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Poly(imino ketone)s as New High-Performance Polymers

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ABSTRACT: A series of novel poly(imino ketone)s (PIK) have been synthesized via palladium-catalyzed polycondensation (Hartwig−Buchwald reaction) of aromatic dichloro or dibromo ketones with various aromatic diamines. The influence of the halogen-containing monomers, concentration, temperature, and catalyst ligands on the polycondensation reaction and on the polymer polydispersity was investigated. These polymers showed good thermal stability with high decomposition temperatures. FT-IR spectra of the PIKs revealed that in the solid state intermolecular and intramolecular hydrogen bonding (N−H···O═C) are present. A model compound was synthesized and characterized by standard spectroscopic methods in order to assist in the structure proof of the polymer. The mechanical behavior of the PIK polymers suggests that they can be considered as a new class of high-performance polymers.

Introduction

In the 1980s high-performance polymers were considered the most promising class of polymers for special applications in automotive, aircraft, and spacecraft industry or medicine[1] due to their outstanding physical properties.[2−9] However, because of their high production costs, only a few types have been commercialized. One example is semicrystalline poly(arylene ether ketone)s (PEKs).[3−9] Much research effort has been dedicated to the structural variation of PEKs to control and improve their properties.[2] Poly(arylene ether ketone)s can be prepared via a polycondensation using electrophilic or nucleophilic aromatic substitution.[3−6] In the latter case fluoride has been employed as a leaving group. The nitro group has rarely been used because of the generation of nitrite ions that become reactive and cause side reactions at elevated temperatures.[10a−e]

Another example of aromatic polymers are poly(arylene amide)s (PAAs). They are materials with high thermal stability, good chemical resistance, and high tensile properties.[11,12] However, their high glass transition temperatures (T_g) and insolubility in organic solvents seriously limit their processability.[13,14]

A third type of aromatic polymers is polyaniline (PANI). It was not used as a high-performance polymer but as a conducting material.[15] It has attracted considerable attention due to its simple synthesis, good environmental stability, and high electrical conductivity. Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization.[16] Recent work has shown that polyaniline prepared at room temperature is of fairly low molecular weight[17] and contains defect sites.[18] Considerable effort has been made to develop relationships between synthetic conditions and properties of polyaniline obtained by electrochemical polymerization.[19] By contrast, little attention has been paid to the chemical polymerization.[20−22]

In this paper, we report the synthesis of aromatic poly(imino ketone)s (PIKs) using the Hartwig−Buchwald reaction.[23a−o] These polymers are promising candidates as high-performance polymers and can be considered as a hybrid structure of poly(arylene ether ketone)s (PEKs), polyaramides (PAAs), and polyaniline (PANI) (Figure 1). The catalytic amination reaction of arylene halides with primary amines using palladium complexes has become an important synthetic procedure for a variety of arylene amines including pharmaceuticals, electronic materials, and ligands for metal catalysts. The Pd-catalyzed aryl amination has also been applied to polycondensation reactions to give various polyamines and its related poly(iminoarylene)s with no or scarcely cross-linked structures.[24a−c] Herein our aim is to use this method for synthesizing poly(imino ketone)s (PIKs) as a new polymer structure. We expected the polycondensation of different aromatic dihalides with primary aromatic diamines using the catalytic system generated from tris(dibenzylideneacetone)dipalladium(0) $Pd_2(dba)_3$ and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) (Figure 3) to produce soluble poly(imino ketone)s (PIKs). The use of inexpensive monomers with bromine or chlorine leaving groups instead of expensive fluorine containing monomers is, as has already been shown for PEEKKs (poly(ether ether ketone ketone)s), very attractive for obtaining aromatic polymers.[9] We expect that the amino and carbonyl groups in PIKs would result in intermolecular

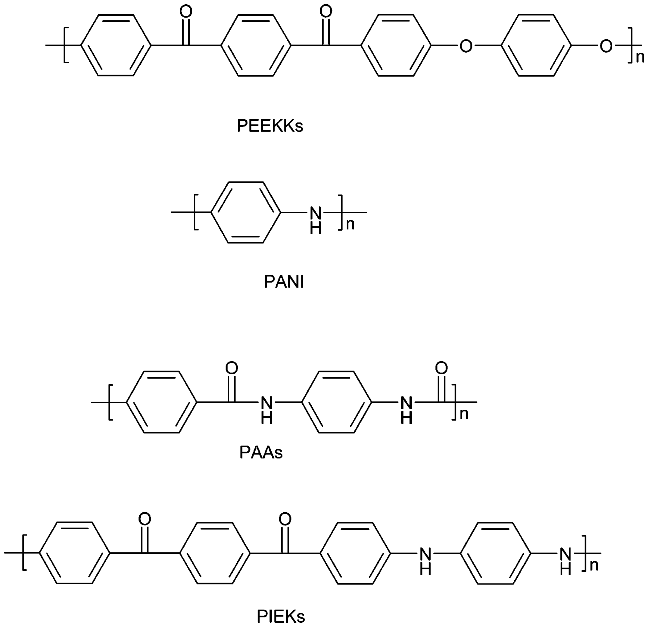

Figure 1. PIK as hybrid material of PEK, PANI, and PAA.

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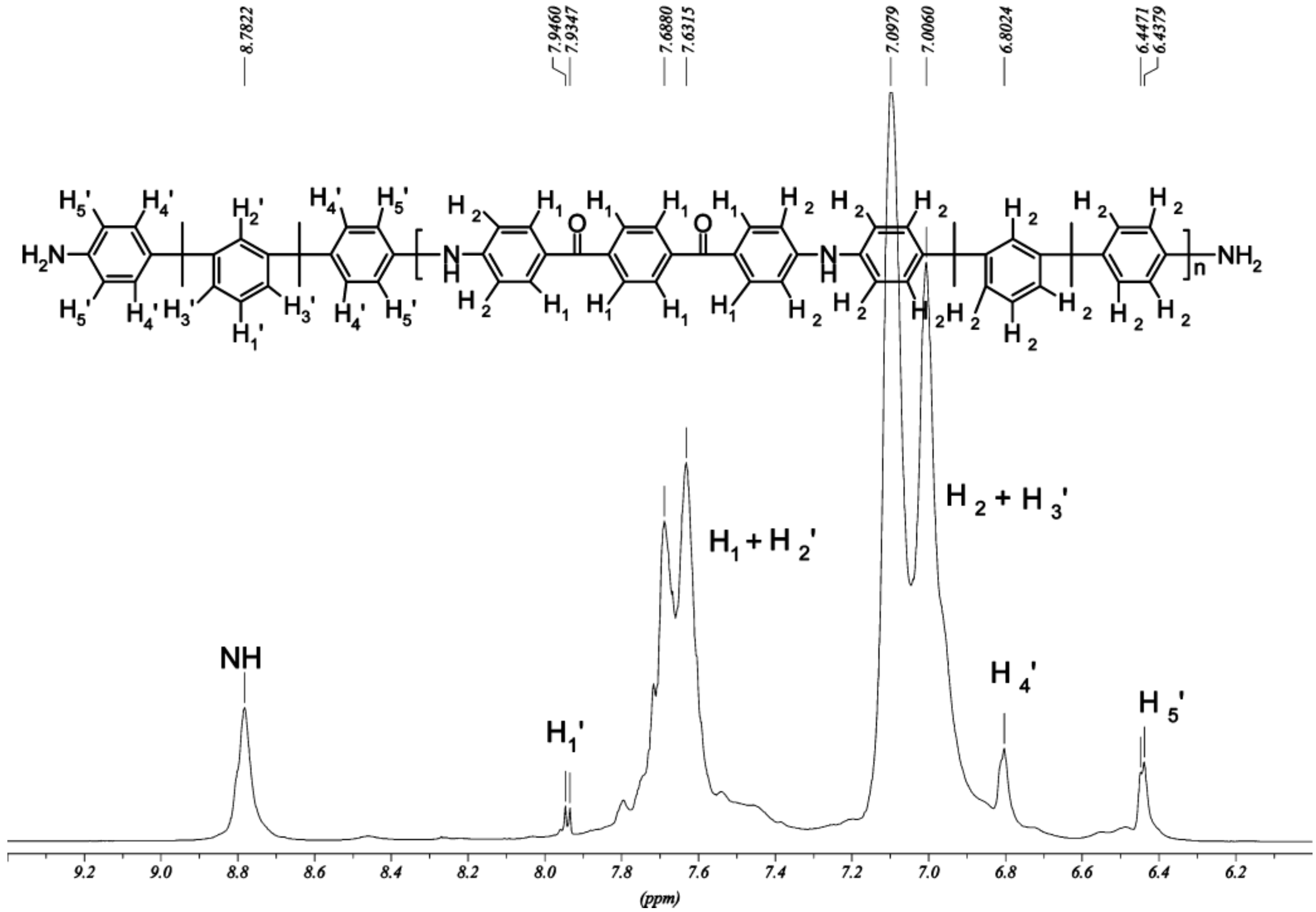


Figure 2. ^{1}H NMR (700 MHz) spectrum of polymer **13** recorded in DMSO-d_6 at 100 °C.

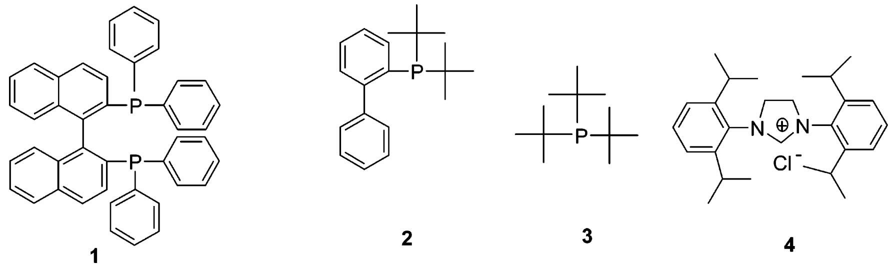


Figure 3. Complex ligands of the catalyst applied in the Buchwald−Hartwig reaction (**1**: BINAP; **2**: di-*tert*-butylphosphinobiphenyl; **3**: P(tBu)$_3$; **4**: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride).

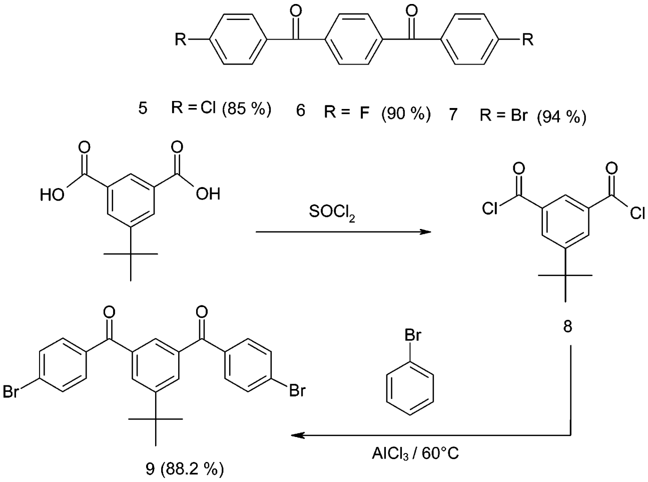
hydrogen bonds like in KEVLAR, leading to good thermal and mechanical properties that are essential requirements for high-performance polymers.[25]

Experimental Section

Materials. 1,4-Bis(4-chlorobenzoyl)benzene (**5**), 1,4-bis(4-fluorobenzoyl)benzene (**6**), and 5-(*tert*-butyl)isophthaloyldichloride (**8**) were synthesized according to literature procedures.[26−28] 1,4-Bis(4-bromobenzoyl)benzene (**7**) was synthesized according to a modified literature procedure[29] (see below), and 1,3-bis(4-bromobenzoyl-5-*tert*-butyl)benzene (**9**) was synthesized as shown in Scheme 1. Other materials and reagents were obtained from different commercial sources and used without further purification.

Measurements. Melting points of purified compounds were determined on a Büchi melting point apparatus at a heating rate of no greater than 1 °C/min and are uncorrected. FTIR spectra were recorded on a Nicolet 320 FTIR spectrometer. UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 15. Elemental analyses were performed on a Perkin-Elmer model 2400 CHN analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AMX250 Hz, Bruker AC300 Hz, and Bruker AMX700 Hz NMR spectrometers in $CDCl_3$, CD_2Cl_2, or DMSO-d_6, depending on the solubility of the material being analyzed. Mass spectra were measured on a Fisons Trio 2000 under electron impact or field desorption conditions. Intrinsic viscosity was measured at 25 °C in DMF or in THF, using a Cannon-Ubbelohde viscometer. The intrinsic viscosity value [η] was obtained by measuring specific viscosity $\eta_{sp} = \eta/\eta_0 - 1$ and reduced viscosity $\eta_{red} = \ln(\eta/\eta_0)$ at four different concentrations, plotting $\eta_{sp/c}$ vs c and extrapolating to zero concentration. DSC was performed on either a DSC I Mettler TC 10 A or a DSC II Mettler TC 11. The DSC curves obtained during the second heating scan were taken into consideration. The samples were heated at a rate of 10 °C/min under flowing nitrogen gas. T_g values were identified as the midpoint of the change in endothermic baseline from the second heating after a quench cooling from the first run. Thermogravimetric analysis (TGA) was performed on a Mettler TC 10A at a heating rate of 10 °C/min under air and nitrogen

Scheme 1. Synthesis of 1,3-Bis(4-bromobenzoyl-5-*tert*-butyl)benzene (9)



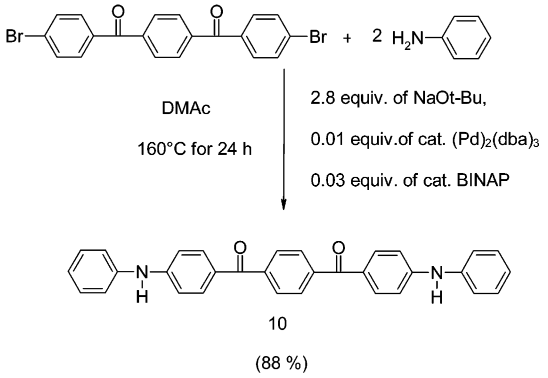
atmosphere. GPC measurements were used to determine molecular weights and molecular weight distributions by universal calibration generated with narrow molecular weight distribution polystyrene standards using tetrahydrofuran or dimethylformamide as eluent.

Synthesis. Synthesis of 1,4-Bis(4-bromobenzoyl)benzene (7) (Modified Procedure).[28] 40 g of anhydrous powdered aluminum chloride (0.3 mol) was added to a stirred solution of 25.4 g of terephthaloyl chloride (0.125 mol) and 255.14 g of bromobenzene (1.63 mol). After an exothermic reaction which raised the temperature to 30 °C, the solution was stirred at room temperature for 12 h and then heated at 95 °C for 2 h. After cooling, the solution was poured into cold aqueous hydrochloric acid to precipitate a solid which was isolated by filtration. The cream-colored solid was thoroughly washed with water, sodium bicarbonate solution (10%), and water and then dried at 100 °C in air. The crude product was recrystallized from *N*,*N*-dimethylacetamide (DMAc) or toluene to give **7** as colorless crystals. Yield: 52.2 g, 94%; mp 274–275 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 100 °C): $\delta = 7.86$ (s, 4H, H_3), 7.76 (d, 4H, H_2, m to Br), 7.73 (d, 4H, H_1, O to Br). MS (EI): 444.10. Anal. Calcd for $C_{20}H_{12}Br_2O_2$ (444.12): C, 54.09; H, 2.72; Br, 35.98. Found: C, 54.00; H, 2.70; Br, 35.56. IR spectra (KBr pellet): 840, 843 cm^{-1} (p-disubstituted benzene); 1640 cm^{-1} carbonyl group).

Synthesis of 1,3-Bis(4-bromobenzoyl-5-*tert*-butyl)benzene (9) (Scheme 1). A mixture of 5-*tert*-butylisophthalic acid (25 g, 0.113 mol) and $SOCl_2$ (250 mL) was stirred at reflux for 24 h. The excess $SOCl_2$ was distilled off under vacuum, and the resultant acid chloride was used in the following Friedel–Crafts benzoylation without further purification. Bromobenzene (230.6 g, 1.469 mol) was added to the acid chloride, and the solution was cooled in an ice–water bath. Anhydrous aluminum chloride (36 g, 0.27 mol) was added slowly such that the temperature did not exceed 5 °C. The obtained red suspension was stirred at room temperature for 16 h and then at 60 °C for 4 h. The reaction mixture was allowed to cool to room temperature and poured into a mixture containing ice–water and concentrated HCl. The pale yellow precipitate was washed with water and sodium bicarbonate solution (10%), resulting in a colorless solid which was dried in an oven. Two recrystallizations from chloroform/petroleum ether gave **9** as colorless crystals. Yield: 49.8 g, 88.2%; mp 167–68 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, rt): $\delta = 8.01$ (s, 2H, m to *t*-Bu group), 7.84 (1H, p to *t*-Bu group), 7.65 (dd, 4H), 7.49 (d, 4H), 1.36 (s, 9H, *t*-Bu group). ^{13}C NMR (62.5 MHz, CD_2Cl_2, rt): $\delta = 195.2$, 152.7, 137.6, 136.4, 132.9, 132.1, 131.0, 128.1, 126.4, 35.4, 31.2. MS(*m*/*z*): 499.60 (molecular peak). Anal. Calcd for $C_{24}H_{20}Br_2O_2$ (500.23): C, 57.63; H, 4.03; Br, 31.95. Found: C, 57.04; H, 3.89; Br, 31.62.

Synthesis of 4,4′-Bis(4-anilinobenzoyl)benzene (10) as a Model Compound (Scheme 2). An oven-dried resealable Schlenk flask was evacuated and backfilled with argon. The flask was charged with $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol, 2 mol %), BINAP (37.4 mg, 0.06 mmol, 6 mol %), and NaO-*t*-Bu (538 mg, 5.6 mmol). The flask was evacuated, backfilled with argon, and then capped with a rubber septum. DMAc (5 mL), 1,4-bis(4-bromobenzoyl)benzene (888 mg, 2.0 mmol), aniline (373 mg, 4 mmol), and additional DMAc (2 mL) were added through the septum. The flask was fitted with a reflux condenser, and the mixture was heated to 160 °C with stirring for 24 h. The resulting solution was allowed to slowly cool to room temperature and subsequently poured into cold water, filtered through Celite, and dried. The crude material was purified by flash chromatography on silica gel and recrystallized from toluene to afford **10** as yellow crystals. Yield: 825 mg, 88%; mp 248–50 °C. ^{1}H NMR (250 MHz, DMSO-d_6, rt): $\delta = 8.77$(S, NH); 7.56 (s, 4H, H_6); 7.50 (d, 4H, H_5); 7.13 (t, 4H, H_4); 7.03 (d, 4H, H_3); 6.93 (d, 4H, H_2), 6.80 (t, 2H, H_1). ^{13}C NMR (62.5 MHz, DMSO-d_6, rt): $\delta = 193.1$ (C3), 148.8 (C7), 140.8 (C8), 132.5 (C2), 129.4 (C5), 128.8 (C1), 126.3 (C10), 122.3 (C4), 119.8 (C11), 119.7 (C9), 113.7 (C6). MS (*m*/*z*): 468.9 (molecular peak), 467.9, 422.6, 300.3, 285.3, 238.9, 195.8 (100%), 166.7, 151.0; FTIR (KBr pellet): γNH at 3341 cm^{-1}; γC=O at 1633 cm^{-1}, γC–H aromatic at 3049 cm^{-1} and C–N at 1338 cm^{-1}; UV recorded in DMF λ_{max} at 296.7 and 374.1 nm. Anal. Calcd for $C_{32}H_{24}N_2O_2$ (468.55): C, 82.03; H, 5.16; N, 5.98. Found: C, 81.54; H, 4.93; N, 5.20.

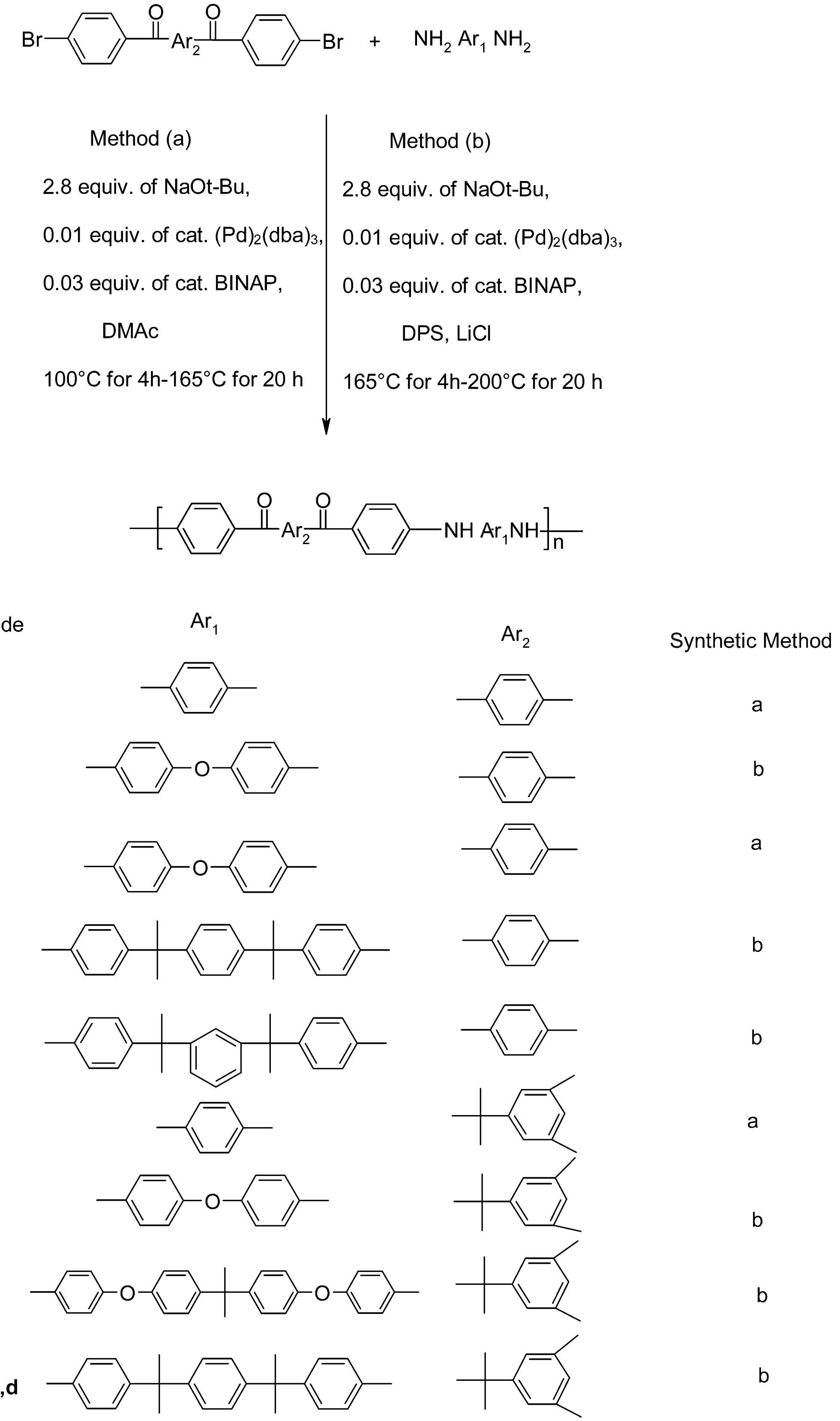
Scheme 2. Synthesis of Model Compound 10



Synthesis of Poly(imino ketone)s (Scheme 3). Method a. To a Schlenk flask equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, dibromo compound (4 mmol), diamine (4 mmol), sodium *tert*-butoxide (1.076 g, 11.2 mmol), tris(dibenzylideneacetone)dipalladium(0) (36.6 mg, 0.04 mmol), BINAP (74.8 mg, 0.12 mmol), and dimethylacetamide (6–8 mL) were added. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated five times. The flask was immersed with continuous stirring in a 100 °C oil bath for 4 h and in a 165 °C oil bath for 20 h. The resulting polymer solution was allowed to slowly cool to room temperature, filtered, and subsequently poured into cold water, filtered, washed with water and methanol, and then dried at 100 °C under vacuum. The elemental analyses of typical polymers **11a**, **11c**, and **14a** are listed in Table 2.

Method b. To a Schlenk flask equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, dibromo compound (4 mmol), diamine (4 mmol), sodium *tert*-butoxide (1.076 g, 11.2 mmol), tris(dibenzylideneacetone)dipalladium(0) (36.6 mg, 0.04 mmol), BINAP (74.8 mg, 0.12 mmol), lithium chloride (0.96–1.4 g), and diphenyl sulfone (7–10 g) were added. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated five times. The flask was immersed with continuous stirring in a 165 °C oil bath for 4 h and in a 200 °C oil bath for 20 h. The reaction mixture was then cooled to room temperature. The obtained powder was subsequently washed with acetone to remove the solvent and dissolved in dimethylformamide, filtered, precipitated by acetone to ensure removal of salts, washed with water many times, and then dried at 100 °C

Scheme 3. Synthesis of Poly(imino ketone)s (PIKs)



under vacuum. The elemental analyses of typical polymers **11b**, **12a**, **13**, **14b**, **15**, and **16a** are listed in Table 2.

Results and Discussion

The accepted mechanism of the Pd-catalyzed amination involves oxidative addition of the aromatic halides to a palladium(0) species to form an arylene palladium(II) halide. By inductive effect or by resonance, this step should be favored for an arylene bromide substituted with an electron-withdrawing group in the ortho or para position. To investigate the potential of the amination reaction for a polycondensation process, 4,4′-bis(4-anili-

Table 1. Characterization of PIKs (GPC, Intrinsic Viscosity, FTIR, and Yield)

polymer code	$\bar{M}_n$[a]	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[b]	DP[c]	yield (%)	γNH[d]	γC=O[d]	γC−N[d]	[η],[e] g/dL
11a				*f*	95	3318	1631	1312	*f*
11b	12 200	25 300	2.1	25	89.9	3322	1635	1314	0.18
11c	11 100	74 100	6.7	23	92	3320	1638	1316	0.16
12a	15 000	26 300	1.8	24	80	3377	1642	1308	0.19
13	11 700	19 500	1.7	18	88	3360	1644	1307	0.17[g]
14a				*f*	86	3348	1646	1310	*f*
14b	44 200	295 200	6.7	82	88	3384	1644	1327	0.42
15	37 000	139 300	3.8	49	84	3422	1663	1330	0.249
16a	85 900	474 500	5.5	126	90	3364	1646	1328	0.685

[a] By GPC (calibrated by polystyrene standards). [b] Polydispersity index. [c] Degree of polymerization determined from number-average molecular weight. [d] FTIR (KBr, pellet). [e] [η] = intrinsic viscosity measured at 25 °C in DMF. [f] Not measured due to poor solubility. [g] Measured at 25 °C in THF.

Table 2. Elemental Analysis for Poly(imino ketone)s

polymer code	formula (mol wt %)[c]	elemental analysis[a] (%)				moisture uptake[b]
			C	H	N	
11a	$(C_{26}H_{18}N_2O_2)_n$	calcd	79.98	4.65	7.17	
	$(390.4411)_n$	found	76.70	4.86	6.89	3.60
		corrected	79.46	4.69	7.14	
11b	$(C_{32}H_{22}N_2O_3)_n$	calcd	79.65	4.60	5.81	
	$(482.5383)_n$	found	77.52	4.73	5.67	2.62
		corrected	79.55	4.61	5.82	
11c	$(C_{32}H_{22}N_2O_3)_n$	calcd	79.65	4.60	5.81	
	$(482.5383)_n$	found	76.80	4.78	5.80	3.63
		corrected	79.59	4.61	6.01	
12a	$(C_{44}H_{38}N_2O_2)_n$	calcd	84.31	6.11	4.47	
	$(626.7979)_n$	found	83.10	6.19	4.33	1.42
		corrected	84.28	6.10	4.39	
13	$(C_{44}H_{38}N_2O_2)_n$	calcd	84.31	6.11	4.47	
	$(626.7979)_n$	found	82.62	6.21	4.34	2.03
		corrected	84.19	6.08	4.43	
14a	$(C_{30}H_{26}N_2O_2)_n$	calcd	80.69	5.87	6.27	
	$(446.5486)_n$	found	74.83	6.23	5.86	6.85
		corrected	79.96	5.80	6.26	
14b	$(C_{36}H_{30}N_2O_3)_n$	calcd	80.27	5.61	5.20	
	$(538.6458)_n$	found	74.60	6.08	4.85	6.97
		corrected	79.80	5.66	5.19	
15	$(C_{51}H_{44}N_2O_4)_n$	calcd	81.79	5.92	3.74	
	$(748.9214)_n$	found	77.69	5.99	3.68	4.93
		corrected	81.52	5.69	3.50	
16a°	$(C_{48}H_{46}N_2O_2)_n$	calcd	84.42	6.79	4.10	
	$(682.9054)_n$		79.81	7.18	3.81	5.70
			84.36	6.77	4.03	

[a] For C and N corrected value = found value × (100% + moisture uptake %). For H corrected value = found value × (100% − moisture uptake %). [b] Moisture uptake (%) = $(W - W_0)/W_0 \times 100\%$. W is the weight of polymer sample after standing at room temperature; W_0 is the weight of polymer sample after drying in a vacuum at 100 °C for 10 h. [c] In g mol^{-1}.

nobenzoyl)benzene (**10**) was synthesized as a model compound by a palladium-catalyzed amination of 1,4-bis(4-bromobenzoyl)benzene (**7**) with aniline as a primary aromatic amine using NaO-*t*-Bu as a base and BINAP (**1**) (Figure 3) as a ligand.

The isolated yield was 88% after column chromatography, while there were no minor undesired products detected by ^{1}H and ^{13}C NMR spectroscopy, (FD$^+$) mass spectra, or thin-layer chromatography.

Polymer Synthesis. Reactions of electron-poor aromatic halides and electron-rich amines give the highest yields in the amination protocol.[30] Thus, we attempted polycondensation of 1,4-bis(4-bromobenzoyl)benzene (**7**) and 1,3-bis(4-bromobenzoyl-5-*tert*-butyl)benzene (**9**) as electron-poor arylene bromides with a series of electron-rich primary aromatic diamines. The results of the Pd-catalyzed polycondensation of these aromatic bromides with different aromatic diamines are listed in Table 1. Two methods were developed for the synthesis of poly(imino ketone)s (Scheme 3).

In both methods the combination of $Pd_2(dba)_3$ and BINAP was used as an efficient catalyst. In method a, DMAc was used as a solvent at a temperature of 100 °C for 4 h followed by 165 °C for 20 h. In method (b) diphenyl sulfone (DPS) was applied as a solvent at a temperature of 165 °C for 4 h and then 200 °C for 20 h, and lithium chloride was added to hinder intermolecular and intramolecular hydrogen bonding of the PIK products and to thus increase the solubility. The relative amounts of monomers and DPS were adjusted to maintain a solid content of 30−36% during the polycondensation process. The reactions of the dibromo monomers **7** and **9** with the arylene diamines having electron-donating substituents provided the corresponding PIKs in 80−95% yields without undesired side products (work-up method a or b).

The polymer solubility depended on the nature of the solvent, the molecular weight, and chemical structure of the polymer. Polymers **11b**, **11c**, **12a**, **13**, **14b**, **15**, and **16a** could be dissolved in aprotic solvents such as NMP, DMAc, DMSO, and DMF while only swelling was observed in other common organic solvents such as chloroform and dichloromethane. The complete dissolution process took from a few minutes (polymer **11b** in

Table 3. Different Experimental Conditions for the Polycondensation of 2,2-Bis[4-(4-aminophenoxy)phenyl]propane with 1,3-Bis(4-bromobenzoyl-5-*tert*-butyl)benzene To Form Polymer 15

run	temp (°C)	concn of monomers (%)	solubility	yield (%)	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	DP
1	100	18	DMF, DMAc, THF	92	4000	1000	4	1.3
2	100	36	DMF, DMAc, THF	90	10000	2000	5	2.6
3	165	24	DMF, DMAc, THF	98	11000	7000	1.6	9
4	165	30	swelling in DMF, DMAc, THF	95				
5	165	36	swelling in DMF, DMAc, THF	96				
6	100−165	36	DMF, DMAc, THF	96	42000	10000	4.2	13

DMF) up to several hours (polymer **16a** in DMF about 24 h).[31]

The molecular weights of the reprecipitated polymers were measured by GPC (calibrated by polystyrene standards). The M_n values are in the range of 11 100−85 900 and the M_w values in the range of 19 500−474 500. The polydispersities vary from 1.7 up to 6.7 (Table 1). Especially, with increasing molecular weights the polydispersity increases drastically.[32]

The elemental analysis of the polymers showed that in all cases the determined carbon and nitrogen content were lower than the calculated ones. This can be explained by the hygroscopic nature of the imino groups of these polymers. The uptake of water was in the range of 1.4−7.0% as calculated from the weight change of the vacuum-dried polymer samples after exposure to air at room temperature for 10−12 h. Therefore, the measured elemental analysis values were corrected by elimination of the amount of absorbed water (Table 2). Similar to the study performed on hygroscopic polyaramides,[33] the experimental data were then in good agreement with the calculated ones.

Intermolecular and Intramolecular Hydrogen Bonding. Hydrogen-bonding interactions of polymers have frequently been studied by FTIR spectroscopy.[34,35] Therefore, IR spectra of all PIKs (KBr pellets) were recorded, giving results in good agreement with the proposed structure. The characteristic absorptions for carbonyl groups $\gamma(C{=}O)$ appeared between 1631 and 1663 cm^{-1} and for aromatic amino groups $\gamma(NH)$ between 3318 and 3422 cm^{-1} (Table 1). Obviously, because of hydrogen bonding, a significant broadening and lowering of the absorption frequency of the bands ($\gamma(C{=}O)$, $\gamma(NH)$) are observed.[36] This effect is known to be a function of the degree and strength of the hydrogen bonding.[37,38] This clearly indicates that N−H···O=C interactions within the same molecule (intramolecular hydrogen bonding) or from neighboring molecules. Intermolecular hydrogen bonding is very likely as the solubility of all polymers is limited but can be drastically improved by the addition of lithium chloride known to break hydrogen bonds.[7] This confirms our assumption that these polymers may be considered as analogous materials to polyaramides. Comparing the frequencies of the N−H bond of the crystalline model compound **10** (3341 cm^{-1}) with those observed in the polymers (**12a, 13, 14a, 14b, 15**, and **16a**: 3377, 3360, 3348, 3384, 3422, and 3364 cm^{-1}), a shift to higher frequencies is observed. This suggests that the hydrogen bonding in PIKs is weaker than in the crystalline model compound.

^1H NMR (700 MHz) spectra of all the soluble polymers were recorded. As an example, the spectra of **13** are shown in Figure 2 (DMSO-d_6 at 100 °C). From the ^1H NMR spectra we can conclude that polymer **13** contains a low concentration of amino end groups (resonances at 6.4 ppm). The concentration corresponds to less than 5 mol % end groups per repeat unit. Bromine end groups are not detectable, but they cannot be excluded as they are expected in the same region as the resonances of the proton H_1. As the concentration of end groups in polymer **13** is very low, the corresponding ^{13}C NMR signals were not detectable.

Table 4. Pd-Catalyzed Polycondensation of 1,3-Bis(4-bromobenzoyl-5-*tert*-butyl)benzene (9) with 4,4′-(1,4-Phenylenediisopropylidine)bisaniline Using Different Ligands[a]

run	polymer code	ligand[b]	yield[c] (%)	M_n[d]	M_w[d]	DP[f]	M_w/M_n[g]
1	**16a**	1	90	85 900	474 500	126	5.5
2	**16b**	2	80.9	28 000	142 000	41	5.1
3	**16c**	3	78	5 000	59 000	7	8.5
4	**16d**	4	73	5 000	52 000	7	9.6
5[e]			0				

[a] The polycondensation of electron-poor 1,3-bis(4-bromobenzoyl-5-*tert*-butyl)benzene (4 mmol) was carried out in the presence of Pd_2 $(dba)_3$ (0.12 mmol), ligand (P/Pd ratio = 3/1), and NaO-*t*-Bu (11.2 mmol) in diphenyl sulfone at 165 °C for 4 h and at 200 °C for 24 h. [b] **1** = BINAP; **2** = di-*tert*-butylphosphinobiphenyl; **3** = $P(tBu)_3$; **4** = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. [c] Reprecipitated polymer. [d] Calibrated by GPC (DMF) polystyrene standards. [e] No catalyst was added. [f] Degree of polymerization determined from number-average molecular weight. [g] Polydispersity index.

The end groups were only detected in the case of polymer **13**, as shown from the ^1H NMR spectrum. Remarkably, no end groups were detected in the case of the higher molecular weight PIKs.

During the synthesis of polymer **15**, the effect of concentration and temperature on the molecular weight could be followed. Upon increasing the temperature from 100 to 165 °C and the concentration from 18% to 24%, M_w increased from 4000 to 10 000 and M_n from 1000 to 7000, while upon increasing the concentration form 24% to 36% at temperature 165 °C, M_w increased from 11 000 to 42 000 and M_n from 7000 to 10 000. A temperature of 165 °C and a concentration of 36% are more suitable for the palladium-catalyzed polycondensation to produce polymer **15** with higher molecular weight (Table 3).

To test which ligand would be most suitable for the polycondensation process to form PIKs, we attempted the amination of 1,3-bis(4-bromobenzoyl-5-*tert*-butyl)benzene (**9**) with 4,4′-(1,4-phenylenediisopropylidine)bisaniline in diphenyl sulfone using different ligands from **1** to **4** (Figure 3, Table 4).

It appears that ligand **1** gives better yields, higher molecular weight, and lower polydispersity of the polymer than ligand **2** and that both are superior to **3** and **4**.

The reactivity of the halogen-containing monomers (**5**−**7**) was studied during the polycondensation process to form polymer **12a** (Table 5). The use of 1,4-bis(4-bromobenzoyl)benzene (**7**) gave polymer **12a** in better yield higher molecular weight than 1,4-bis(4-chlorobenzoyl)benzene (**5**) while 1,4-bis(4-fluorobenzoyl)benzene (**6**) is totally unreactive. It is known that for aryl

Table 5. Pd-Catalyzed Polycondensation of Different 1,4-Bis(4-halobenzoyl)benzenes with 4,4-(1,4-Phenylenediisopropylidine)bisaniline[a]

run	polymer code	R	yield[b] (%)	M_n[c]	M_w[c]	M_w/M_n[d]	DP
1	**12a**	Br	80	15 000	26 300	1.8	24
2	**12b**	Cl	76.6	11 000	16 000	1.5	17
3		F	0				

[a] The polycondensation of electron-poor 1,4-bis(4-halobenzoyl-)benzene (4 mmol) was carried out in the presence of $Pd_2(dba)_3$ (0.12 mmol), ligand (BINAP) (P/Pd ratio = 3/1), and NaO-*t*-Bu (11.2 mmol) in diphenyl sulfone at 165 °C for 4 h and at 200 °C for 24 h. [b] Reprecipitated polymer. [c] Calibrated by GPC (DMF) polystyrene standards. [d] Polydispersity index.

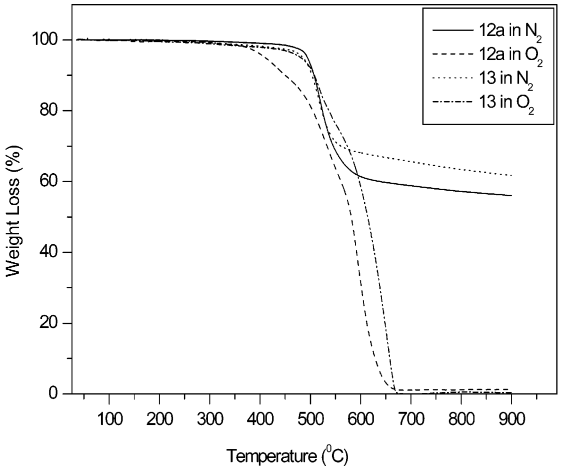


Figure 4. TGA of the polymers **12a** and **13** (in N_2, and in O_2 10 °C/min).

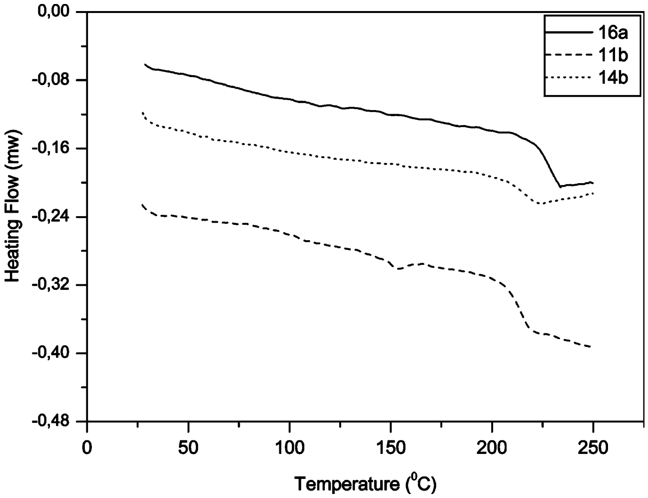


Figure 5. DSC of PIKs (in N_2,10 °C/min, second scan).

amination the reactivity decreases strongly with increasing electronegativity of the halogen atoms, and oxidative addition is rate-limiting.

Thermal and Thermomechanical Behavior. All PIKs showed high thermal stability and a high char yield in nitrogen at 600 °C. Typical TGA traces in air and in nitrogen are shown in Figure 4 for polymers **12a** and **13**. The thermal stability was evaluated by a 5% weight loss (Table 6). TGA curves revealed that the polymers were thermally stable up to 323−494 °C. The 50% weight losses of the polymers took place at over 900 °C for polymers **11a**, **12a**, **13**, **14a**, and **15** in nitrogen and for polymers **11b** and **14b** in both air and nitrogen. Char yield is an easy and important measurement which correlates to the ability to sustain combustion.[39] The maximum char yield at 600 °C was obtained for polymer **11a** (83%), and the minimum was obtained for polymer **16a** (54%) in nitrogen.

By comparing for example the TGA thermograms of **12a** and **13** (Figure 4), it was observed that in air a 50% weight loss of those polymers took place at 580 and 610 °C, respectively, but in nitrogen the 50% weight loss was not observed up to 900 °C. In air the char yield at 600 °C was 34% and 59%, but in nitrogen the char yield at 600 °C was 61% and 68%.

Differential scanning calorimetry (DSC) of PIKs up to 250 °C showed a single T_g, and the absence of a melting temperature suggested an amorphous polymer structure. A representative DSC thermogram of the polymers is shown in Figure 5. The glass transition temperatures of these copolymers are listed in Table 6. All polymers show high T_gs ranging from 202 to 227 °C, being comparable with the T_gs of modified polyterephthalamides bearing pendent groups connected to the polymer backbone with ester linkages.[40] Only polymer **13** gave in a lower T_g at 154 °C. The T_gs are higher than those of the related PEKs which range from 129 to 167 °C[41] and lower than those of aromatic polyamides which amount to 292−319 °C.[42] This can be explained by the

Table 6. Thermal Behavior of PIKs

polymer code	O_2/N_2	T_5[a]	T_{10}[b]	T_{50}[c]	W_{500}[d]	W_{600}[e]	char yield at 600 °C[f]	T_g onset[g]
11a	O_2	323	345	353	95	97	3	*h*
	N_2	482	538	>900	6	17	83	
11b	O_2	435	516	>900	8	22	78	212
	N_2	494	534	>900	6	22	78	
12a	O_2	407	444	582	19	66	34	220
	N_2	494	507	>900	7	39	61	
13	O_2	478	507	613	8	41	59	154
	N_2	485	502	>900	9	32	68	
14a	O_2	335	337	344	94	98	2	*h*
	N_2	387	461	>900	17	29	71	
14b	O_2	365	426	>900	21	30	70	215
	N_2	363	425	>900	23	32	68	
15	O_2	356	413	567	26	64	36	202
	N_2	328	391	>900	30	40	60	
16a	O_2	370	461	715	22	47	53	227
	N_2	366	458	742	23	46	54	

[a] T_5 = temperature of 5% weight loss. [b] T_{10} = temperature of 10% weight loss. [c] T_{50} = temperature of 50% weight loss. [d] W_{500} = weight loss at 500 °C, determined from TGA curve. [e] W_{600} = weight loss at 600 °C, determined from TGA curve. [f] The remaining of the polymer at 600 °C. [g] From the second heating traces of DSC measurements conducted with a heating rate of 10 °C min^{-1} in nitrogen. [h] Not detected up to 250 °C.

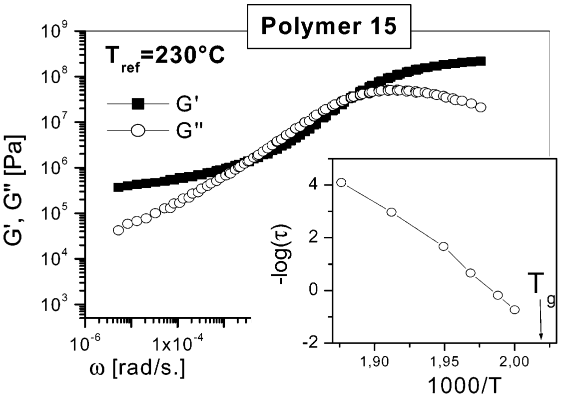


Figure 6. Mechanical behavior of polymer **15** as determined by means of the dynamic small-amplitude shear deformation with various deformation frequencies and at various temperatures. The properties are represented by frequency dependencies of the real (G') and imaginary (G'') components of the complex shear modulus (master curves at the reference temperature of 210 °C). The inset shows the temperature dependence of the segmental relaxation time.

hydrogen bonding in PIKs which is weaker than that in polyamides while PEKs have no hydrogen bonding.

The mechanical behavior of the polymers has been examined by means of dynamic mechanical testing performed at various temperatures and various frequencies with a small-amplitude sinusoidal deformation.[43] An example of the mechanical behavior determined for polymer **15** is shown in Figure 6. The results indicate that the polymer exhibits a spectrum of viscoelastic properties characteristic for linear amorphous entangled polymers. The two relaxation processes: (1) segmental relaxation at high frequencies detected as the cross-points of the storage (G') and loss (G'') modulae on the frequency scale and (2) chain relaxation at low frequencies (not visible) are controlling the behavior.

These relaxations separate three states characteristic for amorphous polymers: (1) the glassy state with the high value of the elastic modulus ($G' \sim 1$ GPa) at high frequencies, (2) the intermediate rubbery state with the modulus of the order of 1 MPa (the low-frequency part of Figure 6), and (3) the flow regime at low frequencies with $G' \ll G''$ both varying with frequency in a characteristic way (not visible).[44] The inset in Figure 6 shows the temperature dependence of the segmental relaxation time which indicates that the relaxation time slows down to nearly 100 s when the polymer is approaching the glass transition temperature (T_g) from higher temperatures. In the presented example, the rubbery plateau is very well developed and extends over many orders of magnitide of the frequency scale, indicating a high molecular weight of polymer **15**. The terminal relaxation and the flow range are not seen in the present data because the high T_g and the high molecular weight of this polymer shift the detection range of such a behavior to very high temperatures (above 250 °C). Summarizing the first results, one can conclude that PIKs can be considered as a new class of high-performance polymers. They exhibit high T_gs ($T_g > 140$ °C) and excellent thermal stability ($T_D > 320$ °C) combined with good mechanical properties (storage (G') and loss (G'') modulae $< 10^8-10^9$ and extended rubber plateau) comparable to polyaramides or PEK.[45] Furthermore, because of the lack of amide bonds, these polymers should be more stable under hydrolyzing conditions.

Conclusions

Soluble poly(imino ketone)s with high molecular weights have been obtained by a Pd-catalyzed polycondensation (Buchwald−Hartwig reaction) of aromatic dibromides and aromatic amines. Various poly(imino ketone)s were synthesized by using different monomers. Four different ligands were used successfully in the Pd-catalyzed process of which the Pd/BINAP system was found to be the most effective catalyst; however, we do not know whether this is due to steric or electronic reasons. The obtained polymers may be considered as an analogue to polyaramides since hydrogen bonding is observed by broadening of the associated imino group (NH) vibrational bands, while the solubility is enhanced. On the other hand, because of the incorporated benzophenone and ether moieties, one can expect similarities to poly(ether ketone)s (high Young modulus, low entanglement molecular weight).[46] All these expectations are already confirmed by initial mechanical and TGA measurements, indicating that PIKs can be considered as a new class of high-performance polymers with a good mechanical behavior and high thermal stability. These investigations are presently extended and will be supported by dielectric spectroscopy. One major advantage in comparison to the established PEKs and polyaramides is already obvious. In comparison to PEK, one can use cheaper monomers, e.g., chloro- or bromo-functionalized aromatic ketones instead of the corresponding difluoro structures. Also, the synthesis of “activated“ intermediates as is the case for the preparation of polyaramides by converting the aromatic esters to e.g. acid chlorides is avoided. Furthermore, many diamines and dibromo compounds are readily available or easy to synthesize giving a fast access to numerous new polymers with optimized properties such as thermal stability, mechanical behavior, or solubility.

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