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Poly(phenylene sulfide−phenyleneamine) (PPSA): The First Hybrid Structure of Poly(phenylene sulfide) and Polyaniline

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ABSTRACT: High molecular weight poly(phenylene sulfide−phenyleneamine) (PPSA, $M_n = 1.5 \times 10^5$) was synthesized via a poly(sulfonium) cation through an acid-induced polycondensation reaction of [4-(methylsulfinyl)phenyl]phenylamine. To our best knowledge, the new polymer represents the first hybrid structure of poly(phenylene sulfide) (PPS) and polyaniline (PAni). In contrast to these two intensively studied polymers, PPSA exhibits a high solubility in solvents, such as THF, DMF, DMSO, and NMP. DSC and X-ray studies revealed the completely amorphous structure of PPSA, which cannot even be influenced by annealing the polymer at temperatures above the glass transition. Furthermore, electronic properties were studied by cyclic voltammetry, and preliminary doping experiments for elucidating the electrical conductivity were carried out.

I. Introduction

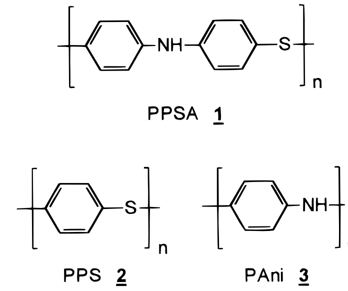
Poly(phenylene sulfide) (PPS) (**2**) and polyaniline (PAni) (**3**) are heteroatom-containing polymers with unique properties. While PPS provides a good level of chemical and thermal stability,[1] PAni is important due to its ability to form electrically conducting films.[2] These special properties, as well as the ready accessibility of both materials (PPS is prepared from 1,4-dichlorobenzene with sodium sulfide by the Phillips process, and PAni can be obtained by chemical or electrochemical oxidation of aniline), prompt great interest in these polymers in industry. Whereas PPS is already widely used for thermal and chemical resists,[3] PAni promises to play a very important role for applications, such as electromagnetic shielding or corrosion inhibition.[4]

A combination of PPS and PAni to compound **1** with alternating phenyleneamine and phenylene sulfide building blocks, should result in a new material, displaying a wide range of properties (Chart 1). These include mechanical stability and also, due to its electron-rich character, electrical conductivity, hole transport ability, or corrosion inhibition. This so-called poly(phenylene sulfide−phenyleneamine) (PPSA, **1**) not only combines the structural features of PPS and PAni but may also additionally serve as a precursor polymer to the polyaminyl radical **5**, which can be conceived as an organic analogue of the inorganic poly(sulfur nitride) **4** (Scheme 1).

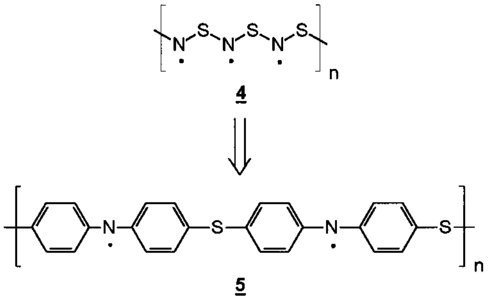
This inorganic material, which is synthesized by the polymerization of tetrasulfur tetranitride, shows metallic conductivity and becomes even superconducting at liquid helium temperatures.[5] However, there is no use for poly(sulfur nitride) in industrial applications due to the difficult and dangerous synthesis of the material.[6] Therefore, the inclusion of carbon-based fragments into the thiazyl backbone is of great interest, since it would allow modification of the properties of $(SN)_x$.[7]

Recently, we introduced the combination of PPS (**2**) and PAni (**3**) to give PPSA (**1**).[8] In this publication, a convenient and highly efficient synthesis of PPSA with full experimental and analytical details will be presented. In addition, we present our investigations on the physical consequences of this hybrid structure, including mechanical and electrical properties.

Chart 1. PPSA (1), First Hybrid Structure of PPS (2) and PAni (3)



Scheme 1. Polyaminyl Radical 5 as an Organic Analogue of Poly(sulfur nitride) (4)



II. Results and Discussion

II.1. Model Reactions. In principle, **1** is accessible by formation of either amino or sulfide bridges. For the latter method, Tsuchida et al. recently developed a simple synthetic tool for producing diphenyl sulfide units.[9] It has been used for the synthesis of high molecular weight PPS and is based on an acid-induced condensation reaction of (methylsulfinyl)arenes (Scheme 2). The protonation of an aromatic sulfoxide (**6**) follows an electrophilic attack toward another activated aromatic ring under formation of a sulfonium cation. The

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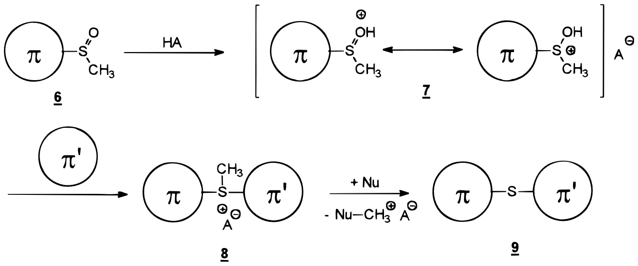
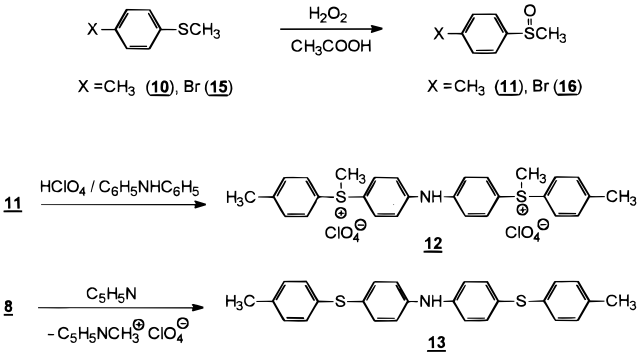
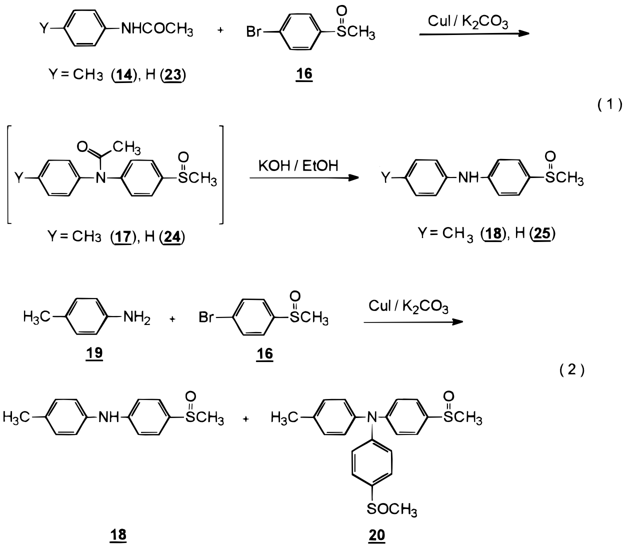
Scheme 2. Proposed Mechanism for the Acid-Induced Condensation Reaction of (Methylsulfinyl)arenes with Activated Aromatic Building Blocks



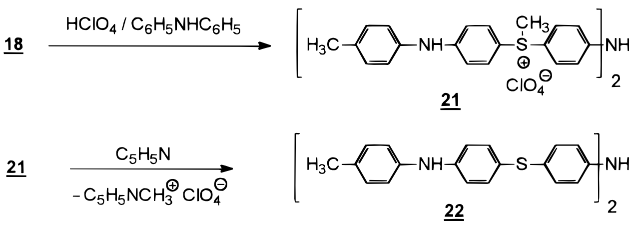
Scheme 3. Synthesis of 4,4′-Bis(4-tolylthio)diphenylamine (13)



Scheme 4. Cu(I)-Catalyzed Coupling Reaction of Amides 14, 19, and 23 with 4-Bromo(methylsulfinyl)benzene (16) (Goldberg Reaction)



Scheme 5. Synthesis of 4,4′-Bis[(4′-methyldiphenylamine-4)thio]diphenylamine (22)



resulting sulfonium salt **8** can be isolated and demethylated quantitatively by a nucleophile in a separate step to the neutral diphenyl sulfide unit **9**.

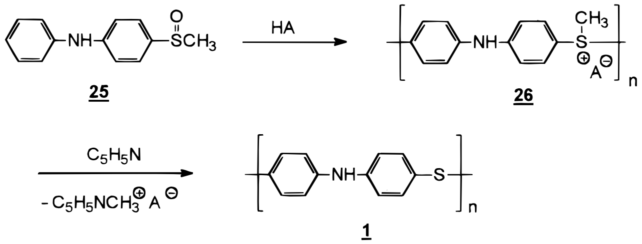
This method appeared to be particularly encouraging for the preparation of PPSA. However, as our system contains amino groups, which in principle can be protonated by strong acids and hence deactivate the phenyl unit toward a nucleophilic attack at the sulfur, we developed our approach to PPSA starting from model reactions. These enabled the investigation of the suitability of this condensation reaction in the presence of diphenylamine units as well as the optimization of the reaction parameters.

The model compound 4,4′-bis(4-tolylthio)diphenylamine (**13**) was formed by the condensation of (4-methylsulfinyl)toluene (**11**) and diphenylamine. The sulfoxide **11** can easily be synthesized in 80% yield by oxidation of 4-(methylthio)anisole (**10**) with hydrogen peroxide (Scheme 3). The acid-induced condensation of **11** with diphenylamine leads quantitatively to 4,4′-bis[(4-tolyl)methylsulfonium perchlorate]diphenylamine (**12**), which can clearly be proven by the ^{1}H NMR spectrum. A distinctive signal at $\delta = 3.73$ is attributed to the three protons of the methylsulfonium group. The aromatic protons show up in two AA′BB′ systems, indicating a coupling reaction only in the position para to the amino group. This para-regiospecificity is confirmed as well by an absorption band in the IR spectrum at 809 cm^{-1}, which is typical for 1,4-phenylene linkages. The high regioselectivity could be explained by the bulky methyl sulfoxide group, which hampers an attack at the position ortho to the amino group. Demethylation of **12** is carried out by treatment with boiling pyridine, affording 4,4′-bis(4-tolylthio)diphenylamine (**13**) in 95−98% yield. The ^{1}H NMR spectrum shows only one signal for the benzylic methyl group at $\delta = 2.27$, while the lack of a signal for the methylsulfonium group proves the quantitative demethylation. As for the sulfonium salt **12**, **13** shows an absorption band in the IR at 810 cm^{-1}, which clearly demonstrates the 1,4-linkage of all phenylene units.

The polymerization through this type of condensation reaction was further encouraged by the synthesis of the next higher model compound, 4,4′-bis[(4′-methyldiphenylamine-4)thio]diphenylamine (**22**). Toward that end, it was necessary to first synthesize the 4-(methylsulfinyl)-4′-methyldiphenylamine (**18**). This can be achieved by the Cu(I)-catalyzed coupling of *N*-acetotoluidine **14** and 4-bromo(methylsulfinyl)benzene (**16**) (Goldberg reaction).[10] The latter can be obtained in high yield by the oxidation of 4-bromothioanisole (**15**) with hydrogen peroxide. The intermediate compound, *N*-aceto-4-(methylsulfinyl)-4′-methyldiphenylamide (**17**), is deprotected without isolation and **18** can be obtained after workup in 70% yield (Scheme 4, eq 1). If this coupling reaction is carried out with the unprotected toluidine **19** under the same conditions, both amino protons are substituted to give **20** and the yield of **18** is dramatically reduced (Scheme 4, eq 2).

Treatment of **18** with diphenylamine and perchloric acid leads to 4,4′-bis[(4′-methyldiphenylamine-4)methylsulfonium perchlorate]diphenylamine (**21**) in high yields (Scheme 5). The expected structure of this model compound is proven by the ^{1}H NMR spectrum with the distinctive signal at $\delta = 3.65$, which is attributed to the six protons of the methylsulfonium groups. The IR spectrum shows an absorption band for the C−H deformation at 820 cm^{-1}, which again indicates the exclusive 1,4-linkage of the phenylene units. After **21** is treated with boiling pyridine, model compound **22** is obtained as a colorless solid in 91% yield. The mass

Scheme 6. Synthesis of PPSA (1)



spectrometric analysis shows exclusive formation of **22** without any side products. The ^{1}H NMR spectrum confirms the expected structure with two signals for the amino protons and one signal for the remaining benzylic methyl groups. In the ^{13}C NMR spectrum only 12 aromatic carbon signals can be detected, which clearly indicates the high regioselectivity for this type of condensation reaction in the para position.

The successful preparation of the two model compounds **13** and **22** indicates that the acid-induced coupling reaction of (methylsulfinyl)arenes is suitable not only for systems containing diphenyl sulfide building blocks but also for systems with diphenylamine units. A deactivation of the diphenylamine building block by protonation of the amino group does not take place. Hence, polymerization toward the PPSA structure by this concept seems to be very promising.

II.2. Polymerization Reactions. The AB-type monomer **25** required for the polymer synthesis is obtained analogously to **18** by the Cu(I)-catalyzed reaction of **23** and **16** (Scheme 4, eq 1). The N-acetylated intermediate **24** is deprotected directly without isolation, affording **25** in 70% yield. The polymerization is carried out by adding the monomer to strong acids, namely perchloric acid, trifluoromethanesulfonic acid, sulfuric acid, or methanesulfonic acid (Scheme 6). The solution is stirred for 24 h, and the precursor polymer, poly[methyl(4-(phenylamino)phenyl)sulfonium salt] (**26**), is precipitated and isolated in nearly quantitative yield by pouring the highly viscous reaction mixture into water. Weak acids such as acetic acid do not lead to any reaction. The polysulfonium salt is soluble in solvents such as DMSO, DMF, and NMP. However, decomposition is observed in neutral solutions, while acidified solutions are perfectly stable. This could be ascribed to a partial premature demethylation of the methylsulfonium group by the amine. If the solution is acidified, the amino group is in equilibrium with its protonated form and hence much less nucleophilic, which is in agreement with the observations described above. The ^{1}H NMR spectrum shows just one signal for the amino proton at $\delta = 9.58$ and one AA′BB′ system for the aromatic protons at $\delta = 7.95$, 7.41, while the methylsulfonium protons result in one signal at $\delta = 3.70$. Signals that correspond to end groups were not detected, possibly due to the high molecular weight. The structure of the polysulfonium salt **26** is confirmed by ^{13}C NMR spectroscopy as well, in which only four aromatic carbons at $\delta = 146.6$, 131.8, 118.7, and 117.4 are observed. The methylsulfonium group leads to one signal at the expected position of $\delta = 24.1$. The absorption of the phenylic C−H stretching in the IR at 820 cm^{-1} is again in agreement with the exclusive para substitution. The UV/vis spectrum shows merely a broad absorption with a maximum at 364 nm ($\epsilon = 24\,200$). A determination of the molar mass by size-exclusion chromatography was not successful because of interactions with the column material, which are due to the polyionic structure.

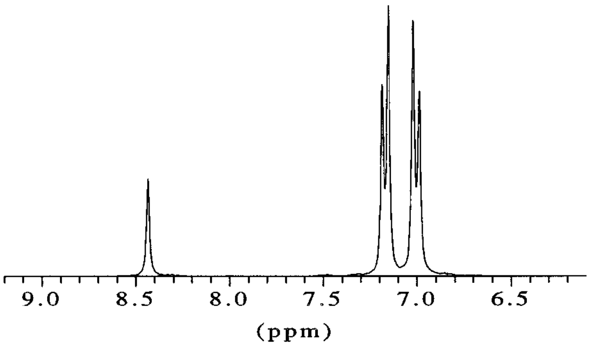
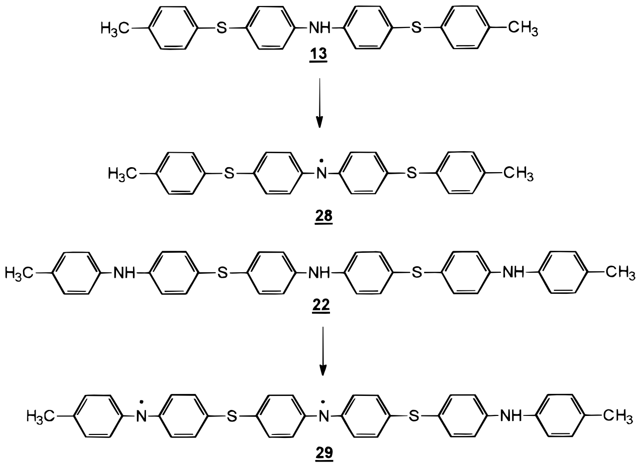


Figure 1. ^{1}H NMR spectrum (250 MHz, 300 K, d_6-DMSO) of **1**.

Scheme 7. Generation of the Radicals 28 and 29 by UV Irradiation of a Dibenzoyl Peroxide-Containing Solution of Amines 13 and 22 in Toluene



Similarly to the synthesis of the model compounds **12** and **21**, **26** was demethylated to the title compound **1** by refluxing in pyridine. PPSA was precipitated by pouring the clear solution into water, yielding a colorless material with low density in 98% yield. Unlike PPS **2** and PAni **3**, PPSA is structurally well-defined and very soluble in solvents such as THF, DMSO, DMF, and NMP. The ^{1}H NMR spectrum is in good agreement with the spectrum of the precursor polymer **26** (Figure 1). Only one signal for the amino group at $\delta = 8.41$ and an AA′BB′ system at $\delta = 7.21$, 7.03, corresponding to the aromatic protons, were detected. The ^{13}C NMR spectrum gave only four aromatic signals ($\delta = 142.7$, 132.6, 125.7, and 118.0), demonstrating the well-defined structure of the polymer (Figure 2).

The UV/vis spectrum of **1** corresponds well with the UV/vis spectrum of the fully reduced form of PAni (leucoemeraldine base).[11] It shows a broad absorption at 332 nm ($\epsilon = 25\,300$), which is hypsochromically shifted by 30 nm compared to the polysulfonium salt **26**. This shift is observed as well for the transition from the model sulfonium salts **12** and **21** to the neutral compounds **13** and **22**. In solution, PPSA exhibits a weak fluorescence with emission maxima at 390 and 410 nm (excitation wavelength of 350 nm, THF).

The molecular weight of the polymer was determined by size-exclusion chromatography in THF with polystyrene as standard. It is very sensitive to the strength of the acid used for the polymerization reactions and increases generally with greater acid strength (Table

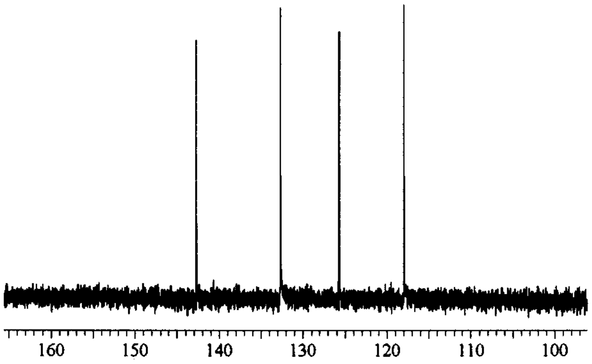


Figure 2. ^{13}C NMR spectrum (62.5 MHz, 300 K, d_6-DMSO) of **1**.

Table 1. Molecular Weights of PPSA Samples Obtained by Polymerization in Different Acids and Determined by GPC in THF with Polystyrene Standard (H_0 = Acidity Function)

acid	$10^{-4}M_n$	$10^{-4}M_w$	M_w/M_n	H_0
CF_3SO_3H	15	39	2.6	−15
$HClO_4$	12	21	1.7	−14
H_2SO_4	1.8	12	6.7	−12
CH_3SO_3H	5	15	3.1	−8
CF_3COOH	0.8	1.1	1.4	−2
CH_3COOH				2

1). This corresponds with the results obtained by Tsuchida et al. for the synthesis of PPS.[9] To obtain such high molecular weights as listed in Table 1, it is very important to use a highly purified monomer as well as a very pure acid. The low molecular weight and the broad distribution of PPSA polymerized with concentrated sulfuric acid is explained by the high viscosity of the acid, which hampers a high conversion of the monomer. The given molecular weight of the polymer, obtained by the reaction with perchloric acid, has been determined after several reprecipitations. In the case of the perchloric acid, the reprecipitation was necessary, due to the fact that very broad and multimodal molecular weight distributions were obtained, whereas this was not the case for the polymers synthesized with other acids. This could be explained by a partial oxidation during the polymerization process through the perchloric acid. Due to the narrow molecular weight distribution of 1.7 after reprecipitation, this polymer was also used for an additional molecular weight determination by membrane osmometry in DMF. The determined value of M_n = 110 000 ± 10 000 corresponds very well with the data obtained by GPC and renders this standard method as very reliable for the determination of the molecular weight of PPSA.

In contrast to the almost insoluble PPS and PAni, PPSA is well soluble in solvents such as THF, DMF, NMP, and DMSO. The solubility of PPS in THF is lower than 0.1% w/w;[12] that of PAni (emeraldine form) amounts to 0.25% w/w in DMF, 0.32% w/w in DMSO, and 4.0% w/w in NMP.[13] However, even a 20% w/w solution of PPSA in THF can be easily obtained. The well-defined structure of the polymer with a lack of cross-linking might be one reason. Furthermore, X-ray diffraction measurements result only in a diffuse peak at $2\theta = 20°$. This indicates that PPSA is a completely amorphous polymer, which should contribute to the high solubility as well. The amorphous character of the PPSA could be explained by its more irregular repeating unit, compared to PPS and PAni, which is due to the different bond-angles of the phenylene units between the amino and sulfur bridges. From the crystal structure of compound **27**, which was obtained by the substitution reaction of thiophenol with 4,4′-diiododiphenylamine, it can be demonstrated that the difference of the bond angles is more than 21° (Chart 2: bond angles C7−S1−C4 = 105.4°; C1−N1−C13 = 126.5°; C16−S2−C19 = 104.2°).[14] This large difference should result in a poorer packing of the polymer chains and hence in the amorphous character of PPSA.

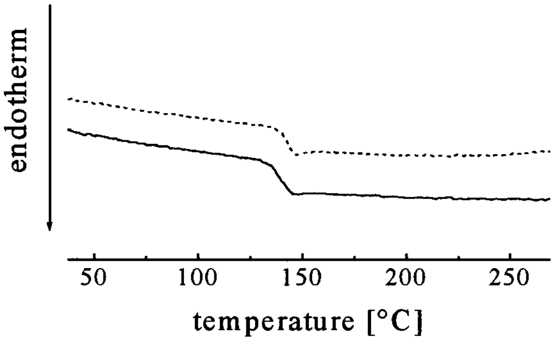
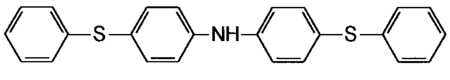
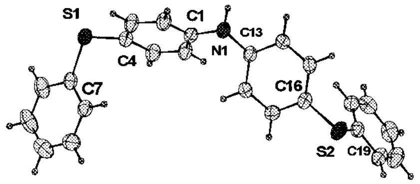


Figure 3. DSC thermogram of PPSA **1** (heating-rate 10 °C/min, in N_2, ------PPSA sample annealed at 170 °C for 4 hours,—PPSA-sample not annealed).

Chart 2. Crystal Structure of 27



27



II.3. Thermal and Mechanical Properties. Thermogravimetric analysis of PPSA shows that the polymer is stable up to 380 °C, which is comparable to PPS (370 °C),[15] whereas PAni in the emeraldine base form decomposes in the range 400−500 °C.[16] The glass transition temperature (T_g) of PPSA, measured by differential scanning calorimetry (DSC), is 145 °C (Figure 3). T_g has additionally been determined by dynamic-mechanical analysis. The master curve, which was obtained by time−temperature superposition, fits well to the WLF equation. The maximum of the loss tangent (tan δ), which describes the cooperative motions of the polymer chains and hence corresponds to the glass-transition temperature, appears at around 150 °C. This is in good agreement with the data obtained by DSC. It is notable that the T_g of PPSA is about 60 °C higher than that of PPS (89 °C).[17] This discrepancy can be ascribed to interactions of the PPSA chains by hydrogen bonding, which result in stiffer polymer chains and hence in a higher glass transition. The T_g for PAni is only known for the emeraldine oxidation state, which has been determined to be 220 °C.[18] Since the emeraldine form of PAni consists of diphenylamine and diimine units, the stiffness of the chain compared to PPSA should be much higher, which is in agreement with the higher T_g.

The DSC measurement of PPSA shows neither a premelt crystallization exotherm nor a melting transition. Even annealing of a sample at temperatures above 170 °C does not lead to any change in the DSC. This is in sharp contrast to the results obtained for PPS and PAni. PPS, which is quenched from the melt, still shows a low crystallinity (≈5%). If this sample is heated to 121 °C, which is about 30 deg above the glass transition temperature, it crystallizes rapidly with a maximum crystallinity near 65%.[19] Similar results were observed for the thermal behavior of PAni. The leucoemeraldine base, which was obtained in an amorphous form by reduction of the emeraldine base, can be transformed to the semicrystalline form by annealing the sample to 300 °C, reaching 40% crystallinity.[20] The more complex structure of PPSA, compared to PPS and PAni, obviously hampers organization of the polymer chains, which has already been mentioned above. Therefore, a thermal transition from the amorphous to a semicrystalline state seems to be not yet possible for PPSA.

Due to the high solubility of PPSA in different solvents, it is readily solution processible. Flexible films with a thickness of up to 50 mm, which are optically clear, colorless, and free-standing, can be obtained from a THF solution by slow evaporation of the solvent or by spin-coating. These films exhibit a very high stability under argon and in the dark. However, if they are exposed to light and oxygen, they become colored and decompose, which might be explained by oxidation of the amino groups. We used these films for the investigation of the mechanical properties of PPSA. The modulus of elasticity *E* was determined to be 1.3 GPa with a maximum extension of 110%, which is typical for amorphous polymers. In comparison, PPS exhibits a much higher modulus of elasticity, which is about 2.3 GPa with an extension of only 10% and results from the high crystallinity of the material. Mechanical analysis has also been done on PAni films by Xiabin et al.,[21] but without any specification of the oxidation state of the samples. They measured a modulus of elasticity of about 1.6 GPa with a maximum extension of 10%. Hence, our results show that PPSA is much softer than PPS and PAni and is not comparable in its mechanical stability to PPS. However, it is much more flexible and extendable, due to its amorphous character.

II.4. Electronic Properties. II.4.1. Cyclic Voltammetry. The close structural relationship between PPSA and PPS, or PAni, raises the question of its electrochemical properties. Therefore, cyclic voltammetric measurements have been carried out on the model compound **13** and on PPSA. Investigations on **13** were carried out in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at −30 °C. The cyclic voltammogram shows that the oxidation of **13** is a chemically reversible process, in which up to two electrons can be removed. The first wave that occurs at a potential of $E_{1/2} = 0.65$ V is due to the generation of a radical cation, whereas the second wave at $E_{1/2} = 1.21$ V results from the formation of the dication (Figure 4). Since these values are in the same range as those for 4,4′-disubstituted diphenylamines, the model compound **13** can be characterized electrochemically as a diphenylamine system.[22,23] Further scans at potentials over 1.6 V lead to irreversible oxidation. The nature of this process is not fully understood yet, but further investigations are underway. The electrochemical studies on PPSA were carried out on a film deposited on a platinum electrode from a 1.5% w/w solution of the polymer in DMF, by slow evaporation of the solvent under reduced pressure. The measurements were performed as multiscan experiments in acetonitrile at −30 °C with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The cyclic voltammetry shows a broad redox band in the range of 0.6−1.2 V (Figure 5), instead of independent peaks observed in the model compound, due to its polymeric nature. The stability of the polymer film to multiple cyclic voltammogram scans is limited by up to 15 scans, which is due to electrochemical degradation.

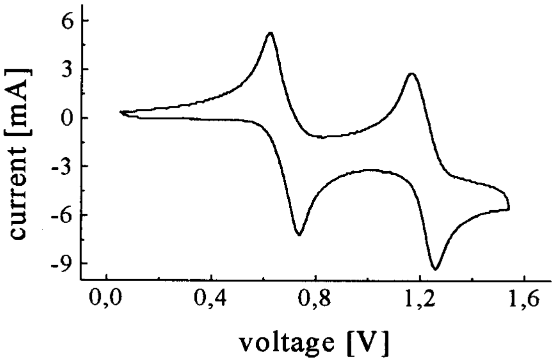


Figure 4. Cyclic voltammogram of the model compound **13** (−30 °C, dichloromethane/Bu_4NPF_6 V vs $Ag/AgNO_3$).

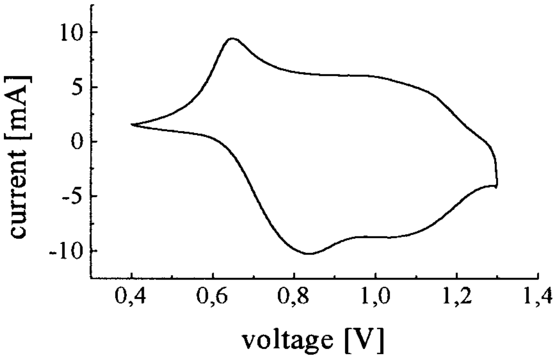


Figure 5. Cyclic voltammogram of a PPSA-film (−30 °C, acetonitrile/Bu_4NPF_6, V vs $Ag/AgNO_3$).

The low oxidation potential of PPSA, which is still about 0.5 V higher than that of PAni,[24] determines our polymer to be an electron-rich material, which can be oxidized easily. Therefore, we are focusing our interest now on the investigation of the suitability of PPSA as a hole-transport material for LED devices. As the polymer meets all the requirements for hole-transport ability, such as low oxidation potential, amorphous structure, or high thermal stability, it appears to be a very promising candidate for this special kind of application.

II.4.2. ESR Measurements. As mentioned above, another important aspect is the structural similarity of the dehydrogenated product **5** of PPSA to the highly conductive poly(sulfur nitride) **4**. First of all, it was necessary to find a practical synthetic approach for obtaining the polyaminyl radical **5**, which then could be characterized by ESR spectroscopy. We first investigated the generation of multiradicals on the model compounds **13** and **18**. Transformation of both oxidatively with PbO_2 and $KMnO_4$ into their hydrazine derivatives was attempted, which should have yielded the aminyl radicals followed by thermal or photochemical cleavage. Unfortunately, it was not possible to obtain any well-defined structures of the hydrazine derivatives, and therefore we tried to generate the radicals directly from the model compounds. The radical **28** can be obtained by UV irradiation of a solution of the model compound **13** in toluene containing dibenzoyl peroxide. The low *g*-value (2.00374) and the coupling constants ($a_{H0} = 0.338$ mT, $a_{Hm} = 0.133$ mT, $a_N = 0.802$ mT), which are typical for aminyl radicals, enable the presence of a nitroxy radical to be ruled out.[25] Irradiation of the next higher model compound **18** in the presence of dibenzoyl peroxide yielded the diradical **29**, confirmed by ESR spectroscopy. This diradical showed a zero-field splitting of 1.76 mT (135 K, toluene, glass), from which a distance of the aminyl centers of 1.17 nm was found by point dipole estimation. This value is in good agreement with the calculated distance of 1.02 nm.[26]

Unfortunately, it was not possible to get any evidence for the existence of the triradical, starting from the model compound **18**. This might be due to the fact that we worked with low radical concentrations and that side reactions occurred during the measurements. Further experiments on the conversion of PPSA into the polyradical **5** are in progress.

II.4.3. Conductivity Measurements. Oxidative doping of PPS (**2**) can increase its electrical conductivity up to 200 S/cm,[27] while PAni is one of the few commercially available conductive polymers with conductivities up to 100 S/cm.[28] The structural relationship of PPSA to PPS and PAni immediately raises the question of its electrical conductivity properties. The undoped polymer is insulating with conductivities lower than 10^{-9} S/cm. As PPSA is an electron-rich material, only the p-type-doping (oxidative doping) seems to be a feasible method. Preliminary doping tests were carried out on free-standing films, and the conductivities were determined by four point measurements with a linear test geometry (direct current).

As dopants, we used bromine, iodine, antimony pentachloride, and iron(III) chloride. The use of bromine led to decomposition of the film, while iodine as the dopant resulted in only very low conductivities. The best results were obtained for films doped with $SbCl_5$ in chloroform and with $FeCl_3$ in acetone/chloroform, showing conductivities of 0.2 and 1.4 S/cm, respectively. The black films retained their flexibility after doping, and the conductivity remained unchanged for several weeks in dry air. Compared to PPS and PAni, the measured conductivities of PPSA are low. We explain this by the low crystallinity of the polymer, but further investigations are in progress.

III. Conclusion

The present paper reports a convenient and efficient synthetic route for the preparation of high molecular weight poly(phenylene sulfide−phenyleneamine) (PPSA) via an acid-induced condensation reaction of 4-(methylsulfinyl)diphenylamine. The polymer, which represents the first combination of the industrially significant poly(phenylene sulfide) (PPS) and polyaniline (PAni), is structurally well-defined and thermally stable up to 380 °C and can be obtained in high yields. Due to its amorphous structure, it is highly soluble and is therefore easily film-processible. First investigations of the electronic properties determined the material to be an electron-rich polymer, which can be easily oxidized. Furthermore, doping experiments yielded maximum conductivities of 1.4 S/cm (after doping with iron(III) chloride), which are low compared to PPS and PAni. Systematic investigations on the physical consequences of this hybrid structure have not been carried out yet but are underway. Additionally, the concept of polycondensation of (methylsulfinyl)arenes will be extended to further heteroatom-containing monomers, as well as to the buildup of other topologies, such as dendritic or ladder-type structures.

Experimental Section

General Methods. Commercial grade reagents were used without further purification. Solvents were purified, dried, and degassed following standard procedures. ^{1}H- and ^{13}C NMR spectral data were obtained on a Varian Gemini 200 and Bruker DRX-250 spectrometer. Gel-permeation chromatographic (GPC) analysis utilized PL-gel columns (three columns, 10 μm gel, pore widths: 500, 10^4, and 10^5 Å) connected with ultraviolet/visible (UV/vis) detectors. The UV/vis spectra were recorded on a Perkin-Elmer Lamda 9 spectrophotometer, and the emission spectra, on a Spex fluorescence spectrometer. The thermal analysis was carried out using a Mettler DSC 30 differential scanning calorimeter and a Mettler 500 thermogravimetric analyzer. The wide-angle X-ray (WAXS) measurement was taken on a Philips PW 1820 powder diffractometer using Cu Kα radiation at room temperature.

Crystal Structure Determination of 27. Crystals suitable for X-ray analysis were grown by isothermal removal of the solvent (ethanol). The crystal structure determination was carried out on a Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation at room temperature. Unit cell dimensions were obtained from 25 reflections with $\vartheta > 20°$, $a = 7.722$ (1) Å, $b = 20.208$ (2) Å, $c = 25.770$ (2) Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, space group *Pbca*, $D_x = 1.309$ g cm^{-3}, $\mu = 24.018$ cm^{-1}. A total of 3800 reflections were measured (ϑ−2ϑ scans) of which 2648 were observed ($I > 3\sigma(I)$). The structure was solved by direct methods (SIR92).

The refinement was done by full-matrix least squares analyses with anisotropic temperature factors for C, N, and S. The hydrogen atoms were refined in the riding mode with fixed isotropic temperature factors. An empirical absorption correction was applied. The final *R* indices were $R = 0.052$, $R_w = 0.061$ (unit weights).

General Procedure for the Oxidation of Aromatic Methyl Sulfides. The oxidation of 4-methylthioanisole (**10**) is used as an example. A 250-mL, round-bottom flask was charged with a Teflon-covered magnetic bar, 90 mL of glacial acetic acid, and 4-methylthioanisole (**10**) (5.8 g, 42 mmol). A solution of hydrogen peroxide (35%, 3.8 mL, 44 mmol) in 20 mL of glacial acetic acid was added dropwise to the reaction mixture at room temperature. After stirring for 24 h, the mixture was poured into water, affording a white precipitate, which was filtered and washed with water. Recrystallization from ethanol gave pure sulfoxide **11** as a white crystalline solid.

4-(Methylsulfinyl)toluene (11): yield 5.2 g (80%); mp 43 °C; ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.37 (3H, s, CH_3), 2.67 (3H, s, $SOCH_3$), 7.25 (2H, d, $J = 8.0$ Hz), 7.51 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 21.8, 44.4, 123.9, 130.5, 141.2, 146.3. Anal. Calcd for $C_8H_{10}OS$: C, 62.30; H, 6.54; S, 20.79; S. Found: C, 62.05; H, 6.59; S 21.01.

4-Bromo(methylsulfinyl)benzene (16): yield 7.3 g (80%); mp 86 °C; ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.73 (3H, s, $SOCH_3$), 7.65 (2H, d, $J = 8.3$ Hz), 7.80 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 43.4, 124.4, 126.1, 134.2, 146.2. Anal. Calcd for C_7H_7BrOS: C, 38.37; H, 3.22; Br, 36.47; S, 14.63. Found: C, 38.32; H, 3.28; Br, 36.51; S 14.73.

General Procedure for the Coupling Reaction of Amides 14 and 23 with 4-Bromo(methylsulfinyl)benzene 16 (Goldberg Reaction). The synthesis of 4-(methylsulfinyl)-diphenylamine (**25**) is used as an example. A 25-mL, round-bottom flask was charged with a Teflon-covered magnetic bar and a thoroughly ground mixture of acetanilide **23** (3.4 g, 25 mmol), 4-bromo(methylsulfinyl)benzene (**16**) (5.5 g, 25 mmol), K_2CO_3 (3.4 g), and CuI (0.5 g). The reaction was allowed to proceed at 160 °C under argon for 16 h. The resulting highly viscous mixture was taken up in dichloromethane and filtered over Hyflo and the filtrate thoroughly washed with EtOAc. After the combined organic fractions were concentrated by vacuum distillation, the residue was dissolved in EtOH (50 mL), containing potassium hydroxide (1.7 g) and heated to reflux for 30 min. The clear solution was cooled and poured into 400 mL of water. The precipitate was filtered off and recrystallized from EtOAc, yielding **25** as a white crystalline solid.

4-Methyl-4′-(methylsulfinyl)diphenylamine (18): yield 4.3 g (70%); mp 122 °C; ^{1}H NMR (200 MHz, 300 K, $CDCl_3$) δ (ppm) 2.46 (3H, s, CH_3), 2.63 (3H, s, $SOCH_3$), 6.85 (1H, s, NH), 7.06−6.98 (6H, m), 7.42 (2H, d, J = 8.5 Hz); ^{13}C NMR (50 MHz, 300 K, $CDCl_3$) δ (ppm) 21.3, 44.0, 115.9, 121.3, 126.1, 130.4, 132.9, 133.8, 139.2, 148.5. Anal. Calcd For $C_{14}H_{15}NOS$: C, 68.55; H, 6.17; N, 5.71; S, 13.05. Found: C, 68.31; H, 6.15; N, 5.52; S, 13.14.

4-(Methylsulfinyl)diphenylamine (25): yield 4.1 g (70%); mp 135 °C; ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.70 (3H, s, $SOCH_3$), 6.96 (1H, t, J = 7.2 Hz), 7.17 (2H, d, J = 7.4 Hz), 7.19 (2H, d, J = 8.7 Hz), 7.31 (2H, t, J = 7.3 Hz), 7.53 (2H, d, J = 8.7 Hz), 8.56 (1H, s, NH); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 43.5, 115.8, 118.8, 121.5, 125.7, 129.6, 135.0, 142.3, 146.8. Anal. Calcd For $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.06; S, 13.86. Found: C, 67.58; H, 5.70; N, 6.01; S, 13.92.

General Procedure for the Acid-Induced Condensation of (Methylsulfinyl)arenes 11 and 18 with Diphenylamine. The synthesis of 4,4′-bis[(4-tolyl)methylsulfonium perchlorate]diphenylamine (**12**) is used as an example. A 25-mL, round-bottom flask was charged with a Teflon-covered magnetic bar and 15 mL of perchloric acid. Sulfoxide **11** (1.54 g, 10 mmol) and diphenylamine (0.84 g, 5 mmol) were added at 0 °C. After the addition was complete, the solution was warmed gradually to room temperature over a period of 1 h. The reaction was allowed to continue at room temperature for 48 h. The mixture was poured into ice−water and stirred for additional 3 h, after which the precipitate was filtered off, washed with water and methanol, and dried under reduced pressure.

4,4′-Bis[(4-tolyl)methylsulfonium perchlorate]diphenylamine (12): yield 3.2 g (99%); ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.41 (6H, s, CH_3), 3.73 (6H, s, SCH_3), 7.39 (4H, d, J = 8.7 Hz), 7.54 (4H, d, J = 8.4 Hz), 7.91 (4H, d, J = 8.4 Hz), 7.92 (4H, d, J = 8.7 Hz), 9.58 (1H, s, NH); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 21.2, 27.5, 116.8, 118.8, 125.3, 129.6, 131.5, 132.1, 144.6, 146.6. Anal. Calcd For $C_{28}H_{29}Cl_2NO_8S_2$: C, 52.34; H, 4.55; Cl, 11.03; N, 2.18; S, 9.98. Found: C, 52.16; H, 4.86; Cl 11.60, N, 2.13; S, 9.21.

4,4′-Bis[(4′-methyldiphenylamine-4)methylsulfonium perchlorate]diphenylamine (21): yield 3.9 g (95%); ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.29 (6H, s, CH_3), 3.65 (6H, s, SCH_3), 7.06−7.20 (12H, m), 7.36−7.40 (4H, m), 7.75−7.90 (8H, m), 8.87 (2H, s, NH), 9.52 (1H, s, NH); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 20.7, 28.1, 112.2, 115.3, 118.4, 118.7, 121.2, 130.2, 131.3, 131.9, 132.6, 137.9, 146.4, 150.1. Anal. Calcd For $C_{40}H_{39}Cl_2N_3O_8S_2$: C, 58.25; H, 4.77; Cl, 8.60; N, 5.09; S, 7.77. Found: C, 57.33; H, 4.89; Cl 8.53, N, 4.99; S, 7.95.

General Procedure for the Demethylation of the Sulfonium Perchlorates 12 and 21 with Pyridine. The demethylation of 4,4′-bis[(4-tolyl)methylsulfonium perchlorate]-diphenylamine (**12**) is used as an example. A 50-mL, round-bottom flask was charged with a Teflon-covered magnetic bar, sulfonium perchlorate **12** (4.8 g, 7.5 mmol), and pyridine (25 mL). The mixture was refluxed under argon for 5 h. After cooling, the clear solution was poured into 100 mL of water and filtered and the precipitate washed thoroughly with water and methanol. Drying under vacuum yielded **13** as a white solid.

4,4′-Bis(4-tolylthio)diphenylamine (13): yield 2.97 g (96%); mp 93 °C; ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.27 (6H, s, CH_3), 7.12 (4H, d, J = 8.5 Hz), 7.14 (8H, m), 7.31 (4H, d, J = 8.5 Hz), 8.58 (1H, s, NH); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 20.8, 118.1, 123.5, 129.2, 130.1, 134.1, 134.3, 136.1, 143.2. Anal. Calcd For $C_{26}H_{23}NS_2$: C, 75.51; H, 5.51; N, 3.39; S, 15.50. Found: C, 75.69; H, 5.65; N, 3.30; S, 15.65.

4,4′-Bis[(4′-methyldiphenylamine-4)thio]diphenylamine (22): yield 4.1 g (91%); mp 164 °C; ^{1}H NMR (200 MHz, 300 K, DMSO-d_6) δ (ppm) 2.24 (6H, s, CH_3), 6.97−7.10 (16H, m), 7.16−7.24 (8H, m), 8.15 (2H, s, NH), 8.37 (1H, s, NH); ^{13}C NMR (50 MHz, 300 K, DMSO-d_6) δ (ppm) 20.6, 116.5, 117.9, 118.6, 123.5, 126.5, 129.8, 129.9, 131.9, 133.3, 140.2, 142.5, 144.3. Anal. Calcd For $C_{38}H_{33}N_3S_2$: C, 76.60; H, 5.58; N, 7.05; S, 10.76. Found: C, 76.60; H, 5.46; N, 6.93; S, 11.01.

Preparation of Poly[methyl(4-(phenylamino)phenyl)-sulfonium trifluoromethanesulfonate] (26). A 25-mL, round-bottom flask was charged with a Teflon-covered magnetic bar and 12 mL of trifluoromethanesulfonic acid. 4-(Methylsulfinyl)diphenylamine (1 g, 4.8 mmol) was added at 0 °C. After the addition was complete, the solution was warmed gradually to room temperature over a period of 1 h and stirred for 24 h. The highly viscous mixture was poured into ice−water and stirred for additional 12 h. The white precipitate was filtered off, washed with water and methanol, and dried under reduced pressure. Yield 1.7 g (98%). ^{1}H NMR (200 MHz, 300 K, DMSO-d_6): δ (ppm) 3.70 (3H, s, CH_3), 7.41 (4H, d, J = 8.7 Hz), 7.95 (4H, d, J = 8.7 Hz), 9.58 (1H, s, NH). ^{13}C NMR (50 MHz, 300 K, DMSO-d_6): δ (ppm) 24.0, 117.4, 118.7, 131.8, 146.6. Anal. Calcd For $C_{14}H_{12}F_3NS_2O_3$: C, 46.28; H, 3.31; N, 3.86; S, 17.63. Found: C, 46.41; H, 3.42; N, 3.98; S, 17.42.

Preparation of Poly(phenylene sulfide−phenyleneamine) (PPSA, 1). A 100-mL, round-bottom flask was charged with a Teflon-covered magnetic bar, polysulfonium salt **26** (1.5 g, 4.1 mmol), and 50 mL of pyridine. The mixture was refluxed for 6 h under argon. After cooling, the clear solution was poured into 500 mL of water and stirred for 3 h. The white polymer was filtered off, washed with water and methanol, and dried under reduced pressure. Yield 0.8 g (98%). ^{1}H NMR (250 MHz, 300 K, DMSO-d_6): δ (ppm) 7.03 (4H, d, J = 9.2 Hz), 7.21 (4H, d, J = 9.2 Hz), 8.41 (1H, s, NH). ^{13}C NMR (62.5 MHz, 300 K, DMSO-d_6): δ (ppm) 118.0, 125.7, 132.6, 142.7. Anal. Calcd For $C_{12}H_9NS$: C, 72.35; H, 4.65; N, 7.04; S, 16.06; Found: C, 72.40; H, 4.70; N, 6.91; S, 16.28.

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