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Gels of Two-Step Rigid Polyamide Networks

Shaul M. Aharoni

Polymer Science Laboratory, Allied-Signal, Inc., Research and Technology, Morristown, New Jersey 07962

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ABSTRACT: Gels of two-step networks were made by first preparing linear polyamides with reactive sites along the chain and then cross-linking by reacting them in solution with connector species in a second step. By using stiff, linear polyamide chains and connector species of varying rigidity, we prepared here gels of fully rigid, semirigid, and semiflexible networks. We then studied their behavior. When all the *accessible* reactive sites on the chain and all the end groups of the connector species are reacted, a defect-free network is obtained. *When low-defect gels of two-step fully rigid and semirigid networks are swollen to equilibrium in a good solvent, their modulus increases above its magnitude in the higher concentration "as-prepared" state.* This is contrary to the cases of semiflexible networks, highly defective rigid networks, and "normal" flexible networks. The above unique behavior is due to the fact that in the swollen low-defect rigid network gels most of the stiff segments are straight and cannot stretch further, while in the as-prepared gels a significant fraction of the stiff segments are bent, allowing for straightening, gel swelling, and easier deformation. A description of the structure of the two-step rigid networks and their defects is presented.

Introduction

Permanent gels of covalently linked rigid polymer networks can be made in one or two steps. In this paper it will be shown that the behavior of low-defect two-step rigid gels is different from that of their one-step analogues and of gels made from flexible networks. The most dramatic difference is the fact that the static shear modulus, G, of such low-defect two-step rigid gels in the swollen state is higher than that in the "as-prepared" more concentrated state.

In the one-step method, we start with a solution of the appropriate monomers, whose average functionality is above 2.0, and conduct the polymerization in a single step. When the synthesized network is rigid, it is characterized by stiff segments connected by rigid branchpoints, as in the compositionally typical fragment I (Chart I). Structurally, however, the stiff all-para segments exist in either straight or bent shape, with each bend being introduced by a syn placement of an amide group in an otherwise all-anti segment, or vice versa. The coexistence in well-formed gelled networks of bent and straight stiff segments is responsible for their very high modulus and low total strain during macrodeformation and makes possible and explains their low degree of swelling during equilibration in good solvents.

In the pregel stage, the growing highly branched polymeric entities conform with the fractal model.[1,2] We therefore call such species fractal polymers (FPs). When the total polymer concentration in the reaction mixture, C_0, is above a certain critical threshold, C_0^*, the system eventually gels and becomes immobile. We have previously demonstrated that, in the case of rigid network gels, their static shear modulus is extremely high[3-5] relative to gels of comparable concentration made from flexible polymers. Their modulus is practically independent of temperature;[5] under externally applied stress their deformation to break is very small;[1,5,6] and their swelling in the good solvent *N,N*-dimethylacetamide (DMAc) is to a large extent attributable to network defects and imperfections.[6] These are brought about by incomplete reaction of the available functionalities in the reaction mixture. Almost all the fully rigid, semirigid, and semiflexible networks we have previously synthesized and described were prepared by the one-step method.[1-5]

The second method requires the preparation of high molecular weight (high-M) linear polymer chains in a first step and then, after purification and in a new reaction mixture, cross-linking them many times along the chain. We call this a two-step method. Here we consider only the cross-linking achieved by the use of a suitable cross-linking agent present in solution with the cross-linkable linear polymer. A variant of the two-step method in which the cross-linking involves only the reactive chain ends will not be considered in this work. In the case of flexible polymers, it is maintained[7] that the one-step and two-step methods are expected to produce two different kinds of molecular networks. We will show here that such differences are present and are amplified in the case of rigid network gels.

Two-step networks prepared from high-M linear stiff chains may be fully rigid, semirigid, or semiflexible, depending on the nature of the cross-linking species and on the extent of reaction. When the cross-linking species are rigid and short, then the resulting network is fully rigid. When reacted at both ends, the short cross-linking species serve as connecting struts between the stiff linear chains, preventing them from approaching closer or drifting apart in the gel; they will henceforth be called connectors. The semirigid gels can be prepared from stiff linear chains and somewhat flexible, rather short connector species. This may allow for higher overall gel elasticity and, probably, increased cross-linking efficiency. The semiflexible gels may be prepared from the linear stiff chains and long flexible cross-linking species. If the latter are sufficiently long and flexible, then the gel will reflect to a large extent their flexible nature and to a lesser extent that of the stiff chains.

Gels of two-step fully rigid, semirigid, and semiflexible networks were prepared in this work from linear stiff aromatic polyamides. Their modulus G was measured in the as-prepared state and after being equilibrated in several good and poor solvents. A few one-step rigid networks similar to those previously described[1-5] were prepared for comparison and their moduli determined at various degrees of swelling. The behavior of the low-defect two-step fully rigid and semirigid networks, to be described below, was unexpected and astounding.

Because we emphasize in this work the broad structural features of two-step rigid networks and not their specific

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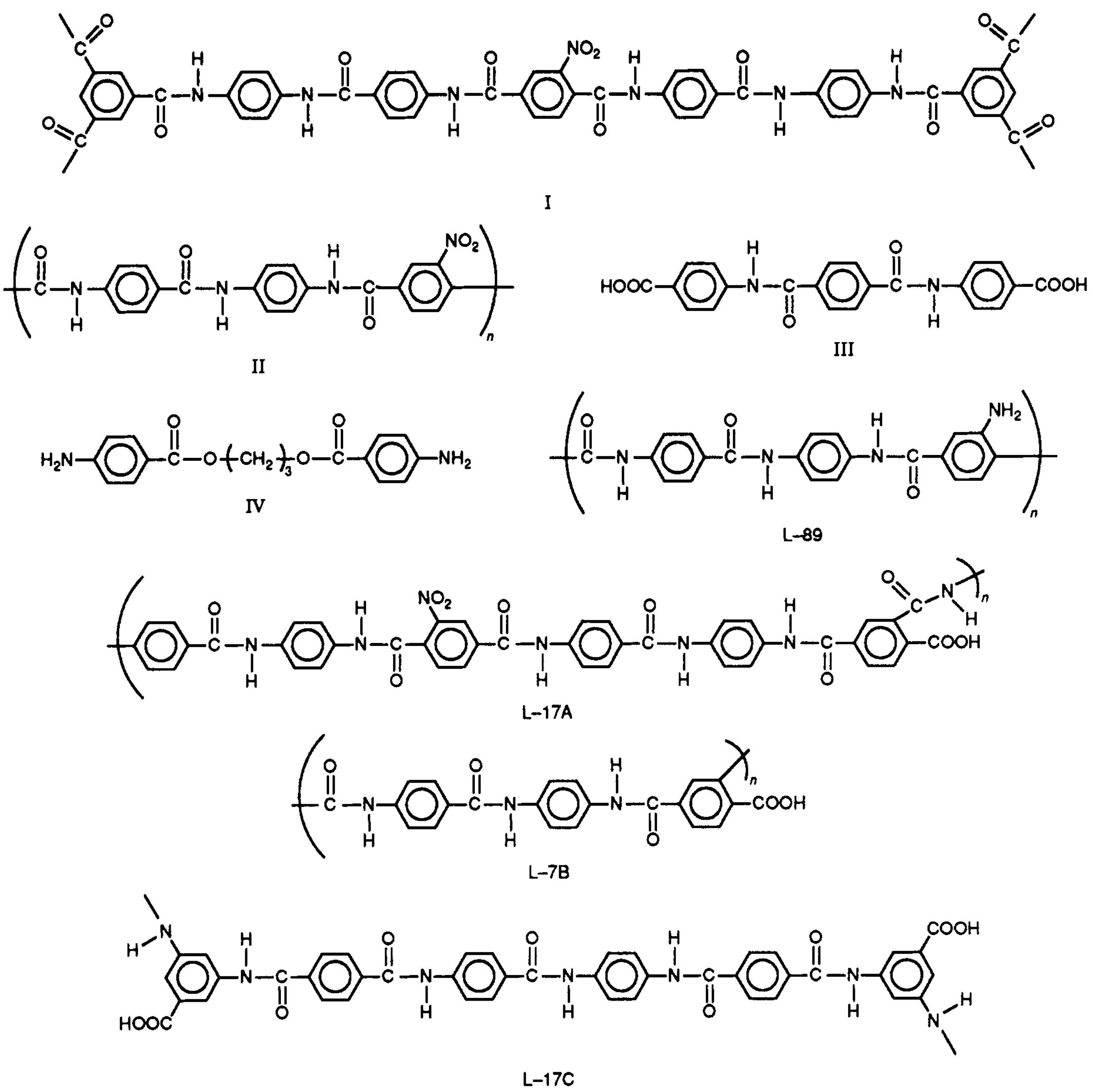
Chart I



details, the compositions and structures of the individual linear stiff polyamides and connector species will be given in the Experimental Section together with all other experimental details. The gelled networks will be described and characterized in the Results section. In the last section the two features unique to gels of two-step rigid networks will be discussed.

Experimental Section

Synthesis. All syntheses were performed by either a Schotten–Baumann-type reaction where acid chloride is reacted with amine or a Yamazaki[8] type reaction where a carboxylic acid is reacted with aromatic amine. Both reactions create amide groups. In order to keep the monomers and polymeric products in solution, the reactions were carried out in a solution of 5 wt % LiCl in DMAc, an excellent solvent mixture for aromatic polyamides. The Schotten–Baumann-type reaction was carried out at temperatures from ambient to close to 85 °C, depending on monomer and polymer solubility. The Yamazaki reactions were all conducted at temperatures from ca. 95 °C up to ca. 115 °C. A slight molar excess of triphenyl phosphite (TPP) and pyridine was used in the Yamazaki reactions and only pyridine for the Schotten–Baumann ones. In both reactions the presence in the system of reagents, unreacted species, and reaction byproducts substantially lowered the solvent quality to be poorer than either DMAc or DMAc/5% LiCl.

The monomer 4,4′-diaminobenzanilide (DABA) manufactured by the Wakayama Seika Kogyo Co. was obtained from Kennedy and Klim, Inc., and was used without further purification. The same monomer was obtained from the Sandoz Corp. but required two or more recrystallizations from 10:1 methanol/acetone to become sufficiently pure for polymerization. The monomer trimethylene glycol bis(*p*-aminobenzoate) was obtained from the Polaroid Corp. under the name Polacure and recrystallized from methanol prior to use. All other monomers, reagents, and solvents were purchased from chemical supply houses at the highest available purity and used as received.

High-*M* Linear Aromatic Polyamides with Reactive Sites. Two kinds of high-*M* linear aromatic polyamides were prepared. In one, all backbone amide groups are in the para positions of the aromatic rings. In this case, all the reactive sites are attached to the rings in positions ortho to the stiff backbone. In the second kind, an occasional symmetrically trisubstituted ring is introduced, bearing a reactive site such that the 1 and 3 positions become part of the stiff chain and the 5 position carries the reactive site. It is important to realize that when a linear polyamide chain containing, for instance, 20% meta-substituted and 80% para-substituted rings is laid flat, its end-to-end distance is only about 5% shorter than that of a wholly para-substituted chain of the same contour length.[6,9,10] Therefore, the insertion of some 1,3,5-trisubstituted rings in the positions where subsequent cross-linking is supposed to occur is not expected to significantly affect the overall rigidity of the resulting network. This was, indeed, found to be the case.

The *all-para*-polyamide was prepared in two steps: first a poly(*p*-benzanilidenitroterephthalamide) was prepared as previously described[3,4,11] by reacting under Yamazaki conditions equimolar amounts of DABA and nitroterephthalic acid (NTPA) to obtain II (Chart I). After workup and purification, this polymer may be converted to poly(*p*-benzanilideaminoterephthalamide) (coded L-89; Chart I) by such procedures as hydrogenation with metallic zinc or tin in concentrated HCl, or a $SnCl_2{\cdot}2H_2O/HCl$ mixture,[12] or with a sodium borohydride complex[13] in a manner similar to that described by Wu and Tesoro.[14] A rhodium-containing complex of the borohydride may alternatively be used.[15] The intrinsic viscosity of the nitro precursor was $[\eta]$ = 1.37 dL/g and that of the amine progeny L-89 was $[\eta]$ = 0.84 dL/g. From the viscosity of the nitro polymer we obtained a weight-average molecular weight M_w = 12 140 by using the relationship[11]

$$[\eta] = 5.93 \times 10^{-5} M_w^{1.068}$$

This molecular weight corresponds to about 90 aromatic rings per chain and an average chain contour length of 580 Å.

Three high-*M* linear stiff polyamides containing meta substitution were prepared. The first, with reactive carboxylic groups in the ortho position to the backbone, was prepared in three steps as follows: 1,2,4-benzenetricarboxylic anhydride was heated to dissolution in a large excess of methanol and swirled hot for several minutes to yield 100% monomethyl ester of 1,2,4-benzenetricarboxylic acid. ^1H and ^{13}C NMR spectroscopy indicated that 70% of the ester groups were on the 1 position and 30% on the 2 position. The purified product was reacted under Yamazaki conditions with NTPA and DABA in a 1:1:2 molar ratio, to obtain a stiff linear polyamide with an average distance of l_0 = 46.5 Å between bends. In the last step, the polymer was dissolved in DMAc containing an excess of LiI and kept at ≥150 °C for 2 h. Under these conditions the LiI selectively hydrolyzes the methyl ester[16] to produce a linear polyamide (coded L-17A) whose idealized repeat unit is shown in Chart I. From its intrinsic viscosity of 0.59 dL/g, an $M_w \simeq 20\,000$ was estimated by analogy with previous work.[17] This corresponds to about 160 rings and a chain contour length of a little over 1000 Å. The second polyamide (coded L-7B; Chart I) was prepared in a similar fashion from a 1:1 molar ratio of the monomethyl ester of 1,2,4-benzenetricarboxylic acid and DABA, followed by hydrolysis of the ester group. The average distance between chain bends is l_0 = 27 Å, and the intrinsic viscosity of 0.31 dL/g indicates a molecular weight of about 7000 and a chain length of about 350–400 Å. The third stiff polyamide containing meta substitution was prepared in a Schotten–Baumann-type reaction from a 1:1:2 molar ratio of DABA, 3,5-diaminobenzoic acid, and terephthaloyl chloride. This procedure was previously employed in order to obtain carboxy-substituted poly(*m*-phenyleneisophthalamide).[18,19] The linear polyamide (coded L-17C) with an idealized repeat unit of that shown in Chart I had an intrinsic viscosity of 0.40 dL/g in concentrated H_2SO_4, from which a molecular weight of $M_w \simeq 10\,000$ was estimated.[20] This corresponds to a chain contour length of over 500 Å.

Connector Species. Several connector species were used in the second step to form gels of covalently bonded networks from the linear polyamides described above. The rigid connector 60B was prepared from 2:1 *p*-aminobenzoic acid and terephthaloyl chloride (III in Chart I). Fully rigid networks were made from the stiff linear polyamides and, separately, 60B, NTPA, and DABA. The Polacure molecule (IV in Chart I) is significantly more flexible, but because of its shortness, the networks made with it were not substantially flexible and we classify them as semirigid.

A flexible cross-linking species, namely, dicarboxy-terminated poly(ϵ-caprolactam) with a degree of polymerization (DP) of about 30 and $[\eta]$ = 0.18 dL/g, was prepared by us in accordance with Sorenson and Campbell[21] from 30:1 ϵ-caprolactam and sebacic acid. The number-average molecular weight, M_n, of this connecting species (coded F-30) is about 3400 and its contour length about 300 Å.

Gelled Networks. All two-step gelled networks were prepared from the high-*M* stiff linear polyamides and the connecting species described above. A modification of the Yamazaki procedure designed to handle gelled products[3-5] was employed in all cases. For the purpose of this work, all second-step polymerizations were conducted at 105–110 °C with a residence time at that temperature of 4 h from the onset of gelation. The network concentration in the as-prepared gels, C_0, was calculated in all cases but one on the basis of the concentration of the high-*M* linear precursor. In the gelled network coded N-32A, prepared from the linear stiff polyamide L-89 and the long flexible connector F-30 in about equal weights, C_0 was calculated from the combined weight of both polymeric species.

Several one-step rigid gels for comparison were prepared in solution from the appropriate monomer mixtures, as described previously.[1-5]

Swelling–Deswelling Procedures and Modulus Determination. After synthesis, the gelled networks were cut into ca. 1-cm-thick slabs with a very sharp blade. Their equilibrium shear modulus, *G*, was measured at ambient temperature (21–23 °C), in most cases without immersion in solvent. Within experimental error, there was no difference between the modulus of the slabs measured out of solvent and those at equilibrium in solvent. The modulus was determined from the extent of uniaxial deformation of the gel by a flat surface under at least four different loads. The displacement was measured by a Humboldt universal penetrometer equipped with a flat tip whose surface area could be adjusted such that the displacement was always limited to fractions of a millimeter. The data scatter depended on the modulus, the higher it was the larger the scatter. It ranged from fractions of 1% for the softer gels up to about 5% for the most rigid ones. To minimize the scatter, we measured in this study each specimen at least twice and used up to six specimens per sample. Then, all these values were averaged to give the result for each gel.

After the modulus of the as-prepared gels was measured, the slabs were weighed and transferred into a large excess of DMAc. It took several solvent changes for them to reach equilibrium in pure DMAc. This process required from 1 to 6 weeks, depending on the thickness of the gel slabs and on the nature of the network. In all cases, the gel was considered to be in equilibrium when no change in its weight and modulus could be detected within 48 h from being placed in a fresh batch of the equilibration solvent. After reaching equilibrium in DMAc and modulus determination, the gel slabs were transferred to a different solvent or solvent mixture and the equilibration process was started anew. Not all the gels underwent the same number and order of equilibration steps. Most networks experienced 3–6 such steps but one, the semiflexible N-32A, underwent 8 equilibration and modulus cycles.

Characterization. Dilute-solution viscosities of the high-*M* linear stiff polyamides and the connecting species F-30 were measured in DMAc/5% LiCl or concentrated sulfuric acid at 25 °C in internal dilution Cannon-Ubbelohde glass viscometers with a solvent efflux time longer than 100 s. The structures and purity of the polymers and all connector species used in this study were confirmed by ^1H and ^{13}C NMR spectra obtained in appropriate deuteriated solvents at 50.3 and 100.6 MHz on Varian XL-200 and Varian XL-400 Fourier transform NMR spectrometers.

In order to estimate the degree of cross-linking obtained in fully rigid gelled networks, several of them together with their respective precursor polymers were subjected to the following procedure: After the network formed in the second step, the reaction was allowed to continue for 4 h. Then some of the gel was passed through a blender to obtain fine-grained particles. These were exhaustively extracted to remove all unreacted connector species and finally dried to constant weight under dynamic vacuum at 120 °C. Then, weighed aliquots of the dry network were placed in DMAc/5% LiCl containing either 4-iodoaniline or 3,4,5-triiodobenzoic acid in large excess. The networks swelled in the solvent containing the iodinated species, and when equilibrium was reached, pyridine and TPP were added. After several additional hours, a Yamazaki reaction was initiated at 105 °C and allowed to continue for not less than 6 h. Then the reaction mixture was cooled overnight down to ambient temperature. The swollen gel particles were filtered and repeatedly extracted in hot DMAc to remove all unreacted iodinated species. They were then dried as above and submitted to Robertson

Table I
Gels of Two-Step Networks Prepared from Stiff Polyamide L-89[a]

code	connector	ratio	C_0, %	G at C_0	C_1, %	G	C_2, %	G	C_3, %	G	C_4, %	G	C_5, %	G	C_6, %	G	C_7, %	G	C_8, %	G
N-92A	NTPA	1:1	10.0	0.44	3.90	0.67	7.65	2.18	7.66	2.18	8.18	2.81	10.21	5.61	10.25	6.09				
N-92B	NTPA	1/2:1	10.0	0.40	4.07	0.71	7.12	2.05	7.14	2.22	8.11	2.96	9.89	5.76	10.00	6.53				
N-92C	NTPA	1/3:1	10.0	0.36	3.17	0.87	5.58	2.01	5.61	2.27	6.91	3.14	7.81	4.27	7.67	3.81				
N-92D	60B	1:1	10.0	1.05	6.34	1.22	12.77	3.23	12.89	3.09	10.17	2.54	10.19	2.54	10.31	2.86				
N-92E	60B	1/2:1	10.0	1.00	7.76	1.98	13.12	4.45	13.57	4.44	8.76	2.48	8.75	2.48	8.80	2.69				
N-92F	60B	1/3:1	10.0	1.00	6.99	2.37	11.48	5.08	11.69	5.08	7.11	2.42	7.13	2.48	7.15	2.77				
N-92G	NTPA	1:1	7.5	0.29	2.45	0.43	4.38	1.65	4.37	1.62	4.86	2.01	5.56	4.64	5.48	3.97				
N-92H	60B	1:1	7.5	0.67	4.49	1.14	9.64	2.22	9.86	2.22	5.66	1.21	5.64	1.48	5.63	1.43				
N-92J	NTPA	1:1	5.0	0.046	1.39	0.037			1.81	0.87	1.91	1.09	2.04	1.32	2.09	1.76				
N-92K	60B	1:1	5.0	0.44	2.69	0.43	6.25	2.37	6.49	2.18	4.37	1.32	4.40	1.25	4.28	0.75				
N-92L	NTPA	1:1	3.0						did not gel											
N-92M	60B	1:1	3.0	0.062	1.42	0.077	1.89	0.92	2.07	1.27	2.12	1.35	2.37	1.87	2.37	1.90				
N-32A	L-30	0.225:1	9.3	0.265	6.26	0.192	4.70	0.18	4.12	0.18	4.01	0.19	6.62	0.93	7.80	1.66	7.85	1.66	5.08	0.187

[a] The N-92 series are all fully rigid gels. N-32A is a semiflexible gel. The moduli G are at the respective concentrations C_0 or C_i and in 10^5 N/m^2. Ratio is the ratio of connector end groups to stiff-chain reactive sites. C_i values are in weight percent.

Laboratory, Inc., Madison, NJ, for iodine analysis. The amounts of carboxylic acid and amine groups left unreacted after the cross-linking step were determined from the weight percent iodine in each sample. A similar procedure was used to determine the fraction of reactive sites of the linear stiff polyamides actually accessible for reaction with the connector end groups, except that in this case the polymers were dissolved prior to the reactions with the iodinated species and that the purification was by means of repeated precipitation of the polyamides in solvents for the monomeric species.

Results

Fully Rigid, Semirigid and Semiflexible Two-Step Network Gels. When taken out of the reaction vessel, almost all the as-prepared two-step network gels were as clear as tinted glass. A few exhibited a slight haze, and the semiflexible N-32A was transluscent. Upon equilibration in DMAc the optical quality of all the gels improved. Even N-32A became fully transparent upon equilibration in the better solvent DMAc/5% LiCl. When immersed in poor solvents such as methanol or methanol/DMAc mixtures, the gels shrank and several showed varying degrees of transluscence or opacity. Except for the semiflexible N-32A, the development of such optical effects occurred only when C was substantially higher than C_0. At these concentrations, the degree of transluscence or opacity appeared to grow with increased concentration of the polyamide network in the shrunken gel. The semiflexible N-32A showed higher sensitivity to solvent quality and developed intense opacity upon deswelling from the good solvents even when its concentration of $C \simeq 7.8\%$ was still below $C_0 = 9.3\%$. We believe the opacity to be an indication of microsyneresis, where microscopic fluctuations in polymer concentration develop in the gels. Importantly, this phenomenon was observed to always be linked with the development of rather high moduli, above those expected from extrapolations of the moduli of the optically clear gels at $C \leqslant C_0$. The inordinately high values of G obtained from the transluscent or opaque gels at $C \gg C_0$ (and of N-32A at $C > 7.8\%$) are recorded only for the sake of completeness, in Table I for two-step networks and in Table V below for one-step networks. They will not be discussed further, nor will they be shown in the figures below. Upon reswelling in good solvents, the gels became clear again and their moduli decreased. In the case of all low-defect fully rigid and semirigid two-step networks, the moduli remained higher than their values in the more concentrated, as-prepared state. In the cases of the rigid one-step networks, of highly defective fully rigid two-step networks and of semiflexible networks, the moduli upon reswelling and clarifying decreased to below their values at C_0 and were proportional to C.

As a family, the gels of low-defect fully rigid and semirigid two-step networks are endowed with moduli about 2 orders of magnitude larger than those of common flexible networks of comparable concentrations.[22] The moduli of the two-step networks are of the same order of magnitude as those of the one-step rigid network gels,[1,5] being slightly higher for low-defect two-step rigid networks equilibrated in good solvent. It was interesting to find that the modulus of our semiflexible N-32A gel at $4\% < C \leqslant C_0 = 9.3\%$ is significantly higher than the modulus of common flexible networks at comparable concentrations. It is important to note here that, as a group, the two-step network gels are much more resilient and do not fall apart as easily and in such a brittle manner as rigid gels of one-step networks.[1,5] Furthermore, once equilibrated in a given solvent, the gels exhibited moduli completely insensitive to the duration of immersion. Within experimental error, identical moduli were measured on several two-step network gels over a period of 178 days and on a few one-step rigid gels over a period of exactly 1 year.

The two-step networks are listed in two tables together with their connector species, the ratio of connector end groups to stiff polymer reactive sites (calculated from the structures), the network concentration in the as-prepared state, C_0, and the concentrations C_i at each state of equilibrium, $i = 1, 2, 3, ...$, and the respective static shear modulus, G. In Table I are listed the two-step networks prepared from the linear polyamide L-89. In Table II are listed the networks made from the polyamides L-7B and L-17C.

The position of the reactive sites on the aromatic rings along the stiff chains exerts a strong influence on the final degree of cross-linking. The three linear polyamides L-17C, L-7B, and L-17A were reacted at $C_0 = 10.0\%$ with varying amounts of DABA under otherwise identical conditions. The qualitative results in Table III indicate that polymer L-17C with carboxyl groups in the meta position form nice gels. Polymer L-7B, whose carboxyl groups are ortho to the chain, gelled only when the number of connector end groups was substantially lower than the calculated number of stiff-chain reactive sites. Polymer L-17A has carboxyl groups only in ortho positions, and the distance between them is twice the distance in L-7B. Polymer L-17A did not gel at all even though some cross-linking did occur, as demonstrated by an increase in the intrinsic viscosity of the reaction products relative to the precursor polyamide.

A more quantitative correlation between the ortho or meta positioning of the reactive group on the polyamide chain rings and the accessibility of these sites to attack by

Table II
Gels of Two-Step Networks Prepared from Stiff Polyamides L-17C and L-7B[a]

code	linear polymer	connector	ratio	C_0, %	G at C_0	C_1, %	G	C_2, %	G	C_3, %	G
N-19A	L-17C	DABA	2:1	10.0	2.03	7.07	1.306	7.07	1.647	6.99	3.15
N-19B	L-17C	DABA	1:1	10.0	2.44	8.77	3.05	8.64	3.151	8.58	3.27
N-19C	L-17C	DABA	1/2:1	10.0	1.69	7.95	2.314	7.89	2.611	7.81	2.61
N-19D	L-17C	DABA	1/3:1	10.0	1.20	6.95	1.724	7.07	1.966	6.99	2.29
N-22A	L-17C	DABA	1:1	11.0	3.97	9.67	5.71	9.61	6.09	9.55	8.31
N-22B	L-17C	DABA	1/3:1	10.0	1.11	6.55	2.69	6.50	2.86	6.54	2.77
N-19L	L-7B	DABA	1/2:1	10.0	0.441	2.74	0.127	2.35	0.143	2.33	0.176
N-19M	L-7B	DABA	1/3:1	10.0	1.079	4.24	0.485	4.09	0.545	4.25	0.545
N-22C	L-17C	Polacure	2:1	10.0	1.36	6.18	2.77	6.04	2.94	6.00	3.39
N-22D	L-17C	Polacure	1:1	10.0	2.44	8.21	5.08	8.12	5.08	8.12	5.71
N-22E	L-17C	Polacure	1/2:1	10.0	2.08	6.81	4.69	6.69	4.57	6.64	4.46
N-22F	L-17C	Polacure	1/3:1	10.0	1.71	6.10	2.54	6.02	2.94	6.04	2.77

[a] N-22C through N-22F are semirigid gels. All others are fully rigid. The moduli G are at the respective concentrations and in 10^5 N/m^2. Ratio is the ratio of connector end groups to stiff-chain reactive sites. C_i concentrations are in weight percent.

Table III
Gel Formation as a Function of the Reactive Site Location on a Stiff Precursor Chain[a]

code	precursor chain	position	ratio of connector end groups to chain reactive sites	results
N-19A	L-17C	meta	2:1	gelled
N-19B	L-17C	meta	1:1	gelled
N-19C	L-17C	meta	1/2:1	gelled
N-19D	L-17C	meta	1/3:1	gelled
N-19J	L-7B	ortho	2:1	did not gel
N-19K	L-7B	ortho	1:1	did not gel
N-19L	L-7B	ortho	1/2:1	gelled
N-19M	L-7B	ortho	1/3:1	gelled
N-19E	L-17A	ortho	2:1	did not gel
N-19F	L-17A	ortho	1:1	did not gel
N-19G	L-17A	ortho	1/2:1	did not gel
N-19H	L-17A	ortho	1/3:1	did not gel

[a] All stiff poyamides contain carboxyl groups attached to aromatic rings in the meta or ortho position to the backbone. All were reacted with DABA at C_0 = 10.0% under otherwise identical conditions.

the end groups of the rigid connector species was gathered from the results of the reactions with iodinated aromatic molecules described in the Experimental Section. The results are presented in Table IV. Here we find that the highest attainable level of substitution of the meta-positioned L-17C is 95.7% while that of the ortho-positioned polymers L-17A and L-89 is only 37.2% and 28.5%, respectively. From Table IV we also learn that the fraction of the accessible reactive sites that are reacted in the gels is rather high and that when an excess of connector species is present, many of the connectors are reacted at only one end. This leaves the other ends open to subsequent reaction, provided a mobile species can reach them. The last entry in Table IV indicates that when "infinite" networks do not form, some connector species are attached to the stiff chain at one end, but the fraction of connector species reacted at both ends is negligible. This is, of course, exactly as expected.

In general, when the connector species end groups were about equal in number to the accessible reactive sites on the linear stiff polyamides, the second step of network formation was extremely rapid and gelation occurred in a matter of seconds to minutes. As the ratio of end groups to accessible reactive sites deviated from 1 in either direction, it took longer for the system to gel. From this it is evident that the higher the network perfection, the faster it forms and that this is achieved when the number of connector end groups matches the number of accessible reactive sites on the stiff linear chains. The level of cross-linking is substantially higher than that expected under the assumption that the stiff chains and connector species are fully rigid and completely immobile. We believe this incongruency to be due to the fact that the stiff chains and connector species are neither fully rigid nor completely immobile. In recent solid-state ^{13}C NMR relaxation studies,[23] we have found that they do perform torsional motions. Furthermore, the activation energy for syn/anti interconversions is in the range of only 5–7 kcal/mol[6,9] and the energy difference between these placements is only 0.3 kcal/mol.[24] Thus, the stiff chains can easily undergo syn/anti interconversions with the associated torsions and chain bending. All these motions contribute to reactive-site mobility and increased cross-link efficiency.

The results in Tables I and II indicate that the level of imperfections in the networks reveals itself in both the degree of swelling in DMAc and the moduli of the DMAc-equilibrated two-step gels. This is graphically shown in Figure 1, where C is plotted against the ratio of end groups to calculated reactive sites, and in Figures 2 and 3, where the moduli G at C_0 and C_3 are plotted against the same ratio. In all three figures the curves pass through broad peaks centered at the concentration of accessible reactive sites in the respective precursor stiff polyamide. These concentrations are marked by ticks on the abscissas. Importantly, the peaks appear at the same location for both as-prepared and DMAc-equilibrated gels. The very low moduli of N-19L and N-19M in Figure 3 and the direction of their slopes clearly reflect the very high level of imperfections present in networks prepared from the polyamide L-7B with ortho-positioned reactive sites and the very small number of accessible such sites.

A survey of the data in Tables I and II reveals that the modulus of swollen gels of fully rigid and semirigid two-step networks with low levels of defects is higher than that in the as-prepared state. This surprising behavior is not observed in highly defective fully rigid networks, such as N-19L and N-19M in Table II, or in networks in which the connector species between the stiff polyamides is very long and flexible as in the semiflexible N-32A in Table I. The results of sequences of modulus measurements on low-defect rigid two-step gels are shown in Figure 4. The arrows along the curves indicate the chronological sequence of equilibration for each gel, starting from the as-prepared state. The curves for N-32A and N-19L, respectively, semiflexible and highly defective rigid gels, are also shown in the figure.

In the course of this work we found that defects in two-step rigid networks are caused by either or a combination of the following: relatively low C_0, low efficiency of some second step reactions, very short or very long rigid connectors lowering the cross-linking efficiency, and strong deviations from stoichiometry of connector end groups and accessible stiff-chain reactive sites. A 2:1 deviation resulted in the "normal" behavior of the two-step rigid

Table IV
Cross-Linking Efficiency as a Function of Ratio of Connector End Groups to Stiff Chain Reactive Sites

code	ratio of connector end groups to stiff-chain reactive sites	stiff-chain sites left unreacted after cross-linking step: % wt iodine	stiff-chain sites left unreacted after cross-linking step: % subst	connector attached at one end with available amine at the other end: % wt iodine	connector attached at one end with available amine at the other end: % subst	connector reacted at both ends,[a] %
L-89	none	21.90[b]	28.5			
L-17C	none	14.16[c]	95.7			
N-19A (from L-17C)	2:1	1.78[c]	15.0	16.19[b]	57.3	23.4
N-19B (from L-17C)	1:1	0.57[c]	4.8	1.14[b]	4.0	86.9
N-19C (from L-17C)	1/2:1	1.38[c]	11.6	1.03[b]	3.6	80.5
N-19D (from L-17C)	1/3:1	2.06[c]	17.3	1.27[b]	4.5	73.9
L-17A	none	4.62[c]	37.2			
N-19F (from L-17A)[d]	1:1	1.19[c]	11.5	7.26[b]	28.8	-3.1

[a] Obtained by subtraction of groups reacted in both previous columns from available sites in the respective linear stiff polyamide. [b] Determined by reaction with 3,4,5-triiodobenzoic acid. [c] Determined by reaction with 4-iodoaniline. [d] Did not gel after a 6-h reaction time.

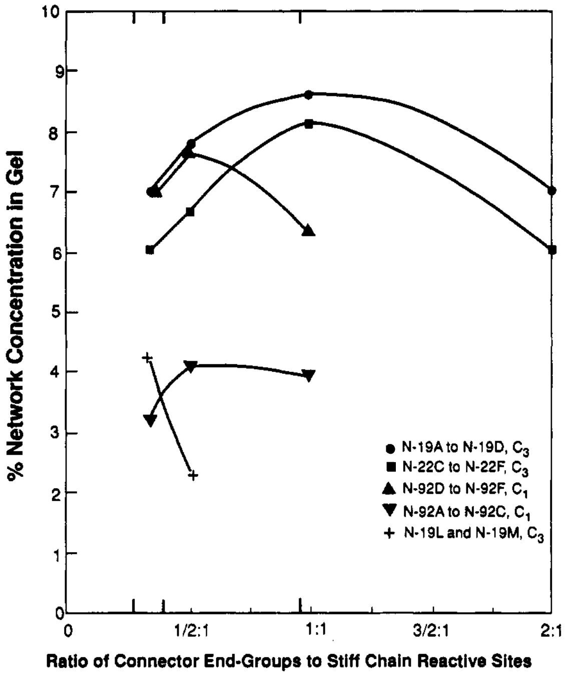


Figure 1. Network concentration in swollen gels as a function of the ratio of connector end groups to the calculated stiff-chain reactive sites. All "as-prepared" concentrations were 10.0%. Networks were equilibrated with DMAc. Tick marks on the abscissa indicate concentrations of accessible reactive sites.

gels 49A1 and 49A2 in ref 1.

Gels of One-Step Rigid Networks. Several gels of rigid networks were prepared by a single-step Yamazaki procedure in solution from the appropriate monomer mixture. They were made for comparison with gels of two-step networks of similar chemical composition and for verification of our previous observations[1-5] that the moduli of gels of one-step rigid networks show the normally expected direct dependence on C. The results are listed in Table V. From them we find that, indeed, $G \propto C$. Furthermore, it is apparent that this relationship holds true for rigid gels of varying average segment length, l_0, and branchpoint functionality, f. It should be noted that one full year lapsed between C_3 and C_4 of gels N-25B, N-60M, and N-60L with changes in G practically within our experimental scatter and minute decreases in C for two out of the three gels. It may be that this very small change in C is due to a small number of very slow interconversions from syn to anti (or anti to syn) placements of the backbone amide groups, allowing for small increases in gel volume.[6,9]

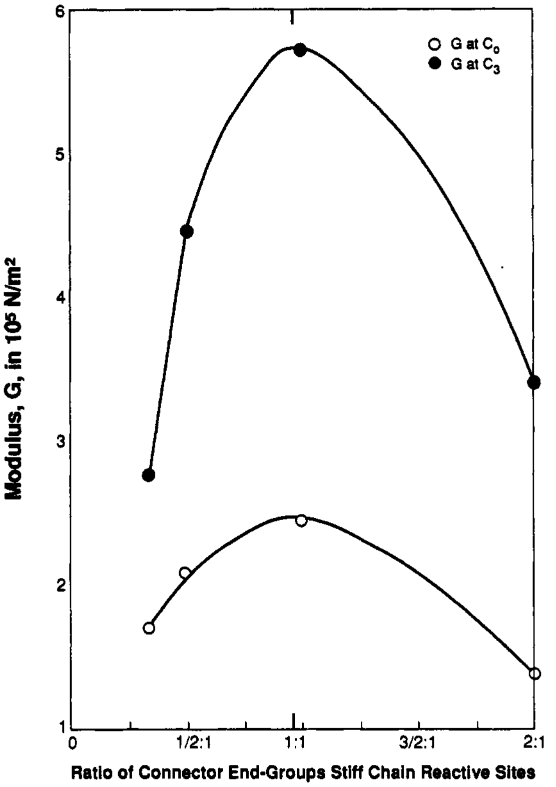


Figure 2. Modulus of gels N-22C through N-22F as a function of the ratio of connector end groups to calculated stiff-chain reactive sites. A further description is in the caption to Figure 1.

In Figure 5 are shown the chronological equilibration steps of networks N-25B and N-60M in improving quality solvents. Also shown are four old one-step networks with $f = 3$, characterized by three different l_0 lengths and two C_0 concentrations (series N-88). In this case, only the moduli at C_0 and the final concentration C are available. Here, too, the modulus G at $C < C_0$ is smaller than the modulus at C_0. The observations in this work on one-step rigid gels are consistent with all the previous observations on such gels[1-5] and with the normal behavior of gelled polymeric networks.

Discussion

In this section two main issues will be discussed. The first one deals with the fact that the static shear modulus of gels of low-defect fully rigid and semirigid two-step networks is higher in the swollen equilibrium state than in the as-prepared state. The second one is a description of the structure of two-step networks consisting of stiff precursor linear polyamides and rigid connector species.

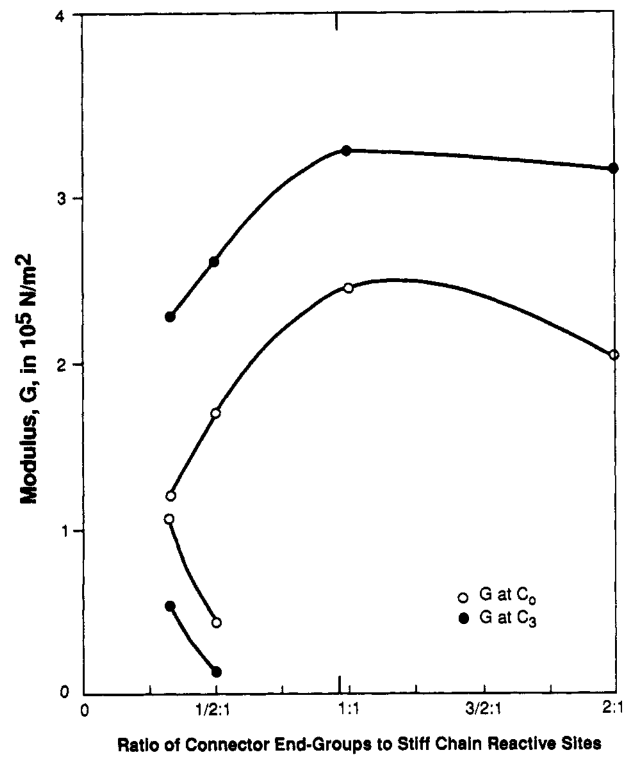


Figure 3. Modulus of low-defect gels N-19A through N-19D and of highly defective gels N-19L and N-19M, all as a function of the ratio of connector end groups to the calculated stiff-chain reactive sites. Ticks on the abscissa stand for the concentration of accessible reactive sites on stiff linear chain L-17C.

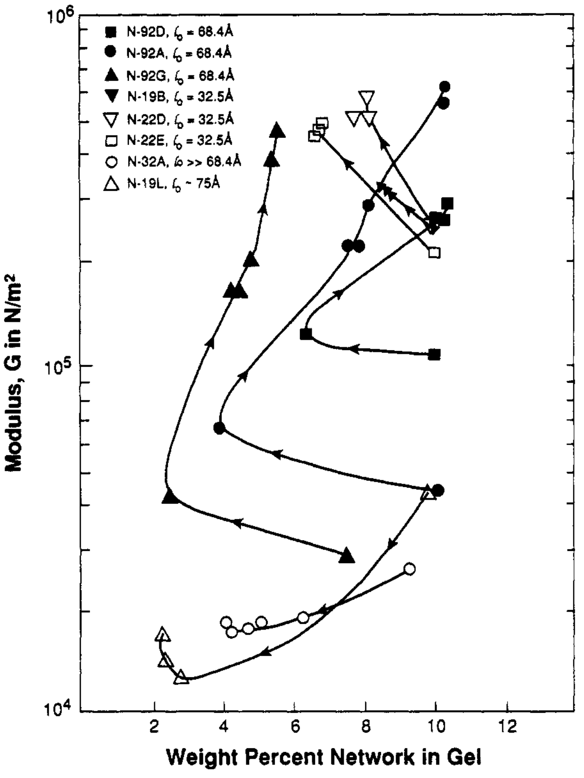


Figure 4. Chronological sequence of the equilibrium modulus of two-step network gels. All networks have a branchpoint functionality $f = 3$. Arrows indicate the chronological sequence of equilibration steps from the as-prepared state. An additional description is given in the text.

Figure 6 contains all the structural elements and will serve as a visual aid in discussing both issues. In it, the linear stiff chains and attached connector species in the gel are drawn in perspective, with their parts closer to the viewer shown in wider lines and the parts farther from the viewer shown in narrower lines. Entities parallel to the plane of the page are shown in uniform thickness lines. Angular breaks in the linear stiff chains, of 20° or thereabouts, are clearly shown in the figure but without specifying whether they involve one or two anti/syn placements.[6,9]

In all our work with rigid gels they never secreted or imbibed solvent nor changed volume when deformed under external stress.[1,2,5] This is also the case with two-step rigid networks. Under such circumstances, the product of the deformations, λ_i, of the gelled networks is

$$\lambda_1\lambda_2\lambda_3 = 1$$

and when the gel is constricted in one direction, $-\lambda_1$, it expands in the other two directions, λ_2 and λ_3. In the case of common flexible gels, such deformations are made possible to a large extent by changes in the configurations of flexible Gaussian coils away from their state of equilibrium. These changes require relatively small energy investment, which accounts for the low moduli of gels of common flexible networks. In the case of low-defect rigid network gels, this mode of deformation is not available. The stiff segments are relatively short. They are fully extended or contain a small number of bends. The branchpoints are rigid. Because of these three structural features and because small changes in segmental end-to-end distances and in relative branchpoint positions are brought about in a defect-free network probably by pairs of anti/syn (or syn/anti) interconversions,[6] the configurational changes of Gaussian coils are precluded. All this results in rigid networks that can deform only slightly and with a substantial investment of energy—hence, the high modulus.

When a low-defect two-step rigid network is prepared and then immersed in a good solvent, it imbibes some and swells. At equilibrium, it swells much less than a comparable highly defective gel. In the latter case, relatively large amounts of solvent may concentrate in pockets close to the defects, as these regions offer the least resistance to swelling. When the rigid gel has no, or only a very small number of, pockets near imperfections for the solvent to concentrate in, its total swelling at equilibrium is low. This small swelling is accommodated by stiff segment straightening. For segments anchored into the rigid network by effective branchpoints at both ends, the most likely straightening mechanism is by pairs of syn/anti interconversions.[6] For segments connected to the network at one end only, a single syn/anti interconversion will suffice.[6,9] Under these conditions, the population of bent stiff segments in low-defect two-step rigid gels will substantially decrease in favor of the straight stiff segments, making the swollen rigid gels rich in them. When such a gel is deformed, during modulus measurement for instance, the large population of straight stiff segments cannot stretch further in the λ_2 and λ_3 directions, reducing the ability of the system to accommodate strains and deformations. Therefore, the modulus of low-defect two-step rigid network gels is expected to increase once the gels are swelled to equilibrium in a good solvent. The modulus will remain high as long as the fraction of straight stiff segments in the swollen low-defect rigid gels stays significantly higher than it was in the as-prepared gelled network. The fact that in two-step networks the precursor linear polyamides are extended and much longer (400–1000 Å in our case) than the sizes of the highly branched fractal polyamides right below the gel point (100–200 Å)[2] may contribute to the development of less defective

Table V
Gels of One-Step Rigid Networks[a]

code	branchpoint functionality	segment length, Å	C_0, %	G at C_0	C_1, %	G	C_2, %	G	C_3, %	G	C_4, %	G
N-26A	3	23	10.0	7.95	8.92	4.69	8.95	5.08	8.86	5.05		
N-26B	3	23	10.0	9.14	8.73	3.39	8.82	3.39	8.74	3.26		
N-25B	3	19	7.6	3.45	6.47	2.01	6.13	1.68	5.79	1.25	5.78	1.31
N-60M	3	65	7.5	3.59	4.28	1.81	12.17	4.35	7.04	2.81	6.78	2.86
N-60L	6	65	7.5	5.31	6.98	5.04	7.74	5.54	7.00	5.08	6.90	5.08

[a] The moduli G are at the respective concentrations C and are given in units of 10^5 N/m^2.

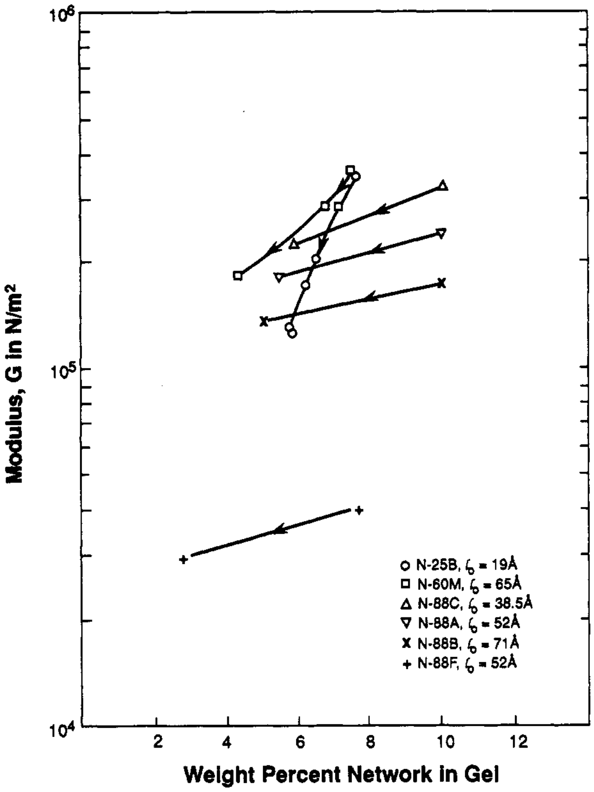


Figure 5. Chronological sequence of the equilibrium modulus of one-step network gels. All networks have a branchpoint functionality $f = 3$. Arrows indicate the chronological sequence from the as-prepared state.

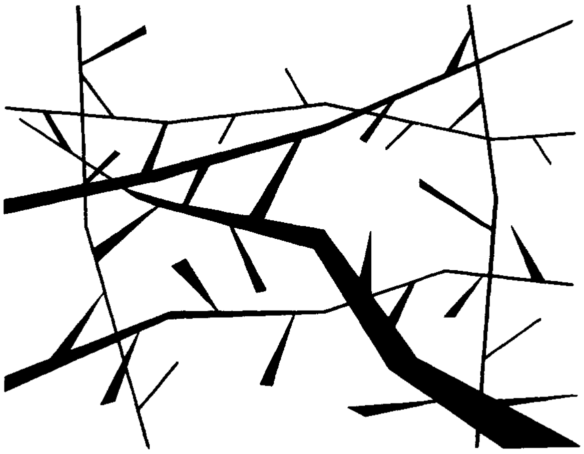


Figure 6. Schematic of the two-step rigid network gel in perspective. The network is constructed from stiff linear polyamide chains and an excess of rigid connector species. Solvent is not shown. Additional explanations are given in the text.

networks than in the one-step systems. This may increase the probability of modulus growth with gel swelling. In our case such higher moduli were indeed observed in low-defect two-step rigid gels. Because such a behavior was not observed in one-step rigid gels, we are led to believe that they, as a family, contain much more imperfections than the low-defect two-step rigid gels.

Now, when highly defective rigid networks are immersed in a good solvent, they swell much more than their low-defect analogues. The swelling of the highly defective regions of the rigid network is in addition to, and in general is substantially larger than, the swelling of the low-defect regions. We believe that essentially the same swelling mechanism is operable in one-step rigid gels and in highly defective two-step rigid gels. The difference is, probably, in the distribution of the solvent-rich pockets. In the one-step rigid gels these pockets may appear in relatively high frequency at the interfacial zones between the precursor fractal polymers,[2] while in the highly defective two-step rigid gels they may occur at random throughout the network. In both kinds of rigid networks, beyond a small level of swelling associated with anti/syn interconversions and stiff segment straightening, the degree of swelling is proportional to the level of network imperfections. Because an enhanced level of imperfections increases the average contour distance between effective branchpoints, the modulus of highly defective rigid networks decreases with increased imperfection concentration. This was observed in this and previous works and is valid for one-step and two-step rigid networks.

The above is, of course, inconsistent with common flexible and even semiflexible networks. In these, a substantial solvent uptake and large gel swelling are easily accommodated by relatively small configurational changes of initially loose Gaussian coils. Even after swelling the flexible segments between cross-links are far from straight and taut and may accommodate a substantial further deformation without increases in modulus. Such a behavior was observed here with the semiflexible gel N-32A and in our previous work in flexible networks with or without rigid branchpoints.[1,3-5]

It is important to recognize that the thermodynamic solvent–segment interactions are the same in chemically identical rigid networks prepared by either a one-step or two-step procedure. The identical behavior of the solvent was observed by solution- and solid-state ^{13}C NMR studies of highly concentrated swollen one-step and two-step networks of identical chemical composition[23] and in the dilute-solution viscosity and dynamic light scattering behavior of the same[25] and similar[17] systems. Furthermore, in the present work we found that equilibrating gels of two well-formed two-step networks (N-19B and N-22A in Table II) in DMAc at 150 °C resulted in a minute weight decrease (1.7% for N-19B and 1.5% for N-22A) and no measurable change in the modulus from C_3 in Table II at room temperature. This insensitivity to temperature is identical with our previous observations on well-formed one-step rigid systems.[5] These facts weigh against the possibility that in the two-step rigid systems the solvent molecules somehow contribute to an enhancement of the modulus upon swelling and do not do the same in the one-step analogues.

We now turn to the second discussion topic, namely, the structure of two-step networks made from stiff linear polyamide chains connected by rigid connector species. We believe that a good definition of a defect-free two-step gelled network is one in which all accessible reactive sites on the stiff chains are reacted with the connector species and all connector species are reacted at all their end groups. That is, a network where no accessible reactive sites and no connector end groups are left unreacted. Figure 6 is an example of a highly defective two-step rigid network. Here, a large excess of the connector species was used, resulting in many of them remaining attached at only one end to a single stiff chain, like the barbs of a barbed wire. The rest of the connector species, reacted at both ends, act as struts between the stiff chains. If the level of network perfection is sufficient, and at present we have no way of quantifying it, then upon swelling in a good solvent the bends in the stiff chains and, probably, rigid struts will straighten and the modulus will increase. Conversely, when there are too few connector units in the network, then they are all reacted at both ends, but some of the accessible reactive sites on the stiff chains are left unreacted. We understand that the constraints on mobility imposed by the stiff polyamide chain and the rigid connector struts greatly reduce the cross-linking efficiency, as compared with flexible chains and cross-linkers. The rigidity and diameter of the chain and connector species also tend to strongly reduce the accessibility of ortho-positioned stiff-chain reactive sites. Placing the reactive sites in meta positions when possible greatly increases their accessibility to the rigid connector species. We believe that in the case of flexible precursor chains the difference between meta- and ortho-positioned reactive sites is not as large as that in stiff chains and the accessibility of these sites is substantially higher.

Conclusions

When gels of rigid networks are prepared, some of the stiff segments are straight while others are bent. When swollen in a good solvent, the population of the straight stiff segments grows at the expense of the bent segments. Since the straight segments cannot stretch further, the resistance of the swollen rigid gel to deformation should be higher than that in the as-prepared state. In this work we demonstrate that this is indeed what happens when gels of two-step rigid networks are low in defects and are prepared from stiff polymer chains and fully rigid or semirigid connector species. In the case of highly defective rigid networks or of flexible ones, this unusual behavior is not observed. Instead, the usual, direct dependence of the modulus on concentration is seen.

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