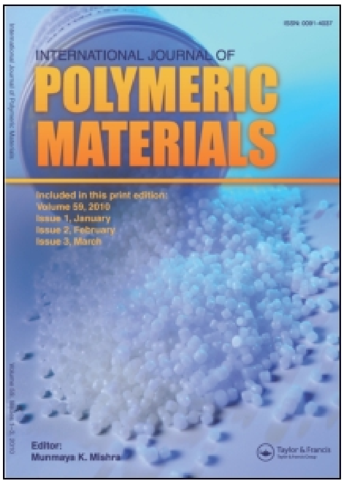

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Shaul M. Aharoni[a]
[a] Polymer Science Laboratory, Research & Technology, Allied-Signal Inc., Morristown, New Jersey, USA

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The Deformation of Rigid Gels of One-Step Polyamide Networks and Their Constituent Stiff Segments

SHAUL M. AHARONI

Polymer Science Laboratory, Research & Technology, Allied-Signal Inc., P. O. Box 1021R, Morristown, New Jersey 07962, USA

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When a gel of rigid polyamide network is prepared in solution by a single step polymerization, some of its stiff segments are straight and others are bent. The motional freedom of the majority of the segments is greatly constrained by having fully or mostly reacted multifunctional rigid branchpoints at both their ends. A minority of the segments are less constrained because they are attached to the network at one end only. We believe that a most efficient mechanism for bending of constrained straight stiff polyamide segments is by a pair of syn-anti interconversions occurring in the same segment. For polyamides these are the least energy consuming changes in which 180° rotations around the ring-to-carbonyl or ring-to-nitrogen bonds take place at an activation energy as low as 4 kcal/mol. In this way, significant translations of one branchpoint relative to the other take place without any torsions of the moving branchpoint and with the bent portions of the stiff segment defining no or almost no "cone of rotation" in space. Conversely, the most efficient straightening mechanism for constrained bent stiff segments is the reversal of the above process, i.e., two placement interconversions occurring per segment. Stiff segments attached to the network at only one end can easily deform by a single interconversion, of course.

During macrodeformation the gels maintain constant volume. In this deformed state, the size of the populations of straight and bent stiff segments changes from the relaxed state. In the directions where the stressed sample increases its dimensions, the population of straight segments grows at the expense of the bent segments. In the perpendicular directions where the dimensions of the gel decrease, the population of bent segments increases at the expense of the straight ones. The inability of straight stiff segments to stretch results in increases in modulus with deformation. After the stress is removed the populations of straight and bent segments revert back to their original size. From the above it is obvious that the deformation of rigid gels is not affine. Similarities exist between deformation and swelling, except for the fact that in the swollen gel the population of straight segments increases isotropically throughout the sample which is not the case in the deformed gel. The strong effects of network imperfections are discussed in the context of rigid network swelling.

KEY WORDS Gels, networks, rigid stiff-segments, deformation

INTRODUCTION

Permanent isotropic gels comprise covalently bonded polymeric networks swollen with solvent. According to the nature of their segments and branchpoints (crosslink junctions), the networks are broadly divisible into two major groups: flexible and rigid. Evidence in the literature is mounting[1–5] that flexible networks and gels are inhomogeneous on the macroscopic scale. This contradicts the fundamental assumption of homogeneity underlying the currently accepted theories aimed at explaining the properties of the flexible systems.[6-11] In the systems discussed herein, highly branched rigid macromolecules nucleate in solution and grow at random from the appropriate monomer mixture by a continuous one-step polymerization. The fractional amounts of the different monomers combine with their size to define the *average* length, ℓ_0, of the stiff segments between rigid branchpoints. The branchpoint functionality, f, is dictated by the functionality of the rigid monomers, with $f \geqslant 3$. A typical segment with $\ell_0 = 38.5$ Å constrained in an "infinite" network by two fully reacted branchpoints with $f = 3$ is shown in Figure 1. For brevity, the segments and branchpoints will be called here "network components." From the nuclei the branched macromolecules randomly grow in size and number, aggregate in clusters of increasing size and, finally, form an "infinite" network encompassing the whole solution, provided it is sufficiently concentrated.[12-14] In the pre-gel state the growing highly branched rigid polyamide macromolecules were found[13,14] to conform with the fractal model. We therefore call them fractal polymers (FPs). Due to the branchpoint rigidity, segmental stiffness and the large size of ℓ_0 relative to the segmental cross-sectional diameter, d, and common solvent molecules, the FPs and gelled network progenies are remarkably open structured on scales smaller than ℓ_0 and highly draining for normal size solvent molecules. The fact that ℓ_0 is an *average* length and not a single value combines with the 3-dimensionality of the growing entities to greatly reduce the probability for either frustration of segmental growth[15] or "segmental crowding"[16] as one progresses from the center to the exterior of the FPs. The occasionally incomplete reaction of network components further reduces the chances of frustration or crowding in the interior of the fractal polymers. The crowding effect is substantially due to all segments being of identical length. In our case, ℓ_0 is only an *average* length, allowing the mass to be distributed more uniformly throughout the volume of the FPs, and for the formation of a small number of intramolecular cyclic structures. These reduce both crowding and frustration. A 2-dimensional schematic representation of a FP with $\ell_0 = 38.5$ Å, f = 3 and $60\,000 < M_n < 70\,000$ is shown in Figure 2. The relatively uniform segmental density may be the reason why, when studied by small-angle x-ray scattering intensities,[13] our rigid FPs behave as surface fractals and not as mass fractals. The central solid dot in Figure 2 stands for the nucleus of the FP. The diameter of

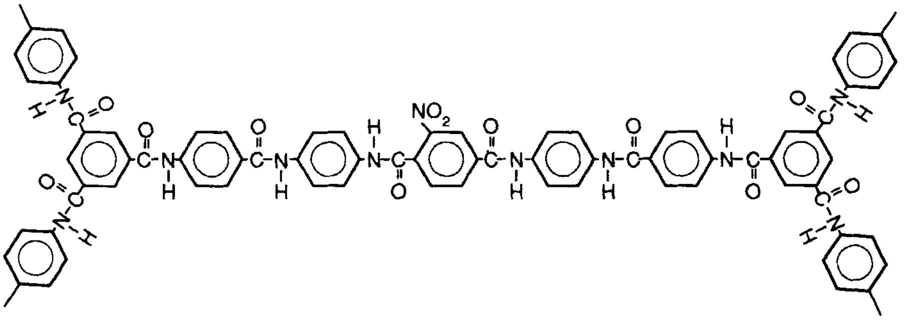

FIGURE 1 Typical stiff segment with fully reacted rigid branchpoints. ℓ_0 = 38.5 Å and f = 3.

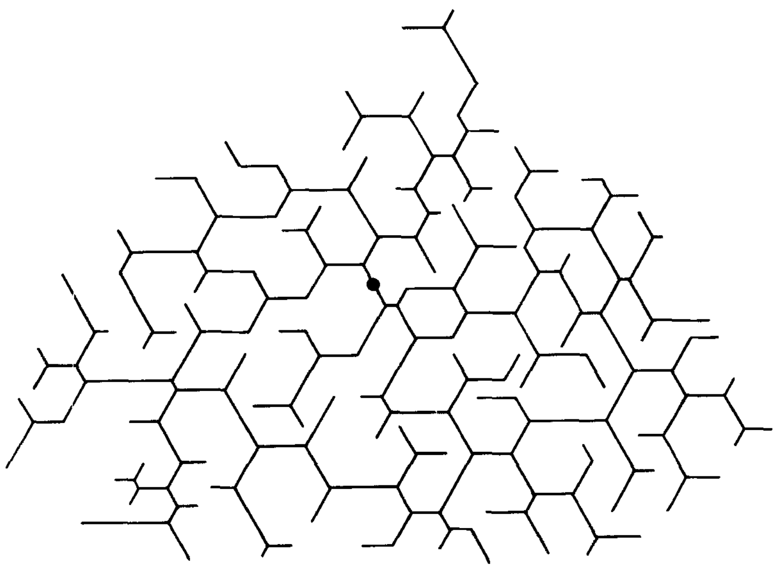

FIGURE 2 A fractal polymer with $\ell_0 = 38.5$ Å, $f = 3$ and $60\,000 < M_n < 70\,000$. Because ℓ_0 is an average length, some intramolecular cyclization may occur and the segmental density in the interior tends toward uniformity. Note the highly open structure of the rigid FPs.

normal solvent molecules is about half that of the solid dot, explaining the highly draining nature of the rigid fractal polymers.[12,13]

In the one-step process of network formation, the growing FPs aggregate at random and form interpolymer covalent bonds with or without the participation of monomers and low-M oligomers. Due to monomer depletion, especially in the interiors of the FPs, only small amount of additional growth takes place in the interiors. Because of the participation of monomers and oligomers in the interpolymer bonding, the material density in the "interfacial" regions is close to that of the FPs interiors. This is at variance with the case where no monomers or oligomers were present and the properties of the gels reflected the size of the precursor fractal polymers.[14] In the 3-dimensional reality, the segments in the final network are truly isotropic in space, especially when considered on macro-scale. This is due to the stiff segments being held less rigidly to the triangular grid of Figure 2, not all segments being straight and many FPs randomly join together to form the "infinite" network. Therefore, in the gelled one-step rigid networks we have macroscopically homogeneous systems whose "building blocks" maintain some fractal nature on a microscopic scale. The macro-uniformity of the rigid gels is clearly demonstrated by their blemishless optical appearance and by their isotropic response to mechanical stresses experienced during modulus determinations.[12,13] Small-angle x-ray intensities, supported by light scattering, end-group titrations and porosimetry measurements, reveal the fractal nature of the pre-gel species as well as the post-gel "infinite" network in both the solvent-swollen state and the dry, collapsed state.[13] Beyond the gel point, the incorporation of monomers and low-M oligomers in the network tends to cloud the fractal nature of the system. Monomers and oligomers not incorporated in the "infinite" network may form fractal polymers which are topologically trapped in the network without being covalently bonded to it.

The modulus G of our typical gelled rigid networks is of the order of 10^6 to 10^7 dyne/cm^2, depending on concentration, on ℓ_0 and on f. This is about the same as the plateau modulus, G_N^0, of pure high-M flexible chain polymers and about 100 times larger than G of gels of such flexible polymers at comparable concentrations.[17] On the other hand, our typical G values are about 10^{-4} the magnitude of 10^{11} dyne/cm^2 extrapolated[18] for randomly oriented molecules of poly(p-phenylene terephthalamide) in the bulk.

The assumption of Gaussian behavior of networks[19-21] is predicated on the segments and branchpoints being flexible and the distance between crosslinks large. In the case of rigid networks the segments are stiff, the branchpoints rigid and the distances between them are relatively short. Therefore, the Gaussian statistics assumptions are invalid in the case of rigid networks and gels. Our covalently-bonded one-step rigid polyamide networks do not conform with the models of Doi and Kuzuu,[22] where the rods are not connected and may slide past one another, or Boue *et al.*[23] where the branchpoints are flexible, or of Jones and Marques[24] where the rigid network is taken to be homogeneous and the deformation affine. The three models treat molecular segments as if they were greatly miniaturized cylindrically-shaped rods. In the limit of small deformation, each such rod has an effective elastic constant for bending, k, which scales as

$$k \propto d^4/L^3 \tag{1}$$

where L is the length of the rod.[25] This leads to deformations in which the segments bend smoothly at a constant curvature under an applied stress.[22,24] Proportionality (1) holds only when the material of the rod is isotropic.[22,25] It is not expected to be valid when the rod is in fact a stiff macromolecule bending only at specific sites along its length by the mechanism of isomeric interconversions as explained by the rotational isomeric state (RIS) model.[26-28]

In the following sections a qualitative description will be presented, first of the deformations of unconstrained stiff polyamide segments as described by Aharoni, Hatfield and O'Brien,[29] then of stiff segments motionally constrained at both ends by fully or mostly reacted rigid branchpoints and, finally, of ensembles of such segments in the gelled rigid network. The descriptions will be limited to the low deformation regime where fractures and sample failure are not expected to take place.

DEFORMATION OF INDIVIDUAL STIFF POLYAMIDE SEGMENTS

We believe that stiff aromatic polyamide segments may bend or straighten out by syn-anti interconversions of their amide groups. This may not be the only mode of segmental deformation but, in light of the very low activation energies associated with these interconversions and the large displacements they facilitate, it is a very likely deformation mechanism. Molecular simulation procedures are presently being developed in our laboratories[30] to test this point. In this paper, the syn-anti interconversion mechanism will be described in a more qualitative manner, without recourse to the computer simulation results to be published in the future.

In order to gain insight into how constrained stiff polyamide segments deform, one must first understand the deformation mechanism of unconstrained segments. Therefore, we shall start our discussion of segmental deformations by describing deformations of unconstrained stiff polyamide segments and then move to the description of constrained ones. Because the discussion is limited to the low deformation regime, bond stretching and valence angle alterations play no significant role in segmental deformation. Trifunctional rigid branchpoints will be used for the purpose of illustration without reducing the generality of the discussion.

(a) Unconstrained stiff polyamide segments

An unconstrained stiff segment may deform by one or more of the following deformation modes: changes in bond length, changes in valence angles or changes in torsional angles. The total potential energy for rigid segment deformation may respectively be described in terms of the three deformation modes:

$$V_{tot} = V_s + V_v + V_t \tag{2}$$

The energy requirements for bond stretching, V_s, and valence angle changes, V_v, are at least an order of magnitude larger than for the torsional mode, V_t, making changes in torsional angles the primary mode of segmental deformation.[29] The possible contributions of hydrogen bonds with solvent molecules or with other segments to the energetics of segment deformation are expected to be rather small, if they exist at all. This is due to the isotropic nature and relative dilution of the rigid gels, and the fact that such contributions were found, in studies of model compounds,[29] to be small. Therefore, the effects of hydrogen bonds are neglected in this study.

To describe the deformation of a rigid polyamide segment typical of our networks, let us consider the segmental fragment in Figure 3. In it are defined the three skeletal amide torsional angles, α, β and ω. The respective activation energies for rotation, E_α, E_β and E_ω, correspond to the peaks in the potential energies V_t for torsion around the respective bonds. In the case of aromatic polyamides, π-electron delocalization, V_π, and non-bonded interactions, V_{nb}, combine to produce V_t:

$$V_t = V_\pi + V_{nb}. \tag{3}$$

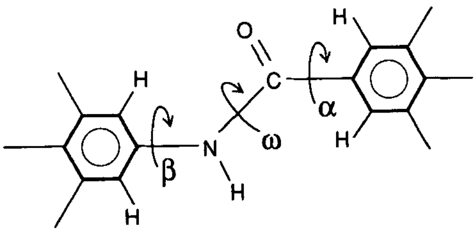

FIGURE 3 Aromatic polyamide segmental fragment with the angles α, β and ω indicated.

In a previous paper[29] data for unconstrained systems, mostly small molecules, were presented showing that E_α falls in the range of 7 to 9 kcal/mol, E_β lies at about 14–18 kcal/mol and E_ω is above 20 kcal/mol. The value of E_ω is in good accord with activation energies used in calculating the structure and behavior of unconstrained linear stiff polyamides[31–33] analogous to our networks. The experimental values of E_α and E_β are somewhat higher than the calculated values of only about 3 to 4 kcal/mol for both E_α and E_β.[34,35] From the shapes and magnitudes of the energy wells[31] it is obvious that 180° interconversions around α and β are more likely to take place than around the central amide bond, and that small departures of the α and β angles from their equilibrium minima are more likely to occur than deformations of the amide group out of planarity. For example, a $\pm 20°$ departure from the minimum of both α and β requires the investment of ca. 5 kcal/mol if we consider the experimental results[29] and only ca. 2 kcal/mol if we consider the calculated values,[35] while a similar departure for ω is associated with an energy investment of 12 kcal/mol or more. It should be noted that the experimental activation energies were obtained from systems in which rotations are not hindered by crowding and where at least one end of each deforming molecule is free to perform torsional motions. Only such motional freedom allows the movement of a section of the stiff polyamide segment in the swollen network to take place. This isomerization movement is effected by a rotation around a *single* bond and with it the moving stiff section defines a "cone of rotation" in space.[36,37] Front and side views of the cone of rotation of an unconstrained stiff polyamide section are shown in Figure 4. Here the rotation is around the central amide bond.

Let us now investigate the geometry and energetics of a stiff aromatic polyamide segment unconstrained in at least one end, responding to an applied force **F** by a single torsional rotation. The force **F** is vertically applied from top to bottom in the plane of the page. Two types of interconversions may take place: one is a torsional motion around the central amide bond as depicted in Figure 3, and the other is an anti-syn interconversion of two amide groups relative to an aromatic ring in between them. In Figure 4 the angle 2ψ is taken to be 120°, which is very

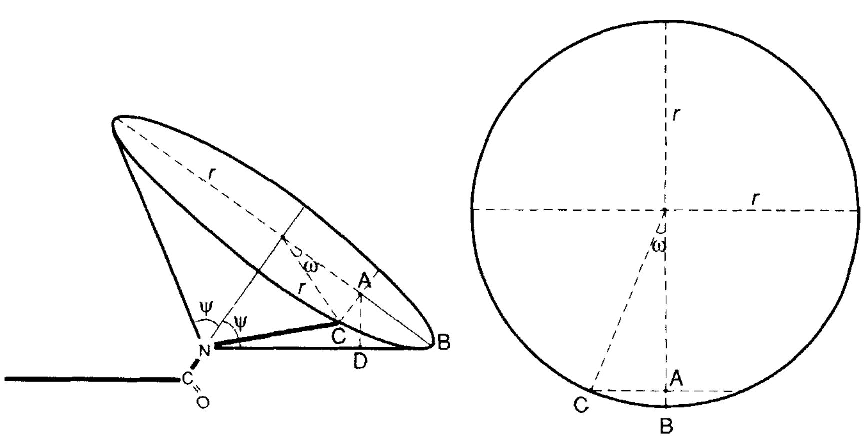

FIGURE 4 Side- and front-view of the cone of rotation the unconstrained section of the segment defines in space upon rotation around the central amide bond. The distance $\overline{AD}$ is the motion in the direction of an applied force **F** and $\overline{AC}$ is the motion in the perpendicular direction.

close to reality, and we calculate the deformations brought about by a change in ω from 0° to 20°. The radius of the cone of rotation is denoted by r which for $2\psi = 120°$ is equal to 0.866 ℓ where ℓ is the length of the moving stiff section. In general, the distance $\overline{AB} = (1 - \cos \omega)r$, the distance $\overline{AC} = (\sin \omega)r$ and the distance $\overline{AD} = \sin(90 - \psi)\,(1 - \cos \omega)r$. The distance $\overline{AD}$ is the change in position of the tip of the moving section in the direction of the applied force **F**. For $2\psi = 120°$ and $\omega = 20°$ we obtain $\overline{AB} = 0.053\ \ell$, $\overline{AC} = 0.294\ \ell$ and $\overline{AD} = 0.026\ \ell$. That is, a 2.6% change in the position of the section tip in the **F** direction requires a lateral movement over ten times larger. The potential energy associated with a 20° deviation from planarity of the amide group is ca. 12 kcal/mol, and to complete the rotation and go from planar trans to planar cis amide, an energy barrier of $E_\omega \cong 20$ kcal/mol must be surpassed. Most importantly, to perform such a rotation around the central amide bond a large cone of rotation must be generated and, when both ends of the deforming segment are anchored in a rigid network, drag half of this network with the moving segmental section. It is obvious that ω-angle torsions are not favored from both energetic and topological considerations even when the segment is not motionally constrained. When the stiff polyamide segment is fixed at both ends in a gelled rigid network, the segmental and sectional movements necessary for a single rotation around the central amide bonds appear to be impossible to perform.

A single interconversion from anti to syn is shown in Figure 5C. In this case a 20° change in the chain direction is easily achieved by changing one placement from anti to syn or vice versa. When the end of the moving section is unconstrained, this section defines a cone of rotation where $2\psi = 20°$. This leads to the radius r of the cone of rotation being $r = 0.174\ \ell$. Hence, for $\omega = 20°$, $\overline{AB} = 0.01\ \ell$, $\overline{AC} = 0.06\ \ell$ and $\overline{AD} = 0.01\ \ell$. This small displacement in the direction of **F** requires a calculated ca. 2 kcal/mol while the completion of the anti-syn interconversion requires less than 5 kcal/mol and creates a rather large displacement in the same direction, namely 0.347 ℓ. Upon comparison we find that surmounting energy barriers of less than 5 kcal/mol by anti-syn interconversions contributes 0.347 ℓ displacement in the direction of the applied force while a 20° torsion around the central amide bond contributes only 0.03 ℓ displacement at the much higher cost of ca. 12 kcal/mol. We find, hence, that in the case of unconstrained stiff polyamide segments, a most energy efficient mechanism allowing for the largest displacements of branchpoints in the direction of the applied force is a complete anti-syn or syn-anti interconversion per segment. These interconversions are most likely effected by 180° rotations around the ring-to-carbonyl or ring-to-nitrogen bonds. However, when both ends of the stiff polyamide segment are fixed in a network and cannot perform torsional movements or inscribe in space cones of rotation, then the segmental deformations become somewhat more complicated.

(b) Stiff polyamide segments constrained at both ends

In the ideal situation all stiff polyamide segments are solidly fixed by their fully reacted rigid branchpoints into the rigid network. As a consequence, the branchpoints themselves are constrained from performing torsional movements and changing their angular orientation relative to each other. Most importantly, the torsional

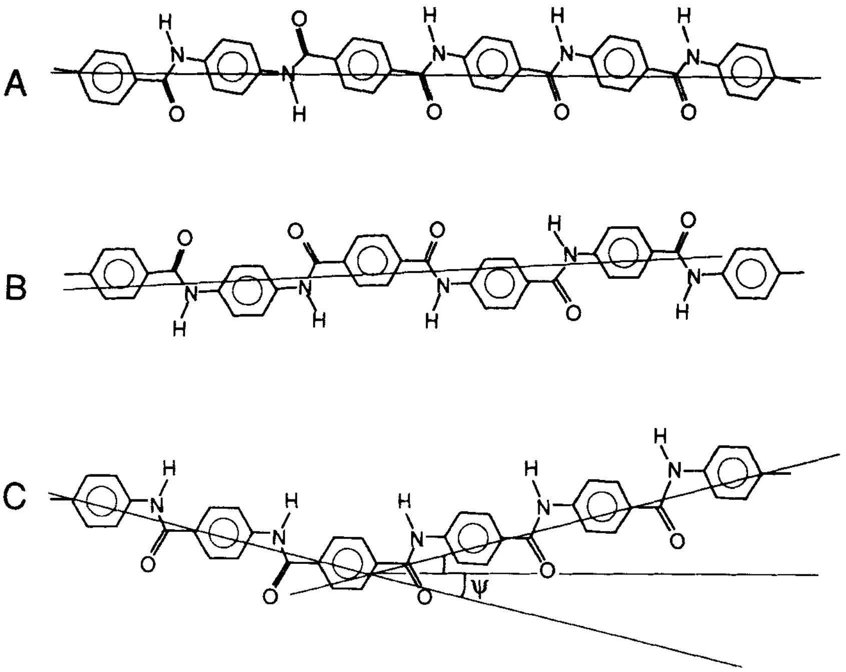

FIGURE 5 Bending of an unconstrained stiff aromatic polyamide segment by a single anti-syn interconversion. (A) Fully anti segment. (B) Fully syn segment. (C) A fully anti segment with one syn placement. A fully syn segment with one anti placement produces the same bend.

restraints of the branchpoints and the great reduction of their freedom of movement in the network practically eliminate modes of segmental deformation requiring that segments or their sections defined in space cones of rotation of substantial size. Therefore, models and systems employing unconstrained stiff segments may be useful to describe individual linear stiff polyamide macromolecules, but are incapable of correctly describing the kind of segmental deformations and torsional rotations taking place in gelled polyamide networks where the majority of the stiff segments are constrained at both ends by being connected to fully or mostly reacted rigid branchpoints. For the moment we neglect the less constrained stiff segments even though such segments can support loads and transmit stress.

A proposed mechanism for bending of stiff aromatic polyamide segments attached at both ends into a rigid gelled network by means of rigid branchpoints is graphically shown in Figure 6. Accordingly, one or more *pairs* of anti-syn interconversions per stiff segment are needed. Each pair of interconversions may isomerize simultaneously, or one interconversion may send local stresses along the segment and force small deviations, V_{ti}, from the equilibrium state of several amide groups, all in the same direction. When the sum of the energies involved in these deviations exceeds the energy needed for a single interconversion,

$$\sum_i V_{ti} \geqslant E_\alpha \tag{4}$$

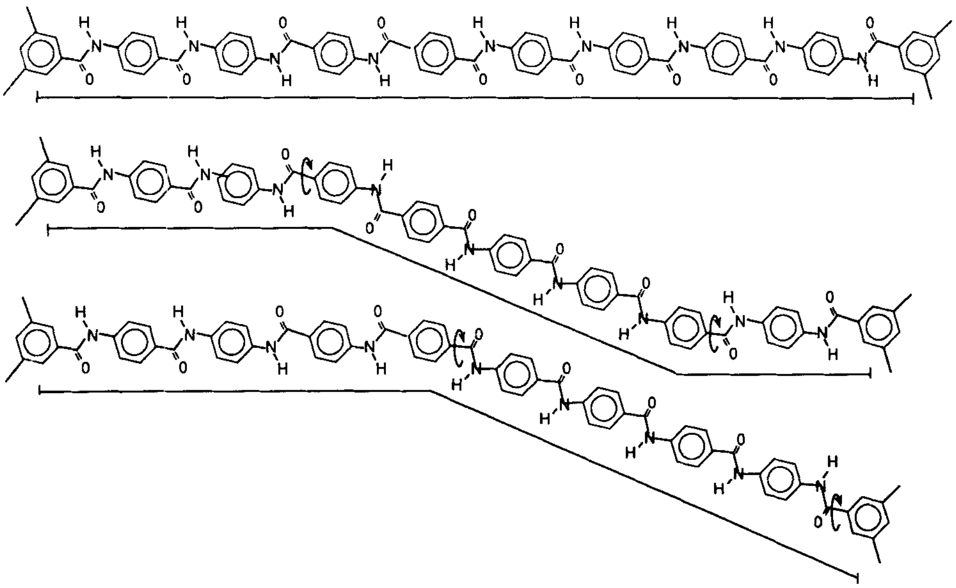

FIGURE 6 Bending of a stiff aromatic polyamide segment constrained at both ends by fully reacted rigid trifunctional branchpoints (top). The bends are effected by a pair of interconversions per segment (see arrows). The displacement of a branchpoint from its initial position is dictated by the total length of the segment and by the length of the section between the interconverting placements (middle and bottom).

then this interconversion suddenly occurs and the stiff segment relaxes in its newly deformed state. Such kind of motion, whether simultaneous or in sequence, generates practically no cone of rotation because the movements of the section between the two interconverting placements and that of the portion of the segment being displaced, are largely restricted to the plane containing the applied force **F**. By such means an easy displacement of branchpoints in the direction of **F** is achieved. The magnitude of this displacement depends, of course, on the length ℓ_0 of the segment and on the length of the section between the two interconversions. The spatial distance between the branchpoints decreases somewhat with bending, but this is true for all cases where rodlike segments are bent or curved.

In a previous work[29] it was shown by solid-state carbon-13 NMR and IR spectroscopy that a small fraction of the network amide C(O) atoms are slightly decoupled from their neighbors. This effect was more noticeable in networks strained by collapsing than in networks in the equilibrated gels. In a solid-state ^{13}C-NMR relaxation study[38] the values of $T_{1\rho c}$ of several typical networks in the dry and solvent-swollen states were measured over a broad range of temperatures. All carbonyl carbons exhibited a single, much slower $T_{1\rho c}$ than all the ring carbons in the pre-gel FPs and in the post-gel "infinite" network, and their activation energy for relaxation was substantially smaller than the activation energy for relaxation of the ring carbons. The experimental results of both works[29,38] indicate that the amide carbonyl in the pre-gel FPs and in the post-gel "infinite" network are substantially decoupled from the ring carbons, reinforcing our belief that individual stiff polyamide segments can most easily bend by performing rotations around the amide-to-ring bonds. The fact that the fraction of decoupled carbonyls observable by IR and ^{13}C-NMR spectroscopy increased in strained systems, appears to support the mechanism in which the pair of interconversions takes place in sequence and not simultaneously. Additional work is needed, however, to prove this point.

DEFORMATION AND SWELLING OF ONE-STEP RIGID POLYAMIDE NETWORK GELS

(a) The network

An essentially defect-free rigid network consists of stiff polyamide segments connected to one another by rigid branchpoints. The majority of the segments are constrained from bending by a single interconversion and other torsional movements by virtue of the branchpoints at both their ends being fully reacted. Similarly, most branchpoints are prevented from performing torsional motions by their fully or mostly reacted functionalities. However, segments and branchpoints connected to the "infinite" network at only one point are free to perform the "forbidden" movements indicated above. It should be borne in mind that because the difference between syn and anti placements in stiff aromatic polyamides is only about 0.3 kcal/mol,[29,33] there is practically no energetic advantage to either placement. Therefore, during the one-step polymerization the stiff segments add to the growing FPs and network either straight or bent, and the completed rigid network contains both straight and bent stiff segments.

Because of the relative shortness of the segments and the statistics of placements, the large majority of bent segments will be singly- or doubly-bent. We believe that pairs of interconversions are the easiest mode of deformation, contributing the largest displacements to constrained stiff segments. This means that the swelling and the deformation of gelled rigid networks are associated with changes in the populations of straight and doubly-bent segments. Unless changed under stress to doubly- or triply-bent, the once-bent segments behave as the straight ones in that they contribute to the overall strength and modulus of the gelled network, but are not directly associated with swelling or deformation. It is important to mention here that upon equilibration in a good solvent the change in populations of straight and bent segments occurs more or less uniformly throughout the volume of the gel, but under stress the changes in populations reflect the local strains in it. These points will be elaborated on later. From the above it is obvious that gels of rigid networks do not deform affinely, with some segments experiencing larger deformations than others and some not deforming at all.

(b) Deformation of rigid gels under linear compression

Under linear compression the rigid gels, as a rule, maintain constant volume:

$$\lambda_1\lambda_2\lambda_3 = 1 \qquad (5)$$

where λ_i are the sample deformations in three dimensions. This is evident from the fact that no "sweating" or other forms of solvent loss were observed when the measurements were conducted with the gel not immersed in solvent[12,13,14] and no weight was added when the measurements were performed with the gels submerged in solvent.[12] The observed incompressibility is in agreement with expectations.[39] When compressed, it was repeatedly observed[12,13,14,40] that the most rigid gels failed in a highly brittle fashion and tolerated a linear compression, λ, of the order of only 2%. The tolerance gradually increased, approaching 20% in the case of the more pliable gelled networks characterized, say, by $\ell_0 = 52$ Å, $f = 3$ and $C_0 = 5.0\%$. At higher compressions the gels developed brittle cracks leading to catastrophic failure of the specimens. It should be emphasized here that the deformability and swelling capabilities of gels of rigid networks appear to be directly related to the levels of network imperfection.[13] We will touch upon these effects in the next section.

When gels of rigid networks deform macroscopically, the population of straight segments in the directions undergoing positive strain ($\lambda > 1$) grows at the expense of the bent segments but the deformation is limited by the fact that the straight segments cannot stretch further. In the perpendicular directions, where the gels experience negative strains ($\lambda < 1$, compression), the population of the straight segments decreases in favor of the bent ones. A simplistic two-dimensional picture of this, neglecting all excluded volume effects, is shown in Figure 7. Here, a relaxed gel of a rigid polyamide network with $f = 3$ is shown in the lefthand panel. Because they are the ones most likely to experience interconversions, essentially all bent segments are shown doubly-bent. In the righthand panel of Figure 7 the same network is shown as deformed by the force **F**. Some of the network was squeezed out of the picture by the force **F**. In both panels of Figure 7, segments denoted by

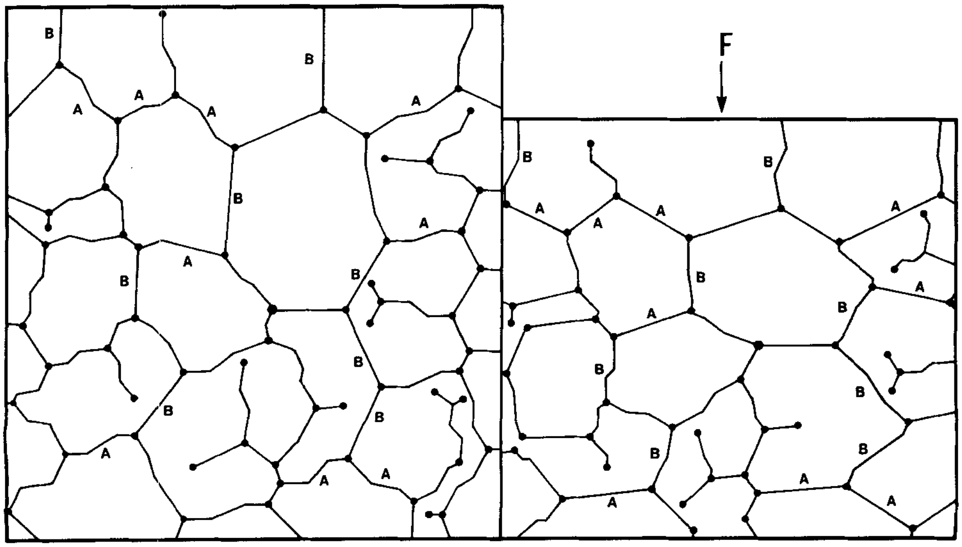

FIGURE 7 Two-dimensional representation of a gel of rigid network with stiff polyamide segments and rigid $f = 3$ branchpoints. The lefthand panel is the relaxed gel and the righthand panel is the gel strained by the applied force **F**. Additional explanations in the text.

A are those that were bent in the relaxed state and straightened out under stress. Segments denoted by B are those that were straight in the relaxed gel and bent under stress. Naturally, many additional segments retained their shape even though their spatial positions were changed as the gel deformed. We note, therefore, that while the ratio of A to B segments in the deformed gel as a whole may not change during deformation, the *local* spatial distribution is changed. In the volume sensing the applied stress the average direction of the A segments is mostly perpendicular to **F** while the average direction of the B segments is largely in the **F** direction. As a result of these deformations, the branchpoints will be displaced both in the **F** direction and in perpendicular directions and with them the whole network. In reality, however, the resistance to the applied stress, i.e., the modulus, reflects not only the energy requirements for the interconversions in A and B segments but also excluded volume effects and the constant length of the straight stiff segments. After the applied stress is removed, the recoil of the gel reflects the reversal of the above processes.

In light of all of the above we conclude that the deformation of rigid gels under stress and the small part of the swelling which is independent of network imperfections, are both made possible by the coexistence in the gelled networks of straight *and* bent stiff segments.

(c) Swelling

After being prepared in an uninterrupted one-step polymerization at polymer concentration C_0, the "as-prepared" gelled networks may be carefully swelled in a good solvent[12,13,14] until the equilibrium concentration C is reached. The swelling ratio, C_0/C, is directly dependent on ℓ_0 and inversely on f. It ranges from less than 1 vol/vol percent for the most rigid and brittle gels with networks having very short ℓ_0 and $f = 6$, up to 300 vol/vol percent for gelled networks with $f = 3$ and long ℓ_0. Among the very rigid gels, showing less than about 15–20% swelling, no unreacted functionalities could be found by various titration methods.[12,13,41] The softer gels with increasing swelling ratios, contained unreacted functionalities in correspondingly growing amounts.[12,13,41] This indicates that the majority of the network swelling may be attributed to various network imperfections correlatable with the presence of unreacted functionalities, and also that a smaller part of the swelling exists which is independent of such imperfections. We believe that this smaller swelling of the rigid networks is associated with changes in segmental configurations generated by syn-anti and anti-syn interconversions. These, in turn, are reflected in the above mentioned changes in NMR and IR spectra.[29]

The response of the rigid gels to the rate of swelling during equilibrium and to linear compression during modulus determination supports our belief that the macroscopic deformation of the gels is associated with deformations of some stiff segments. During equilibration, when the difference in quality between the imbibed and expelled solvents is kept small, no cracks appear in the rigid gels. Under such conditions equilibration is achieved in a matter of weeks or months. When the quality of the solvents is greatly different, a visible moving front may appear in the gel between the solvents, usually accompanied by brittle cracks in or very close to the front.

When "as-prepared" gels of one-step rigid networks swell to equilibrium in a good solvent, their modulus G decreases. The primary cause for the reduction of G is the aveage drop in concentration of network components per unit volume of the gel. A secondary contribution to the decrease in G is the enhanced nonuniformity of the network, especially in regions of lower segmental concentration as described previously.[1,5,14] Two smaller effects act in the opposite direction, increasing the modulus upon going from C_0 to C. Such a behavior was actually observed by this author[42] in gels of rigid two-step networks. One of these effects is the appearance of non-covalent interactions between motionally constrained network components that did not exist in the "as-prepared" system. The second opposite effect is due to the inability of straight stiff segments to stretch, as described before. Since the population of straight segments increased during swelling at the expense of the bent ones, we observed[42] that the contributions to modulus due to the unstretchability of straight stiff segments became more noticeable as the level of perfection in rigid two-step network increases. However, in the case of the one-step rigid network gels all effects leading to an increased modulus are much smaller than those leading to the reduction of the modulus upon swelling, with the overall result that G decreases upon swelling from C_0 to C.

The dramatic effects of network imperfections can be gathered from the following experimental observations: Consider a rigid gel (1) prepared at a relatively high concentration $C_0(1)$. Upon swelling to equilibrium its concentration drops to C(1). A chemically identical different gel (2) is now prepared at a concentration $C_0(2)$ such that $C_0(2) = C(1)$. When the modulus of both gels is measured, one finds that the modulus of the swollen gel (1) at C(1) is higher than the modulus of gel (2) at $C_0(2)$ even though $C(1) = C_0(2)$. This observation is due to the fact that networks prepared at lower concentrations contain a higher density of imperfections than networks prepared at higher concentrations. Such a performance pattern was repeatedly observed by us[12,14,41] on many series of rigid gels where C_0 was altered but ℓ_0 and f kept constant. In addition to demonstrating the effects of imperfections, these observations also instructed us that the power dependence of G on C_0 is much larger than that of G on the concentration ratio C/C_0. In other words, the modulus of the imperfect rigid gel depends not only on the network concentration at the time of measurement but also on how did it get there.

CONCLUSIONS

When gels of rigid polyamide networks are prepared in solution by a single step polymerization from the appropriate monomer mixtures, some of their stiff segments are incorporated into the networks straight and some bent. In highly perfect networks the majority of the stiff segments are motionally restrained by having the rigid multifunctional branchpoints at both their ends fully or mostly reacted. A minority of the network components are less constrained by virtue of being attached to the "infinite" network at one point only. We believe that a most efficient mechanism for bending of motionally restrained straight stiff segments is by two rotational isomeric interconversions taking place in the same segment. In the case of aromatic polyamides, anti-syn and syn-anti are the least energy consuming interconversions in which 180° rotations around the ring-to-carbonyl or ring-to-nitrogen bond take place with an activation energy of less than 5 kcal/mol. In this way, large translations of one branchpoint relative to the other take place without any torsions of the moving branchpoint and with the bent portions of the stiff segment defining no or almost no "cone of rotation" in space. The most efficient mechanism for straightening of constrained bent stiff segments is the reversal of the above process. Stiff segments attached to the network through only one branchpoint can easily deform by a single interconversion, as was shown previously.[29] When the rigid gels are deformed their volume remains constant. Under deformation the population of straight and bent stiff segments change from their sizes in the undeformed, relaxed state. In the directions where the gel is positively strained, the population of straight segments increases at the expense of the bent segments. However, because straight stiff segments cannot stretch, an increasing resistance to deformation ensues. In the perpendicular directions, where the dimensions of the gel decrease, the population of bent segments increases at the expense of the straight ones. From the above it is clear that the deformation of rigid gels is not affine. Substantial similarities exist between deformed gels and ones swollen to equilibrium. The important difference is that in the swollen gel the population of the straight stiff segments increases at the expense of the bent segments isotropically throughout the sample unlike the case during deformation.

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