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Structural Study of Doped and Undoped Polythiophene in Solution by Small-Angle Neutron Scattering

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Small-angle neutron-scattering studies have been carried out on solutions of the conjugated polymer poly-3-butylthiophene. At room temperature positive interchain interactions occur even at concentration as low as 0.1 g/l. At $T=65\,^{\circ}\mathrm{C}$ the statistical length $b=55$ Å of isolated neutral chains has been measured. Upon doping of the polymer chains, a large conformational transition occurs. In the dilute regime, the charged polymer chains are in a rodlike state. Doped–conjugated-polymer solutions do not behave like common polyelectrolytes.

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The electrical and nonlinear optical properties of conjugated polymers have received much attention during the last few years. These properties are largely determined by the geometry of the conjugated macromolecules and the charge distribution along the chains. However, detailed structural information for most conjugated polymers is not available.

Small-angle neutron scattering (SANS) has been used for obtaining geometrical information on macromolecules. Recently, conjugated alkylthiophene polymers have been synthesized, which are soluble and can be doped to form a conductive solution.[1] This makes it possible for the first time to study the chain conformation by SANS for both the undoped and the doped polymers in the same solvent. Although π-conjugated structures tend to yield relatively stiff chains with attractive interchain interactions, single-chain conformations can be determined in dilute solutions where chain interaction is negligible. This has been shown for solutions of the polydiacetylenes p3BCMU and p4BCMU.[2,3]

All conducting polymers are presumed to undergo large geometry changes upon doping, leading to a substantial modification of the band structure. These changes are the result of polaron and bipolaron formations which have been proposed as the dominant charge configuration for alkylthiophenes.[4,5] SANS can then be used to investigate the change in chain conformation with increased doping level. We present here the first experimental study on the structure of a conducting polymer in solution.

The poly-3-butylthiophene was synthesized and purified as described elsewhere.[1] Two types of samples were used, one with $M_w=49\,000$ and a weight distribution of $M_w/M_n=1.5$ used for the neutral solutions, and another with $M_w=22\,000$ and $M_w/M_n=5$ used for the doped solutions. Deuterated nitrobenzene was used as solvent. Most of our results for the neutral polymer solution were obtained with a polymer concentration of 1 mg/cm^3, well below the overlap concentration $c^*\approx 20$ mg/cm^3. Doping was achieved by our preparing a solution of $\mathrm{NOSbF_6}$ and adding it to the polymer solution.

The SANS experiments were performed in Grenoble (Institut Laue–Langevin high flux reactor), with use of the diffractometers D11 and D17 in the scattering-vector range $4.5\times10^{-3}<q<3\times10^{-1}$ Å^{-1}. The scattering function measured is given by

$$G(q,c)=\Sigma(q,c)m/K^2cN\,, \tag{1}$$

where $\Sigma(q,c)$ is the observed differential cross section in cm^{-1} after subtraction of the flat background given by the solvent, K^2 is the contrast factor in cm^2, c is the polymer concentration in g/l, N is Avogardro's number, and $m=138$ g/mol is the molar mass of the monomer repeat unit.

We have done absolute measurements using a standard calibration.[6] This allows one to check the isolated-chain conformation through the determination of the mass per unit length. Semiempirical modified neglect of diatomic overlap calculations give a monomer repeat unit length of $a=3.90$ Å.[7] With a molar mass $m=138$ g/mol, this leads to a mass per unit length of $M_l=35.4$ g Å^{-1} mol^{-1}.

The single-chain scattering function is

$$g(q)=(M_w/m)P(q)\,, \tag{2}$$

with $P(q)$ the normalized scattering factor of the chain such that $P(0)=1$. Several theoretical models have been developed to describe the scattering functions and the conformations of macromolecules in solution.[8] For a Gaussian coil, the asymptotic law is

$$\lim_{q\to\infty} q^2g(q)=12M_l/mb(1-6M_l/q^2M_wb)\,. \tag{3}$$

By our plotting $q^2g(q)$ vs q, a plateau of height $12M_l/mb$ is found, where b is the statistical length. For a wormlike chain with persistence length, Des Cloizeaux[9] has given the asymptotic law

$$\lim_{\substack{L\to\infty\\ q\to\infty}} \frac{L}{b}P(q)=\frac{\pi}{qb}+\frac{4}{3(qb)^2}\,, \tag{4}$$

where L is the contour length. By our replotting $qg(q)$ vs q, a plateau of height $\pi M_l/m$ is found in the q range where a rodlike structure can be observed. The statistical length of the chain is calculated with the model of Yoshizaki and Yamakawa.[10]

In Fig. 1, $qg(q)$ is plotted versus q for neutral chains of poly-3-butylthiophene in solution at various temperatures with a polymer concentration $c=1$ mg/cm^3. No kinetic effects have been observed for a given temperature during any of the experiments. The observed large intensity at low-q values clearly shows that more than one macromolecule scatters coherently at room temperature. The shape of the scattering curves implies that a significant attractive interchain interaction occurs in the solution with a strong temperature dependence. This still occurs at polymer concentration as low as 0.1 mg/cm^3. Such a behavior eliminates the possibility of our measuring the single-chain conformation at room temperature. The scattering function given by the isolated-chain structure is screened at low q values because of the positive interchain interaction; while at higher q values, since the chain is not an infinitely thin thread, the finite lateral extension of the side groups will change the overall q dependence of the total scattering function.[3,11]

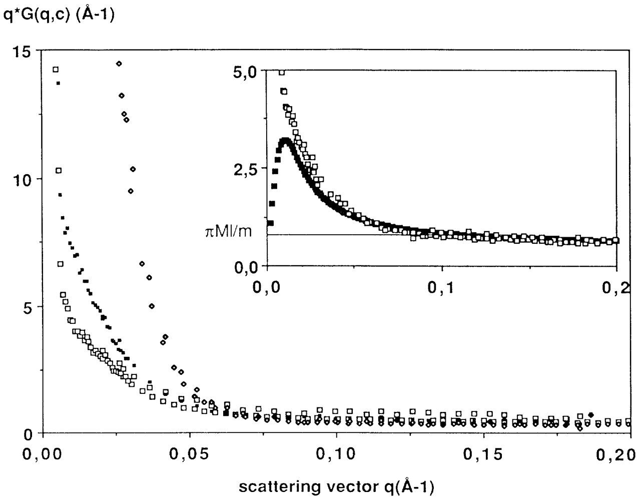

FIG. 1. $qg(q)$ plot of n-butylthiophene neutral chains in nitrobenzene solvent: $T=25\,°\mathrm{C}$ (◇); $T=55\,°\mathrm{C}$ (■); $T=65\,°\mathrm{C}$ (□). Inset: $qg(q)$ plot of n-butylthiophene neutral chain in nitrobenzene solvent at $T=65\,°\mathrm{C}$ (□); fit with numerical calculation (Ref. 10) is shown with constraints given in the text (■).

Higher temperatures were investigated in order to decrease the interchain interaction through the increase of the thermal fluctuations. Only at the lowest q values do we find a residual interchain contribution, which results in a small difference between calculated[10] and experimental data in the q range higher than 0.02 Å^{-1} (see inset in Fig. 1).

With a $q^2g(q)$ plot, a plateau height of 0.06 is found in the q range from 0.04 to 0.06 Å^{-1}. By application of Eq. (3) and use of the calculated value of M_l, a statistical length $b=51$ Å is obtained. To take into account the finite lateral extension, we use a Guinier approximation. If we set R_c^2, the mean square radial radius of gyration, in the q range where $q<1/R_c$, the scattering function becomes

$$g(q)=g_0(q)\exp(-\tfrac{1}{2}q^2R_c^2)\,, \tag{5}$$

where $g_0(q)$ corresponds to the infinitely-thin-thread scattering factor. With this approximation the best fit obtained with the wormlike chain model[10] gives $M_l=35$ g, $b=55$ Å, and $R_c=3.5$ Å (see inset in Fig. 1). The former value agrees very well with the value calculated for an isolated chain of poly-3-butylthiophene. If we assume that the scattering length density of the lateral groups is very close to the nuclear density, which is correct for the alkyl groups, the value of $R_c=3.5$ Å leads to a total geometric extent for the lateral groups of $L_c=12.1$ Å.

One may consider the polymer as an infinitely thin ribbon of mass per unit area, M_s, which can then be deduced from $q^2g(q)=0.14$ in the q range 0.18 to 0.25 Å^{-1} using

$$q^2g(q)=2\pi M_s/m\,. \tag{6}$$

The experimental data yield $M_s=3.1$ g/Å^2 mol, from which a value of the ribbon width of $W=11.5$ Å is deduced, very close to the L_c value given by the fit. The present result is not a definite experimental proof that an isolated chain state has been measured. Nevertheless, we can expect that the conformation of the isolated chain will be not very different from the one measured for the following reasons: Absolute measurement gives the height expected from the structure of the monomer unit. The values obtained in different ways, with Eqs. (3)-(6) in the q range between 0.04 and 0.25 Å^{-1}, are identical.

Several conclusions follow from these numbers describing the conformation of poly-3-butylthiophene in nitrobenzene at 65 °C. First, this is indeed a true solution. The excess scattering intensity below $q\approx 3.5\times 10^{-2}$ Å^{-1} shows that residual interchain interactions are attractive. Second, the polymer is a fairly flexible coil. Its statistical length should be compared to the corresponding values for a typical semirigid conjugated polymer, polydiacetylene [$b=275$ Å at 65 °C (Ref. 3)], and for a typical flexible polymer, polystyrene [$b\approx 20$ Å (Ref. 11)].

The first experiment done on doped solutions are displayed in Fig. 2. Two polymer concentrations, 0.5 and 2.40 mg/cm^3, were used. The dopant molecules NOSbF$_6$ were dissolved in deuterated nitrobenzene and added to the polymer solution at room temperature. The nominal dopant concentration is one dopant molecule per monomer repeat unit. Overall neutrality is insured by the SbF$_6{}^-$ counterions. The near-infrared absorption spectrum is identical to the one observed by Hotta *et al.*[12] A maximum absorption at 830 nm and a broad peak around 1800 nm are observed.

The structure of the doped chains in solution leads to completely different scattering curves depending on the neutral-polymer concentration. A q^{-2} behavior is observed for $c_p = 2.4$ mg/cm^3, while for $c_p = 0.5$ mg/cm^3, a q^{-1} behavior is observed in the investigated q range. If we assume that repulsive interchain interactions do not drastically alter the low-q scattering behavior, the q^{-1} dependence of the dilute solution means that the chains are more rigid in the doped state. Our results provide a lower limit for the statistical length equal to $b = 850$ Å. Therefore, the conformational change upon doping at low polymer concentration corresponds to a transition from a coil to an extended conformation close to that of the rod structure.

Since up to now, no structural study has been performed on doped solutions, the most reasonable approach is to compare the present experiments with those done on polyelectrolytes. In salt-free solutions, a peak in the scattering curve is observed with a q-value position that varies with a $c^{1/2}$-like dependence on concentration.[13,14] The origin of the peak has been related to a liquidlike ordering of rods or to the concept of a correlation hole.[15,16] The observed q^{-1} behavior in our experiment requires that such a peak, should it exist, will be below the lowest q value used, i.e., at $q < 8 \times 10^{-3}$ Å^{-1}.

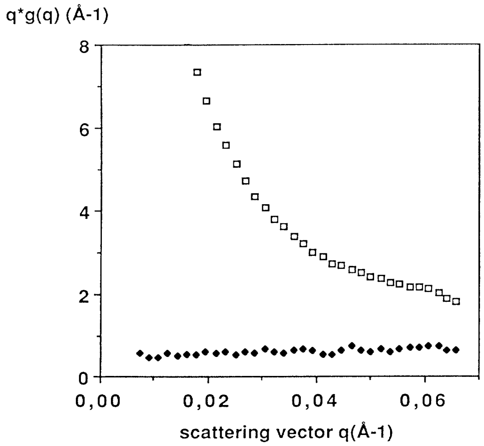

FIG. 2. $qg(q)$ plot of the chain n-butylthiophene doped with NOSbF$_6$: $c_p = 0.5$ mg/cm^3 and $c_d = 100\%$ (◆), $c_p = 2.4$ mg/cm^3 and $c_d = 100\%$ (□).

Odijk and Houwart have shown that the persistence length L_p of a polyion near the rod limit is the sum of two contributions[17]: $L_p = L_0 + L_e$, with L_0 the intrinsic rigidity and L_e the rigidity due to electrostatic interactions. The magnitude of L_e depends on the existence of counterion condensation around the polyelectrolyte, that is, on the effective charge density along the chain and on the Bjerrum length Q,

$$Q = e^2/Dk_BT\,, \tag{7}$$

with e the elementary charge, D the dielectric constant of the medium, k_B the Boltzman constant, and T the temperature. For nitrobenzene Q is 15 Å.

In the strong-coupling limit $A < Q$, Odijk has given an expression for the electrostatic persistence length (half of statistical length)[16]:

$$L_e = 1/16\pi AQc\,. \tag{8}$$

Here, A is the average distance between charges along the chain, and c is the monomer concentration. Although the precise maximum doping level in polythiophene solutions is not known, it is estimated from optical spectroscopy studies[12] not to exceed 50%, which compares with about 33% measured for the solids. If we assume 50%, with $c = 0.5$ mg/cm^3, expression (8) gives $b = 150$ Å, markedly lower than the measured one. Even if one assumes a 100% doping level, the calculated statistical length $b = 310$ Å is still far too low.

An alternative is to consider the rod-limit case without condensation, even partial, of counterions. The electrostatic persistence length is[17]

$$L_e = Q/4A^2k^2\,, \tag{9}$$

with $k^2 = 4\pi Qc_-$ and c_- the counterion concentration. For $c = 0.5$ mg/cm^3, the corresponding counterion concentration leads to a Debye length $k^{-1} = 50$ Å. With one charge per monomer unit (100% doping level) the statistical length is then $b = 2L_e = 1200$ Å, while for 33% doping the length is reduced significantly to $b = 130$ Å. These results would suggest a highly doped state of the chains at low polymer concentration without counterion condensation.

Very high doping levels (100% or beyond) are in conflict with the measured values in the solid state. However, the doping mechanism in solution can be very different. In the solid state, the doping process will be controlled by chain packing and dopant diffusion in a dense medium which are the limiting factors for maximum doping level and which are not important in solution.

We know of no example of a 100%-doped conductive polymer and we would think that our samples in solution probably do not contain one charge per thiophene ring. One could argue that such a high doping level will lead to a drastic change in the electronic band structure of the conjugated polymer which is not supported by the results of spectroscopy. Indeed, the assumption of very high doping levels is only necessary if one stays within the framework of the conventional polyelectrolyte theory. For usual polyelectrolytes the charges are located at fixed points, generally the end side groups. Therefore, it is logical to use the dielectric constant of the solvent to take into account the effect of the repulsive electrostatic interaction. In our case, the charges are mobile along the backbone of the conjugated polymer and the role of solvent polarizability can be smaller.

In salt-free solutions of dilute conventional polyelectrolytes, the electrostatic persistence length L_e is usually much larger than the intrinsic length L_0. This is most likely not true for doped-conjugated-polymer solutions. The doping process is associated with a large change in electronic structure, i.e., a change from an aromatic-type backbone to a quinoid-type structure, where the bond between rings has a double-bond character. This will lead to a much stiffer chain and therefore to a large increase of L_0.

The differences to conventional polyelectrolytes are also evident from the upper curve in Fig. 2. If a correlation hole is present it should be observed at a concentration $c=2.4$ mg/cm^3, since the overlap concentration c^* of chains with molecular weight $M_w=22000$ (contour length $L=620$ Å) will be equal to $c^*=M_w/NL^3=0.15$ mg/cm^3 for the chain rodlike state.

At $c=2.4$ mg/cm^3, a decrease of the magnitude of the density fluctuations due to Coulombic interactions should be observed. Instead, the scattering function shows a q^{-2} behavior. It follows that the density fluctuations are much larger than the average density, which is inconsistent with the expected behavior of polyelectrolytes. A reasonable hypothesis is that a nonhomogeneous charge distribution occurs along the chain as a result of the repulsive interaction between mobile charges on different chains.

In conclusion, poly-alkylthiophenes in solution undergo a dramatic conformational change upon doping. Conventional polyelectrolyte theory cannot account for the observed large persistence length.

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