Extremely High Molar Mass Hyperbranched Poly(arylene ether)s from a New Semifluorinated AB$_2$ Monomer by an Unusual AB$_2$ + A$_2$ Polymerization Approach

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ABSTRACT: A new AB$_2$ monomer [3,5-bis(4-fluoro-3-trifluoromethylphenyl)phenol] has been successfully prepared by the Pd(0)-initiated coupling reaction of 4-fluoro-3-trifluoromethylphenylboronic acid and 3,5-dibromophenol. This monomer led to a high molecular weight hyperbranched polymer (M_w = 230 000 g/mol) by self-condensation. Several hyperbranched polymers have also been prepared successfully by condensing the AB$_2$ monomer with different diphenols (A$_2$) in different molar ratios. Here, the stoichiometric (2:1) AB$_2$/A$_2$ products **2c** and **3c** showed extremely high weight-average molecular weights of 3 730 000 and 4 470 000 g/mol without any gelation under the specified reaction conditions. The products have been well characterized by SEC, DSC, TGA, FTIR, and NMR techniques. The degree of branching of the AB$_2$ product could be determined by proton NMR for a medium molar mass sample and was found to be 0.5. The AB$_2$ self-condensed hyperbranched poly(arylene ether) showed a glass transition temperature (T_g) as high as 199 °C and the 10% weight loss temperature as high as 573 °C in N$_2$, whereas the extremely high molar mass products **2c** and **3c** of the AB$_2$/A$_2$ approach did not show a T_g up to 350 °C and similar high thermal stability. Homogenous and stable films could be prepared from these new polymers which are prone to self-cross-linking by heating especially for the AB$_2$/A$_2$ products. High hydrophobicity of the polymers combined with high thermal stability renders those materials highly interesting for microelectronics application.

Introduction

Hyperbranched polymers are a special type of dendritic polymer and a relatively new class of macromolecules. They are receiving much attention in recent years[1–5] from both academia and industry since Flory's original theoretical report[6] in 1952. Because of their unique architecture, these macromolecules show excellent solubility in organic solvents and low viscosity. One-pot self-polymerization of AB$_x$ monomers (where $x \geq 2$) is one of most common routes to prepare hyperbranched polycondensates.[7–10] The polymerization of AB$_x$ monomers to generate highly branched soluble polymers as described by Flory resulted in a general high interest in branched polymers and the comparison of their relative properties with those of linear analogues. The irregular branched hyperbranched polymers, in contrast to dendrimers, are polydisperse systems in terms of both molecular weight characteristics and their degree of branching.[10,11]

Hyperbranched aromatic polyethers can be prepared through nucleophilic aromatic substitution reactions of AB$_x$ type monomers.[1] In addition to common electron-withdrawing groups such as sulfone and ketone, certain heterocycles can activate aryl halides toward aromatic nucleophilic substitution. Several hyperbranched poly(arylene ether)s from AB$_2$ monomers have been reported in the literature that include poly(ether sulfone),[12] poly(ether ketone)s,[14–16] poly(etheroxazole),[18] poly(ether phenyl phenyl quinoxaline)s,[19–21] poly(phenylene oxide),[22,23] poly(arylene ether imide),[24–26] poly(arylene ether ketone imide)s,[27,28] and poly(arylene ether phosphine oxide)s.[29,30]

Increasingly, hyperbranched polymers are synthesized also by the A$_2$ + B$_y$ approach from easily available monomers. Several groups have attempted a facile A$_2$ + B$_3$ approach toward hyperbranched polymers.[31] Although the A$_2$ + B$_3$ synthetic approach for hyperbranched polymers shows many advantages (such as facile preparation, scaling up, easy to tailor structure, etc.) over the AB$_x$ polymerization approach, it has as intrinsic problem that gelation is unavoidable at the critical conversion of the functionalities. The success of this approach is dependent upon many factors, including the ratio of functionalities, solvent and reagent purity, and the reaction time and temperature. Several polymer architectures have been prepared by this approach, e.g., polyamides,[32] polycarbonates,[33] and polyimides.[34,35] However, very few reports exist on the synthesis of hyperbranched poly(arylene ether)s by adapting A$_2$ + B$_3$.[36] Recently, we have reported several hyperbranched polymers from a new B$_3$ monomer adapting an A$_2$ + B$_3$ approach.[37] There are a few reports on preparation of hyperbranched polyphenylenes by the AB$_2$ + AB approach.[1,38] We will now demonstrate that also the AB$_2$ + A$_2$ approach can also be used as an extension of A$_2$ + B$_3$ and AB$_2$ + AB methods of condensation resulting in nongelled products.

In general, poly(arylene ether)s possess high glass transition temperatures, excellent thermal stability, and mechanical strength and can be used as moldable or castable tough matrix resins.[39–41] Among the possible applications, poly(arylene ether)s are used as insulating materials in microelectronics (interlayer dielectrics and intermetal dielectrics) and as membrane materials, e.g., for gas separations. Fluorine-containing polymers are of special interest because of their low dielectric constants and remarkably low

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water absorption. Hexafluoroisopropylidene (6F) groups in the polymer backbone enhance polymer solubility (commonly referred to as the "fluorine effect") without forfeiture of thermal stability.[42] They also increase the glass transition temperature with concomitant decrease of crystallinity. The bulky $-CF_3$ group also serves to increase the free volume of the polymer, thereby improving various properties of polymers including gas permeabilities and electrical insulating properties.[39−41,43] Because of all these interesting properties of the fluorinated polymers, considerable attention has been devoted to the preparation of new classes of fluorine-containing polymers.[39−44] It is expected that fluorinated hyperbranched poly(arylene ether)s will lead to further reduction in dielectric constants as higher fractional free volume results from highly branched structure.

The present work describes the synthesis and characterization of a new trifluoromethyl activated AB$_2$ monomer [3,5-bis(4-fluoro-3-trifluoromethylphenyl)phenol] and of the hyperbranched poly(arylene ether) obtained by self-condensation of the synthesized monomer. The work has been further extended to the preparation of several poly(arylene ether)s by the AB$_2$ + A$_2$ approach using diphenol as A$_2$ monomer. The polymers have been characterized by SEC, FTIR, and NMR techniques, and the thermal properties have been evaluated by DSC and TGA techniques. Surface properties of the spin-coated films on silicon wafer have also been investigated.

Experimental Section

Methods. Elemental carbon, hydrogen, and nitrogen of the compounds were analyzed by the pyrolysis method using Vario EL (Elementar, Germany) elemental analyzer. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DRX 500 spectrometer using CDCl$_3$ as solvent and as internal standard [$\delta(^1H)$ = 7.26 ppm; $\delta(^{13}C)$ = 77.0 ppm]. The ^{19}F NMR spectra were referenced on external C$_6$F$_6$ [$\delta(^{19}F)$ = −162.9 ppm]. FT-IR spectra were recorded with a Bruker IFS66 V/s spectrometer using a Golden Gate ATR device (diamond internal reflection element). DSC measurements were made on a DSC Q 1000 of TA Instruments with ramping rate of 20 °C/min under nitrogen. Glass transition temperature (T_g) was determined from the second heating run using the half-step method. Thermal decomposition behavior of these polymers was investigated on a TGA Q 5000 of TA Instruments at a heating rate of 10 °C/min under nitrogen. Determination of the molar masses was performed by size exclusion chromatography (SEC) equipped with HPLC pump (Knauer, Germany) coupled with differential refractive index (RI) detector (ETA-2020, WGE Dr. Bures, Germany) and a multiangle laser light scattering detector (MALLS) DawnEOS (Wyatt Technologies). PL Mixed B-LS chromatography column (Polymer Laboratories, Ltd., UK) was used with THF as a solvent with a flow rate of 1 mL/min. The evaluations were made with the software ASTRA 4.9 (Wyatt Technology Corp.). In order to obtain reliable information about the molar mass distribution of the samples, linear fit of the molar mass/elution volume dependence has been performed using the Corona Software (Wyatt Technology Corp.). Water contact angle of the spin-coated films were measured using an OM40 microinstrument from Dataphysics, Filderstadt, Germany. The volume of the water droplets used for measurements was 2 μL. Atomic force microscopy (Digital Instruments, Inc., Santa Barbara, CA) (AFM) imaging was performed using a Dimension 3100 and a CP microscope (Park Scientific Instrument, Inc.) in the tapping mode.

Starting Materials. 4,4′-Isopropylidenediphenol (BPA), 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), tetrakis(triphenylphosphine)palladium(0), 4-aminophenol, and toluene (anhydrous) were purchased from Aldrich and used as received. 5-Bromo-2-fluorobenzotrifluoride was purchased from Fluorochem, UK, and was used as received. *N*-Methyl-2-pyrrolidone (NMP, E. Merck,

Germany) was purified by stirring with NaOH and distilled from P$_2$O$_5$ under reduced pressure. All other solvents and chemicals were purchased from Aldrich and E. Merck, Germany, and used as received.

Synthesis of 3,5-Bis(4-fluoro-3-trifluoromethylphenyl)phenol; AB$_2$ Monomer. In a first step 5-bromo-2-fluorobenzotrifluoride was converted to its boronic acid derivative as described in previous literature.[40] A 1000 mL three-necked round-bottom flask was charged with 4-fluoro-3-trifluoromethylphenyl boronic acid (23 g; 111.15 mmol), 3,5-dibromophenol (10 g; 39.6 mmol), toluene (350 mL), water (350 mL), Na$_2$CO$_3$(37 g, 2864.865 mmol), and Pd(PPh$_3$)$_4$ (1.37 g; 1.19 mmol, 3 mol % with respect to dibromophenol). The reaction mixture was intensively stirred and refluxed for 72 h. The mixture was neutralized by addition of dilute HCl. The organic layer was separated, and the aqueous layer was extracted by 400 mL of toluene; the combined organic layer was filtered over Al$_2$O$_3$ (type 100−125 mesh, activity 1, bed length 40 cm, and diameter 4 cm) column to remove the catalyst Pd(PPh$_3$)$_4$. The column was washed with 500 mL of toluene; finally, the compound was obtained after removal of the toluene. The compound was further purified by recrystallization from 1:10 mixture of toluene/hexane. Recrystallized yield: 12.4 g (74.6%); melting point: 165 °C. Anal. Calcd for C$_{20}$H$_{10}$F$_8$O (418.30 g mol^{-1}): C, 57.37%; H, 2.40%. Found: C, 57.21%; H, 2.42%. IR (KBr) (cm^{-1}): 3280, 1606, 1515, 1428, 1324, 1053, 829, 647. ^1H NMR (CDCl$_3$): 7.81 (2H, dd, H^6), 7.76 (2H, m, H^{10}), 7.30 (2H, t, H^9), 7.24 (1H, t, H^4), 7.03 (2H, d, H^2), 4.95 (1H, s, OH). ^{13}C NMR (CDCl$_3$): 159.44 (dq, C^8), 157.22 (C^1), 141.30 (C^3), 137.05 (d, C^5), 132.46 (d, C^{10}), 125.84 (dq, C^6), 122.55 (q, C^{11}), 118.77 (dq, C^7), 118.10 (C^4), 117.39 (d, C^9), 131.88 (C^2). ^{19}F NMR (CDCl$_3$): −62.43 (d, F^{11}), −117.45 (q, F^8).

Synthesis of Hyperbranched Poly(arylene ether) [hbp(hw)] from the AB$_2$ Monomer by Self-Condensation. Polymerization reaction was carried out in a 50 mL three-necked round-bottomed flask equipped with a stir bar, a Dean−Stark trap fitted with a condenser, and a nitrogen inlet. The flask was charged with 3,5-bis(4-fluoro-3-trifluoromethylphenyl)phenol (1 g; 2.39 mmol), K$_2$CO$_3$ (0.495 g; 3.58 mmol), NMP (10 mL), and toluene (25 mL). The mixture was heated to reflux (140−150 °C, oil bath temperature) for 3 h as water was removed azeotropically with toluene. After removing the toluene from Dean−Stark trap, the reaction temperature was increased to 180 °C and maintained for 8 h. The reaction mass was cooled to room temperature, and the polymer was recovered by precipitation from a 50/50 mixture of 300 mL of water/methanol containing few milliliters of HCl. The precipitate was isolated and washed several times with boiling water to remove any inorganic impurities and then dried under vacuum at 50 °C for overnight. The mass was redissolved in THF (15 mL) and precipitated in excess methanol and dried under vacuum at 70 °C for 24 h. ^1H NMR (CDCl$_3$): 8.0−7.85 (H$^{6'}$), 7.85−7.6 (H^6, H^{10}, H$^{10'}$), 7.55 (H$^{4',dend}$), 7.51 (H$^{4',lin}$), 7.47 (H$^{4',term}$), 7.35−7.2 (H$^{2'}$, H^9), 7.2−7.1 (H$^{9'}$). ^{13}C NMR (CDCl$_3$): 159.7 (C^8), 157.6 (C$^{1'}$), 155.0 (C$^{8',dend}$), 154.9 (C$^{8',lin}$), 154.8 (C$^{8',term}$), 142.3 (C$^{3',dend}$, C$^{3',lin}$), 142.0 (C$^{3',term}$, C$^{3',lin}$), 136.5 (C$^{5',lin}$), 136.4 (C$^{5',term}$),135.5 (C$^{5',dend}$), 136.4 (C$^{5',lin}$),132.7 (C^{10}), 132.2 (C$^{10'}$), 126.3 (C$^{6'}$), 125.9 (C^6), 123.2 (q, C$^{11'}$), 122.5 (q, C^{11}), 122.3 (q, C^7), 121.9 (C$^{4',term}$), 121.85 (C$^{4',lin}$), 121.8 (C$^{4',dend}$), 119.9 (C$^{9'}$), 118.9 (dq, C^7), 117.6 (d, C^9), 117.4 (C$^{2',dend}$, C$^{3',lin}$), 117.3 (C$^{2',term}$, C$^{3',lin}$). ^{19}F NMR (CDCl$_3$): −62.6 (d, F^{11}), −63.0 (s, F$^{11'}$), −116.8 (F^8).

Synthesis of Hyperbranched Poly(arylene ether)s from AB$_2$ + A$_2$ Monomers. Hyperbranched polymers **2a−2c** and **3a−3c** were prepared by reacting the AB$_2$ monomer with two different diphenols, namely 4,4′-isopropylidenediphenol (BPA) and 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), respectively, in different molar ratios. The quantity and molar composition of the AB$_2$ and diphenol (A$_2$) monomers used are given in Table 1.

The weighed amount AB$_2$ monomer, A$_2$ monomer, K$_2$CO$_3$, 20 mL of NMP, and 25 mL of toluene was charged in a 100 mL

Table 1. Feed Composition of the AB$_2$ and A$_2$ Monomers and Amount of Added Potassium Carbonate

| polymer | AB$_2$/A$_2$ (OH/F) | A$_2$ (g/mmol) | | AB$_2$ (g/mmol) | K$_2$CO$_3$ (g/mmol) |
		BPA	6FBPA		
2a	1:1 (3:2)	0.2728/1.195		0.5/1.195	0.594/4.30
2b	3:2 (7:6)	0.2183/0.956		0.6/1.434	0.554/4.01
2c	2:1 (4:4)	0.1910/0.836		0.7/1.673	0.462/3.34
3a	1:1 (3:2)		0.2728/1.195	0.5/1.195	0.594/4.30
3b	3:2 (7:6)		0.2183/0.956	0.6/1.434	0.554/4.01
3c	2:1 (4:4)		0.1910/0.836	0.7/1.673	0.462/3.34

Scheme 1. Reaction Scheme and Structure of the AB$_2$ Monomer
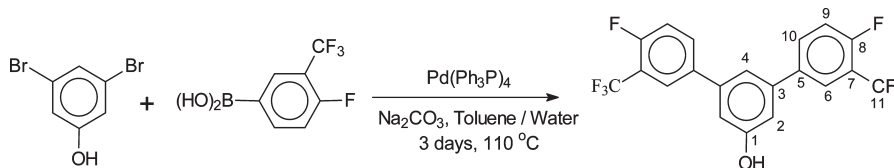
three-necked round-bottom flask equipped with a stir bar, nitrogen inlet, and a Dean–Stark apparatus. The reaction temperature was slowly raised to 150 °C and maintained for 8 h. During this period toluene was removed from it to remove the water formed in the acid–base reaction between phenol and base. The reaction temperature was raised to 180 °C, and the reaction was continued for another 3 h. The reaction mixture was then poured into 500 mL of water/methanol mixture (1:1) containing 10 mL of HCl. The precipitate obtained was collected by filtration, dried under vacuum at 50 °C for overnight, and reported as crude yields. The powdered products obtained were further purified by reprecipitation from dichloromethane (CH$_2$Cl$_2$) solution into methanol. The precipitated product was washed with methanol and dried under vacuum at 50 °C for 12–14 h.

The ^{1}H and ^{13}C NMR spectra of samples **2c** and **3c** (AB$_2$/A$_2$ = 2:1; A/B = 1:1) are shown in Figure 3. For samples with excess of A groups (**2a**, **2b**, **3a**, and **3b**) additional signals due to unreacted A-sites of the AB$_2$ and A$_2$ monomer, respectively, were observed. A detailed signals assignment failed due to the complexity of the structure and distinct signal overlap. ^{19}F NMR (CDCl$_3$): 2 series: −62.7 and −62.9 (F$^{11'}$); 3 series: −62.9 (F$^{11'}$), −65.0 (F^{17}).

Results and Discussion

AB$_2$ Monomer Synthesis. The scheme of synthesis of 3,5-bis(4-fluoro-3-trifluoromethylphenyl)phenol named as AB$_2$ monomer is shown in Scheme 1. It comprises, first, the synthesis of 4-fluoro-3-trifluoromethylphenylboronic acid from 5-bromo-2-fluorobenzotrifluoride and, finally, the palladium-catalyzed cross-coupling reaction of 4-fluoro-3-trifluoro-methylphenylboronic acid with 3,5-dibromophenol, adopting the reaction protocol as reported in earlier literature.[40] The coupling reaction was very efficient as it resulted in very high yield of the AB$_2$ monomer. The chemical structure and purity were confirmed by spectroscopic methods.

Polymer Synthesis. The syntheses of the hyperbranched poly(arylene ether)s were achieved by two different approaches from the AB$_2$ monomer. First, the self-condensation of the AB$_2$ monomer leads to hyperbranched poly(arylene ether)s of different molecular weight depending on the solution concentration and reaction time. In general, high solution concentration and longer reaction time lead to high molecular weight products. At first the self-condensation of the AB$_2$ monomer was done with a solution concentration of 5 wt % for 3 h at 150 °C and then for further 3 h at 180 °C that produced a product of weight-average molecular weight (M_w) of 8000 with polydispersity index of 1.70. On increasing the reaction time to 8 h at 180 °C, the M_w increased to 52 900

with a PDI of 3.4. The M_w of the AB$_2$ self-condensation product was further increased to 231 300 with a PDI of 2.0 when the solution concentration was increased to 10 wt % and yields of the syntheses were also increased accordingly (Table 2).

The hyperbranched copoly(arylene ether)s were prepared by an AB$_2$ + A$_2$ approach. The synthesized AB$_2$ monomer was reacted with two different commercial diphenols at three different molar ratios (Table 1). The detailed reaction scheme and structures of the polymers are shown in Scheme 2. Here, the reactions were carried out at lower concentration; about 4 wt % of solution concentration was maintained to avoid any gelation. Particularly, the 2:1 molar reactions of AB$_2$/A$_2$ resulted in gelation when the solution concentration was 10 wt %. Also, some changes were done in terms of the reaction time and temperature, though the total reaction time was kept the same with 11 h. In AB$_2$ + A$_2$ polymerizations, the reaction temperature was slowly raised to 150 °C and maintained for 8 h; finally, the reaction temperature was increased to 180 °C, and the reactions were continued for another 3 h. These changes were required to avoid any gelation in the 2:1 molar reactions of AB$_2$/A$_2$. The yields of the polymer synthesis are reported in Table 2. It can be seen from the Table 2 as the functional equivalence of −OH to −F approaches 1 the yield of the synthesis increased in accordance with development of higher molar masses with M_w values even 4 million g/mol. However, there was no gelation in any of the reactions under the stated reaction conditions. To check the reproducibility of the synthesis, **2c** was synthesized twice under the same reaction conditions. Both times there was very high molecular weight development (first batch, $M_w \sim 3\,426\,000$; second batch, $M_w \sim 3\,730\,000$) without any gelation.

On the first glance the lack of gelation in the AB$_2$/A$_2$ system is very surprising. However, a high number of soluble hb polymers is reported also by the A$_2$ + B$_3$ approach.[1] In that case, high molar mass samples are usually difficult to achieve when the equivalency of A:B functionality is given, since the gel point is reached theoretically already at a functional group conversion of only 71%. Thus, usually an off-stoichometric A:B ratio is chosen to reduce the danger of gelation by shifting the critical conversion to higher values. When using A$_2$/B$_3$ in the ratio 3:4 (meaning A/B = 1:2, having high excess of B functionality) the critical conversion can be shifted to 87%,[1] but due to the high stoichiometric imbalance, again rather low molar mass products result. In our case, with AB$_2$/A$_2$ = 2:1, which corresponds to stoichiometric ratio of

Table 2. Physical Properties of the Hyperbranched Polymers

polymer	yield (%)	η_{inht}	M_w (g/mol)	MWD	T_g (°C)	5% weight loss temperature (°C)	10% weight loss temperature (°C)	residue at 800 °C (%)	average contact angle (deg)	std dev (deg)
hpb(lw)	75	0.14	52 900	3.4	128	366	397	47		
hpb(hw)	91	0.16	231 300	2.0	199	518	573	56	97.3	1.2
2a	71	0.12	27 300	1.7	235	476	530	59	92.3	1.4
2b	83	0.28	254 000	6.0	282	518	548	62	92.7	1.2
2c	92	0.30	3 730 000	3.0	n.d.[a]	524	549	62	93.7	2.0
3a	72	0.08	35 100	1.8	204	473	512	52	92.6	1.0
3b	81	0.12	154 000	1.9	270	474	535	54	93.3	1.2
3c	89	0.30	4 470 000	2.2	n.d.	530	554	57	95.6	0.4

[a] n.d.: not detected up to 350 °C.

Scheme 2. Reaction Scheme and Structure of the Hyperbranched Poly(arylene ether)s
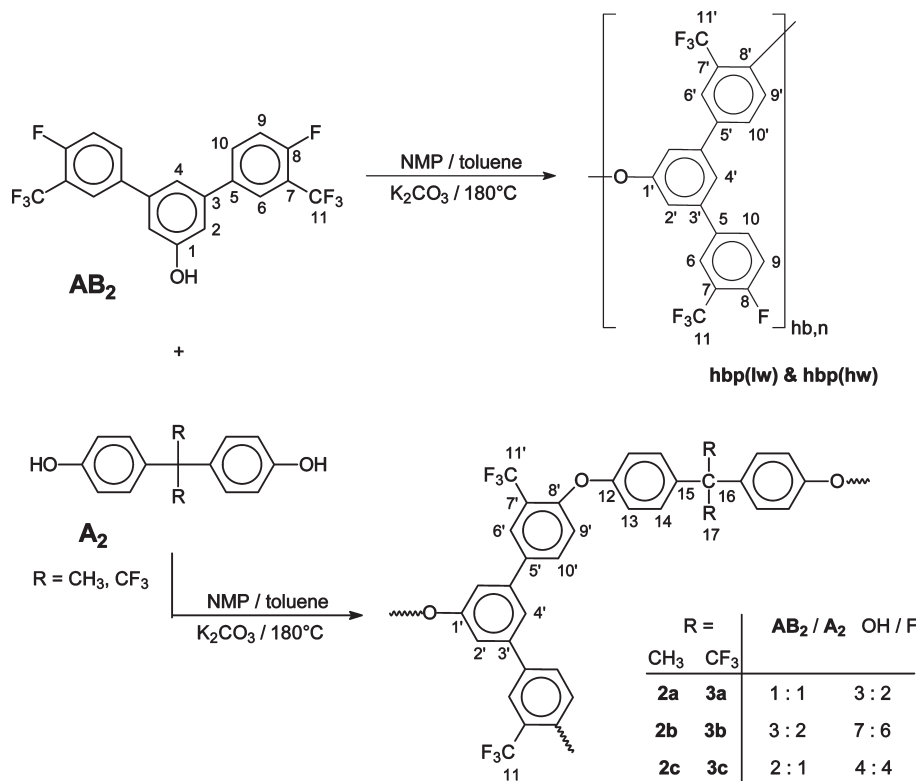
the functionalities, only half of the A functional groups contribute to potential gelation since the other half undergoes common self-condensation of the AB_2 monomer. Roughly speaking, the critical conversion in this case is shifted from about 70% to nearly 90% keeping equivalency of the functional groups and, thus, without impairing the achievable molar mass. In a previous theoretical study the "diluting" effect on the critical functionality ratio on adding A_x to AB_2 was to some extent predicted[45] and could now be verified with this study. Nevertheless, as outlined above, the reaction conditions, like monomer concentration, have to be optimized since compared to the pure AB_2 system, the critical conversion lies below 100%.

Polymer Characterization. *Polymer Solubility and Molecular Weight Determination.* The polymers prepared under optimized conditions exhibited good solubility in common organic solvents like previously reported for linear semifluorinated poly(arylene ether)s and the hyperbranched poly(arylene ether)s derived from the analogues B_2 and B_3 monomer, respectively.[37,40] It was attempted to obtain 10% (w/v) solutions of all polymers in several organic solvents. All the polymers were soluble in chloroform and THF at room temperature; also toluene appears to be a fairly good

solvent for these polymers, despite its low polarity compared to the solvents that are commonly used for poly(arylene ether)s. These polymers were not soluble in DMSO even on reflux, while they are soluble in amide solvents such as NMP, DMF, and DMAc at room temperature, although these types of dipolar aprotic solvents have similar polarities.

Chromatographic characterization has been carried out in order to assess the molar masses of the homopolymer based on AB_2 monomer in comparison to the copolymers obtained after co-condensation of AB_2 and A_2. In the case of the homopolymers, homogeneous narrowly distributed samples have been obtained. In contrast to that, the copolymers possess broadly distributed molar masses. Figure 1 shows the typical refractive index (RI) chromatograms for a hyperbranched homopolymer [hbp(lw)] and a hyperbranched copolymer (**2a**). The copolymer **2a** is showing significantly broader distributions than the homopolymer. A closer look into the light scattering (MALLS) chromatograms of the copolymers gives us an insight into a slight bimodality of the chromatograms, showing the existence of species with very high molar mass along with the main molar mass distribution. This is typical also in $A_2 + B_3$ hb systems indicating a system very close to the gel point. However, the low intensity

of the refractive index chromatogram indicates that these species are in very low concentration.

The development of the molar masses in an analogous series (comparison a, b, c) showed a similar trend. As more and more functional equivalence is reached (a to c), the molecular weight of the AB_2/A_2 reaction products increased, as expected. However, the trends of molar mass distributions of the samples are not consistent. One would expect that in general the polydispersity increases going from samples a to c. However, because of amplified cleaning steps for the polymers after the polymerization, which led to loss of certain part of the sample and fractionation but to various extents for each sample, a comparison of the samples regarding polydispersity is not possible. In addition, fractionation of the polymers by repeated precipitation explains also the observed rather low polydispersities for hb polymers.
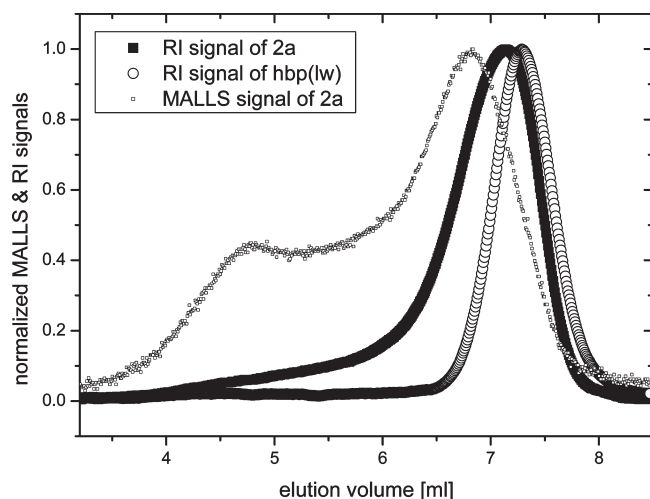
Figure 1. RI chromatograms of homopolymer hbp(lw) and the copolymer **2a** and MALLS chromatogram of the copolymer **2a**.
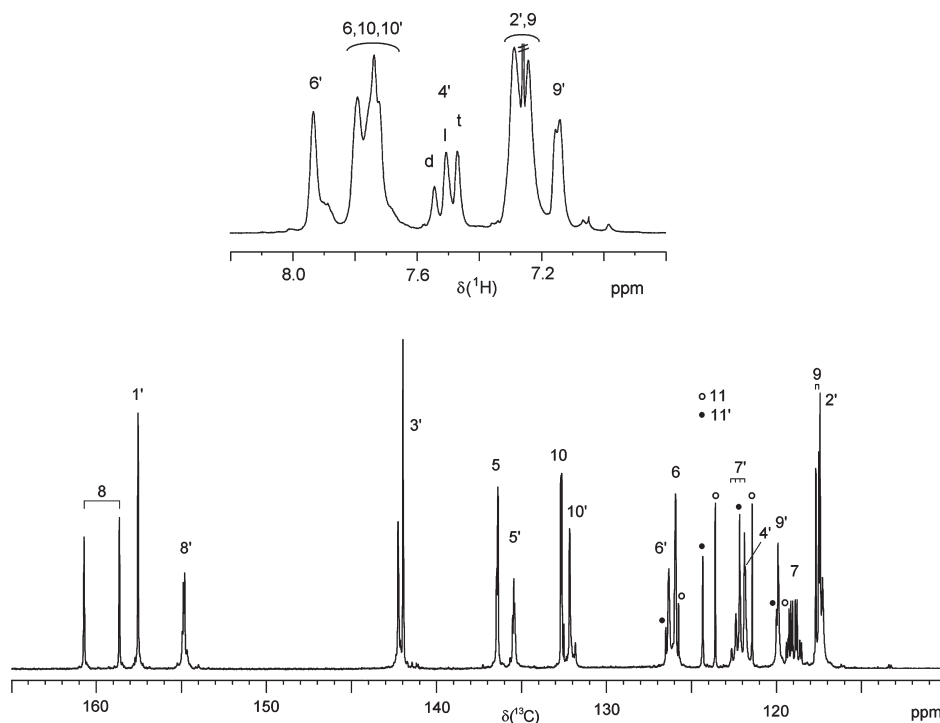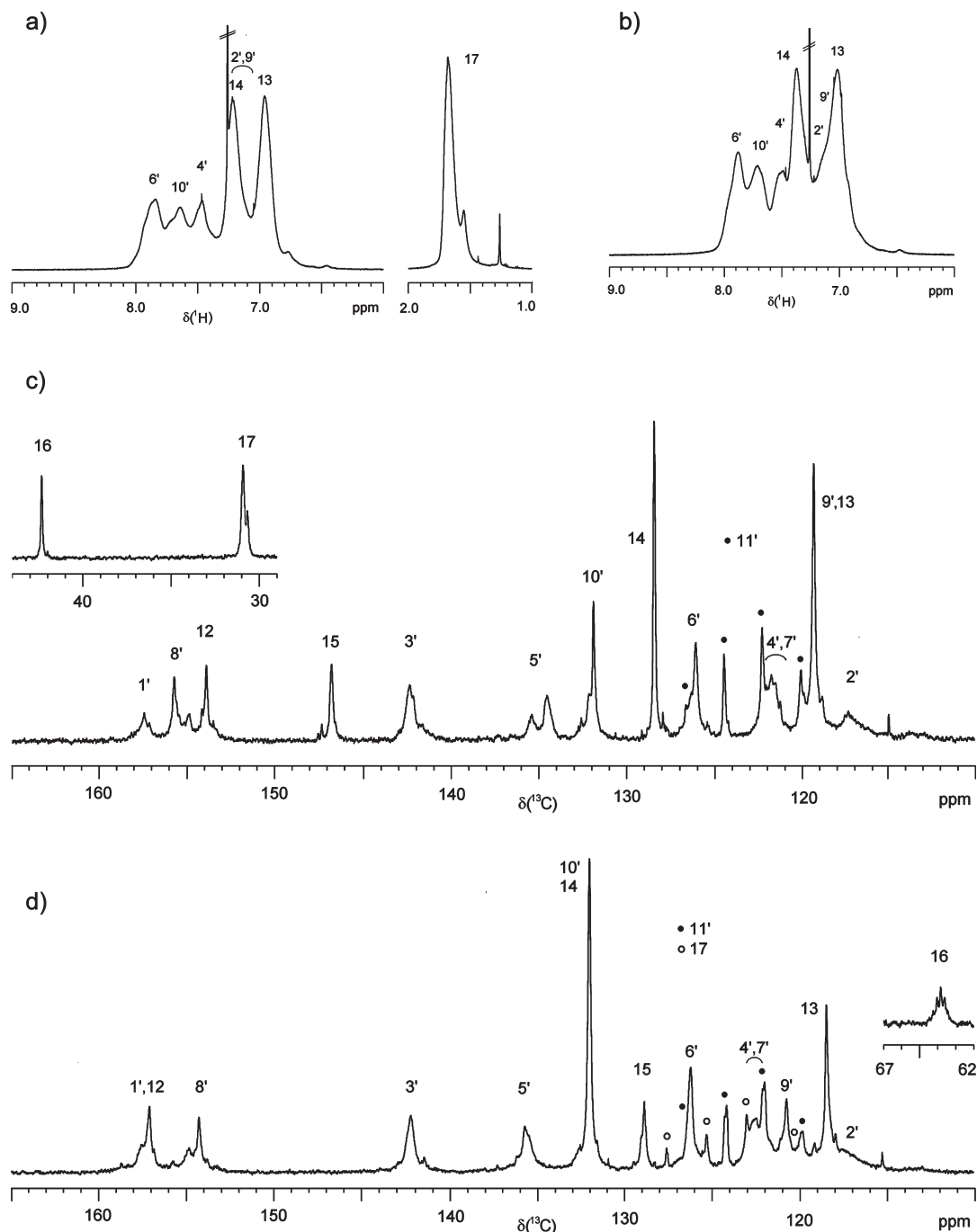
Confirmation of the desired poly(arylene ether) structures was done by FT-IR and more detailed by combination of ^1H, ^{13}C, and ^{19}F NMR. The FT-IR spectra of these polymers show bands caused by the aryl ether linkages ($1140-1050$ cm^{-1}) that are generated in the polymer-forming reaction and also the stretching frequencies ($1240-1150$ cm^{-1}) corresponding to CF_3 groups.[37,40]

Spectroscopy. Figure 2 depicts the ^1H and ^{13}C NMR spectra of the low molecular weight polymer hbp(lw). A complete signal assignment by combination of 1D and 2D NMR methods confirms the hyperbranched poly(arylene ether) structure (see also Experimental Section) and the absence of a significant amount of byproduct. Three signals occur for H$_{4'}$ caused by the three characteristic substructures of a hyperbranched polymer from AB_2 monomer, i.e., by dendritic (d), terminal (t), and linear (l) units. Thus, the degree of branching (DB) could be calculated according to the equations introduced by Fréchet et al. [$DB_{Fréchet} = (t + d)/(t + l + d)$][46] and Frey et al. [$DB_{Frey} = 2d/(2d + l)$].[47] The content of t units (30%) was significantly larger than the content of d units (20%), which is in accordance with a relatively low molecular weight of this polymer.[48−50] Otherwise, the content of d and t units should be rather equal. $DB_{Frechet}$ is calculated to be 0.5, whereas DB_{Frey} gives a more realistic value of 0.44.

As the molecular weight increases for hbp(hw), broadening of the ^1H NMR signals prevents an accurate determination of the content of subunits. However, the ratio of b and B units can be determined by ^{19}F NMR from the corresponding CF_3 signals. It increases from 45:55 in hbp(lw) to 50:50 in hbp(hw), a value characteristic for a DB = 0.5. Thus, the polymerization follows a random process as expected for an AB_2 monomer with well-separated functionalities.

It was also attempted to characterize the $AB_2 + A_2$ condensation products by ^1H and ^{13}C NMR. As illustrated by the NMR spectra of **2c** and **3c** in Figure 3 distinct signal broadening and overlap hampers a detailed signal assignment, but the copolymer structure can be confirmed. For

Figure 2. ^1H and ^{13}C NMR spectra of the hyperbranched AB_2 homopolymer hbp(lw). Solvent: CDCl$_3$. Atom numbering according to Scheme 2.

Figure 3. ^{1}H (a, b) and ^{13}C NMR spectra (c, d) of the (AB$_2$ + A$_2$) polymers **2c** (a, c) and **3c** (b, d). Solvent: CDCl$_3$. Atom numbering according to Scheme 2.

samples with excess of A groups (**2a**, **2b**, **3a**, and **3b**) additional signals due to unreacted A-sites of the AB$_2$ and A$_2$ monomer, respectively, were observed. Full conversion of B functionalities could be proved for all samples by absence of the corresponding ^{19}F signal at about −116.5 ppm.

Thermal Properties. The thermal properties of all the polymers determined by TGA and DSC are summarized in Table 2. A high thermal stability is characteristic for all the polymers. TGA curves of hyperbranched polymers are shown in Figure 4. The hyperbranched polymers obtained from the self-condensation of the AB$_2$ monomer showed thermal stability dependence on molecular weight. As the molecular weight increases, the thermal stability increases and accordingly hbp(hw) showed higher thermal stability

than the analogous hbp(lw). The thermal stability of the hyperbranched polymers prepared by AB$_2$ + A$_2$ approach mainly depends on the content of residual functional groups in the polymer which is related to the initial AB$_2$/A$_2$ ratio. Especially, the polymers **2c** and **3c** (2:1 molar products) with low content of unreacted end groups and high molecular weight showed excellent thermal stability in nitrogen and the 10% weight loss temperature values which were even higher than that of their analogous linear polymers.[40,41] Mainly, the absence of any reactive functional groups prevents early stage decomposition.

The DSC curves of all the hyperbranched poly(arylene ether)s are shown in Figure 5, and the glass transition temperatures (T_g) are summarized in Table 2. It can be seen
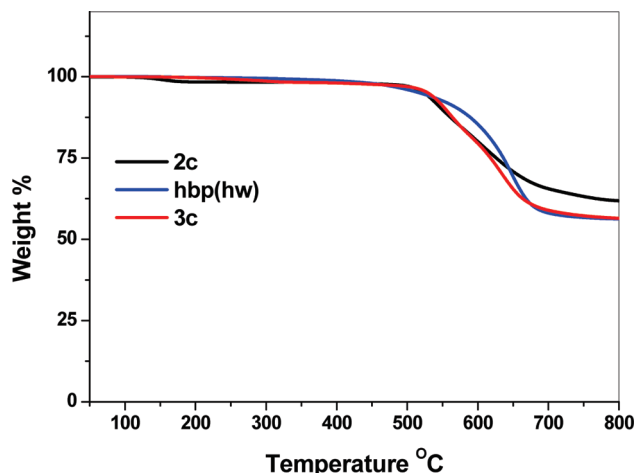
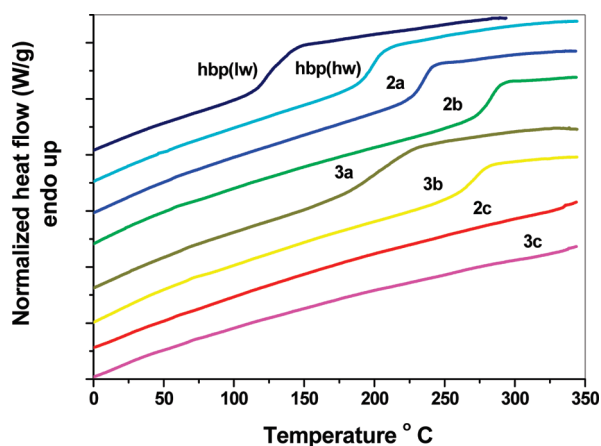**Figure 4.** TGA thermograms of the hyperbranched polymers.

Figure 5. DSC plots of the hyperbranched polymers.

from the Table 2 that the glass transition temperature of the hyperbranched polymers greatly depends on the molecular weight. The hbp(lw) showed considerably lower T_g than the analogous high molecular weight hbp(hw). It can be seen from Figure 5 that, except for **2c** and **3c**, all other polymers showed a distinct glass transition. The hyperbranched polymers **2c** and **3c** did not show any glass transition up to 350 °C. Glass transition temperature is one of the important parameters to decide the use of polymers as coating materials in microelectronics, and it is expected that the polymer have T_g above 350 °C.[39] This could be a positive aspect of these hyperbranched poly(arylene ether)s for such application. In general, the glass transition temperatures of the AB_2/A_2 polymers are dependent on the molecular weight of the hyperbranched polymers as the type of end group present is the same for all the nonequivalence functional reactions. Except for the 1:1 molar products, the 3:2 and 2:1 molar hyperbranched poly(arylene ether)s exhibited higher glass transition temperatures relative to their linear analogues derived from 1,3-bis(4-fluoro-3-trifluoromethylphenyl)benzene or 1,4-bis(4-fluoro-3-trifluoromethylphenyl)benzene and BPA and 6FBPA, respectively.[40] Somewhat, this finding is contrary to the findings of Lie and Long in case of hyperbranched poly(aryl ester)s[51] but might be related to the high molar mass products with low number of unreacted groups achieved in our case.

Polymer Film Properties. It was attempted to prepare freestanding films of these poly(arylene ether)s by casting 15 wt %
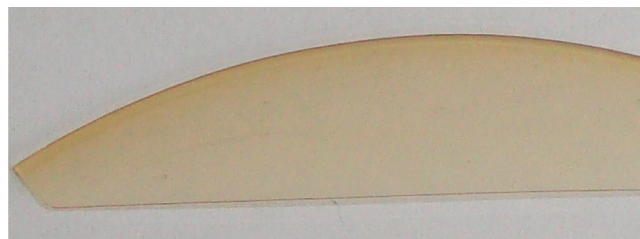

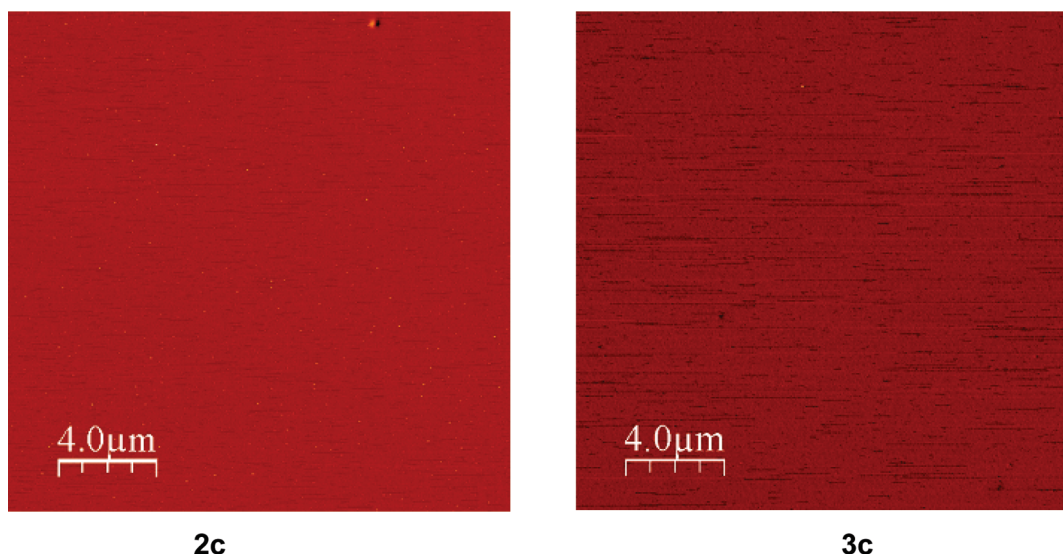**Figure 6.** Film of hyperbranched polymer **2c** of thickness 90 μm.

solutions of these polymers in CH_2Cl_2 on Petri dishes. Transparent pale yellow films were obtained after controlled evaporation of the CH_2Cl_2 at 30 °C and putting the Petri dishes under vacuum at 100 °C for 5 h (Figure 6). However, the films are brittle in nature, and none of these hyperbranched polyethers provide films of measurable mechanical strength as expected for high-T_g hyperbranched polymers.[37] When the oven temperature was increased to 300 °C for 5−6 h, the texture and color of the films on the Petri dishes did not exhibit noticeable change, but the films became completely insoluble in all the organic media that were studied as solvents for these polymers except hbp(hw) and hbp(lw), possibly due to postpolymerization of remaining functional groups.[37] This observation suggests that these hyperbranched poly(arylene ether)s can be used for dielectric coatings, an application that does not demand free-standing films, but requires cross-linked films on a substrate after high-temperature baking. Though the dielectric constant of these polymers have not yet been evaluated, the dielectric constant values ($\varepsilon = 2.67 \pm 0.2$) obtained for the analogous linear poly(arylene ether)s[40a] permits anticipation that these hyperbranched polymers will exhibit even lower dielectric constants due to the more void space arising because of highly branched structure of these polymers.

Though, the polymer films were brittle in nature, the water absorption properties of the hyperbranched polymers (**2c** and **3c**) were investigated by immersing the films of **2c** and **3c** in deionized water. The equilibrium water sorption was reached within 24 h. The films from hyperbranched polymer **2c** and **3c** showed negligibly low water absorption attributed to the presence of hydrophobic trifluoromethyl groups. Low water absorption is another very important criteria for that materials used in low dielectric constant application.[39]

Contact Angle Measurements and Surface Texture. The preparation of thin films was realized via spin-coating on silicon wafers with a native SiO_2 layer of ∼2 nm. The hyperbranched polymers were dissolved in chloroform to obtain 2 wt % solutions. The polymer solutions were filtered several times through Millipore 0.2 μm Teflon filters. Thin films were prepared by spin-coating process at a speed of 2400 rpm onto the silicon wafers, which were cleaned with dichloromethane in an ultrasonic bath for 20 min followed by further cleaning in a 1:1:1 mixture of 29% ammonium hydroxide, 30% hydrogen peroxide, and water for 1.5 h at 65 °C. AFM phase image of the thin films of hyperbranched polymers **2c** and **3c** coated on silicone wafers showed smooth surfaces without any detectable feature indicating a good film quality and prove also the homogeneity of the polymers and their suitability as coatings (Figure 7).

Contact angle is an important parameter which is often used as a measure of the hydrophobicity of a polymer surface. For the films on silicon wafers, advancing contact angle were measured using water as a medium to investigate surface wettability. Contact angles were measured as average values over a large number of measurements on the coated silicon wafer, and the mean contact angle (CA) has been

Figure 7. AFM phase images of hyperbranched polymers **2c** and **3c** coated on silicone wafers.

reported. The water contact angles values of the polymer coated wafers are given in Table 2. The values indicate the hydrophobic nature of the coated surface.

Conclusion

A novel AB$_2$ monomer has been synthesized and characterized. This AB$_2$ monomer leads to the formation of hyperbranched poly(arylene ether)s by self-condensation. The molecular weight of the self-condensation products mainly depends on the reaction time and concentration of the reaction medium. The high molecular weight product showed excellent thermal stability and high glass transition temperature. The work was further extended to prepare hyperbranched polymers by the AB$_2$ + A$_2$ approach, i.e., by condensing AB$_2$ with two different diphenols (A$_2$). The molecular weights of the resulting products were depending on the molar concentration of AB$_2$/A$_2$. Very high molecular weight products were obtained for 2:1 molar reactions where a functional equivalence was achieved. The polymerization proceeded smoothly for very high molar mass products without significant problems, and gelation could be avoided for most monomer ratios selecting suitable conditions. As compared to the also common A$_2$ + B$_3$ approach, here the critical conversion is shifted to very high values avoiding gelation without the need of stoichiometric imbalance, pointing to a new alternative to fine-tune molar masses and properties of hyperbranched polymers. The high solubility of the products allowed their structural characterization by NMR and chromatographic techniques.

The hyperbranched poly(arylene ether)s showed excellent thermal stability and very high glass transition temperatures. Despite very good solubility and formation of high molar mass products, it was not possible to obtain free-standing films from these polymers with measurable mechanical strength since the highly branched structures prevents the formation of polymer entanglements. However, this does not restrict the use of these polymers, particularly in the fields where free-standing films are not needed. High glass transition temperatures in combination with very good thermal stability suggest the use of these polymers as low-*k* coating materials in inter-layer dielectrics. It was found that by heating cross-linking in solution cast films could be achieved especially from AB$_2$ + A$_2$ products due to postpolymerization of remaining functional groups.

Thin films of the hyperbranched polymers were prepared on silicon wafers via spin-coating. Smooth surfaces were obtained without any detectable feature indicating a good film quality. The water contact angle value of the thin films indicates that the hyperbranched polymers are hydrophobic in nature.

Though dielectric constant values of these hyperbranched polymers were not investigated, the outstanding properties of these polymers and previously reported dielectric constant[40a] of analogous linear poly(arylene ether) suggests their application in the field of low dielectric constant coating.[39]

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