The principal results are as follows:

For lightly cross-linked gels, the longitudinal osmotic modulus M_{os} determined by osmotic and mechanical measurements is in accord with that obtained from dynamic light scattering. The ratio R of these two quantities increases as the gel heterogeneities increase.

SAXS measurements of the mean-square concentration fluctuations $\langle \Delta c^2 \rangle$ associated with the heterogeneities in the fully swollen gels are in reasonable quantitative agreement with that deduced from the ratio R. The values of $\langle \Delta c^2 \rangle$ increase strongly with increasing cross-link content.

Estimates of the correlation length from three independent measurement techniques, namely, SAXS, dynamic light scattering intensity, and collective diffusion measurements, yield values that are consistent with one another.

Over the concentration range studied, the shear and volume elastic moduli both follow a one-third power dependence as a function of the concentration c, even for the most heterogeneous sample, but their numerical values diverge from each other as the cross-linking density increases.

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Registry No. (Acrylamide)(*N*,*N*'-methylenebisacrylamide) (copolymer), 25034-58-6.

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Gels of Rigid Polyamide Networks

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ABSTRACT: Gels were prepared comprising highly branched networks of rigid rodlike segments and a good solvent. Several networks in which some flexibility was built into the chain were prepared for comparison. All these systems show a remarkably steep approach to the gel point and large viscosity increases beyond it. Fractionation and end-group titrations show that the higher the rigidity of the network the less sol is extractable and the lower its molecular weight, indicating that due to segmental rigidity, individual highly branched macromolecules can hardly diffuse out of the "infinite" network, while more flexible macromolecules diffuse out with greater facility. The modulus of the gels increases with increased network concentration. This holds for gels equilibrated and immersed during measurements in good as well as in poor solvent. The modulus of the equilibrated immersed rigid networks appears to be insensitive to temperature changes over the range 23–150 °C. In networks with more flexibility, the modulus of the immersed gels drops with temperature, and the drop appears to be associated with increased swelling of the gels. It seems that the segments between branch points, even those termed "flexible" in this study, are far too short and too rigid to conform with Gaussian statistics and for the gels to behave accordingly. A schematic description of the rigid network structures is proposed.

Introduction

In the term "gel" are included such disparate systems as lamellar mesophases, inorganic clays, vanadium pentoxide gels, phospholipids, certain disordered proteins, and, of course, three-dimensional or network polymers.[1] Polymeric gels are capable, in general, of absorbing large amounts of solvent and, like all other gels, exhibit properties of solids such as modulus and shape retention. In this paper we describe a new class of network polymeric gels with remarkable properties. For the purpose of this work we define polymeric gel as a system consisting of a polymer network swollen with solvent and a polymer network as a three-dimensional polymeric structure excluding the occluded solvent. The polymeric gels may be categorized in two major classes: thermoreversible gels and permanent gels. The thermoreversible gels undergo a transition from an immobile gel below a certain characteristic temperature, to a spontaneously flowing solution above it. The links between the polymeric chains are transient in nature and support a stable polymeric network only below the characteristic "melting" point. Prominent among such links are polymer–polymer and polymer–

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solvent hydrogen bonds, polymeric microcrystals holding together swollen networks, entwined helical structures promoted or supported by particular solvents, and specific interactions between certain polymers and solvents, operating over a typical interval. The nature of these interactions is not fully understood at present. In ref 2–6 examples are given of the above thermoreversible gels.

The permanent gels consist of solvent-logged covalently bonded polymeric networks. One family of such networks is formed by cross-linking preexisting high molecular weight (high M) linear macromolecules. Rubber vulcanization is an obvious example. Another family is that of networks formed by branching during the polymerization process due to the incorporation of multifunctional monomers in the growing chains. This family is divisible into two groups, depending on the polymerization characteristics. In the case of addition polymerization such as free radical or anionic polymerizations, a relatively small number of highly branched, high-M macromolecules are present in the reaction mixture together with a relatively large mass fraction of unreacted monomers. Gels of polystyrene cross-linked with divinylbenzene are a good example. In the case of condensation polymerization, such as polyesterification, polyamidation, or the formation of polyurethanes, the relative number of the high-M highly branched macromolecules is not greatly changed from the above, but instead of unreacted monomers, the reaction mixture contains a changing distribution of lower M macromolecules, reaching down to oligomeric size. The molecular weight and molecular weight distribution of the macromolecules change during the condensation, resulting in a polymeric network encompassing the whole reaction volume, with whom are interpenetrated and in whose voids and irregular surfaces are nestled other macromolecules of lower molecular weight. At the point of gelation, only a very small weight fraction of the polymerizable material is in the form of unreacted monomeric species, and the molecular weight distribution becomes extremely broad.[7] The polyamide networks described in this work were all prepared by condensation polymerization using the Yamazaki[8] procedure modified to accommodate gelled networks. Strict stoichiometry between amine and carboxyl groups was maintained in all cases.

Once a gelled network of flexible chain polymers is formed, the polymerization reaction does not necessarily stop. In fact, it is well-established that the reaction continues beyond the gel point,[7,9,10] involving a substantial fraction of intramolecular reactions.[10,11] In inorganic systems such as silica, too, the chemical reactions leading to gelation continue beyond the gel point, causing changes in the composition, structure, and properties of the gel.[12,13] In the case of flexible chain polymers, the reaction vessel appears to be filled with highly branched macromolecules which keep on growing beyond the gel point just as they did before. Gelation occurs when a sufficient number of these macromolecules link together to prevent steady-state flow. At this point the resulting network, ostensibly a single giant highly branched macromolecule, pervades the whole reaction volume. Within this very same volume are present, however, many more macromolecules that are not chemically attached to the network; they can be extracted out of the gelled system by the use of appropriate solvents. In the case of flexible polymer systems, it is easy to visualize how the flexible network swells in the right solvent and the flexible macromolecules comprising the sol fraction diffuse out of the gel, probably by a reptation-type[14] process. This may not be the case when both the cross-linked network and the interpenetrated highly branched macromolecules consist of highly rigid segments preventing or, at least, inhibiting chain motions necessary for the transport of such macromolecules in such a network. One aim of this work is to find whether highly branched rigid macromolecules are formed during the pre- and postgelation polymerization and whether they are trapped in the giant swollen network or can be extracted out as can the flexible chains. In light of the fact that the existing theories of flexible network formation are based on several hypotheses which are not here valid,[15–17] an agreement between our results on rigid networks and predictions for flexible networks cannot be expected.

The simplest theory of rubber elasticity[7] relates the tensile modulus, E, to the concentration of elastically effective network strands, ν; the gas law constant, R; and the absolute temperature, T, by the relation

$$E/3 = g\nu RT \tag{1}$$

where g is a front factor introduced to allow for effects of several theoretical approximations.[18,19] In terms of measured quantities

$$E/3 = (F/A)/(\lambda - \lambda^{-2}) \tag{2}$$

in which F is the tensile force, A is the original cross-sectional area, and λ is the extension ratio (length under load divided by length without load). It is assumed that λ values are within the range of linear behavior. When measured after sufficiently long times to be the equilibrium values, E in eq 2 is called the equilibrium linear tensile modulus. It is this value that is related by eq 1 to ν, the concentration of elastically effective strands after the relaxation of all possible chain couplings or entanglements.[20] For rubbery or solvent-filled systems, where the Poisson ratio is essentially 0.50, the tensile modulus relates to the shear modulus, G, as

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

A major uncertainty in (1) lies in the definition of ν: what is the meaning of "elastically effective network strands" and how are they to be counted? What is the exact relationship between the number and functionality of junction points and the number of elastically effective strands? How and when should interactions such as entanglements, which are not permanent in their nature, be counted? These problems are rather controversial[19–26] and not fully resolved at present.

Another problem with eq 1 is the nature of its dependence on T. This equation applies if the elasticity of the system is due solely to the change in the conformational entropy of the polymeric chains and the length of the chain sections between cross-links is large enough to enable the calculation by statistical means of the entropy as a function of extension.[27,28] The existence of rather long flexible strands between cross-link points is the cause of the temperature dependence of the conformational entropy and a cornerstone of the theory of rubber elasticity.

In systems where no crystallization or other "ripening" phenomena take place with time, the plateau modulus for a melt or concentrated solution appears to vary by a power slightly greater than two.[18,23,26,28]

$$E(\text{or } G)(\text{gel}) = E(\text{or } G)(\text{network})C^{2.2} \tag{4}$$

where C is the volume concentration of polymer in the system. When cross-linked, one obtains E (or G) $\propto$ number of cross-links and $C^{2.2}$ where C is the volume concentration of the network in the gel.

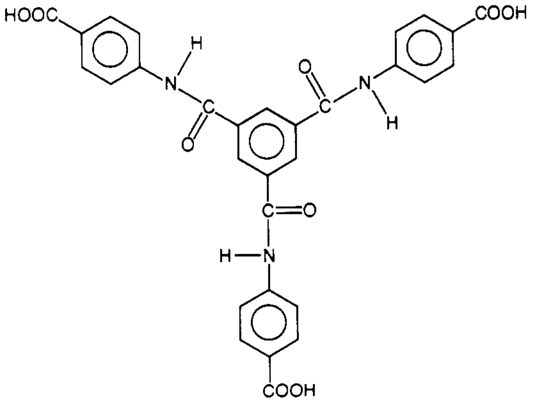
In isotropic gels of rodlike polymers the situation is dramatically different. Here, the change in the conformational entropy with temperature is negligibly small and the more important factor is the deformation energy of the individual stiff polymer chains.[29] In such an energetic gel, E decreases with T.[27] It is important to recognize, however, that the theory of rodlike isotropic gels[29] treates rods which are not permanently connected to one another and can slip by each other.

It is conceivable that gels of permanently cross-linked highly rigid networks will be practically independent of temperature. Since such chains will not, or hardly, undergo conformational changes, their modulus should not increase with temperature. Because we deal with an isotropic gel in which the rigid chains are all connected to one another, they can neither slip by nor be sufficiently displaced from their initial positions to substantially bend one another. Therefore, their modulus will not be significantly reduced with increased temperature, except for the effects of gel expansion with temperature. A reduction in modulus may occur if some flexibility is built into the rigid chain segments, allowing for a low level of, say, trans–gauche configurational changes to take place. This may reduce the modulus by reduction of the resistance to stress and/or by enhanced gel swelling with temperature.

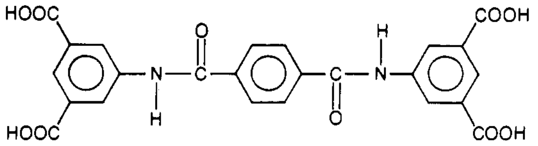
A second purpose of this study is to measure G as a function of network concentration in the gel and as a function of T, for gelled networks of highly branched macromolecules permanently connected to each other. The results will be compared with existing theories of elasticity. We speculate that the rodlike networks open up new possibilities: A successful description of the standard flexible system is to think of any chain surrounded by a tube of the others. Typically, the Kuhn step length of such a polymer is much smaller than the radius of the tube. For networks whose elements are rigid, as the case may be with many liquid-crystal polymers, one can get the rigid segments between functions much longer than the tube radius defined by the surroundings. Such an extreme case will have elastic behavior dominated by bending and not by random flight entropy. Clearly very high moduli can be expected in this case.

Experimental Section

(a) Monomer Synthesis. Two monomers were prepared in solution below room temperature by a Schotten-Baumann-type reaction. The monomer *N,N′,N″*-tris(*p*-carboxyphenyl)-1,3,5-benzenetriamide (TCPBT) was prepared in a mixture of *N,N*-dimethylacetamide (DMAc) and pyridine from excess *p*-aminobenzoic acid and 1,3,5-benzenetricarboxyloyl chloride. Upon termination, the reaction mixture was poured into a large excess of water. The precipitated solids were filtered off and washed repeatedly with hot methanol to remove unreacted reagents and reaction byproducts. The clean product was then dried in a vacuum oven at ca. 150 °C. This trifunctional monomer and, occasionally, 1,3,5-benzenetricarboxylic acid (BTCA), was used to introduce trifunctional branch (cross-linking) points into the growing polymer network. The monomer bis(3,5-dicarboxyphenyl)terephthalamide (BDPT) was prepared in a DMAc/pyridine mixture from terephthaloyl chloride and an excess of 3,5-dicarboxyaniline. The workup of this tetrafunctional monomer was identical with the one for the trifunctional monomer above. In both cases, the Schotten-Baumann-type reaction was allowed to proceed for up to 16 h at room temperature after a stay at lower temperatures for not less than 4 h. The yields were ca. 75% and 65% for the purified trifunctional and tetrafunctional monomers, respectively. Carbon-13 NMR spectra obtained from solutions of the monomers in deuteriated DMAc served to verify their structure and purity.

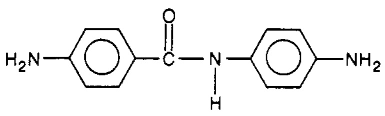


TCPBT

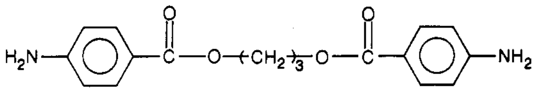


BDPT

The aromatic monomer 4,4′-diaminobenzanilide (DABA) was obtained from Sandoz Corp. and recrystallized twice from 10:1 methanol/acetone prior to use. The monomer trimethylene glycol di(*p*-aminobenzoate) was obtained from the Polaroid Corp. and recrystallized from methanol prior to use. It will be identified below as Polacure. All other monomers, reagents, and solvents were obtained from chemical supply houses at the highest available grade and used as received.



DABA



(b) Polymer Synthesis. All the polyamide networks, and several comparable linear polyamides, were prepared by the use of the Yamazaki procedure[8] modified to handle cross-linked systems in a fashion similar to the one previously described by Aharoni.[30,31] Besides monomers with an equivalent number of amine and carboxyl residues, the reaction mixture contains DMAc with or without 5 wt % anhydrous LiCl, pyridine, and triphenyl phosphite (TPP). All polymerizations were conducted in the temperature range 103–115 °C. The reactions were allowed to continue for 3 h after the systems gelled, except for the kinetic studies of rigid networks where the reactions were rapidly quenched shortly after the viscosity reached the upper limit of the viscometer. For the purpose of this work, the gel point is defined as the point in time when the magnetic spinning egg (1-in. long) rather abruptly ceases to rotate and cannot be put in motion again by stopping and restarting the stirrer. At the same point, air bubbles stopped moving and remained trapped in the gel. As a rule, a rather rapid reduction in the depth of the vortex preceded the gel point of all rigid networks.

In several cases, the kinetics of gelation were followed as is described below: in the thermostated hot oil bath, there were placed a beaker with pure DMAc and the round-bottom flask containing the reaction mixture except for the triphenyl phosphite. The oscillating sphere of a Nametre direct readout viscometer was placed in the DMAc beaker. The assembly was heated up to the desired reaction temperature and brought to equilibrium. Then the viscometer sphere was rapidly and carefully wiped clean and about half the reaction mixture was poured into a beaker and the viscometer sphere immersed in the mixture. After equilibrium was reestablished, the appropriate amounts of TPP were added to the beaker and round-bottom flask and thoroughly stirred. The reaction time, t, was counted from the moment, t_0, the TPP was fully stirred in the hot mixture. A very slight reduction in viscosity was observed over the next few minutes, reflecting, we believe, the decrease in viscosity of the added TPP as it heats up to reach the temperature of the equilibrated mixture. In this fashion, the changes in viscosity of the reaction mixture were monitored before and after the gel point, covering the range from about 2 cP, the viscosity of the hot reaction mixture prior to polymerization, up to about 145 000 cP, the upper limit of the Nametre viscometer. The cessation of motion of the stirring egg in the round-bottom flask served to estimate the point at which the network in the flask and the beaker gels. After the reaction was terminated and the gel in the beaker cooled, it was broken apart and removed from the viscometer sphere, the latter was carefully cleaned with brass wool and solvent and readied for the next run.

(c) Network Purification, Equilibration, and Sol/Gel Determination. Except for the kinetic studies, all polymerizations were conducted in round-bottom flasks, which were broken in a plastic bag in order to retrieve the cross-linked network. In no case where a self-supporting gel was formed did we observe any solvent separating out of the gel; the gelled network encompassed the whole volume of the reaction mixture. Thus, the concentration of polymer in the reaction medium, C_0, is clearly determined by the concentration of monomers charged. After sacrificing the reaction flasks, the network systems were cut into about 1-cm-thick slabs for the purpose of mechanical studies or passed through a blender filled with methanol or water for the purpose of sol/gel fractionations and end-group analyses.

The cut slabs were immersed in large volumes of DMAc, allowing the unpolymerized part of the reaction mixture to diffuse out of the gels and the pure DMAc to diffuse in. The DMAc was replaced several times, at a faster rate initially, until all the ingredients of the initial reaction solution were leached out of the now optically blemishless transparent gels. The solvent-exchange process took about 10 weeks until the gels asymptotically reached their equilibrium swelling state with DMAc. The replaced solvent of each gel was collected and at the end poured into an at least 10-fold amount of water. In practically all cases where rigid networks were prepared, no water-insoluble products were obtained, however.

Many slabs were transferred from the good solvent DMAc to the poor solvent formamide. In this case, the solvent exchange was repeated several times over a few weeks and was reflected by a gradual decrease in the size and increased opacity of the network slabs, except for the most rigid among them.

The volume expansion or shrinkage upon equilibration of the networks in solvent was obtained in two ways with good agreement among them. Slabs of the cross-linked network containing the reaction solution were weighed and their dimensions measured. After equilibrium in either good solvent (DMAc) or poor solvent (formamide), their dimensions were remeasured and weights determined. From the dimensional changes, weight changes, initial concentration, C_0, and densities of solvent and polymers, the volume/volume concentration, C, of the polymers in the equilibrated gels were determined. The swelling ratios, C_0/C, were all calculated in terms of volume.

It was found that specimens showed a propensity to crack and develop internal fissures when first equilibrated in DMAc at ambient temperature and then heated during the modulus measurements. This occurred more frequently in the more rigid samples having shorter distances, l, between branch points and/or higher branch-point functionality. For the purpose of measuring the volume change of samples as a function of temperature and in order to avoid cracking, the following high-temperature equilibration procedure was adopted: At the end of the polymerization, the gelled network was transferred hot into hot DMAc without being allowed to cool. The temperature of the DMAc was maintained at around 100 °C. After several replacements of the hot solvent, the samples ceased swelling and there were no impurities in the wash. For the purpose of modulus and volume measurements, the temperature of the gel together with the immersion solvent was brought up to 150 °C. The modulus was measured after 30-min equilibration at this temperature. The volume was measured both by weighing the specimens and converting to volume and by measuring their dimensions, after several hours at 150 °C. After a very slow cooling to room temperature, the weight and dimensions of the specimens were determined again. From the differences, the volume change of the samples as function of temperature was calculated. Because of rapid solvent evaporation at 150 °C, dimensional measurements were found to be more reliable than weighing. The results of volume changes were averaged from not less than two specimens per sample.

For sol/gel determinations, the as-synthesized networks were comminuted in a blender full with methanol or water. The choice between these depended on the nature of the monomers and their solubility or insolubility in methanol. The immersion liquid was replaced several times until there was no odor of pyridine or phenol present. Then the polymer particles were dried under high vacuum at temperatures in the 160–190 °C range. The dry polymer was carefully weighed and then placed in a large excess of DMAc to swell. After reaching equilibrium, the DMAc was replaced several times and saved. This process took about 2 weeks. Then the swollen polymer was filtered and immersed in methanol to shrink. The shrunk polymer was filtered again and dried down in an oven as before. After the product was cooled, it was weighed and the lost weight, when measurable, was counted as the sol fraction. The ratio of the lost weight to the recovered weight is the sol/gel ratio. The methanol filtrate was combined with the saved DMAc and the mixture poured into a 10-fold volume of water. When a precipitate formed, it was collected by filtration, dried, and weighed. The agreement between this weight and the above-mentioned lost weight was fair.

(d) Titrations for Carboxyl and Amine End Groups. Most samples used for the purpose of end-group titrations were equilibrated for over 6 months in pure DMAc. In all cases the swollen gels were dried to constant weight and then coarsely ground. Samples of about 1.00 g each were weighed with a high-sensitivity electric balance and placed in 20 mL of DMAc to swell again. After swelling, a methanolic solution of ca. 0.01 N KOH (aqueous 0.01 N NaOH was found to be equally useful) was added and the samples were allowed to equilibrate for over 72 h at ambient temperature. To this mixture, 100 mL of distilled water was added and the mixture back-titrated with an ca. 0.01 N aqueous HCl solution. A solvent blank and the trifunctional TCPBT monomer (MW = 567) were used to determine the boundary conditions. All the samples were titrated potentiometrically to pH 7.00. Titrations for amine end groups were conducted in the same manner, except that aqueous HCl was added first to the samples in DMAc, and alcoholic KOH solutions were used after equilibration for back-titration. Several of the samples were titrated more than once, and quite a few titrations were carried repeatedly forward and backward through pH 7.00, to ensure that the results are not controlled by the diffusion rate of the titrants into the gels.

(e) Tensile Modulus Measurements. Equilibrated slabs of polymer networks were placed in pans of the equilibrating solvent in such a fashion that the solvent will reach the top surface of the slabs. The pans were placed on a hot plate capable of maintaining constant temperature in the range of interest, and the temperature of the solvent-filled slabs was allowed to equilibrate with the external solvent in the pan for about 30 min prior to modulus measurements. This process was repeated for each sample at each temperature in each solvent.

The equilibrium modulus, $E/3$, was determined from the depth of penetration of a flat surface into the gel under four different loads. The penetration depth was measured with a Humboldt universal penetrometer equipped with a flat penetration surface. The flat surface could be changed such that the softer gels were tested with larger area surfaces than the more rigid cells. The displacement was measured only after all motion ceased, ensuring that the measured modulus is an equilibrium modulus. Because of the relatively large area of the flat surface, it penetrated the gels only slightly, resulting in a simple negative extension deformation and not a shear deformation as in the case of spherically shaped penetrating tip.[32,33] The modulus $E/3$ was calculated according to eq 2 and all the results below are presented in terms of the modulus G ($G = E/3$). After allowing for imperfect contact between the gel slab and penetrometer surface at the lowest load, the results from the three higher loads were linear and within about ±5% from one another.

To make sure that no chain scission or internal cracking occurred during the slow exchange from DMAc to formamide, several of the slabs equilibrated in formamide were reimmersed in DMAc and, over about 2 months, reequilibrated in pure DMAc. Their moduli were measured at room temperature and above and were found to be, within experimental error (±5%), the same as

Table I
Rigid Rodlike Networks

					l,[c] Å	
code	descriptn	branch-pt functionality	f[a]	C_0,[b] %	identical	av
R-10C	PBT-TCPBT	3	3.000	10.0	32.5	
R-11A2	PBT-TCPBT	3	2.400	10.0		52
R-11A	PBT-TCPBT	3	2.400	10.0		52
R-11B	PBT-TCPBT	3	2.333	10.0		71.5
R-11C	PBT-TCPBT[d]	3	2.166	10.0		130
R-11D	PBT-TCPBT[d]	3	2.100	10.0		208
R-10C	PBNT-TCPBT	3	3.000	10.0	32.5	
R-12A	PBNT-TCPBT	3	2.400	10.0		52
R-12B	PBNT-TCPBT	3	2.333	10.0		71.5
R-12C	PBNT-TCPBT	3	2.166	10.0		130
R-12D	PBNT-TCPBT	3	2.100	10.0		208
R-8	PBNT-BTCA	3	2.400	10.0		38.5
R-11	PBNT-BTCA	3	2.333	10.0		58
R-14	PBNT-BTCA	3	2.250	10.0		77.5
R-18	PBNT-BTCA	3	2.166	10.0		116.5
R-29	PBNT-BTCA[d]	3	2.125	10.0		155.5
R-37C	PB-BTCA	3	3.000	7.5	19	
R-37D	PB-TCPBT	3	3.000	7.5	32.5	
R-37H	PB-TCPBT	3	3.000	7.5	32.5	
R-37B	PB-BDPT	4	4.000	7.5	19, 12.7	

[a] Average acid functionality. [b] Polymerization concentrations. [c] Chain contour length. [d] Incomplete network: gel falls apart upon swelling in good solvent.

Table II
Semiflexible and Flexible Networks

					l, Å	
code	descriptn	branch-pt functionality	f	C_0, %	identical	av
SF-37E	Polacure-TCPBT	3	3.000	7.5	38.3	
SF-37F	Polacure-BDPT	4	4.000	7.5	25.5, 12.7	
F-37G	Polacure–sebacic acid–TCPBT	3	2.400	7.5		~50
F-37J	Polacure–sebacic acid–BDPT	4	3.000	7.5		~50

were measured initially in DMAc. This satisfied us that no measurable damage was done to the networks during the solvent exchanges, heating, and cooling sequences and moduli measurement procedures. It should be noted that if the changes from good to poor solvent, or vice versa, are too rapid, the network gels tend to develop cracks and break up. The severity of this phenomenon appears to be directly related to the network rigidity.

(f) Other Characterization Techniques. Carbon-13 NMR spectra confirming the structure and purity of the synthesized monomers were obtained with a Varian XL-200 Fourier transform NMR spectrometer from about 10% solutions in solvents such as DMAc-d_9, and DMF-d_7, using tetramethylsilane as an internal reference.

The crystallinity levels of several gels were determined from their wide-angle X-ray diffraction (WAXD) patterns. The WAXD patterns were collected at ambient temperature on a Philips APD 3600 automated diffractometer operating in parafocus mode and using monochromatized copper Kα radiation.

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 preferred solvent for these measurements was concentrated sulfuric acid.

Results

(a) Networks and Their Structural Characteristics. The polyamide networks prepared in this study are listed in Tables I and II. In Table I are enumerated the networks whose segments between the branch points are rigid and rodlike. They are all prefixed by R. The rigid rodlike networks are divisible into four different families. Their molecular structures are abbreviated in the second column of Table I: PBT-TCPBT is poly(benzanilide–terephthalamide) with trifunctional branch points comprising TCPBT; PBNT-TCPBT is poly(benzanilide–nitroterephthalamide) with the same trifunctional branch points; PBNT-BTCA is poly(benzanilide–nitroterephthalamide) with trifunctional branch points consisting of 1,3,5-benzenetricarboxylic acid; PB is polybenzanilide. It was polymerized with either the trifunctional branch points BTCA or TCPBT or the tetrafunctional BDPT. The branch-point functionality column is self-evident. Average acid functionality was calculated by dividing the total number of carboxyl groups by the total number of acid molecules reacted with the aromatic diamines to form the polyamide networks. When there are no diacids in the reaction mixture, the diamines react with the multiacids and the distances between one branch point and another are all identical. Provided all functional groups are reacted, there is no distribution of distances in this case. This is reflected in the last two columns of Table I, where, for networks with identical distances between branch points, the chain contour length, between branch points, l, are listed in the "identical" column. The distances were measured by using the projection of the trans C–C bonds in the alkylene segments of flexible and semiflexible chains or following the axes between branch points in the case of the rigid rodlike networks.

A simple way to increase the distance between branch points is to replace incremental amounts of the multiacid branch points by the appropriate amounts of diacids. Such replacements are reflected by the decreased average acid functionality, f, in the fourth column of Table I. The resulting distances between the branchpoints, l, are listed in the last column. Due to the presence of the diacids, the distances between the branch points are not identical anymore. An average l, calculated on the basis of the molar composition of monomers and their structures,[34-39] is given in the last column of Table I. In the polymerization concentration column are listed the volume/volume percent concentration, C_0, of the polymer network in the reaction mixture, calculated from the weights and densities of charged monomers, the volumes of solvents and addi-

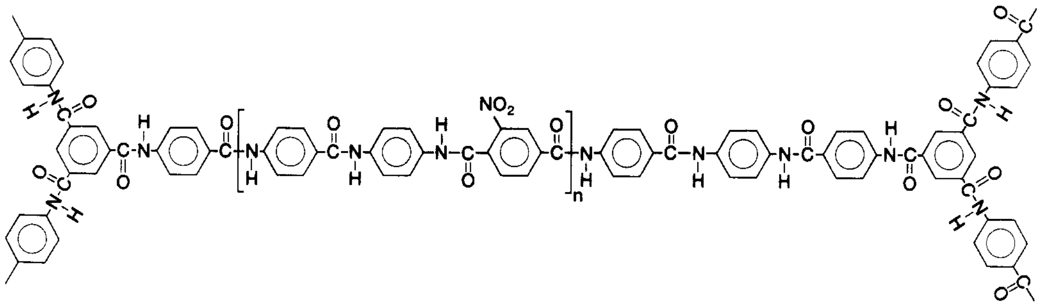


Figure 1. Molecular fragment of PBNT-TCPBT. Elimination of the nitro group results in PBT-TCPBT. Notice the symmetric trifunctional branch points.

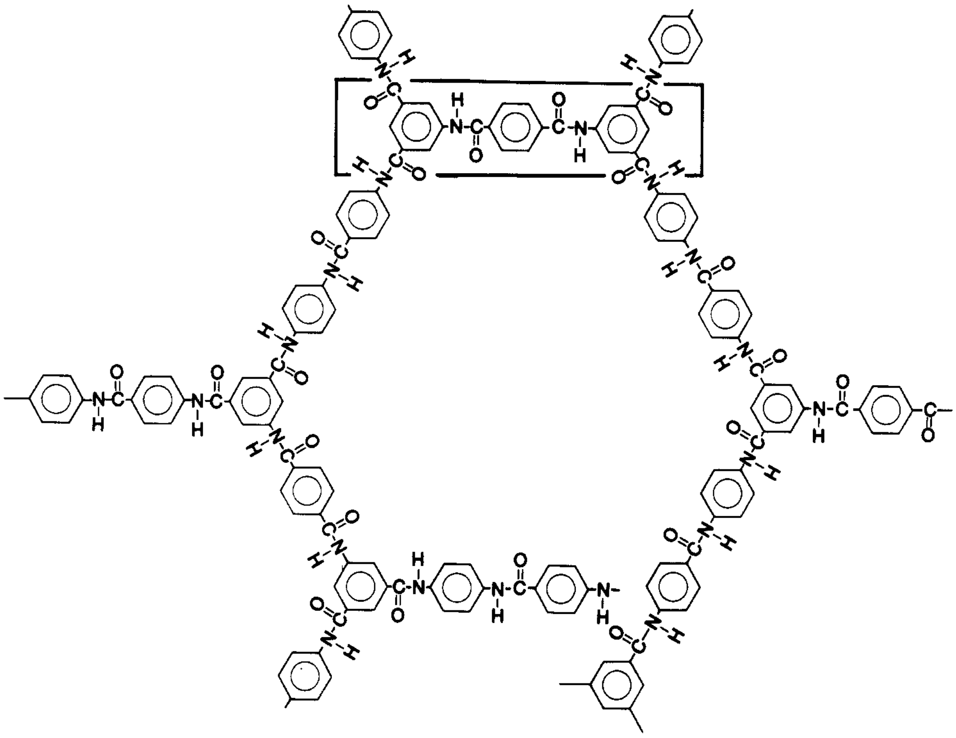


Figure 2. Molecular fragment of the tetrafunctional nonsymmetrical PB-BDPT. One tetrafunctional branch point is enclosed in a box for clarity.

tional reagents, and the expected weight loss during the polycondensation reaction. A molecular fragment of PBNT-TCPBT is shown in Figure 1. When the nitro group is removed, PBT-TCPBT is obtained. If the network comprises only *p*-benzanilide and TCPBT, then identical rods of four aromatic rings are present between all trisubstituted aromatic rings. This is the case for PB-TCPBT in Table I. Because of the elongated shape of the BDPT tetraacid, the situation is somewhat more complex with the tetrafunctional network PB-BDPT. A molecular fragment of this network is shown in Figure 2 to aid in understanding its structure. For clarity, one nonsymmetrical tetrafunctional branch group is marked in a box.

Four semiflexible and flexible networks of series -37 listed in Table II were prepared for the sake of comparison with their rigid counterparts. The semiflexible networks are prefixed by SF and the flexible networks by F. The two semiflexible networks consist of the semiflexible diamine Polacure and the branch providers TCPBT and BDPT. The two flexible networks contain three monomers each: the semiflexible Polacure, the flexible sebacic acid, and the TCPBT triacid or BDPT tetraacid. Because of the presence of sebacic acid, the *l* value is a calculated average and not the identical distances present in both semiflexible networks. An additional group of five semiflexible networks (SF-93 series) was synthesized from Polacure, isophthalic acid, and 1,3,5-benzenetricarboxylic acid in varying proportions. Their end-group analyses and swelling ratios were consistent with those of the semiflexible networks in Table II. Because they were not characterized, the SF-93 series will not be further discussed.

Although labeled "flexible" and "semiflexible", these networks are far from being flexible as is commonly perceived. In the case of SF-37E, for example, the semiflexible segment starts and ends in the middle of an aromatic ring. Between these two rings, each segment contains two additional pairs of para-substituted rings, with the segmental flexibility being limited to the $O-(CH_2)_3-O$ sequence of the Polacure monomer. However, because of the rigidity of the branch points and adjoining aromatic rings and associated amide groups, the conformational changes of the $O-(CH_2)_3-O$ sequences are highly restricted. A change from gauche to trans, or vice versa, within these sequences, will require a translational displacement of the branch points and associated aromatic rings by about 1 Å.[40] Such displacements are strongly restrained by the connectivity of the network. Similar arguments, although not as restrictive, can be made in the case where sebacic acid is copolymerized into the network. The important conclusion is that the flexible and semiflexible networks are not really flexible in the conventional sense. This is borne out by the relatively modest strains the gels of these networks can support before failing. Therefore, we do not believe that our "flexible" and "semiflexible" gels are comparable to common flexible gels.

During the polymerizations it was noted that the reaction mixtures of the rigid rodlike PBT–TCPBT polymers, prepared at $C_0 = 10\%$, increasingly hazed up with the progress of the reaction even before the system gelled. The resulting gelled network was not fully transparent but became transparent during swelling and equilibration in the good solvent DMAc. All other polymers in Tables I and II produced fully transparent gels which remained so after equilibration in DMAc. All transparent gels were fully isotropic with no apparent preferred orientation. The isotropic nature of the networks was further corroborated by uniform swelling in all directions during the equilibration studies in DMAc and by the similarity of moduli measured on slabs cut at different orientations from the gelled initial reaction product.

The ability to form a network encompassing the whole reaction volume resulting in shape-supporting gel is strongly dependent on the average acid functionality, f, in the reaction mixture. Thus, for $f = 2.400$, the total monomer concentration in the feed must be $C_0 = 3\%$ or higher in order for a shape-supporting gel to be formed. The exact concentration depends on the structure of the participating monomers. At $f = 2.166$ the concentration C_0 must exceed about 10% and at $f = 2.100$ the monomer charge must exceed 11.5% of the reaction mixture. This, however, was the highest monomer concentration that could be dissolved in the hot reaction mixture. The lowest concentration where self-supporting gels can be obtained is termed the critical concentration, C_0^*.

The intrinsic viscosities of two of the rigid rodlike samples that failed to form self-supporting gels were determined in dilute solutions. The two polyamides R-11C and R-11D had intrinsic viscosities of 0.87 and 0.54 dL/g, respectively. Some visible gel particles were filtered off R-11C and far smaller amounts of such gels were noticed in R-11D. By analogy to previous work on similar linear polymers, we estimate the minimum weight average molecular weight, M_w, of the rigid rodlike branched R-11C by $M_w \simeq 9000$ and that of R-11D by $M_w \simeq 5000$.[41] Microscopic observations on many dried up minute gel particles comprising rigid rodlike networks revealed them to be rather porous, ramified, and brittle particles, more or less spherical in gross shape.

(b) Gelation Kinetics. Gelation kinetics were evaluated by measuring the increase in viscosity of the reaction mixture with time, as described in the Experimental Section. Only highly branched systems were studied. The results are presented in Figure 3. An examination of the data reveals that a brief incubation period preceded the onset of rapid increase of the viscosity. During this incubation period, a slight decrease in viscosity may occasionally occur, reflecting, we believe, the decrease in viscosity of the added TPP upon heating from ambient to reaction temperature. Once the viscosity starts increasing, it takes off rather dramatically, especially in the cases of rigid or semiflexible networks. The flexible network shows the same incubation period as the others, but the viscosity increases far slower than the others and reaches a far lower viscosity plateau long after the system gelled. At about the same reaction temperature that rigid and semiflexible networks increase in viscosity in a very similar fashion to levels exceeding our ability to measure. Among these, the gel point was ascertained only for the trifunctionally branched semiflexible SF-37E. The gelation occurred at a viscosity of about 200 cP, very similar to the flexible network gel, and is accompanied by a change in slope of the viscosity versus time curve.

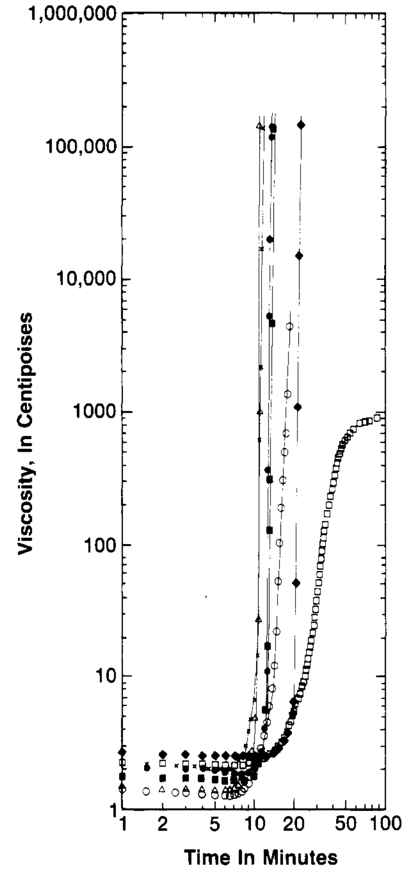


Figure 3. Viscosity of polymeric network gels as a function of polymerization time. Systems polymerized at about 115 °C: Rigid networks (●) R-37B, (×) R-37C, (■) R-37D; semiflexible networks (○) SF-37E, (△) SF-37F; flexible network (□) F-37G. System polymerized at 103 °C: (◆) R-37H. All networks at $C_0 = 7.5\%$.

The viscosities of all other systems increased too rapidly to ascertain quantitatively the point of gelation. However, qualitative observations indicate that the gel point of all the systems we studied (all at $C_0 = 7.5\%$) occurred between 200 and 1000 cP. A comparison of the curves of the trifunctional PB-TCPBT, R-37D, and R-37H indicates that a reduction of the reaction temperature from 115 to 103 °C increased the incubation period by about 5 min but did not change significantly the subsequent rapid increase in viscosity.

It is important to recognize that the polycondensation and network formation in all our systems continue after the respective gel points, and that at the same concentration the viscosity of the flexible network gel is far lower than that of the rigid and semiflexible networks.

(c) End-Group Titration and Sol/Gel Fractionation. The procedures employed for sol/gel fractionation and end-group analyses were described in the Experimental Section. It is important to note that the end-group titrations were performed only on the gel component of the samples and never on the sol/gel mixture. The results of all sol/gel fractionation experiments are listed in Table III. They are in general agreement with the results in ref 31. The results of end-group titrations are tabulated in Table IV. The most important observation gathered from Table III is that the highly branched rigid networks produce a very small fraction of extractable sol. This fraction rapidly increases in instances where the formed gel fails to maintain its integrity when swelled in a good solvent,

Table III
Sol/Gel Fractions of Network Gels

code	descriptn, rigidity	branch-pt functionality	f	C_0, %	wt % gel	wt % sol
R-37B	PB-BDPT, rigid rod	4	4.000	7.5	100	0
R-37D	PB-TCPBT, rigid rod	3	3.000	7.5	100	0
R-12A	PBNT-TCPBT, rigid rod	3	2.400	10.0	99	1
R-12D	PBNT-TCPBT, rigid rod	3	2.100	10.0	98	2
R-8	PBNT-BTCA, rigid rod	3	2.500	10.0	99	1
R-11	PBNT-BTCA, rigid rod	3	2.333	10.0	95	5
R-14	PBNT-BTCA, rigid rod	3	2.250	10.0	93	7
R-18	PBNT-BTCA, rigid rod	3	2.166	10.0	90	10
R-29[a]	PBNT-BTCA, rigid rod	3	2.125	10.0	67	33
SF-37F	Polacure–BDPt, semiflexible	4	4.000	7.5	97.9	2.1
SF-37E	Polacure–TCPBT, semiflexible	3	3.000	7.5	71.0	29.0
F-37G	Polacure–sebacic acid–TCPBT, flex	3	2.400	7.5	62.5	37.5
F-37J	Polacure–sebacic acid–BDPT, flex	4	3.000	7.5	65.9	34.1

[a] Incomplete network: gel falls apart upon swelling in good solvent.

Table IV
Carboxyl and Amine End-Group Analysis by Titration

code	descriptn	rigidity	branch-pt functionality	f	M_n per carboxyl	M_n per amine
	solvent blank				290 000	
55B	TCPBT monomer		3		576	NA
R-37B	PB-BDPT	rigid rod	4	4.000	9 280	28 400
R-37H	PB-TCPBT	rigid rod	3	3.000	9 850	28 600
R-10C	PBT-TCPBT	rigid rod	3	3.000	*b*	52 500
R-11A	PBT-TCPBT	rigid rod	3	2.400	23 500	48 700
R-11B	PBT-TCPBT	rigid rod	3	2.333	*b*	31 000
R-11C	PBT-TCPBT (a)	rigid rod	3	2.166	66 700	36 550
R-11D	PBT-TCPBT (a)	rigid rod	3	2.100	40 000	42 000
R-12A	PBNT-TCPBT	rigid rod	3	2.400	30 800	77 000
R-12B	PBNT-TCPBT	rigid rod	3	2.333	14 800	56 500
R-12C	PBNT-TCPBT	rigid rod	3	2.166	19 000	49 900
R-12D	PBNT-TCPBT	rigid rod	3	2.100	12 900	38 750
F-37G	Polacure–sebacic acid–TCPBT	flex	3	2.400	175 000	143 000
F-37J	Polacure–sebacic acid–BDPT	flex	4	3.000	200 000	180 000

[a] No shape-supporting gel is formed. [b] End point was reached in the first drop of titrant. Values are too large to be determined accurately.

R-29, or when no self-supporting gel was formed, as was the case with R-11C and R-11D. A comparison of the rigid R-12A and R-8 with the flexible F-37G and F-37J, all with the same average functionality, clearly shows the very large sol fraction of the flexible networks as compared with the negligibly small sol fraction of both rigid networks. A comparison of R-37D with SF-37E, identical systems except for the replacement of the rigid DABA monomer by the more flexible Polacure, clearly reveals the very same trend.

The molecular weight of the sol fraction of F-37J was estimated from its intrinsic viscosity of 0.50 dL/g to be about M_w = 15 000, by analogy with the linear comparable poly(ester amide) in ref 42.

The titration results in Table IV indicate that a small number of amine and carboxyl groups are present in the gel fraction of the networks. A comparison of the rigid networks with the semiflexible and flexible ones qualitatively reveals a trend toward higher molecular weight per titratable group as the network becomes more flexible. It appears that with enhanced flexibility, the chances improve for intermolecular contact and bond formation, as well as intramolecular cyclization. Additionally, the extraction of macromolecules not covalently connected with the macroscopic network becomes more efficient as the flexibility of the network and extractable molecules increases. Because the incubation period before the onset of rapid viscosity increase and gelation was about the same for all the evaluated networks, one can reject the argument of lower reactivity of the more rigid networks leading to lower molecular weight per end group in the rigid networks.

When the titration results of the rigid networks are considered together with their sol/gel fractionation and with the intrinsic viscosities of systems that failed to form shape-supporting gels, one reaches the conclusion that gels of branched rigid macromolecules contain one or a few giant macromolecules pervading the whole volume of the reaction mixture and forming a covalently bonded network. Nestled and interwined in this network there exist a much larger number of macromolecules whose number-average molecular weight per reactive group is, in general, below 100 000 for rigid systems and reaches up to 350 000 for the semiflexible and flexible ones.

As will become apparent below, there appears to exist no direct correlation between the molecular weight per end group of a shape-supporting network and the modulus or degree of swelling of its gel in a good solvent.

(d) Network Equilibration and Modulus. Large specimens were used for the equilibration studies and the subsequent modulus determinations. Although durations of about 3 months were allowed for the equilibrations and extractions, we believe that, at least in the case of rigid networks, a substantial fraction of the higher M individual macromolecules were not extracted out of the gels prior to the mechanical testing. This belief is based on the titration results presented above. For clarity, the results of volume changes upon equilibration in good solvent (DMAc) and poor solvent (formamide) are listed in Table V together with the modulus G, in dyn/cm^2, measured at ambient temperature on the equilibrated specimens. The modulus of two flexible gels was measured also on the as-prepared samples, at C_0 = 7.5%. The percent polymer

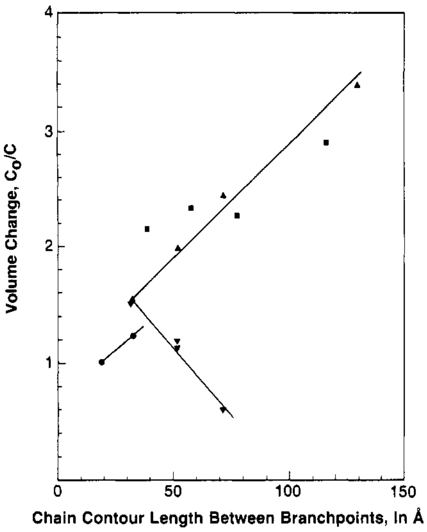


Figure 4. Volume change as function of chain contour length between branch points for networks equilibrated in DMAc. Families: (●) R-37, C_0 = 7.5%; (▲) R-10, R-12, C_0 = 10.0%; (■) R-8, R-11, R-14, R-18, C_0 = 10.0%; (▼) R-10, R-11A, R-11B, C_0 = 10.0%, hazed prior to gelation.

in the equilibrated gel, C, was determined from comparisons of the weights of the equilibrated gels with the weights of the constant-weight dried-up networks, followed by conversion from weight to volume fractions. The as-prepared concentration, C_0, was calculated from the monomer charges in the reaction mixture. The f and l columns are self-explanatory.

The volume change upon equilibration in DMAc is plotted as function of chain contour length between branch points l in Figure 4. Here, values above 1.0 indicate a network swelling during equilibration, and values smaller than 1.0 reflect the network shrinkage. The molecular mechanism of swelling and colapse of the rigid gels will be discussed in a forthcoming paper. In general, highly branched and cross-linked networks swell very little, with the increase in swelling following the increase in distance between branch points (cross-links in the case of fully reacted systems). It is obvious that the three rigid rodlike members of series R-10, R-11A, R-11B do not follow the trend. This behavior is due to the development of crystallinity during the polymerization of this series and is not typical of the systems under study. The reasons for the rather erratic swelling behavior of the flexible and semiflexible members of the -37 series, in Table V, is not understood at present.

Four samples from the -37 series were equilibrated in DMAc at room temperature and at 150 °C. The results indicate that the tetrafunctional, densely branched rigid rodlike R-37B shows no change in its volume over the temperature interval indicated. The trifunctional rigid rodlike R-37D may have shown very small volume changes, but these fall within our experimental margin of error, making the changes suspect. On the other hand, the trifunctional semiflexible SF-37E and the tetrafunctional flexible F-37J both showed a substantial increase in volume with temperature. In terms of network concentration in the gels, SF-37E changed from C = 8.38% at room temperature to C = 7.07% at 150 °C. F-37J changed from C = 9.87% at room temperature to C = 8.51% at 150 °C. The ratio of volume at 150 °C to volume at room temperature is 1.19 and 1.16, respectively. Equilibration in poor solvent leads to a shrinkage of the networks with $C < C_0$.

The ambient temperature equilibrium modulus, G, of the equilibrated gels is plotted against C in Figure 5. The

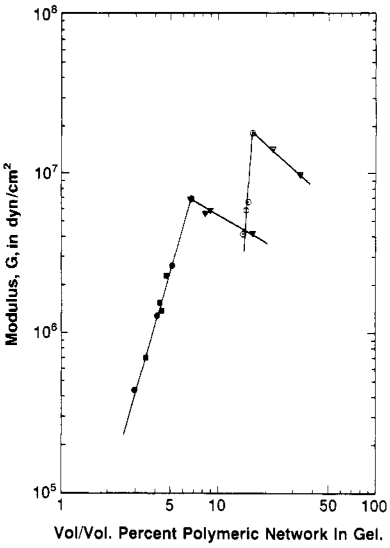


Figure 5. Room temperature modulus, $G = E/3$, versus concentration C of rigid rodlike gels. Solid symbols: equilibrated and measured in DMAc. Empty symbols: equilibrated and measured in formamide. (○, ●) R-12 series; (■) R-8, R-11, R-14, R-18 series; (▽, ▼) R-10, R-11A, R-11B series.

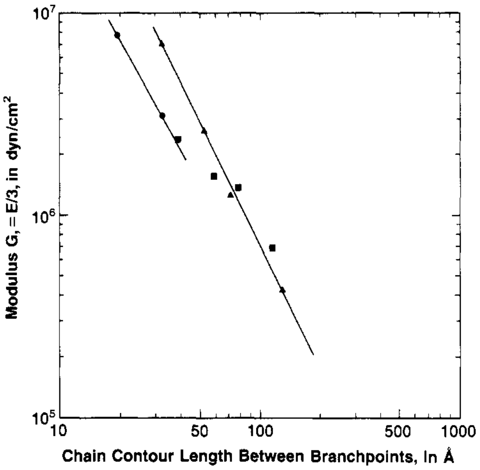


Figure 6. Room temperature modulus, $G = E/3$, of rigid rodlike networks equilibrated and measured in DMAc, plotted against the chain contour length between branch points.

atypical results of series R-10, R-11A, R-11B are presented only for the sake of completeness. The results can be summarized as follows: the rigid rodlike gels show a very high power dependence on C. The modulus and C increase upon collapse of the networks in poor solvent. In the good solvent DMAc, the modulus of the rigid rodlike gels shows a power dependence on C described by

$$G \propto C^{3.15}$$

This power law increases for the rigid rodlike networks in the poor solvent formamide.

When the moduli of rigid rodlike networks prepared at C_0 = 10% and equilibrated in DMAc are plotted against l in Figure 6, the following power law is observed:

$$G \propto l^{-2.11}$$

Because they developed intense optical opacity, the results for networks collapsed in formamide may reflect a possible macroscopic phase separation. Such a phase separation may render a dependence of G on l meaningless and the dependence of G on C questionable.

Probably the most important experimental results of this work are presented in Figure 7. Here, the modulus G =

Table V
Gels Equilibrated in DMAc and Formamide and Their Modulus, G, at Ambient Temperature

					N,N-dimethylacetamide			formamide		
code	descriptn	f	l, Å	C_0, %	C, %	vol exp	G, dyn/cm^2	C, %	vol exp	G, dyn/cm^2
R-37B	rigid rod PB	4.000	19/12.7	7.5	7.50	1.00	7.66×10^6			
R-37D	rigid rod PB	3.000	32.5	7.5	6.10	1.23	3.07×10^6			
R-10C	rigid rod PBT	3.000	32.5	10.0	6.72	1.49	6.98×10^6	16.60	0.60	18.31×10^6
R-11A2	rigid rod PBT	2.400	52	10.0	8.9	1.12	5.79×10^6			
R-11A	rigid rod PBT	2.400	52	10.0	8.42	1.19	5.63×10^6	22.27	0.45	14.65×10^6
R-11B	rigid rod PBT	2.333	71.5	10.0	16.78	0.60	4.19×10^6	32.81	0.30	9.77×10^6
R-10C	rigid rod PBNT	3.000	32.5	10.0	6.72	1.49	6.98×10^6	16.60	0.60	18.31×10^6
R-12A	rigid rod PBNT	2.400	52	10.0	5.05	1.98	2.62×10^6	15.76	0.63	6.66×10^6
R-12B	rigid rod PBNT	2.333	71.5	10.0	4.10	2.44	1.25×10^6	15.11	0.66	5.89×10^6
R-12C	rigid rod PBNT	2.166	130	10.0	2.96	3.38	0.43×10^6	14.50	0.69	4.19×10^6
R-12D	rigid rod PBNT	2.100	208	10.0			too soft			too soft
R-8	rigid rod PBNT	2.400	38.5	10.0	4.65	2.15	2.29×10^6			
R-11	rigid rod PBNT	2.333	58	10.0	4.30	2.33	1.53×10^6			
R-14	rigid rod PBNT	2.250	77.5	10.0	4.40	2.27	1.37×10^6			
R-18	rigid rod PBNT	2.166	116.5	10.0	3.45	2.90	0.69×10^6			
R-29	rigid rod PBNT	2.125	155.5	10.0			too soft			
SF-37E	semiflex Pol'cr	3.000	38.3	7.50	8.38	0.89	0.456×10^6			
F-37G	flex sebacic a.	2.400	~50	7.50	a	a	1.00×10^5			
F-37G	flex sebacic a.	2.400	~50	7.50	3.51	2.14	0.873×10^5			
F-37J	flex sebacic a.	3.000	~50	7.50	a	a	1.53×10^6			
F-37J	flex sebacic a.	3.000	~50	7.50	9.87	0.76	2.31×10^6			

[a] As-prepared sample, in gelled reaction mixture.

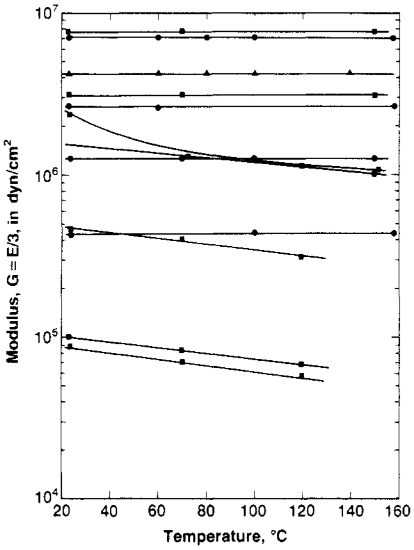


Figure 7. Modulus, $G = E/3$, of networks equilibrated and measured in DMAc, as a function of temperature. (■) -37 series; (●) R-12 series; (▲) R-11B.

$E/3$ was measured as function of temperature on samples first equilibrated and then immersed in DMAc. Wide-angle X-ray diffraction patterns indicated no crystallinity in any of the gels in Figure 7. The results indicate that the rigid rodlike networks are insensitive, within the framework of our accuracy, to changes in temperature from room temperature up to the boiling point of DMAc. However, when a measure of flexibility was introduced into the segments between the cross-links (in samples F-37G and F-37J as prepared and samples SF-37E, F-37G, and F-37J after equilibration in DMAc), a decrease in modulus is brought about by increases in the temperature. From the slope of log modulus G versus $1/T$, an activation energy of 0.5 to 2.0 kcal/mol was obtained for all these polymers. Such a low activation energy is probably associated with some strongly cooperative phenomenon occurring upon heating of the flexible and semiflexible gels. In general, we note that (a) the modulus decreases with an increase in l (as shown above), (b) tetrafunctional branch points are more efficient in increasing the modulus than the trifunctional analogues, and (c) the addition of the flexible sebacic acid monomer did not increase dramatically the rate of modulus decrease with temperature obtained by the introduction of the semiflexible monomer Polacure.

Only seven measurements of modulus as a function of temperature were conducted in formamide on rigid networks equilibrated in this poor solvent. The moduli were higher than the corresponding ones in DMAc and showed insensitivity toward temperature changes over the range of ambient to 100 °C.

Discussion

When all functional groups stoichiometrically present in the reaction mixture react with one another to form covalent bonds, a single "infinite" macromolecule is expected to be produced either by direct covalent linkage or by entanglements which do not permit two or more large units to be separated. Its level of branching reflects the average functionality of the available monomers. Gels of highly branched covalently bonded polymers are visualized by current theory as infinite polymeric networks pervading the whole volume of the system and swollen by suitable diluents.[1,7,43] Interpenetrated with the infinite macromolecules are highly branched macromolecules of lower molecular weight.[7,44,45] In the case of flexible backbone polymeric networks, the macromolecules nestled in and interpenetrated with the infinite network can be extracted out as the sol fraction. Their behavior is reminiscent of, but not necessarily identical with, the diffusion of branched or star molecules in a network of infinitely long rods.[46-48] The lower M macromolecules form in the reaction mixture because some of the functional groups in the growing polymer molecules failed to form intermolecular covalent bonds. Therefore, the presence in the system of significant amounts of titratable reactive groups may be taken as an indication that lower M macromolecules are present, besides the infinite polymeric network. Because these molecules are highly branched, the relationship between their molecular weight and the number of reactive end groups is not straightforward, but one can get an appreciation of their size from their molecular weight per end group.

In our case of rigid rodlike networks, extractions failed to remove the highly branched macromolecules out of the infinite network, except for a few instances in which the functionality *f* was small. With increased flexibility, larger sol fractions were extracted. There are two possible explanations for the negligible sol fraction of the rigid gels and the much larger sol fraction obtained from the flexible ones: (a) the species comprising the flexible networks are less reactive than those in the rigid networks or (b) because of the flexibility of the infinite network and the lower *M* branched macromolecules in it, the latter can be extracted out of the "infinite" network.[1,7,14,43-48] The diffusion of highly branched lower *M* rigid macromolecules through an infinite network of similar rigidity is hindered by the inability of molecular segments to move significantly out of the way. Thus, the negligible amounts of sol in the case of rigid networks have nothing to do with the level of reactivity of the end groups.

Of the two possibilities above, the first cannot be valid. First, the incubation period before the viscosity takes off was observed above to be very similar for rigid and flexible networks, indicating similar reactivity of the respective monomers. Furthermore, it was demonstrated by Aharoni et al.[49] that the flexible sebacic acid is highly reactive in Yamazaki procedures. The semiflexible monomer Polacure was found also to be highly reactive.[42] In fact, it was demonstrated in the past that practically all monomeric species employed in this study are highly reactive under the Yamazaki conditions.[30,31,42,49] Therefore, we reject the first explanation. On the other hand, the combination of the end-group titration results, in Table IV, with the sol/gel fractionation, in Table III, leads us to believe that the higher the rigidity of the network and the smaller is *l*, the more impeded is the diffusion of such highly branched molecules out of the infinite network, and the smaller is the sol fraction. This appears to be clearly the case when the almost insignificant sol fraction of the rigid rodlike R-11C is considered: from intrinsic viscosity measurements we estimate its M_w by only 9000. At the same time, the molecular weight per end group in the gel fraction is in the tens of thousands. (Systems that failed to form self-supporting gels should not be compared with nicely gelled ones.) The extraction becomes more facile with enhanced chain flexibility and increased *l*. This is especially clear in the case of the flexible networks: they leave behind in the infinite network only a small amount of individual macromolecules characterized by a molecular weight (M_n) of about 200 000 per end-group, while the substantial sol fraction (sample F-37J) has an estimated molecular weight (M_w) of only 15 000. This means that the lower end of the molecular weight distribution was extracted out of the infinite network of the flexible polymers while the higher *M* macromolecules were not. The latter still seem to have far lower molecular weights than theory predicts. In the case of the rigid networks, we believe that most of the individual macromolecules were not extracted from the gel and this is the reason for the negligibly small amounts of sol and for the molecular weight per end group being so small relative to the corresponding values for the flexible systems.

The fact that the dried gel particles were highly ramified and the dried self-supporting network gels were generally ramified and highly corrugated, together with the very rapid increase in viscosity during polymerization, is reminiscent of fractal growth characteristics[50-55] and invites the evaluation of our systems in the light of fractal theory. We have insufficient data to prove the fractal growth nature of our systems. However, a plot of ln reduced viscosity, ln η_s, versus time of the seven polymers in Figure 8 indicates that one or two straight lines describe well five of these polymers. In the cases of the flexible F-37G network and when the polymerization was conducted at 103 °C (R-37H), three straight lines could be passed through the data points of each polymer. This linearity is one of the criteria[51] for fractal growth. log–log plots of the same data produced essentially the same results. The slopes of the curves of η_s versus *t* for all these polymers are extremely steep, making it practically impossible to obtain dependable power laws free of unacceptably large error estimates.

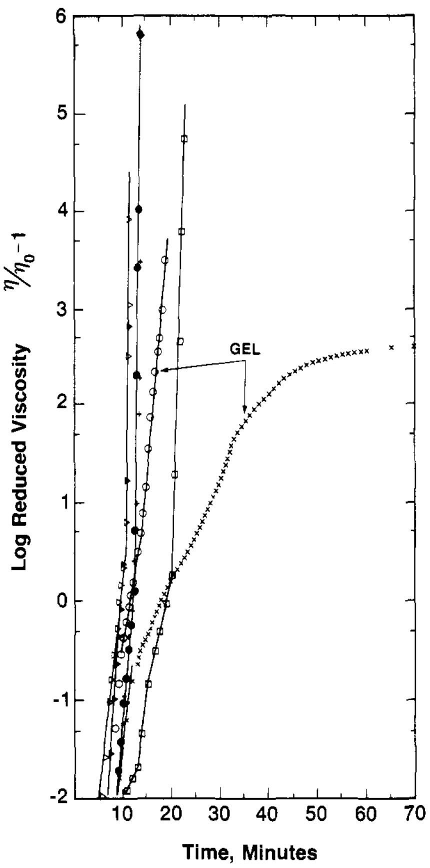


Figure 8. log reduced viscosity versus polymerization time of the -37 series. (○) -37E; (●) -37B; (×) -37G; (△) -37C; (▲) -37F; (□) -37H; (+) -37D. All at C_0 = 7.5%.

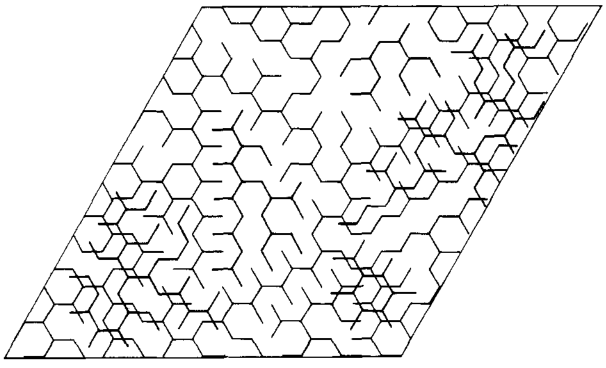


Figure 9. Trifunctional rigid rodlike network gel. Two-dimensional idealization of three-dimensional system. All branches at 120°. Light lines: part of the "infinite" network, all on a triangular lattice. Heavy lines: branched macromolecules not covalently connected to the "infinite" network. Some on a triangular lattice and some displaced off-lattice.

As can be gathered from Figures 1 and 2, the distances between branch points in the rigid rodlike networks are far larger than the chain diameter. This allows for substantial macrmolecular interpenetration without significantly disturbing the spatial distribution and directionality

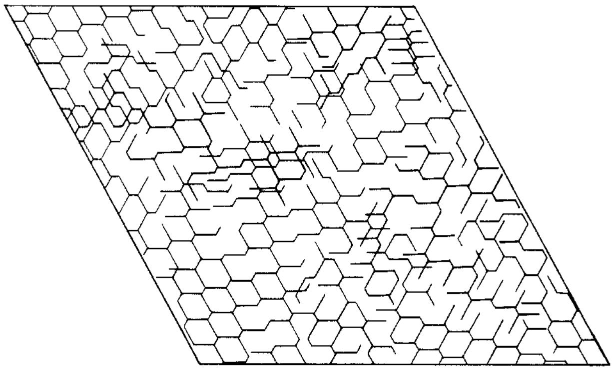


Figure 10. Tetrafunctional rigid rodlike network gel. Description as in Figure 9.

of segments in either the rigid network or the rigid lower M highly branched macromolecules intertwined in it. A schematic two-dimensional representation of the perceived three-dimensional structure is shown in Figures 9 and 10. In Figure 9, the branch points are trifunctional and symmetric, while in Figure 10 they are tetrafunctional and not symmetric. In both figures the heavy lines represent the lower M individual macromolecules and the lighter lines represent a part of the "infinite" network. Notice that in both cases the lower M macromolecules can be positioned on the lattice of the infinite network and also off this lattice in such a manner than their segments occupy spaces in between the segments of the rigid infinite network. The representations in Figures 9 and 10 hold true irrespectively of whether the polymeric networks in the gels follow better the fractal growth model or the percolation model. Of course, the real-three dimensional model is not amenable to a simple drawing.

The modulus versus temperature results in Figure 7 are in disagreement with prevailing theory: the moduli of the rigid network gels appear to be independent of temperature within the ±5% margin of error of our determinations, and the moduli of the more flexible network gels fall with temperature. All the network gels in this figure were determined to be fully amorphous by X-ray diffraction. Theory expects the modulus of the flexible networks to increase[56] and that of the rigid gels to decrease with temperature.[27,29] We believe that several important factors account for the deviation of our results from theory: *the relatively short distances between branch points, the connectedness of the rigid segments, and the general inability of the rigid networks to conform to normal, Gaussian statistics.* Because of the rigidity of the para-substituted aromatic amides, the number of virtual bonds between branch points should be counted as one, in the case of the rigid rodlike networks. Even when we, liberally, count each aromatic ring as a virtual bond, we stay most commonly below 10 such bonds between branch points and never exceed 30. When such short segments, rigid or otherwise, are anchored at both ends by the branch points, their ability to change position and their deformability are greatly reduced. Furthermore, the presence of individual highly branched macromolecules in the "infinite" network may affect significantly the absolute modulus values as well as their dependence on temperature.

Similar to our results, there exist in the literature systems that do not behave according to theory. For instance, the modulus of highly cross-linked networks of the copolymer made from ethyl acrylate and ethylene glycol dimethyacrylate becomes independent of temperature[57] above the transition interval, while the lightly cross-linked analogues show the expected modulus increase with temperature. It should be further noted that deviations from theoretical expectations were observed in the case of flexible networks, when studied under compressive deformation,[58] a configuration similar to our test procedure.

The segmental rigidity of the rigid networks in this study is consistent with the high rigidity of rodlike polyamides of similar composition observed experimentally[41,59] and deduced from the calculated very large characteristic ratio.[39] Spectroscopic studies indicate that the potential barrier to rotation of the bonds in the rigid rodlike polyamide segments is not less than about 10 kcal/mol[60] and generally resides close to 20 kcal/mol.[60,61]

In Figure 7 it was shown that the modulus of five gels of semiflexible and flexible networks decreases with temperature. The modulus at the highest measurement temperature was about 65–70% of its value at room temperature. The equilibration experiments indicated a corresponding volume expansion of about 1.16. This corresponds to about a 14% decrease in network concentration. Thus, we find a dependence of the modulus G on C of about

$$G \propto C^2$$

which dominates over the linear dependence of G on T.

Data in Table V teach us that at room temperature the modulus of the flexible gels depends on C as

$$G \propto C^{3.17}$$

The agreement with the 3.15 power dependence of the rigid rodlike networks is interesting yet probably fortuitous. The thermal expansion of networks swollen in the good solvent DMAc is likely to stretch the flexible segments beyond their extension at room temperature. The associated change in network concentration apparently produces a lower power dependence of G on C than when the change in concentration is not accompanied by changes in the segmental extension. Even in the case of the rigid rodlike gels alone, our experimentally determined 3.15 power dependence of G on C does not fit with any of the current theories. It lies between the power of 2 proposed very recently for systems consisting of disordered rods[62] and is substantially lower than 5, calculated to be the lowest power dependence for systems fitting the discrete percolation model.[62] The observed power dependence is also lower than the fifth power dependence of modulus on concentration proposed by Doi and Kuzuu.[29] In their model, however, the rodlike macromolecules are free to slide by one another, and as a result the elasticity of the gel is independent of the rod lengths. This model, of course, has little in common with the system studied here. While cataloguing these results we also note that the transport theory of Doi and Edwards[63] gives coefficients proportional to C^3, but they are entropic in origin.

Again, in the case of the flexible swollen networks, our 3.15 power dependence of G shows that we are remote from the semidilute limit[43] of 2.25 or the 0.5 power dependence of the deswelled flexible networks.[64]

This is, of course, new territory and an understanding of the specifics of the above relationships, as well as the rather high power dependence of G on C for both rigid rodlike and flexible gels, requires additional experimental and theoretical work.

One final point. The changes in viscosity with reaction time, t, were followed for six members of the -37 series. The results are presented in Figure 3. During the polycondensation, it was noticed that gelation occurs at viscosities of 200 cP or somewhat higher. Based on this, a log–log plot of viscosity versus $(t_c - t)$, in minutes, was constructed for the above polymers, t_c being the gelation time. Beyond $(t_c - t) = 0.3$ min., a linear portion of the curve could be found for all but one (R-37B) of the networks. Among these, the slopes were −1.96, −2.40, −2.46, and −2.5 for SF-37E, R-37D, F-37G, and SF-37F, respectively, and −0.93 for R-37C. These increases in viscosity upon approaching the gel point show much higher power dependence on time than the expectations based on percolation theory[65,66] and several experimental results obtained from flexible systems.[66-68] It should be noted, however, that the literature results relate to gelation processes that are very much slower than the rapid gelation of our systems.

Conclusions

Gels were prepared comprising a good solvent and highly branched networks of rigid rodlike segments. A few networks in which some flexibility was built into the chain were prepared for comparison. All these systems show a remarkably steep approach to the gel point and large viscosity increases beyond it. Fractionation and end-group titrations indicate that the higher the rigidity of the network, the less sol is extractable and the lower its molecular weight. The conclusion is that due to segmental rigidity, individual highly branched macromolecules cannot diffuse out of the infinite network, while more flexible macromolecules diffuse out with greater facility.

The modulus of the gels increases with increased network concentration. This holds for gels equilibrated in good as well as in poor solvent. The modulus of the equilibrated rigid networks appears to be insensitive to changes of temperature over the range 23–150 °C. In networks with more flexibility, the modulus drops with temperature, and the drop appears to be associated with increased swelling of the gels when immersed in a good solvent. A schematic description of the rigid network structures is proposed.

We are satisfied that the segments between branch points, even those termed flexible in this study, are far too short and too rigid to conform with Gaussian statistics and for the gels to behave accordingly. Theory of these systems is only now starting,[60] and we hope that now that experimental results are becoming available, a more elaborate theory in which the network rigidity and the short distance between branch points are taken into consideration will emerge.

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Registry No. TCPBT, 120360-51-2; BDPT, 120360-52-3; BTCA, 4422-95-1; (PBT)(TCPBT) (copolymer), 120360-53-4; (PBNT)(TCPBT) (copolymer), 120360-55-6; (PBNT)(BTCA) (copolymer), 120360-54-5; (PB)(BTCA) (copolymer), 71604-69-8; (PB)(TCPBT) (copolymer), 120360-56-7; (PB)(BDPT) (copolymer), 120360-57-8; (TCPBT)(Polacure) (copolymer), 120360-58-9; (BDPT)(Polacure) (copolymer), 120360-59-0; (TCPBT)(Polacure)(sebacic acid) (copolymer), 120360-60-3; (BDPT)(Polacure)(sebacic acid) (copolymer), 120360-61-4; *p*-aminobenzoic acid, 150-13-0; terephthaloyl chloride, 100-20-9; 3,5-dicarboxyaniline, 99-31-0.

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Miscibility Control by Hydrogen Bonding in Polymer Blends and Interpenetrating Networks

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ABSTRACT: Interpenetrating polymer networks (IPNs) were synthesized from miscible blends of poly[(1-hydroxy-2,6-methylene)phenylene] and poly(methyl methacrylate) by using two types of cross-linking agents at different temperatures. The extent of hydrogen bonding in the blends and IPNs was controlled by changing the temperature of the cross-linking reaction and by reducing the density of the hydrogen bond acceptor groups in the chain, using copolymers of methyl methacrylate and styrene. Fourier transform infrared spectroscopy was employed to measure the extent of hydrogen bonding. A critical value of hydrogen bonding interaction was needed for miscibility to be maintained in these blends and IPNs.

Introduction

The miscibility of dissimilar polymers is favored by exothermic intermolecular interactions. Of the many different types of interactions commonly encountered, hydrogen bonding has been the subject of many recent investigations[1-6] because the formation of hydrogen bonds lends itself in many cases to quantitative spectroscopic measurements, and a wealth of information in the literature on hydrogen bonding between small molecules can be used as guides for polymer studies. More recently, the theory of hydrogen bonding in polymer blends has been formulated so that thermodynamic quantities can be evaluated and phase diagrams calculated from these quantities.[7]

The aim of this research is to study the minimum amount of interpolymer hydrogen bonding needed to maintain a single phase. Our approach consists of varying the density of interacting groups in the chain, determining the fraction of hydrogen bonded groups, and correlating the extent of interaction to phase behavior.

A second objective of our investigation concerns hydrogen bonding in interpenetrating networks (IPNs) derived from miscible blends. Hydrogen bonding formation and dissociation in polymers are thermally reversible.[8] However, if the cross-linking reaction for IPN synthesis takes place at an elevated temperature at which a large proportion of hydrogen bonds have dissociated, it is conceivable that the restricted segment mobility in the network may hinder the full recovery of hydrogen bonds upon cooling. If the temperature is further increased to the point at which the remaining hydrogen bonds is no longer sufficient to maintain the blend as a single phase, it is an open question whether the network formed in the heterogeneous state is able to revert to the miscible state, upon cooling, through the reestablishment of hydrogen bonds. This aspect of IPN properties has been addressed, in part, by Coleman and co-workers.[9] It constitutes a primary element of our study.

To answer the above questions, we have chosen the pair poly(methyl methacrylate) (PMMA) and a phenol–formaldehyde resin, *o,o*-poly[(1-hydroxy-2,6-methylene)phenylene] (PHMP). The two polymers are miscible over the entire range of blend compositions, and spectroscopic evidence of hydrogen bonding between the hydroxyl group of PHMP and the carbonyl group of PMMA has already been reported.[8] The density of the hydrogen bond acceptors in the chain was varied by using a series of methyl methacrylate copolymers containing styrene units. Styrene was selected as the comonomer because the solubility parameter of polystyrene, 9.05, is very close to that of PMMA, 9.24. Consequently, the "copolymer" contribution to miscibility change[10] is expected to be small, and as a first approximation, the styrene segment in the copolymer can be considered as a diluent for the carbonyl group to reduce the number of available interaction sites.

Experimental Section

Materials. (a) Poly[(1-hydroxy-2,6-methylene)phenylenes] (PHMP) were synthesized from phenol and formaldehyde at 165 °C in the presence of calcium hydroxide as catalyst.[11] The reaction condition results in highly specific ortho–ortho methylene linkages without noticeable amounts of side reactions,[12] as confirmed by infrared spectra and by chemical shifts in proton and carbon-13 NMR spectroscopy.

(b) Copolymers of methyl methacrylate and styrene were synthesized by radical polymerization at 70 °C, using azobis(isobutyronitrile) as initiator. The reaction was allowed to proceed to about 10% conversion, and the polymer was isolated and purified by precipitation from methyl ethyl ketone solution into hexane twice. The composition of the copolymer was determined by UV spectrophotometry, using the absorption at 262 nm for the styrene units. The 13 copolymers are designated as COP90 (83.5), 80 (79.2), 70 (72.2), 60 (60.7), 50 (48.9), 40 (37.2), 38 (36.3), 36 (35.6), 34 (34.3), 32 (31.7), 30 (30.4), 20 (16.9), and 10 (9.3), with the weight percent MMA indicated by the number in parentheses. The intrinsic viscosities of these copolymers were determined in toluene at 30 °C. The values increase systematically from 0.359 dL/g for COP90 to 0.516 for COP10. As points of reference, PMMA with an intrinsic viscosity of 0.327 has a viscosity-average molecular weight of 147 000, while PS with an intrinsic viscosity of 0.528 has a calculated molecular weight of 135 000. The 13 copolymers have similar T_g values, about 100 °C.

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