanol, and dried under vacuum at 100–120 °C.

Homogeneous Hydrolysis. General Procedure. A 500-mL flask fitted with a glass/Teflon stirrer was charged with 250 mL of 85–98% sulfuric acid, and poly(ketal ketone) (10 g) was added over 10–20 min to the stirred acid. After 0.5–5 h, the polymer was coagulated by carefully pouring the acid solution into stirred ice water (2 L). The polymer was recovered by filtration, ground in water in a Waring blender, and then stirred 3 or 4 times in boiling water and dried under vacuum. Thoroughly washed polymer showed very low residual sulfur. Elemental Analysis: 79.49% C, 4.15% H, 16.12% O, 0.066% S (found); 79.58% C, 4.11% H, 16.31% O (calcd).

Mass Spectral Analysis of Poly(ketal ketone) 3b. Pyrolysis at 350–400 °C of the poly(ketal ketone) in the solid probe of the Finnigan 4023 quadrupole mass spectrometer showed that the molecular weight of the only volatile component (after removal of trace amounts of water or solvent at lower temperatures) was m/z 44 with a major fragment at m/z 29. Monitoring the m/z 44 ion at 350 °C showed a qualitatively exponential decrease in formation of this species over 20 min, which is consistent with the TGA behavior (Figure 2). Because of the close similarity of the mass spectra of ethylene oxide and acetaldehyde, pyrolysis–gas chromatography (400 °C/2-min pyrolysis probe temperature, 10-ft × $^1/_8$-in. Poropac C/0.19% picric acid column with a liquid nitrogen trap at the front of the column, programmed from 50 to 100 °C at 10 deg/min after removal of trap, FID) of poly(ketal ketone) was used to establish the identity of the volatile component as acetaldehyde by comparison of its GC retention time with authentic samples. Acetaldehyde may well be a secondary rearrangement product of ethylene oxide under the pyrolysis conditions.

Poly(oxybenzophenone) 1 Properties. Samples for mechanical and dynamic mechanical property determinations were prepared by compression molding properly dried polymer powder in a 20-mil cavity mold at 400 °C. Shear cut strips ($^1/_8$ in.) were placed between the grips of an Instron tester and the stress–strain measurements obtained. The pendulum impact strength was determined by allowing a pendulum arm to break the strips held tightly in the grips and measuring the loss in energy (recorded as pendulum impact strength). The dynamic mechanical data were obtained with a torsion pendulum as previously described.[22] The results are discussed in the text. The environmental stress rupture testing was conducted on $^1/_8$-in. strips subjected to various stress levels. The environment was introduced by saturating a cotton swab attached to the center of the specimen. The swab was covered with aluminum foil to suppress evaporation of the test solvent. As expected, **1K** was not crazed and not brittle after exposure for 4 h under 4000 psi stress to acetone, toluene, 2-butanone, or ethyl acetate nor after exposure for 8 h under 6000 psi stress to carbon tetrachloride or isopropyl alcohol.

Polyketones 1E and 1N. Poly(oxybenzophenone) **1E** was a commercially available sample (Stilan, Raychem Corp.). The nucleophilic displacement polyketones (parts b and c of Scheme I) were prepared in diphenyl sulfone from the corresponding monomers following published methods.[10] A 100-mL glass resin kettle (fitted with a glass stirrer, nitrogen inlet, condenser, thermometer, and Therm-O-Watch temperature controller) was charged with 4-fluoro-4′-hydroxybenzophenone (10.81 g, 50 mmol), potassium carbonate (3.4553 g, 25 mmol), 4,4′-difluorobenzophenone (0.0541 g, 0.248 mmol), and diphenyl sulfone (22.9 g). The reaction mixture was heated to 220 °C, held for 20 min, heated to 340 °C, and held 1 h. The hot mixture was poured into a pan,

cooled, ground to a fine powder, extracted twice with boiling acetone and twice with boiling water, and dried overnight under vacuum at 120 °C. The reduced viscosity (in concentrated H_2SO_4) was 2.56 dL/g. A similar procedure was used to prepare the polymer from DHBP and 4,4'-difluorobenzophenone (Scheme Ib).

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Mechanism of Acetylene Polymerization by the Titanium Tetrabutoxide/Triethylaluminum Catalyst System

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ABSTRACT: The dependence of the trans isomer content on acetylene polymerization conditions was examined for the titanium tetrabutoxide/triethylaluminum catalyst system. In toluene at 25 °C and at low ratios of Al/Ti, *trans*-polyacetylene was the exclusive product. As the temperature was lowered, the cis isomer became predominant. Increases in the Al/Ti ratio led to a decrease in the trans isomer content. When tetrahydrofuran was added to polymerizations, the trans isomer was obtained at all ratios of Al/Ti. No effects of catalyst concentration on the isomeric makeup of the polymer were observed. These results are interpreted in terms of the likely organometallic species responsible for the polymerization.

Introduction

Recent interest in the polymerization of acetylenes has been sparked by the observation that polyacetylene becomes highly conductive on oxidation or reduction.[1,2] Much work has addressed the question of whether the polymerization occurs by an insertion mechanism or alternatively by a metathesis route.[3] Nutation NMR techniques indicate that acetylene[4] and substituted acetylenes[5] polymerize via successive insertion reactions with titanium catalysts, while substituted acetylenes polymerize via a metathesis route using molybdenum-based catalysts.[5]

Polyacetylene serves as the prototype conducting polymer, and there has been much synthetic effort to ameliorate its intractability. Copolymers,[6-8] blends,[9,10] and graft and block copolymers[11-14] have been investigated as potentially tractable forms of polyacetylene, but each approach has had severe limitations. Improved conducting polymers might result from a better understanding of the organometallic species that catalyze the polymerization. In this way, desirable polymers may be prepared by ap-

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