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One-Pot Synthesis and Characterization of Soluble Poly(aryl ether−ketone)s Having Pendant Carboxyl Groups

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ABSTRACT: Aromatic poly(ether−ketone)s having pendant carboxyl groups have been obtained by direct, one-pot, Friedel−Crafts copolycondensation of 4,4′-diphenoxybenzophenone with a mixture of terephthaloyl chloride (TC) and trimellitic anhydride acid chloride (TAAC), over a wide range of TAAC/TC molar ratios, in the presence of anhydrous aluminum chloride. The syntheses were performed as precipitation−polycondensations, and the polymers were obtained in particulate form. Besides globular particles of polymer, small quantities of elongated, needlelike particles were observed when the mole ratio TAAC/TC was less than 1. Use of X-ray microdiffraction with synchrotron radiation has revealed that the needlelike material consists of a cyclic compound containing 10 phenylene units, i.e., the crystals are of a [2 + 2] macrocyclic dimer. The polymers obtained are soluble in strong acids and in mixtures of methanesulfonic acid or trifluoroacetic acid with chlorinated hydrocarbons. The molecular structures of the polymers were confirmed by ^{1}H and ^{13}C NMR spectroscopy. Reaction of TAAC with 4,4′-diphenoxybenzophenone produced mainly *meta*-orientation of the resulting ketone linkages. The size of the polymer particles, their molecular weights, and the melting behavior of the products obtained depend on the TAAC/TC ratio used. *Ortho*-keto acid residues, formed during reaction of anhydride groups of TAAC with 4,4′-diphenoxybenzophenone, exhibit ring−chain tautomerism. A carboxyl-containing aromatic polyketone derived from *p*-terphenyl, and thus having with no ether linkages in the main chain, was prepared by analogous chemistry, and functional derivatives of carboxy-substituted polyketones were also obtained and characterized.

Introduction

Poly(aryl ether−ketone)s are high-performance engineering thermoplastics possessing remarkable chemical stability, reasonably high glass transition and melting temperatures, and good mechanical properties.[1−4] Most polymers of this type are semicrystalline, high-temperature, and solvent-resistant materials, which have received increasing commercial and industrial interest over the past two decades. Poly(aryl ether−ketone)s can be obtained in two ways.[1−3] The first approach involves nucleophilic aromatic substitution in which a diaryl ether linkage is formed. The second approach involves Friedel−Crafts electrophilic substitution, in which a diaryl ketone linkage is obtained. Although, in principle, poly(ether−ketone)s can be synthesized by both methods, the efficiencies of the preparative methods can be very different, and only electrophilic substitution reactions can yield polyketones without ether linkages in the main chains.

For many applications, however, modification of poly(aryl ether−ketone) properties is desired. One effective method of varying polymer properties involves the incorporation of pendant functional groups. Among these, carboxylic acid groups are of considerable interest. Both the carboxyl groups themselves and more highly reactive derivatives such as acyl chlorides can be used for further chemical transformation. In addition, incorporation of carboxylic acid groups can significantly affect surface, mechanical, and physicochemical properties and the morphology of the modified polymer. This functionalization can be achieved either by postsynthesis chemical modification of the polymer chain or by direct synthesis using functional monomers. Up to now, preformed polyketones, especially the commercial poly(ether−ether−ketone) known as PEEK, obtained through nucleophilic substitution, have been used for functionalization. Thus, publications describe surface carboxylation of PEEK films by selective wet chemistry,[5] bromination of methylated PEEK followed by hydrolysis of the dibromomethyl-substituted polymer,[6] and oxidation of aldehyde groups to give carboxylated PEEK.[7] Other work describes the condensation of dihalides with 4,4-bis(4-hydroxyphenyl)pentanoic acid[8] and 2-(4,4′-dihydroxybenzhydryl)benzoic acid.[9]

It is well-known that electrophilic reactions of aromatic *ortho*-diacid anhydrides with aromatic hydrocarbons result in *ortho*-keto acids. Therefore, it seemed plausible that electrophilic polyketone preparations using monomers containing anhydride groups could afford polymers having free carboxylic functions. Electrophilic condensation of benzene-1,2,4,5-tetracarboxylic dianhydride with aromatic and heterocyclic compounds via electrophilic substitution in the presence of aluminum chloride, followed by intramolecular cyclodehydra-

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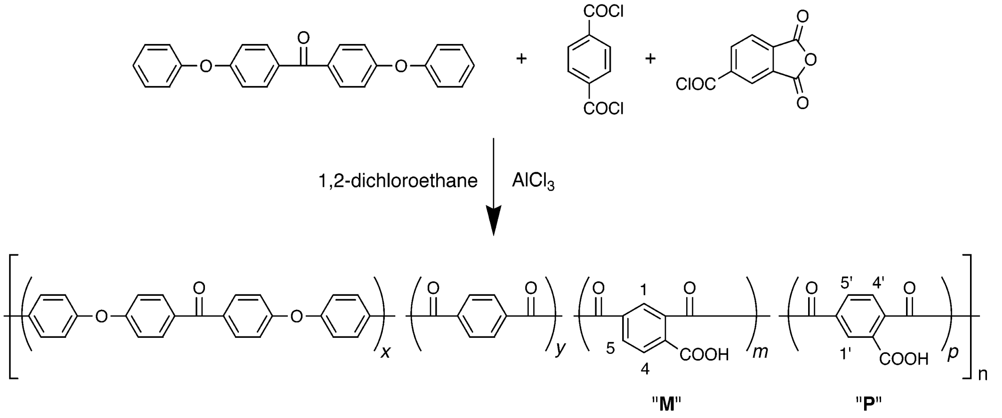
Scheme 1. Synthesis of Carboxy-Functionalized Poly(aryl ether−ketone)s ($x = y + m + p$)



tion of the intermediate polyketoacids, has been reported to give insoluble products, supposedly polyquinones,[10,11] and insoluble, infusible copolymers of pyromellitic dianhydride with biphenyl and diphenyl ether have also been described.[12] A recent publication[13] describes a more successful preparation of soluble carboxyl-containing poly(ether−ketone−ketone) (PEKK) by electrophilic condensation of diphenyl ether and benzene-1,2,4,5-tetracarboxylic dianhydride. It was noted, however, that apparently low-molecular-weight products were obtained.[13] The polymers obtained contained two carboxylic functions per repeat unit, but high-molecular-weight polymers with lower levels of carboxylic acid functionality were not reported. Such materials could prove suitable for the fabrication of nanofiltration or reverse osmosis membranes. Moreover, low degrees of modification could provide copolymers with increased hydrophilicity but with otherwise similar properties to the parent polymer.

The aim of the present work was to devise a flexible, one-step preparation of a family of poly(aryl ether−ketone−ether−ketone−ketone) (PEKEKK)-type copolymers containing pendant carboxylic groups and thus having the general composition shown in Scheme 1. The synthetic approach to these materials involved an electrophilic copolycondensation (Scheme 1) of 4,4′-diphenoxybenzophenone with terephthaloyl chloride (TC) and trimellitic anhydride acid chloride (TAAC), and the success of this technique led to synthesis of a carboxyl-containing aromatic polyketone based on *p*-terphenyl whose polymer structure has no ether linkages in the main chain.

Experimental Section

Materials and Measurements. Terephthaloyl chloride, 1,2-dichloroethane, and trimellitic anhydride acid chloride were obtained from Aldrich and were distilled prior to use. 4,4′-Diphenoxybenzophenone was prepared as described in the literature[14] and was purified by recrystallization from a methanol−benzene mixture. Differential scanning calorimetry (DSC) analysis showed mp 146 °C and 99.92% purity. Anhydrous aluminum chloride was sublimed before use. *p*-Terphenyl was used as received from Acros.

Inherent viscosities of 0.2% (w/v) polymer solutions in methanesulfonic acid (MSA) or in concentrated sulfuric acid were measured at 25 °C using a Schott-Gerate CT semiautomated viscometer. Proton and ^{13}C NMR spectra were recorded using a Bruker AMX-300 spectrometer operating at 75.47 MHz for ^{13}C. The polymers were dissolved in a mixture of chloroform-*d* and trifluoroacetic acid to give 6% (w/v) solutions. Scanning calorimetry (DSC) measurements were carried out using a Mettler DSC 20 system, under a nitrogen atmosphere, at a scanning rate of 20 °C min^{-1}. Mass spectra (MALDI−TOF) were obtained using an SAI TofSpec instrument with dithranol as matrix and sodium trifluoroacetate as cationizing agent.

Polymer Syntheses. Polymer syntheses were carried out in 1,2-dichloroethane using the general precipitation−polycondensation technique described in the literature.[14,15]

Results and Discussion

Polymer Synthesis and Particle Morphology. Methods for the preparation of the poly(ether−ketone) PEKEKK are well documented in the literature.[15−17] It has thus been reported that precipitation−polycondensation of terephthaloyl chloride with 4,4′-diphenoxybenzophenone affords high-molecular-weight polymer in particulate form and that although the bulk of the product comprises near-spherical particles, minor amounts of needlelike particles are also generally observed.[15,18] In the present work we have investigated the precipitation−polycondensation approach as a route to functionalized polyketones, with a gradual increase of TAAC/TC ratio according to the Scheme 1.

First, condensation of 4,4′-diphenoxybenzophenone with terephthaloyl chloride alone was performed according to ref 15. As in the previous reports, small amounts of elongated, needle-shaped particles along with spherical polymer particles were observed (Figure 1a). It was previously suggested that the needlelike particles might be polymer whiskers.[18] However, studies using the X-ray microdiffraction technique (ID13 beamline at the European Synchrotron Radiation Facility in Grenoble) have now revealed that the needlelike particles in fact consist of a macrocyclic compound containing 10 phenylene units; i.e., the needlelike crystals comprise a [2 + 2] cyclic dimer. Full crystallographic details will be reported in a later publication, but a preliminary view of this macrocycle is given in Figure 2. Mass spectroscopic analysis (MALDI−TOF) of the needlelike particles showed a strong molecular ion ([M + Na]$^+$) at $m/z = 1016$, confirming the identity of this component as the [2 + 2] macrocyclic dimer. Formation of cyclic structures during step-growth polymerizations is well-known,[19−21] and recent work by Kricheldorf and co-workers has shown that the proportion of macrocycles in polymers obtained by step-growth polymerizations can in fact be very large (80−90 wt %).[22,23] It is also remarkable that crystallization of the pure macrocyclic dimer occurs even in the presence of a large excess of aluminum chloride, which generally is supposed to complex strongly with product ketone units. (It should

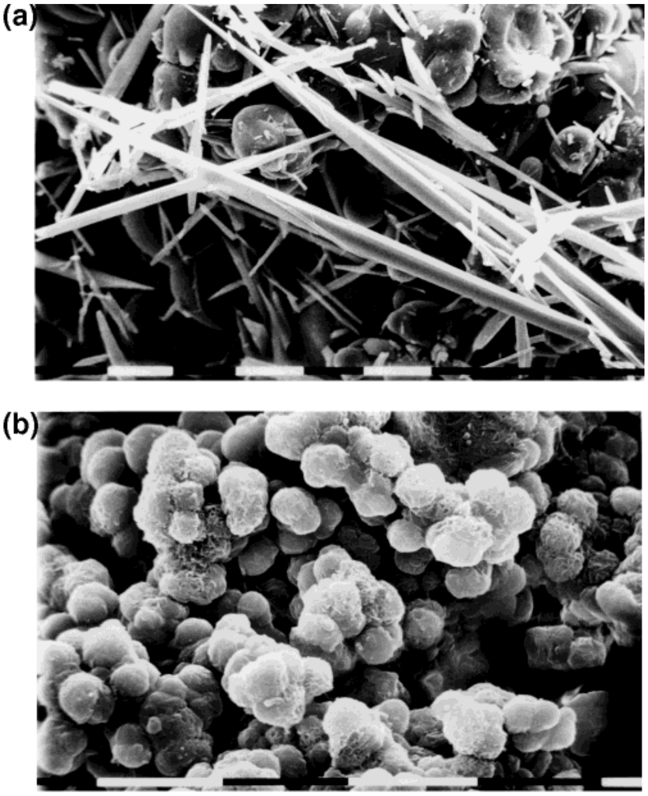


Figure 1. (a, top) SEM of polymer **1**. Scale bar: 10 μm. (b, bottom) SEM of polymer **11**. Scale bar: 10 μm.

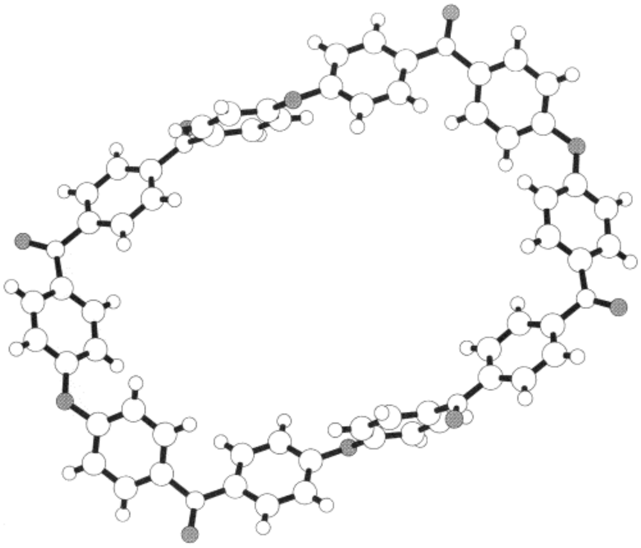


Figure 2. X-ray crystal structure of the macrocyclic dimer.

however be noted that Friedel–Crafts acylation has been used previously for the synthesis of macrocyclic oligomers.[24])

Second, condensations of 4,4′-diphenoxybenzophenone with increasing TAAC/TC molar ratios were carried out to produce aromatic polyketones with different degrees of functionalization. On the whole, syntheses proceeded very similarly to conventional precipitation–polycondensations, with a homogeneous reaction solution at the beginning of the synthesis being transformed into a dispersion by the end of the reaction. A transparent, tough, and flexible film was formed on the walls of the reaction flask, though only in preparations with low TAAC/TC ratios (up to 50 mol %). This suggests a decrease of molecular weight of samples when the relative proportion of TAAC increases. For all 11 preparations (Table 1), white or yellowish particles were produced, and their morphology were studied by scanning electron microscopy (SEM). In polymer **1**, the particle morphology matches the description in the literature for polymers produced at low monomer concentration (<0.1 M).[15,18] Spherical particles of ca. 0.1 mm diameter were aggregated to form larger particles about 1 mm across, together with needlelike particles some 150–250 μm long and 1–5 μm wide (Figure 1a). The same type of elongated particles were also observed in polymers **2**–**5**, which were obtained using a relatively high concentration of terephthaloyl chloride (TAAC/TC < 50%), but for the rest of the samples (**6**–**11**) only aggregates of spherical polymer particles were observed. The size of the spherical particles in the aggregates was found to be dependent on the relative proportions of TAAC and TC, with the diameter of the spheres decreasing as the proportion of trimellitic anhydride chloride increased. Polymer particles thus typically ranged in size from 20 to 30 μm for polymer **1** down to ca. 5 μm for polymer **11** (Figure 1b).

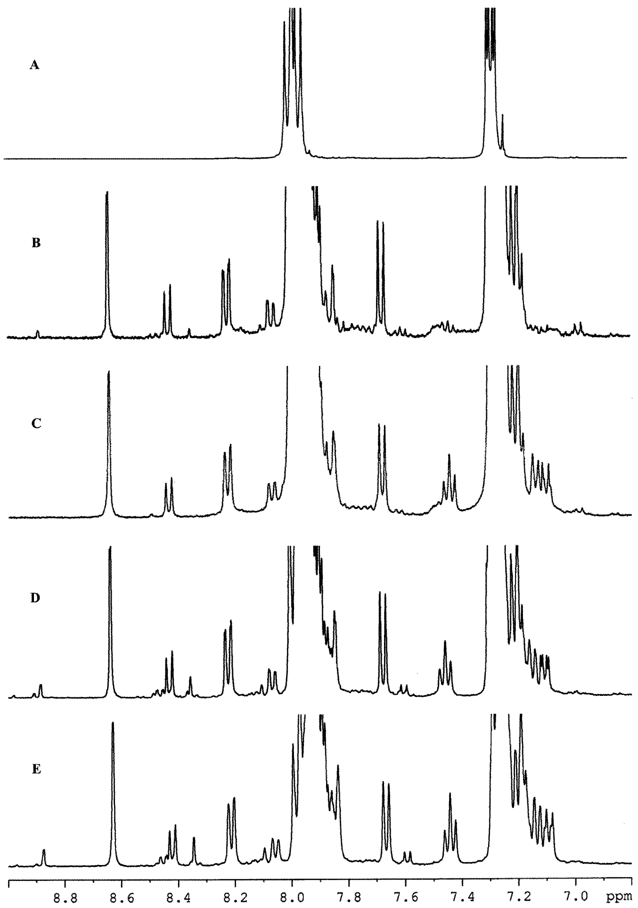


Figure 3. ^{1}H NMR spectra of polymers **1** (A), **4** (B), **5** (C), **9** (D), and **11** (E).

Polymer Structure. The good solubility of the carboxylated copolymers in mixtures of $CDCl_3$ and trifluoroacetic acid has allowed analysis of their structures by NMR spectroscopy. In principle, two different types of acylation can occur with trimellitic anhydride acid chloride, affording either *meta*- (“**M**”) or *para*-orientation (“**P**”) of the resulting ketone groups (Scheme 1). Figure 3 shows the ^{1}H NMR spectra of polymers **1**, **4**, **5**, **8**, and **11**, with increasing content of TAAC residues. The last sample, **11**, is the polymer formed by polycondensation

Table 1. Solubility of Copolymers[a]

sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
TAAC/(TC + TAAC) (mol %)	0	10	20	30	40	50	60	70	80	90	100
H_2SO_4	+	+	+	−	−	−	−	−	−	−	−
CH_3SO_3H	+	+	+	+	+	+	+	+	+	+	+
$CHCl_2COOH$	+	+	+	+	+	+	+	+	+	+	+
TFA	+	+	+	+	+	+	+	+	+	+	+
DMF	−	−	−	−	−	−	−	−	−	−	−
NMP	−	−	−	−	−	−	−	−	−	−	−
DMAc	−	−	−	−	−	−	−	−	−	−	−

[a] + = soluble at room temperature; ± = swells; − = insoluble.

Table 2. Characterization of Copolymers

sample	TAAC/ (TC + TAAC) (mol %)	yield (%)	η_{inh} (dL g^{-1}) (MSA)	T_g (°C)	T_m (°C)
1	0	96	3.90[a]	175	390
2	10	96	1.92[a]	176	370
3	20	94	2.18	186	346
4	30	98	1.80	196	
5	40	89	0.79	206	
6	50	95	0.52	221	
7	60	83	0.19	207	
8	70	84	0.14	nd	
9	80	93	0.05	nd	
10	90	84	0.03	nd	
11	100	83	0.24	nd	
12[b]	50	90	0.22[a]	nd	413

[a] Measured for 0.2% solutions of the polymers in concentrated sulfuric acid. [b] Polymer **12** is discussed in the text.

of 4,4′-diphenoxybenzophenone with pure TAAC. For polymer **1**, produced in the absence of trimellitic anhydride chloride, the ^1H spectrum shows a simple pattern of resonances, and their assignment was made according to ref 15. Two groups of signals (multiplets at 7.22−7.30 and 7.92−8.02 ppm) correspond to protons adjacent to oxygen and protons adjacent to carbonyl, respectively. The presence only of two sets of signals in the spectrum of polymer **1** makes it very straightforward to identify the signals associated with the TAAC residues in the copolymers. As the relative proportion of TAAC increases, two new sets signals of various multiplicities appear in the spectra of polymers **2**, **3**, **4**, **6**, **7**, **8**, **9**, **10**, and **11**. Two-dimensional ^1H NMR (COSY), selective ^1H decoupling, and calculation of predicted chemical shifts by means of an additive calculation scheme[25] enabled these resonances to be assigned.

Singlets at 8.89 (H1′), 8.63 (H1), doublets at 8.48 (H5′), 7.60 (H4′), 8.22 (H5), and 7.68 (H4) point to the presence of both **M** and **P** structures (Scheme 1) in copolymers **2**−**4**. It is clear from the NMR spectra that the proportion of **M** units is invariably higher than that of the **P** units for all the copolymers, and it is remarkable that the spectrum of polymer **5** suggests a complete absence of any **P** units whatever. The reason for such high selectivity is not yet understood. Regarding polymer **5**, new signals in the NMR spectrum—a triplet at 7.43 and a multiplet at 7.18−7.08 ppm—appear. These resonances arise from side-reactions leading to *ortho*- and *meta*-acylation of the phenoxy groups of 4,4′-diphenoxybenzophenone.[15] Evidently, the regioselectivity of the polymer-forming reaction decreases with increase of TAAC content. Apart from **M** and **P** structures**,** there can also be isomers due to different sequence relationships betweenTAAC units in the polymer chain. Because of the different reactivities of acid chloride and anhydride groups, it is probable that the copolymer sequences are not fully random.

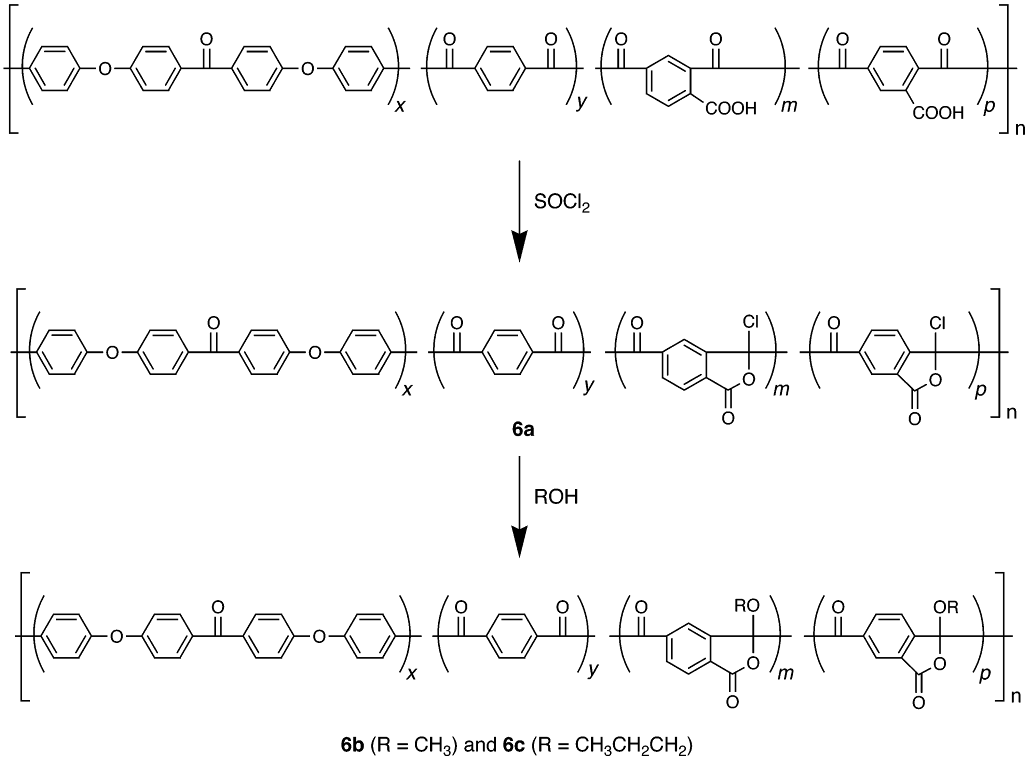
Property Variation with Relative Proportions of TAAC and TC. As can be seen from Table 1, the copolymers generally show higher solubility than polymer **1** and many other linear poly(aryl ether−ketone)s. Despite this, copolymers **4**−**11** are essentially insoluble in concentrated sulfuric acid (normally an excellent solvent for poly(ether−ketone)s), and this anomaly is discussed below.

Viscosity data obtained for solutions of the polymers in methanesulfonic acid (MSA) and thermal characteristics (glass transition and melting temperatures) are given in Table 2. Viscometry studies in MSA showed inherent viscosities ranging from 2.18 dL g^{-1} for **3** to 0.03 dL g^{-1} for **10**. Since polymers **1** and **2** were insoluble in MSA, their viscosities were measured in 98% H_2SO_4 and were found to be 3.95 and 1.92 dL g^{-1}, respectively. The introduction of trimellitic anhydride acid chloride clearly induces a dramatic decrease in molecular weight, but it is worth noting that flexible films could still be cast from the solutions of polymers **1**−**6**, i.e., those containing up to 50 mol % of TAAC. Differential scanning calorimetry (DSC) revealed the presence of melting peaks for polymers **1**−**3** only. This indicates a loss of crystallinity as the proportion of TAAC is increased, consistent with the progressive introduction of carboxyl substituents whose presence decreases the ability of the polymer chains to crystallize. Nevertheless, it should be noted that even with relatively high content of TAAC (20−25%) the polymers still remain semicrystalline.

As shown in Table 2, an increase in the proportion of TAAC relative to TC leads to an increase in T_g, but the glass transition becomes progressively weaker with increasing TAAC/TC ratio and is no longer detectable for polymer **8** onward. Polymer yields vary from 83 to 98%, with the lower yields being obtained for low molar mass materials containing a high proportion of carboxyl groups. For such materials, losses would be expected during isolation due to their increased solubility, especially in methanol, which is used to extract residual salts from the final polymer.[15]

Ring−Chain Tautomerism and Functional Derivatives. Incorporation of TAAC residues in the main chain results in the formation of *ortho*-keto acid residues. It is well-known that ring−chain tautomerism can occur in 2-aroylbenzoic and 2-acetylbenzoic acids,[26,27] so that one may expect *ortho*-aroylbenzoic fragments (or their derivatives) in the polymer chain to also undergo ring−chain transformations. Infrared spectroscopy is an effective method for studying ring−chain phenomena. NMR spectroscopy is also widely used but the ring−chain equilibrium data obtained in solution by NMR spectroscopy can differ markedly from the results obtained for the compound in the solid state. The IR spectra of “as-obtained” polymers **2**−**11** show bands at 1727 and 1700 cm^{-1} associated with the carbonyl

Scheme 2. Synthesis of Chlorolactone- and *Pseudo*-Ester-Functionalized Poly(aryl ether−ketone)s



stretching modes of carboxylic acid and ketone groups in chain tautomers.[27] However, treatment of polymers **2**−**11** with thionyl chloride at reflux results in formation of *pseudo*-acid chlorides or chlorolactones (Scheme 2). The intense band around 1780 cm^{-1} is a clear indication of the presence of the lactone structure. To investigate potential modifications of the carboxyl-containing polymers via their *pseudo*-acid chlorides, polymer **6** was treated with thionyl chloride, and polymers **6a**, **6b**, and **6c** containing respectively chlorolactone, methoxy, and propyloxy *pseudo*-ester functionality were obtained by subsequent precipitations in hexane, methanol, or propanol-1.

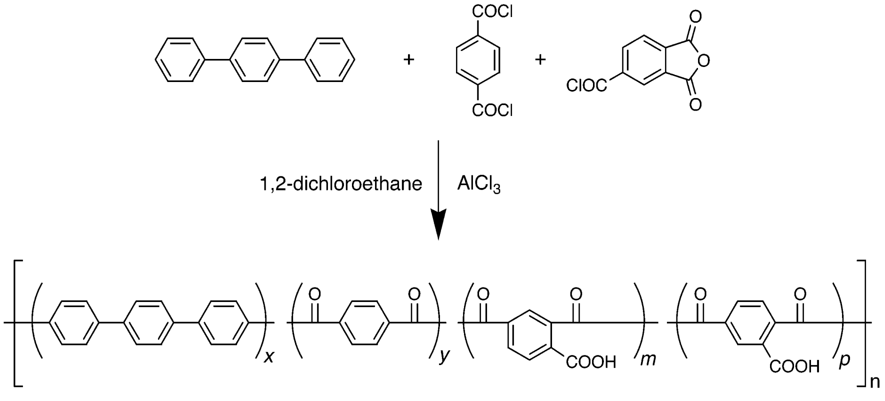
The conversion of carboxylic acid groups to *pseudo*-ester functions was nearly quantitative as indicated by ^{1}H NMR. The IR spectra of the polymers showed an intense band at 1785 cm^{-1}, which confirms the ring-tautomer structure of the polymers. As described in the literature for *o*-benzoyl benzoates,[27] the *pseudo*-ester form of the polymers reported here transforms to the normal ester form in the solid state: evolution of relative intensities of IR bands were observed over several weeks, but the kinetics of conversion between the two forms were not explored. The *pseudo*-acid chloride **6a** was found to undergo very rapid hydrolysis on contact with air. Solubility tests showed that, apart from the above-mentioned solvents, the modified polymers are soluble in 1,1,2,2-tetrachloroethane (TCE), and soluble when heated in dimethyl sulfoxide (DMSO), but precipitate from this solvent on cooling.

As noted above, when the amount of terephthaloyl chloride was less than 80 mol % (samples **4**−**11**), the copolymers were insoluble in 98% sulfuric acid. Since the whole range of polymers was, however, soluble in other solvents (Table 1), it is clear that the polymers, as obtained, are free of cross-linking. On the other hand, *o*-benzoylbenzoic acid has been shown to form a lactol carbonium ion when dissolved in concentrated sulfuric acid.[28] This cation is very reactive and can, in principle, alkylate another polymer chain at the *ortho*-position relative to the ether linkage. The resulting cross-linking might explain the insolubility in H_2SO_4 of those polymers with high densities of carboxylic acid groups on the polymer backbone. The formation of lactol carbonium ion from benzoylbenzoic acid fragments, followed by intermolecular electrophilic substitution reactions leading to cross-links, could be the reason for polymer insolubility in concentrated sulfuric acid. On the whole, ring−chain transformations of polymer-incorporated moieties of *o*-benzoylbenzoic acid are similar to those observed for their monomeric analogues. It is to be noted that chlorolactones are generally more reactive than conventional aromatic acid chlorides.

Thus, electrophilic one-pot copolycondensations of TAAC with TC and 4,4′-diphenoxybenzophenone result in polymers with pendant carboxylic groups. It is anticipated that analogous copolycondensations of TAAC and isophthaloyl chloride or other aromatic or aliphatic acid chlorides with 4,4′-diphenoxybenzophenone would afford similar results. Equally, it is obvious that many hydrocarbons, particularly those containing phenoxy-end groups,[29] can in principle also be used for condensations with TAAC. Perhaps more importantly, even fully aromatic hydrocarbons such as *p*-terphenyl can be used for polymer preparation. We have for example found that reaction of *p*-terphenyl with an equimolar mixture of TC and TAAC gives a soluble polymer **12** having the composition shown in Scheme 3.

According to ^{1}H NMR analysis of polymer **12**, the abundance of *meta*-oriented ketone linkages derived from TAAC moieties is again significantly higher than *para*-oriented ones. It is worthy of note that the use of *p*-terphenyl instead of 4,4′-diphenoxybenzophenone yielded a more highly crystalline material. Thus, the DSC trace of polymer **12** revealed an endothermic peak at about 413 °C. The relatively high melting tempera-

Scheme 3. Synthesis of a Carboxy-Functionalized Poly(*p*-terphenyl−ketone) ($x = y + m + p$ and $y = m + p$)



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ture observed (Table 2) can be related to terephthaloyl−*p*-terphenyl−terephthaloyl sequences in the main chain. (The melting points of *p*-terphenyl and 4,4′-diphenoxybenzophenone themselves are 214 and 146 °C, respectively.)

Conclusions

Electrophilic precipitation−polycondensation of 4,4′-diphenoxybenzophenone with a mixture of terephthaloyl chloride and trimellitic anhydride acid chloride over the complete TAAC/(TC + TAAC) molar ratio range, in the presence of anhydrous aluminum chloride, leads to aromatic polyketones containing carboxylic acid side groups. The proportion of trimellitic anhydride acid chloride in the reaction mixture, relative to terephthaloyl chloride, modulates the size of the polymer particles, the molecular weight, and the thermal properties of the products obtained. Polymers containing trimellitic anhydride acid chloride residues up to 25 mol % retain some semicrystalline character. Along with the globular polymer particles observed for all samples, a minor proportion of needlelike particles appeared in samples containing higher levels of terephthaloyl residues. These particles consist of cyclic [2 + 2] dimer, as is also the case for the homopolymer **1**, derived from terephthaloyl chloride. Decrease of polymer molecular weight with an increase of TAAC/TC molar ratio points to a lower reactivity of anhydride groups in comparison with acid chloride groups. *Ortho*-keto acid residues formed during reaction of anhydride groups show chain−ring tautomeric transformations similar to those observed for *o*-benzoylbenzoic acid. This new synthetic method allows for the preparation of different aromatic polyketones with a wide variety of main-chain compositions and proportions of side-chain carboxyl groups.

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