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Low T_g, Stretchable Polyaniline of Metallic-Type Conductivity: Role of Dopant Engineering in the Control of Polymer Supramolecular Organization and in the Tuning of Its Properties

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Doping of polyaniline with a new family of protonating agents, namely sulfosuccinates with alkyl or alkoxy substituents, is discussed. The resulting polyaniline-sulfosuccinates exhibit a lamellar type structural organization in which stacks of polymer chains are separated by dopant anions. Although structurally similar to previously studied polyaniline-sulfophthalates, polyaniline-sulfosuccinates are better ordered and exhibit better physical properties. In particular, they exhibit metallic-type conductivity down to 210 K and they can be stretched at room temperature to elongations at break, $\Delta l/l_o$, approaching 200%. Mechanical stretching does not affect the temperature range of the metallic conductivity, however, it does induce a 4-fold increase in the room-temperature conductivity of the polymer. Low T_g of polyaniline-sulfosuccinates is also the origin of the low temperature thermochromism − a phenomenon reported so far only for polyaniline-sulfosuccinates and polyaniline-sulfophthalates. Finally, accelerated aging tests carried out at a temperature of 408 K, in ambient conditions, have shown that polyaniline doped with di-(2-butoxyethyl) ester of sulfosuccinic acid is thermally more stable than poly(3,4-ethylenedioxythiophene) doped with ferric tosylate ($Fe^{III}(Tos)_3$) − the system considered so far as the most stable of all conducting polymers.

Introduction

Processibility of conducting polyaniline (abbreviated as PANI) combined with its environmental stability and good mechanical properties are of crucial importance for technological applications of this polymer. In the case of doped electroactive macromolecular systems the above-mentioned properties depend very strongly not only on the chemical constitution of the polymer chain and the dopant anion but also on the supramolecular aggregation induced by the presence of the dopant. Thus, dopant engineering must play a key role in developing new conductive systems of desired properties. Progress in the fabrication of PANI with tunable properties achieved in the past decade is a very good example of this approach. Historically, the first dopants used for the improvement of solution processibility of the conducting form of PANI were surfactant anions such as anions originating from *n*-dodecylbenzenesulfonic acid.[1] Other doping agents frequently used for solution processing of PANI involve other sulfonic acids[2] and in particular (±)-camphor-10-sulfonic acid[3] and 2-acryloamido-2-methyl-1-propanesulfonic acid,[4] in association with suitable solvents such as *m*-cresol or 2,2′-dichloroacetic acid (abbreviated as DCAA).

In our previous paper[5] we focused on the development of new dopants derived from industrially used plasticizers, namely diesters of phthalic acid. We synthesized a series of diesters of 4-sulfophthalic acid with alkyl and alkoxy substituents and studied their effects on the supramolecular organization, electrical, and mechanical properties of doped PANI. We demonstrated that PANI doped with sulfophthalates shows somehow improved

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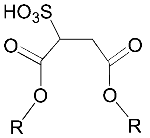
Chart 1



DESSA

mechanical properties while retaining its metallic-like conductivity over a large temperature range. In particular, for *n*-alkyl substituents in the doping ester molecule, the elongation at break ($\Delta l/l_0$) of doped polyaniline increases linearly with the size of the dopant, reaching 80% for polyaniline doped with di-*n*-dodecylester of 4-sulfophthalic acid.[6]

It has been recently reported[7] that in the case of poly(pyrrole) a new type of dopant, namely the anion of di-2-ethylhexyl ester of sulfosuccinic acid (abbreviated as DEHESSA$^-$), strongly improves processibility and mechanical properties of this polymer. Polypyrrole doped with DEHESSA$^-$ shows a stretchability ($\Delta l/l_0$) approaching 150% and a relatively good conductivity of a few S·cm^{-1}. For sure DEHESSA is not unique and other diesters of sulfosuccinic acid can be used as processibility inducing dopants for poly(pyrrole). Moreover, in their acidic form they can dope poly(aniline) via the protonation reaction. Therefore, in this research we have undertaken the task of synthesizing several diesters of sulfosuccinic acid with alkyl or alkoxy substituents and testing them as new protonic dopants for PANI. We have then studied the influence of the chemical constitution of these new dopants on the supramolecular aggregation in doped PANI, its glass transition temperature *T*g, and its mechanical, spectroscopic, and electrical properties.

Experimental Section

Synthesis of Diesters of Sulfosuccinic Acids. The general formula of the sulfosuccinic acid diesters (DESSA) synthesized in this research is depicted in Chart 1.

Two esters with alkyl substituents and two esters with alkoxy ones were synthesized (i.e., di-2-ethylhexyl ester of sulfosuccinic acid (abbreviated as DEHESSA), di-*n*-dodecyl ester of sulfosuccinic acid (abbreviated as DDoESSA), di-(2-butoxyethyl) ester of sulfosuccinic acid (abbreviated as DBEESSA), and di-(2-(2-butoxyethoxy)ethyl) ester of sulfosuccinic acid (abbreviated as DBEEESSA).

DEHESSA was prepared by passing its commercially available sodium salt (Aldrich) in the form of an aqueous solution (Aldrich) through an ion exchange column (Dowex, Aldrich). The resulting diester was then extracted from the aqueous solution with diethyl ether and dried with $MgSO_4$. The solvent was removed by evaporation.

The three other diesters were prepared from sulfosuccinic acid (Aldrich) and the corresponding alcohols: 1-*n*-dodecanol, 2-*n*-butoxyethanol, and 2-(2-butoxyethoxyethanol) (all from Aldrich). No catalyst was required because in this typical acid-catalyzed esterification reaction the strongly acidic SO_3H group of sulfosuccinic acid is the source of protons. In a typical reaction 5.1 g (25.6 mmol) of sulfosuccinic acid in the form of a 70 wt % solution in water was mixed with 76.8 mmol of the corresponding alcohol and heated at 110 °C for 4 h under constant nitrogen flow, which assured an effective removal of water formed in the course of the reaction as a side-product. No special purification procedure was required for DBEESSA because 2-*n*-butoxyethanol is sufficiently volatile to be efficiently pumped off in a high vacuum line. For the diesters with longer substituents a different purification procedure had to be applied due to the low volatility of the alcohols used in the reaction. Typically 100 mL of 1 M HCl was added to the reaction mixture which separated into two phases after a few minutes. The organic phase was recovered, and the crude product was extracted with diethyl ether, dried with $MgSO_4$, and finally pumped in a high vacuum line at 50 °C for ca. 3 h.

The chemical nature of the products was identified by elemental analysis, ^{1}H NMR, and FTIR. One should note here that because of the hygroscopic nature of the synthesized products, especially in the case of diesters bearing alkoxy substituents, elemental analysis had to be fitted assuming some hydration with water molecules. ^{1}H NMR spectra were recorded on a Bruker AC 200 MHz spectrometer whereas FTIR spectra were measured on a Perkin-Elmer Paragon 500 spectrometer.

DEHESSA. Anal. Calcd for $C_{20}H_{38}O_7S\cdot 0.2\ H_2O$: C, 56.36; H, 9.08; S, 7.52. Found: C, 56.38; H, 9.73; S, 6.75. NMR ^{1}H (DMSO-d_6, ppm): 0.85 (12H); 1.28 (16H); 1.48 (2H); 2.9 (2H); 3.60 (1H); 3.90 (4H); 5.7. IR (KBr, cm^{-1}): 3440 (S), 2959 (m), 2931 (m), 2870 (m), 1729 (s), 1460 (m) 1417 (m), 1259 (s), 1169 (m), 1090 (s) 1041 (s), 858 (w), 764 (m), 746 (m).

DDoESSA. Anal. Calcd for $C_{28}H_{54}O_7S\cdot 1.0\ H_2O$: C, 60.84; H, 10.21; S, 5.80. Found: C, 61.20; H, 10.67; S, 5.12. NMR ^{1}H ($CDCl_3$, ppm): 0.87 (6H); 1.26 (36H); 1.63 (4H); 2.09 (2H); 3.2 (2H); 3.77 (1H); 4.22 (4H). IR (KBr, cm^{-1}): 3463 (S), 2950 (s), 2920 (m), 2850 (m), 1728 (s), 1463 (s) 1367 (m), 1237 (s), 1193 (m), 1164 (w), 1092 (s) 1049 (s), 998 (m), 949 (m), 864 (w), 719 (m).

DBEESSA. Anal. Calcd for $C_{16}H_{30}O_9S\cdot 0.75\ H_2O$: C, 46.64; H, 7.70; S, 7.78. Found: C, 46.49; H, 7.51; S, 8.42. NMR ^{1}H (DMSO-d_6, ppm): 0.86 (6H); 1.30 (4H); 1.45 (4H); 2.9 (2H); 3.5; 4.07 (4H); 5.8. IR (KBr, cm^{-1}): 3447 (S), 2960 (m), 2930 (m), 2873 (m), 1734 (s), 1458 (m) 1415 (w), 1384 (m), 1331 (w), 1232 (s), 1169 (m), 1120 (m) 1040 (s), 848 (m), 738 (m).

DBEEESSA. Anal. Calcd for $C_{20}H_{38}O_{11}S\cdot 1.5\ H_2O$: C, 46.77; H, 8.04; S, 6.24. Found: C, 47.23; H, 8.35; S, 5.11. NMR ^{1}H (DMSO-d_6, ppm): 0.88 (6H); 1.30 (4H); 1.45 (4H); 2.83 (2H); 3.5; 4.07 (4H); 4.90. IR (KBr, cm^{-1}): 3297 (S), 2964 (m), 2943 (m), 2871 (m), 1734 (s), 1459 (m), 1242 (s), 1122 (s), 1036 (s), 854 (w), 736 (m).

Synthesis of Polyaniline. PANI was synthesized at −27 °C in a HCl/LiCl water/ethanol solution using $(NH_4)_2S_2O_8$ as the oxidizing agent. The obtained polyaniline hydrochloride salt was then converted to the base form by treatment with an excess of 0.3 M NH_3 (aq) solution. The inherent viscosity of the obtained polymer was measured at 25 °C in a 0.1 wt % solution in 96 wt % H_2SO_4 using an automatic Ubbelohde viscosimeter. The obtained value was 2.25 dL·g^{-1}. The detailed polymerization procedure can be found elsewhere.[8]

Casting of Free-Standing Films of Doped PANI. Free-standing films of protonated (doped) PANI were cast from 0.5 wt % solutions with respect to the PANI base in 2,2′-dichloroacetic acid (abbreviated as DCAA). The ratio of dopant molecule to PANI repeat unit was 0.5 in all cases studied. The solutions were magnetically stirred typically for 3−4 weeks until no evolution in their UV−vis−Near-infrared (UV−vis−NIR) spectra was observed. Films were cast on polypropylene at 45 °C under argon flow. They were then pumped till constant mass in a vacuum line. Typical film thicknesses were ca. 20−30 μm.

Characterization Techniques. Wide-angle X-ray diffraction (WAXD) studies of doped PANI were performed in reflection geometry (Bragg−Brentano) using Cu Kα_1 radiation (1.5406 Å). The scan step was 0.06° (in 2θ) with a counting

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Table 1. Elemental Analysis of Polyaniline Doped with Diesters of Sulfosuccinic Acid

	%C	%H	%N	%S	%Cl
$PANI(DEHESSA)_{0.45}(DCAA)_{0.15}(H_2O)_{0.63}$					
calcd	59.01	7.49	4.50	4.63	3.42
found	58.72	7.41	4.42	4.91	3.35
$PANI(DDoESSA)_{0.5}(DCAA)_{0.3}(H_2O)_{0.50}$					
calcd	60.99	8.22	3.45	3.95	5.24
found	59.83	7.70	4.08	3.81	5.71
$PANI(DBEESSA)_{0.45}(DCAA)_{0.15}(H_2O)_{0.88}$					
calcd	53.15	6.62	4.59	4.73	3.49
found	53.08	7.21	4.44	4.34	3.51
$PANI(DBEEESSA)_{0.5}(DCAA)_{0.13}(H_2O)_{1.0}$					
calcd	53.03	7.05	3.80	4.35	2.41
found	52.41	6.83	3.62	3.84	2.52

time of 15 s/step. The diffractometer was equipped with an 800 channels linear detector with a step of 0.02°.

Small-angle X-ray scattering (SAXS) measurements were performed on a home-built SAXS camera using a FR591 Nonius rotating Cu anode operating with a fine focus at a 6° takeoff angle corresponding to a 0.2×0.2 mm^2 apparent beam size. The beam was $K\alpha/K\beta$ filtered (wavelength Cu $K\alpha$: $\lambda = 1.5418$ Å) and focused in horizontal and vertical directions by total reflection from two curved Franks mirrors (Ni-coated glass optical flats). Scattering patterns were recorded with a two-dimensional position-sensitive gas-filled detector installed 132 mm from the sample. The sample–detector distance was calibrated using silver behenate as a standard.

Differential scanning calorimetry (DSC) experiments were performed on a TA Instrument model DSC 2010 analyzer with a constant dry nitrogen flow using a rate of heating/cooling of 20 K/min. Typically two runs were performed with the following temperature sequence: RT→ 143 K→ 423 K→ 143 K→ 473 K.

Mechanical tests were carried out at room temperature on an Instron apparatus applying a draw rate of 1 mm·s^{-1}. For conductivity and structural studies on oriented PANI–DESSA samples, thin films were mechanically drawn at RT using a drawing speed of 1 mm·min^{-1}.

Solid-state UV–vis–NIR spectra of doped PANI were recorded on a Perkin-Elmer λ900 spectrometer equipped with a cryostat operating in the temperature range of 77–523 K. Spectra were recorded in the range of 303–170 K.

The temperature dependence of the conductivity was determined in the temperature range of 4.2–300 K using a standard four-probe technique. To ensure good electrical contacts four gold lines were evaporated through a mask to which 25-μm golden wires were attached by pressing. The temperature of the sample during the measurement was checked with a rhodium–iron resistance thermometer which was placed in the proximity of the sample. All samples were dynamically pumped prior to the measurements until $d\sigma/dt$ reached 0 (typically 14 h).

The thermal stability of doped PANI was tested by monitoring the conductivity evolution for samples heated in air at 408 K using homemade equipment allowing simultaneous measurements of the conductivity of eight different samples.

Results and Discussion

Elemental analysis data obtained for films of PANI doped (protonated) with diesters of sulfosuccinic acid and cast from 2,2′-dichloroacetic acid (DCAA) solutions are listed in Table 1. Similarly to the PANI protonated with diesters of 4-sulfophthalic acid[5] co-protonation with the solvent molecule takes place as manifested by the presence of chlorine in the elemental analysis of the doped films. Incorporation of water molecules via hydration is also evidenced, thus the general formula describing the doped polymer must be expressed as $PANI(dopant)_x(DCAA)_y(H_2O)_z$. In all cases $x + y$ exceeds 0.5 which means that the excess of the protonating agents is trapped in the polymer matrix either by protonation of amine sites or by another type of dopant/polymer interaction. PANI doped with sulfosuccinates shows also a higher hydration degree as compared to PANI–sulfophthalate systems described in ref 5. Among the former a higher hydration degree is observed for dopants bearing alkoxy substituents as compared to those with alkyl groups.

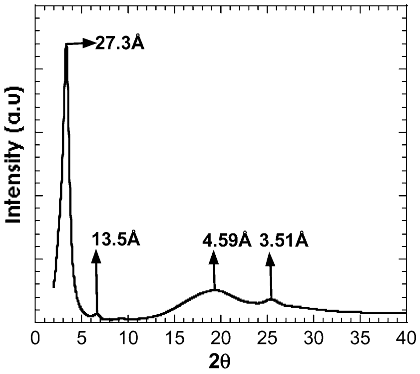

Figure 1. Wide-angle X-ray diffraction (WAXD) pattern of a free-standing film of polyaniline doped with di-2-ethylhexyl ester of sulfosuccinic acid.

PANI doped with diesters of 4-sulfophthalic acid shows a layered-type structure in which stacks of polymer chains are separated by dopant anions.[5] For dopants with longer substituents some interdigitation of the alkyl (or alkoxy) groups must be postulated. In other words, PANI doped with sulfophthalates can be regarded as a comb-shaped polymer in which the side-groups are attached to the polymer backbone by ionic bonds. A recent paper[9] reviewed the capability of such systems to produce a large variety of self-organized supramolecular structures. Self-organized layered, and in some cases lamellar, structures were postulated for several conjugated and nonconjugated polymers doped with surfactant anions.[10–15] Although in the case of PANI–sulfophthalates the formation of a layered-type structure could be evidenced by analysis of their SAXS and WAXD profiles, no direct evidence of a lamellar structure was found as no higher order diffraction peaks were present. However, such second order reflection is clearly seen in the WAXD patterns of PANI–DEHESSA (Figure 1). In addition to a remarkably narrow and intensive reflection at $2\theta = 3.2°$ ($d = 27.3$ Å) we note a second reflection of much lower intensity at $2\theta = 6.5°$-($d = 13.5$ Å). The former reflection is indicative of an extended order in the chain-dopant-chain direction whereas the latter one suggests the presence of a lamellar structure. Apart of being somehow better ordered, PANI–sulfosuccinates show a very close structural similarity to PANI–sulfophthalates. In addition to a strong reflection at small 2θ values (large d values),

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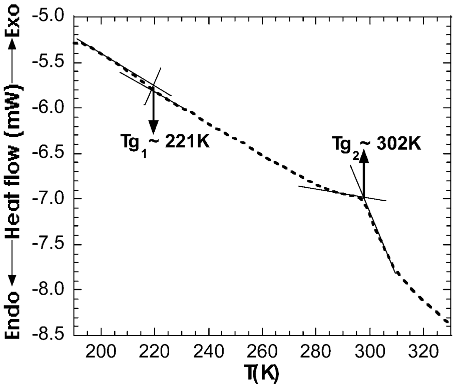

Figure 2. Differential scanning calorimetry (DSC) curves of polyaniline doped with di-(2-(2-butoxyethoxy)ethyl) ester of sulfosuccinic acid.

Table 2. *d*-Spacings Corresponding to Bragg Reflections (WAXD Experiments) Measured for Polyaniline Doped with Diesters of Sulfosuccinic Acid

	d_1 (Å)	d_2 (Å)	d_3 (Å)	d_4 (Å)
PANI−DEHESSA	27.3	13.5	4.59	3.51
PANI−DDoESSA	39.2		4.44	3.49
PANI−DBEEESSA	28.5		4.45	3.52

which is dependent on the size of the dopant, they show two, much broader, dopant-independent reflections at $2\theta = 25.3°$ ($d = 3.5$ Å) and at $2\theta = 19.2°$ ($d = 4.5$ Å) which can be ascribed to the van der Waals distances between stacks of phenylene rings present in the polymer chain and between aliphatic chains of the dopant, respectively. Table 2 contains the set of *d* spacings measured for PANI−sulfosuccinates studied in this research. The obtained values corroborate the generality of the structural model proposed in our previous paper.[5]

In reality, similarly to other doped conducting polymers, PANI−sulfosuccinates are only partially crystalline and are generally regarded as heterogeneous systems in which more ordered (crystalline) parts coexist with less ordered (amorphous) parts. Such a picture is consistent with the observed electrical transport properties of doped PANI[16] as well as with other physical measurements.[17] On the other hand, mechanical properties of partially crystalline polymers are governed by the value of their glass transition temperature (T_g). Recently we have demonstrated[18] that the improved room-temperature stretchability of PANI−sulfophthalates is caused by a dopant-induced lowering of T_g in the doped polymer. Very similar effects are also observed for PANI−sulfosuccinates studied in this research. As seen in Figure 2 two different glass transition temperatures are observed for these systems which we label Tg_1 and Tg_2. The latter one is very distinct, whereas the former is less pronounced but reproducibly observed. This is not surprising considering that in comb-shaped polymers different types of segmental movements can occur. Following the interpretation proposed in ref 18 for PANI−sulfophthalates we attribute the lower temperature transition (Tg_1) to the freezing of the movements of the dopant alkyl or alkoxy branches, whereas the higher temperature transition (Tg_2) is regarded as originating from the movements of the polymer−dopant association because above this temperature doped PANI is stretchable. It should be noted here that although exhibiting nearly the same Tg_2, PANI−sulfosuccinates stretch much better than PANI−sulfophthalates containing the same substituent and consistently show lower values of the Young modulus (Table 3). A typical stress−strain curve recorded for PANI−sulfosuccinate is presented in Figure 3. In fact, the films can be stretched up to $\Delta l/l_0 = 195\%$, i.e., the highest value observed so far for room-temperature stretching of doped conjugated polymers.

Table 3. Glass Transition Temperatures (T_{g1} and T_{g2}), Room Temperature Conductivity (σ_{RT}), Elongation at Break ($\Delta l/l_0$), and Young Modulus Determined for Free-Standing Films of Polyaniline Doped with Diesters of Sulfosuccinic Acid[a]

	T_{g1} (K)	T_{g2} (K)	σ_{RT} (S·cm^{-1})	$\Delta l/l_0$ (%)	Young Modulus (MPa)
PANI−DEHESSA	228	294	110	90	117
PANI−DEHEPSA		*283*	*115*	*28*	*212*
PANI−DDoESSA	249		97	180	94
PANI−DDoEPSA	*243*		*79*	*78*	*225*
PANI−DBEESSA		294	125	130	52
PANI−DBEEPSA		*301*	*172*	*29*	*not measured*
PANI−DBEEESSA	221	302	90	195	46
PANI−DBEEEPSA	*231*	*281*	*97*	*72*	*132*

[a] For comparative purposes the same parameters obtained for polyaniline doped with diesters of 4-sulfophthalic acid, containing the same substituents, are included (in italic).

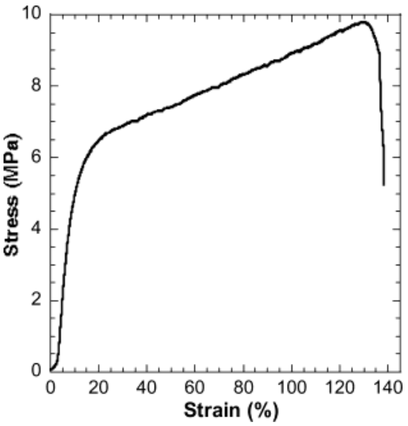

Figure 3. Stress−strain curve recorded for a free-standing film of polyaniline doped with di-*n*-dodecyl ester of sulfosuccinic acid, drawing rate 1 mm·s^{-1}.

In Figure 4 the temperature dependence of the dc conductivity of PANI−sulfosuccinates studied in this research is presented. With the exception of PANI−DBEEESSA, all other samples exhibit more "metallic" character than PANI doped with the corresponding sulfophthalates.[5] Although the temperature zone of the negative value of $d\sigma/d$T is roughly the same in both cases (from RT down to ca. 200−210 K), the reduced conductivity value, σ/σ_{RT}, measured at 4.2 K, is much higher for PANI−sulfosuccinates. The RT values of the conductivity measured for all systems studied are listed in Table 3.

We were tempted to verify whether, taking advantage of the stretchability of PANI−succinates, we are able to induce preferential orientation in their films and in

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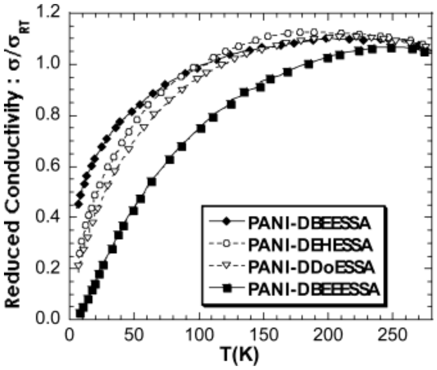

Figure 4. Temperature dependence of dc conductivity measured for polyaniline films doped with diesters of sulfosuccinic acids.

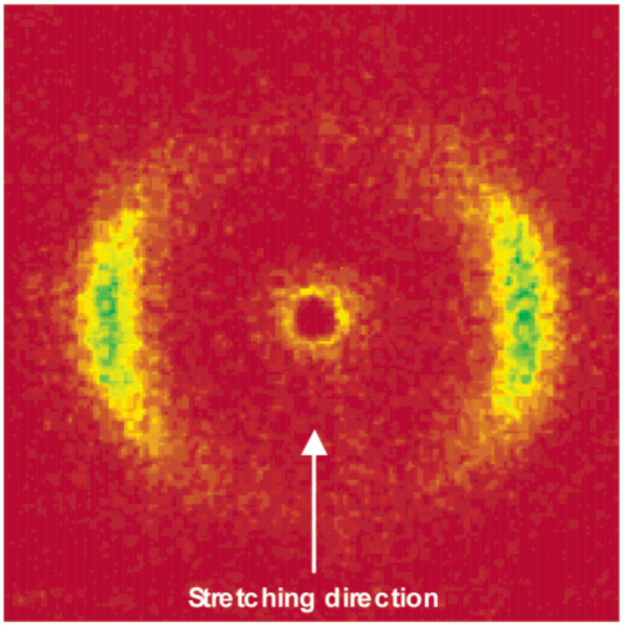

Figure 5. 2D Small-angle X-ray pattern of a free-standing film of polyaniline doped with di-2-ethylhexyl ester of sulfosuccinic acid stretched to $\Delta l/l_0 = 77\%$. The elongation axis is vertical. A side of the square corresponds to 0.688 $Å^{-1}$.

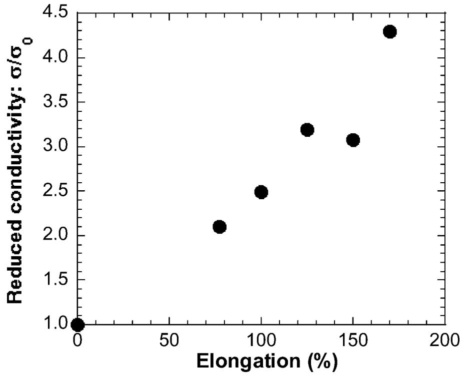

Figure 6. Conductivity increase measured at room temperature for free-standing films of polyaniline doped with di-(2-(2-butoxyethoxy)ethyl) ester of sulfosuccinic acid as a function of their elongation.

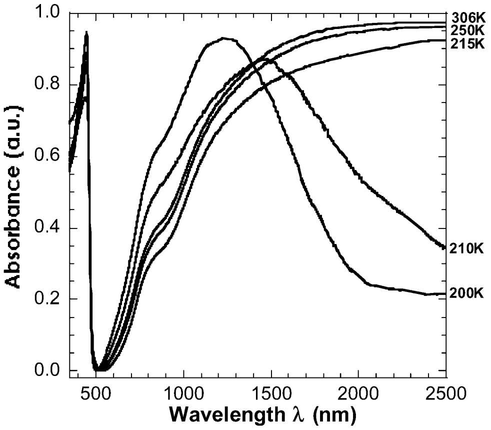

Figure 7. UV−vis−NIR spectra of thin solid films of polyaniline doped with di-2-ethylhexyl ester of sulfosuccinic acid registered for the temperature range 303−200 K.

this manner influence their electrical conductivity. In Figure 5 the two-dimensional SAXS profile, obtained for a PANI−DEHESSA free-standing film stretched to $\Delta l/l_0 = 77\%$, is shown. The observed ring for $q = 0.233$ $Å^{-1}$ corresponds to a distance $2\pi/q$ of 27 Å, i.e., the interlayer chain-dopant-chain distance. An orientation of the doped polymer is clear with the stacking chain-dopant-chain direction perpendicular to the drawing direction. Upon stretching to $\Delta l/l_0 = 77\%$ the conductivity measured at RT increases by ca. 30%; however, the temperature range of the metallic-type behavior does not increase. For PANI−DBEEESSA, which is more stretchable than PANI−DEHESSA, the RT conductivity increases linearly with $\Delta l/l_0$ exceeding four times its initial value for the elongation of 170% (Figure 6).

In addition to their improved stretchabillity, low T_g of PANI−sulfosuccinates also induces other phenomena never previously observed for doped PANI (except PANI−sulfophthalates studied previously in our group).[18] One of them is low temperature thermochromism. Thermochromism is a common phenomenon in poly(thiophene) derivatives and is manifested by reversible changes in their UV−vis−NIR solid-state spectra induced by temperature.[19] Molecular origins of the thermochromism are chain conformational changes occurring above T_g of the polymer. We wanted to verify whether molecular motion in PANI−sulfosuccinates, whose emergence at temperatures in the vicinity of Tg_1 is evidenced not only by DSC (vide supra) but also by the temperature dependence of incoherent quasielastic neutron scattering (IQNS),[20] may induce thermochromism in PANI. In Figure 7 UV−vis−NIR spectra of PANI−DEHESSA, recorded in the temperature range of 200−306 K, are presented. The strong thermochromic effect is manifested by an abrupt narrowing of the broad absorption extending from ca. 520 nm toward near-infrared (NIR). In the simplest interpretation[3] this extended absorption, observed at $T > 210$ K, is indicative of charge carriers (polarons) delocalization. Narrowing of this band, occurring at $T < 210$ K, can be interpreted as a spectroscopic manifestation of the chain conformational changes resulting in the localization of charge carriers. Comparison of the temperature of the thermochromism onset with DSC and IQNS[20] data clearly indicates that the onset of the thermochromism can be correlated with the "freezing" of the dopant movement. In the "frozen" state the dopants impose

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(19) See for example: Inganäs, O. In *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; Wiley & Sons: New York, 1997; vol. 3, p 785.

(20) Djurado, D.; Bée, M.; Combet, J.; Dufour, B.; Rannou, P.; Pron, A.; Travers, J.-P. *ILL Ann. Rep. 2000, Sci. Highlights* **2001**, 62.

unfavorable chain conformations for charge carriers delocalization, whereas in the "mobile" state, their interactions with the chain result in conformations favoring better conjugation and by consequence better charge carriers delocalization. In the case of the poly(semiquinone radical) structure (polaron lattice) of the doped PANI chain, the extent of the conjugation depends on the value of the torsional angle between the phenylene ring and the plane of the PANI chain zigzag. In this aspect, the onset of interactions of PANI chains with "mobile" dopants results in a more planar chain conformation which facilitates charge carriers delocalization. To our knowledge PANI−sulfosuccinates and PANI−sulfophthalates[18] are the only doped PANI systems exhibiting such a low temperature thermochromism. Weak thermochromism was previously reported for PANI protonated with (+)-camphor-10-sulfonic acid. However the effect was registered at a relatively elevated temperature of 413 K consistent with the high T_g of PANI−CSA.[21]

Finally, we were slightly concerned whether the low T_g of PANI−sulfosuccinates might negatively influence their thermal stability. It is known that aging phenomena and degradation processes in polymer systems are usually accelerated at temperatures exceeding T_g because molecular motion frequently facilitates interchain or intrachain interactions between specific functional groups, which may result in reactions leading to the polymer degradation. This is clearly seen in the PANI−CSA system whose degradation, as probed by its conductivity drop, is strongly accelerated at temperatures exceeding 408 K i.e., T_g.[22−23] For comparative purposes we have carried out accelerated aging experiments of PANI−sulfosuccinates and PANI−CSA at 408 K in ambient conditions. The results are presented in Figure 8. All PANI−sulfosuccinates studied in this research are much more thermally stable than PANI−CSA despite their low T_g. Extremely good thermal stability of PANI−DBEESSA should be underlined. The half-life parameter of the latter, $t_{0.5}$, i.e the time required for the conductivity to drop to 50% of its original value, is 314 h. This $t_{0.5}$ value is ca. 15 times higher than that of PANI−CSA measured in the same experimental conditions.[22] Moreover, it is 4 times higher than $t_{0.5}$ of commercially available poly(3,4-ethylenedioxythiophene) doped with ferric tosylate (Fe(III)(Tos)$_3$) which is considered to be one of the most thermally stable conductive polymers.[24−25]

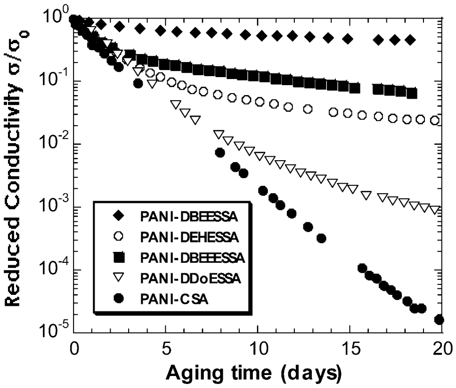

Figure 8. Evolution of dc conductivity measured for films of polyaniline doped with diesters of sulfosuccinic acid aged at the temperature of 408 K in ambient conditions. The results obtained for polyaniline doped with (±)-camphor-10-sulfonic acid are included for comparative purposes.

Conclusions

To summarize, we have synthesized a new family of polyaniline doping agents, namely sulfosuccinates with alkyl or alkoxy substituents. Sulfosuccinate doped PANI shows a layered or lamellar supramolecular organization and has the lowest glass transition temperature of all PANI-based systems. As a consequence it is stretchable at room temperature and exhibits low temperature thermochromism. Finally, PANI doped with sulfosuccinates containing alkoxy substituents can be considered as one of the most thermally stable doped conducting polymers fabricated to date.

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(22) Rannou, P.; Nechtschein, M.; Travers, J.-P.; Berner, D.; Wolter, A.; Djurado, D. *Synth. Met.* **1999**, *101*, 734.

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