Mechanisms of Deformation in Fully Conjugated Conducting Gels. Stretching and Swelling

B. Pépin-Donat and A. Van-Quynh

Laboratoire de Physique des Métaux Synthétiques, UMR 5819 (CEA-CNRS-Université J. Fourier), SI3M/DRFMC, CEA Grenoble, 38054 Grenoble Cedex 9, France

A. Viallat*

Laboratoire de Spectrométrie Physique, UMR 5588 (CNRS-Université J. Fourier), BP 87, 38402 Saint-Martin d'Hères Cedex, France

Received February 4, 2000; Revised Manuscript Received May 18, 2000

ABSTRACT: Uniaxial elongation and swelling of well-defined fully conjugated poly(3-octylthiophene) gels of various functionalities and cross-link concentrations are studied above the melting temperature. The gels exhibit rubber elasticity (elastic modulus E in the range $0.2 < E < 0.7$ MPa) and swell in chloroform. A linear relationship is established between E and the inverse of the mean number of skeletal bonds between consecutive cross-links ($1/N_{av}$). Variations of the transverse relaxation rate of protons attached to the polymer network with $1/N_{av}$ are also linear whether NMR observations are performed on dry unconstrained networks or on fully swollen gels. The results show that the active network chain segments which give rise both to elastic and swelling properties are the linear strands comprised between adjacent cross-links. Moreover, we show that when doped by iodine in chloroform these gels are conducting while they remain swollen.

1. Introduction

Conjugated polymer gels form a fascinating class of materials because in addition to their viscoelastic and swelling properties, they present the electronic transport properties of conjugated polymers.[1,2]

A challenge is to prepare conducting gels in a swollen doped state. Indeed, in this case the solvent molecules separate the network chain segments from one another, and the interchain electronic transport is expected to be limited; i.e., transport should occur preferentially along the connected paths of the network and the conductivity should reflect the network topology. Second, as the presence of solvent lowers crystallization and glass transition temperatures, swollen gels should exhibit the classic properties of rubber elasticity at room temperature. Furthermore, the competition between electronic energy and conformational entropy may lead to coupled effects between conducting and viscoelastic properties such as electromechanical effects.

Recently well-defined fully conjugated gels of poly(3-octylthiophene) (POT) of various cross-link ratios and of different cross-link functionalities have been prepared.[3,4,5] These gels have been swollen in good solvent and doped in the dry state. The statistical structure of these systems was studied in a first paper.[6,7] Their crystalline structures in the solid state[8] and their conducting properties in the doped dry state[9,10] were reported in subsequent papers. The present paper is dedicated to the study of elasticity and swelling of these gels above both their glass and melting temperatures. The first aim is to understand their mechanisms of deformation when they experience either an anisotropic deformation (stretching) or an isotropic deformation (swelling). The second purpose of this paper is to show that these gels can be doped in the swollen state.

This paper is organized as follows. We recall the main structural properties of these gels in section 2. We present experimental aspects in section 3. We describe stretching experiments and we report the values of the elastic modulus of dry gels above the melting temperature in section 4. The NMR approach to the swelling of gels is reported in section 5. Results are discussed in section 6. Finally, we show the first pictures of a swollen conducting doped gel.

2. Structural Properties of These Networks

POT gels were obtained by oxidative copolymerization of octylthiophene with four different fully conjugated cross-links (1,3,5-trithienylbenzenes and 1,2,4-trithienylbenzenes with functionalities f equal to 3 or 6) at various cross-link densities R. Systems corresponding to initial fR values higher than a critical value $fR_c \approx 10^{-3}$ exhibit an insoluble macroscopic gel phase in equilibrium with a sol made of finite-size polymeric clusters. The gel phase was washed to extract the sol[1] for each system. These polymer networks are glassy at room temperature and present a semicrystalline structure in the dry state below their melting temperature (150 °C).[11] The study of the gel fraction G, which reflects the state of connectivity of the polymer networks, of the equilibrium swelling ratio in good solvent, and of the ^{1}H transverse NMR relaxation rate, which characterizes the state of deformation of chain networks induced by the presence of cross-links, has shown that the product fR is the relevant variable to describe the statistical structure of POT gels above the melting temperature.[4] The reduced variable $N_{av} = 2/fR$ represents the average degree of polymerization of linear polymer strands comprised between adjacent cross-links. Moreover, the elementary chain segments which participate in the swelling process are also the linear chain segments comprised between adjacent cross-links. These segments are believed to be disengaged from one another in swollen gels.[6] The way of preparation of these gels leads to the formation of statistical structures and consequently, the number of skeletal bonds of these segments

10.1021/ma000211o CCC: $19.00

determining the network mesh size obeys a statistical distribution which may be broad and whose average value is N_{av}.

3. Experimental Section

The samples were prepared in the laboratoire de Physique des Métaux Synthétiques. Mechanical and NMR measurements were performed in the Laboratoire de Spectrométrie Physique.

3.1. Samples. Preparation of four series of gels by oxidative copolymerization of octylthiophene with four different fully conjugated trithienylbenzenes was reported elsewhere.[1−3] The four series of gels, prepared by using tris(2′-thienyl)-1,3,5-benzene, tris(3′-thienyl)-1,3,5-benzene, tris(2′-thienyl)-1,2,4-benzene and tris(3′-thienyl)-1,2,4-benzene are referenced as **1**, **2**, **3** and **4** respectively. Their functionality is 3 for series **1** and **3** and 6 for the series **2** and **4**. Various networks were made for each series by varying the initial molar fraction of trithienylbenzene moiety, *R*, defined as the ratio of the number of cross-links to the number of octylthiophenes between 0.001 and 0.2. Considering the gels series 3 and 4 prepared using tris(2′-thienyl)-1,2,4-benzene and tris(3′-thienyl)-1,2,4-benzene a rescaling of the product *fR* had to be done to account for the decrease of reactivity of trithienyl-1,2,4-benzene units due to steric hindrance compared to that of trithienyl-1,3,5-benzene units. The scaling factor ϕ is equal to 0.3. This means that the probability that the functional groups attached on the cross-links have reacted is reduced so that the cross-link density has to be rescaled to account for the fact that approximately 30% of trithienyl-1,2,4-benzene units may be considered as cross-links.

3.2 Mechanical Measurements. All mechanical measurements were performed above the melting temperature, i.e. at 156 °C, in the dry state. The samples had a parallelepiped-like shape and their volume could vary from 2 to 5 mm^3. The two ends of each sample were stuck using epoxy glue onto two ceramic pieces. The lower one was fixed. The upper one was a vertical long rod at the end of which was attached a nylon thread. At the other end of the thread, past a pulley, was suspended a small container. Uniaxial stretching was induced by pouring controlled volumes of water in the container. The longitudinal nominal stress was equal to the ratio of the weight of water to the nondeformed section of the sample. The strain corresponded to the displacement of the upper rod measured with a cathetometer. After a stress was imposed a delay of two minutes was waited prior to the measurement of the associated strain.

3.3. NMR Measurements. NMR measurements were carried out on isotropically deformed POT gels, i.e. POT gels swollen with deuterated chloroform. Swollen gels were kept in NMR tubes sealed under nitrogen atmosphere. The relaxation functions of the transverse magnetization were recorded on a pulsed Brüker CXP spectrometer operating at 60 MHz. Paramagnetic interactions, due to the presence of residual paramagnetic iron ions within the samples induced a fast relaxation process. Paramagnetic contribution was eliminated by using a Carr−Purcell spin-echo sequence.

Pseudo-solid spin-echoes were obtained with the following sequence: $(\pi/2)_y-\tau/2-(\pi)_y-\tau/2\text{-}(\pi/2)_{-x}-\tau_1/2-(\pi)_y-\tau_1-(\pi)_y-\tau_1-(\pi)_{-y}-\tau_1-(\pi)_{-y}$, where $(\alpha)_y$ denotes a rotation of angle α around the *y*-axis.

4. Stretching of Dry Gels

4.1. Principle of the Measurements. The modulus of elasticity *E* of dry gels above the melting temperature is derived from the variations of the stress with a strain corresponding to uniaxial elongation. In the framework of the theories developed by Kuhn, Wall, Flory, and Treloar,[12−14] the network is pictured as a collection of statistically independent chains whose end-to-end vectors are transformed affinely in the macroscopic strain. The variation of the nominal stress *F*/*S* (i.e. the force per unit of unstrained area) vs the deformation ratio λ in a uniaxial deformation at constant volume is expressed within this scheme as

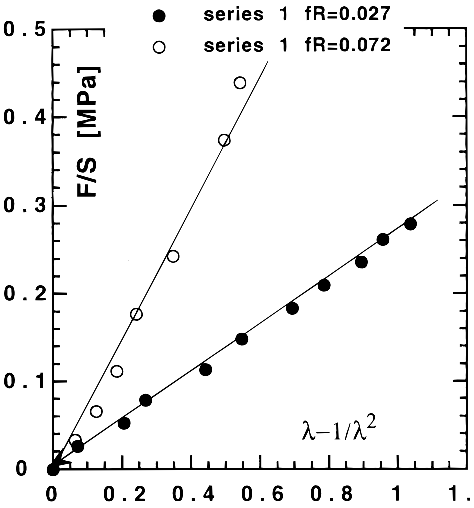


Figure 1. Linear variations of the nominal stress *F*/*S* vs $\lambda - 1/\lambda^2$ (λ is the stretching ratio) for two samples: $R = 0.009$ (filled circles); $R = 0.024$ (open circles). The elastic modulus is equal to the value of the slope of the straight line.

$$\frac{F}{S} = AnkT\left(\lambda - \frac{1}{\lambda^2}\right) \tag{1}$$

where *n* is the number of elastic structural segments in the network per unit volume, that is to say the number of elementary strands effectively connected to two first neighbor cross-links and *A* is a numerical constant which depends on the model used to describe the elasticity of the chains.[13] The average elementary elastic segments can be viewed as the active segments whose collective motions govern the macroscopic deformation of the polymer network.

The elastic modulus *E*, expressed in pascal is then equal to

$$E = AnkT \tag{2}$$

4.2. Elastic Modulus. Uniaxial stretching experiments were carried out on 10 different gels ($0.01 < fR < 0.08$). Experimental variations of *F*/*S* vs $\lambda - 1/\lambda^2$ are clearly linear for all studied gels, in agreement with eq 1. This linear variation is illustrated in Figure 1 for two gels of cross-link ratios *R* equal to 0.009 and 0.024, respectively. Elastic moduli derived from the slope of *F*/*S* vs $\lambda - 1/\lambda^2$ lie in the range 0.2−0.7 MPa. These values are comparable to that ordinary found in elastomers[12,13] and in melts of high molecular weight polymers.[15] The values of elastic moduli obtained for the various gels are given in Table 1.

Experimental variations of *E* with the product *fR* are shown in Figure 2. A linear variation is clearly observed. This result can be interpreted according to eq 2 by considering that 2/*fR* which represents the average segmental spacing between cross-links along the chains is equal to the mean number of skeletal bonds of the average elastic strand $N_{el} = (1/n)a^3$. This result shows that the relevant structural element which governs the elastic uniaxial elongation of these gels is the linear segment comprised between adjacent cross-links. The deformation of this linear segment is in affinity with the macroscopic elongation.

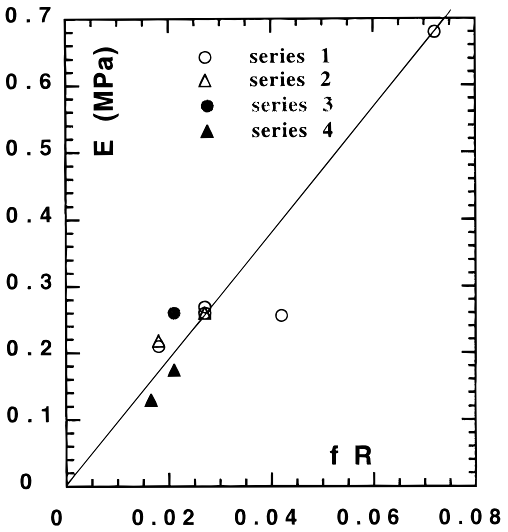


Figure 2. Linear variations of the elastic modulus E with the product fR. Each different symbol corresponds to a series of gels.

Table 1.

series	fR	E (MPa)	Q	χ_c^d (ms^{-1})	χ_c^{sw} (ms^{-1})
series 1	0.3			5.78	
$f = 3$	0.212		5.8	3.9	2.09
	0.112			2.59	0.893
	0.072	0.680	5.7	2.2	0.629
	0.042	0.185	10	1.53	0.395
	0.027	0.260	15.1	1.3	0.285
	0.027	0.269	11	1.31	0.257
	0.018	0.21	22.7	1.14	0.142
series 2	0.042	0.164	9.6	1.26	0.460
$f = 6$	0.027	0.260	11	1.19	0.223
	0.018	0.218	16.1	1.55	0.258
series 3	0.021	0.26	17.4	1.46	0.162
$f = 3$	0.0018	0	sol		
	0.15		5.4	3.4	
series 4	0.021	0.174	17.8	1.52	0.154
$f = 6$	0.0165	0.129	27.3	1.08	0.123
	0.0018	0	sol		

One point deviates from the master curve of E vs fR. It corresponds to a value of $f = 3$ and $R = 0.014$. Its elastic modulus is lower than expected. It is worth noting that enhanced conductivity and enhanced crystalline domain sizes have been observed on this sample[9,11] although gel fraction, equilibrium swelling ratio, and ^{1}H spin−spin relaxation time were not anomalous. This behavior is still unclear.

5. NMR Approach to the Swollen State

In this section we combine NMR with swelling effects to describe the active structural segments which govern the mechanisms of deformation of the networks under swelling. Values of the equilibrium swelling ratios have been previously reported. They are recalled in Table 1.

5.1. Principle of the NMR Approach. The principle of the NMR approach relies on the observation of the relaxation of the transverse magnetization of all protons located on polymer chains. In gels, the chain segments which form the network are subjected to different kinds of topological constraints such as cross-links, slipping links or entanglements. Because of these constraints, the conformational thermal fluctuations existing above the glass transition temperature of the gel are restricted and nonisotropic. These constraints induce a break of time correlations of conformational fluctuations. Therefore, they determine elementary network chain segments which are observed from NMR. The nonisotropic nature of conformational motions of elementary chain segments results in a nonzero average of magnetic dipole−dipole interactions between the spins which belong to such chain segments. In this case, the motional averaging gives rise to residual dipolar interactions which may be strong enough to govern the relaxation of the transverse magnetization by screening the contribution of the dynamics of monomer rotations.[16] The relaxation is then sensitive only to deviations from isotropic rotations.

Starting from one network chain segment, defined by its number N of skeletal bonds and its mean end-to-end vector $\langle \mathbf{r}_N \rangle$, the strength of the residual dipolar interaction existing between all protons located on this segment is expressed from the residual spin Hamiltonian[16]

$$\langle H_D(\mathbf{r}_N,N)\rangle = (3\cos^2\theta_N - 1)\frac{\langle r_N\rangle^2}{\langle {r_N}^2\rangle^2} a^2 \Lambda H_D^0 \qquad (3)$$

where H_D^0 is the dipolar interaction which should be observed along the chain segment in the glassy state, a is the skeletal bond length, θ_N is the angle between the end-to-end vector $\mathbf{r}_N$ and the steady magnetic field, and $\langle {\mathbf{r}_N}^2 \rangle$ is the mean square end-to-end distance of a segment of size N. Λ accounts for angular correlations among three neighboring skeletal bonds of the segment.

The transverse magnetization function assigned to this chain segment is written as

$$m_x(\mathbf{r}_N,N)\,(t) = \mathrm{Tr}\{e^{i\langle H_D(\mathbf{r}_N,N)\rangle t} M_x e^{-i\langle H_D(\mathbf{r}_N,N)\rangle t} M_x\} \qquad (4)$$

and the transverse relaxation function over the whole sample, $M_x(t)$ is the sum of $m_x(\mathbf{r}_N,N)(t)$ over all elementary chain segments of the network.

Equation 3 shows that NMR properties reflect the state of average elongation of all elementary chain segments within the gel.

5.2. Evidence for Residual Dipole−Dipole Interactions. The solidlike relaxation resulting from the nonzero average of proton−proton dipolar interactions can be detected by observing pseudo-solid echoes whose formation at given times of the transverse relaxation curve is specific to the existence of residual dipolar interactions.[16] Considering any polymer gel or polymer system in the melt or in solution, pseudo-solid echoes can be generated whenever monomer units undergo nonisotropic motions, induced by the existence of topological constraints.

Such echoes are clearly detected along the nonexponential relaxation curves observed in swollen POT gels. Typical pseudo-solid echoes are plotted in Figure 3; they are above the transverse relaxation function obtained from the Carr−Purcell sequence. The relaxation function is mainly due to the protons located on octyl side chains which are more numerous that those located on the POT backbone. Therefore, the restriction of the diffusional motion of the polythiophene backbone due to cross-links leads to a restriction of the motion of the short side octyl chains attached to this backbone. Moreover, it is worth noting that although the relaxation rates are slow, pseudo-solid echoes are observed along the whole relaxation curve. Therefore, even the long tail of the relaxation (t > 30 ms) is not governed by the dynamics of monomer rotations but reflects the state

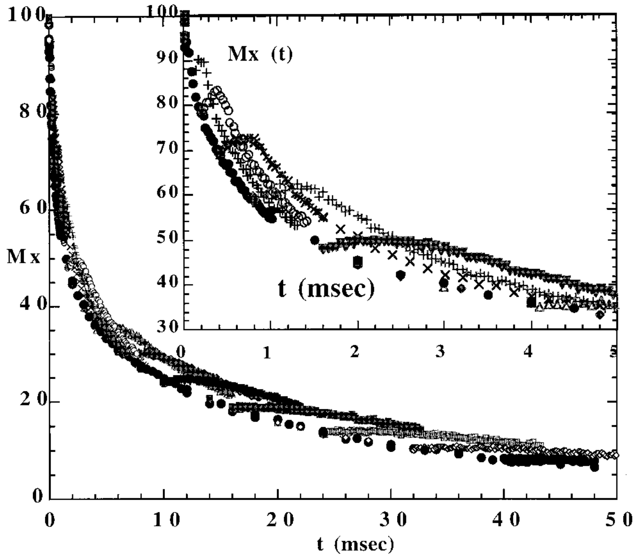


Figure 3. Transverse magnetization relaxation curve of a POT gel characterized by $R = 0.009$ and swollen at the maximum swelling degree with deuterated chloroform. Pseudo-solid echoes are generated at several times.

of average elongation of all elementary chain segments within the gel.

5.3. Analysis of the Relaxation Function. A specific treatment of transverse magnetic relaxation curves has been developed[16] by considering the two easily computable integrals

$$\phi_1 = \int_0^\infty \frac{M_x(t)}{\sqrt{t}}\,dt \qquad \phi_3 = \int_0^\infty \frac{1}{\sqrt{t}}\frac{dM_x(t)}{dt}\,dt \quad (5)$$

The parameter χ_c, homogeneous to a relaxation rate, is defined as the ratio ϕ_3/ϕ_1. It can be expressed as

$$\chi_c \propto \Lambda\langle N\rangle^{-2\nu} \quad (6)$$

where $\langle N\rangle$ is the number of skeletal bonds of elementary chain segments averaged over the whole sample. If the structural chain segment is the segment comprised between two successive cross-links $\langle N\rangle = N_{av}$. In this case, as in the case of vulcanizates prepared from the random cross-linking of long flexible polymer chains, the distribution of the number of skeletal bonds of chain segments defined by two consecutive cross-links may be broad and χ_c reflects the mean size of the gel constitutive segments. The exponent ν depends on the model used to describe the statistic of the chain segments. It is equal to $^1/_2$ for ideal linear segment chains (Gaussian chains) and $^3/_5$ for linear segments which obey excluded-volume statistics.

5.4. Experimental Results. The gels are observed in the state of maximum swelling. Variations of the corresponding NMR parameter χ_c^{sw} are plotted as a function of the product fR in Figure 4. Experimental points lie on a single straight line, as was the case for the NMR parameter χ_c^d measured in the dry molten state (see Figure 4). This result is interpreted as follows. One considers that the swelling process results from the disengagement of chain segments from one another although the exact nature of these active chain segments is not defined a priori. One can therefore picture the swollen structure as an ensemble of cells, each one being determined by a number of bonds whose average value over the whole sample is $\langle N\rangle_{sw}$. The observed master curve is then analyzed according to eq 6: (i) the active chain segments involved in the property of swelling and detected from NMR are the linear segments comprised between adjacent cross-links, i.e., $\langle N\rangle_{sw} = N_{av}$, (ii) the statistical framework is Gaussian, i.e., $\nu = {}^1/_2$. This statistical regime is likely due to the presence of a non uniform network which hinders the process of full disengagement of segments. Chain segments characterized by the mean segmental spacing N_{av} or dangling segments cross-linked only at one extremity may overlap partially, thus resulting in a screening of excluded volume effects.

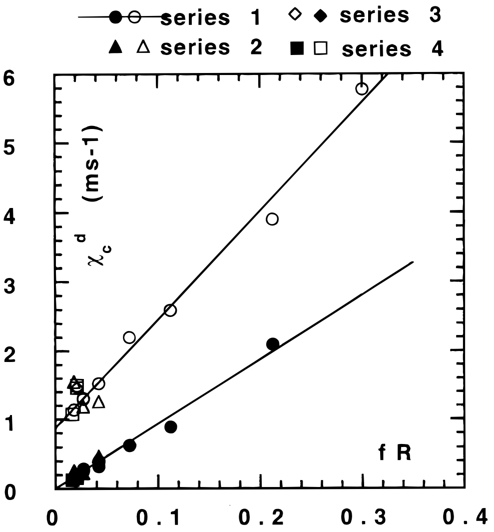


Figure 4. Linear dependence with fR of the NMR structural parameter observed in dry gels χ_c^d (open symbols) and in the swollen state χ_c^{sw} (filled symbols).

It was shown in ref 6 that swollen gels could be pictured as a packing of swollen domains which obey a Gaussian statistics. The swelling ratio could therefore be expressed as $Q \propto N_{av}^{1/2}$. This result is confirmed in this study. Moreover, combination of equation $Q \propto N_{av}^{1/2}$ with eq 6 yields $\chi_c^{sw} \propto Q^{-2}$. Such a relationship was already observed in several long polybutadiene,[17] poly(dimethylsiloxane)[18] and polyethylene[19] chains cross-linked at random whereas elementary chain segments of gels formed from end-linked calibrated polymer precursor obey excluded volume statistics.[20] The similarity of the behavior of POT gels (prepared from random copolymerization of small units) with that of randomly cross-linked elastomers may be due to the fact that these systems are all characterized by a broad distribution of the segmental spacing between adjacent cross-links and the presence of dangling ends in the network structure.

6. Discussion

The main features about experimental results concern the linear relationships obtained between the elastic modulus E, χ_c^d observed from unconstrained dry molten gels, χ_c^{sw} determined from fully swollen gels and the inverse of the mean number of skeletal bonds between consecutive cross-links fR. First, these results strongly corroborate the existence of active network chain segments associated with a given state of gelation and which govern both properties of elasticity and swelling. Second, these results suggest that these segments are the linear strands comprised between adjacent cross-links which are characterized by the average number $N_{av} = 2/fR$. Moreover, these chain segments active both for swelling (detected from NMR in the swollen state) and for elasticity are the same that those detected from NMR on the non deformed gel. It can be therefore considered that the regime of fluctuations that occur in the unconstrained elastomer and which define the elementary chain segments are involved in the elastic response of stretched gels and in the swelling process.

The linear relations between E, Q, and fR are expected to be valid only for gels prepared far enough from the gelation threshold ($fR \gg fR_c$). Indeed, the elastic modulus and the swelling ratio go to zero at the threshold and, close to it, these quantities are known to depend only on the deviation from the gelation threshold which is a function of $fR - fR_c$ and not a function of the single variable fR. In other terms, it is well-known that close to the gel point the active segments of a gel which determine the gel mesh size are large branched chains whose size diverges at the threshold although the mean distance between cross-links, equal to $2/fR_c$, does not diverge. However, the relevant variable $fR - fR_c$ reduces to a function of fR when $R \gg R_c$. The observed proportionality of E vs $1/fR$ therefore indicates that the POT gels studied here are prepared far enough from the threshold so that the gel mesh size is defined by the small linear strands between cross-links. This behavior is similar to that observed for well-connected end-linked gels.

The value of $\chi_c^d(0)$ extrapolated when the cross-link density $R = 0$ is not equal to zero. It reveals the presence of topological constraints in addition to those induced by the covalent cross-links. Among these constraints are slipping links and entanglements which are known to form temporary network structures specific of molten high polymers. Such temporary networks are detected from NMR when the rate of dissociation of these constraints is smaller than the residual dipole−dipole interaction of protons. $\chi_c^d(0)$ is related to the mean size of elementary segments associated with these additional constraints. These structural segments are however not trapped in the cross-linked structure. Indeed, when the gels are fully swollen the NMR structural parameter χ_c^{sw} goes to zero with fR. This result shows that the solvent which separates the chain segments from on another frees all the constraints which are not due to covalent cross-links. The parameter χ_c^{sw} is therefore sensitive only to the chain segments determined by covalent cross-links.

The linear relations of E, χ_c^d, and χ_c^{sw} vs fR lead to the existence of a linear relation between E and χ_c^d. Such a law between E measured on deformed gels and χ_c^d measured on nondeformed dry gels have been already experimentally observed and reported for polymer networks cross-linked at random.[17,21] Even more interesting is the resulting direct proportional law observed between the NMR structural parameter determined in the swollen state χ_c^{sw} and the elastic modulus E. This latter law is illustrated in Figure 5. It is worth emphasising that such a relationship relates in a linear direct way a microscopic NMR parameter measured in a isotropically swollen gel to a macroscopic elastic modulus measured on a dry stretched sample.

7. Doped Gel in the Swollen State

We report qualitative results concerning swelling in the doped state of the sample obtained from 1,3,5 trithienylbenzene ($f = 3$) with a cross-link ratio R equal to 0.006. In the dry state, the sample of was black. A small piece of the sample (0.1 mm thickness) was put on a cover glass and observed by optical microscopy. First, the sample was allowed to swell in an excess of chloroform (with respect to the amount required to reach the equilibrium swelling). The gel became red and its volume increased drastically. Then, a volume v of a solution of iodine in chloroform was added: v corresponded to the amount of iodine required for a doping ratio of 30% assuming the presence of I_3^- after doping. The addition of the iodine solution resulted in a small shrinkage of the volume of the swollen sample (approximately 30%) and in a change in the color (the sample became black) Nevertheless, the volume of the doped sample in chloroform remained significantly higher than that of the unswollen undoped one. Furthermore, the doped sample swollen in chloroform exhibited rubber elasticity and significant conductivity. Figure 6 shows photographs of the sample (magnification of 10) in the three different states: dry (a), swollen doped (b), and swollen undoped (c). No change in the color of the doped swollen gel was observed after several hours. This result suggests that no significant dedoping occurred during this time.

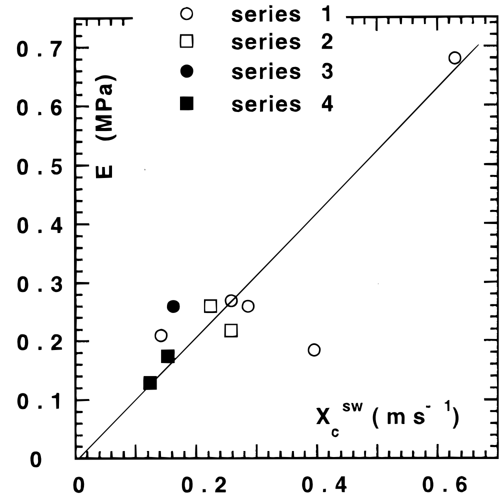
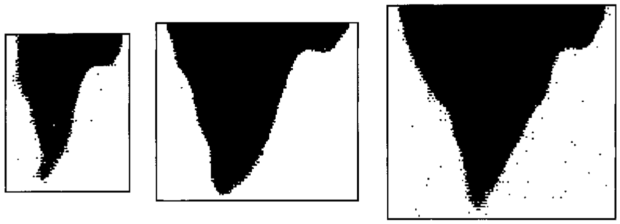


Figure 5. Variation of the modulus of elasticity E vs the NMR structural parameter χ_c^{sw} determined in the swollen state.



dry gel undoped

swollen doped gel

swollen undoped gel

Figure 6. Photographs of the same piece of a POT gel (R = 0.006) in three distinct states: dry (a), swollen doped (b), and swollen undoped (c). As it is shown on the photograph (b) the gel remains swollen after doping. A decrease of the swelling ratio of about 30% is observed upon doping.

8. Conclusion

We have shown that POT gels exhibit the behavior of elastomers. They present rubber elasticity with an elastic modulus of the order of that of high polymer gels and they swell in good solvent. The statistical structure of these gels prepared in the range $fR_c \ll 0.016 < fR < 0.2$ is determined from the size of linear chain segments comprised between cross-links. These segments which are perceived from NMR measurements in the dry molten state control elastic and swelling properties. Their regime of fluctuations also detected from NMR is described within a Gaussian framework in both dry and swollen states. A direct relationship is therefore evidenced between the local microscopic NMR probe and the two macroscopic quantities elastic modulus and swelling ratio.

This work was a necessary step permitting to find a variable which characterizes the statistical structure of these gels in order to understand their mechanisms of macroscopic deformation due to stretching and swelling. Moreover, we have obtained in this work conducting doped gels in the swollen state. This opens the way to the study of conducting properties in 3D gels for which the conducting paths coincide with the polymer chain segments, that is to say when hopping of electrons from one chain segment to another is limited due to the solvent acting as a chain separator. The texture of swollen doped gel is rubberlike, thus suggesting the existence of large conformational fluctuations in this state which make possible electromechanical effects. However, the regime of fluctuations may be drastically different from the Gaussian one since chain segments are expected to exhibit more rigid conformations which favor electronic delocalization. This work is under study at the present time.

Acknowledgment. We thank M. Abkarian for his help in optical video microscopy.

References and Notes

(1) Fizazi, A. *Phys. Rev. Lett.* **1990**, *64*, 2180.

(2) De Gennes, P. G. *C. R. Acad. Sci., Paris* **1986**, 302 Série II, No. 1.1.

(3) Rebourt, E.; Pépin-Donat, B.; Dinh, E.; Nechtschein, M. *Synth. Met.* **1995**, *69*, 293.

(4) Rebourt, E.; Pépin-Donat, B.; Dinh, E. *Polymer* **1995**, *36*, 399.

(5) Rebourt, E.; Pépin-Donat, B.; Dinh, E. *Synth. Met.* **1995**, *69*, 291.

(6) Viallat, A.; Pépin-Donat, B. *Macromolecules* **1997**, *30*, 4679. Pépin-Donat, B.; Viallat, A.; Rebourt, E.; Bras, J. *Synth. Met.* **1999**, *102*, 1506.

(7) Pépin-Donat, B.; Lairez, D.; de Geyer, A.;Viallat, A. *Synth. Met.* **1999**, *101*, 471.

(8) Viallat, A.; Pépin-Donat, B. *Synth. Met.* **1999**, *101*, 122.

(9) Sixou, B.; Pépin-Donat, B.; Nechtschein, M. *Polymer* **1997**, *38*, 1581.

(10) Pépin-Donat, B.; de Geyer, A.;Viallat, A. *Polymer* **1998**, *39*, 6673.

(11) Pépin-Donat, B.; Sixou, B.; de Geyer, A.; Viallat, A.; Won Fah Hin, L. *J. Phys. Chem.* **1998**, *95*, 1225.

(12) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, England, 1975.

(13) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(14) Kuhn, W. *Kolloid Z.* **1939**, *87*, 3.

(15) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley: New York, 1980.

(16) Cohen Addad, J. P. *NMR and Fractal Properties of Polymeric Liquids and Gels*; Pergamon Press: Oxford, England, 1993. Cohen-Addad, J. P. *Physical Properties of Polymeric Gels*; Cohen Addad, Ed.; John Wiley & Sons: New York, 1996.

(17) Cohen Addad, J. P.; Soyez, E. *Macromolecules* **1992**, *25*, 6855.

(18) Cohen Addad, J. P.; Montes, H. *Macromolecules* **1997**, *30*, 3678.

(19) Viallat, A.; Cohen-Addad, J. P.; Cassagnau, P.; Michel, A. *Polymer* **1995**, *37*, 555.

(20) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979. Cohen Addad, J. P. *Phys Rev. B* **1993**, *48*, 1287.

(21) Cohen Addad, J. P.; Phan Thanh, B.; Montes, H. *Macromolecules* **1997**, *30*, 4374.

MA000211O