Gelled Networks Prepared from Rigid Fractal Polymers

Shaul M. Aharoni

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

Received March 9, 1990; Revised Manuscript Received May 25, 1990

ABSTRACT: Macroscopically homogeneous gelled networks, characterized by rigid rodlike polyamide segments averaging 38.5 Å in length connected by stiff trifunctional branch points, were prepared in a single step from fractal polymers, from monomers, and from mixtures of fractal polymers with monomers. The shear modulus, G, of the networks prepared from monomers or from the smallest fractal polymers is high and of similar magnitude. As the radius, R_H, of the fractal polymers increases, the shear modulus of the gelled networks prepared from them decreases as $G \propto R_H^{-3.3}$. The concentration of residual unreacted sites in the networks prepared from the smaller fractal polymers is substantially smaller than in networks prepared from the larger fractal polymers. The critical concentration for the formation of "infinite" networks, C_0^*, is independent of the critical concentration for entanglement, C^*, of the precursor fractal polymers.

Introduction

When polymer networks consist of rigid rodlike segments covalently connected by stiff branch points, the assumptions underlying flexible Gaussian networks[1,2] are not expected to hold true. Primary among those are the long flexible Gaussian segments and the ease of formation of intramolecular closed loops. Thus, the basic papers[3–8] have to be modified when rigid rodlike polymers comprise the network rather than flexible ones. First steps were taken toward modeling polymeric networks and gels comprising rigid rodlike segments connected by flexible[9] and stiff[10,11] branch points. These models, as those for the flexible networks, consider the systems as rather homogeneous. Our experimental work with gels of rigid rodlike polyamide networks interconnected by stiff branch points[12,13] indicated that when the networks were prepared from monomers by a single-step (one-step) polymerization, the homogeneity assumption is not consistent with physical reality. In this case, the growing highly branched polymeric entities in the pregel state were found to conform with the fractal model.[13] Therefore, we shall call these entities fractal polymers (FPs). Recent experimental[14] and theoretical[15] treatments of flexible networks describe them as microheterogeneous systems. The above suggested to us that the size of the fractal polymers at the gel point may affect, or maybe even dominate, the properties of their respective gelled network progenies.

In order to test this important point, we have altered the one-step polymerization procedure described in ref 12 and 13. In the present work, aliquots were withdrawn from the reaction mixture as the reaction progressed in the pregel state, and the polymer was immediately precipitated, then carefully purified, and finally characterized. The fractal polymers were further reacted in solution either alone or mixed with the appropriate monomers at a polymeric product concentration of $C_0 = 5.0\%$ and lower. Then the modulus and other properties of the resulting networks were determined in the "as-prepared" state and after equilibration in the excellent solvent *N*,*N*-dimethylacetamide (DMAc).

Experimental Section

The preparation of rigid rodlike gelled polyamide networks by a single step from either monomers or FPs was achieved by the use of the Yamazaki procedure[16] as modified by Aharoni for the preparation of cross-linked systems.[12,13,17,18] The fractal polymers were similarly prepared by terminating the reaction at various stages during the pregel stage.[12,13] For the purpose of this study, these polymeric products were washed first with 1:10 DMAc/methanol, then twice in boiling methanol, then in water, and finally in methanol prior to careful drying under dynamic vacuum at ca. 120 °C. Spectroscopic and chromatographic analyses indicate the above sequence to remove residual reagents, reaction byproducts, monomers, and low molecular weight (low-*M*) oligomeric species. The purified fractal polymers were then characterized by dilute and concentrated solution viscosity and static and dynamic light scattering techniques. After characterization they were redissolved in DMAc/5% LiCl at ca. 100 °C, the solution was cooled back to ambient temperature, pyridine and triphenyl phosphite (TPP) in the appropriate amounts were added, DMAc/5% LiCl was added to bring the polymer concentration to $C_0 = 5.0\%$ (w/v), and then the solution was heated to ca. 110 °C for the polymerization reaction to proceed in the absence of monomers and low-*M* oligomers. To determine the critical concentration for network formation, C_0^*, the above procedure was repeated at decreasing C_0 until C_0^* was reached, where the formed network did not fill anymore the whole volume of the reaction medium. After gelation all the reactions were allowed to continue for 3 h and then terminated. The reaction vessels were then broken, and the gels were retrieved and sliced into slabs ca. 1 cm thick for mechanical testing and equilibration in pure DMAc. These procedures were described in detail.[12,13]

Dilute and concentrated solution viscosities of the soluble fractal polymers were measured in DMAc/5% LiCl at 25 °C in internal dilution Cannon-Ubbelohde glass viscometers with solvent efflux time longer than 100 s and at 23 °C in an oscillating-sphere Nametre direct-readout viscometer. Weight-average molecular weight, M_w, of pregel samples was measured on their solutions in DMAc/5% LiCl in a low-angle light scattering Chromatix KMX-6 instrument. The hydrodynamic radius, R_H, and molecular weight distributions were determined from diffusion measurements in a Langley-Ford LSA-II photon correlation spectrometer (PCS) by taking numerical transforms of the photon correlation data using our enhanced version of Provencher's CONTIN program.[19]

The amounts of free carboxylic acid and amine groups present in gelled networks prepared at $C_0 = 5.0\%$ were measured in 5:1 DMAc/H_2O by first conducting a titration with methanolic KOH using phenolphthalein as indicator and then conducting a back-titration with aqueous HCl using bromophenol blue to indicate the end point. The carefully purified gels were first ground and dried at 150 °C to constant weight and then immersed in the solvent mixture at close to 100 °C. After the mixture cooled, methanolic KOH was added. After swelling in the solvent mixture for several days, the suspensions were back-titrated with the HCl. The titrations required not less than 3 KOH and 6 HCl incremental additions and took about a week to reach each end point and remain there. From the amounts of dry network samples and the titrated KOH and HCl solutions, the amounts of free end groups in the polymer were calculated. In this series the amounts of carboxyl and amine were about equal.

0024-9297/91/2224-0235$02.50/0

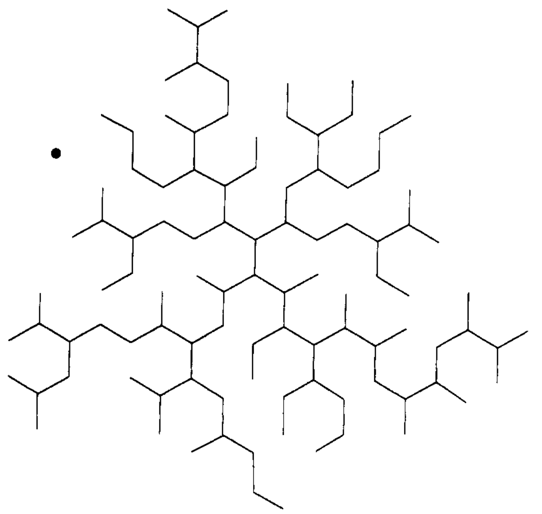
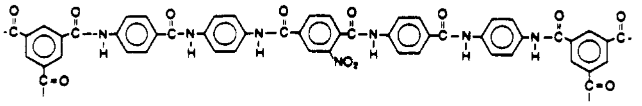


Figure 1. Two-dimensional representation of a rigid rodlike fractal polymer with l_0 = 38.5 Å and stiff trifunctional branch points. The solid dot stands for a solvent molecule ca. 7 Å in diameter.

The equilibrium shear modulus, G, was determined from linear compression measurements of the gelled networks. These and all other procedures were described in ref 12 and 13 in detail.

Results

All the rigid rodlike networks and fractal polymers (FPs) in this study were prepared as described above. They were made from a 2:1:2/3 molar ratio of 4,4′-diaminobenzanilide (DABA)/nitroterephthalic acid (NTPA)/1,3,5-benzenetricarboxylic acid (BTCA). Networks prepared from FPs had, of course, the same chemical composition. The same monomer mixture was used in the two cases where FPs and monomers were used together. The polymerization proceeds through the creation of amide groups, with segmental tips and unreacted sites at branch points being divided about evenly between amine and carboxyl moieties that can be further reacted if and when desired. The 2:1:2/3 monomer ratio produces networks or FPs characterized by stiff trifunctional branch points linking together rigid rodlike aromatic polyamide segments whose *average* length, l_0, is 38.5 Å:



A two-dimensional representation of such a fractal polymer, with $M_n \cong 68\,000$, is shown in Figure 1. The solid dot in the figure corresponds in size to a molecule of DMAc. Dilute-solution viscosity measurements[13] indicated that the rigid fractal polymers are porous to solvents and highly draining. The relative emptiness of the FPs is in agreement with theoretical expectations.[20] By holding the length l_0 constant we were able to follow the effects of polymer concentration and the size of the fractal polymers on the properties of the gelled networks without having to account for the strong effects of changes in l_0 on the same properties.[12] The characteristics of the fractal polymers subsequently used for the preparation of rigid gels are listed in Table I. The critical concentrations for the formation of gelled "infinite" networks, C_0*, were determined by sequences of one-step polymerizations of monomers or FPs at decreasing C_0, down to C_0 = 1.0%. The C_0* values are listed in Table I together with the relevant parameters of the corresponding FPs.

The viscosities, η, of the four fractal polymers 45XB, 72A, 74B, and 45XG are plotted in Figure 2 on log–log paper against the polymer weight percent concentration, c. To eliminate the effects of minor differences in the DMAc/5% LiCl solvent viscosity, η_s, the plotted viscosity η is defined as the solution viscosity η_0 less η_s. Depending on the solvent batch, η_s fell in the range 3.5–4.2 cP, reflecting the exact amounts of LiCl in the DMAc and the levels of moisture in the solvent. In the dilute-solution regime the power dependence of η on c gave the proportionality

$$\eta \propto c^{\alpha_1} \tag{1a}$$

with α_1 falling in the interval 0.70–1.13, straddling the theoretically expected value of 1.0. In the concentrated-solution regime

$$\eta \propto c^{\alpha_2} \tag{1b}$$

with $2.78 \leqslant \alpha_2 \leqslant 3.10$ for the three fractal polymers for which sufficient data points are available. The magnitude of α_2 is substantially smaller than normally encountered with flexible linear polymers. Importantly, while the solutions of the two smaller FPs, 45XG and 74B, move smoothly from the dilute to the concentrated regime, the solutions of the two large FPs, 45XB and 72A, clearly pass through a well-defined semiconcentrated regime. The presence of three concentration regimes for the large fractal polymers is in agreement with the theoretical prediction of Muthukumar[21] for such systems.

In the case of linear flexible polymers, the critical concentration for entanglement, C*, is defined as the point where the solution viscosity clearly deviates from the dilute-solution behavior. In our case, C* lies at ca. 6% for 45XG, 4% for 74B, and ca. 0.8% for both 45XB and 72A. The change from semiconcentrated to concentrated solution occurs at C**, which falls at 4–5% concentration for the two larger FPs. log–log plots against c of the specific viscosity, η_{sp}, or reduced viscosity, η_{sp}/c, merely accentuate the breaks in the curves at C* and C** but do not affect their positions measurably.

All networks in this study were prepared at C_0 = 5.0% and lower. The equilibrium shear modulus, G, of the networks prepared at C_0 = 5.0%, measured on the "as-prepared" gelled networks and at the equilibrium concentration C after immersion in DMAc, is given in Table II. The values of G at C are given here only for completeness and will not be discussed in this paper. As indicated in Table II, the time it took for the C_0 = 5.0% networks to form and gel dramatically increases with the size of the precursor FPs. Furthermore, these networks decreased in macroscopic rigidity from the relatively brittle 59Q to the very soft 74C, which barely could maintain its shape. A measure of the increasing fragility of the networks prepared from FPs with increasing size can be gathered from the increased swelling (smaller C) upon equilibration in DMAc and the falling apart of the two networks made from the largest FPs.

In Table III are listed the number-average molecular weight, M_n, per residual unreacted site in the C_0 = 5.0% networks prepared from fractal polymers, as obtained from titrations. Also are listed the M_w and M_n of these FPs, taken from ref 13.

The intensities of small-angle X-ray scattering (SAXS) from fractal polymers and one descendent network were measured in ref 13 and plotted in terms of log (intensity) at the scattering vector q against log q. The FPs and network were all of the same chemical composition, rigid rodlike segments with l_0 = 38.5 Å and stiff trifunctional

Table I
Characteristics of Fractal Polymers Used in, and the Critical Concentration, C_0*, for, Network Formation[a]

FP code	$[\eta]$, dL/g	M_w	M_n	M_w/M_n	R_H, Å	C_0*, %
monomers						1.75
59E	0.26	9 600	3 850	2.5	18.1	2.0
74B	0.39	24 000	~8 000	3.0	27.7	2.4
72A	1.09	320 000	~40 000	~8.0	80	4.15
45XB	1.26	410 000	47 650	8.6	120.3	4.5
59D	1.61	>700 000	156 000		155	5.0

[a] All FPs are chemically identical, rigid polyamides with l_0 = 38.5 Å and stiff trifunctional branch points. M_w and R_H are calculated on the basis of total amount of soluble polymer in the sample. Additional characteristics and correlations are given in ref 13.

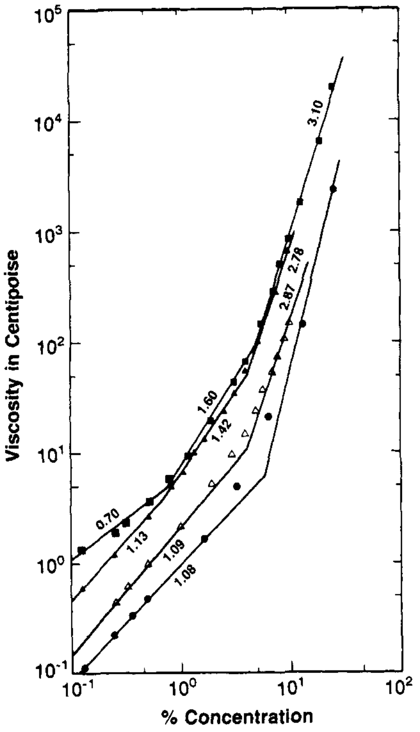


Figure 2. Viscosity as a function of concentration of fractal polymers. Small FPs: (●) 45XG; (△) 74B. Large FPs: (▲) 72A; (■) 45XB.

branch points. The slopes of the lines through the SAXS data points define the scattering exponents which are related to the surface dimensionality, D_s, of surface fractals through[22-24]

$$I(q) \propto q^{-(6-D_s)} \tag{2}$$

For classical surface fractals, having a nonfractal normal density bounded by a fractal surface,[23] the meaningful values of the surface dimension D_s lie in the interval $2 \leqslant D_s < 3$ with $D_s = 2.0$ in the case of smooth surface and increasing toward 3 with increasing corrugation. If, however, the scattering waves are sensitive to the mass of the scattering fractals and not to the nature of their surface, then in the range of validity[22-24]

$$I(q) \propto q^{-D_F} \tag{3}$$

with $1 < D_F < 3$ for mass fractals. The values of D_s from ref 13 are listed in Table IV together with the observed scattering exponents. The D_s values of all the dry samples fall in the range $2.0 \leqslant D_s \leqslant 2.7$, and those of the solvent-swollen samples lie in the interval $2.5 \leqslant D_s \leqslant 3.0$. The fact that the scattering exponents were consistently between 3 and 4 clearly indicates that we observe the surface dimensionality according to proportionality 2 and not the mass dimensionality of relationship 3.[25] No correlation was observed between the D_s values in Table IV and the sample polydispersities in Table I.

The shear moduli, G, of the "as-prepared", C_0 = 5.0% gelled networks are plotted in Figure 3 on log-log paper against the hydrodynamic radius, R_H, of the precursor FPs and against their intrinsic viscosity, $[\eta]$, obtained from dilute-solution measurements. Although some scatter exists, lines can easily be passed through the data points giving the approximate proportionality of G and R_H

$$G \propto R_H^{-3.3} \tag{4}$$

and of G and $[\eta]$

$$G \propto [\eta]^{-3.8} \tag{5}$$

The power of −3.3 in proportionality 4 is close to the theoretically expected power of −3 for the relationship between the modulus and the radius of the precursor cluster.[26] It is higher than the −2.3 power dependence of the compressive strength of polystyrene particles on their diameters, reported by Buscall et al.[27] We have no proof for it, but we believe that the stronger dependence of G on $[\eta]$, as compared with the dependence of G on R_H, may reflect the highly draining nature of our rigid fractal polymers.

Discussion

The major observations of this work are (a) a strong inverse dependence of the modulus of the gelled networks on the size of their precursor fractal polymers, at least when prepared in the absence of extra monomers, (b) the independence of C_0* and C of these networks from the critical concentration for entanglements, C*, of their FPs, (c) the reduction, in the networks, of the interpolymer covalent bond formation with increased size of the fractal polymers, at least for networks prepared at $C^* \lesssim C_0$ = 5.0%, and (d) the development of a well-defined intermediate-concentration regime in solutions of large FPs. The first two observations will be briefly discussed below.

The decrease in the modulus G with increasing precursor FP size is mostly caused by the fact that the modulus is proportional to the density of the fractal polymers in the gel and, hence, inversely proportional to their R_H^{-3}.[26] Two additional factors may contribute somewhat to increase the G–R_H negative power dependence: (a) larger network voids may allow the gelled network to deform more under a given stress, thus reducing its modulus, and (b) the concentration of interparticle amide bonds is smaller in the case of the large FPs than for the small FPs. In networks prepared by a one-step polymerization directly from monomers or from very small FPs, the size of the "building blocks" is small and of the same order of magnitude. Hence their high modulus and its similar magnitude. When monomers and oligomers are present together with fractal polymers in the evolving "infinite" network, the average size of the precursor particles reduces, the modulus of the network increases, and the correlation between modulus and the size of the pure fractal polymer fades away.

Table II
Modulus of Gelled Networks Prepared from Rigid Fractal Polymers at C_0 = 5.0%[a]

network code	made from	R_H of FP, Å	time to gel	modulus, G, at C_0 = 5.0%, dyn/cm^2	equilibrated C, %	modulus, G, at C, dyn/cm^2
45P	monomers only		minutes	2.28×10^6	3.36	1.53×10^6
59Q	FP 59E	18.1	seconds	2.20×10^6	2.55	1.55×10^6
74E	FP 74B	27.7	minutes	0.15×10^6	2.42	0.0915×10^6
74D	FP 72A	80	ca. 1 h	0.025×10^6	2.01	0.015×10^6
74F	FP 45XB	120.3	ca. 4 h	0.007×10^6	*b*	*b*
74C	FP 59D	155	ca. 5 h	0.0032×10^6	*b*	*b*
77A	4% 74B + 1% monomers		minutes	0.266×10^6	2.1	0.0674×10^6
77B	4% 72A + 1% monomers		minutes	0.298×10^6	2.0	0.0525×10^6

[a] All networks made by the same chemistry from the same monomer composition to produce an identical structure with l_0 = 38.5 Å and stiff trifunctional branch points. Networks prepared from FPs were made from well-purified fractal polymers with no additional monomers. [b] Fell apart upon swelling in DMAc.

Table III
Unreacted End Groups in Networks Prepared from Fractal Polymers at C_0 = 5.0%

network code	M_n per residual end group	made from FP	M_w of FP	M_n of FP	M_n of FP/M_n per residual end group
59Q	19 230	59E	9 600	3 850	0.20
74E	57 500	74B	24 000	~8 000	~0.14
74D	4 875	72A	320 000	~40 000	~8.2
79B	5 110	45XB	410 000	47 650	9.3
74C	12 690	59D	>700 000	156 000	12.3

Table IV
Scattering Exponents and D_s Values for Several Members of the 45X Series[a]

		dry samples		solvent-swollen samples	
code	form	scattering exponents	D_s	scattering exponents	D_s
45XE	pregel	3.75	2.25	3.5	2.5
45XF	pregel	3.5	2.5		
45XG	pregel	4.0	2.0	3.3	2.7
45XB	pregel	3.9	2.1	3.35	2.65
45XD	network	3.3	2.7	3.0	3.0

[a] Values rounded within ±0.05.

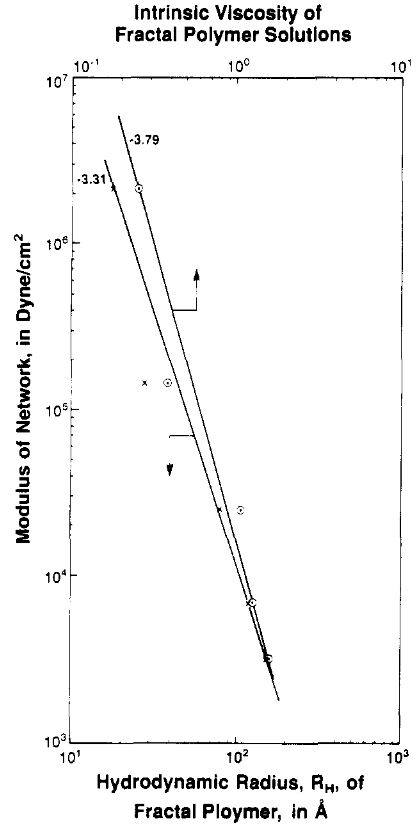


Figure 3. Modulus of chemically identical "as-prepared" networks at C_0 = 5.0% made from precursor fractal polymers as a function of the FP hydrodynamic radius (bottom) and intrinsic viscosity in dL/g (top).

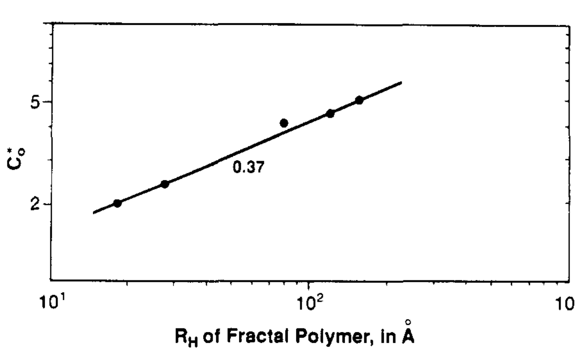


Figure 4. Critical concentration for gelation, C_0*, as a function of R_H of FPs. All are chemically identical, rigid rodlike polyamides with l_0 = 38.5 Å and stiff trifunctional branch points.

A double-logarithmic plot of C_0* from Table I against R_H of the precursor FPs (Figure 4) clearly shows the power dependence

$$C_0^* \propto R_H^{0.37} \tag{6}$$

An identical power dependence of C_0* on $M_w^{1/2}$ was obtained, indicating that $D_F \cong 2$. A comparison of the data in Table I with the concentration C* in Figure 2 indicates that C_0* is substantially smaller than C* for the smaller FPs. For large FPs, $C_0^* > C^*$, with this C_0* being larger than the C_0* of the smaller FPs. Importantly, in the case of the small FPs, networks prepared at concentrations C_0 such that $C^* > C_0 > C_0^*$ form faster and produce a modulus higher than networks from the larger FPs prepared at identical $C_0 > C_0^*$ which is larger than C* for these FPs. The relatively rapid formation of networks from monomers and small FPs at $C_0 < C^*$ tells us that a substantial fraction or most of the interparticle covalent bonds are formed between ramified FP surfaces or relatively thin FP exterior layers and appears not to require deep interparticle penetrations and reactions of previously unreacted sites in the FP interior. This conclusion is supported by the very small number of unreacted end groups present in the C_0 = 5.0% networks made from small FPs (cf. Table III). In the case of the large FPs, C_0 and C_0* are several times larger than C*, indicating a very intense interparticle interpenetration during the network formation. Nevertheless, the modulus of such networks is substantially lower than the modulus of networks made from smaller FPs at the same C_0. The substantial number of residual reactive end groups measured on networks prepared at C_0 = 5.0% from large FPs, the deep interparticle interpenetrations, and the lower modulus combine to instruct us that a smaller concentration of interparticle covalent bonds is created under such conditions. In light of the above and the fact that attempts to prepare gelled networks from several large FPs at $C_0 = C^*$ have failed, we conclude that relatively small amounts of covalent bonds form between large FPs at concentrations $C_0 \geqslant C^*$.

Referring back to Table II, we find that the modulus of gels of chemically identical networks prepared at constant $C_0 > C_0^*$ decreases with the increasing size of the fractal polymers. The closer is C_0 to C_0^* of that particular FP size, the lower is the modulus. The reduction in modulus is especially dramatic for networks 74F and 74C whose C_0^* are very close to their $C_0 = 5.0\%$. The behavior and appearance of our gelled networks indicate a macroscopic homogeneity of a system that is fractal on the macromolecular size scale. Much above C_0^*, say at $C_0 \geqslant 10\%$, the effects of the proximity to C_0^* may wash away.

From the values of M_w, R_H, and $[\eta]$ in Table I the proportionalities

$$M_w \propto R_H^{2.29} \tag{7}$$

and

$$M_w \propto [\eta]^{2.53} \tag{8}$$

are obtained. These are close to the proportionalities

$$M_w \propto R_H^{2.05} \tag{9}$$

and

$$M_w \propto [\eta]^{2.39} \tag{10}$$

derived in ref 13 for the fractal polymers of series 45X, which are chemically identical with the FPs in Table I. These power dependencies reflect a very open structure for the rigid highly branched polymeric entities—when probed on the size scale of solvent molecules. In terms of fractal models, the M_w–R_H power relationships are consistent with the behavior of mass fractals. The growth kinetics studies of the highly branched rigid (and flexible) pregel entities[13] support the percolation model of branched polymers. On the other hand, the SAXS results reported in ref 13 and here, as well as porosimetry measurements on the dry pregel species and postgel network,[13] support a surface fractal behavior. The reasons for the agreement of our systems with both types of fractals are not understood by us at present. The rigid segments in our systems are characterized by an *average* segment length l_0 and are not all of the same length. This segmental length distribution renders our systems inconsistent with common Cayley tree models.[28] It may be that this distribution is a contributing factor to the fractal behavior of the systems described in this work.

In conclusion, we believe that in sufficiently concentrated solutions the one-step rigid networks are created by the concurrent formation of mostly interparticle covalent bonds and continuous FP aggregation with varying degrees of interpenetration. In our case, amide groups serve as the interparticle covalent bonds holding together an "infinite" network. We should note here that the above description may not fit two-step networks in which preformed long linear chains are cross-linked in a second step either at the chain ends or at reactive sites along the chain. The heterogeneities of such networks may better be described along the lines of the recent communication of Bastide and Leibler.[14]

Finally, we believe the above observations may be transferrable to flexible networks prepared by a single step from monomers or, as was done in this work, from FPs obtained in the pregel stage and purified to remove monomers and oligomeric species. Due to intraparticle cyclization and entanglements, highly probable in flexible systems and less likely in the rigid rodlike ones, the dependence of the flexible-network properties on the size and/or dimensionality of its precursor fractal polymers may not be as discernible as in the case of the gelled rigid networks.

Acknowledgment. The author thanks Dr. K. Zero for obtaining the light scattering results and the referees for most helpful comments and suggestions.

References and Notes

(1) Dusek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.
(2) Flory, P. J. *Discuss. Faraday Soc.* **1974**, *57*, 7.
(3) James, H. M.; Guth, E. *J. Chem. Phys.* **1943**, *11*, 455; **1947**, *15*, 669.
(4) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(5) Wall, F. T.; Flory, P. J. *J. Chem. Phys.* **1951**, *19*, 1435.
(6) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapters XI, XIII.
(7) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1958.
(8) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapters V, VII.
(9) Boue, F.; Edwards, S. F.; Vilgis, T. A. *J. Phys. (Paris)* **1988**, *49*, 1635.
(10) Ball, R. C.; Kantor, Y., unpublished.
(11) Jones, J. L.; Marques, C. S. *J. Phys. (Paris)* **1990**, *51*, 1113.
(12) Aharoni, S. M.; Edwards, S. F. *Macromolecules* **1989**, *22*, 3361.
(13) Aharoni, S. M.; Murthy, N. S.; Zero, K.; Edwards, S. F. *Macromolecules* **1990**, *23*, 2533.
(14) Bastide, J.; Leibler, L. *Macromolecules* **1988**, *21*, 2647.
(15) Kruger, B.; Schafer, L.; Baumgartner, A. *J. Phys. (Paris)* **1989**, *50*, 3191.
(16) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373.
(17) Aharoni, S. M. *Macromolecules* **1982**, *15*, 1311.
(18) Aharoni, S. M.; Wertz, D. H. *J. Macromol. Sci., Phys.* **1983**, *B22*, 129.
(19) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213, 229.
(20) Alexander, S. *Phys. Rev. B* **1989**, *40*, 7953.
(21) Muthukumar, M. *J. Chem. Phys.* **1985**, *83*, 3161.
(22) Martin, J. E. *J. Appl. Crystallogr.* **1986**, *19*, 25.
(23) Schmidt, P. W. In *The Fractal Approach to Heterogeneous Chemistry*; Avnir, D., Ed.; Wiley: Chichester, 1989, pp 67–79.
(24) Martin, J. E.; Hurd, A. J. *J. Appl. Crystallogr.* **1987**, *20*, 61.
(25) Daoud, M.; Martin, J. E. In *The Fractal Approach to Heterogeneous Chemistry*; Avnir, D., Ed.; Wiley: Chichester, 1989; pp 109–130.
(26) Martin, J. E.; Adolf, D.; Wilcoxon, J. P. *Phys. Rev. A* **1989**, *39*, 1325.
(27) Buscall, R.; Mills, P. D. A.; Goodwin, J. W.; Lawson, D. W. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4249.
(28) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

Registry No. (BTCA)(DABA)(NTPA) (copolymer), 82914-79-2.