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Phase-transfer catalyzed synthesis of poly(etherketone)s

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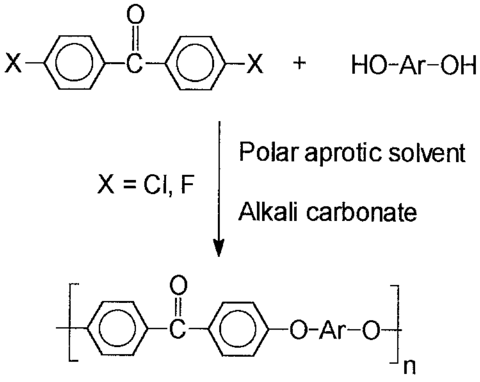
Summary:

A novel synthetic method for the preparation of high molecular weight aromatic poly- (etherketone)s is described. N-Alkyl(4-N´,N´-dialkylamino)pyridinium chlorides **1**, **2** and **3** were used as phase-transfer catalysts in polycondensation reactions of 1,4-bis(4-chlorobenzoyl)benzene (**4**) with aromatic diphenols via nucleophilic displacement. The polycondensations were significantly promoted and, moreover, the results achieved in terms of molecular weight and reaction time were comparable to polymerizations conducted with 1,4-bis(4-fluorobenzoyl)benzene (**5**), which is a considerably more reactive monomer.

Introduction:

Aromatic poly(etherketone)s, which are useful as high performance engineering thermoplastics, have been studied intensively (1). They are generally prepared by step-growth polymerization of activated aryldihalide monomers with aromatic diphenolates in a dipolar aprotic solvent, or via Friedel-Crafts coupling of aromatic diacyl monomers with arylethers (1-12). The former method involves formation of an ether linkage by nucleophilic aromatic substitution (S_NAr) as the polymer-forming reaction (equation 1).



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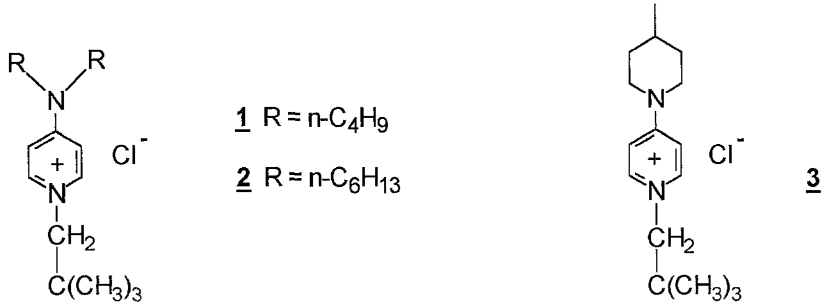
In a nucleophilic aromatic substitution reaction, activating groups such as sulfone, keto or azo units are required to allow nucleophilic displacement of the aromatic halide (1). Both, the nature of the electron-withdrawing groups and of the halide have a marked influence on the course and rate of the reaction. Commercially available semicrystalline poly(etherketone)s are prepared exclusively by the reaction of difluoroaryl monomers such as 4,4′-difluorobenzophenone (6) or 1,4-bis(4-fluorobenzoyl)benzene (5) with hydroquinone (7) in the presence of alkali carbonates. High molecular weight polymers have not been synthesized from dichloroaryl monomers in an industrial scale, since their reactivity is considerably lower than that of the corresponding difluoro compounds. Amorphous poly(etherketone)s can be synthesized from less reactive aromatic dichloro monomers, but long reaction times are required (13). Since dichloro monomers are much cheaper than the corresponding difluorides, the exploration of new synthetic methods better suited for the polycondensation of dichloroarylketone monomers is of practical importance. The course of a poly(etherketone) synthesis is further influenced by the reacitivity of the alkali metal phenolates used as nucleophilic components. The more soft the alkali metal counter ions are, the higher is the nucleophilicity and thus the reactivity of the corresponding phenolates (14). Industrially, sodium or potassium carbonates are used to form the alkali metal phenolates. As a result, the carbonates and the corresponding phenolates exhibit only low solubility in aprotic solvents (15).

We examined the influence of phase-transfer catalysts in polycondensation reactions of dichloroarylketone monomers with bisphenols in order to overcome the above described problems in poly(etherketone) synthesis. Conventional phase-transfer catalysts such as tetraalkylammonium chlorides are not stable under basic conditions and high temperatures. They decompose by both nucleophilic attack and Hofmann elimination and are therefore not suitable for poly(etherketone) synthesis. D.J. Brunelle et al. (16,17) reported that N-alkyl salts of 4-dialkylaminopyridines are effective phase-transfer catalysts (PTC) to promote nucleophilic displacement reactions even if unpolar solvents were used. N-Neopentyl(4-N′,N′-dialkylamino) pyridinium chlorides 1, 2 and 3, however, are thermally stable up to 300°C (16).



1 $R = n\text{-}C_4H_9$

2 $R = n\text{-}C_6H_{13}$

3

Scheme 1: Structures of the phase-transfer catalysts 1, 2 and 3.

The high stability of these compounds even under basic conditions can be explained by a resonance stabilization of the positive charge in the pyridine ring. Also, the pyridinium salts are sterically hindered and therefore less susceptible to nucleophilic attack. Finally, decomposition by Hofmann elimination is decreased due the absence of ß-hydrogens in the neopentyl group.

These results encouraged us to use the pyridinium type salts **1**, **2** and **3** in polycondensation reactions via nucleophilic displacement. In the present paper a phase-transfer catalyzed polycondensation of the less reactive dichloroaryl monomers 1,4-bis(4-chlorobenzoyl)benzene (**4**) is reported, which represents an alternative route towards high molecular weight poly(etherketone)s.

Experimental:

The bisphenols **8** and **9** were synthesized by condensation reactions of phenols with the corresponding aliphatic ketones using mercaptoacetic acid as catalyst according to a modified literature procedure (18).

2,2-Bis(4-hydroxyphenyl)pentane (**8**)

A mixture of 50 mmol 2-pentanone (43.08 g), 2 mol phenol (188.2 g) and 5 mmol mercaptoacetic acid (0.46 g) was saturated with hydrogen chloride gas. The red mixture was stirred for 24 h at room temperature in an argon atmosphere. The reaction mixture was poured into hot water and remaining reactants were removed by steam destillation. Recrystallization of the residue from toluene afforded the product as a colorless solid in 90 % yield (m.p.: 149 °C, lit. [18] m.p. 147°C). Elemental analysis: C, 79.65%; H, 7.86% (calculated for $C_{17}H_{20}O_2$); found: C,79.61%; H, 7.89%.

2,2-Bis(4-hydroxyphenyl)heptane (**9**)

9 was prepared analogous to **8**. The yield of the colorless purified solid was 85 % (m.p.: 139 °C, lit. [18] m.p. 136°C). Elemental analysis: C, 80.24%; H, 8.51% (calculated for $C_{19}H_{24}O_2$), found: C, 79.88%; H, 8.23%.

1,4-Bis(4-chlorobenzoyl)benzene (**4**) (m.p. 257°C-258°C, lit. [13] m.p.:257 °C) and 1,4-Bis(4-fluorobenzoyl)benzene (**5**) (m.p.: 214°C,lit. [13] m.p. 214°C) were obtained from Hoechst AG, Frankfurt/Main .

Synthesis of the phase-transfer catalysts:

N-Neopentyl(4-dibutylamino)pyridinium chloride (**1**), N-neopentyl(4-dihexylamino) pyridinium chloride (**2**), N-neopentyl-4(4'-methylpiperidinylene)pyridinium chloride (**3**) were synthesized according to reference 16.

Polymerization:

General procedure:

50 mmol diphenol (**8**, **9**), 50 mmol (**4**),150 mmol anhydrous potassium carbonate and 0 - 5 mmol phase-transfer catalyst were placed in a 250 ml four-necked round-bottomed flask equipped with a mechanical stirrer, an argon inlet, a water separator and an addition funnel. The reaction unit was evacuated and flushed with high-purity argon were repeated several times. Dimethylacetamide (DMAc) (100-120 ml) and toluene (40 ml) were added dropwise. The stirred mixture was then heated under argon to 60°C. The reaction unit was subsequently evacuated and flushed with argon again and finally an argon stream was passed through. The mixture was heated to 155°C for 3 h while the toluene-water azeotrope was removed by distillation. The reaction temperature was kept constant until a very viscous solution was obtained. The polymer was then precipated by pouring the hot solution slowly into a blender containing a water/acetic acid mixture. The resulting precipitate was subsequently washed with water and methanol and finally boiled in methanol.

^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm) of **10**:7.84 (m, 8H, phenylene), 7.22 (s, 4H, phenylene), 7.03 (m, 8H, phenylene), 2.12 (m, 2H, methylene), 1.68 (s, 3H, methyl), 1.16 (m, 2H, methylene), 0.92 (t, 3H, methyl).

^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm) of **10**:195.38, 162.87, 153.78, 146.92, 141.59, 133.15, 130.15, 129.86, 129.48, 120.44, 117.73, 46.47, 45.15, 28.62, 18.77, 15.48.

^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm) of **11**:7.84 (m, 8H, phenylene), 7.27 (s, 4H, phenylene), 7.04 (m, 8H, phenylene), 2.09 (m, 2H, methylene), 1.67 (s, 3H, methyl), 1.28 (m, 4H, methylene), 1.13 (m, 2H, methylene), 0.81 (t, 3H, methyl).

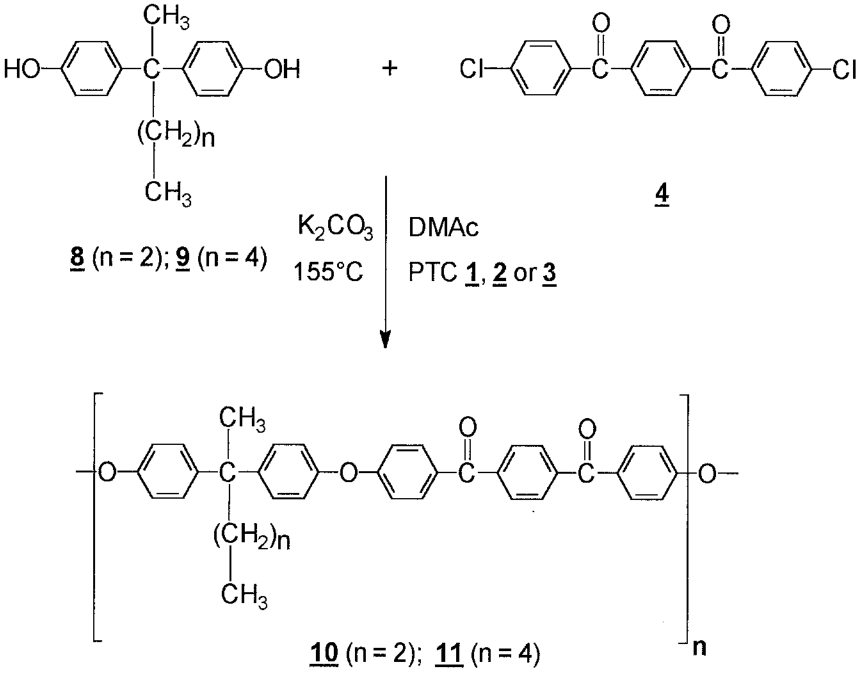
^{13}C-NMR (125 MHz, $CDCl_3$, δ / ppm) of **11**:195.25, 162.85, 153.72, 147.05, 141.59, 133.27, 131.83, 130.15, 129.62, 120.35, 117.82, 46.33, 42.81, 33.22, 28.89, 25.18, 23.09, 14.88.

Measurements :

Molecular weights were determined using a set of 4 Styrogel columns with THF as solvent. Differential scanning calorimetry (DSC) was carried out using a scanning rate of 10°C and a sample size of 10 mg. The only distinctive feature of the DSC thermograms was T_g. The NMR spectra were recorded using a Varian (Gemini 200) 200 MHz spectrometer.

Results and discussion:

The phase-transfer catalyzed poly(etherketone) synthesis of dichloroarylketone monomers with bisdiols was studied using a standard monomer mixture containing 2,2-bis(4-hydroxyphenyl)pentane (8) or 2,2-bis(4-hydroxyphenyl)heptane (9) and 1,4-bis(4-chlorobenzoyl)benzene (4) (equation 2).



8 (n = 2); 9 (n = 4)

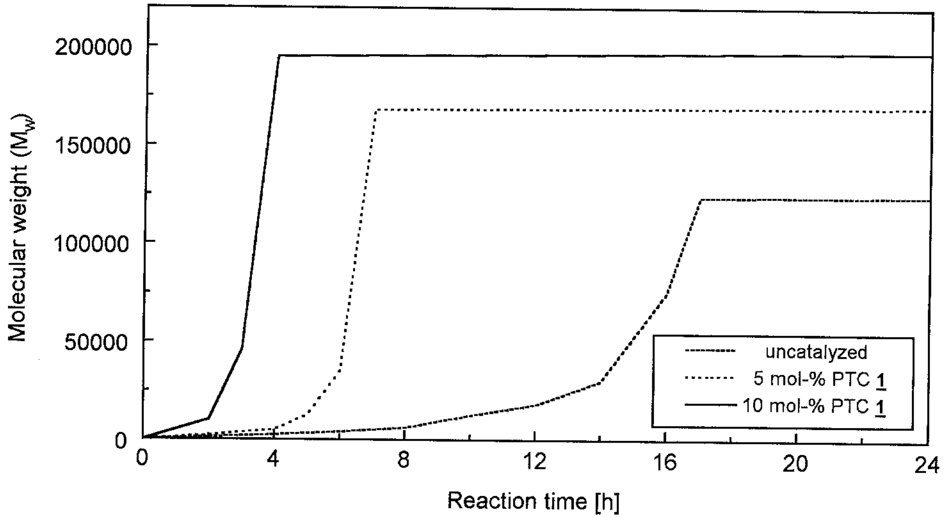
4

10 (n = 2); 11 (n = 4)

(2)

High molecular weight amorphous poly(etherketone)s were obtained, which exhibited excellent solubility in chloroform, dichloromethane and tetrahydrofuran. The polymers can therefore easily be characterized by NMR (see experimental part) and GPC. The above reactions were used as models for a kinetic study, since they allow the course of the condensation to be monoitored, e.g., by correlation of reaction time and molecular weight (or viscosity) as determined by GPC of aliquots (Scheme 2).

Polymer 10 was obtained by condensation of 8 with the dichloroaryl monomer 4 in the absence of phase-transfer catalysts (M_W > 100000), but a reaction time of 17 h was required. With PTC 1 (5 mol % relative to the monomer amount), high molecular weight products (M_W >170000) are formed within 7 h. This corresponds to a 2.4-fold decrease in reaction time. A 3.8-fold decrease in reaction time is observed when the amount of 1 is raised to 10 mol %. Furthermore, the catalyzed reactions result in material of higher molecular weight than the uncatalyzed reactions (table 1). This difference in molecular weight suggests that chain terminating reactions, e.g. by reductive elimination of chlorine from oligomeric end groups (19), becomes less important, due to the shorter reaction times.



Scheme 2: Formation of polymer **10** by phase-transfer catalyzed polycondensation.

The results of poly(etherketone) synthesis with 4 and the bisphenols 8 and 9 are summarized in Table 1. Analogous results are obtained with PTC 2 or 3. When 9 is used as the bisdiol, the above results are further confirmed, since comparable values of molecular weight and reaction time were obtained (table 1).

Table 1: Conditions and results of poly(etherketone) synthesis

Monomers: dihalide / bisphenol	Phase-transfer catalyst	Amount of catalyst (%) [a]	Reaction time (h)	M_w
4 / 8	uncatalyzed	----------	17	124200
4 / 9	uncatalyzed	----------	17.5	120900
4 / 8	1	5	7	174200
4 / 8	1	10	4.5	193700
4 / 9	2	10	5	196000
4 / 9	3	10	4.5	202300
5 / 8	----------	----------	2	225500
5 / 9	----------	----------	1.75	232100

[a] related to the amount of monomers.

We assume that the significant decrease of the reaction time is caused by an increased solubility of anionic species in the presence of the phase-transfer catalysts 1, 2 or 3. Both the potassium carbonate and especially the mono- and oligomeric potassium phenolates exhibit low solubility in aprotic solvents (15). Furthermore, the exchange of potassium cations against pyridinium ions, which represent the much softer counter ions compared with the potassium ions, improves the nucleophilicity and thereby reactivity of the phenolic species (14).

A comparison of the above described phase-transfer catalyzed preparation of amorphous poyl(etherketone)s with the currently used method based on the application of difluoroarylketone monomers shows, that the molecular weights attained, the reaction times required, and the polymer properties are all comparable (table1, 2).

Table 2: Characterization of synthesized polymers.

Polymer	$h_{inh.}$ [a]	T_g (°C)[b]	M_w [c]	Film [d]
12	1.26	158	225500	Clear, tough
13	1.27	153	232100	Clear, tough
10	1.18	158	193700	Clear, tough
11	1.20	153	202300	Clear, tough

[a] Inherent viscosity, 0,5 % solution at 20°C.

[b] Differential scanning calorimetry at a heat rate of 10°C/min.

[c] Weight-average molecular weight by GPC in chloroform solution.

[d] Cast from chloroform solution.

Conclusion:

It was shown that the phase-transfer catalysts based on N-alkylated pyridinium salts 1, 2 and 3 promote poly(etherketone) synthesis via nucleophilic displacement by increased solubility and nucleophilicity of the phenolic species. The difference in reactivity of 1,4-bis(4-chlorobenzoyl)benzene (4) and the corresponding difluoroaryl monomer 5 can be nearly compensated as demonstrated in condensation reactions of 4 and 5 with the bisphenols 8 and 9. Moreover, the chain terminating reactions observed in poly(etherketone) synthesis using dichloroarylketone monomers were minimized, which was shown by the significantly higher molecular weight polymers obtained in the catalyzed polymerisations.

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