Macromolecules **1992,** *25,* 1510–1515

Networks and Gels of Stiff Zigzag Polyamides

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Received August 20, 1991; Revised Manuscript Received October 25, 1991

ABSTRACT: Two series of stiff zigzag polyamide network gels were prepared from monomers in solution by one-step polymerization. Within each, all stiff segments are of identical length, l = 19 Å and l = 32 Å, respectively. The bends between segments are rigid and of 120°. The distances between branchpoints, l_0, are average ones and were controlled by the appropriate monomer mix in the reaction bath. In general, the series with l = 19 Å produced networks with low defect concentration and the series with l = 32 Å was characterized by rather highly defective networks. Upon equilibration in DMAc, the 19-Å zigzag series exhibited shear moduli, G, very close to those of rigid rodlike network gels of comparable concentrations and 1 or 2 orders of magnitude larger than comparable gels of flexible chains. The power dependence of the modulus on the equilibrium concentration and on l_0 is intermediate between that observed for rigid rodlike network gels and that theoretically expected from swollen flexible chain networks. The more defective series, with l = 32 Å, showed huge drops in G with small decreases in the concentration, reflecting their defective nature. Their moduli do not follow power law dependence on either l_0 or the concentration. In the poor solvent formamide, both series shrink and undergo microsyneresis. The results in poor solvent are, hence, given but are not discussed.

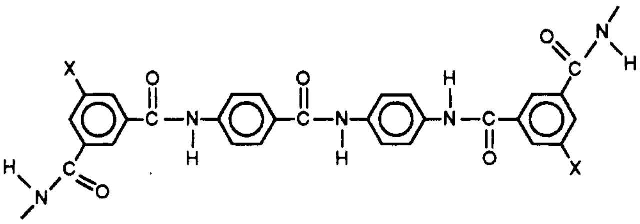
Introduction

Several years ago, we prepared and characterized[1,2] two novel series of unbranched aromatic polyamides. Instead of being "rodlike" in shape, each chain of these linear polymers consisted of many stiff segments. In each polymer, all the segments were of identical length l. They were connected by either rigid or single-atom freely rotating joints, defining an angle of about 120° between adjacent segments and giving the chain an overall appearance of a zigzag line. They will henceforth be called zigzag polyamides. It was found that, in dilute solution, the behavior of the zigzag polyamides with freely rotating joints followed the expectations from freely rotating random coils in which each stiff segment behaves as a single virtual bond.[1] The stiff zigzag polyamides with rigid joints behaved about the same,[2] with the random-coil chains being slightly more expanded. The behavior of all the zigzag polyamides in dilute solution was found to be affected by their equilibrium rigidity,[2] yet in no case did they exhibit lyotropic mesomorphicity at higher concentrations or thermotropic liquid crystallinity in the bulk. This stands in contradistinction to the fact that chemically similar, oligomeric rodlike polyamides with lengths comparable to the segments in our zigzags do exhibit lyotropic liquid crystallinity.[1-3]

We felt it would be interesting to find how permanent networks of stiff zigzag polyamides behave in the dry bulk and in gels swollen to equilibrium in good or poor solvents. Results of this investigation are presented in this paper.

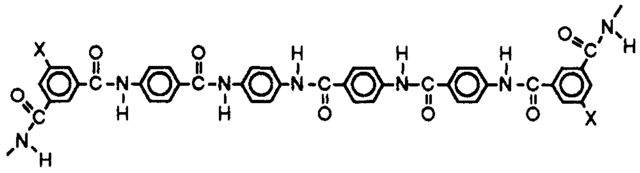
Experimental Section

Two series of rigid zigzag polyamide network gels were prepared in solution from the appropriate monomer mixture by a one-step condensation reaction. The choice of monomers was such that for each series the length, l, of all segments between bends was *identical*, while the contour length between branchpoints, l_0, was an *average* length, except for the first member of each series where $l = l_0$. In series Z-19, when they are straight, all segments are 19 Å long



where X stands for H at the 120° bends between segments in a chain and for the secondary aromatic amide at the branchpoints. For series Z-19, three commercially available monomers were used, keeping a strict stoichiometry between the total amine and total carboxyl groups. The monomers were isophthalic acid 1,3,5-benzenetricarboxylic acid and 4,4-diaminobenzanilide (DABA). By changes in the ratio of the two acids, the average distance l_0 was controlled.

When straight, all segments in the Z-32 series are 32 Å long



where X keeps the same meaning as above. For this series, the acid monomers had to be separately prepared. The trifunctional monomer 1,3,5-tris(carboxyphenyl)benzenetricarboxamide (TCPPT)

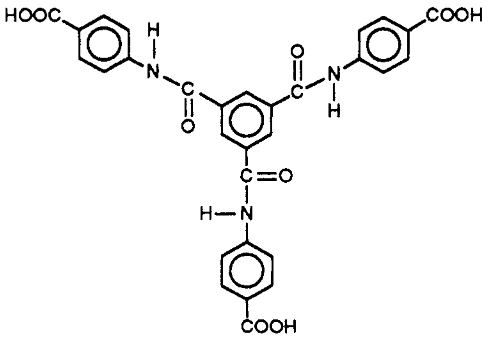


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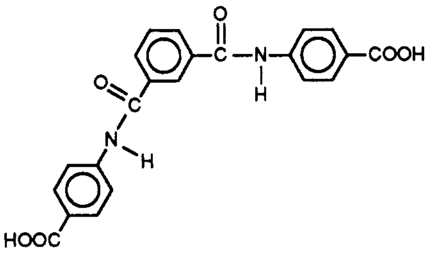
Table I
Properties of One-Step Trifunctional Zigzag Polyamide Stiff Networks and Gels

				mol wt titration per group			equilib in DMAc		equilib in formamide	
code	C_0, vol %	l, Å	l_0, Å	carboxyl	amine	gel, wt %	C, %	modulus G, N/m^2	C, %	modulus G, N/m^2
Z-19E	10.0	19	190	26 700	31 900	90	1.89	1.14×10^5	7.66	4.69×10^5
Z-19B	10.0	19	114	8 000	37 200	97	2.98	1.57×10^5	12.32	7.49×10^5
Z-19H	10.0	19	57	30 800	39 850	98	5.12	2.23×10^5	21.51	7.32×10^5
Z-19C	10.0	19	38	36 400	42 000	99	7.18	2.81×10^5	20.53	6.46×10^5
Z-19A	10.0	19	19	20 000	36 600	99	9.07	3.94×10^5	11.20	4.72×10^5
Z-19J	11.5	19	190	6 700	31 000	NA	3.41	1.97×10^5	10.69	5.26×10^5
Z-19D	11.5	19	57	40 000	50 100	NA	6.66	2.60×10^5	25.96	8.32×10^5
Z-19F	5.0	19	57	10 800	28 800	NA	1.64	1.11×10^5	6.29	3.28×10^5
Z-32A	10.0	32	32	14 800	29 500	NA	5.55	3.97×10^5	11.44	4.73×10^5
Z-32B	10.0	32	64	12 500	30 300	NA	3.28	5.48×10^4	11.07	2.62×10^5
Z-32C	10.0	32	96	>290 000[a]	43 500	NA	2.52	1.94×10^3	8.58	0.76×10^5
Z-32D[b]	10.0	32	192	57 150	47 000	NA		too soft to measure, $[\eta] = 0.84$ dL/g[c]		
Z-32E[b]	10.0	32	320	>290 000	38 000	NA		too soft to measure, $[\eta] = 0.67$ dL/g[c]		

[a] The level of resolution of our titrations. [b] No shape-supporting gel was formed. [c] Solutions contain some insolubles. Gels were dissolved by heating for 3 h at 140 °C in DMAc/LiCl.

was prepared in a mixture of *N,N*-dimethylacetamide (DMAc) and pyridine from 1,3,5-benzenetricarboxyloyl chloride and a molar excess of 4-aminobenzoic acid. Details of this preparation are given by Aharoni and Edwards.[4] The difunctional monomer bis(carboxyphenyl)isophthalamide (DCPIP) was prepared in a similar fashion from isophthaloyl chloride and excess 4-aminobenzoic acid. By use of DABA with the desired ratios of TCPPT to DCPIP, an *identical* $l = 32$ Å was obtained during the one-step polymerization, together with a controlled *average* l_0.



The one-step polymerization was conducted in DMAc containing 5% LiCl(DMAc/LiCl) at about 105 °C in the presence of a slight molar excess of both triphenyl phosphite (TPP) and pyridine. Details of this procedure and of the subsequent purification were all described in great detail by Aharoni and associates[4-8] and need not be repeated here. It suffices to say that a strict balance between the amine and total carboxyl groups in the monomer mixture was maintained in all polymerizations.

The monomer DABA was obtained from Sandoz Corp. and twice recrystallized from 10:1 methanol/acetone prior to use. Even so, the material retained a light gray-beige color, indicating the presence of a trace amount of dark impurities. All other monomers, reagents, and solvents were obtained from chemical supply houses at the highest available purity and used as received. The structures of TCPPT and DCPIP and their reasonable purity were verified by means of proton and carbon-13 NMR spectroscopy using a Varian XL-200 Fourier transform NMR spectrometer. Solutions (10%) in deuteriated solvents containing TMS as the internal reference were generally used.

The procedures used for sample preparation and equilibration of the permanent gels in pure DMAc (good solvent) and formamide (poor solvent), for the determination of the shear modulus, *G*, by means of linear compression experiments, for the sol/gel fractionation, and for titrations for carboxyl and amine end groups were all described in detail in refs 4 and 7.

The crystallinity indices of several networks and linear polyamides were estimated from their wide-angle X-ray diffraction (WAXD) patterns. These were collected at room temperature on a Philips APD-3600 automated diffractometer operating in parafocus mode and using monochromatized Cu Kα radiation. The density of dry networks was determined by pycnometry in mixtures of 1,2-dichloroethane with either methanol or carbon tetrachloride. Dilute-solution viscosities of polymer solutions were measured at 25 °C in internal dilution Cannon-Ubbelohde glass viscometers with solvent efflux times longer than 100 s. The solvents used for these measurements were either DMAc/LiCl or concentrated sulfuric acid.

Results and Discussion

All the networks and gels prepared in this study are listed in Table I together with the volume concentration during polymerization, C_0, the equilibrated volume concentration, C, the lengths l and l_0, the titrated molecular weight, M_n, the gel fraction, and the intrinsic viscosity, $[\eta]$, of two systems that were too imperfect to maintain their shape and were substantially soluble after prolonged heating in DMAc/LiCl.

The moduli, *G*, were obtained from the purified gels equilibrated in either DMAc or formamide. The moduli obtained at ambient temperature (ca. 20 °C) are listed in Table I. These are about 2 orders of magnitude higher than the moduli obtained from flexible-chain gels of comparable concentrations.[9] It should be mentioned in this context that no measurable difference was found in the modulus of specimens measured fully immersed in the equilibrating solvent and out of it. Also, no solvent secretion was observed for the stiff zigzag polyamide gels under the conditions used for modulus measurements.

In Table II we present data extracted from Table V of ref 4. Here, PBNT stands for networks from poly(*p*-benzanilide nitroterephthalamide) and PBT for networks from poly(*p*-benzanilide terephthalamide). The PBNT and all the stiff zigzag polyamide networks swell nicely in neat DMAc while PBT requires the stronger solvent DMAc/LiCl in order to swell and become optically clear. Cross-polarized light microscopy indicated that all the above gels are isotropic in nature. For the purpose of structural comparison, the zigzag polyamides, PBNT, and PBT are about the same.

When the entries in Tables I and II are compared, one finds that, for the same C_0 and comparable l_0, the modulus of the stiff zigzag gels is lower than that of the rigid rodlike gels. The difference, however, is not large. With respect to swelling there is no clear pattern: in DMAc the zigzag and PBNT gels appear to swell to about the same level. In formamide, the gels turn opaque upon shrinking, indicating the onset of local, microscopic phase separation known as microsyneresis. In formamide at $C < C_0$, the intensity of the opacity appears to be directly related to the degree of shrinking. Such a behavior was previously noted[4] in the behavior of PBT in pure DMAc. As will be seen below, the moduli obtained from formamide-

Table II
One-Step Trifunctional Rigid Rodlike Polyamide Gels Equilibrated in DMAc and Formamide and Their Modulus, *G*, at Ambient Temperature[a]

			N,N-dimethylacetamide		formamide	
code	description	l_0, Å	*C*, %	modulus *G*, N/m²	*C*, %	modulus *G*, N/m²
R-10C	rigid rod PBNT	32.5	6.72	6.98×10^5	16.60	18.31×10^5
R-12A	rigid rod PBNT	52	5.05	2.62×10^5	15.76	6.66×10^5
R-12B	rigid rod PBNT	71.5	4.10	1.25×10^5	15.11	5.89×10^5
R-12C	rigid rod PBNT	130	2.96	0.43×10^5	14.50	4.19×10^5
R-12D	rigid rod PBNT	208		too soft to measure		not measured
R-8	rigid rod PBNT	38.5	4.65	2.29×10^5		not measured
R-11	rigid rod PBNT	58	4.30	1.53×10^5		not measures
R-14	rigid rod PBNT	77.5	4.40	1.37×10^5		not measured
R-18	rigid rod PBNT	116.5	3.45	0.69×10^5		not measured
R-29	rigid rod PBNT	155.5		too soft to measure		not measured
R-10C	rigid rod PBT	32.5	6.72	6.98×10^5	16.60	18.31×10^5
R-11A2	rigid rod PBT	52	8.9	5.79×10^5		not measured
R-11A	rigid rod PBT	52	8.42	5.63×10^5	22.27	14.65×10^5
R-11B	rigid rod PBT	71.5	16.78	4.19×10^5	32.81	9.77×10^5

[a] All network gels were synthesized at concentration C_0 = 10.0‰ (v/v).

equilibrated samples do not adhere to power law dependence on l_0 and show much a wider scatter than the values obtained from the DMAc-equilibrated ones. All the results obtained from the gels equilibrated in formamide will be given for completeness, while the discussion will concentrate on the gels equilibrated in DMAc.

The stiff polyamide segments in rodlike and zigzag networks can be completely straight or bent. Using the rotational isomerization model concepts, in the straight segments the amide group placements are either all anti or all syn. Bends, each of about 20°, in the segments occur when a single placement converts through a 180° amide flip from anti to syn or vice versa.[10] That is, instead of only ring flipping we have in the polyamide segment some amide flipping, too. When intersegmental H-bonds do not play a major role, as is the case in the gelled networks, the activation energy for such anti–syn interconversion is relatively small[10,11] and, especially in the absence of intersegmental H-bonds, identical with ring flipping.[12] The energies of the two placements are about the same,[13] making the anti placement only slightly more favorable than the syn placement. This results in both anti and syn placements being inserted into the segments during polymerization. Hence, some stiff segments will be straight and others bent. The recent results of Cain et al.[12] indicating that 180° flips are a primary mode of relaxation to the practical exclusion of flips or librations of substantially smaller amplitude support our belief that in rigid networks one of the modes of segmental bending is by 180° flips of the amide groups, i.e., anti–syn interconversions. The important fact to realize is that because of the segmental stiffness and shortness and because of the branchpoint rigidity, the random-coil model and Gaussian statistics, usually employed to describe flexible chain networks, are not applicable in our case.

For temperature effect studies, slabs of equilibrated gels were fully immersed in large volumes of the equilibrating liquid, slowly brought up to the desired temperature, and then kept there for at least 30 min prior to the linear compression measurement at that temperature. The results are presented in Figure 1. From it, we conclude that gels of stiff zigzag polyamides prepared at higher concentrations or with shorter l_0 are insensitive to temperature changes in the range of 20 °C < $T \leq$ 120 °C. This is similar to our previous observations on rigid rodlike network gels.[4] Gels prepared in relatively dilute concentrations or with the longest l_0 showed a slight reduction in *G* with temperature. By analogy with the observations on gels of rigid rodlike networks,[4] we interpret this to be caused by the more defective network gels slightly swelling with improvement in solvent quality upon heating.

Unlike the nonexistent or minor effects of temperature, changes in the average distance l_0 strongly affect the swelling of the "as-prepared" gels upon immersion in the good solvent DMAc. In Figure 2, the volume changes of members of the series Z-19 and Z-32 prepared at C_0 = 10.0% are plotted against the distance l_0 of the various networks. The volume changes are linear with l_0, but the slope of the Z-32 series is substantially steeper than that for the Z-19 series. We believe this reflects the generally higher defect concentration present in the Z-32 series.

When the results of the DMAc-equilibrated gels in Figure 2 are plotted in terms of equilibrated concentration *C* against l_0, a power dependence of *C* on l_0 emerges, provided C_0 is the same for all gels. This is clearly evident in Figure 3 where all C_0 = 10.0%. Here for series Z-19

$$C \propto l_0^{-0.86}$$

and for series Z-32

$$C \propto l_0^{-0.71}$$

Similar data are shown in Figure 4 for all our shape-supporting stiff zigzag gels. Here the trends are all the same as in Figure 3, but because of the small number of samples with C_0 = 11.5% and C_0 = 5.0% power laws for such samples could not be obtained.

The moduli, *G*, of the Z-19 series gels appear to follow a power law dependence on *C*. The results are graphically shown in Figure 5, where it should be noted that for C_0 = 10.0% the values of *C* correspond to C/C_0. It is interesting to note that the moduli for each equilibration liquid all fall on a single line, having rather small scatter for DMAc-equilibrated samples, and do not reflect a measurable dependence of *G* on the initial C_0 of the stiff zigzag gels. For DMAc-equilibrated gels the power law is

$$G \propto C^{0.77}$$

which for C_0 = 10.0% is far higher than the theoretically expected $G \propto C^{0.333}$ for flexible gels.[14-17] For formamide-equilibrated gels the power law dependence is

$$G \propto C^{0.81}$$

That is, both power dependencies are essentially the same:

$$G \propto C^{0.8}$$

This power law dependence of *G* on *C* is much smaller

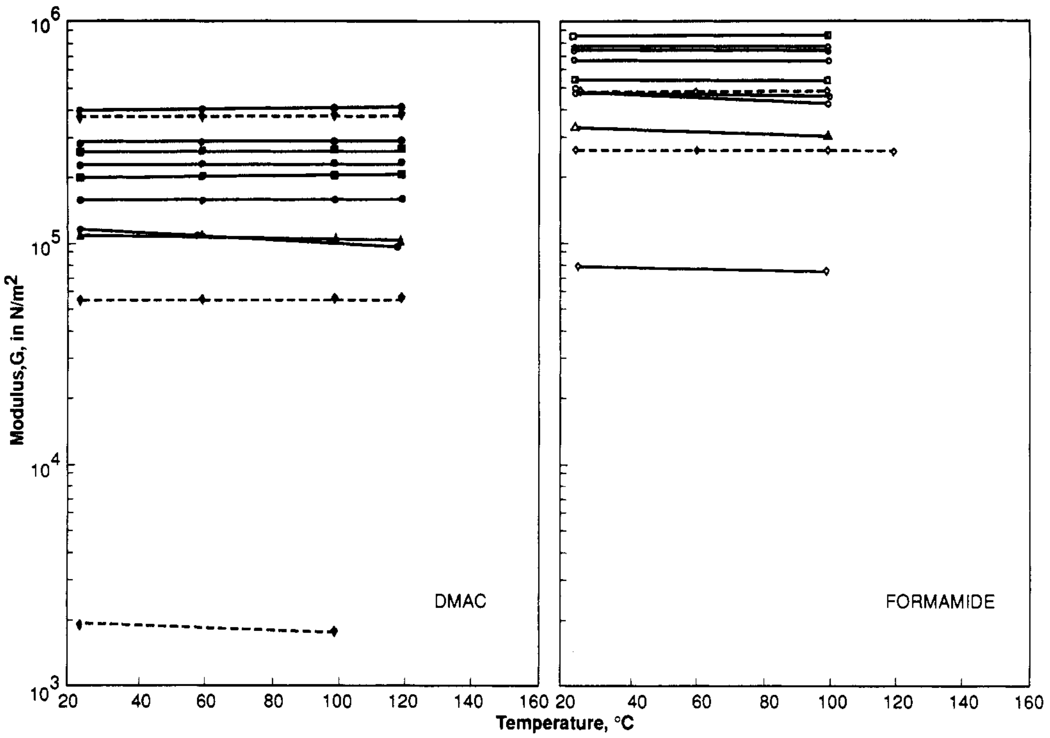


Figure 1. Modulus, G, as function of temperature for stiff zigzag polyamide gels equilibrated in DMAc and formamide: (●, ○) Z-19, C_0 = 10.0%; (■, □) Z-19, C_0 = 11.5%; (▲, △) Z-19, C_0 = 5.0%; (♦, ◇) Z-32, C_0 = 10.0%.

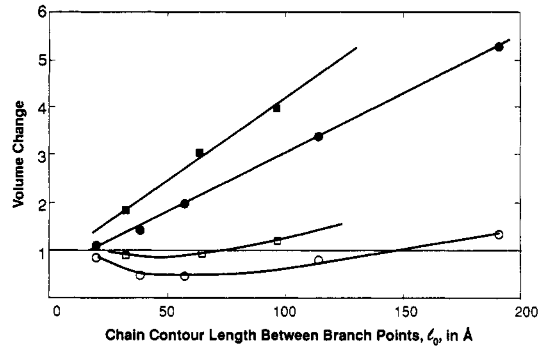


Figure 2. Volume changes upon equilibration as function of l_0 of gels synthesized at C_0 = 10.0%. Solid symbols: DMAc-equilibrated. Open symbols: formamide-equilibrated. Circles = Z-19 series, squares = Z-32 series. 1.0 = as-prepared volume of gel.

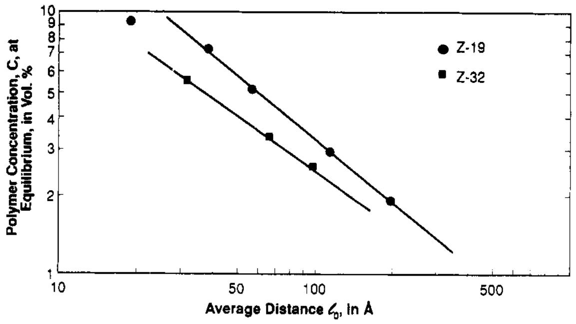


Figure 3. Swelling upon equilibration in DMAc of stiff zigzag polyamide gels prepared at C_0 = 10.0 v/v %.

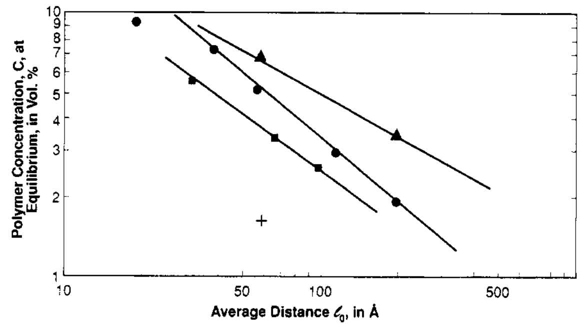


Figure 4. Swelling upon equilibration in DMAc of stiff zigzag polyamide gels: (●) series Z-19, C_0 = 10.0%; (▲) series Z-19, C_0 = 11.5%; (+) series Z-19, C_0 = 5.0%; (■) series Z-32, C_0 = 10.0%.

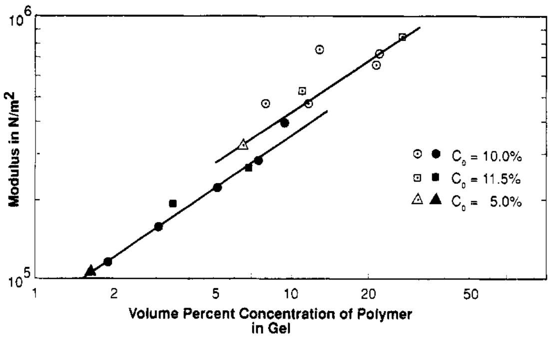


Figure 5. Modulus, G, of series Z-19 as a function of polymer concentration upon equilibration in DMAc (solid symbols) and formamide (open symbols).

than the $G \propto C^{3.15}$ previously observed in the case of DMAc-equilibrated rigid rodlike networks.[4]

When the results of series Z-32 are added to those in Figure 5, Figure 6 is obtained. Clearly, the moduli of series Z-32 show huge drops with small decreases in C, even though Z-32A, in which $l = l_0$, falls in the same range as the Z-19 series. When the moduli of the DMAc-equilibrated gels are plotted against l_0, in Figure 7, the same pattern is obtained: the moduli of series Z-19 show a moderate inverse dependence on l_0

$$G \propto l_0^{-0.55}$$

while for series Z-32 the drop in G with l_0 is very large and does not follow a power law dependency. We believe that the huge drops in C and G for series Z-32 and the remarkable softness of Z-32D and Z-32E indicate that beyond Z-32C the networks are not infinite anymore.

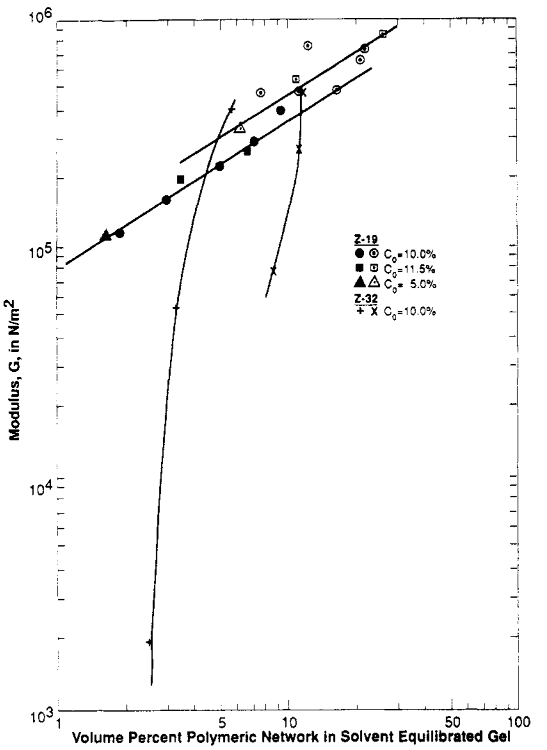


Figure 6. Modulus, G, vs concentration, C. Solid symbols and +: DMAc-equilibrated. Open symbols and ×: formamide-equilibrated.

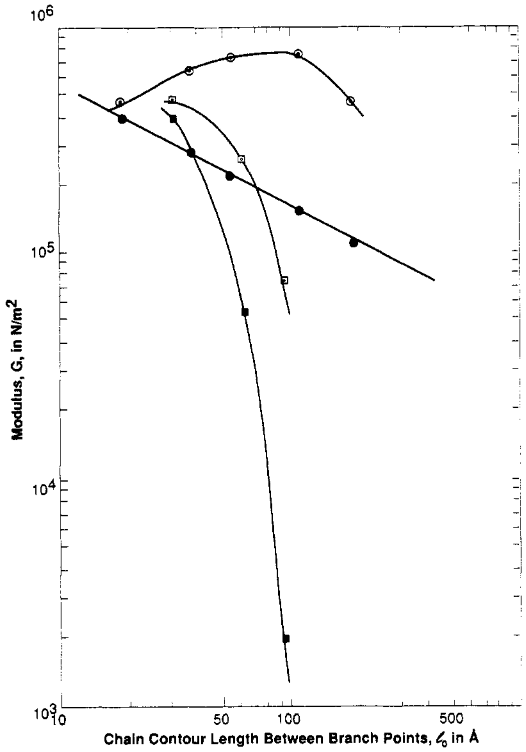


Figure 7. Modulus, G, vs l_0 of series Z-19 and Z-32 polymerized at C_0 = 10.0%. Solid symbols: DMAC-equilibrated. Open symbols: formamide-equilibrated. Circles: Z-19. Squares: Z-32.

As was the case with the dependence of G on C, the above dependence of G on l_0 is much weaker than in the case of rigid rodlike network gels where $G \propto l_0^{-2.11}$.[4] The reasons for the differences in power law dependency between rigid rodlike and stiff zigzag networks are not understood by us at present, but we should emphasize that the power law dependency of the stiff zigzag gels is intermediate between the one observed for rigid rodlike gels and the one theoretically expected for gels of flexible networks prepared at one concentration, C_0, and then equilibrated to a new concentration, C.

Table III
Densities and Crystallinity Indices of Aromatic Polyamide Networks and Unbranched, Un-Cross-Linked Stiff-Chain Polyamides[a]

code	description	l, Å	l_0, Å	density, g/cm³	crystallinity, %
	Rigid Networks				
Z-19E	stiff zigzag network	19	190	1.347	0
Z-19B	stiff zigzag network	19	114	1.344	0
Z-19H	stiff zigzag network	19	57	1.345	0
Z-32E	stiff zigzag FPs	32	320	1.365	0
Z-32D	stiff zigzag FPs	32	192	1.362	0
Z-32C	defective stiff zigzag network	32	96	1.360	0
A1703-11B	stiff rodlike network		72	1.428	~15
A1703-11C	defective stiff rodlike network		120	1.435	26
A1703-11D	failed stiff rodlike network		195	1.447	39
	Unbranched Stiff Chains				
A0500-14C	stiff zigzag	26		1.326	5
A0500-14D	stiff zigzag	39		1.339	1
A0500-14B	stiff zigzag	46		1.304	0
A0500-13D	high-M rodlike			1.433	>90
A0500-13B	high-M rodlike			1.453	>90
A0500-9B	oligomeric rodlike			1.536	100

[a] All measurements on purified, as-prepared systems after vacuum drying at ca. 125 °C to constant weight.

When all the solvent was removed from the DMAc-equilibrated gels, the networks collapsed to produce clear or translucent very tough solids. Their density, ρ, was measured and is listed in Table III together with the density of other relevant aromatic polyamide networks and linear polymers. Also listed are the crystallinity levels of these systems as measured by WAXD. The most striking fact is that the stiff zigzag networks collapse to the density range expected from amorphous flexible polymers and that, at the same time, they retain their amorphicity. This is rather similar to the behavior of unbranched stiff zigzag chains with random l[18] and is dramatically different from stiff zigzag chains in which all the lengths l are identical. In the latter case, entries A0500-14C, -14D, and -14B in Table III, a low level of crystallinity is present in the as-prepared polymers and it increases dramatically to 25% and higher upon thermal annealing.[2] Stiff rodlike networks and unbranched rodlike polymers have densities and crystallinity indices higher than stiff zigzag networks and chains, and the density appears to grow linearly with percent crystallinity.

The entries in Table III instruct us that the various stiff zigzag networks collapse to about the same density independently of l_0 and almost independently of l. The fact that the fractal polyamides Z-32E and Z-32D collapse to the same density interval as the three Z-19 and Z-32C networks indicates that network imperfections do not control the final density. In light of the above, we believe that the ability to collapse reflects a substantial degree of segmental and, probably, branchpoint and bend deformability. This allows the segments in the collapsing dry networks to pack close to one another but in such a random pattern as to prevent ordering and the onset of crystallization. This is consistent with our previous observations on the solution properties of stiff zigzag chains,[1,2] where the chains were found to be sufficiently flexibile to adopt the shape of an expanded random coil in which each stiff segment corresponds to a virtual bond.

Conclusions

Gels of stiff zigzag polyamide networks were prepared by a one-step polymerization in solution at concentration

C_0 and then purified and equilibrated in the good solvent DMAc and the poor solvent formamide. The DMAc-equilibrated gels prepared from well-formed stiff zigzag networks exhibit large shear moduli, G, very close to the moduli of gels of comparable concentrations prepared from rigid rodlike networks. These moduli are about 2 orders of magnitude larger than the moduli of comparable concentration gels prepared from flexible chain networks. The power law dependence of the modulus on the concentration C and on the distance l_0 is intermediate between the theoretical expectations from flexible chain networks and that experimentally observed for rigid rodlike networks. Formamide-equilibrated stiff zigzag networks generally shrank to $C > C_0$ and concomitantly turned opaque, indicating microsyneresis. Their moduli did not follow a power law dependence on either l_0 or C. Highly defective networks show a large drop in G with modest decreases in C and no power law dependence, for both DMAc- and formamide-equilibrated gels.

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