Topological Polymer Networks with Sliding Cross-Link Points: The “Sliding Gels”. Relationship between Their Molecular Structure and the Viscoelastic as Well as the Swelling Properties

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Received March 7, 2006; Revised Manuscript Received December 6, 2006

ABSTRACT: Topological polymer networks with sliding cross-link points, the “sliding gels” (also called slide-ring gels), are a new class of supramolecular networks based on intermolecularly cross-linked α-cyclodextrins/poly(ethylene glycol) polyrotaxane precursors. The cross-link points of such networks are not fixed but can slide along the template chain of the polyrotaxanes. The main parameters governing the sliding gel properties are the number of cyclodextrins per polyrotaxane, the cross-linking density, and the nature of the swelling solvent. Small-angle neutron scattering, swelling measurements, and mechanical spectrometry were used to understand the unusual physical properties and their relation to the molecular structure of the sliding gels. The swelling as well as the viscoelastic properties are found to be solvent dependent reflecting the structural changes of the network. Indeed, in water, the number of cross-link points (topological and physical) increases as opposed to dimethyl sulfoxide (DMSO) leading to higher modulus values, while the persistence length of the sliding gel strands increases in DMSO as opposed to water leading to a shift of the tan(δ) peak, the transition point between the two observed viscoelastic regimes, toward higher frequencies.

1. Introduction

Polymer gels are often classified following the type of cross-link points. Until recently only two main classes of polymer gels have been considered: the one with chemical bonds (permanent cross-link points) and the other with physical bonds (reversible cross-link points). A novel class of gel materials, so-called topological network, has been recently proposed by de Gennes[1] and was characterized by the sliding character of the cross-link points (also called slide-ring cross-link points). The topological network architecture is obtained by the intermolecular cross-linking reaction of precursor polyrotaxanes.[2−5] The main characteristic of the sliding cross-link points is to allow a sliding motion of the constitutive template network chains through the figure-of-eight junctions. The sliding network architecture was, for the first time, experimentally realized by the use of high molecular weight polyrotaxanes, with chemical structures based on α-cyclodextrin macrocycles (α-CDs) threaded along a template poly(ethylene glycol) (PEG)[6−8] and their intermolecular bridging with a cross-linker through the hydroxyl groups of the α-CDs, forming thus the cross-linking network points in the form of figure-of-eight. Figure 1 shows schematically the molecular architecture of the studied gels where only few α-CDs participate to the formation of the cross-link points. The sliding gels are expected to have unusual chemical, physical, and mechanical properties due to the theoretical ability of the cross-linking points to slide along the template polymer chain.

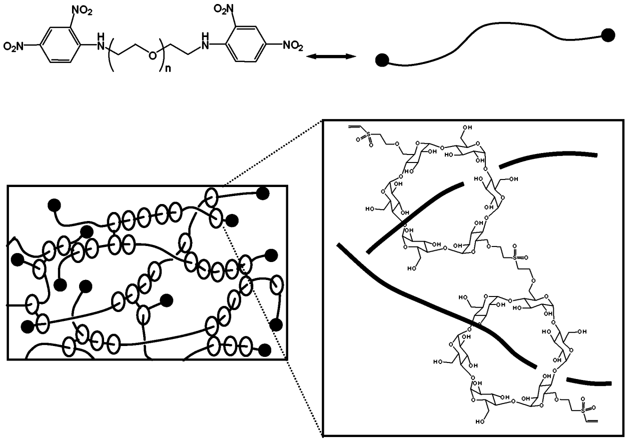

Figure 1. Schematic representation of the molecular architecture of a sliding gel obtained by reaction between α-CDs/PEG polyrotaxanes and divinyl sulfone.

Three pertinent parameters governing the unusual properties of this new class of topological materials are the complexation degree, N, defined as the number of α-CDs per template PEG chain, the cross-linker fraction, K, defined as the ratio of the mole number of cross-linker, n_c on the mole number of α-CDs, n_{CD} and the interactions between the swelling solvent and the constitutive parts of the network.

The aim of this work was to systematically study the physical, chemical and mechanical properties as well as their relation to the molecular structure of this new class of topological networks as a function of the three previously mentioned parameters governing their structure. For this study swelling measurements,

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10.1021/ma0605043 CCC: $37.00 © 2007 American Chemical Society
Published on Web 01/13/2007

small-angle neutron scattering (SANS) and mechanical spectrometry were used.

2. Experimental Section

2.1. Synthesis of the Sliding Gels. The preparation of the polyrotaxane precursors and the formation of the sliding gels are reported in the Supporting Information section and have been extensively described in previous publications.[5,9]

2.2. Methods and Measurements. ^{1}H NMR Measurements. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Bruker 300 Ultrashield 300 MHz with an internal lock on the ^{2}H-signal of the solvent. The complexation degree was determined by comparison of the integrations of the CH-1 signal of α-CD at 4.8 ppm to the signal between 3.4 and 3.9 ppm, which corresponds to CH-3, CH-6, and CH-5 of α-CD and the CH_2 of the BA-PEG.

Swelling Measurements. The swelling degrees (S) were determined by a gravimetric technique, and the calculations were based on the gel weight according to the equation

$$S\,(\%) = \frac{W_S - W_D}{W_D} \times 100 \tag{1}$$

where W_S and W_D are, respectively, the weights of the swollen and dried gel.

For SANS study, the swelling volume ratio (Q) was determined by a volumetric technique and calculated according to the following equation:

$$Q = \frac{V_S}{V_D} \tag{2}$$

V_S and V_D are, respectively, the volumes of the swollen and dried gel.

These experiments were realized in distilled water and DMSO and the swelling capacity of the gels was measured at room temperature (22 ± 1 °C). For the weight measurements of completely swollen gels, the excess of water or DMSO on the surface of the gel was wiped off with filter papers. The dried gels measurements were obtained after 48 h in an oven at 50 °C.

Small-Angle Neutron Scattering Measurements. SANS measurements were carried out at the Laboratoire Léon Brillouin (LLB, CEA, Saclay, France) and at the Institut Laue-Langevin (ILL, CEA, Grenoble, France). The use of these two diffractometers allows the study of the sliding gels by SANS on a large range of scattering vectors q. The PAXY instrument was used at the LLB to study the sliding gels structure in the intermediary domain. The sample-to-detector distance was fixed at 5 m with a wavelength of $\lambda = 12$ Å (5×10^{-3} Å^{-1} < q < 4×10^{-2} Å^{-1}). Absolute intensities corrected for detector sensitivity were obtained by normalization to the scattering from Plexiglas with reference to the direct beam. For the sliding gels study at very low q, the D11 diffractometer at the ILL was used using an incident wavelength of $\lambda = 12$ Å. The sample-to-detector distance was prone to 36.7 m and the resulting q range explored was 7.4×10^{-4} Å^{-1} < q < 6.7×10^{-3} Å^{-1}. The scattered neutron intensity calibration was performed using the signal from a 1 mm thick water sample. Heavy water (D_2O) was used as swelling solvent during all the experiments. The sample cell for all experiments on the PAXY and D11 diffractometers consisted of 1 mm thick quartz windows separated by a 2.5 mm O-ring. Corrections for incoherent background, detector response and cell window scattering were applied to all measurements.

Dynamical Mechanical Measurements. The experimental setup used is a Rheometrics-RSA II strain controlled spectrometer. This RSA II spectrometer is equipped with one normal force transducer (1kFRT) that can detect normal forces within the range 0.001−10 N. The instrument is equipped with a STD motor having a strain resolution of 0.05 μm and an angular frequency range between 10^{-3} and 100 rad·s^{-1}. The configuration chosen for mechanical spectrometry was the parallel plates configuration. The samples (typically, diameter of 12.75 mm and thickness of 3 mm) were immersed in distilled water or DMSO during all the experiments in order to maintain the same state of solvent content in the material, thus avoiding sample drying and deswelling during the time of the experiments. Mechanical spectrometry was carried out at angular frequencies from 0.001 up to 100 rad·s^{-1} with a strain amplitude of 2.5%. A pre-strain of 5% was applied to the sample before the start of the test in order to ensure that the sample was always in compression during the experiments.

3. Results

The physical, chemical and mechanical properties of the topological networks and their relation to their molecular architecture, which is governed by the complexation degree N and the cross-linker fraction K were recognized in an earlier work.[5] These promising results led us to consider a more systematic study of the properties and the internal structure of the sliding gels as a function of these two relevant parameters. Moreover a third parameter had to be considered in order to properly apprehend the molecular mechanisms underpinning the sliding gels in view of their topological architecture: the swelling solvent quality. Hence the swelling behavior of the sliding gel as a function of two different kind of swelling solvents (one poor (H_2O) and one good solvent (DMSO) of the polyrotaxane precursors) has been studied to understand the network/solvent interactions and their influence on the molecular structure of the sliding gel.

For this purpose polyrotaxane precursors with a well-defined degree of complexation N have been synthesized according to the procedure reported previously.[9] These syntheses allowed us to obtain polyrotaxanes with a controlled N by varying the initial ratio R_0 between the α-CDs and PEG and the thermal cycle during the complexation process. The complexation degree N of each polyrotaxanes used in this work was in the range 22−90 as reported in the Supporting Information. The intermolecular cross-linking reaction between the polyrotaxane chains was carried out with divinyl sulfone (DVS) as cross-linking agent according to the procedure already described.[5] More precisely the topological cross-link points were formed by bridging, via the DVS molecule, the hydroxyl groups of two α-CDs threaded on different polyrotaxanes. This reaction allowed us to synthesize swollen topological networks of polyrotaxanes. By control of the cross-linking density, soft to hard sliding gel materials could be obtained. The degree of cross-linking density is related to the cross-linker fraction K defined following the equation

$$K = \frac{n_C}{n_{CD}} \tag{3}$$

where n_C and n_{CD} are, respectively, the cross-linker and α-CDs mole numbers introduced in the pregel solutions.

All characteristics of the sliding gels prepared for this study are reported in the Supporting Information. For the rest of this study, the sliding gels are denoted by GxRy, where x represents the complexation degree N and y the volume V in microliters of cross-linker incorporated in the pregel solution.

3.1. Influence of Cross-Linker Fraction K in Water. In Figure 2, the influence of the cross-linker fraction ($3.25 \le K \le 9.43$) as a function of the swelling degree S in water of several sliding gels prepared from polyrotaxanes with different complexation degrees ($22 \le N \le 80$) is presented. For all the sliding gels, the swelling behavior shows the same tendencies with the cross-linker fraction K. Two swelling regimes appear with increasing cross-linker fraction K in water. For low K, a quasi-linear decrease of the swelling degree is observed. The highest swelling degree for these sliding gels is reached for the G80R40

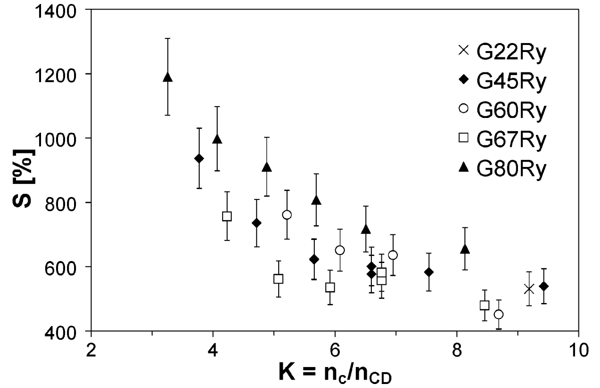

Figure 2. Influence of the cross-linker fraction *K* on the swelling degree *S* in water: (×) G22R*y*; (◆) G45R*y*; (○) G60R*y*; (□) G67R*y*; (▲) G80R*y*.

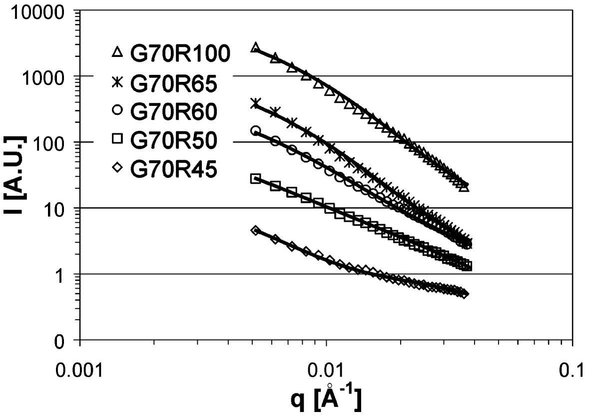

Figure 3. Neutron scattering functions and their fitting curves for sliding gels prepared from a 70 α-CDs polyrotaxane precursor with different cross-linker fraction *K*: (◇) G70R45 (*K* = 3.76); (□) G70R50 (*K* = 4.18); (○) G70R60 (*K* = 5.02); (×) G70R70 (*K* = 5.86); (△) G70R100 (*K* = 8.37).

Table 1. Correlation Lengths, ξ and Ξ, for the G70R*y* Obtained from the Form Factor (4)

	ξ (Å)	Ξ (Å)
G70R45	65	850
G70R50	65	790
G70R60	58	700
G70R70	53	675
G70R100	50	610

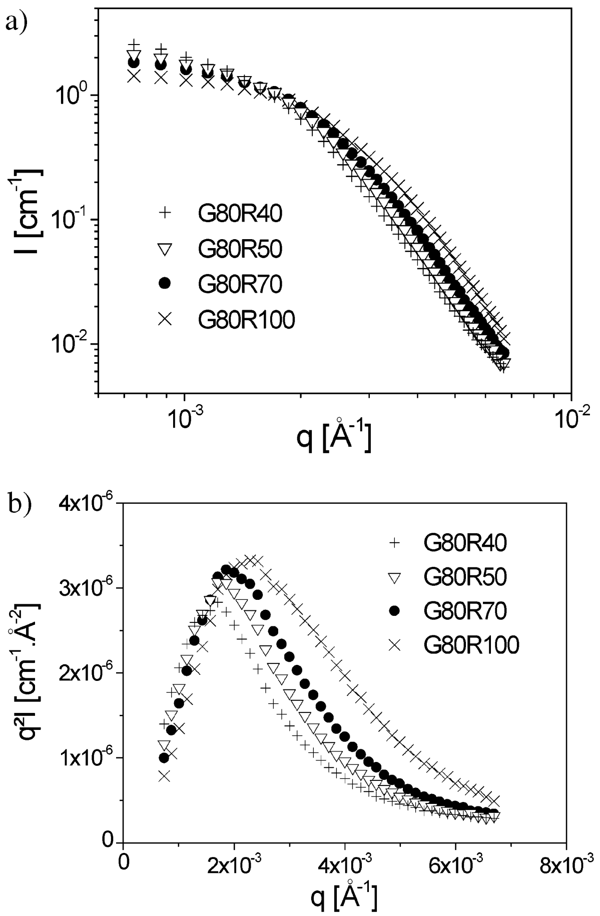

Figure 4. Neutron scattering functions for the G80R*y*: (+) G80R40 (*K* = 3.25); (▽) G80R50 (*K* = 4.07); (●) G80R70 (*K* = 5.69); (×) G80R100 (*K* = 8,13). Key: (a) *I*(*q*) = *f*(*q*); (b) Kratky plot $q^2I(q) = f(q)$.

gel with *S* about 1200%. For higher *K*, a quasi-stationary regime is achieved with a plateau close to 500% for all sliding gel series.

Small-angle neutron scattering (SANS) on the PAXY diffractometer at LLB was performed in a series of the sliding gels with increasing cross-linker fraction. The experiments were done with sliding gels in an isotropic equilibrium swollen state in D_2O as swelling solvent and in a *q* range visualizing the network mesh size as well as large structural heterogeneities. In Figure 3, the SANS data obtained for sliding gels series G70R*y* are presented. The scattering intensities of the sliding gels are clearly dependent on the cross-linker fraction *K*. With increasing *K*, the scattering intensities increase. Moreover an excess of scattering intensities is also observed for the lowest *q* values. This result is attributed to the presence of large heterogeneities: the so-called Benoît−Picot effect.[10] The fitting of the scattering intensities with a single squared Lorentzian function was not possible for the lowest *q* because of the excess scattering, a signature of large structural heterogeneities in the swollen network. In an attempt to relate the scattering data with the molecular structure of swollen gels with large structural heterogeneities, the form factor (eq 4) developed by Mallam et al.[11,12] has been adopted. This form factor introduces two scattering contributions: a Lorentzian, $I_F(q)$, comparable to that of semidilute solutions and a stretched exponential representing a "solidlike" contribution, $I_S(q)$, arising from the static fluctuations due to the structural heterogeneities in the gel.

$$I(q) = I_S(q) + I_F(q) = I_S \exp(-(q\Xi)^{0.7}) + \frac{I_F}{1 + q^2\xi^2} \quad (4)$$

where the correlation lengths ξ and Ξ are associated with a molecular characteristic correlation length of the topological network and a characteristic correlation length related to the heterogeneity size respectively.

In Table 1, a summary of the fitting of the SANS data is presented. The correlation length ξ was found to have values ranging from 65 to 50 Å for the less to the most cross-linked gels respectively and is related to the persistence length of the network. The correlation length Ξ also depends clearly on the cross-linker fraction *K*. It was found in the range 850−610 Å for the less to the most cross-linked gels respectively and corresponds to the characteristic length scale of the large structural heterogeneities. It clearly appears that the correlation lengths ξ and Ξ decrease with increasing *K*, implying that the mesh size as well as the distance between the heterogeneities decreases (i.e., the density of heterogeneities increases) with an increase in the cross-linking density of the network.

In Figure 4, the SANS data obtained for sliding gels series G80R*y* in D_2O as swelling solvent and in a very low *q* range

Table 2. Experimental Data for the G80R*y* Sliding Gels

	n_C (mmol)	K	Q	$I(q \to 0)$ (cm^{-1})	q_{max} (Å^{-1})	D_{app} (Å)	R_P (Å)
G80R40	0.4	3.25	12.90	3.92	2.29×10^{-3}	4480	2240
G80R50	0.5	4.07	10.97	3.03	2×10^{-3}	4120	2060
G80R70	0.68	5.69	9.08	2.21	1.86×10^{-3}	3830	1915
G80R100	0.95	8.13	7.55	1.66	1.71×10^{-3}	3350	1875

(7.4×10^{-4} Å^{-1} $\leq q \leq 6.7 \times 10^{-3}$ Å^{-1}) are presented. For the highest scattering vector region (Figure 4a), the scattering intensity increases with increasing K, a similar behavior observed with the series of G70R*y* gels. In this very low q range a crossover in the scattering intensities with a value close to $q = 1.7 \times 10^{-3}$ Å^{-1} was observed. For q values beyond this crossover point, the tendency of the scattering intensities are reversed with respect to cross-linking densities of the network and the lowest cross-linked system scatters more. This observation is attributed to the swelling degree evolution with the cross-linking density of the network. Previously, in the case of nontopological swollen gels including heterogeneities, Bastide et al.[13] have shown that the scattering intensity for $q \to 0$ is directly related to the volume concentration of elementary strands and to the concentration differences between strongly cross-linked zones (the heterogeneities named frozen aggregates) and the homogeneous matrix of the network. Assuming this treatment is valid in the case of topological swollen gels, we can transpose this analysis to the sliding gels. In topological networks with heterogeneities, this dilution effect, produced by increasing the swelling degree, leads to an increase of the concentration fluctuations between the frozen aggregates and the homogeneous network matrix. This effect is more pronounced for the low cross-linked sliding gels and explains the higher level of scattering intensity at $q \to 0$ for the sliding gels exhibiting the highest swelling degrees. Moreover a second contribution must be taken into account to explain fully the observed scattering intensities with increasing K at $q \to 0$. At low q values, the spatial correlations between the heterogeneities become weaker. Thus, the scattering contribution due to the heterogeneities in the total scattering intensity is weaker at $q \to 0$. In order to rationalize these observations, a scaling law (eq 5) was proposed by Bastide et al.[13] and Daoud et al.[14] to correlate the volume concentration of elementary φ strands (or the volume swelling ratio Q) with the scattering intensity for $q \to 0$:

$$I(q \to 0) \propto \varphi^{-t} \propto Q^{t} \tag{5}$$

where $I(q \to 0)$ is the experimental scattering intensity for $q \to 0$.

In Table 2, the summary of the experimental data for the sliding gel series of G80R*y* is presented, and Figure 5 shows the correlation between the scattering intensity for $q \to 0$ and the swelling ratio Q. The exponent of the scaling law is comparable to that observed before for chemical cross-linked gel systems[15] and corresponds fairly well with the theoretical exponent value of 5/3 predicted by Daoud et al.[14] The high value of this exponent reveals the dilution effects for gels with a high swelling capacity. In Figure 4b a treatment of the scattering data for the gel series of G80R*y* in the Kratky representation is presented. A correlation peak is observed for a scattering vector value q_{max} which is attributed to a characteristic correlation length related to the density fluctuations in the sliding gel. The position of the correlation peak has an obvious relationship with the cross-linker fraction K. With decreasing K, the correlation peak is shifted toward the low q values. In fact the observed maximum is due to the presence of heterogeneities in the form of particles the size of which decreases with increasing K. Several previous workers[16−18] used the Guinier and Fournet[19] analysis to obtain an indication for the inter-particle distances D_{app} between the heterogeneities. Strictly speaking this treatment is only valid for uniform spherical particles on a face-centered cubic lattice. Indeed, the average distance between the centers of the particles was correlated with the q_{max} position according to the equation

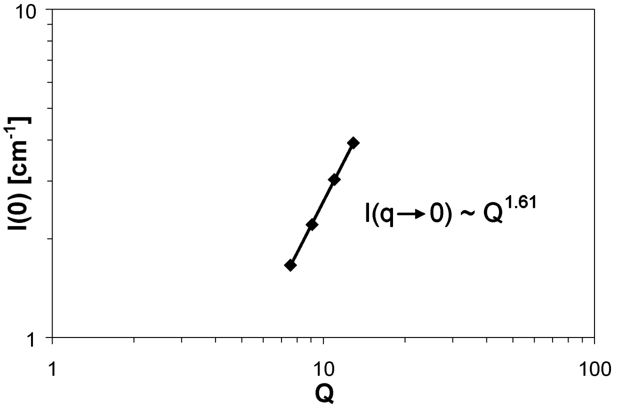

Figure 5. Scaling law $I(0) = f(Q)$ established for G80R*y* sliding gels.

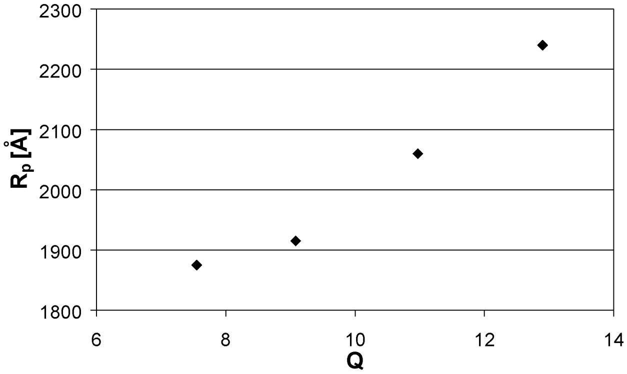

Figure 6. Evolution of the particles radii R_P with the swelling ratio Q for the G80R*y*.

$$D_{app} = 1.22\left(\frac{2\pi}{q_{max}}\right) \tag{6}$$

where D_{app} is the average distance between the centers of the particles.

A reasonable approximation in estimating the radii of the particles, R_P, is to consider them being equal to $D_{app}/2$. In Table 2 are reported the results obtained according to the approximation above. The values of R_P indicate the presence of clusters of highly physically cross-linked polyrotaxane chain stacks formed via the hydrogen bonds between the α-CDs. The size of these clusters is directly related to the increase of the cross-linker fraction which prevents the swelling of these clusters by the solvent. These arguments can be confirmed by the results presented in Figure 6, where the variation of R_P with the swelling ratio Q of the studied sliding gels clearly shows the cross-linker fraction effect on the swelling ability of the heterogeneities. Indeed, the higher K is, the lower the swelling ratio Q of the sliding gel.

The mechanical spectrometry in compression was performed in order to evaluate the cross-linker fraction influence on the viscoelastic properties of these topological materials. Figure 7

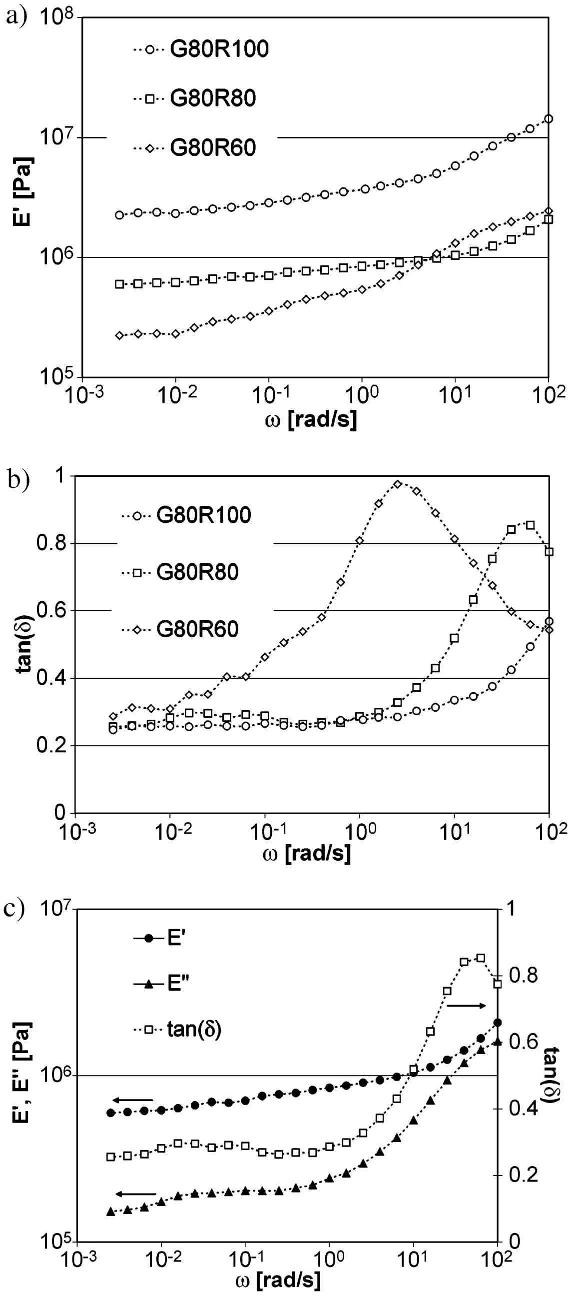

Figure 7. Frequency sweep tests for the G80R*y* sliding gels in water. (a) E' vs ω: (◇) G80R60; (□) G80R80; (○) G80R100. (b) tan(δ) vs ω: (◇) G80R60; (□) G80R80; (○) G80R100. (c) Viscoelastic spectra of G80R80: (●) E'; (▲) E''; (□) tan(δ).

shows the viscoelastic spectra for the G80R*y* sliding gels series. With increasing *K*, the elastic and loss moduli increase but the frequency dependence of the moduli appears more complex. In Figure 7c, the E' and E'' do not show a unique plateau but rather two corresponding to two different viscoelastic regimes. The transition between these regimes is clearly observable with the loss angle δ evolution with a pronounced tan(δ) peak at the transition region (see Figure 7b). It can be noticed that, with an increase in the cross-linker fraction *K* and thus the cross-linking density, the transition shifts from a low to a higher frequency even though the global moduli values are higher. These experimental observations have been found on all the tested sliding gels whatever the polyrotaxane complexation degree *N* was.

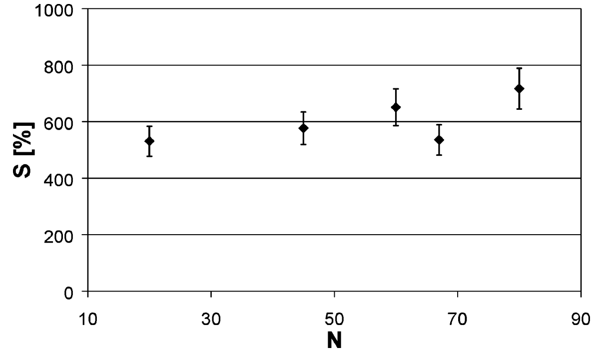

Figure 8. Influence of the complexation degree *N* on the swelling degree *S* in water of the sliding gels G*x*R70 at a fixed cross-linker volume $V = 70$ μL.

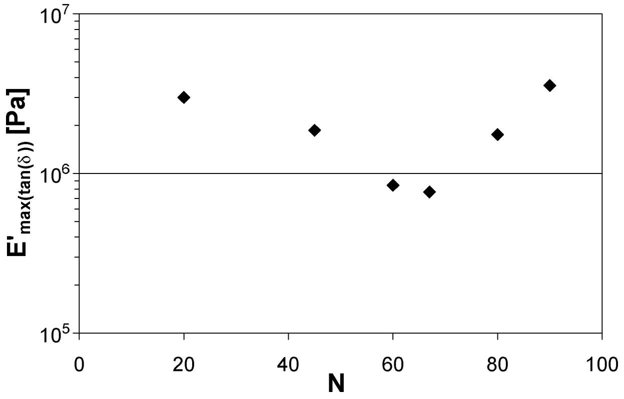

Figure 9. $E'_{\max(\tan(\delta))}$ vs complexation degree *N* for G*x*R70 in water.

3.2. Influence of the Complexation Degree *N* in Water. The complexation degree *N* is another parameter for the conformation of the polyrotaxanes and as a consequence also for the properties of the sliding gels. Assuming that two monomer units of BA-PEG are covered by one α-CD,[20] the complexation degrees for the polyrotaxanes used in this study are in the range of 10% to 35% with respect to the theoretical full coverage for a template BA-PEG chain of 20 kg mol^{-1}. In fact, the increasing complexation degree, *N*, plays a considerable role in the conformation evolution of the polyrotaxane precursor chain going from a Gaussian chain behavior (low *N*) with excluded volume to a rodlike chain (high *N*) with a high persistence length.[9] It should be expected that sliding networks synthesized with polyrotaxane precursor chains with various complexation degrees will lead to topological network materials with different viscoelastic properties and various swelling behaviors. However the swelling degree *S*, for a given weight fraction $\Phi = 0.15$ of the gel, appears to be slightly dependent on the complexation degree *N* as shown in Figure 8. This unexpected result can be attributed to the high level of cross-linking density of the series of gels studied in this work which have been designed for viscoelastic characterization experiments. The high level of cross-linking density seems to overshadow the influence of the complexation degree on the swelling behavior of the sliding gels.

The influence of the complexation degree on the sliding gels viscoelastic properties was also explored by mechanical spectrometry. Dynamical frequency sweep experiments in compression were carried out in order to evaluate the $E'_{\max(\tan(\delta))}$ which was defined as the elastic moduli value at the tan(δ) peak. $E'_{\max(\tan(\delta))}$ is related to a specific dynamic state of the sliding network and allows to describe the same state of relaxation for all sliding gels studied. Figure 9 shows $E'_{\max(\tan(\delta))}$ vs the complexation degree *N* for six sliding gels prepared with a cross-linker mole number $n_C = 0.7$ mmol. The $E'_{\max(\tan(\delta))}$ values at

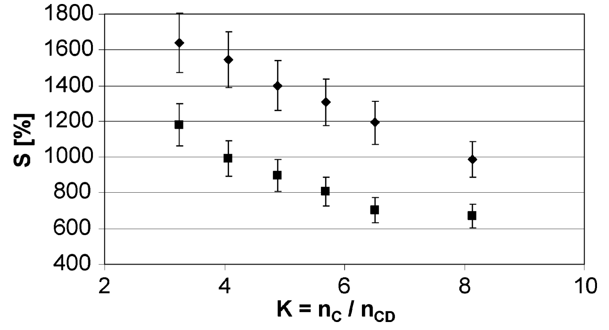

Figure 10. Swelling degree *S* evolution with regard to the cross-linker fraction *K* for the G80R*y* in water (■) and DMSO (◆).

constant cross-linker mole number do not follow a monotonous dependence with the complexation degree *N*. An experimental minimum was observed for a complexation degree $N = 67$ and is attributed to two antagonist effects. With increasing *N*, the number of topological cross-link points decrease due to more probable intramolecular bridging between the α-CDs threaded on a same polyrotaxane while the persistence length of the network strands increases due to the formation of molecular channels promoted by this intermolecular chemical bridging and the physical interactions between the α-CDs belonging to the same template chain. Thus, on one hand the average number of the cross-link points is higher at low complexation degree leading to high moduli levels. On the other hand, the formation of α-CD tubes around the template chains is promoted with the increase of *N*, leading to an increase of the rigidity of the elementary elastic strands of the sliding network, resulting to higher moduli levels.

3.3. Influence of the Cross-Linker Fraction *K* in DMSO. The influence of solvent on the polyrotaxanes conformation is also noticeable. Karino et al.[21] have shown that the conformation of the same polyrotaxane in sodium deuteroxide (NaOD) is characterized by a Gaussian conformation with excluded volume while in DMSO-d_6 the polyrotaxane chain adopts a more rigid rodlike conformation. This difference was rationalized by the fact that the electrostatic repulsions between charged α-CDs present in NaOD prevent thus the attractive interactions and as a consequence hinder the establishment of α-CDs transient tubes around the template chain. It should be expected that this polyrotaxane conformation could be preserved on the sliding gels synthesized with the same polyrotaxane precursor chains when swollen in different solvents having each a different quality with the polyrotaxane chain.

Figure 10 shows the swelling degree *S* of the G80R*y* sliding gels series for various *K* in distilled water and in DMSO. The swelling degree *S* appears higher in DMSO than in water and reaches values almost twice as high in the region of low *K* sliding gels. Two viscoelastic regimes, separated with a transition marked by tan(δ) peak, are observed in DMSO as well (Figure 11). Furthermore, increasing the cross-linker fraction *K* leads to the same tendencies as in water: (i) an increase of the complex moduli; (ii) a shift of the tan(δ) peak toward the highest frequencies. Nevertheless, as compared to measurements in water, the behavior in DMSO has shown much lower moduli and a tan(δ) peak shift toward the lower frequencies. The two viscoelastic regimes found in DMSO are characterized by two plateaus for E' as already observed in water. However, as opposed to E'' behavior observed in water, E'' increases monotonically in DMSO at low frequecies until a maximum corresponding to the transition between the two viscoelastic regimes. This original behavior, as previously reported,[22] is more pronounced for the less cross-linked gels where the E'' power law dependence is close to the value 1, characteristic of low viscous dissipations.

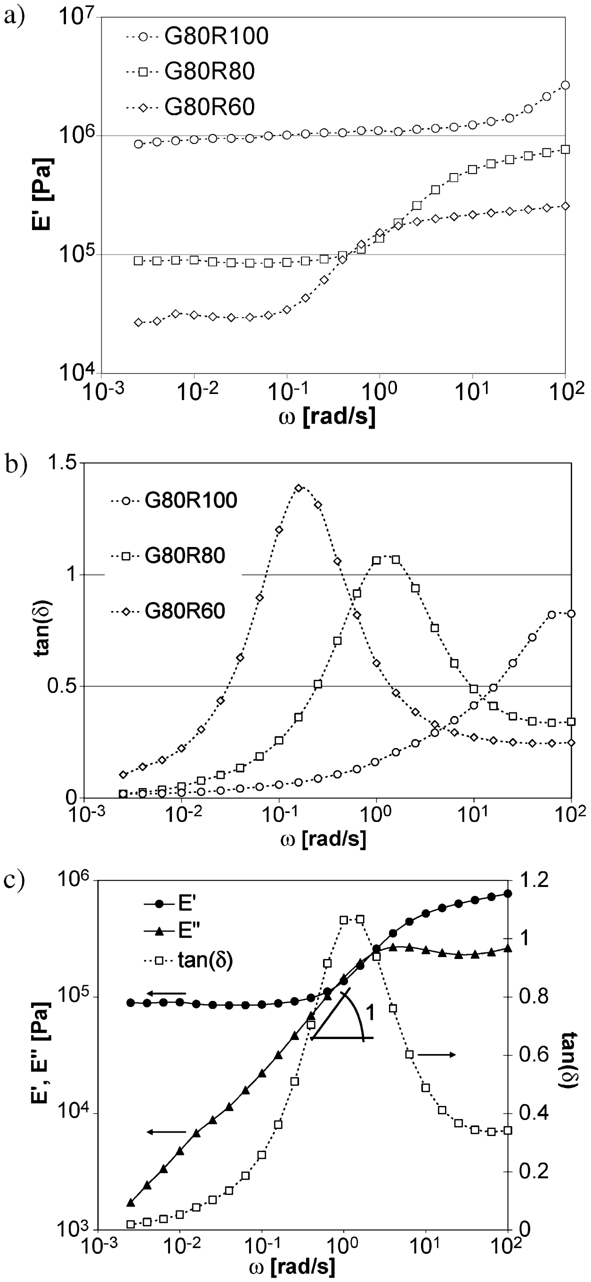

Figure 11. Frequency sweep tests for the G80R*y* sliding gels in DMSO. (a) E' vs ω: (◇) G80R60; (□) G80R80; (○) G80R100. (b) tan(δ) vs ω: (◇) G80R60; (□) G80R80; (○) G80R100. (c) Viscoelastic spectra of G80R80: (●) E'; (▲) E''; (□) tan(δ).

4. Discussion and Conclusion

The internal structure of the sliding gels, characterized with SANS, is complex with molecular and supramolecular organization length scales. At the molecular level, a correlation length close to 50 Å was measured and was assigned to a characteristic correlation length of the sliding network strands. At the submicroscopic scale, non-homogeneous huge aggregates of about 0.1 μm have been evidenced as a consequence of a statistical cross-linking reaction.[15] These heterogeneous aggregates, composed essentially from stacks of hydrogen-bonded α-CDs threaded on PEG segments, are due to the collapse of the polyrotaxane network strands in water. The size and the density of the aggregates depend on the quality of the swelling

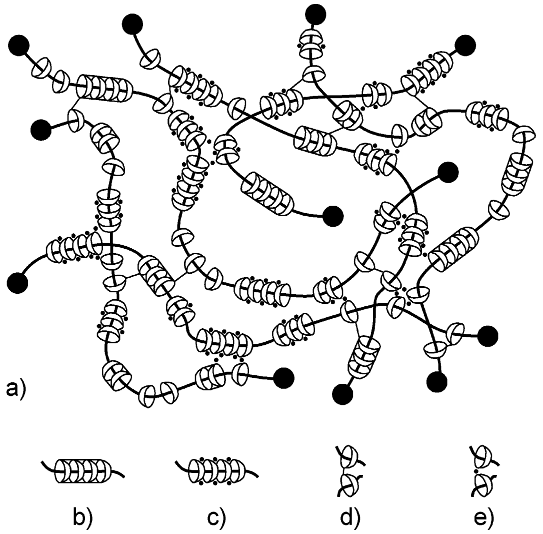

Figure 12. (a) Schematic view of the sliding gel at the molecular level showing: (b) chemically bonded α-CD tube, (c) physically bonded α-CD tube, (d) chemical cross-link between α-CDs, and (e) physical cross-link between α-CDs.

solvent. Indeed, an opaque sliding gel in water becomes translucent when it is swollen in DMSO. Thus, the swelling solvent has a considerable influence on the internal structure of the sliding gels, particularly on the heterogeneities. The use of DMSO as swelling solvent, due to its better affinity with the polyrotaxane network strands, helps to swell the collapsed part of the network and prevents the stacks of hydrogen-bonded α-CDs and consequently the establishment of extra intermolecular hydrogen bond bridges between the polyrotaxane chains. Consequently, the heterogeneities fade out leading to a more homogeneous gel where the intermolecular hydrogen bond bridges between the polyrotaxane chains are significantly attenuated. However, the intramolecular hydrogen bond interactions between the α-CDs belonging on the same polyrotaxane chain are always effective both in water and DMSO[9,12] and lead to the formation of α-CDs transient molecular tubes. Figure 12 shows a molecular model for the internal structure of the sliding gels where both chemical and physical intramolecular bonds are considered as cross-link points between the α-CDs belonging to the same or to different polyrotaxane network strands. Also, the presence of α-CDs molecular tubes around the polyrotaxane network strands, due to the physical or chemical bonding between intra-polyrotaxane α-CDs, is also envisaged. The number, the nature and the ratio between all these types of bonds considered above depend strongly on the cross-linker fraction, the swelling solvent and the complexation degree.

The proposed molecular model of the sliding gels (Figure 12) allows to explain their specific viscoelastic properties as a function of the cross-linker fraction. The viscoelastic characterization of the sliding gels swollen in water or DMSO has led to two main observations: with increasing *K*, the modulus levels increase and the tan(δ) peak related to the transition between the two E' plateaus shifts toward the highest frequencies. The observed transition between the two plateaus is similar to a rubber−glass transition of elastomeric materials.[23] This behavior is also known for end-linked star−polymer structures[24] and multicomponent associative polymer networks.[25] At the molecular level, this transition corresponds to a mobility decrease of the constitutive strands of the network with the increase of the frequency. This transition is attributed to different strand dynamics of the sliding gel network as a function of the frequency. At low frequencies, an efficient relaxation of the network strands is possible, while, at higher frequencies, this relaxation is slowed down due to the presence of α-CD tubes increasing the persistence length of the strands and thus leading to the higher modulus plateau. The explanation of the tan(δ) peak shift toward the higher frequencies with increasing *K*, is less obvious at first sight. This shift can be rationalized as follows (see Figure 13). For the low cross-linker fraction (Figure 13a), the attractive hydrogen bond interactions between the intra-polyrotaxane α-CDs lead to the formation of transient α-CD tubes around the polyrotaxane network strands. Thus, the network strands exhibit a high persistence length which contributes unfavorably to the relaxation processes while the establishment of low number of cross-link points results in low moduli levels. For the high cross-linker fraction (Figure 13b), the hydrogen bonding interactions between the intra-polyrotaxane α-CDs are prevented due to the modification of the hydroxyl functions with the cross-linker molecules. This chemical modification produces polyrotaxane strands with a lower persistence length contributing favorably to the relaxation processes. As already pointed out by SANS experiments, a high cross-linker fraction introduces a high number of aggregates and cross-link points which lead to high moduli levels.

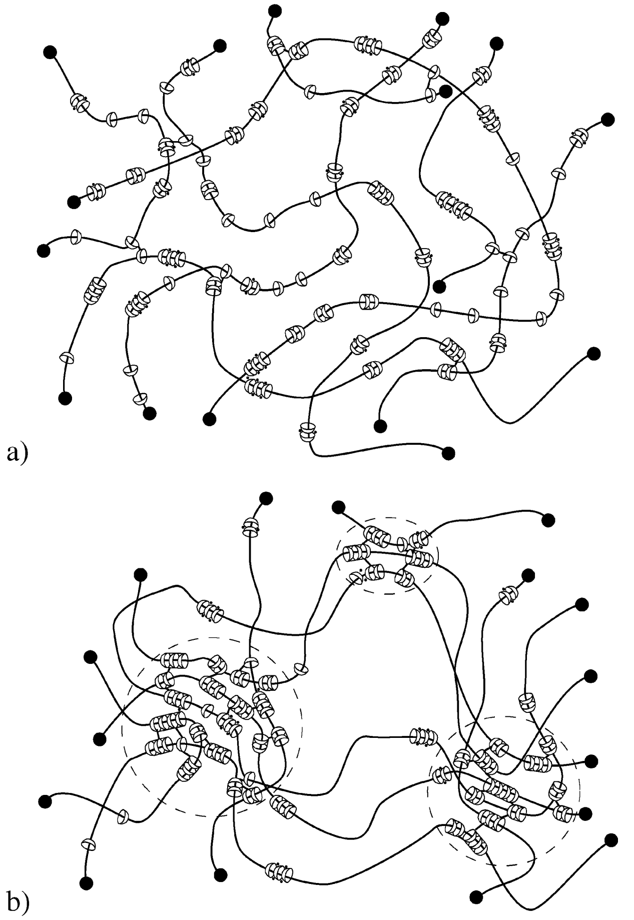

Figure 13. Schematic view of the sliding gel at its equilibrium swelling in the same solvent for (a) low cross-linker fraction *K* or (b) for high *K*. The dashed lines highlight the aggregates which are favored at high *K*.

The proposed molecular model of the sliding gels also allows to explain the difference of swelling behavior between the two solvents (water and DMSO). The swelling behavior of the sliding gels studied in water and DMSO have led to two main observations: (i) the presence of different hydrogen-bonding density and intramolecular/intermolecular hydrogen-bonding ratio in DMSO and water, and (ii) the sliding gels had a more pronounced ability to swell in DMSO, as opposed to water, leading to a network expansion. These observations are related to the different solvent interactions of the polyrotaxane chains in DMSO and water. Indeed the establishment of the hydrogen bonding interactions between inter-polyrotaxane α-CDs is more favorable in water inducing a collapse of the polyrotaxane network resulting in large heterogeneities which can explain the different swelling behavior of the sliding gels in the two solvents. The DMSO, as a better solvent than water for the polyrotaxane precursors, is more able to swell the heterogeneities as can be indirectly seen by the quasi-linear decrease of the swelling degree with increasing K (see Figure 10). In the case of water, however, a plateau is obtained for the highest K due to the lesser ability for this solvent to swell the cross-linked aggregates. These aggregates were certainly present at the time of dissolution of the polyrotaxane precursors in sodium hydroxide solution, just before the cross-linking reaction step for the preparation of the sliding gels. The use of a dissociating solvent such as DMSO or DMAC/LiH, as reported by Araki et al.[26] for the high molecular weight polyrotaxanes, during the cross-linking reaction step should prevent the aggregate formation in the sliding gels.

The viscoelastic properties are also dependent on the swelling solvent. In DMSO viscoelastic measurements at low frequencies have shown for E'' a power law dependence close to 1 and E' higher than E''. It results a dominant elastic response over the viscous component at low frequencies. This peculiar behavior can be attributed to the sliding motions of α-CDs cross-link points. In fact in DMSO, sliding motions of α-CDs are favored in comparison to water since hydrogen bonds between α-CDs belonging to two different polyrotaxanes mostly vanish in DMSO. Consequently in this swelling solvent the network expansion as well as the sliding motion of α-CDs are enhanced. The effective sliding motion is overshadowed in water where the chains collapse due to the formation of numerous hydrogen bonds. Frozen aggregates are formed slowing down the sliding motion. To have more insight into the different viscoelastic behavior of the sliding gels in water and DMSO, the dependence of the $E'_{\max(\tan(\delta))}$ and the position of tan(δ) peak in the frequency range as a function of the cross-linker fraction K for the G80Ry sliding gels both in water and DMSO were analyzed (Figure 14). The dependence of $E'_{\max(\tan(\delta))}$ with K follows an exponential law for both swelling solvents. The absolute values of the moduli are higher in water than in DMSO for all the sliding gels. For high K, $E'_{\max(\tan(\delta))}$ in water and DMSO seem to converge to a same value. Thus, $E'_{\max(\tan(\delta))}$ does not depend on the swelling solvent for the highest K, which is due to the fact that the high density of cross-links prevents all motions and overshadows the sliding mobility in the topological network. For a given gel, the tan(δ) transition shifts toward the lowest frequencies in DMSO as opposed to water. Indeed in water, the network collapse increases the probability of intermolecular hydrogen bonding interactions between the α-CDs threaded along different polyrotaxane chains while the larger swelling degree in DMSO results in a large network expansion and favors the hydrogen bonding interactions between the intra-polyrotaxane α-CDs. Thus, for a given sliding gel at a fixed cross-linker fraction, the persistence length of the polyrotaxane strands is higher in DMSO than in water, due to the formation of transient α-CD tubes, leading to a tan(δ) peak shift toward the low frequencies.

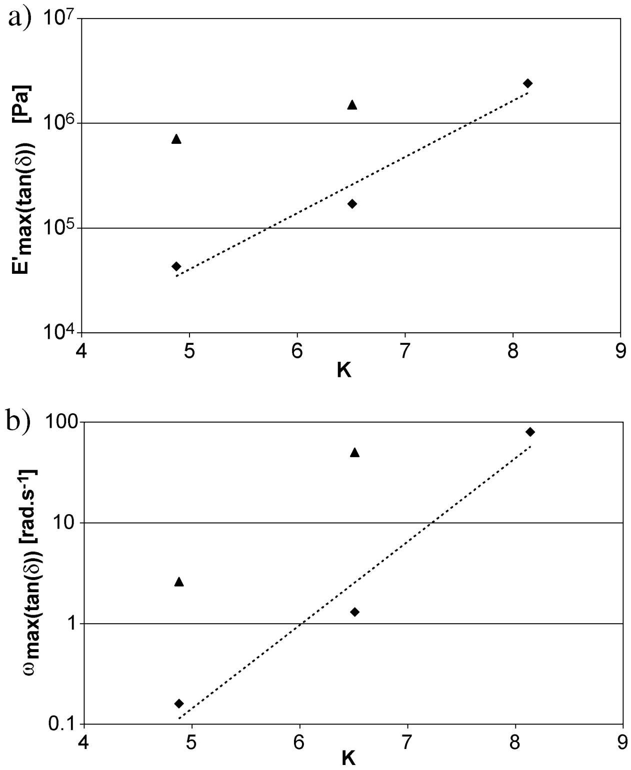

Figure 14. Evolution of $E'_{\max(\tan(\delta))}$ and $\omega_{\max(\tan(\delta))}$ for the G80Ry sliding gels. (a) $E'_{\max(\tan(\delta))}$ vs K: (◆) $E'_{\max(\tan(\delta))}$ in DMSO; (▲) $E'_{\max(\tan(\delta))}$ in water. (b) $\omega_{\max(\tan(\delta))}$ vs K: (◆) $\omega_{\max(\tan(\delta))}$ in DMSO; (▲) $\omega_{\max(\tan(\delta))}$ in water.

In summary the sliding gel molecular structure is complex and strongly influenced by three main parameters: the complexation degree N, the cross-linker fraction K and the swelling solvent interactions with the constitutive components of the sliding network. The SANS study reported in this paper has firmly established the heterogeneous structure in water of the sliding gels as previously observed by Karino et al.[21] and recently reported by Shinohara et al.[27] Aggregates of polyrotaxane network strands are formed during the statistical cross-linking reaction in sodium hydroxide solution which mostly are promoted by the stacks of hydrogen bonded α-CDs. These aggregates are dispersed in a diluted network matrix. It was demonstrated that the presence of the heterogeneities is greatly dependent on the swelling solvent. In DMSO, a good solvent, the heterogeneities fade out rendering the gel more homogeneous and then the sliding cross-link points contribute mainly to the peculiar viscoelastic properties of the sliding gels. Thus, the sliding motion of the cross-link points along the template chain particularly at low frequencies in DMSO revealed the sliding characteristics of the topological networks. This sliding characteristic motion is a unique signature of the molecular dynamics encountered in topological polymer networks with sliding cross-link points. This sliding motion is expressed in the viscoelastic behavior by weak viscous dissipation underlining the very effective relaxation mechanism on this new class of materials: the “sliding gels”.

Acknowledgment. The authors are grateful for financial support from the Grant ANR JC00S SUPRAGEL and from the Région Alsace.

Supporting Information Available: Text giving experimental details including materials used, preparation of the polyrotaxanes precursors, and formation of the sliding gels and a table giving parameters for the synthesis and characterization of the sliding gels. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0605043