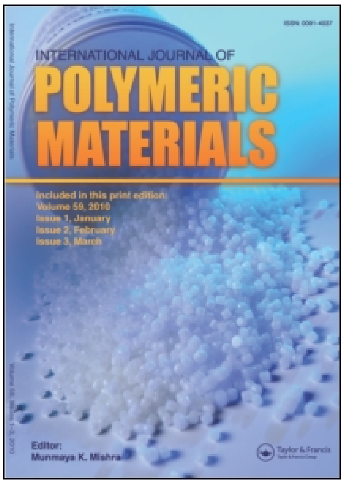

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Shaul M. Aharoni[a]
[a] Allied Signal Inc., Research and Technology, Morristown, New Jersey, USA

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Interfractal Porosity in Gels of Rigid Aromatic Polyamide Networks and its Consequences

SHAUL M. AHARONI

Allied Signal Inc., Research and Technology, P.O. Box 1021, Morristown, New Jersey 07962, USA

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Gels of rigid aromatic polyamide networks are brittle in nature. They may be prepared in a single step from monomers, or from precursor fractal polymers (FPs) purified from monomers, dimers and higher oligomers. The relationship between the concentration at which the network gels are prepared and the size and number of interfractal voids is discussed. The modulus of gels prepared exclusively from FPs was found in an earlier work to show an inverse power dependence on the size of the precursor FPs. It is suggested here that, in a fashion similar to yet not identical with ceramics and other polycrystalline materials, the dependency may be associated with the number and size of interfractal flaws surpassing a critical size for the initiation and propagation of flaw-initiated cracks. At present we cannot exclude total porosity from consideration, but flaws much smaller than whole FPs appear to be ineffective in crack initiation and catastrophic propagation.

KEY WORDS Fractal, interfractal, porosity, voids, imperfections, network, rigid, modulus, mechanical properties

INTRODUCTION AND PREVIOUS RESULTS

Three-dimensional, "infinite" networks and their gels may respectively be prepared in the bulk or solution by any of three methods: (a) Reacting an appropriate mixture of difunctional and higher-functionality ($f \geqslant 3$) monomers in a single step to obtain a network with junction functionality f. (b) Preparing in one step long linear chains decorated along their length with many reactive sites, and in a separate second step reacting these sites by the addition of chemical reagents or by irradiation to crosslink the system. (c) Preparing in a first step linear chains end-capped with reactable groups and in a second step reacting them together or with a high-functionality crosslinker to form a network from end-linked precursor chains. These methods are applicable to the creation of flexible and rigid networks and gels, but the efficiency of network formation decreases, and the number concentration of network defects and flaws increases, with the increase in the stiffness of the network segments and junction points. The increased number concentration of network defects, and the associated increase in the number of unreacted sites, are especially noticeable as one progresses from stiff worm-like precursor chains to rodlike chains employed in methods (b) and (c) above.

When the one-step polymerization method is used, highly branched pre-gel polymers form first. With the advent of the reaction, polycondensation in our case, and the depletion of monomers and other low molecular weight (low-M) fragments, an increase occurs in the number concentration of unreacted sites belonging to the growing pre-gel polymers. If the reaction is conducted in dilute solution at concentrations C_0 lower than a characteristic critical concentration for "infinite" network formation, C_0^*, then the highly branched particles will cease growing when the monomer supply is depleted, but an "infinite" network will not form. When the reaction is conducted in the bulk or at concentrations C_0 high above C_0^*, then the highly branched polymers will grow interpenetrated with one another and the "infinite" network will be highly interwoven with itself and with highly branched polymers trapped in the network but not necessarily covalently bonded to it. Mathematically, the highly branched pre-gel polymers behave as Cayley trees with non-uniform branch length. Physically, rigid polyamide highly branched polymers were found to conform with the surface fractal model.[1] We, therefore, call them interchangeably trees or fractal polymers (FPs). In Figure 1 a two FPs fragment of a dilute solution rigid network is schematically and 2-dimensionally shown. In this extreme case the rigid FPs, with $f = 3$, were first prepared at $C_0 < C_0^*$. Then all monomers and other low-M species were removed and the concentration increased to $C_0 = C_0^*$. At this concentration a small number of interfractal covalent bonds form; a number as small as one bond per FP is sufficient for gelation to occur. Such a preparation creates "infinite" gels most dilute in polymeric material and,

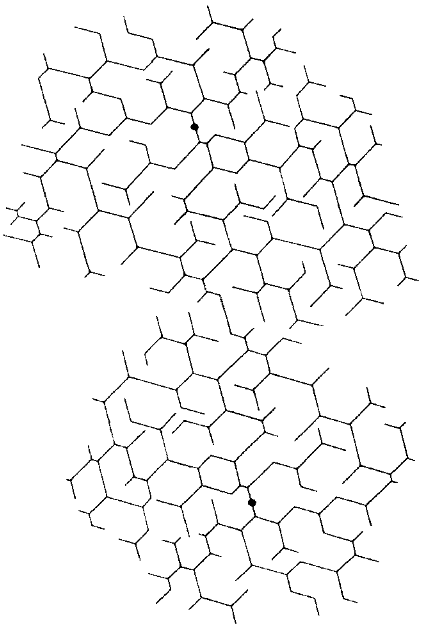

FIGURE 1 Onset of network formation in dilute solution at C_0^*: Two fractal polymers connected by a single covalent bond.

since there are no additional reactive species around, the network mass will not grow when the polycondensation time is increased. Because of the segment stiffness and branchpoint rigidity of FPs such as rigid polyamides, once a small number of interfractal bonds are formed, the probability of increasing this number by prolonging the reaction time is very small. For conciseness, networks prepared at C_0^* from FPs in the presence or absence of monomers, etc., will be called herein C_0^* networks.

In Figure 2, the other extreme is schematically shown. Here the network was formed in solution at high concentration and with the progress of reaction beyond the gel-point the monomers were completely depleted. In the figure one tree is shown in the plane and the dots indicate locations where segments belonging to other FPs cross this plane. The high segmental interpenetration and the overall network density are rather obvious. In this case the spatial distribution of unconsumed network reactive sites will be much more uniform than in the dilute solution case, because the segment-tips and unsatisfied branchpoints of each FP are so deeply embedded in a multiplicity of similar FPs. The rigid network in the gel will be in this case far more uniform than in the dilute solution case, and interfractal voids of sizes significantly larger than intrafractal voids will either not exist at all or be present in a very small number.

Light scattering studies[1-3] indicate that in dilute solutions the rigid polyamide FPs behave as porous particles of more or less spherical shape. When gelled networks were formed of them at C_0^* and slightly higher, $C_0 \gtrsim C_0^*$, and the ensuing brittle gels subsequently broken, they broke in a highly brittle manner and the fracture surfaces were found by scanning electron microscopy (SEM) to be poly-

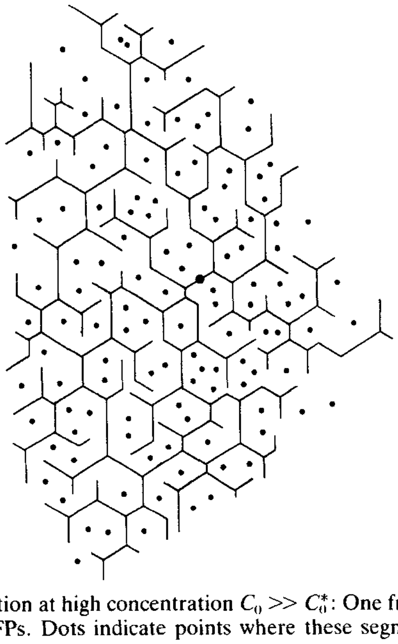

FIGURE 2 Network formation at high concentration $C_0 >> C_0^*$: One fractal polymer interpenetrated by segments of many other FPs. Dots indicate points where these segments cross the plane through the "tree."

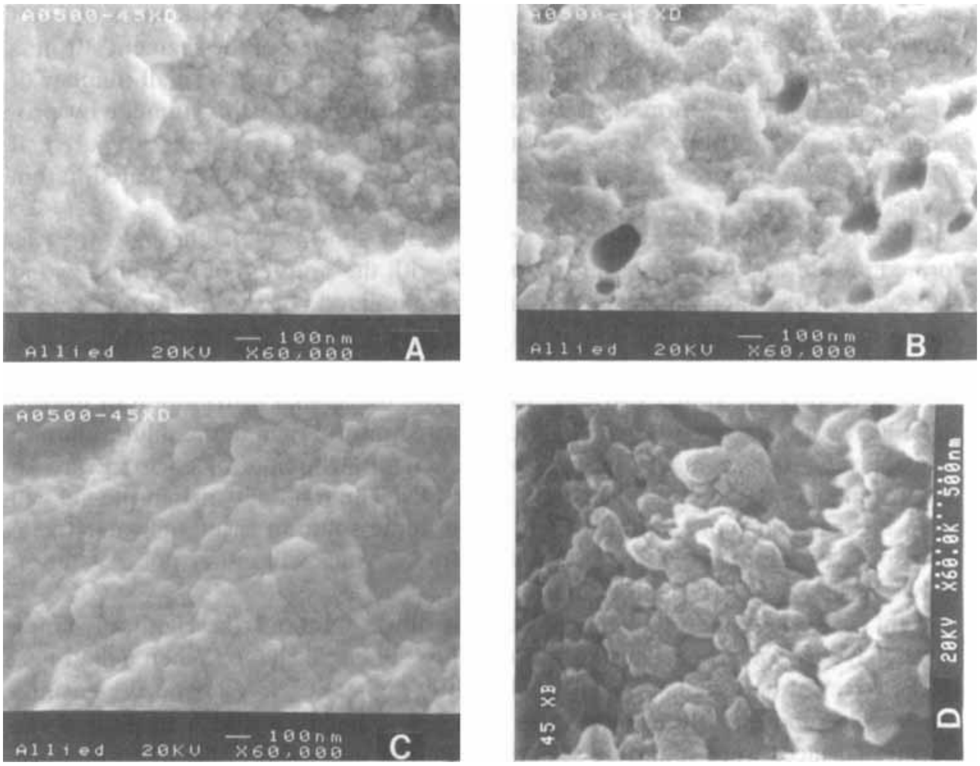

FIGURE 3 Scanning electron microscope photographs of fracture surface of two rigid polyamide network gels prepared in one step from monomers at $C_0 = 3.0\%$. Notice the polyhedral shape of the primary particles, of sizes in the range of 20 to 80 nanometers. Original magnification: 60,000×.

hedral in nature. In Figure 3 we show four fracture surfaces of two gels of rigid polyamide networks prepared at $C_0 = 3.0\%$[1] and observed by SEM at 60,000× magnification. The appearance of the primary particles, of sizes 20 to 80 nanometers in diameter, is the same in all micrographs. In these gelled networks the shape of the primary particles is that of polyhedra, obtained by slight compression of moderately-soft spheres. The size of the polyhedral particles is consistent with the size of the largest precursor fractal polymers withdrawn from the reaction mixture right before the gel point and measured by light scattering techniques.[1,3] The rather clear definition of the polyhedral interfaces is a good indication that when rigid network gels are prepared from monomers in one step at concentrations slightly higher than C_0^*, the density of network material in the interfractal and interstitial areas is lower than in the interior of the FPs and relatively large interfractal voids are likely to be present. During failure, the cracks follow the regions with lowest network-material concentration, which are the weakest regions and are, of course, preferentially located in the interfractal surface regions and interstitial voids.

A similar morphology in an unrelated system was recently reported by Pearson and Yee.[4] When a sufficient amount of poly(phenylene oxide) (PPO) is present in a blend with epoxy resin, the PPO tends to organize itself around the growing crosslinked epoxy particles. When these are close together, they press upon one another (cf. Figures 3 and 8 in Reference 4), and develop polyhedral morphology in which the PPO clearly defines the interfaces of the adjacent polyhedra. Although the size of the epoxy polyhedra is far larger than the size of our FPs, the similar morphology indicates that when pressed together the growing one-step epoxy particles and polyamide FPs in the rigid network gels created at $C_0 \geqslant C_0^*$ adopt the same polyhedral shape. This is, of course, consistent with expectation.

The effects of porosity, i.e., total void content, on certain properties of solid materials are well recognized in diverse fields such as soil mechanics,[5,6] mechanical and other properties of ceramic and polycrystalline materials,[7-17] composites,[18,19] material packing,[20] porosimetry[21-23] and bulk polymers.[24,25] Similar effects of porosity on the structure and behavior of liquids were previously described by Bernal[26-28] and Scott.[29] On the other hand, every farmer or gardener knows that while the total void content of various soils is about the same,[5] a given volume of fine-grained clay contains a large number of small pores contributing to high water retention while coarse-grained sands have only a small number of large pores responsible for rapid drainage and low water-retention capacity. The existence of deserts depends, hence, on the large average pore size and not the total porosity of their sands.

Recently we have observed that when gels of rigid polymer networks are prepared at $C_0 \geqslant C_0^*$ from pre-gel highly branched FPs in the absence of monomers and other low-M species, their shear modulus, G, shows a strong inverse power dependence on the size of the precursor FPs[1,3]:

$$G \propto R_H^{-3.3} \tag{1}$$

where R_H is the hydrodynamic radius of the FPs as measured by means of photon correlation spectroscopy (PCS). In a subsequent section we speculate on whether this power dependence is due to the total porosity in the rigid network gel or the average size of the interfractal flaws in the final network. Because in the molecular-size scale of interest one may not be able to differentiate between various flaws, we shall hereby use voids, pores, cracks and flaws interchangeably.

VOID-SIZE AND POROSITY EFFECTS

According to Griffith's theory of the strength of brittle materials,[30] the fracture stress, σ_f, is given by

$$\sigma_f = (2\gamma E/\pi Q)^{1/2} \tag{2}$$

where γ is the specific surface energy, E is the tensile modulus, and Q is a critical flaw size. When the size of voids or other flaws in a brittle material is larger than Q, these will continue to grow under stress and catastrophic failure will ensue. When the size of the flaws in the brittle material is smaller than Q, their growth will be arrested and the applied stress, σ, will not reach σ_f. The failure stress is, hence, inversely proportional to the size of flaws in the brittle system:

$$\sigma_f \propto Q^{-1/2} \tag{3}$$

In the case of granular systems such as ceramics or polycrystalline compacts, the size of the critical flaw initiating failure is equal to the sum of the larger among the precursor grains plus an adjacent void.[7] From random packing studies of spheres[26–29] and from packing studies on less regular species such as soil particles,[5,6] we know that the size of the interstitial voids is directly dependent on the size of spheres or grains, the larger the solid particles the larger the voids in between them. One can, then, relate the fracture stress to the size, g, of the precursor grain, which can be taken as the largest grain size, g_0, which is in turn equal to the largest void size, r_0, in the system[14,16]:

$$Q \simeq (g + r) = g_0 \tag{4}$$

$$\sigma_f = (2\gamma E/\pi g_0)^{1/2}. \tag{5}$$

Equation (5) tells us that, through the association of large void size with large grain size, the larger the grains in a brittle solid the lower its fracture strength. Furthermore, Equations (2) and (5) state that for a system with constant γ and constant g and r, the fracture strength and tensile modulus are related[13]:

$$\sigma_f \propto E^{1/2} \tag{6a}$$

By analysis of experimental results, Dutta *et al.*[13] obtained, however, a power dependency of

$$\sigma_f \propto E^n \tag{6b}$$

where n is slightly larger than 1.00.

Ceramics, polycrystalline compacts and, certainly, gelled rigid networks created exclusively from rigid FPs may be considered to be statistically isotropic. In the case of rigid networks this was experimentally verified.[1,3] For such systems the expression relating the tensile modulus, E, to the shear modulus, G, is

$$G = E/2(1 + \nu) \tag{7}$$

where ν is Poisson's ratio. For incompressible fluids ν = 0.50 and for elastomers it is slightly smaller. In the case of gels comprising mostly of solvent, ν can safely be approximated by 0.50. Equation (7) then reduces to

$$G = E/3 \tag{8}$$

Combining Equations (6) and (8) we find

$$\sigma_f \propto G^n \tag{9}$$

with the theoretical value of n set at $\frac{1}{2}$ while experimentally it was found to be slightly larger than 1.00.

Griffith's theory of the strength of brittle materials, hence, links the strength and tensile and shear moduli with the size of the largest flaws in the system and not with the total void content, i.e., the porosity of such materials. Through the association with void size, an association of σ_f, E and G with the precursor grain size is established.

Independently of void or flaw size, dependence of σ_f and E on the porosity of polycrystalline ceramics was demonstrated in the literature. Based on their open pore, connected grain model, Wagh and associates[15,16] obtained the empirical dependencies

$$\sigma_f = \sigma_0(1 - p)^t \tag{10}$$

$$E = E_0(1 - p)^m \tag{11}$$

where p is the volume fraction porosity in the material and σ_0 and E_0 are, respectively, the strength and tensile modulus of the defect-free material. Relationships (10) and (11) are conceptually similar to earlier dependencies on porosity suggested by Duckworth[31] and Dutta *et al.*[13] According to Wagh *et al.*,[15,16] the magnitude of the exponent t depends on m as

$$t = m + 0.5 \tag{12}$$

but the value of m is not fixed and was shown to vary from one polycrystalline material to another within the range of $2 \leq m < 4$ and be dependent on the grain and pore size distribution.[16] Krstic has theoretically shown[12] that E and σ_f are dependent in a complicated manner on the sizes of pores and the cracks emanating from them in brittle solids. Experimental data presented by him show that when the porosity of a series of samples of the same material is kept constant but the pore size varies, both E and σ_f decrease with increasing pore size. If, however, the porosity also changes, then its effects appear to dominate and the contribution of pore size variations becomes clouded.[12]

The packing density

$$D = 1 - p \tag{13}$$

of closed-packed hard spheres of identical diameter is 0.7405 ($= \pi 2^{1/2}/6$). The D values of single-diameter cylinders and prisms are 0.91[32] and 1.00, respectively. It has been shown by Bondi[33,34] that the packing density of flexible linear macromolecules fluctuates very close to 0.74. A linear macromolecule may be visualized, then, as a string of hard spheres of close dimensions. When a 3-dimensional array of hard spheres is closely packed, no motion is possible without the introduction of long-range order. That is, at $D = 0.74$ only crystalline arrangements of hard spheres are possible. It was shown by Bernal[26] that this constraint on mobility takes place when the average distance between spheres in each direction reaches about 0.95 of the highest possible linear packing density in that direction. The packing density at which mobility is facilitated without long-range order is, therefore,

$$D \leq 0.7405(0.95)^3 = 0.6346 \tag{14}$$

corresponding to dense random packing (DRP), determined experimentally to cluster around 0.634–0.637[28,29,35–38] in studies using hard spheres of identical diameters. The packing density below which the ensemble loses its coherence is called loose random packing (LRP) and its experimental values concentrate in the $D = 0.60$ to 0.61 interval.[29,35,37,39] Critical compressibility values obtained by Rigby[40,41] for spherical and non-spherical molecules are very close to one another and do not show great sensitivity to changes in the ratio of surface area to molecular length. When the hard spheres in the randomly packed ensemble are not of identical size but have a modest size distribution, then their DRP is rather close to the DRP of identical spheres whose size is similar to that of the major contributor to the distribution.[42–44] The LRP is expected to behave in a similar manner. As the disparity increases between the sizes of spheres in the mixture, the packing density increases, especially when the volume fraction of the small spheres is kept low to only fill the interstitial volumes of the larger spheres.[44]

BACK TO ONE-STEP RIGID POLYAMIDE NETWORKS

In our work with rigid aromatic polyamide networks the polycondensation reaction[1–3,45,46] was carried in solution and the obtained stiff gels were isotropic in character. In such gels the critical concentration C_0^* was found to be dependent of the branchpoint functionality and the average length, l_0, of network stiff segments between branchpoints. In no case could we prepare stiff gels of "infinite" rigid aromatic polyamide networks at concentrations C_0^* lower than about 2%. Moreover, when network gels were prepared at concentrations $C_0 > C_0^*$ and subsequently swelled in a good solvent to equilibrium, they swelled as a rule to concentrations C not lower than about 2%.

Unlike gels of flexible polymer networks, the gelled rigid networks generally fail in a brittle fashion. Depending on the level of network perfection the rigid gels may elastically deform before failure, the higher the concentration of network flaws the larger the pre-failure elastic strain. Even in instances of significant elastic strain, say, over 100%, the fractures in the gels were brittle in nature with smooth surfaces and no rough tearing characteristics. Furthermore, upon failure the gelled networks recoiled back to their original shape and dimensions with no permanent plastic deformation in evidence. Depending on the absence of network defects and on f and l_0, the brittle glass-like nature of the gels and their fracture surfaces may carry to polymer concentrations as low as ca. 2%. We believe that the brittle nature of the rigid network gels allows us to consider them in the terms widely accepted in the description of ceramic and other polycrystalline brittle materials.

When the polycondensation reaction leading to gelled rigid networks was conducted at $C_0 < C_0^*$ or, alternatively at $C_0 > C_0^*$ but arrested before the gel point, soluble pre-gel polymers were obtained. When these were purified and analyzed, they were found to be highly branched with molecular weights directly dependent on polymerization time.[1,3] Solution viscosity, light scattering, small-angle x-ray scattering and porosimetry measurements revealed that the rigid highly branched pre-gel species are porous in nature, have highly ramified exteriors, and behave in conformity with the fractal model.[1] The diameters of the ones obtained right before the gel point, fell in the interval of 20 to 80 nanometers, much smaller than the sizes of the primary grains in ceramics and other polycrystalline materials.

In a separate study[3] rigid aromatic polyamide FPs were prepared, characterized by identical f and l_0 but of increasing molecular weights, R_H and, consequently, radius of gyration, R_G. The unreacted terminals of segments and branchpoints were decorated about evenly with amine and carboxyl groups. When the purified FPs of each batch were reacted with each other at $C_0 \geqslant C_0^*$, rigid stiff gels of "infinite" networks formed, containing all the solvent in the reaction bath. It is important to emphasize here that the networks were created from the FPs in the absence of monomers, dimers and other low-M oligomers. For rigid polyamide network gels created exclusively fro FPs, the C_0^* was found to be directly dependent on the size of the precursor FPs[3] as:

$$C_0^* \propto R_H^{0.37} \tag{15}$$

The shear modulus of the nascent gels, all of which were prepared at $C_0^* < C_0 = 5.0\%$ from FPs only, followed proportionality (1), decreasing with increased R_H in a -3.3 power dependence. In the case of rigid network gels formed exclusively from rigid FPs the relationship between the size of the FPs and the properties of their network progeny is clear and unclouded by contributions from monomeric and similar small species. Unlike this, in the usual case FPs of ever-increasing size participate in the creation of networks together with monomers, dimers, oligomers, etc. Then the relationship between precursors' size and network properties is not clear.

As was mentioned above, when a network is prepared in solution at C_0^*, the amount of network material in the ensuing gel is minimal. Modeling each rigid FP as a sphere or, better, as a polyhedron in a 3-dimensional Voronoi tesselation,[47] one finds that the total interfractal void volume, along the interfaces and in the interstices between them, is the highest sustainable by the rigid network. From the minimal packing density when mobility is arrested, Equation (14) above, the interfractal porosity of the gelled rigid networks at C_0^* is expected to be $1-0.63 =$

0.37. The similarity of this value to the experimental power in proportionality (15) may be of significance or completely fortuitous, we do not know at present. From Figure 2 we learn that, unlike the DRP of solid spheres where the porosity remains constant, a high degree of interpenetration and growth of one FP in others takes place in the case of rigid FPs when the network gels are prepared at $C_0 > C_0^*$. The larger the ratio C_0/C_0^* the higher the number concentration of interpenetrated FPs and parts of FPs residing in one another and in the gelled network.[2] It is important to recognize here that the distance l_0 is not affected by changes in C_0. This distance is entirely controlled by the ratio of difunctional to higher-functionality monomers in the reaction mixture.

Rigid polyamide FPs were recently simulated by a computer using a POLYGRAPH program with energy minimization.[48] Their mass density was found to be rather low yet more or less uniform in their interiors and rapidly falling off in the highly corrugated exterior shells. Dendrimers of the same molecular weight had similar features, except for the mass density in their interiors being very high. This is rather similar to the results for flexible dendrimers recently obtained by Mansfield and Klushin[49] from Monte Carlo calculations. The results, in Table I, indicate that the FPs are internally highly porous, especially relative to the rather compact dendrimeric structure, and their porosity increases with the increase in the average segment length, l_0. It is obvious, then, that such porous FP structures may each be capable of accommodating many other FPs or parts thereof within its pervaded volume. Most of the rigid networks in our studies were prepared in one step from 4:1 and 5:1 molar ratio 4-aminobenzoic acid to 3,5-diaminobenzoic acid and similar monomers, resulting in mass volume fraction of about 2%, as in the last two entries in the table.

When gelled rigid networks are prepared at C_0^* from rigid FPs in the absence of monomers, etc., then the average size of the interfractal voids in the final network changes with the average size of the precursor FPs: the larger the FPs the larger the voids. This, of course, is identical with all results obtained in DRP studies including those using mixtures of various-size spheres.[37] When the rigid gels are prepared at C_0^* using FPs of a given average size, then in the resulting C_0^*-network

TABLE I

Polymer volume fraction in polyamide fractals with 200 aromatic rings each. Molecular modeling by computer simulation with energy minimization after each iteration[a]

Monomers	Segment length, Å	Mn	Volume fraction
3,5-DABA, *Dendrimer*	6.4	27970	0.75
3,5-DABA, *Fractal*	6.4	27480	0.24
1:1 PABA/3,5-DABA	12.8	26008	0.18
4:1 PABA/3,5-DABA	32	24904	0.02
		31046	0.02
5:1 PABA/3,5-DABA	38.5	>30000	<0.02

[a] Computer modeling results obtained by Dr. W. B. Hammond on August 29, 1992.

All entries except for the first one are fractals. 3,5-DABA = 3,5-diaminobenzoic acid, PABA = *p*-aminobenzoic acid.

Mn = number average molecular weight.

Volume fraction = volume of polymer mass divided by volume of sphere defined by R_G of fractal.

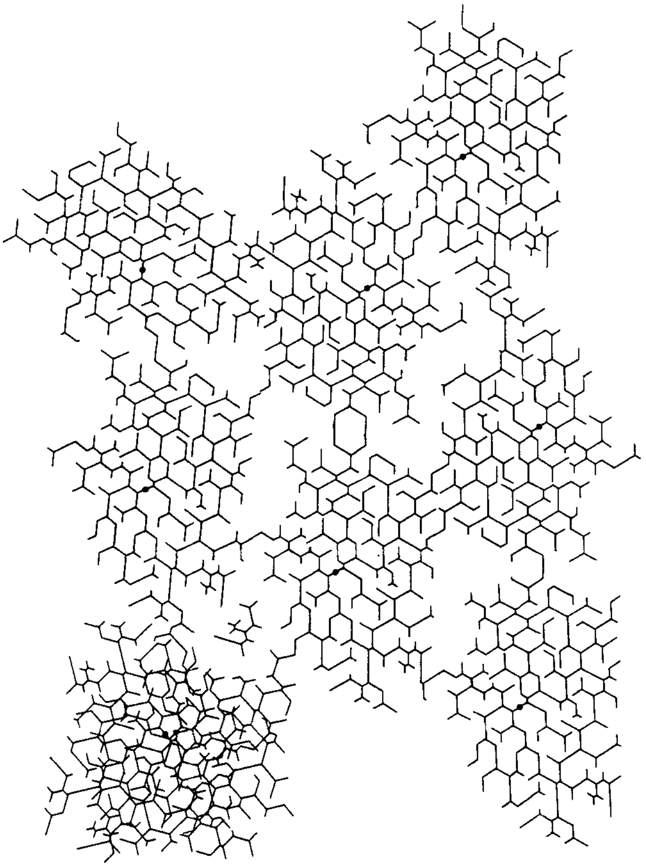

FIGURE 4 Gelled network from rigid FPs, formed at C_0^*. Notice size of interfractal voids.

not only the total interfractal void content is at its peak but the average interfractal void size is the largest. At larger void content and void size no "infinite" rigid network may be created. The above is schematically (and 2-dimensionally!) shown in Figure 4. In it, one FP of the C_0^*-network is interpenetrated by another which may or may not be a covalently-bonded part of the C_0^*-network. By analogy with the ceramic and polycrystalline solids mentioned above[7,12,15-17] the largest interfractal voids are comparable in size to the precursor FPs. The analogy is especially appropriate in light of the fact that ceramics are considered to be fractal in nature with multiple generations of agglomerates[10] each of which is a fractal ensemble of much smaller primary particles.[10,11,50-52]

As the concentration of FPs in solution increases above C_0^*, the size and number of the interfractal voids decrease. This is because at $C_0 > C_0^*$ increasing number of FPs in the network are interpenetrated by others and these invade not only the FP precursors of the network but also the interfractal voids of the C_0^*-network. The FPs in excess of C_0^* may participate as covalently-bonded additions to the original C_0^*-network, as separate networks interwoven with the C_0^*-network, or merely as individual FPs and FP-aggregates trapped in the C_0^*-network. A mixture

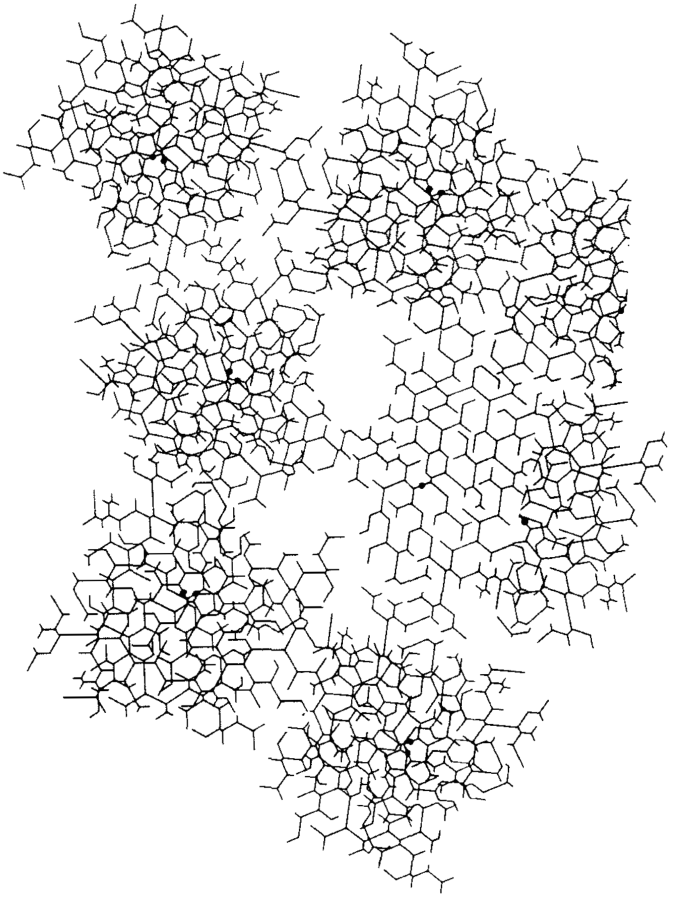

FIGURE 5 Gelled network from rigid FPs, formed at about $2C_0^*$. Notice that the size and number of interfractal voids have decreased.

of these three possibilities is a most likely occurrence. A 2-dimensional schematic representation of a simple $C_0 > C_0^*$ network is shown in Figure 5. In it, parts of separate network and FPs are shown interwoven with the original C_0^*-network.

An important assertion of the Griffith theory of strength of brittle materials[30] is that voids, cracks, and other flaws must be of a certain critical size Q in order to contribute to flaw-initiated failure. Flaws smaller than Q may grow under an applied stress and then contribute to failure, or not grow under the stress and not contribute to failure. In the case of the rather porous FPs in our rigid network gels, intrafractal voids or pores appear not to contribute to flaw-initiated failure of the networks. We reach this conclusion because the shear modulus and failure characteristics were the same within experimental error for network gels identically prepared at a concentration somewhat higher than C_0^* from our smallest FPs and, in parallel, directly from the corresponding monomers.[1,3] In networks prepared directly from monomers the interfractal definition is blurred and intra- and interfractal voids are expected to be of about the same size. This will be even more pronounced when the networks are prepared from monomers at increasing concentrations above C_0^*. We therefore believe that interfractal voids of sizes comparable with the intrafractal voids do not contribute meaningfully to void-initiated failure of the rigid network gels and do not increase in size to surpass the critical size Q. This picture is consistent with Equations (4) and (5) above, placing the size of Q as equal or larger than the largest grain size in the system, FP in our case. Therefore, in each rigid network gel made from FPs in a one-step polycondensation, the flaws may be divided into two categories: One is the intrafractal flaws and interfractal flaws of comparable size that do not contribute to flaw-initiated failure of the gelled network; The second is the larger interfractal flaws that are larger than Q or may grow under stress to become so and contribute to the failure of the network.

Accepting the concept of DRP for networks created exclusively from rigid FPs, we draw the conclusion that in C_0^*-networks the interfractal void fraction is about 0.37. As C_0 increases, both the number and size of the large interfractal flaws decrease and they are expected to finally vanish at $C_0 >> C_0^*$. Since flaws of size Q and larger are comparable in size to the larger primary grains in the system,[7,30] in our rigid networks where the FPs are the primary grains flaws of size $\geqslant Q$ are all interfractal and not intrafractal ones; i.e., in C_0^*-networks the magnitude of Q changes together with the FP size and is comparable to the R_H or R_G of the precursor FPs. This leads to a preferential decrease in the number and size of flaws equal or larger than Q with increases in network concentration above C_0^*: a small additional amount of network mass will reduce the size and number of the larger voids substantially more than of the smaller voids.

When a gelled rigid network is swelled to equilibrium in a good solvent, the degree of swelling mostly reflects the number and size of flaws in the network. This is especially noticeable in one-step rigid networks, even one with $f = 6$[53] which is supposed to be fully rigid,[54,55] but was also observed in two-step rigid networks especially prepared in non-stoichiometric manner in order to vary the level of network imperfections.[56] Because in the interfractal voids and flaws there is less than average polymer mass, there is less local resistance to swelling and the imbibed solvent preferentially, yet not exclusively, concentrates in such sites during network swelling. This is similar to previous observations[57,58] on gelled networks of flexible polymers.

The reduction in modulus upon swelling is, however, as a rule lower than the reduction in modulus obtained from gelled rigid networks synthesized at the lower concentration. Thus, for example, a rigid network synthesized at $C_0^* < C_0 = 5.0\%$ and then swelled to equilibrium at $C_0^* < C = 2.5\%$ will have much higher modulus than a chemically identical network synthesized at $C_0^* < C_0 = 2.5\%$. The reason for the difference is, of course, that when synthesized at $C_0^* < C_0 = 2.5\%$ the gelled network contains many more and larger flaws than when synthesized at $C_0 = 5.0\%$. The swelling from $C_0 = 5.0\%$ to $C = 2.5\%$ lowers the network concentration in the gel and reduces the modulus, but because the network is less defective than when prepared at $C_0 = 2.5\%$, the reduction in modulus is by far smaller.[1-3,56] Figure 6, a composite of several rigid networks prepared at various C_0 and measured there and at various C, is typical.

Flawless rigid network gels, consisting of rigid branchpoints and rodlike segments

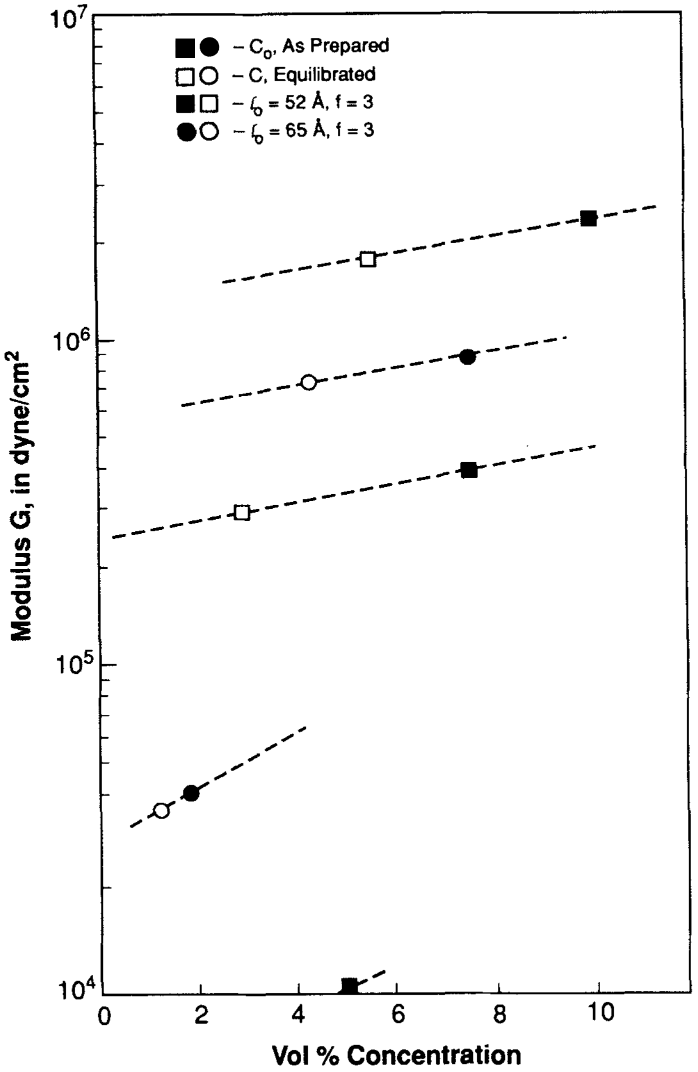

FIGURE 6 Shear modulus vs. polymer concentration in gelled rigid networks prepared in one step from monomers. C_0 is the concentration during network formation and C is the concentration upon swelling to equilibrium in a good solvent. (Networks: polyamides, solvent: DMAc.)

as envisioned by Jones and associates,[55,59] are incapable of significantly swelling or shrinking from the concentration C_0 in which they created. For these networks, substantial volume changes must be accompanied by irreversible bond rupture. In the case of flawless aromatic polyamide C_0^*-networks the gel swelling is expected to be somewhat larger but not much above ca. 20 volume percent[53,60]; for networks prepared at $C_0 > C_0^*$ the swelling is expected to be even smaller. This is because aromatic polyamide segments are created during the polycondensation reaction in both extended and bent configurations[60] and the segments themselves may reversibly deform in several bending modes, many of which are of twist-bending nature.[60-63] Experimentally, one-step rigid polyamide networks with $f = 3$ generally swelled more than ca. 20%, often surpassing 100% volume change.[1-3,60] This was especially noticeable in networks with large l_0. In cases of small l_0 and $C_0 > C_0^*$, especially when $f > 3$, swelling as low as 1% was measured. It is obvious, then, that when relatively large swelling appears in such rigid networks, it is controlled to a large extent by network defects and not by the extension and stretching of individual stiff segments.

The -3.3 power dependence of the modulus of nascent network gels made exclusively from FPs on the size of these FPs,[3] appears at first glance to be straightforward and consistent with observations on ceramics and polycrystalline solids and the theoretical models based on total porosity developed to explain such observations.[7-17] The situation becomes, however, muddied when it is realized that the concentration $C_0 = 5.0\%$ at which these gels were prepared[3] from FPs is almost identical with C_0^* of the largest FPs and grows to about $2C_0^*$ as the FPs get smaller and their C_0^* decreases. Upon an increase in the concentration C_0 above C_0^* we encounter in such rigid gels, hence, not a mere decrease in total porosity but a concurrent decrease in the average size of the interfractal voids and a reduction in the number fraction of voids equal in size to Q or larger. The power dependence of the modulus on the size of the precursor FPs may, then, be associated not only with the number and size of voids equalling or surpassing the critical void size for catastrophic failure, but also with the total interfractal porosity in the rigid gels. At present, we cannot exclude from consideration either of these dependencies. A similar situation exists in the field of ceramics and polycrystalline materials, were certain systems depend on total porosity, others on void size and yet others on both.[7,12,14,64]

An alternative approach to resolve the modulus and, especially, the strength dependence of the one-step rigid gels prepared at $C_0 > C_0^*$ on the size of the FPs at the gel-point may be by the use of the fractal model. By this we do not mean the description or treatment of fracture surface in terms of surface fractal models[65,66] nor do we mean systems where the failure passes through the cores of FPs, as in the case of minimal path for transport in networks when these are modeled as Cayley tress.[67] What we have in mind is simulations of invasive percolation fluid into systems comprising compacts or aggregates of impenetrable substances whose surface is fractal in nature. In such aggregates the voids in between the impenetrable particles are themselves of fractal character.[68] We believe that the propagation of cracks through the weakest areas in a one-step gel created from precursor FPs, i.e., the interfractal surfaces and interstitial regions, can be modeled in a similar fashion. Whether the calculations will produce results consistent with experiment is yet to be seen.

CONCLUSIONS

Gels of rigid polymer networks created at $C_0 \gtrsim C_0^*$ from precursor polyamide FPs to the exclusion of monomers and small oligomers, may be modeled by analogy with dense random packing of solid spheres, or with Voronoi polyhedra. The power dependence of the modulus of such gels on the average size of the FPs appears to be associated more with the size and number of interfractal voids surpassing a critical size for failure, than with the total void content. The number and size of interfractal flaws sufficiently large to affect failure may both contribute concomitantly to failure and low modulus. This becomes evident as we proceed to increase the polycondensation concentration C_0 above C_0^*, where the total interfractal void fraction is estimated to be 0.37. Even though we believe that void size and number beyond Q dominate, the available data are insufficient to exclude total porosity from consideration.

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