Synthesis of Polyphenylene from a *cis*-Dihydrocatechol, a Biologically Produced Monomer

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ABSTRACT: Benzene is oxidized by oxygen utilizing the dioxygenase enzyme contained in the microorganism *Pseudomonas putida*. Genetic manipulation produced a variant that gave exclusively the initial oxidation product of benzene the *cis*-dihydrocatechol (**2**) in practical quantities. Derivatives of the latter, in particular the methyl carbonate, can be obtained pure and are very stable. They polymerize in the absence of solvent with radical initiators to give a polymer (**4**). The latter is soluble in solvents such as acetone and methylene chloride and readily forms coherent coatings and films. On heating methanol and CO_2 are expelled and polyphenylene is formed as a coating or film. The aromatization process is catalyzed by bases and can occur well below the glass-transition temperature of the precursor polymer of 185 °C. The aromatization can occur under homogeneous conditions in the basic solvent *N*-methylpyrrolidone. Surprisingly, these partially aromatized molecules are soluble even at conversion to 30% phenyl groups. The latter studies can be used to measure the glass transition of polyphenylene that was found to be 283 °C. Neutron scattering studies have shown that the precursor polymer is a random coil. Viscosity measurements show that there is a coil–rod transition on aromatization in *N*-methylpyrrolidone. Crystallographic data on polyphenylene crystallized above its glass transition and the thermal and electrical properties are described.

Introduction

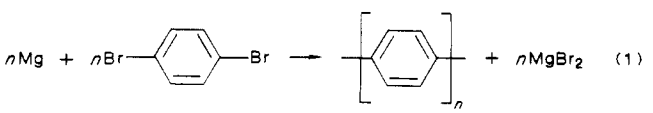
The majority of linear polymers containing the aromatic nucleus are synthesized by using polycondensation techniques. Examples include poly(ethylene terephthalate) (PET), poly(teraphthalamide) (Kevlar), poly(phenylene ether sulfone) (PES), poly(phenylene ether ether ketone) (PEEK), etc.

An advantage to this synthetic route is that molecular fragments joining the aromatic nuclei can be chosen so as to give melt processability. The disadvantage to this method of synthesis is that the molecular fragments joining the phenyl groups are more susceptible to thermal, oxidative, and photochemical attack. These facts have been extensively debated over the last 20 years and form part of the knowledge built up on the relationship between molecular structure and stability in polyaromatic materials. The expectation is that polyphenylene would be the most thermally stable structure of all the linear polyaromatics, and consequently various attempts have been made to synthesize this material.

One route to polyphenylene is the direct polymerization of benzene using a technique developed by P. Kovacic and others.[1-3] The process is known as an oxidative cationic polymerization and requires large quantities of cupric chloride.

The precise structure of the polymer produced is not known but contains a mixture of 1,2 and 1,4 units plus chemical defects.[3] The products are more correctly defined as oligomers rather than polymers since the chain lengths are between 10 and 15 phenylene residues. Moreover, it is difficult to remove completely all the $CuCl_2$ from what is rather an intractable solid. Notwithstanding these criticisms this is a successful route to polyphenylene, and powders are produced that can be fabricated by sintering techniques into various shapes.[2]

A second synthesis of polyphenylene (eq 1) is that due to Yamamoto[4] in which *p*-dibromobenzene polymerizes in the presences of magnesium using a nickel catalyst. This



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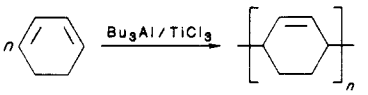
is one of the few examples of Grignard chemistry being used directly to form a macromolecule. Molecular weight measurements indicate that the growth does not go beyond 10–12 phenylene residues. This is because the polymer separates as a crystalline solid, and further polymerization to higher molecular weight is not possible.

An early attempt to use polymers of cyclohexadiene as a route to polyphenylene was by Marvel and co-workers[5-8] and involved the direct polymerization of cyclohexa-1,3-diene using a Ziegler catalyst (eq 2). This produced poly(cyclohexene) containing 1,4 and 1,2 units. Aromatization of polymers with structure **1** was attempted by reacting it with bromine followed by pyrolysis to eliminate HBr.

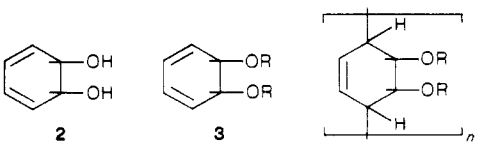


(2)

The purity of the products formed by this method is highly suspect as there are a number of bromo-substituted intermediates that might be formed and aromatization would be incomplete. Furthermore, the fact that reactants and potential products are both insoluble in solvents makes control of the chemistry difficult.

An additional complication is having HBr as the leaving group. Readdition of the latter to unsaturated intermediates formed in the reaction is possible. It is doubtful therefore that this route ever produced "clean" polyphenylene. It is more likely that the structure consisted of small numbers of the fully aromatized molecules admixed with partially aromatized segments.

This paper describes the synthesis of 5,6-*cis*-dihydroxycyclohexa-1,3-diene (DHCD, **2**), the study of the polymerization of its derivatives **3**, and the conversion of the polymers formed **4** into polyphenylene.



2 **3** **4**

The advantage of this particular diene is that the polymer formed is soluble in a variety of solvents because of the presence of the solubilizing group OR, where R can

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be CH_3CO, $CH_3O{\cdot}CO$, etc. Moreover, on aromatization the leaving group ROH is an organic acid that normally cannot add to an unsaturated hydrocarbon in the manner of HBr. Finally this possibility can be completely eliminated by using the methylcarbonic acid which at aromatization temperatures decomposes into methanol and carbon dioxide.

Although it is possible to produce compounds of the type **2** by conventional organic chemistry, it is more economic to use microbial oxidation of aromatic hydrocarbons. The additional advantage to this route is that the 5,6-*cis*-dihydroxycyclohexa-1,3-diene formed is the only isomer. Moreover, derivatives of the latter are polymerizable whereas 5,6-*trans*-dihydroxycyclohexa-1,3-diene obtained by conventional synthetic organic chemistry polymerizes with difficulty.

Experimental Section

Fermentation. DHCD was produced by the batch fermentation of *Pseudomonas putida* in an LKB 1601 fermenter with working volume of 3–4 L. The cells were grown in a mineral salts medium with ethanol as carbon source. Temperature was maintained at 30 °C and pH kept constant at 7.5 by automatic addition of NaOH or HCl. Benzene was supplied by passing the in-flowing air (1.2 L min^{-1}) through a round-bottom flask containing benzene, and the oxygen tension in the fermenter was maintained at 5% saturation by regulation of the relative amounts of air and oxygen added to the culture. The production of DHCD was monitored by the intensity of the UV absorbance at 260 nm. When accumulation reached the maximum level, the culture was centrifuged to remove cell debris and the product extracted into methylene chloride by using a continuous counter current extraction method. The methylene chloride solution was then concentrated under reduced pressure to a glycol concentration of 0.25–0.30 g mL^{-1} and three times the volume of *n*-pentane slowly added to the warm solution. The DHCD crystallized out and was recovered by filtration. After being washed with pentane, the pure product was dried and stored at −40 °C.

Derivatization. The derivatization of DHCD is exemplified by the synthesis of the diacetate, DHCD–DA. The diol (1.3 mol) was dissolved in pyridine (4.2 mol) in a round-bottom flask and cooled to −10 °C. Acetic anhydride (4.0 mol) was then added dropwise under nitrogen while the temperature was maintained below 0 °C. After addition the reaction was left stirring at 0 °C for 1 h and then allowed to warm to room temperature. The product was concentrated by removing pyridine on a rotary evaporator at 40 °C and the concentrate added to diethyl ether (800 mL) in a separating funnel. This solution was then washed three times with 300-mL aliquots of 10% aqueous sodium bicarbonate and three times with similar quantities of water. After the solution was dried over sodium sulfate, the ether was removed by rotary evaporation to yield the DHCD–DA as a slightly yellow liquid. This was purified by fractional vacuum distillation at 70 °C (0.1 mmHg) to give a product of 99.5% purity in 80% yield.

Bulk Polymerization. Pure DHCD–DA (15 g, 76.5 mmol) and azobis(isobutyronitrile) (53 mg, 0.32 mmol) AZBN initiator were placed in a 50-mL round-bottom flask and degassed by pumping followed by flushing with nitrogen three times. The reaction mixture was then heated to 70 °C and allowed to polymerize for 72 h. The resulting solidified reaction mass was dissolved in chloroform (100 mL) with stirring and the polymer (12 g, 80% yield) recovered by precipitation into hexane (1 L). The molecular weight of the polymer was determined by gel permeation chromatography (GPC) in chloroform solution using a refractive index detector and confirmed by low-angle laser light scattering, LALLS, using a Chromatix KMX6 instrument.

Polymerization Kinetics. Most of the kinetic data was obtained for bulk polymerizations up to 10% conversion performed in dilatometer tubes. The monomer and initiator were simply mixed, degassed, and poured into the dilatometer under nitrogen atmosphere. The variations of rate with initiator concentration and temperature were obtained in this way. Monomer dependence was determined by dilatometry of benzene solutions of the monomer using exactly the same experimental procedure.

Dispersion Polymerization. Monomer (1.0 g of DHCD–DA), initiator (7 mg of AZBN), and dispersomer (50 mg of X190-242, a comb polymer with poly(methyl methacrylate) backbone and poly(12-hydroxystearic acid)/glycidyl methacrylate side chains in the ratio 2:1 supplied by ICI Paints Division, Slough, UK) were placed in a 50-mL round-bottom flask and degassed three times. Heptane (7 mL) was then added and the mixture stirred under nitrogen at 80 °C in a water bath. Polymerization was continued for 48 h and the polymer recovered by filtration.

Aromatization. The aromatization of the polymers of DHCD derivatives in the solid state was studied by thermogravimetric analysis (TGA) under nitrogen or in vacuo by using a Perkin-Elmer TGS-2 instrument. Samples of the polymer were loaded into the machine and weight loss monitored as a function of temperature at a fixed heating rate, typically 10 °C/min, or isothermally as a function of time at a given temperature, typically 300 °C.

Aromatization in solution was performed by heating the polymer (5% w/v) in *N*-methylpyrrolidone at 150–200 °C. Aliquots were removed at appropriate intervals and quenched by precipitation into methanol. These samples were then characterized by GPC as described above, intrinsic viscosity at 30 °C in chloroform, infrared, and TGA. The latter two techniques provide means of determining the degree of aromatization of the polymer. In infrared this is by comparison of the carbonyl absorption in the precursor monomer at 1750 cm^{-1} with the aromatic absorption of the resulting phenylene rings at 810 cm^{-1}. The only complication with this infrared method occurs with the dimethylcarbonate derivative, DHCD–DMC, which shows an additional absorption of 1810 cm^{-1} appearing during the early stages of aromatization and eventually disappearing again as aromatization is completed. The peak at 1810 cm^{-1} is typical of a carbonyl absorption in a strained ring structure, and the phenomenon has been interpreted as the formation of cyclic carbonate groups (see Table IX) produced by the elimination of dimethylcarbonate. On further heating these groups aromatize with loss of water and carbon dioxide. TGA provides the weight loss to complete aromatization and, by comparison with the theoretically calculated result, an estimate of the degree of aromatization occurring during the solution process can be made.

Crystallinity. The X-ray diffraction profile of crystalline polyphenylene shows three characteristic maxima at *d* spacings of 4.5, 3.9, and 39.2 Å equivalent to 2θ values of 19.4, 22.4, and 27.6°. In addition there is normally a characteristic broad diffraction halo peaking at around $2\theta = 19°$ from the amorphous polyphenylene in the sample. The degree of crystallinity can be determined by using a computer program to perform a least-squares fit of four Lorentzian profiles at these 2θ values on the observed diffraction pattern. The ratio of the sum of the areas of the three crystalline peaks to the total area of the diffraction pattern including the amorphous halo then gives the desired result.

Glass-Transition Temperature. Samples of the precursor polymer were converted to intermediate levels of aromatization by heating at 300 °C under nitrogen for varying periods. The extent of aromatization was calculated by the infrared and TGA to complete aromatization methods described above. The glass-transition temperature of each sample was then determined by differential scanning calorimetry (DSC) at 10 °C/min using a Perkin-Elmer System 7 instrument.

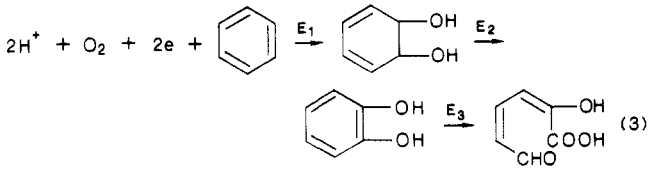
Neutron Scattering. Measurements were made in the solid state on protio/deuterio plaques prepared by solution casting. The relevant components were solution blended in 1,2-dichloroethane at 2% w/v concentration, and the solution was reprecipitated into 10 times its volume of methanol. The polymer blend was reclaimed and dried in vacuo for 24 h at 60 °C. This blend was then redissolved in 1,2-dichloroethane at concentration of 30% w/w, an appropriate amount placed into a moulding frame, and the solvent removed by controlled evaporation at 25 °C. This procedure produced clear void free plaques 32 mm × 17 mm × 0.5 mm thick which were used in the experiments.

All samples were prepared by using the same matrix polymer (H_{12}) in which M_w = 353 K and M_w/M_n = 2.6. The deuteriated (D_{12}) equivalent tag molecules were prepared by molecular fractionation of a 1% solution in acetone at 30 °C using methanol as nonsolvent of polymer in which M_w = 812 K and M_w/M_n = 2.24.

Neutron scattering experiments were made on samples containing 10% by weight of the D_{12} tag molecule, but one sample was studied at 5% tag loading from which the concentration dependence of molecular weight was estimated. Details of the samples are provided in Table V. Details of the SANS measurements are given by Ballard and Schelton[14] and other references given in this review paper.

Results and Discussion

Microbial Oxidation of Benzene. Although microorganisms able to oxidize benzene were known in the literature[10,11] because of their sensitivity and poor rates of oxidation, they lack the robustness necessary for large scale manufacture of **2**. From a manufacturing site contaminated with hydrocarbons over many decades we were able to isolate a new organism, *Pseudomonos putida* 11767. This organism exhibited a high rate of benzene oxidation and was substantially more tolerant of high benzene concentrations. The course of the oxidation within the bacterial cell is shown in eq 3.



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The dioxygenase E_1, with the assistance of the cocatalyst nicotinamide adenine dinucleotide in its protonated form (NADH), reacts with oxygen to form **2**, the complete oxygen molecule is used in this process, and the protons are supplied by the cocatalyst. Subsequently **2** is aromatized by E_2, and NAD^+ is converted back to NADH. A third enzyme, the dioxygenase E_3, converts catechol to a muconic acid. By genetic manipulation we produced a variant of 11767 which lacked enzyme E_2 needed to oxidize **2**.

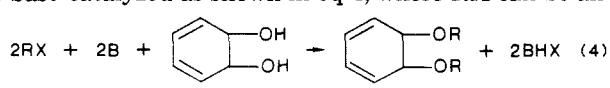
Since DHCD is water-soluble, it diffuses out of the cell into the surrounding aqueous media and accumulates therein. The organisms presently available will tolerate up to 0.5% liquid benzene in water, and the product accumulates to the extent of 40–50 g/L without inhibiting the oxidation. Yield on benzene is nearly 100%, and DHCD is the only oxidation product. With use of this genetically modified organism, a process has been developed for the kilogram scale production of DHCD. The organism is used as a catalyst in a well-mixed aerated aqueous solution to which benzene and ethanol are added.[12,13]

Ethanol is oxidized to carbon dioxide by other enzymes in the organism, thereby supplying the energy required by enzyme E_1 to drive the oxidation of benzene. At the end of the process DHCD is isolated by extraction with methylene chloride.

This process is now operated in 1000-L reactors to produce DHCD and substituted *cis*-dihydrocatechols, some of which are used as chemical intermediates for fine chemical manufacture.

Derivatives of DHCD. DHCD dehydrates at temperatures in excess of 60 °C to give phenol and water. This aromatization process is catalyzed by strong acids.

In basic solutions or neutral media DHCD is quite stable and can be stored indefinitely below 0 °C. Derivatization of the latter can be carried out at and above pH 7.4 without the formation of phenol, and the predominant reactions are base-catalyzed as shown in eq 4, where RX can be an



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acid chloride, anhydride, or iodide and B an organic tertiary base. The alkylation or acylation is accomplished in pure pyridine or dimethyl sulfoxide. If phosgene is the acid chloride a cyclic carbonate is the product. In Table I are summarized the properties of these derivatives.

Table I
Properties of Derivatives of DHCD

derivative	bp, °C	mp, °C
diacetate (DHCD–DA)	70 (0.1 mmHg)	40
dipivalate (DHCD–DP)	110 (0.1 mmHg)	30
dibenzoate (DHCD–DB)		93
bis(*p*-nitrobenzoate)		166
bis(*p*-bromobenzoate)		159
dimethoxycarbonyl (DHCD–DMC)	105 (0.1 mmHg)	36
diethoxycarbonyl (DHCD–DEC)	110	liquid
dimethyl ether (DHCD–DME)	70 (10 mmHg)	liquid

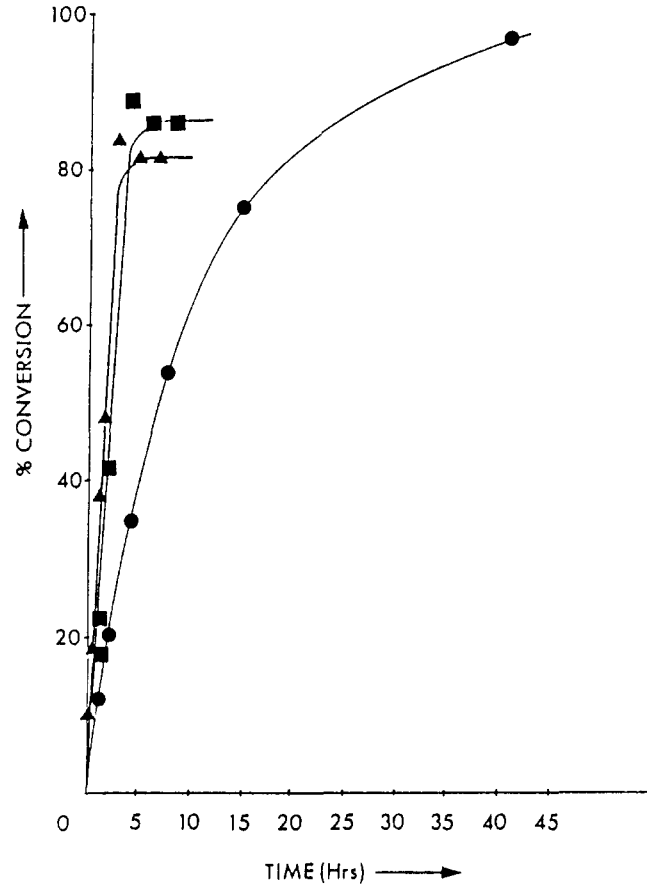


Figure 1. Conversion time curves for the polymerization of various cis glycol derivatives using benzoyl peroxide as initiator: ●, DHCD–DA; ▲, DHCD–DB; ■, DHCD–DMC; temperature, 90 °C; $[M]_0/[I]_0 = 156$.

Polymerization of DHCD Derivatives Using Radical Initiators. Initial experiments on the polymerization of DHCD and its derivatives were unsuccessful because of contamination by small amounts of impurities, including traces of phenol. Moreover it was found that the initiating radicals facilitated the formation of phenol, which inhibits polymerization, when pure DHCD was used. On the other hand, most of the acyl derivatives could be polymerized by using radical initiators either as the pure compound or dispersed in an organic solvent in which it is not soluble.

Studies of the Homopolymerization of DHCD. Initial rates of polymerization of DHCD derivatives were measured by using dilatometry and at high conversions by weighing the polymer produced. In Figure 1 is shown a typical conversion time curve obtained gravimetrically by using benzoyl peroxide as initiator. Most effective polymerizations were obtained in the absence of solvent, and with these conditions polymerization would proceed almost to completion without difficulty. In Figure 2 is shown the

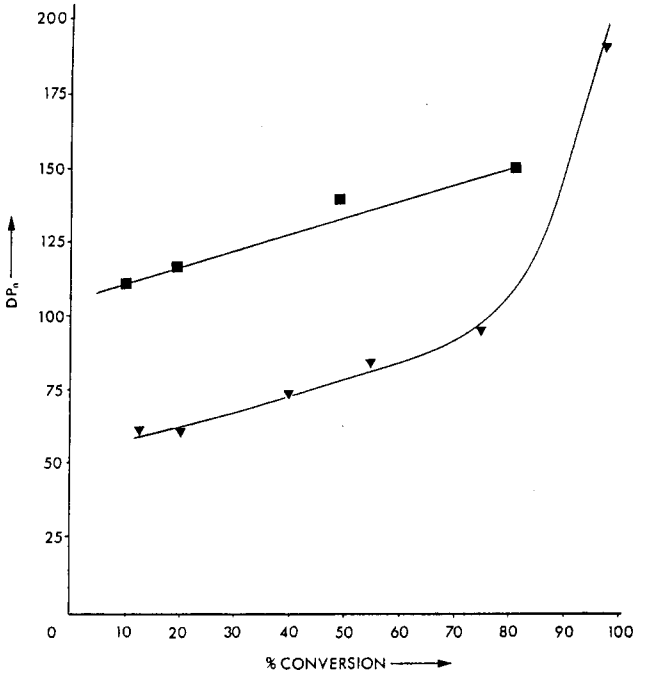


Figure 2. The degree of polymerization as a function of conversion. Conditions of polymerization as for Figure 1: ■, DHCD-DB; ▼, DHCD-DA.

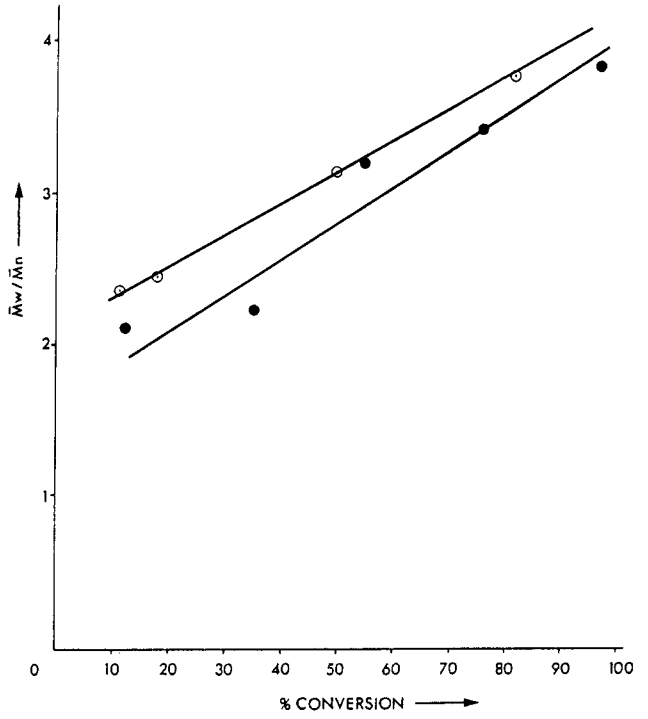


Figure 3. The dispersity as a function of conversion. Conditions of polymerization as for Figure 1: ○, DHCD-DB; ●, DHCD-DA.

variation in molecular weight as represented by the number average degree of polymerization (DPn). If the latter is compared with the dispersity given in Figure 3, it is evident that the bulk polymerization of these monomers is not dissimilar from the polymerization of acrylic esters.

The relationship between monomer and catalyst concentration and polymerization rate was obtained from initial rate studies and is illustrated in Figures 4 and 5. Equation 5 summarizes the results of these experiments, where $[M]_0$ and $[I]_0$ are the initial monomer and initiator concentrations, respectively.

$$R_P = \frac{-d[M]}{dt} = k[M]_0^{3/2}[I]_0^{1/2} \quad (5)$$

Table II
Comparison of Ratios at 90 °C of Kinetic Parameters for Propogation (k_p) and Termination (k_t) for the Polymerization of Vinyl Monomers[14]

monomer	$k_p/k_t^{1/2}$	monomer	$k_p/k_t^{1/2}$
styrene	0.05	DHCD-DMC	0.04
methyl methacrylate	0.10	DHCD-DA	0.02

Table III
Polymerization of DHCD-DMC at 50 °C and 3000 atm in Benzene as Solvent

$[M]_0$, mol/L	$[C]_0$, mol/L	convn, %	M_w	M_n
2.44	0.0077	75.6	523 770	149 065
2.44	0.031	90.3	422 430	134 580
2.44	0.015	76.3	431 360	157 130
4.11	0.015	70.0	563 050	171 720

Table IV
Effect of Deuteriation on the Initial Rate of Polymerization of the DHCD-DA at 40 °C

monomer	10^5R_p, L mol^{-1} s^{-1}	M_w
$C_6H_6(OCOCH_3)_2$ (H_{12})	5.75	66 600
$C_6D_6(OCOCH_3)_2$	5.85	55 390
$C_6H_6(OCOCD_3)_2$	6.82	71 530
$C_6D_6(OCOCD_3)_2$ (D_{12})	7.32	171 810

The values of the molecular weights of the polymers obtained at these low conversions gave a clearer relationship between the reciprical of DPn and the square root of the initiator concentration. This is shown in Figure 6 and is a general feature of the polymerization of vinyl monomers such as styrene and methyl methacrylate.

The molecular weight of the polymer is sensitive to the concentration of monomer, and the presence of an aromatic solvent reduces it markedly. High molecular weights can only be obtained in the absence of solvent. Also, the reaction temperature is a parameter to which the molecular weight is even more sensitive, and there is a reduction by a factor of 5–10 in molecular weight if the polymerization is carried out at 90 °C compared to 60 °C.

Measurements of molecular weight in the course of rate measurements also revealed that there was a linear relationship between rate of polymerization and the reciprocal of the number average degree of polymerization. From this information we derive values of $k_p/k_t^{1/2}$ for the acetate and methylcarbonate derivatives. A comparison between these values with those obtained for styrene and methyl methacrylate[14] is shown in Table II.

The plots of 1/DPn vs Rp and 1/DPn vs $[cat.]^{1/2}$ have positive intercepts. This suggests there is a significant transfer of activity from the propagating chain to monomer. This view is supported by eq 5 which shows an unusually high order with respect to monomer concentration. The effect of temperature on polymerization rate is summarized in Figure 7. The energy of activation derived from the slope is 16.9 kcal/mol.

It was also found that the polymerization had a marked pressure coefficient and that the rate at 3000 atm was 5–7 times greater than experiments conducted at atmospheric pressures. Also as shown in Table III molecular weights are not significantly higher.

The deuteriated analogues of DHCD are readily obtained by replacing benzene in the microbial oxidation with deuteriobenzene (C_6D_6). The sequence of reactions that follow are identical, except there is a marked kinetic effect. A comparison was made between the deuteriated and protonated acetate monomers in polymerization. For this purpose we determine the initial rate of polymerization in the pure monomer containing 1% of an initiator and the molecular weight of the polymer produced. The results

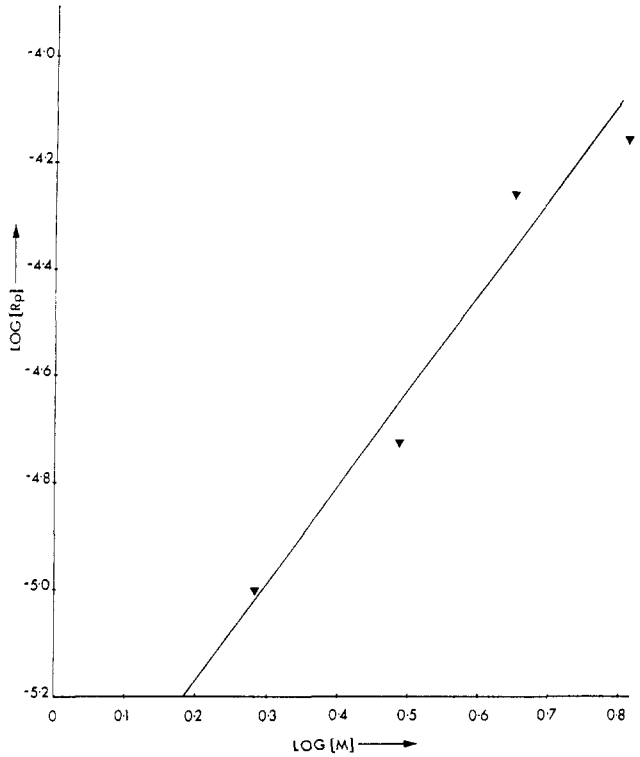


Figure 4. Initial rates of polymerization of DHCD–DA as a function of monomer concentration at 90 °C using benzoyl peroxide, $[I]_0$ = 5.68 mmol/L, in benzene as solvent.

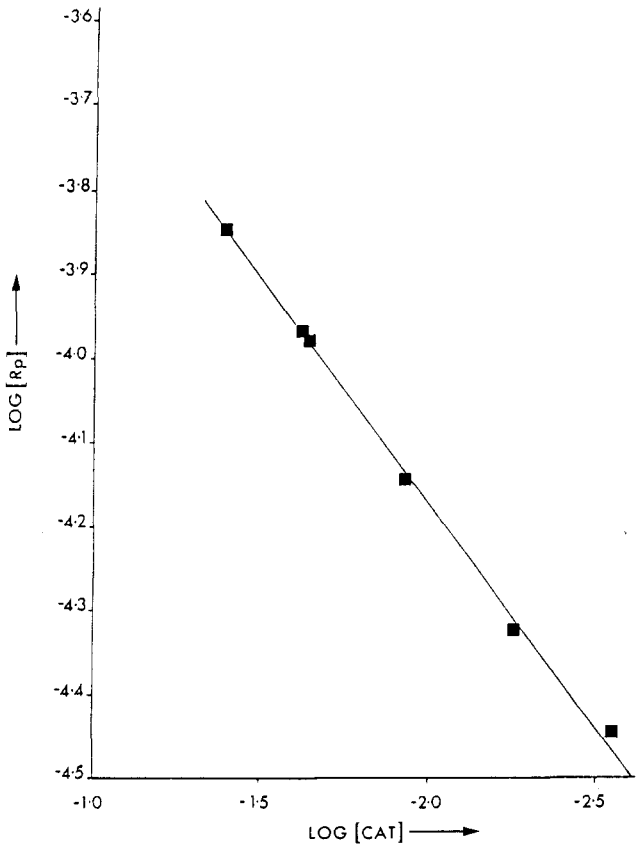


Figure 5. Initial rates of polymerization of DHCD–DA as a function of catalyst concentration at 90 °C using benzoyl peroxide ($[M]_0$ = 6.37 mol/L).

obtained are given in Table IV.

The most important effect of deuteriation was to produce a marked increase in molecular weight of the polymer produced. This is well-known in radical polymerization

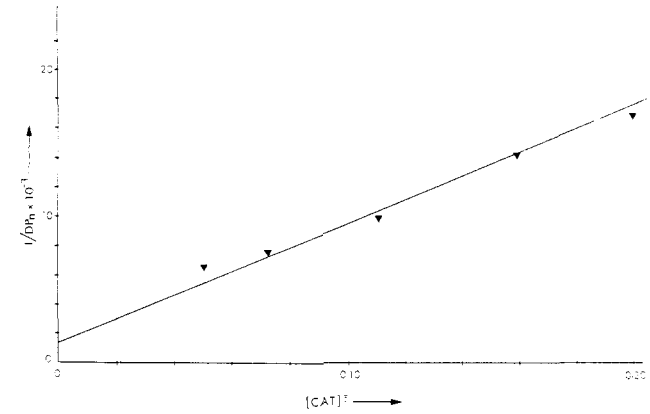


Figure 6. Relationship between number average degree of polymerization (DP) and catalyst concentration for the polymerization of DHCD–DA at 90 °C in the absence of solvent ($[M]_0$ = 5.5 mol/L).

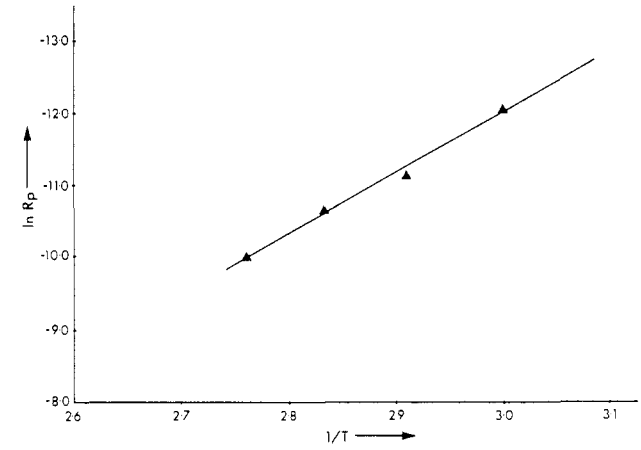


Figure 7. Arrehenius plot of polymerization rate against temperature for DHCD–DA.

of vinyl monomers and is due to the retardation of the bimolecular termination reaction and possibly to differences in the rate of allylic proton or deuteron abstraction from monomer leading to degradative chain transfer.

Polymerization in organic diluents, in which the polymer is insoluble, has been achieved by using dispersing agents. The latter consists of a polymethyl methacrylate backbone with side chain derived from 12-hydroxystearic acid. Powders of the polymers derived from DHCD acetate, benzoate, and methylcarbonate have been obtained. The polymer consists of spherical particles with a reasonable narrow distribution of particule sizes that can be controlled in the range 20–400 μm. Although all the derivatives of DHCD can be polymerized by using dispersion techniques, the benzoate and methylcarbonate do so at particularly high rates and give polymers with molecular weights of up to one million. A preliminary look at the kinetics of the polymerization has been carried out which shows that at low conversion

$$R_p = k[M][I]^{1/2} \quad (6)$$

where [I] is the concentration of the radical generator azobis(isobutyronitrile). Similarly, disperity is less than two at low conversions, with a normal growth mechanism for the macromolecule.

Conformation and Structure of Poly(DHCD–DMC) in the Solid State. The availability of the fully deuteriated species make conformational studies in solution and in the solid state possible. The use of small-angle neutron scattering (SANS) to measure M_w and the radius of gyration (R_w) by taking advantage of the differing scattering

Table V
Neutron Scattering Study of Poly(DHCD-DMC) in the Solid State

sample code	D_{12} content, %	$10^{-6}M_w$ (LALLS)	M_w/M_n (GPC)	$10^{-6}M_w$ (SANS)	$10^{-6}M_w$ (SANS corr.)	R_w, Å
blend 1	10	2.10	1.5	1.53	1.94	364
2	10	1.5	1.4	1.0	1.2	320
3	10	0.860	1.7	0.530	0.627	230
4	10	0.460	1.4	0.368	0.467	174
5	10	0.250	1.9	0.188	0.238	119
1A 10F	10	1.6	1.8	1.46	1.86	326
2A 5F	5	0.440	1.6	0.424		171
2A 10F	10	0.440	1.6	0.382	0.485	172

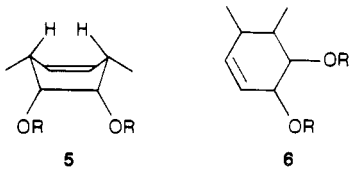
lengths of the proton and deuteron is well established.[9] These experiments were carried out in collaboration with Dr. Manfred Stamm and will be reported in detail in a later publication.

Void free plaques (32 × 17 × 0.5 mm) were obtained of mixtures of poly(DHCD–DMC) containing 5 and 10% of the fully deuteriated analogue. All samples were prepared by using the same matrix polymer (H_{12}) in which M_w = 353 000 and M_w/M_n = 2.6. The tag molecules (D_{12}) were prepared by fractionation of a polymer in which initially M_w = 812 000 and M_w/M_n = 2.24. Fractionation was effected by using mixtures of acetone and methanol at 30 °C. The data obtained are given in Table V. Molecular weights of the fractions were measured by laser light scattering (LALLS) in solution and in the solid state using neutron scattering (SANS). It was necessary to correct the SANS values of M_w for the fact that they were not independent of polymer concentration. The latter are closer to the LALLS values. These corrected SANS values were used to derive the curve shown in Figure 8. From the latter we obtained the relationship:

$$R_w = 0.26(M_w)^{1/2} \quad (7)$$

This equation is typical of a polymer chain in which there is a Gaussian distribution of chain segments around the center of mass.

In the macromolecule infrared and ^1H NMR analyses show that the DHCD-DMC residues are predominantly the result of 1,4-addition reaction in the polymerization. These residues constitute 85% of the polymer and probably have a "boat" shape configuration as shown in **5**. The



5 **6**

remaining residues are the result of a 1,2 addition reaction during the polymerization as shown in **6**. The admixture of these two structural entities results in a nonlinear molecule that the SANS data show has a random coil configuration.

Thermal Conversion to Polyphenylene. The polymers of DHCD derivatives can be aromatized by heating as fibers or films in the solid state and in solution. The process can be followed by using thermogravimetric analysis, infrared spectroscopy, or ^1H NMR spectroscopy. Typical results are shown in Figures 9 and 10.

The principal reactions leading to polyphenylene are shown in eq 8. The process is accompanied by elimination of two molecules of the acid for each phenylene group formed. Thus ROH produced in the examples given in

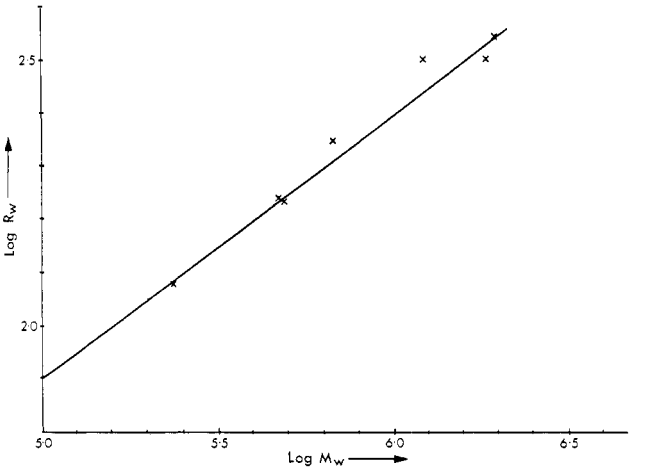


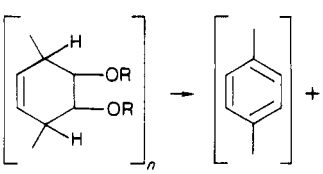
Figure 8. Plot of R_w against M_w using data in Table V.

Table VI
Kinetic Data for the Aromatization of Various Derivatives of Poly(DHCD) Obtained from Thermal Gravimetric Analysis Results at 300 °C

derivative	first-order rate const, min^{-1}	half-life, min
poly(DHCD–DA)	0.046	15
poly(D_6–ring DHCD–DA)	0.021	33
poly(D_{12} DHCD–DA)	0.012	58
poly(DHCD–DP)	0.037	19
poly(DHCD–DB)	0.034	20

Table VII
Kinetic Data for the Aromatization of Poly(DHCD-DMC) from Thermal Gravimetric Analysis

temp, °C	first-order rate const, min^{-1}	half-life, min
300	0.12	6
280	0.066	11
260	0.022	32



(8)

Figure 9 are acetic acid, benzoic acid, and pivalic acid from the acetate, benzoate, and pivalate derivatives, respectively. For practical reasons the preferred derivatives is the dimethylcarbonate. The eliminated acid in this case is methylcarbonic acid, which decomposes to give methanol and carbon dioxide.

In Tables VI and VII are summarized the kinetic data obtained from initial rate of decomposition for the thermal

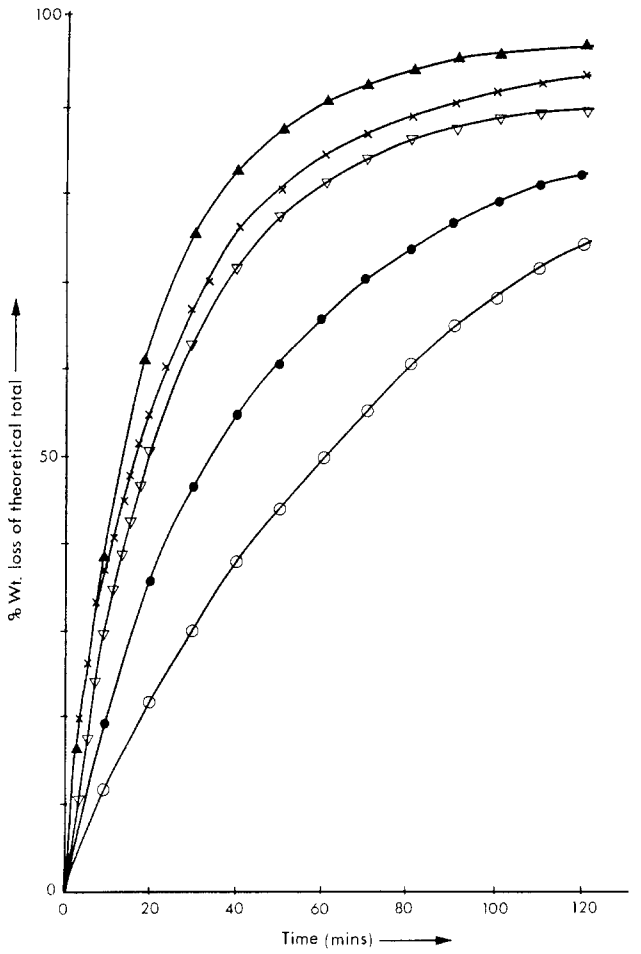
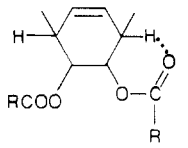


Figure 9. Thermal conversion to polyphenylene at 300 °C: ▲, poly(DHCD–DA); ▽, poly(DHCD–DP); ×, poly(DHCD–DB); ●, poly(D^6-ring DHCD–DA); ○, poly(D^{12} DHCD–DA).

aromatization. The latter process probably proceeds via a cyclic intermediate **7** and is successful because the carboxylic acid is a good leaving group. The kinetic data for the deuteriated polymers show that the presence of the D atom in the ring slows the aromatization process markedly, consistent with an intermediate of type **7** being formed.



7

The methylcarbonic acid and methylthiocarbonic acid derivatives of DHCD differ from the simple carboxylic acids in that the aromatization can be catalyzed by strong tertiary nitrogen bases and metal salts. Figure 11 is typical of the effect and shows that the potassium bromide catalyzes the aromatization and thereby reduces the temperature at which the process occurs. Additional information is given in table VIII, which shows that *n*-octylamine is far more effective in this role than metal salts. The role of the base in catalyzing the aromatization of the methylcarbonate derivatives is at present not understood.

N-Methylpyrrolidone is a good solvent for poly(DHCD–DMC) and also catalyzes the aromatization. Surprisingly the partially aromatized polymer is soluble in this solvent up to 35 mol % aromatized. At degrees of aromatization less than this the polymer can be isolated and dissolved in solvents such as methylene chloride, chloroform, etc. In Figure 12 is shown a typical decomposition curve. This shows that the aromatization process is autocatalytic in this solvent. In other words the partially aromatized polymer transforms cyclohexene residues more readily into phenylene groups. This suggests that the presence of phenylene residues adjacent to the cyclohexene residues facilitates aromatization. In Table IX is given the ap-

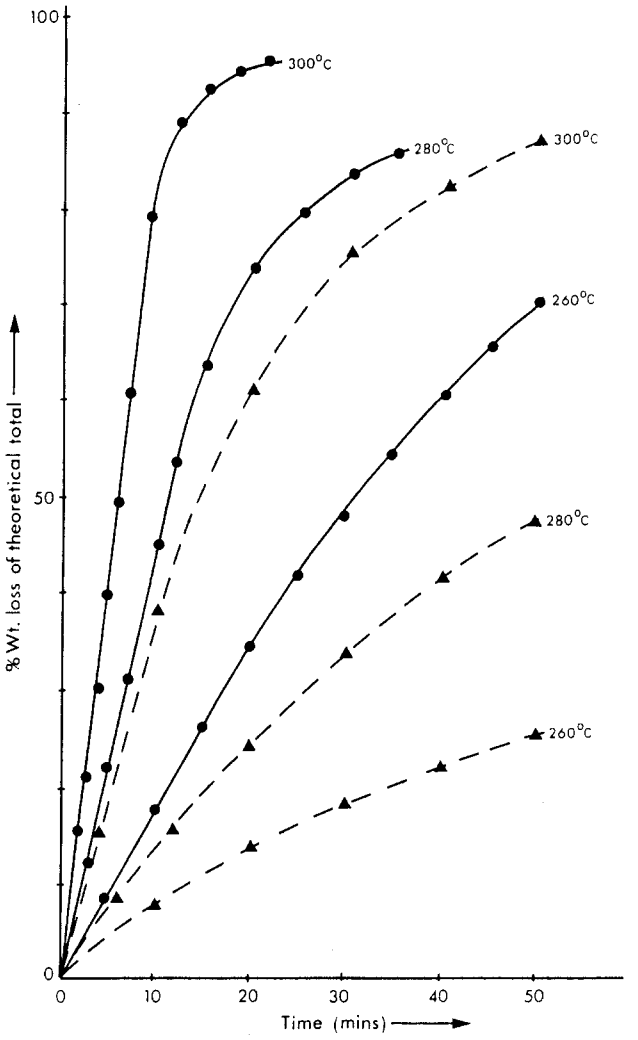


Figure 10. Thermal conversion to polyphenylene at different temperatures: ●, poly(DHCD–DMC); ▲, poly(DHCD–DA).

Table VIII
Catalyzed Thermal Conversion of Poly(DHCD–DMC) to Polyphenylene

cat.	mol % (w/w)	temp, °C	first-order rate const, min^{-1}	approx. half-life min
NaI	2	260	0.733	1
		250	0.386	2
		240	0.115	6
		230	0.052	13
		220		
KI	2	260	2.251	0.3
		250	1.547	0.5
		240	0.554	1
		230	0.262	3
		220	0.080	9
CsI	2	260	2.558	0.2
		250	1.585	0.4
		240	0.684	1
		230	0.478	2
		220	0.173	4
KBr	0.5	220	0.074	9
	2.0	220	0.145	5
$(CH_3(CH_2)_7)_3N$	0.5	240		1
	0.5	220		2

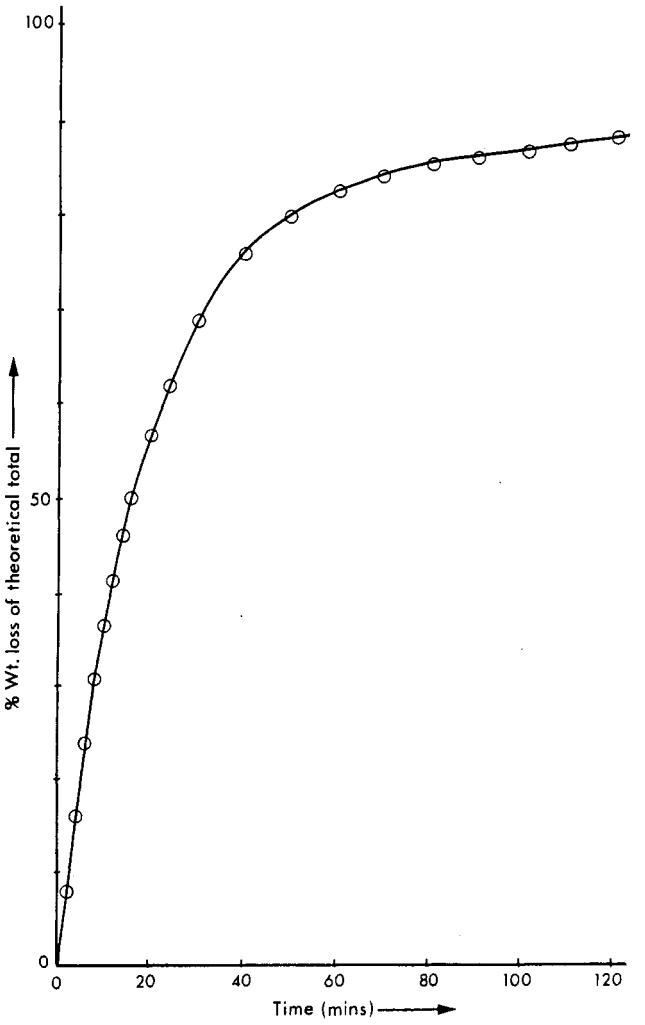


Figure 11. Catalyzed thermal conversion of poly(DHCD–DMC) at 220 °C (catalyst, KBr; concentration, 2% w/w).

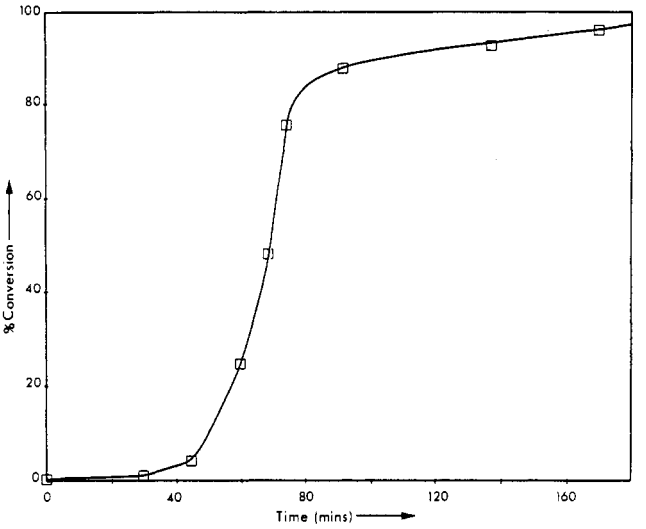


Figure 12. Aromatization of poly(DHCD–DMC) in *N*-methylpyrrolidone as solvent. The process was followed by using thermogravimetric analysis (temperature, 170 °C; polymer concentration, 5% w/w).

proximate composition of a partially aromatized polymer in which 35 mol % of phenylene groups are present. The cyclic carbonate residues (see Experimental Section) are fully aromatized at the much higher temperature of 260 °C.

Aromatization in solution enable any changes in molecular weight to be measured. A typical example is given

Table IX
Composition of Partially Aromatized Poly(DHCD–DMC)

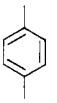
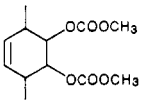
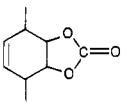
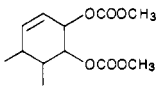
type of residue	amount, mol %	anal.
	30	IR, 810 cm^{-1}
	50	IR, 1750 cm^{-1}
	5	IR, 1810 cm^{-1}
	9	^1H NMR
	6	^1H NMR

Table X
Solution Aromatization of Poly(DHCD–DMC) at 148 °C in NMP[a]

		GPC results	
time, min	aromatization, %	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	0	139 700	2.34
40	6	140 800	2.27
166	15	139 000	3.11
176	16	169 000	4.02
188	18	193 800	4.06
210	20	243 700	6.46
217	22	320 900	7.63
229	26	331 200	12.10

[a] Initial concentration 15% w/v.

in Table X. It might be expected that with the accompanying weight loss due to aromatization there would be a progressive decline in molecular weight so that when the process is complete it would be a third of its initial value. In fact we observe no change at all up to 15% aromatization followed by a doubling of molecular weight at 26% aromatization.

It is evident from Table X that aromatization does not produce chain scission for if this was the case of the molecular weight would be reduced significantly. The apparent increase in molecular weight is due to the fact that the conversion of the precursor molecule into polyphenylene is accompanied by a major conformational change. Poly(DHCD–DMC) has been shown to be a random coil in solution by SANS; polyphenylene on the other hand is a rigid rod in which the Kuhn length is very long. The data in Table X in which the molecular weights are obtained by comparison with standard polystyrene molecular weights cannot be correct because as the number of phenylene residues in the polymer increases, there is a progressive increase in hydrodynamic volume. This can be demonstrated by comparing the intrinsic viscosities of polymers with different degrees of aromatization as shown in Figure 13.

It is known that the viscosity of a solution of a macromolecule is predominantly dependent on the size of the molecule, expressed as the root-mean-square radius of gyration $(\bar{S}^2)^{1/2}$ and not on the nature of the polymer.[15] This definition leads to the expression

$$[\eta] = \Phi\left(\frac{\bar{S}^2}{M}\right)^{3/2} M^{1/2}\alpha^3 \qquad (9)$$

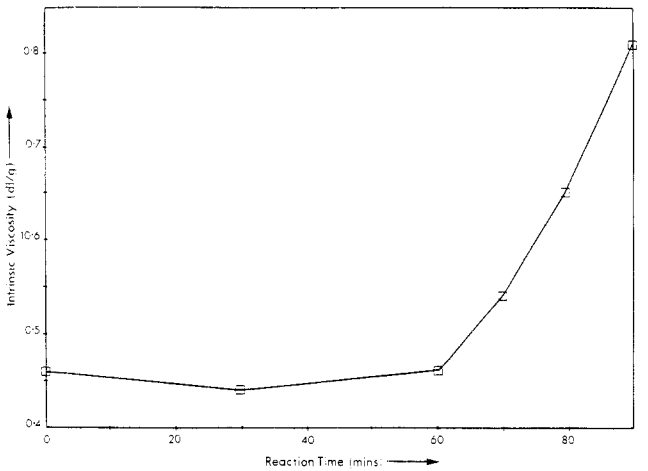


Figure 13. Aromatization of poly(DHCD–DMC) in *N*-methylpyrrolidone as solvent. Samples removed and intrinsic viscosities determined by dilution. A sharp increase in intrinsic viscosity occurs at 20% conversion.

where Φ is a constant, M is the molecular weight, and α is a parameter expressing deformation of the molecular dimension owing to the polymer solvent interaction. It is evident from (9) that at a constant molecular weight, $[\eta]$ is markedly dependent on the volume of the molecule V_e, given by

$$V_e = 4\pi(\bar{S}^2)^{3/2}/3 \qquad (10)$$

The aromatization process is accompanied by a transition from a random coil to a configuration which consists of a random arrangement of rigid rods separated by flexible sections of unaromatized molecules. As the aromatized fraction increases, the flexible units decline and the average length of the rodlike polyphenylene sections increases. This is shown clearly in Figure 13, where the intrinsic viscosity remains constant for the first 20% of conversion to phenylene units, but after this a marked increase in intrinsic viscosity occurs. Since this parameter is a measure of hydrodynamic volume, it must be concluded that this increase results, at least in part, from an increase in the radius of gyration of the molecule as a consequence of chain segments becoming straight as the phenylene units are formed. It is also possible that association of individual chains, through their aromatized segments by π–π interaction to form larger agglomerates, contributes to the observed increase in viscosity.

Solid-State Properties of Polyphenylene. Polyphenylene produced by the chemistry so far described is available as a thin film, on a variety of substrates such as glass, metals, ceramics, or plastic films with thermal transitions in excess of 300 °C. Solutions of the precursor polymer can also be spun at concentrations of about *20%* and, on aromatization, fibers are produced. Polyphenylene is a very stiff molecule, and it is not possible to draw the fibers. Any orientation of the polyphenylene molecules can only occur during the aromatization process but becomes increasingly more difficult as the extent of aromatization exceeds 50%.

Polyphenylene obtained by this route is pale yellow in color and is not contaminated by inorganic substances. In the unannealed state it is 60% crystalline. By controlled aromatization above 185 °C, crystallinities of *75–80%* can be obtained.

The absence of color suggests that the structure is not coplanar. In Table XI are given the principle X-ray reflections obtained on a polymer powder whose crystallinity was approximately *60%*. These have been compared with

Table XI
X-ray Diffraction of Polyphenylene and *p*-Terphenyl Model Compounds

polyphenylene[a] principal reflections	*p*-terphenyl[16] principal reflections	*p*-terphenyl[16] structural feature
4.5	4.40	distance between phenyl groups in same molecule in the direction of the principle molecular axis
3.9	3.89	distance between similar centers of phenyl groups in adjacent molecules all lying in the same plane
3.2	3.00	distance between planes of molecules

[a] This paper.

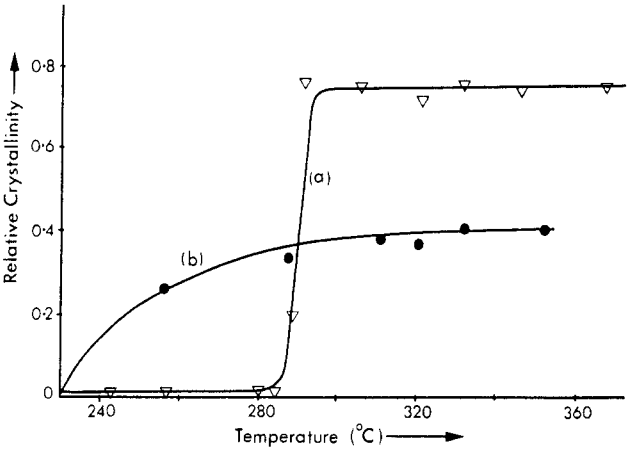


Figure 14. The effect of annealing temperature on the crystallinity in polyphenylenes obtained under differing aromatization conditions: (a) amorphous polyphenylene obtained at 150 °C; (b) semicrystalline polyphenylene obtained at 240 °C (annealing time 17 h).

those reported in the literature for para-linked oligophenyls. The most complete study is due to Rietweld, Maslen, and Clews[16] of *p*-terphenyl in which X-ray diffraction was supplemented by neutron diffraction to identify the positions of the hydrogen atoms.

Aromatization of the precursor molecule below its glass-transition temperature (185 °C) produces predominantly amorphous polyphenylene powder or coating. Subsequently annealing this powder and following the development of crystallinity at different temperatures produces the results shown in Figure 14a. At temperatures below 290 °C there is no recognizable increase in crystallinity. At this temperature there is a step change in the level of crystallinity. Annealing at temperatures above the latter produces a very high level of crystallinity. If the precursor molecule is aromatized above its glass-transition temperature, then the crystallinity of the polymers obtainable on subsequent annealing is shown in Figure 14b. It would appear that small crystals formed during the aromatization process impede the further reorganization of the macromolecules so that the maximum possible crystallinity is not achievable.

These small crystals are absent from the polymer produced by aromatization below 185 °C. It is evident that the onset of crystallinity in Figure 14a is associated with the increase in chain mobility and determines therefore the glass-transition temperature as 285 °C for amorphous polyphenylene.

In Figure 15 is shown the variation in the glass-transition temperature of the precursor molecule with the extent of aromatization. It shows an increase in T_g from the flexible

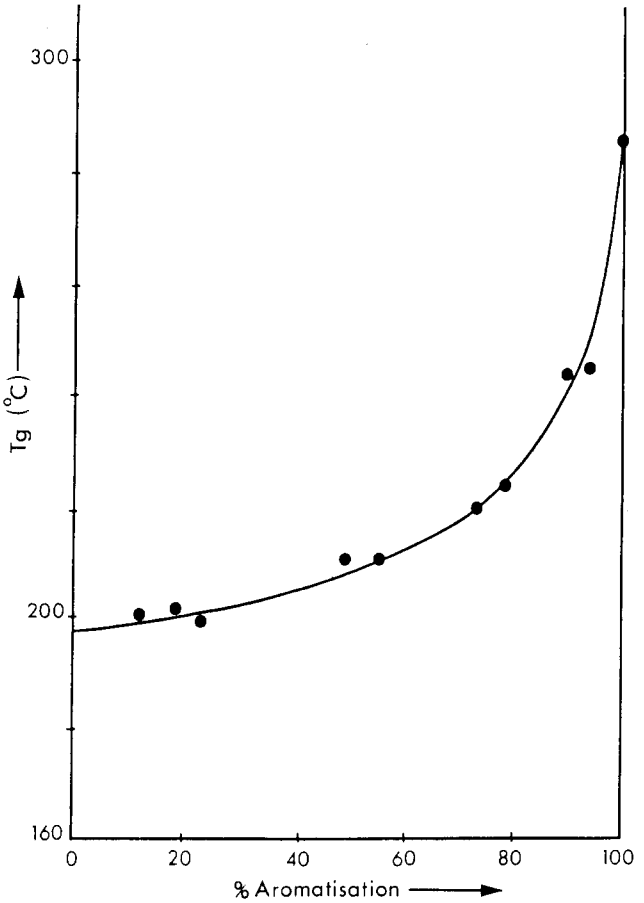


Figure 15. Glass-transition temperatures for polymers with different degrees of aromatization. The figure of 100% aromatization was obtained from Figure 14a. Measurements carried out by using a differential scanning calorimeter.

precursor molecule with increasing rigidity of the molecule as more phenyl groups are formed. The curve finally approaches the T_g of pure amorphous polyphenylene asymptotically. The shape of the curve suggests that the phenyl groups are being formed initially (up to 30%) in blocks and are not randomly distributed along the chain. In the latter case the T_g would increase much more rapidly with the degree of aromatization.

The thermal stability of polyphenylene coatings is to some extent related to the thermal treatment during the aromatization process. It is advantageous to carry out the latter in an inert atmosphere, completing the process by heating at 260 °C and finally at 320 °C to remove the amine catalyst and oligomers. In Figure 16 it is shown that such coatings can be used at temperature close to 400 °C and in the absence of oxygen even at temperatures of 500 °C although there is a significant weight loss initially, probably due to loss of higher oligomers. The films remain coherent, are not carbonized, and still retain their good electrical insulation characteristics. Total thermal breakdown only occurs at a significant rate at 600–800 °C. At these temperatures, in an inert atmosphere, oligophenyls are produced of general composition H-$(C_6H_4)_n$-H where n = 3–11. No benzene or diphenyl is produced. The reason for the absence of the latter is not clear.

The oxidative stability in air is superior to most other aromatic polymers and coatings can withstand temperatures of 350 °C for short periods without significant breakdown. The behavior at 380 °C in air is compared in Figure 16 with that in pure nitrogen.

Polyphenylene coatings previously described have electrical conductivities of 10^{-14}–10^{-15} Ω^{-1} cm^{-1} and in this

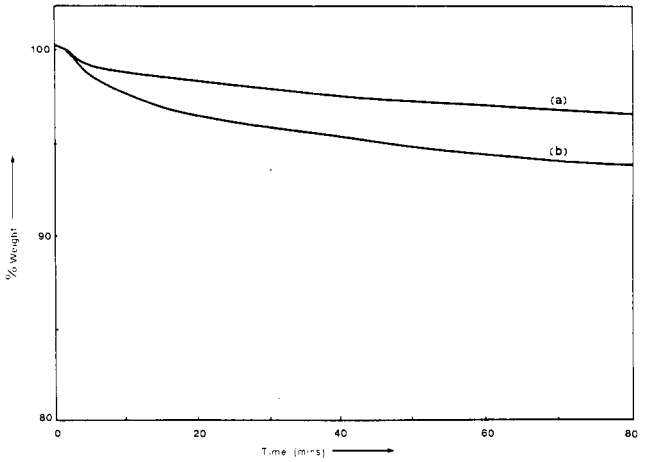


Figure 16. Thermal gravimetric analysis of a polyphenylene coating at 380 °C. Sample previously heated to 320 °C in nitrogen for 24 h: (a) in nitrogen, initial *1.48%* loss due to residual higher oligomers; (b) in air.

Table XII
Electrical Conductivity of Polyphenylene

dopant		conductivity, Ω^{-1} cm^{-1}	empirical formula
sodium naphthalide	n type	0.6×10^{-2}	
ferric chloride	p type	1.5×10^{-2}	$(C_6H_4)_{0.49}(FeCl_4)_{0.12}$
AsF_5	p type	1×10^{2}	$(C_6H_4)(AsFs)_{0.42}$

condition are very good electrical insulators. They have the added advantage of being free of inorganic contaminants.

In Table XII are given examples of the effect of n- and p-type dopants on the electrical conductivity. The polyphenylene films are pale yellow in color, but on treatment with sodium naphthalide they become black and their conductivity markedly increases to give a semiconductor. This behavior is repeated with the strong electron acceptors such as ferric chloride and arsenic pentafluoride. The coatings can be used also as an organic cathode in an electrochemical cell in which lithium trifluoromethyl sulfate is the electrolyte

$$me^- + (C_6H_4)_n + mLi^+ \rightarrow (C_6H_4)_n^{m-} \cdot mLi^+ \quad (11)$$

In their electrical behavior the high molecular weight polyphenylene films prepared so far apparently differ little from the oligomeric polyphenylenes previously reported in the literature.[2]

EXAFS has proved to be a unique tool in providing structural information to help understand the mechanism of conductivity and stability of doped polyphenylene. For $FeCl_3$ doping under anhydrous conditions, it has been shown that Fe is bound in a tetrahedrally coordinated $Fe^{III}Cl_4^-$ with an Fe–Cl distance of 2.19 Å. This is quite different from $FeCl_3$ (solid) which is octahedral with an Fe–Cl distance of 2.34 Å.

A subsequent paper will describe these results in more detail and give information of the effect of copolymerization on the electrical conductivity.

Conclusions

The method described for producing polyphenylene is being used in the study of (1) polymeric electrodes that combine ionic and electron conduction; (2) alignment layers for liquid crystal display systems; (3) production of carbon structures; (4) protective coating for thermally stable polymers in chemically aggressive environments; (5) catalysts are being developed that will enable a predominantly linear polymer to be prepared.

Acknowledgment. The work described was carried out in ICI's Corporate Laboratory whose enlightened management made it possible for polymer chemists to use microbiological techniques, an unusual combination of skills. The authors listed in the title were the original team responsible but many others participated in examining the value of this approach to polymer synthesis. These included Paul Holmes, Phillip Cheshire, Anthony Pickering, Alan Nevin, David Twose, W. Moran, and D. Platt.

Registry No. DHCD, 17793-95-2; DHCD (homopolymer), 110851-46-2; DHCD-DA, 86504-11-2; DHCD-DA (homopolymer), 86504-12-3; DHCD-DMC, 86504-09-8; DHCD-DEC, 110851-44-0; DHCD-DME, 110851-49-5; DHCD-DP, 86504-08-7; DHCD-DP (homopolymer), 86504-19-0; DHCD-DB, 86504-06-5; DHCD-DB (homopolymer), 86504-13-4; DHCD (bis(*p*-nitrobenzoate) derivative), 110851-42-8; DHCD (bis(*p*-bromobenzoate) derivative), 110851-43-9; $FeCl_3$, 7705-08-0; AsF_5, 7784-36-3; benzene, 71-43-2; acetic anhydride, 108-24-7; neutron, 12586-31-1; sodium naphthalide, 3481-12-7.

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High Molecular Weight Polysilanes with Phenol Moieties

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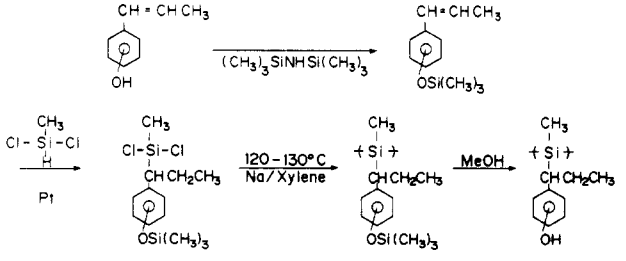
ABSTRACT: High molecular weight polysilanes substituted with pendant phenol moieties were prepared by sodium condensation of dichlorosilanes, whose phenolic OH groups were protected with trimethylsilyl ethers. [2-[[3-[(Trimethylsilyl)oxy]phenyl]methyl]ethyl]methyldichlorosilane (Me-m-1) could homopolymerize to form high molecular weight polysilane (PSi(Me-m-1)). However, monomers substituted with 4-hydroxyphenyl moieties did not give high polymers. The position of the OH in the benzene ring and the number of carbons between Ph and Si seem to determine whether or not the polymer has polysilane structure. The polymer (P(Me-m-1) (M_w 110 000)) with 3-hydroxyphenyl moieties was prepared by gentle hydrolysis of PSi(Me-m-1) in methanol without serious molecular weight decrease. Solubility, photolysis, and thermal stability for the P(Me-m-1) were compared with those for the polysilanes reported previously.

Introduction

Since polysilanes soluble in solvent were synthesized by the reaction of dichlorosilanes with sodium dispersion in *dodecane*, toluene, or xylene,[1,2] many kinds of polysilanes have been reported.[3-7] Recent interest on polysilane syntheses was concentrated on the preparation of high molecular weight polysilanes with functional groups.[8-10] The reason is that high molecular weight polysilanes are potentially useful as UV photoresists,[11] radical photoinitiators,[12] impregnating agents for strengthening ceramics,[13] and precursors for silicon carbide fibers.[14] Synthesizing polysilanes with functional groups would be desirable to make the polysilane application wider.

Recently, polysilanes with halogen moieties in the side chain were synthesized[7] from polysilanes substituted with a double bond, followed by addition of HX to the double bond. However, there have not been any reports published on hydrophilic polysilanes. The authors' goal was to synthesize high molecular weight polysilanes substituted with phenols and to determine the characteristics of these polymers.

Scheme I
Syntheses of Polysilanes with Phenols



Determining how to protect OH moiety was an important point. The protecting group used must have durability to withstand synthesis reagents during monomer and polymer syntheses. In addition, after syntheses, the protecting group must be removed under mild conditions, because the Si–Si bond is easily attacked by base and acid. The trimethylsilyl moiety was selected to achieve these purposes.

Scheme I shows monomer and polymer syntheses. Introduction of the phenol moiety to Si by a Grignard reagent was reported previously;[15] however, the authors' attempts to prepare [[(trimethylsilyl)oxy]phenyl]chloro-

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