Chlorinated Hydroquinones in Thermotropic Melt Polyesters

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ABSTRACT: Selective monochlorination of hydroquinone by SO_2Cl_2 is a preferred synthetic route to chlorohydroquinone. The product mixture, without purification, may be polymerized with terephthalic acid and other comonomers, such as 6-hydroxy-2-naphthoic acid, to provide high-strength fibers. Successive *in situ* chlorination, acetylation, and polymerization constitute a simple, single-reactor process with an inexpensive starting material. Chlorination by SO_2Cl_2 took place almost exclusively in the para position of monoaryl- or alkyl-substituted hydroquinones. Polymers therefrom, e.g., the polyterephthalates of 2-chloro-5-phenylhydroquinone or its *tert*-butyl analog, melted significantly lower and had T_g higher than in the absence of chlorine. They provided crystalline, high-strength fibers, with a tenacity of 20–26 gpd and good strength retention at high temperatures. A prime cause of these effects is electronic dissymmetry across the hydroquinone moiety, optimally enhanced by steric dissymmetry.

Introduction

The preferred melting range for thermotropic polyesters, for high-strength fibers, is about 280–340 °C. This accommodates melt extrusion (spinning) below thermal decomposition temperatures while providing for heat strenthening of fibers above a useful threshold temperature of about 265 °C. The latter process is a buildup of molecular weight to a degree of polymerization of 100 or more, necessary for high fiber tensile strength, by transesterification in the solid state. It is uniquely effective with thermotropic polymers because the molecular chains are well aligned in the fiber axial direction, in the fully extended conformation, and therefore do not deorient or shrink during heat strengthening.

With a few exceptions, copolymerization is usually required to bring melting temperatures down to the desired range. Copolymer modifications of poly(2-chloro-1,4-phenylene terephthalates) have been particularly useful for providing fibers of very high strength. Examples of comonomers are 4,4′-oxydibenzoic acid,[1] 2,6-naphthalenedicarboxylic acid,[2] and 6-hydroxy-2-naphthoic acid (2,6NE),[3] at levels of about 15 mol %. The best polymerization method for thermotropic polyesters containing chlorohydroquinone (ClPG) is acetolysis reaction between acetates and carboxylic acids. The diacetate of ClPG is thermally stable, in contrast with the free diol, at the high temperatures needed for melt polymerization. Aromatic hydroxy compounds, including ClPG, may be converted quantitatively to acetate by reaction with acetic anhydride.

The best-known synthetic route to ClPG has been addition of HCl to benzoquinone, which is relatively expensive. ClPG is formed in high yield, together with small amounts of dichlorohydroquinones. Purification is necessary to remove other minor byproducts which adversely affect polymerizability and fiber properties. This paper describes chlorination of hydroquinone (PG) and monosubstituted hydroquinones by sulfuryl chloride to provide monochlorinated products in high yield. The crude mixture of reaction products may be used directly, without further purification, for the synthesis of copolymers capable of high fiber tensile properties. This opens the way for a single-reactor process for ClPG-containing polymers whereby ClPG and its diacetate are formed intermediately *in situ*. Chlorinated alkyl- or aryl-substituted hydroquinones (2-Cl-5-RPG) are new intermediates giving polymers with lower melting point and spinning temperatures than nonchlorinated, related hydroquinones and higher glass transition temperatures than practically all other thermotropic polyester fiber compositions.

Nomenclature

A shorthand notation for monomers and polymers in this paper to permit immediate recognition of structure is built around use of PG to denote hydroquinone (P = 1,4-phenylene; G = glycol = diol). Thus, ClPG is chlorohydroquinone, 2,5-DClPG is 2,5-dichlorohydroquinone, TriClPG is trichlorohydroquinone, PhPG is phenylhydroquinone, and so on. T is common usage for terephthalic acid. 2,6N is 2,6-naphthalenedicarboxylic acid. 2,6NE is 2-hydroxy-6-naphthoic acid.

Polymer codes are combinations of the codes for basic diols, diacids, or hydroxy acids of which they are composed. Separated by hyphens, an AA–BB type polymer, is indicated. Separation by a diagonal slash indicates a mixed AA–BB/AB copolymer type. Mole ratios of monomers are shown in parentheses. The following are examples: ClPG/T/2,6NE(42.5/42.5/15.0); ClPG-T/2,6N(70/30).

Tensile properties of fibers are expressed in gpd (grams per denier); 1.00 gpd is approximately 0.88 dN/tex (decinewton per tex). As benchmarks, nylon 66 industrial fibers and Kevlar aramid fibers have tensile strengths of 10 and 23 gpd, respectively.

Experimental Section

Chlorinations. The hydroquinone (0.166 mol) in 300 mL of acetic acid, under a slow flow of nitrogen, at 21 °C was treated with successive 2.00-mL additions of SO_2Cl_2 (0.15 mol). After each addition, the mixture was stirred for an additional 20 min, at which point a small aliquot was withdrawn for analysis. For each aliquot volatiles were evaporated off at 21 °C, after which the residue was quantitatively derivatized with bis(trimethylsilyl)-trifluoroacetate. This material was then analyzed by gas chromatography, using a 10-ft column containing 10% OV-17 on Chromosorb W (80/100), programmed at 4 °C/min from 150 to 240 °C. Peak areas were equated to the quantity of each component present. In some cases the identity of certain peaks was determined on the basis of logical deduction, without experimental confirmation, but usually by comparison with retention time for a pure specimen. Figures 1–4 were established in this way. In the case of Cl_2 chlorinations, aliquots of Cl_2/acetic acid solutions were sequentially combined with PG/acetic

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acid solutions. Likewise, for brominations, Br_2 in ether was added to PG/ether.

ClPG from Hydroquinone. Benzoquinone (105 g, 0.94 mol) in dioxane (300 mL) was combined with a stirred solution of dioxane (150 mL) saturated with HCl. After 20 min HCl was passed through the solution for 1 h. Excess HCl was removed by bubbling nitrogen through the solution for 20 min; solvent was distilled off. GC analysis of the residue, pertaining only to volatile components, showed 91.96% ClPG, 3.70% PG, 1.90% 2,5-DClPG, 1.36% 2,6-DClPG, 0.60% 2,3DClPG, and 0.48% other constituents. Quantitative acetylation of this "ClPG" residue, followed by melt polymerization at up to 340 °C with the appropriate monomer to form "ClPG"/T/2,6NE (42.5/42.5/15.0), gave a rubbery material which failed to form a fluid melt, even at 400 °C. Heating was accompanied by excessive bubble formation.

Bromination of PG. Hydroquinone (165 g; 1.5 mol) in ether (2000 mL; ca. 8% solids) was treated dropwise with Br_2 (240 g, 82 mL, 2.5 mol) with stirring at 0–15 °C during 2 h. After 30 min ether was evaporated off to provide 281 g of BrPG; mp 103–106 °C (lit.[5] mp 110–111 °C); brownish solid. GC analysis showed 86.7% BrPG, 4.7% PG, and 6.3% DBrPG isomers. Successive crystallizations from benzene and toluene gave mp 107–109 °C (95.1% BrPG).

Representative Example of the Elements of the Single-Reactor Process: ClPG/T/2,6NE(42.5/42.5/15.0). PG (55.0 g, 0.50 mol) in acetic acid (500 mL), as a stirred solution/slurry at 21 °C, was treated dropwise with SO_2Cl_2 (67.5 g, 0.50 mol) during 1.5 h. After 1 h, volatiles (acetic acid, SO_2, HCl) were removed *in vacuo*, leaving a residue of slightly off-white solid (74 g) consisting of 79.5% ClPG, 12.9% DClPG isomers, and 7.66% PG. Other byproducts were essentially nil. This reaction product (13.2 g) was refluxed with acetic anhydride (40 mL) during 3 h. Subsequent addition of terephthalic acid (14.11 g, 0.085 mol) and 2,6NE (6.90 g, 0.03 mol) was followed by stirring and heating in a Wood's metal bath from 150 up to 320 °C during 107 min, during which acetic acid distilled off. The stirred viscous melt was finally subjected to a vacuum of 0.2–0.5 Torr during 6 min at 320–330 °C. The polymer softened on a gradient hot bar at 270 °C, and long fibers could be pulled from the anisotropic melt at 315 °C.

Representative Fiber Processing. A molded plug of the above polymer was extruded through a 0.23-mm-diameter orifice at 300 °C and fibers were wound up at 550 m/min. The yarn was piddled into a basket and heat-treated under zero tension in an oven under a slow flow of nitrogen at 180–283 °C during 4 h and then at 282 °C for 16 h. Tenacity/elongation/modulus for as-spun and heat-treated fibers were, respectively, 4.4 gpd/1.4%/375 gpd and 15.3 gpd/4.0%/432 gpd.

2-Chloro-5-phenylhydroquinone Diacetate. PhPG (124 g, 0.666 mol) in acetic acid (1200 mL) under a nitrogen bleed was treated with SO_2Cl_2 (90 g, 5.4 mL, 0.666 mol) during 3 h at room temperature with stirring. Exit gases were conducted through water to dissolve byproduct SO_2 and HCl. Evaporation of volatiles was followed by refluxing with acetic anhydride (600 mL) containing pyridine (2 mL) for 5 h. Acetic acid/acetic anhydride were distilled off and the residue was fractionally distilled through a 25-mL Vigreux column at about 165 °C/0.5 Torr. Crystallization from ethanol and then methanol gave 2-Cl-5-PhPG diacetate: mp 100.5–102.5 °C; 99% purity by GC; structure confirmed by NMR analysis.

2-Chloro-5-*tert*-butylhydroquinone diacetate was distilled at 130 °C/0.7 Torr and crystallized from ethanol: mp 73–76.5 °C; 96.9% purity by GC; identified by NMR.

2-Chloro-5-methylhydroquinone diacetate was recrystallized from ethanol: mp 110–111.5 °C; 99.6% purity by GC; identified by NMR.

1-Chloro-2-hydroxy-6-naphthoic Acid. The methyl ester of 2,6NE (60.6, 0.30 mol) in acetic acid (600 mL) under nitrogen at room temperature was treated with SO_2Cl_2 (40.5 g, 24.3 mL, 0.30 mol) during 3 h. SO_2 and HCl were removed by purging with nitrogen. Product crystallized from the solution: 50 g; mp 155–156.5 °C; 96.3% purity. This methyl ester of 1-Cl-2,6NE (40 g) was refluxed 24 h in a solution of KOH (19 g) in MeOH/H_2O (50/50). The cooled, filtered solution was acidified with HCl. The filtered, washed methyl 1-Cl-2,6NE product, 35 g, had mp 245–255 °C. This was acetylated to give mp 262–264 °C; 100% purity by GC; identity confirmed by NMR.

Table 1. Reactions of Chlorine with Hydroquinone

reaction products (by GC)	1.0 equiv of Cl_2 with 5% PG in AcOH at 21 °C/2 h	2.1 equiv of Cl_2 with 5% PG in AcOH at 21 °C/2 h	1.0 equiv of Cl_2 with 50% PG in AcOH/H_2O (75/25) at 90 °C/2 h
PG	65.6[a]	44.0	48.3
ClPG	21.8	17.3	42.6
2,5DClPG	1.62	2.42	2.28
2,3DClPG	6.95	30.6	1.42
TriClPG	0.13	0.47	0.24
higher boilers	3.05	0.24	5.11

[a] Values in percent.

Results and Discussion

Chlorination of Hydroquinone. Chlorine reacts incompletely and with poor selectivity with PG in acetic acid solution at 21 °C. Table 1 shows that with an equimolar amount of chlorine, 66% PG remains unreacted and that ClPG is extensively chlorinated further to afford a mixture of ClPG (22%) and isomeric 2,3- and 2,5-dichlorohydroquinones (12%). Higher ratios of chlorine to PG increased the degree of chlorination (e.g., 2 mol equiv of chlorine reduced residual PG to 44%), with dichlorohydroquinones now the predominant products (Table 1).

Following a literature procedure,[4] the reaction of chlorine with PG at a much higher concentration (50 vs 5%) and higher temperature (90 vs 21 °C) in acetic acid/water (75/25 w/w) again gave incomplete chlorination, with 48% unreacted PG, but a higher yield of ClPG relative to other components (Table 1). The reaction products were also contaminated with an unacceptably high level of high-boiling, thermally unstable materials. The presence of water profoundly changes the mechanism of chlorination as revealed by a comparative absence of polychlorinated hydroquinone. Evidently HCl and HOCl are produced by reaction of chlorine with water, whereupon the latter oxidizes PG to benzoquinone, which then reacts with HCl. Benzoquinone also accounts for high-boiling byproducts. The distribution of chlorinated products from reaction of benzoquinone, as discussed later, is similar to that shown in Table 1 for the aqueous acetic acid reactions.

For reduced substrate reactivity, as a possible way to improve selectivity of chlorination in glacial acetic acid, the diacetate of ClPG was treated with chlorine. At 21 °C there was no reaction in the absence of a catalyst. Catalyzed chlorination again showed little selectivity, with large yields of di- and trichlorinated hydroquinones.

Reduced reactivity on the part of the halogenating agent did, however, lead to a strong preference for restricting reaction to attack on PG to form monohalohydroquinone rather than competing attack of a ClPG as well to form dihalohydroquinones. In initial experiments the reaction of bromine with PG in ether at an equimolar ratio gave bromohydroquinone (BrPG) in over 80% yield. Dioxane bromide, a 1:1 molecular complex, was reported to afford BrPG in over 90% yield.[5]

Sulfuryl chloride has been shown to be a selective chlorinating agent, e.g., in reaction with phenol to form 4-chlorophenol in 100% yield; variable yields of 2- and 4-chlorophenols, depending on temperature, result from use of chlorine.[6] As an inexpensive liquid, bp 67 °C, SO_2Cl_2 is easily handled. Its chlorination byproducts are HCl and SO_2, which are easily removed from a reaction mixture, e.g., by aeration.

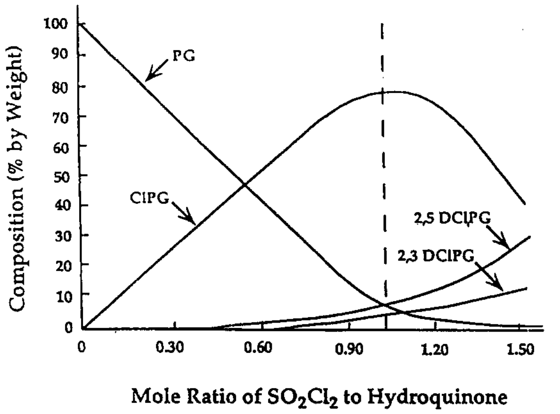


Figure 1. Chlorination of hydroquinone.

Table 2. Composition by Weight of Product Mixture from Reaction of SO_2Cl_2 with 8% PG in Acetic Acid at Various Ratios at 21 °C

	retention time (min)	mol of SO_2Cl_2/mol of PG			
		1.00	1.10	1.20	1.50
PG	5.41	9.3 (10.2)[a]	6.9 (7.5)	2.6 (2.8)	0.03
unknown A[b]	7.50	0.80	0.20	0.18	0.02
ClPG	8.10	78.4 (79.9)	80.4 (81.5)	78.1 (79.9)	44.1
unknown B[b]	9.80	0.42		0.02	0.00
2,5DClPG	10.25	7.2 (6.5)	7.4 (6.6)	12.0 (10.9)	32.6
2,3DClPG	11.75	3.8 (3.5)	5.0 (4.4)	7.0 (6.4)	22.7
other products	>12.00	0.16	0.26	0.08	0.18

[a] Molar compositions in parentheses. [b] Unknowns A and B are almost certainly monoacetylated PG and ClPG from acid-catalyzed esterification by acetic acid and disappear in analysis of the fully acetylated mixture.

PG is chlorinated rapidly and quantitatively by SO_2Cl_2 in acetic acid[7] or ethyl acetate[8] at 21 °C. Maximum yields of ClPG (ca. 80%) were achieved with a SO_2Cl_2:PG mole ratio of 1.0–1.2, giving a white product containing minor amounts of 2,3DClPG, 2,5DClPG, unreacted PG, and negligible other products (Figure 1). Contaminants, which could interfere with the ability of the crude reaction products mixture to provide high molecular weight polymer and high-strength fibers, are absent. If a purer ClPG product is desired, the reaction products may be purified, e.g., by distillation as the diacetate, in which case ethyl acetate[8] would be a preferred reaction medium because it can dissolve PG at higher concentrations than acetic acid.

Figure 1 shows the change in composition of a solution in acetic acid at 21 °C wherein PG is treated with successive increments of SO_2Cl_2 at 21 °C. In the early stages where PG is in excess, ClPG exclusively is formed, but as the concentration of ClPG exceeds that of PG, it starts to undergo dichlorination. The compositions of the product mixtures, using 1.0, 1.1, and 1.2 mol of SO_2Cl_2/mol of PG, for maximal ClPG formation, are shown in Table 2. Good reproducibility of composition of the chlorination products mixture, very important if such a mixture is to be incorporated in a polymeric/fiber product, was confirmed for the arbitrarily selected case of SO_2Cl_2:PG ratio of 1.50 and concentration of 9.0% (partial slurry) in acetic acid at 21 °C. (At an early stage in the chlorination this became a homogeneous solution.) At PG concentrations in acetic acid of, say, up to 10%, where the limits of solubility are exceeded only to a modest degree, there is no significant dependence of reaction product composition on concentration. However, where the proportion of slurry becomes appreciable, there is a marked divergence in the composition of the product mixture. The product mixture was much the same for a 20% solution of PG in ethyl acetate[8] and a 5% PG solution in acetic acid.

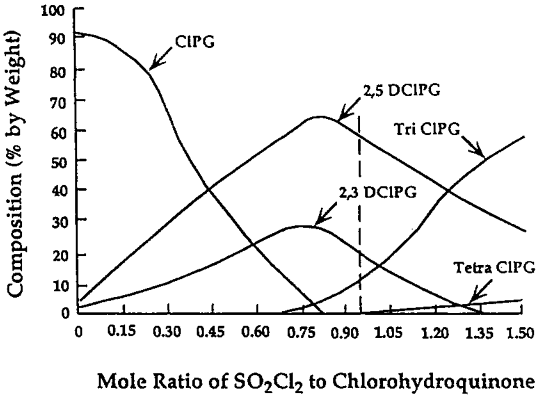


Figure 2. Chlorination of chlorohydroquinone.

Figure 2 shows the course of chlorination of ClPG in acetic acid at 21 °C with incremental amounts of SO_2Cl_2. This, of course, represents the polychlorination of PG. (Starting material was actually 92% ClPG together with minor amounts of isomeric dichlorohydroquinones.) ClPG ultimately disappears as progressive chlorination provides a mixture containing 67% 2,5DClPG and 30% 2,3DClPG. These, in turn, are converted to trichlorohydroquinones, and ultimately tetrachlorohydroquinone starts to appear. Probably tri- and tetrachlorohydroquinones, as well as ClPG, but not 2,3- or 2,5DClPG, can be prepared in high yield via SO_2Cl_2 in the appropriate proportions.

The product mixtures from 1.0, 1.1, and 1.2 mole ratios of SO_2Cl_2:PG all contain about 80% ClPG (Table 2). (The differences in minor component content may influence spinnability and fiber properties. From time to time certain comonomer combinations have provided polymer melts which exhibit atypical flow properties in failing to undergo good attenuation in spinning; this ultimately led to mediocre fiber strength. A probable cause is incompatibilities of oligomeric species in the polymerizing melt, leading to a certain amount of block copolymer character.) ClPG/T/2,6NE (42.5/42.5/15.0 mole ratio) was selected as a suitable basic composition for comparing the effect of replacing ClPG by crude "ClPG" (chlorination reaction products). Siemionko reported[3] that the same copolymer made from purified ClPG gave heat-treated yarn tenacity/elongation/modulus of 27.5 gpd/4.3%/507 gpd. The polymer was prepared from preformed acetate monomers and spun at 320–326 °C. Comparable data for the "ClPG" crude product mixture are shown in Table 3 ("ClPG" content is based on the moles of PG used for its preparation). It is apparent that "ClPG" from 1.0- and 1.1-mole SO_2I_2 give superior heat-treated fibers compared with that from 1.2-mole SO_2Cl_2. These copolymers are considered broadly comparable with the Siemionko control. Insolubility of all these copolymers in organic solvents made it impossible to assess their molecular weight in terms of inherent viscosity. However, an indirect indicator of molecular weight is tenacity of as-spun fibers which, at ca. 4 gpd, is typical of many thermotropic polyesters. The higher strength of the control in Table 3 indicates appreciably higher molecular weight, although this cannot be construed as an indicator that heat-treated fibers will also be stronger. Liquid crystallinity in all melts was established by the thermooptical test described in ref 2. The intensity of transmitted light, relative to incident light, passing through a polymer specimen between crossed polarizers is measured continuously as temperature is raised. Thermotropic polymers show a substantial increase in transmittance at the melt (or flow) temperature. Transmitted light diminishes to zero at the clearing

Table 3. Tensile Properties of "ClPG"/T/2,6NE (42.5/42.5/15) for "ClPG" Derived from Reaction of Varying Proportions of SO_2Cl_2 with PG[a]

		as-spun			heat-strengthening					
SO_2Cl_2:PG mol ratio	spinning temp (°C)	T	E	M_i	T	E	M_i	(T	E	M_i)
1.0	290–300	4.5	1.4	383	15.6	4.0	441	(21.0	4.3	575)
1.1	306–314	5.1	1.4	425	14.6	3.7	440	(16.3	4.2	410)
1.2	370	3.6	1.1	370	7.3	2.1	384	(9.9	2.4	510)
control:pure ClPG plied yarn (3)	320–326	7.3	1.9	485	24.3	4.3	447	(—	—	—)
synthetic "ClPG" mixture[b] (cf. SO_2Cl_2:PG = 1)	320	5.5	1.5	451	14.8	4.0	418	(17.1	4.5	444)

[a] Properties are average of five tests, with highest tenacity in parentheses (gpd units). [b] "ClPG" contained 78.9% (molar) ClPG, 10.2% PG, 6.46% 2,5DClPG, and 3.46% 2,3DClPG.

temperature, where the melt loses its liquid crystalline character. For the "ClPG"-containing copolymers of Table 3, initial pyrolytic weight loss occurs at 375–390 °C, which is well below clearing temperatures.

The lower strength of the fiber from "ClPG" from 1.2-mole SO_2Cl_2 may be an artifact of the polymerization conditions because related synthetic "ClPG" mixtures consisting of (a) 80% ClPG + 20% 2,3DClPG and (b) 80% ClPG + 20% 2,5DClPG both were consistent with excellent fiber properties (17 and 23 gpd,[3] respectively). A synthetic "ClPG" mixture of preformed diacetates, to simulate the "ClPG" product from 1.0-mole SO_2Cl_2, gave quite comparable fiber properties (Table 3).

In addition to providing a "ClPG" product which may be used directly without further purification or separation, SO_2Cl_2 chlorination makes possible a simplified single-reactor polymerization process. Inexpensive hydroquinone in acetic acid may be chlorinated *in situ*, with evolution of byproduct HCl and SO_2 as gases. With addition of acetic anhydride, at elevated temperatures the "ClPG" diol mixture may than be quantitatively acetylated. With addition of the remaining monomers required and removal by distillation of acetic acid and unconsumed acetic anhydride, temperature is raised to promote acetolysis polymerization and further acetic acid formation. The environmentally acceptable byproducts may be recycled as acetic acid and/or acetic anhydride.

A single-reactor process is not possible for a ClPG reaction mixture from benzoquinone and HCl, even though the ClPG yield may be over 90%, because minor byproducts interfere with polymerization to a spinnable polymer melt. Such a product mixture, prepared in dioxane, contained the following volatile components: ClPG, 92.0%; PG, 3.70%; 2,6DClPG (probably), 1.36%; 2,5DClPG, 1.90%; 2,3DClPG, 0.6%; other volatile constituents, 0.48%. Preparation of "ClPG"/T/2,6NE (42.5/42.5/15.0) from such a mixture gave a rubbery material which never became a fluid melt below 400 °C, with polymerization and heating accompanied by excessive evolution of volatile byproducts other than acetic acid.

It is of interest to compare ClPG/T/2,6NE polymers[3] with the analogs from BrPG, which was briefly investigated in terms of direct bromination of PG by bromine, as discussed earlier. BrPG/T/2,6NE (42.5/42.5.15.0) has a melt temperature substantially lower than that of the ClPG and MePG analogs (275, 320, and 310 °C, respectively). Pure BrPG led to fiber properties comparable with those from ClPG in analogous compositions. Tenacity/elongation/modulus was 17.2 gpd/4.5%/440 gpd for the heat-treated fiber. The melt temperature lowering capability of bromine, compared with chlorine, is not sufficient to make possible melt processing of BrPG-T homopolymer. Melting point lowering is associated with the comparatively greater bulk of a bromine versus a chlorine substituent, which is 25 or 50% depending on whether volume is calculated using atomic radii[9] (1.27 vs 1.00, respectively) or half-distance between atomic centers in diatomic molecules (1.53 vs 1.00, respectively). BrPG-based polymers and fibers could undoubtedly be produced from PG by a single-reactor process but it is not certain that byproduct polybromohydroquinones, which would be present as minor components, would have adequate thermal stability for melt-spinning at ca. 300 °C. Although BrPG-based thermotropic polyester fibers would provide superior fire resistance to ClPG-based analogs, there appear to be no significant advantages as high-strength fibers to warrant in-depth investigations.

Table 4. Effect of PG Concentration in Acetic Acid of Composition of Reaction Product Mixture from Reaction with 1.00 mol of SO_2Cl_2 at 21 °C

	concn of PG in acetic acid (w/w)		
	16.7% (slurry)	9.9% (slurry)	4.8% (solution)
PG	14.2	9.3	13.8
ClPG	68.9	78.4	77.9
2,5DClPG	9.6	7.2	4.9
2,3DClPG	6.7	3.9	3.0

Chlorinated Alkyl- or Arylhydroquinones. The use of ClPG in thermotropic polyester compositions is a particular application of the general principle that asymmetric substitution, particularly with a single substituent, is an effective means of reducing melt temperatures. Melting point lowering parallels the size of the substituent. Shape of substituent also plays a role. Some examples are shown in Table 5.

Pletcher[1] observed that copolymers based on 2-methyl-5-ethylhydroquinone had a polymer melt temperature of 282 °C, lower than for 2,5DMePG or 2,5DEtPG and for MePG or EtPG. It seemed likely that placement of a chlorine substituent para to the existing substituent in substituted hydroquinones such as those in Table 4 might lower polymer melting temperatures considerably such that a comonomer would no longer be necessary, and homopolymeric fibers having considerable crystallinity would result. Crystallinity makes a key contribution to good dimensional stability at elevated temperatures and often is concomitant with higher glass transition temperatures. For a great many thermotropic polyesters including those based on ClPG, T_g is about 112 °C. Most such polymers follow approximately the Beaman rule[11] that $T_g = {}^2/_3 T_m$, where T_m is the crystalline melting point in K. Thus, PhPG-T, from phenylhydroquinone (PhPG), has T_g 150 °C and T_m = 349 °C.

In general, alkyl- or arylhydroquinones are chlorinated by SO_2Cl_2 para to the original substituent in high yield and high selectivity, at least as good as for monochlorination of PG.[12] Figure 3 shows that the course of chlorination of PhPG by SO_2Cl_2 in acetic acid at 21 °C is very similar to that of PG itself and can provide close to a 100% yield of 2-Cl-5-PhPG with just over 1.0 mol equiv of SO_2Cl_2. Chlorinations of *tert*-BuPG and MePG again are similar to that of PhPG in Figure 3.

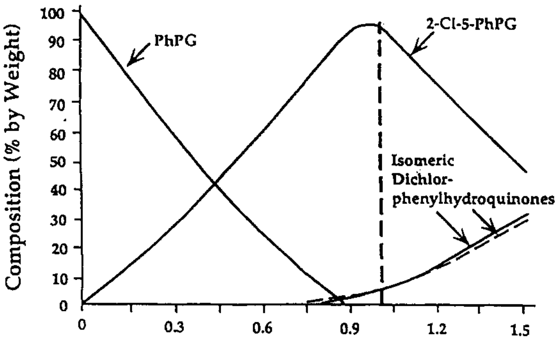


Figure 3. Chlorination of phenylhydroquinone.

As described for the case of "ClPG", it is possible to prepare melt-spinnable polymers based on 2-Cl-5-PhPG, 2-Cl-5-*tert*-BuPG, and 2-Cl-5-MePG by single-reactor chlorination/acetylation/polymerization sequences. For accurate assessment of polymer and fiber properties at the outset, and since these are all novel monomers, pure diacetates were isolated and purified by standard procedures. In the examples studied not only did para substitution by Cl lower the polymer melting temperature but it raised the glass transition temperature; i.e., in relation to Beaman's rule, $T_g > {}^2/_3 T_m$. This is of particular significance in thermotropic polyester fibers where increased T_g translates into increased thermal stability and property retention at elevated temperatures.

With 1.0 mol equiv of SO_2Cl_2, PhPG was converted to about 94% 2-Cl-5-PhPG together with 3% each of 2,3-DCl-5-PhPG and 2,6-DCl-5-PhPG (Figure 3). Its structure was confirmed by NMR analysis. The homopolymer 2-Cl-5-PhPG-T had a melt temperature and spinning temperature 30–40 °C below that of PhPG-T (Table 5). Although the latter may be spun for a limited duration to give strong fibers (T = 25 gpd for optimized yarn), it must be spun right at the limit of its thermal stability. For continuous processing it is necessary to reduce spinning temperature with a modest amount of comonomer. Table 5 shows that for the polyterephthalate of (*p*-chlorophenyl)-hydroquinone and its Me and MeO analogues, spinning temperatures as high as, if not higher than, that of PhPG-T are necessary,[13] thus affirming the profound difference in thermal properties between 2-Cl-5-PhPG and its isomer with a *p*-chlorophenyl substituent. Substitution in the phenyl side group also has an adverse effect on fiber properties (T = 11–15 gpd; Table 5).

The tensile properties of 2-Cl-5-PhPG-T (Table 5) are considered to be in the same range as those of PhPG-T; modulus is somewhat lower but elongation (up to 6.6%) is somewhat higher and may indicate additional toughness. As-spun 2-Cl-5-PhPG-T fibers show an unusually well-defined diffractogram with a crystal size of 107 Å (cf. Kevlar 49 aramid with ca. 80 Å) and an orientation angle of 29°, improving to 11° on heat treatment (PhPG-T also has a high crystallinity and an orientation angle of 13°).

DSC analysis showed that 2-Cl-5-PhPG-T as-spun fibers exhibit a melting endotherm peak at 349 °C (5.4 J/g), moving to 337 °C (12.4 J/g after heat strengthening at 278 and 316 °C (15.0 J/g) after alternative heat strengthening at 294 °C. The melting range, indicated by the peak width, is about 20 °C in each case. The absence of crystallization exotherms in the DSC cooling curves indicates that crystallization is slow. Shifts in melting endotherms suggest that recrystallization occurs in the region of the melting temperatures. Recrystallization is known to occur in PhPG-T whereby melting endotherms at 295 and 340 °C in as-spun fibers, after melting and reheating, are replaced by a single endotherm at 338 °C; heat strengthening at 316 °C caused this to shift to 355 °C. The DSC data for 2-Cl-5-PhPG are puzzling since the fiber is spun apparently well below the initial crystalline melting point (310–320 vs 349 °C). However, the thermooptical test shows a flow temperature of 316 °C and a progressive increase in the transmitted light intensity, i.e., development of the nematic melt phase to beyond 340 °C. This suggests progressive melting of the solid phase, dispersed in the nematic melt such that it does not adversely affect spinning. It is likely that the much longer heating times involved in a spinning operation, albeit below the crystalline melt temperature, enable residual crystalline particles to become homogenized in the melt.

The glass transition temperature of 2-Cl-5-PhPG-T (DSC) is 174 °C, considerably higher than that of PhPG-T (150 °C), ClPG-T copolymers (ca. 112 °C), and many hydroxybenzoic acid-based copolymers (ca. 112 °C). T_g affects retention of tensile strength and modulus on heating fibers at 150 °C (Table 5). The performance of PhPG-T is also associated with its high degree of crystallinity (30 vs 15 J/g for 2-Cl-5-PhPG-T, for respective crystalline melting endotherms) because T_g, a property of noncrystalline regions of the polymer, becomes relatively less important.

While processing temperatures of PhPG-T can be reduced below the thermal decomposition range by chlorination to 2-Cl-5-PhPG, an alternative way to do this is via copolymerization as PhPG/2-Cl-5-PhPG-T. Such copolymers may be produced in any desired ratio by *in situ* chlorination with the appropriate amount of SO_2Cl_2 in a single-reactor process. The copolymer compositions described in Table 6 were, however, prepared in the conventional manner from the pure diacetates. All compositions showed good tensile strength. After an initial drop in melting temperatures and glass transition temperature relative to PhPG-T, on copolymerization with 2-Cl-5-PhPG-T, these values remained more or less constant, suggesting isomorphous crystalline character.

As a readily-available, inexpensive monomer *tert*-BuPG should be an attractive ingredient for thermotropic polyester fibers. However, many *tert*-BuPG compositions of the AA–BB type have proven unsatisfactory. *tert*-BuPG-T has an excessively high melting temperature, in the region of 400 °C. Copolymerization, e.g., with 2,6-naphthalenedicarboxylic acid, reduces melting temperature far less effectively than is the case with ClPG-T. Melts do not attenuate well in spinning, and ultimately fibers have low strength. It seems likely that the large, compact *tert*-butyl group enhances hydrocarbon character, leading to phase separation during polymerization, block copolymer character, and poor flow characteristics.

2-Cl-*tert*-BuPG was obtained in 84% yield, together with 16% isomer, probably 2-Cl-3-*tert*-BuPG, by reaction of *tert*-BuPG with about 1.0 mol of SO_2Cl_2. Relatively pure (97%) 2-Cl-5-*tert*-BuPG was isolated for polymerization studies. The homopolymer, 2-Cl-5-*tert*-BuPG-T, melting at 370 °C, was not suitable for melt spinning, even though its melting temperature was considerably lower than the melting temperature of *tert*-BuPG-T. However, incorporation of as little as 5 mol % of 2,6NE drastically lowered the melt temperature to 308 °C. (With 17% 2,6NE comonomer, T_g remained high but the melting temperature was reduced below the level where fibers could be effectively heat-strengthened.) The 5% 2,6NE copolymer provided excellent heat-strengthened fibers with tenacity/elongation/modulus as high as 27 gpd/6.5%/504

Table 5. Polyterephthalamide Homopolymers Related to PhPG-T

					heat-strengthened fibers			retention at 150 °C	
	T_g	melting endotherm	polymer melt temp (°C)	spinning temp (°C)	tenacity (gpd)	elongation (%)	modulus (gpd)	tenacity (%)	modulus (%)
PhPG-T[12]	150	30	345	340–360	25.0[a]	3.8	520	76	63
2-Cl-5-PhPG	174	15	316	310–320	21.0	5.8	340	75	77
p-ClPhPG[13]			370	365–370	11.2[a]	2.7	379		
p-MePhPG[13]				>340	15.3	3.1	440		
p-MeOPhPG[13]			341	>340	13.0	3.1	440		
ClPG/T/2,6NE[3] (42.5/42.5/15)	112	low			27.5	4.3	507	50	50

[a] Optimized conditions. [b] 1.0-in. filament specimens; all others were 10-in. yarn specimens.

Table 6. PhPG/2-Cl-5-PhPG-T Copolymer Properties (1-in. Filaments)

				tenacity/elongation/modulus	
composition (mol % of 2-Cl-5-PhPG)	melt temp (DSC) (°C)	spinning temp (°C)	T_g (DSC) (°C)	av (gpd/%/gpd)	highest strength (gpd/%/gpd)
100	300–320	310–320	174	20/6.6/315	21/5.8/340
80	302–324	315–320	163	21/6.7/330	22/6.7/350
60	291–317	290–300	162	21/6.5/350	23/6.6/365
40	278–310	305–310	161	18/5.9/325	24/6.7/380
20	310–315	295–300	160	19/5.5/360	23/6.0/390
0	338–347	340–360	150	25/3.8/520 (yarn, 10 in.)	

gpd. Retention of tenacity and modulus at 150 °C, despite high T_g, was only 53 and 57%, respectively, not much higher than for copolymers of ClPG-T with low T_g. This mediocre performance was associated with low levels of crystallinity, partly the result of copolymer character but largely because *tert*-BuPG-containing polyesters have a low tendency to crystallize. Substitution of 10% 4-hydroxybenzoic acid for 2,6NE gave a copolymer spinnable at 295–300 °C to give nonoptimized fibers with tenacity/elongation/modulus of 13.8 gpd/4.1/357, orientation angle of 13°, T_g of 175 °C, and low crystallinity. An unusual characteristics of 2-Cl-5-*tert*-BuPG-based fibers was a substantial increase in modulus (by about 100 gpd) on heat strengthening; this indicates as-spun fibers have rather mediocre chain alignment.

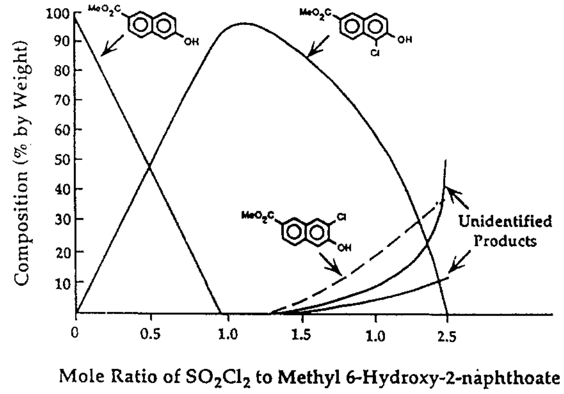
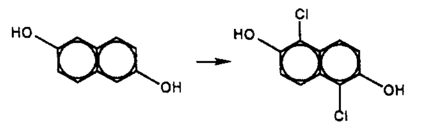


Figure 4. Chlorination of methyl 2-hydroxy-6-naphthoate.

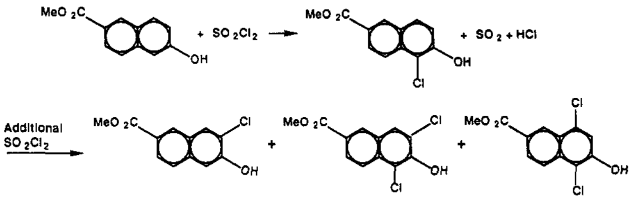
MePG was chlorinated by an equimolar amount of SO_2Cl_2 to form 92% 2-Cl-5-MePG and 8% isomeric 2-Cl-3-MePG (assumed structure). Unlike the cases of PhPG and *tert*-BuPG where Ph and *tert*-Bu groups sterically hinder chlorination at positions ortho to them thus directing chlorination toward the para position, steric hindrance was not a major consideration in the case of MePG. Preference for substitution at the para position must be the result of electronic asymmetry. Using purified monomers, 2-Cl-5-MePG/T/2,6NE (42.5/42.5/15.0), melting range 300–340 °C (by differential thermal analysis), flow temperature 319 °C (by thermooptical test), and T_g of 140 °C, was prepared. Thus, the melting temperature is not much different from that of the analogous copolymers from ClPG or MePG, but T_g is significantly higher (compared with 112 °C). Compared with the analog from 2,5-DClPG with a melting temperature above 370 °C, the drop is considerable. It is inferred that the 2,5-DMePG analog would have a similarly high melting temperature since a related composition, 2,5-DMePG-T/2,6N (70/30), melts about 370 °C (by DTA). It is widely held that substituent size is a major factor in determining melt temperatures of substituted hydroquinone-based polymers. If this were true, it would be expected that copolymers based on 2-Cl-5-MePG would not differ significantly in this way from those based on 2,5DClPG or 2,5DMePG, since methyl and chloro substituents are similar in size. Since a difference exists, there is clearly a large contribution from asymmetric charge distribution affecting the cohesion between polymer chains. This effect is manifest in the lower melting point of the asymmetrically substituted monomers: 111, 140, and 142 °C, respectively, for diacetates of 2-Cl-5-MePG, 2,5-DMePG, and 2,5-DClPG.

2-Cl-5-MePG/T/2,6NE (40/40/20), a somewhat modified composition having a lower melting point of 301 °C (by DSC), was spun to a fiber with tenacity/elongation/modulus of 3.1 gpd/1.0%/300 gpd, having mediocre response to heat-strengthening (9.0 gpd/2.5%/455 gpd). Low fiber luster was indicative of phase inhomogeneity which would be subject to improvement by variation of previous conditions.

Chlorination of Binuclear Phenols. Assuming selective chlorination by SO_2Cl_2, the primary product to be formed in high yield from 2,6-naphthalenediol is likely to be 1,5-dichloro-2,6-naphthalenediol. No selectivity between substitution in the 1 and 5 positions would be expected. A symmetrical monomer of this sort should not lower melt temperatures of the copolymers significantly, compared with the unsubstituted diol. To provide asymmetric substitution, chlorination of methyl 2-hydroxy-6-naphthoate was investigated. The methyl ester, rather than free acid, was selected to ensure adequate solubility in acetic acid. Figure 4 shows that 1.0 equiv of SO_2Cl_2 provided methyl 1-chloro-2-hydroxy-6-naphthoate in 95%



yield. Continued chlorination leads to the formation of three additional products, presumably with chlorine in the 7, 8, and 5,8 positions.



1-Cl-2,6NE, isolated by hydrolysis of the ester, provided a copolymer, ClPG/T/1-Cl-2,6NE (42.5/42.5/15.0), melting somewhat lower than the 2,6NE analog (292 vs 302–312 °C) and giving comparable fiber properties (tenacity/elongation/modulus = 20.6 gpd/4.8%/458 gpd. Since a lower level of 1-Cl-2,6NE (10%) gave a much higher melting point (358 °C) and inferior properties (15.3 gpd/3.4%/578 gpd), this monomer offers no real advantage over 2,6NE. At lower comonomer levels such as 10% 2,6NE, it is difficult to avoid the presence of significant blocks of higher melting ClPG-T in the polymer, which diminish response to heat strengthening at significantly lower temperatures.

Reaction of SO_2Cl_2 with 4,4′-biphenol at equimolar ratio produces a 2:1:1 mixture of 3-chlorobiphenol, 3,3′-dichlorobiphenol, and unsubstituted starting material. With 2 mol of SO_2Cl_2/mol of biphenol a high yield of the symmetrical 3,3′-biphenol will result. By deactivating the positions ortho to OH by acetylation, chlorination is directed toward the 2,2′ positions. This occurs much more slowly than with the free diol but under optimal conditions good yields of 2-chloro- and 2,2′-dichlorobiphenyldiacetate are expected.

Conclusions

Chlorination of PG by SO_2Cl_2 in an organic solvent provides a high-yield (80%), low-cost route to ClPG compared with the commonly used addition of HCl to benzoquinone. Significant byproducts in this reaction are exclusively minor amounts of 2,3- and 2,5DClPG so that the crude mixture of reaction products may be polymerized, without further purification, to high molecular weight thermotropic copolymers. These can be converted into high-strength fibers which are comparable to those made using purified ClPG as demonstrated for ClPG/T/2,6NE. On this basis a simplified, single-reactor process for ClPG copolymers was defined whereby PG in acetic acid is converted *in situ* by SO_2Cl_2 to ClPG, with byproducts SO_2 and HCl removed by aeration; sequentially acetic anhydride addition provides quantitative conversion to diacetate; finally, with addition of other monomeric ingredients and progressive increase in temperature, solvent acetic acid and excess anhydride are distilled off and polymerization proceeds with evolution of additional acetic acid to form a high molecular weight thermotropic melt. The distillates are low-cost, environmentally acceptable, recyclable materials.

PhPG is chlorinated even more selectively under conditions comparable to the case of PG, to form 2-Cl-5-PhPG (about 95% yield). This can be polymerized as the polyterephthalate via the diacetate and spun to fibers of similar strength (above 20 gpd) to PhPG-T. The former provides a significantly lowered melting point and spinning temperatures, well below the threshold of thermal decomposition, close to which PhPG-T must be spun. 2-Cl-5-PhPG-T is a crystalline fiber with T_g substantially higher than those of PhPG-T and ClPG-T copolymers (174 °C vs 150 and 112 °C, respectively). These properties translate into very good retention of tensile properties at elevated temperatures. As an alternative approach, spinning temperatures may be suitably lowered by copolymerizing PhPG with 20 mol % (or less) of 2-Cl-5-PhPG and terephthalic acid. This may be simply done as a single reactor operation by initially treating PhPG in acetic acid with the appropriate amount of SO_2Cl_2 to form the desired amount of 2-Cl-5-PhPG, before proceeding with the acetylation/polymerization sequence. All copolymers have also an elevated T_g (relative to PhPG-T) of 162 °C showing significant crystallinity and possibly isomorphous as heat-strengthened fibers.

SO_2Cl_2 chlorination of the readily available *tert*-BuPG again provides high yields (85%) of 2-Cl-5-*tert*-BuPG which, as polyterephthalate, has a significantly lowered melting point. Copolymerization, e.g., with 5 mol % of 2,6NE, is additionally required to reduce melting temperatures to the preferred region of 300 °C, to facilitate spinning. Fibers had tenacity/elongation/modulus as high as 27 gpd/6.5%/504 gpd but, despite a high T_g of 172 °C, tensile property retention at 150 °C was only modestly better than for ClPG-T copolymers, probably the result of moderate crystallinity. 2-Cl-5-MePG, from chlorination of MePG, provided polymers having significantly lowered melting points compared with analogs from Cl-, Me-, or 2,5-DCl or 2,5-DMePG. Since Cl and Me are of similar size, this effect must be the result of electronic asymmetry across the polymer chains.

Methyl 2-hydroxy-6-naphthoate was selectively chlorinated in the 1 position. 1-Cl-2,6NE as a copolymer constituent lowered the melting temperature by about 50 °C compared with the analog containing 2,6NE.

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