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Outstanding Covalent Conjugated Gels: Electrically Conducting Rubbers

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Summary: Four series of fully conjugated poly(octylthiophene) gels were prepared by oxidative copolymerization of octylthiophene with four different cross-links (trithienylbenzenes) of functionalities f=3 or 6 and by varying the cross-link ratio R. The gels exhibit rubber elasticity and swell in apolar solvents. The gel fraction, the swelling ratio Q, the elastic modulus, and a NMR structural parameter display master curves of variations versus the variable fR, which characterises the statistical structure of the gels. This result shows that the linear chain segments comprised between adjacent cross-links govern the deformation properties of the networks. Transport properties were explored. The gels are photoluminescent. When doped (oxidation by iodine), they are electronically conducting both in dry and swollen states. At large Q intra-chain hopping mechanisms govern the conductivity while at small Q, intermolecular hopping processes are predominant. Cross-links are not a limitation to conductivity.

Keywords: conjugated polymers; electromechanical effects; electron conductivity; gels; poly(octylthiophene)

Introduction

This paper deals with the outstanding properties of a new kind of conducting polymer: covalent conjugated polymer gels of poly(octylthiophene). These systems were prepared with the aim of obtaining networks with interesting transport and mechanical properties like rubber elasticity and the ability to swell in a good solvent. Indeed, the mechanical behaviour of classical 1D conducting polymers is generally far from rubbery. Actually, they are vitreous at room temperature (high glass transition temperatures) because of their strongly associative structure induced by π-stacking. In the dry state, gels of conducting polymers should also exhibit this strongly associative structure in addition to their topological structure. Therefore, they are expected to be glassy at room temperature. In presence of a good solvent, the associative structure should be reduced, leading to lower Tg: rubbery behaviour may be expected. Moreover, since gels have a connected 3D-structure, 3D paths allowing charge transport in the swollen gel should exist, which render the systems conducting.

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In the first part of this paper, we recall the main features of current conjugated polymers. Then the method of preparation of these gels is reported. After a brief review of their properties in the solid dry state, we report macroscopic (gel fraction) and microscopic (NMR) experiments. We discuss the results in relation with the gel statistical structure, that is to say, their characteristic mesh size. We then explore their isotropic (swelling) and uniaxial deformation properties. We investigate their transport properties: conductivity and luminescence. We conclude with electromechanical effects, which were discovered very recently, that result from the coupling between mechanical and transport properties.

Main Features of Current Conducting Polymers

In saturated polymers, carbon atoms are bound by sigma orbitals and the four valence electrons are localized. The electronic band is filled and these polymers are insulators. In conjugated polymers, sp2 hybridization leads to one unpaired electron per carbon atom. The π-electrons can delocalize over many carbon atoms along the polymer chain. The electronic band is half-filled, leading to a possible metallic behaviour. However, in quasi 1D systems, polymer chains tend to distort spontaneously, giving rise to pairing of successive sites along the chain and alternating short and long bonds, or dimerization (Figure 1).

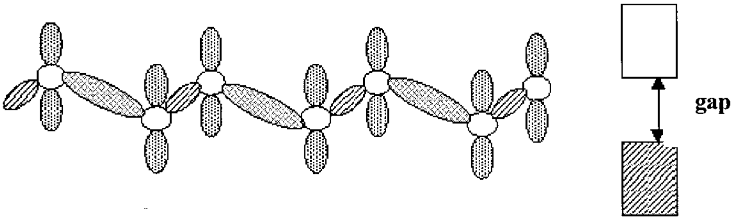

Fig. 1. Dimerized structure of conjugated polymers.

This dimerization opens a gap at the Fermi surface of about 2-3 eV, thereby lowering the energy of the occupied electronic states, which renders the system a semiconductor.

The polymer is transformed into a conductor by doping but, unlike inorganic semiconductors, doping is produced by an oxidation or reduction reaction. For instance, iodine can be introduced, which removes one electron from the chain and forms I_3^-. The charges are stored over small delocalized chain sections of a few units. At the domain walls the conjugation is disrupted and outside these domains the chain is dimerized. A first degree of oxidation gives rise to one charge stored on each domain (polaron). Further oxidation leads to the formation of bipolarons. The existence of the charges causes levels to appear in the gap.

1D-conduction along a chain generally occurs via intrachain electron hopping. Charge must move in the field of close counterions, which must be either numerous or mobile. 3D-conduction in the bulk polymer is different and is still not completely understood: it is generally considered that electrons jump from one chain to another via hopping or tunnelling. This mechanism is governed by the 3D structure of the system, which is not well controlled because of strong chain association due to π-stacking. This 3D structure exhibits a mixture of crystalline zones, vitreous stacked regions and doped zones and is very heterogeneous. The relationship between structure and transport properties of solid conducting polymers is difficult to establish and their conduction mechanisms are generally interpreted within granular models: hopping between conducting grains separated by insulating barriers.[1]

Preparation of Poly(octylthiophene) Gels

Gels are prepared by oxidative polymerization of monomers: octylthiophene with multi-functional cross-links: trithienylbenzene[2] (see Figure 2). We prepared 4 gel series, using 4 trithienylbenzene with functionality f equal to 3 or 6 and cross-link ratios R between 0.001 and 0.2. All reactive units (monomers or cross-links) could react either with themselves or with the others. Figure 3 presents a schematic structure of the networks.

Only the average degree of polymerization between two adjacent cross-links can be known from the stoechiometry. It is equal to $\langle N \rangle = 2/f\,R$. Starting only from monomers, $R = 0$, we obtained linear poly(octylthiophene) chains. When a small amount of cross-links is added, we get finite clusters. Above a critical cross-link ratio, a 3D gel with a large mesh size was found at the end of the reaction, together with a solution of finite clusters. For higher cross-link ratios, we have better connected gels (smaller mesh size) with most of the clusters bound to

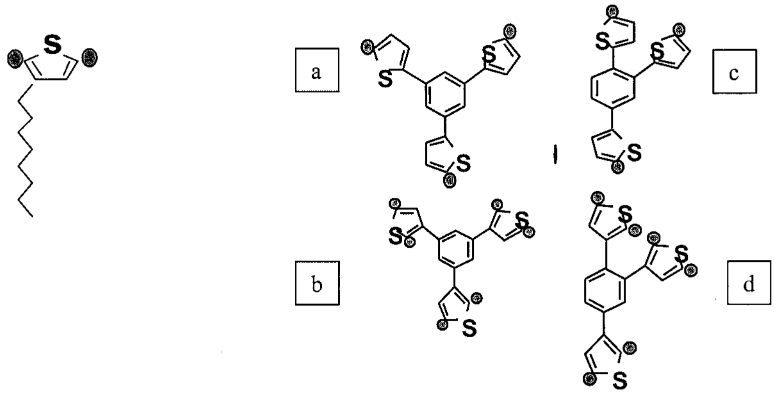

Fig. 2. Structure of the monomer and of the cross-links.

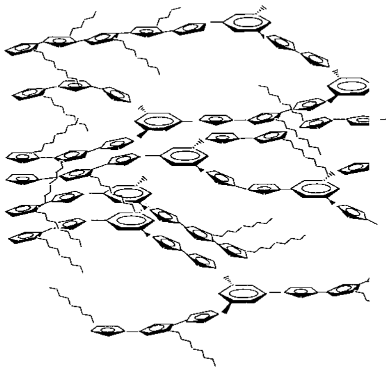

Fig. 3. Schematic network.

the gel phase. In these gels, the observed gel point is very low, since the reaction probability is high (as soon as one cross-link (f = 3) is added to 500 octylthiophene, a gel appears in the reactive medium).

Solid Dry State

In the dry solid-state, the associative structure due to stacking is added to the intrinsic network structure. Therefore, as expected, solid-state properties are not particularly specific to the gel structure. The glass transition temperature Tg ranges between 0°C and 30°C. The gels are semi-crystalline and the melting point is 160°C.[3] Materials are tough at room temperature. Doped, these systems are conductors and the behaviour of the conductivity is similar to that of linear poly(octylthiophene) chains.[4]

Statistical Structure and Mechanical Properties

In this section, the gels are studied in the molten or in the swollen state, where their statistical structure can be explored. We show that, although the mechanisms of the reaction of oxidative polymerization using $FeCl_3$ (insoluble in the reactive medium) is not entirely known and may lead to phase separation phenomena, gel structures are reproducible and depend on the two controllable parameters f and R. We report a relevant variable, which reflects the physical states of gelation of the gels or, in other terms, which is associated with the average mesh size of the network. Drawing master curves of variation of various physical quantities versus this variable allows its determination. These curves of variation are interpreted in order to understand the mechanisms of deformation in dry and swollen gels, i.e., in order to characterize the active statistical chain segments and their collective behaviour.

Gel Fraction

The first physical quantity we measured is the gel fraction G. It was determined by weighing soluble and insoluble fractions obtained at the end of the reaction after extensive washing of the gels . G directly reflects the state of connectivity of the network. It is equal to 0 as long as only finite clusters exist in the system. It is equal to 1 whenever all monomers are attached to one another. In the search for a master curve, a single curve of the variation of G versus the product fR was obtained.[5] Above the gel threshold, as expected, G increases and reaches a plateau where most of finite clusters are finally attached to the gel, which is then well connected.

Nuclear Magnetic Relaxation Experiments

To have a more microscopic insight into the gels, NMR measurements were performed in the molten state and at maximum equilibrium swelling. The background of the study is the following: when one chain segment is submitted to topological constraints, for instance cross-links at both chain extremities, the end-to-end vector of the chain is not equal to zero. This anisotropy results in the existence of dipolar interactions, which govern the relaxation of the transverse nuclear magnetisation. A global relaxation rate, χ , can be measured, which is

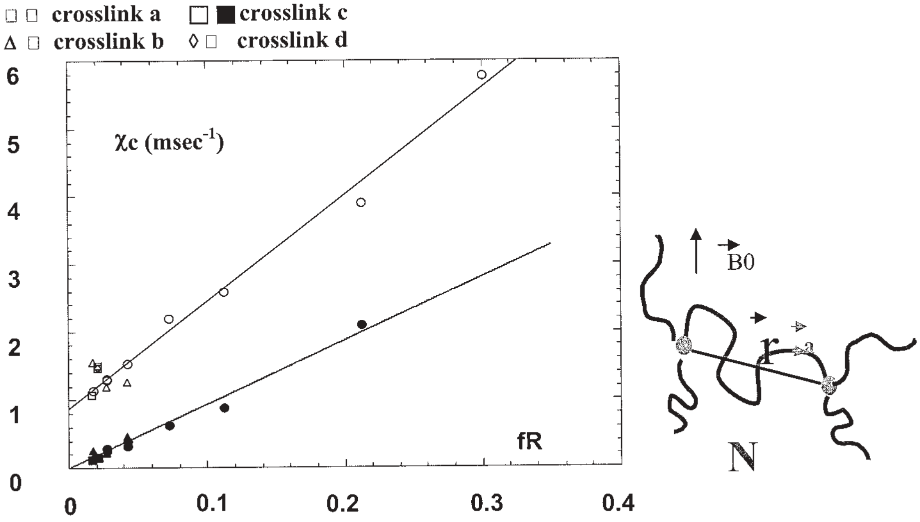

Fig. 4. Linear variations of the structural NMR parameter, χ_c, versus fR.

proportional to the inverse of the square of the end-to-end vectors of these segments, averaged over the whole sample: $\chi \propto \langle r \rangle^{-2} \propto \langle N \rangle^{-2\upsilon}$. If <N> denotes the average degree of polymerization of such chain segments, χ is proportional to $<N>^{-1}$ for Gaussian chains ($\nu = 1/2$).

χ does indeed vary linearly with the product fR (Figure 4), which is proportional to $1/<N>$, where $<N>$ is the average number of units between two cross-links. The active segment detected by NMR is therefore closely linked to the segment between cross-links. In the molten state, χ is not equal to zero at fR=0. This reveals the contribution of temporary entanglement network, which exists in molten linear polyoctylthiophene chains.[5] However, the constraints associated to the entanglement network are not trapped in the gel structure since there are not perceived in the swollen state[i].

Moreover, NMR experiments detect an evolution of the gel structure from the lowest to the highest cross-link ratios and this shows that the way of gel preparation is satisfactory.

Swelling

The gels are able to swell in an apolar solvent like chloroform. Swelling ratios range between 3 and 26. A master curve is obtained by plotting the variations of the inverse of the swelling ratio Q^{-1} as a function the square root of fR. A linear regime at low fR is observed, followed by a plateau (see Figure 5). The linear regime can be understood by picturing the gel by a close packing of disengaged Gaussian chain segments of size N. Indeed, the gel concentration

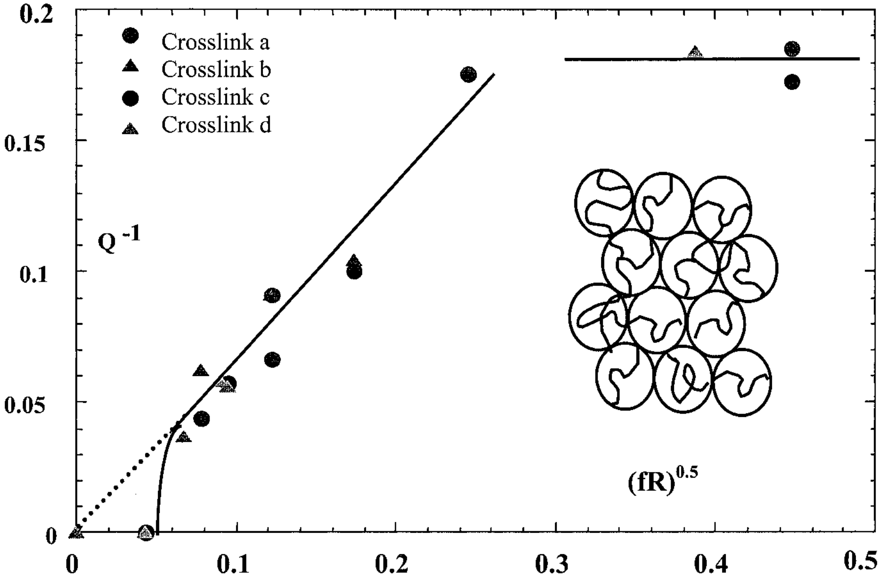

Fig. 5. Variation of the inverse of the swelling ratio with fR.

is then equal to the concentration in each cell: $Q^{-1} \propto N/r^3 \propto N^{1-3v}$ where r is the size of each cell. Assuming that the chains are Gaussian, $\nu = 1/2$, we find that the concentration Q^{-1} varieslinearly with $N^{-1/2}$. Consequently, Q^{-1} varies linearly with $fR^{1/2}$. Therefore, the active elements, which govern the mechanisms of swelling and NMR relaxation are found to be the same (segments comprised between adjacent cross-links).

High values of fR correspond to short average spacings between cross-links, which behave like semi-rigid strands, occupying small statistical volume. The degree of overlapping of the strands is small and no significant disengagement occurs during swelling. The swelling ratio is then constant and probably reflects the increase of free volume of the gel due to solvent.

Elasticity

The elastic behaviour of the gels in molten and swollen states was explored. In the molten state, uniaxial compression and stretching experiments (by suspending fixed weights to the sample) were performed. In the swollen state, DMA experiments (1 Hz, small deformation in the linear zone) were performed on samples swollen in chloroform in controlled atmosphere.

For molten dry gels, the nominal stress at fixed force varies linearly with $\lambda - 1/\lambda^2$, where λ is the stretching ratio. This result can be interpreted within the simplest model of rubber elasticity (affine deformation). We observe a linear variation of E with fR[6] (Figure 6). This result is in agreement with the model developed by Kuhn, Wall, Flory and Treloar where E is

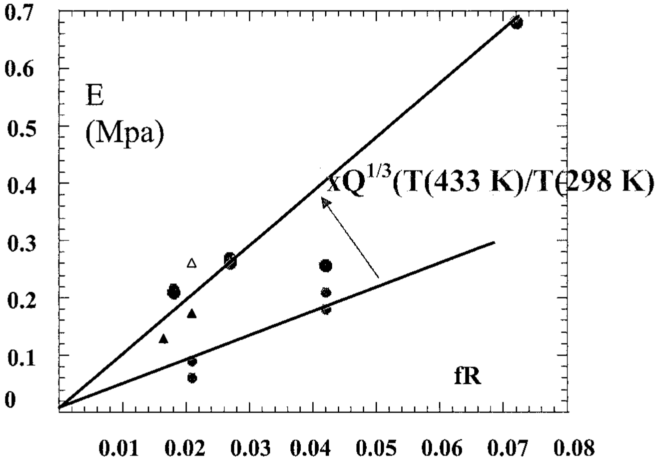

Fig. 6. Variation of modulus of elasticity (E) versus fR.

elongation of these gels in molten and swollen states is the linear segment comprised between directly proportional to the number of elastic structural segments in the network per unit volume. Consequently, the relevant structural element, which governs the elastic uniaxial adjacent cross-links.

Moreover, this classical model also works for swollen gels. In this case, the elastic modulus of swollen gel is predicted to be proportional to: $E \alpha kT/N Q^{-1/3} \phi_0{}^{2/3}$, where ϕ_0 is the volume fraction of the reference state.[7, 8] Indeed, in our experiments, when ϕ_0 is set equal to 1, the curves observed in the swollen and molten state are superimposed by applying the correction factor corresponding to the difference of swelling and temperature of experiments (Figure 6).

Conclusion

The results we obtained can be very satisfactorily interpreted within the framework of classical rubber elasticity theory. These systems are well described within a mean field framework. Our results support that the linear strands comprised between adjacent cross-links govern the properties both of elasticity and swelling.

Transport Properties

Gels were doped with iodine in the swollen state (chloroform). They still remain swollen upon doping, although a small decrease of the swelling ratio is observed. The order of magnitude of the doping level is 1%. Gels become black but remain soft and elastic. Elastic moduli of swollen doped gels increase slightly (they range from 0.4 to 2MPa) but remain in the classical range of elastomers, although doped chains are generally more rigid than neutral chains.

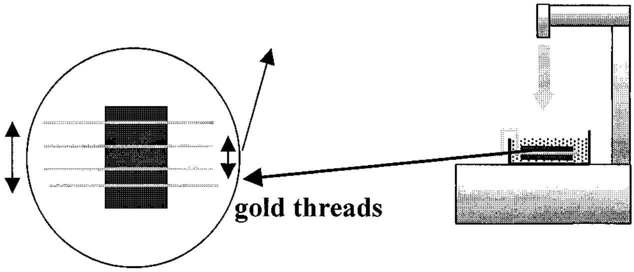

Fig. 7. Experimental device for measurements of resistance versus swelling ratio.

Conduction Properties

In order to measure simultaneously gel conductivity and swelling ratio, four gold threads were introduced into fully swollen doped gels. The swelling ratio was deduced from the distance between the threads observed with a light microscope. Voltage was applied between the two outer threads in order to obtain a constant current of I=1 μA in the whole sample. The voltage V between the two inner threads was then measured. This method (four probes in line: Valdes method modified for infinite sample thickness)[9] permits errors due to contact resistance to be avoided.Both dc and ac (frequencies 100 Hz to 1000 Hz) experiments yield the same results, but ac experiments were preferred in order to avoid polarization phenomena at the electrode. The resistance is simply obtained from the ratio of V/I.

Starting from gels at maximum swelling, we slowly evaporate the solvent in a controlled manner. The resistances and swelling ratios are simultaneously measured during the deswelling of the sample. We observe (Figure 8) that the resistance exhibits first a plateau when the gel begins to deswell, and a strong variation upon swelling. The value of the plateau does not depend on the cross-link ratio. Then a fast decrease of the resistance is observed.

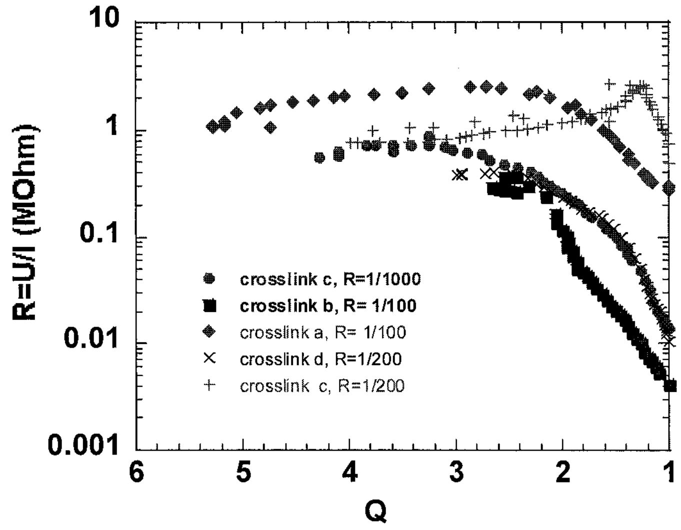

Fig. 8. Variation of the resistance versus the swelling ratio.

Our interpretation is the following. The strong dependence of the resistance upon deswelling cannot be understood as a simple dilution effect of a gel, which would be pictured as a network of non-interacting wires. Actually, in this case, the resistance should not change upon dilution by a non-conducting solvent.

At high swelling ratios, on the plateau, the independence of the resistance with Q indicates that the concentration-dependent mechanisms of inter-chain hopping are not dominant. Therefore, this suggests that intra-chain hopping mechanisms govern the conductivity. Moreover, the constant value of the plateau observed for all cross-link ratios shows that cross-linking is not the limiting factor to the intra-chain conductivity: intra-chain conduction is probably governed by defects along the chain, which induce disruptions of chain conjugation.

Dealing with the domain of small swelling ratios, where the resistance is sharply dependent on the concentration, chain segments are no longer well separated from one another by the solvent. In this case, inter-chain hopping can occur, and they now govern the conductivity. Intra-chain hopping mechanisms no longer dominate. At small swelling ratios, conduction is governed by interchain hopping.

Photo-luminescence

In the neutral state conjugated polymers are photoluminescent. Poly(octylthiophene) gels show a strong red luminescence (600 nm) after excitation by a blue laser at 488 nm The luminescence dramatically decreases upon deswelling, while an increase of the radiative recombination time is observed.[10] This result cannot be interpreted simply by taking into account a dilution effect analogous to that observed for usual dyes. It reveals that a chain association process occurs upon deswelling. This results in an additional 3D structure where charges can delocalize and separate from one another.

Conclusion

These gels exhibit an interesting combination of transport and mechanical properties. Moreover, these properties are expected to be coupled in fully swollen gels since mechanical properties depend on chain conformations, which govern the intra-chain conductivity. Very recently, such an electromechanical effect was observed: swollen doped gels were submitted to a small elongational force. A pulse of voltage of 1 Volt was then applied. A sudden change of the deformation ratio, followed by a slow relaxation was clearly observed. This preliminary results open the field to promising potential applications of these original systems.

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