Polyamide networks with stiff 'liquid-crystalline' segments and trifurcated flexible junctions

S. M. Aharoni*
Polymer Science Laboratory, Allied Signal Inc. Research and Technology, PO Box 1021, Morristown, NJ 07962, USA

and S. F. Edwards
Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge CB3 0HE, UK

(Received 23 April 1993; revised 18 September 1993)

The preparation of a novel family of polyamide network gels is described. In these networks, the segments are stiff and longer than the critical axial ratio for mesomorphic behaviour. The junctions are trifurcated and flexible. The gels were prepared at 10% network concentration. They are intensely birefringent in the relaxed nascent state, unlike fully rigid or flexible network gels. Upon swelling in *N*,*N*-dimethylacetamide (DMAc) to equilibrium, the gels lose their birefringence, which is recovered when the equilibrated gels are heated to less than 120°C and then cooled. The birefringence of the present gels is clearly associated with the coexistence in them of both long, stiff mesogenic segments and flexible trifurcated junctions. X-ray diffraction studies reveal the gelled networks to be fully amorphous. Thermal studies by differential scanning calorimetry indicate very strong attractive interactions between the polyamide networks and DMAc solvent, manifested by pronounced solvent retention in the gels at high temperatures and substantial lowering of both freezing and melting points of the DMAc in the gels relative to its transitions in the bulk.

(Keywords: polyamide networks; liquid crystal; flexible junctions)

INTRODUCTION

The literature is replete with experimental and theoretical studies of flexible networks and gels, their swelling behaviour and mechanical properties. Until recently, rigid networks and gels consisting of *stiff* segments and *rigid* branch-points (SR systems) were not reported. In the past few years, experimental studies of rigid polyamide SR networks and gels have appeared in the literature, describing their synthesis, swelling and deswelling behaviour and some mechanical properties[1–9]. To the best of our knowledge, there exists only one theoretical treatment of rigid polyamide SR networks[10].

Several theoretical treatments appeared recently[11–15] of more general networks and gels comprising *stiff* segments and *flexible* junctions (SF systems) or semi-flexible worm-like chains. We know of no literature publication describing the synthesis, characterization and properties of polyamide SF networks and gels. This is the first paper to describe such systems. In it we describe the structure of the synthesized networks, hot-stage cross-polarized light microscopy observations demonstrating the 'liquid-crystalline' nature of the gelled networks, X-ray studies revealing the amorphous state of the gelled SF networks and supporting the notion that restricted motion of the stiff segments exists in the present networks, and d.s.c. studies indicating that strong attractive interactions exist between the polymer and the solvent in the gelled networks. The SF systems are remarkable in that their nascent and solvent-equilibrated gels exhibit rainbow-coloured birefringence in the relaxed state as well as under stress.

EXPERIMENTAL

Gels of polyamide networks with stiff aromatic segments and trifurcated flexible junctions, SF gels, were prepared in a single step from the appropriate monomer mixtures in solution. All the trifunctional flexible junctions originated from tricarballylic acid residues. The synthesis, gel purification and characterization were described in great detail in previous publications[3–6]. All the SF gels were studied in the 'as-prepared' nascent state and after purification and equilibration with pure *N*,*N*-dimethylacetamide (DMAc). Previously prepared[3–6] trifunctional network gels having stiff segments with rigid branch-points (SR networks), flexible segments with rigid branch-points (FR networks) and flexible segments with flexible junctions (FF networks) were used for comparison. Highly branched pre-gel fractal polymers (FPs) and systems that failed to form gels of sufficient integrity for modulus determination were studied by hot-stage cross-polarized light microscopy and wide-angle X-ray diffraction (WAXD) scans and compared with the SF gels and networks.

---

[*] To whom correspondence should be addressed

0032-3861/94/06/1298–08

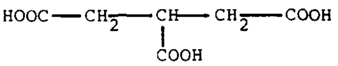
© 1994 Butterworth-Heinemann Ltd

Hot-stage microscopy studies using unpolarized and cross-polarized light were conducted using an Olympus BH-2 microscope equipped with an Olympus exposure control unit and a Mettler FP-82 hot stage controlled by a Mettler FP-80 central processor. Heating and cooling rates were 10 K min^{-1}. The intensity of cross-polarized light passing through the sample was estimated from the inverse time in seconds read off the automatic mode of exposure time in the exposure control unit. WAXD patterns were collected at ambient temperature from the nascent and DMAc-equilibrated gels and from the dry pulverized pure networks and pre-gel species by using a Philips APD 3600 diffractometer operating in parafocus mode and using monochromatized copper K_α radiation. Prior to the X-ray studies, all samples were first checked by optical microscopy to establish sample homogeneity and the absence of any minute crystalline impurities. The samples were then finely chopped in a blender. The gelled networks were scanned at this point. To obtain the dry samples, the chopped particles were transferred to methanol and then water. During this the particles collapsed in size. They were then repeatedly washed in boiling water and methanol before being finally dried to constant weight at 120°C under dynamic vacuum. Soluble pre-gel polymers were prepared similarly, except that they were first dissolved in DMAc and precipitated in a large excess of methanol. Dilute-solution viscosities of pre-gel polymeric species were measured at 25°C on their solutions in DMAc containing 5% wt/vol dry LiCl, using Cannon–Ubbelohde internal dilution glass viscometers with solvent efflux times longer than 100 s. Weight-average molecular weights were estimated from the intrinsic viscosity by using M_w vs. viscosity relationships established in previous work[3,4].

Thermal studies were conducted by using a DuPont model 9900 d.s.c. instrument. Sample sizes were in the 20 to 40 mg range. The samples were kept under nitrogen atmosphere throughout the scans. Heating and cooling rates were 10 K min^{-1}. Cooling to about −55°C was achieved by chilling the d.s.c. cell with 'dry ice'. Cooling to about −75°C was achieved by using a slush of 'dry ice' in acetone. The stiffness of large slabs of gel immersed in the same cold media was evaluated by direct visual observations and by physically touching them with the aid of a glass rod. The temperature of the gel slabs was determined by a thermometer deeply inserted in them and capable of reaching −100°C.

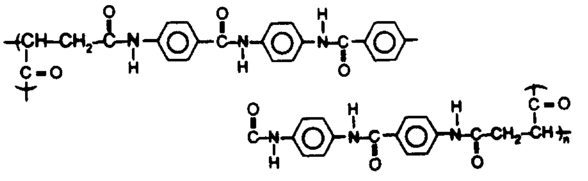
RESULTS AND DISCUSSION

Five networks with stiff segments and flexible junctions (SF networks) were prepared in one-step Yamazaki polycondensation[3–6,16] in solution at polymer concentration $C_0 = 10.0\%$. In all of them the flexible junction originated from the trifunctional aliphatic tricarballylic acid:



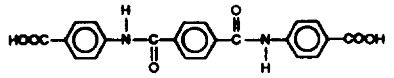
$$\mathrm{HOOC{-}CH_2{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}CH_2{-}COOH}$$

Because the networks were prepared from the monomers in one step, the stiff segments are not all of identical length, and their length is an average one. Two of the networks (SF-62B, SF-62B2) had five aromatic rings between the flexible junctions. These two networks were obtained by the use of a 2:1 molar ratio of 4,4′-diaminobenzanilide (DABA) and terephthalic acid (TPA). The average projected length between junctions is $l_0 = 37$ Å. Because the length and diameter of a *para*-substituted aromatic amide residue are about the same, five aromatic rings lead to an axial ratio for SF-62B and SF-62B2 of $x \simeq 5$.



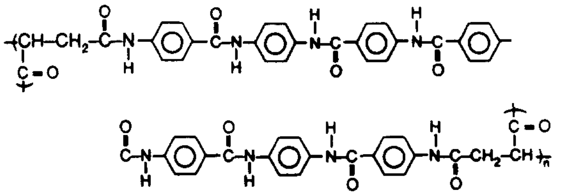
Networks SF-62B and SF-62B2

Two additional networks (SF-62A, SF-66A) of identical composition were prepared in the same way, but with seven aromatic rings between flexible junctions. Their average segment length l_0 is about 50 Å and their axial ratio x is about 7. The stiff segments were each constructed from two DABA residues and one aromatic diacid with three rings:



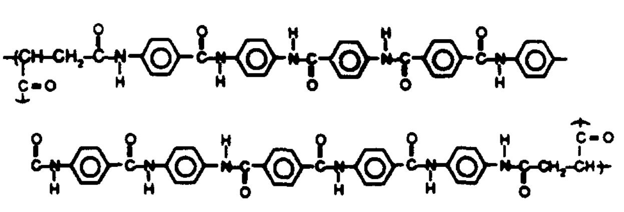
Diacid 60B

The diacid 60B was separately prepared from 2 mol of 4-aminobenzoic acid and 1 mol of terephthaloyl chloride. A typical segment in these networks SF-62A and SF-66A is shown here.



Networks SF-62A and SF-66A

One network (SF-62D) was prepared with an average of 10 aromatic rings per segment, corresponding to an axial ratio of about 10 and $l_0 = 70$ Å between flexible joints. In this case, an average stiff segment contains three DABA residues, one residue from the diacid 60B and one TPA residue.



Network SF-62D

The gelled networks were fully clear during preparation and retained their clarity upon cooling to room temperature and upon equilibrating in DMAc. Attempts to prepare at $C_0 = 10.0\%$ networks with much shorter segments, using only DABA between the tricarballylic acid residues, and longer segments, with 12 and 13 aromatic rings in each, all failed. The short segments produced powdery product instead of a network. The systems with very long segments failed to form self-supporting 'infinite' networks and produced microgel suspensions instead.

Cross-polarized light microscopy studies

In this work the gelled networks were studied in their nascent state at concentration C_0 and after swelling to equilibrium in DMAc at concentration C. They are listed in *Table 1* together with their structural characteristics and their birefringence behaviour at C_0 and C. WAXD patterns obtained from the nascent and DMAc-equilibrated SF gels revealed them to be all amorphous.

The most important information in *Table 1* is the fact that the SF network gels are intensely birefringent in their nascent state and in the DMAc-equilibrated state upon some heating and cooling back to ambient temperature (see below). No similar birefringence was observed by us in the present work or any previous work in any gelled sample of nascent or DMAc-equilibrated SR, FR and FF networks[3–6]. The birefringence of the SF networks, evidenced by strong rainbow coloration, is present in the fully relaxed 'as-prepared' gels and intensifies when these gels are stressed or sheared. The stresses were supplied either by pressing a microscope coverglass on the gels, or by combining such pressure with a shearing motion. The nascent gels of SF-62B and SF-62B2 showed markedly less birefringence than SF-62D, SF-62A and SF-66A. Unlike common lyotropic or thermotropic liquid-crystal polymers (LCPs), the multicoloured birefringent phase in the SF gels is static. Because of their immobility and homogeneity, the appearance of the birefringence in the nascent SF-62D, SF-62A and SF-66A gels is rather uniform throughout the sample and is reminiscent of the stress birefringence often observed in clear amorphous moulded plastic items. Qualitatively, the intensity of the birefringence in our SF gels was markedly higher than common stress birefringence in bulk amorphous polymers. Birefringence with similar uniform appearance was previously observed in other liquid-crystalline systems[17,18].

When the birefringent nascent SF gels are heated on the microscope state at 10 K min^{-1}, they start losing their birefringence rather rapidly at temperatures higher than 120 to 125°C. If the heating is continued such that a substantial fraction of the solvent in the gel is lost, say, at about 150°C, the birefringence is not recovered upon cooling. If the heating is stopped at less than about 130°C, before the DMAc starts escaping the gel, the birefringence is recovered upon cooling.

After swelling to equilibrium in DMAc, the SF-62D, SF-62A and SF-66A gels lost most, but not all, of their birefringence. When the DMAc-equilibrated gels were heated on the microscope stage to no more than 125°C and cooled back to room temperature, an intense rainbow-coloured birefringence appeared during the cooling step and remained at room temperature. This happened with the gels not covered with coverglass and under no stress whatsoever throughout the whole heating and cooling cycle. However, when the DMAc-equilibrated gels were heated to above 150°C, where significant loss of solvent occurred, the birefringence did not reappear upon cooling. The gelled networks SF-62B and SF-62B2 behaved in a similar fashion except that in their case the birefringence was monochromatic and its intensity lower than for SF-62D, SF-62A and SF-66A.

The intensity of the cross-polarized light passing through fully relaxed SF gels was measured as a function of temperature upon heating on the hot stage of the cross-polarized light microscope. Typical results, for DMAc-equilibrated SF-62D and SF-66A, are shown in *Figure 1*. A very sharp loss of cross-polarized light intensity occurs at about 120°C for SF-62D and at 135°C for SF-66A. In a fashion similar to nascent SF gels, this intensity is recovered if the heating is stopped at temperatures lower than the precipitous drop in intensity and the sample is cooled back to ambient temperature.

It is well known that unconnected rod-like particles may exhibit liquid crystallinity when their axial ratio x surpasses a critical value x_c of about 6.4[19–21]. When the rods are connected to one another, the magnitude of x_c becomes substantially smaller, progressing through

Table 1 Comparison of nascent and DMAc-equilibrated SF network gels

Code	l_0 (Å)	C_0 (%)	Birefringence[a]		DMAc-equilibrated C (%)	Birefringence		Microscopy observations
			Relaxed	Stressed		Relaxed	Stressed	
SF-62D	70	10.0	Yes	More	2.55	Yes	More	Intense rainbow-coloured birefringent gel
SF-62A	50	10.0	Yes	More	2.17	Yes	More	Ditto
SF-66A	50	10.0	Yes	More	1.87	Yes	More	Ditto
SF-62B	37	10.0	Some	More	2.62	Faint	More	Uniform monochromatic gel
SF-62B2	37	10.0	Some	More	3.49	Faint	More	Ditto

[a] Birefringence intensity: Yes > Some > Faint

Table 2 Pre-gel fractal polymers and their characteristics

Code	Nature of system	Prepared at C_0 (%)	Observed at C (%)	l_0 (Å)	Intrinsic viscosity (dl g^{-1})	M_w	Birefringence
FP-66L	SF	10.0	20.0	90	0.574	82 000	None
FP-66J	SF	10.0	33.3	15	0.150	3 300	None
FP-45XD	SR	3.0	20.0	38.5	–	> 700 000	None
FP-45XB	SR	3.0	16.7	38.5	1.26	410 000	None
FP-59E	SR	5.0	10.0	38.5	0.26	9 600	None
FP-74B	SR	5.0	10.0	38.5	0.39	24 000	None
FP-69D	SR	20.0	10.0	6.5	–	–	None

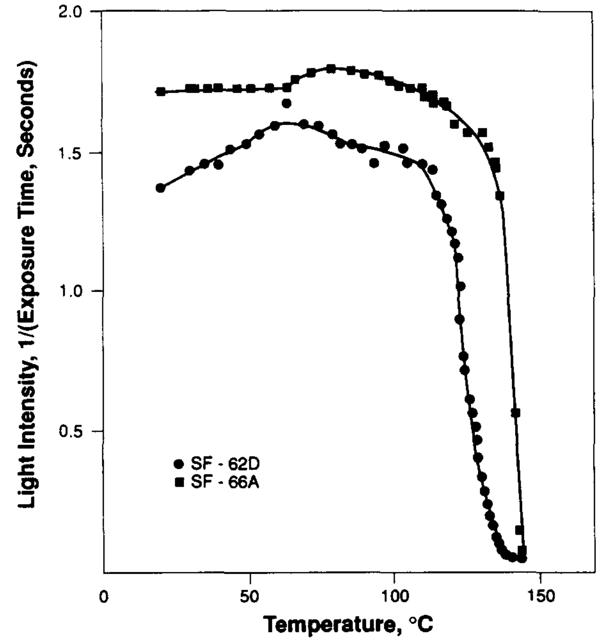


Figure 1 Intensity of cross-polarized light passing through two birefringent gels, as a function of temperature

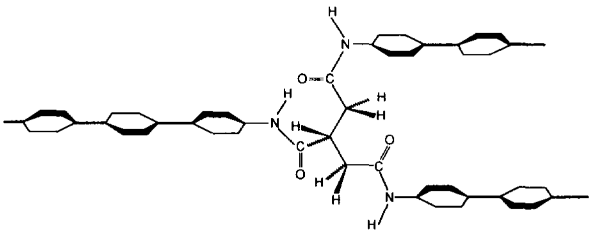


Figure 2 Trifurcated flexible junction, a tricarballylic acid residue, connecting stiff aromatic 'liquid-crystalline' network segments

$5<x_c<6$ for tetrahedral bond angle about a single connecting atom[22], to $3<x_c<3.5$ for highly flexible spacers allowing for complete directional independence of one rod-like segment from its neighbours along the chain[23]. This means that the segment lengths of all the systems in *Tables 1* and *2* (see below) are sufficient to exhibit liquid crystallinity, except for the pre-gels FP-66J and FP-69D. Gelled networks with flexible segments are not expected to be liquid-crystalline and exhibit birefringence in the relaxed state. The fact that none of the SR family showed liquid crystallinity or birefringence indicates that for these to occur the stiff segments cannot be randomly oriented and interconnected by rigid branch-points. A flexible junction is needed instead. The relatively low birefringence exhibited by the amorphous gels SF-62B and SF-62B2 reflects, we believe, the fact that the axial ratio of these networks is about 5. It is just marginally above the critical axial ratio for systems in which the junctions are not fully flexible[22,23] where $x_c \simeq 5$. We are just at the boundary between isotropicity and order[14] and, hence, the modest intensity of the birefringence. The axial ratios of gels SF-62D, SF-62A and SF-66A are substantially larger than x_c, and the birefringence of the nascent and DMAc-equilibrated gels, relaxed or stressed, is, hence, far more intense than for SF-62B and SF-62B2. From the above we also learn that the tricarballylic acid residue is not fully flexible, forcing some directional correlation between the stiff segments attached to it.

We believe that the flexibility of the trifurcated junctions in the SF networks imparts some motional freedom to the stiff segments in the systems. Computer-generated molecular simulations of trifurcated junctions containing tricarballylic acid residues and long, stiff aromatic polyamide segments were studied by us. They are in excellent agreement with observations on space-filling models. In *Figure 2* a trifurcated flexible junction with parts of the three connected stiff polyamide segments is shown. Here, the amide groups in the segments are shown edge-on by a heavy line, and the aromatic rings alternate at ca. ±30° relative to the plane of the amides, as is the case with stiff linear polyamides in the crystalline state. The trifurcated junction was found to be of substantial, but not complete, flexibility, with one of the lowest free-energy conformations being the one schematically shown in *Figure 2*. Here, the tricarballylic acid flexible junction is triangular and planar, and the stiff segments more or less parallel to each other and coplanar in the plane of the paper. Conversions from this preferred conformation to others of similar low free energy are most easily achieved by rotations around the bonds on either side of the $-CH_2-$ groups. Molecular simulations by computer and tests with space-filling models satisfied us that such isomerizations meet with very little resistance. The easy alignment of the stiff segments in parallel arrays, and the ease of reversible interconversions of the flexible junction from flat triangular to trigonal pyramid or similar isomeric states, clearly make facile the organization of the stiff segments of SF gels in collinear arrays extending over relatively large volumes of the gelled networks. We believe that this collinear or parallel organization over large volumes is the cause of the observed birefringence in the SF systems.

We hypothesize that, during swelling in DMAc, an increasing fraction of the trifurcated junctions isomerize from flat triangular to trigonal pyramid or similar isomers. By so doing, the stiff segments lose their parallel alignment and the gel loses corresponding fractions of the initial birefringence. The isomeric change from triangular to trigonal pyramid maximizes the average distance between flexible junctions, allowing more solvent to enter the gel and swell it. When the DMAc-equilibrated SF gels are heated to about 100°C and then cooled, their birefringence reappears. This was especially noticeable in the relaxed SF-62D, SF-62A and SF-66A. No solvent was lost or oozed out of the gels during the heat cycling. We do not understand the process but hypothesize that volume changes and acquired entropy may help the trifurcated junctions in the network to isomerize and the junctions to revert to triangular conformation with parallel segments. The solvent in the gel may be, at the same time, redistributed closer to sites of network defects. If this takes place, and we have no experimental proof of it, then the average distance decreases between junctions in the less defective portions of the gel, parallel and collinear segmental organization can be accommodated, and birefringence reappears.

When shear or stress is applied to the SF gels, the networks deform and an increasing fraction of the stiff segments align in parallel arrays and become collinear. This increases the intensity of the birefringence over the relaxed state, as was clearly observed in this work. Such a behaviour is according to expectations even from systems having long flexible segments[24].

We have previously demonstrated[3–6] the fractal nature of pre-gel polymeric species with stiff segments, prepared in a single step from their monomers. In the present work we have found that solutions of all pre-gel polymer particles, in their nascent state at C_0 and redissolved from the dry state at concentrations $C \gg C_0$, failed to exhibit birefringence. This holds true for both SF and SR systems in the relaxed state and when the solution is sheared. The characteristics of the pre-gel FPs in these solutions are listed in *Table 2*. From the table we learn that the highly branched pre-gel fractal polymers do not exhibit birefringence even when their junctions are flexible and their stiff segments longer than x_c. The failure to show birefringence carries over to very high concentrations. We believe that this behaviour is caused by the FPs being much smaller than a quarter of the wavelength of visible light, and by the random orientation of the segments in each FP and in their aggregates.

Based on the above, we conclude that, in order to exhibit birefringence in the relaxed state, the networks in the nascent and solvent-equilibrated gels must consist of stiff segments with axial ratio larger than x_c and of substantially flexible junctions. The gelled networks must extend over sizes of light wavelength and larger. This behaviour is fundamentally different from that of SR and FF gelled networks, neither of which manifest birefringence in the relaxed state.

Wide-angle X-ray diffraction studies

All the gelled networks were studied by WAXD in their nascent and DMAc-equilibrated forms. In all cases, the gelled networks were found to be amorphous. Several SF systems were studied by X-rays to determine whether they can crystallize when the solvent is removed and the network collapses. These systems are listed in *Table 3*. Four of them did form 'infinite' networks and gelled. Two did not. All systems were prepared for the X-ray studies as described in the 'Experimental' section. The results indicate that five out of the six dry samples contained some crystalline fraction. The presence or absence of crystallinity is apparently independent of whether the systems successfully formed 'infinite' networks. Because the crystallinity appeared in dried samples originating from amorphous gels, we believe it to be inherent to the networks and not caused by, highly improbable, minute crystalline inclusions: the observed crystallinity arises from the network collapsing on itself during drying. An important fact to recognize here is that all the SF systems with relatively long segments exhibit a measure of crystallinity upon drying. Members of the SR family never showed crystallinity when examined in the same manner[4]. As was shown above, the presence of the flexible junctions, and the probable presence of network defects, allows stiff segments to align themselves in parallel arrays during drying, facilitating some crystallization. This could not have happened in the SR networks owing to the rigidity of their branch-points.

Table 3 Crystallinity of dried trifurcated SF networks by WAXD

Code	l_0 (Å)	Formed 'infinite' network	Crystallinity (%)
SF-66L	90	No	17–20
SF-62D	70	Yes	15
SF-66A	50	Yes	6–7
SF-62B	37	Yes	13
SF-62B2	37	Yes	16
SF-66J	15	No	None detected

Because of the low levels of crystallinity, the intensity and definition of the diffraction peaks were low. The systems with the best WAXD patterns were SF-66L (in *Figure 3*) and SF-62D, where the *d*-spacings of four reflections could be determined. These are 4.23, 3.79, 3.19 and 2.13 Å. The linear analogue of our SF networks is poly(*p*-benzanilide terephthalamide) (*p*-BT). A comparison of the above four X-ray reflections with the pattern of *p*-BT[25] points to a correspondence of the four reflections observed in the SF-66L sample with the four most intense reflections observed in *p*-BT. If this is indeed the case, then the four reflections in the SF-66L sample are those of $hkl = 110$, 200, 004 and 006, respectively. The important message from the above is that the crystallites detected by WAXD in the dried SF networks are similar to, but not exactly identical with, those of the linear analogue of the same networks.

The X-ray results in *Table 3* indicate that upon drying all but one of the SF networks were semicrystalline. This is contrary to the SR networks, which never showed

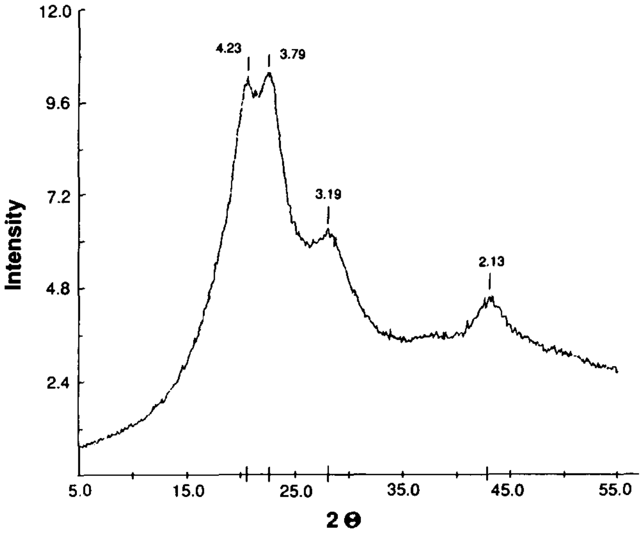


Figure 3 WAXD pattern of dry SF-66L network

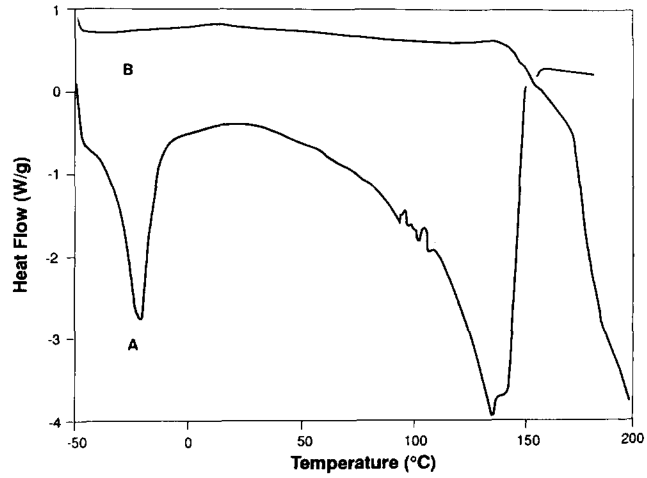


Figure 4 (A) D.s.c. scan of pure bulk DMAc; heating cycle. (B) D.s.c. trace of SR-45XD swollen in DMAc to 10.0% polymer concentration

crystallinity, either as gels or upon drying[4]. The development of crystallinity in the drying SF networks clearly indicates that these networks are endowed with sufficient motional freedom for, at least some of, their stiff segments to form parallel arrays of sizes large enough for X-ray detection. Smaller such arrays, too small for X-ray detection, are most likely to exist in the dry SF networks. These arrays are most likely held together by intersegmental hydrogen bonds, as can be deduced from the largest *d*-spacing in the WAXD patterns. The reason for the absence of crystallinity in the dry SF-66J is, we believe, the inability to pack laterally such short segments when these are connected in most cases at both ends to trifurcated junctions.

D.s.c. studies on solvent–network interactions

The response of all the gelled polyamide networks to changes in temperature turned out to be most interesting. It was followed by d.s.c. and direct observations. In order to appreciate the observations, the d.s.c. scan (A) of pure DMAc in *Figure 4* should be studied. Here, a melting point at −21°C is followed by a rather smooth curve with uniform curvature from ca. 30°C to 135°C. The curvature is endothermic in nature and reflects a slow evaporation of the DMAc upon heating. At about 135°C an abrupt change in the direction of the curve heralds the appearance of vapour bubbles, the initial state of boiling. Upon cooling the sample in preparation for the scan A in *Figure 4*, the DMAc in the d.s.c. cup abruptly froze at −49.1°C, producing an extremely sharp exothermic peak with heat of fusion of 32.62 J g^{-1} (not shown here).

As the gels cooled during the direct visual observations, a temperature interval was reached for each gel in which it became substantially stiffer to the touch. This transition interval was as high as ca. 20°C for the DMAc-equilibrated SF-66A and as low as −5°C for the DMAc-equilibrated SF-62D. In all cases the gels kept their optical clarity upon turning stiffer. In their stiff state the gels were not exactly brittle but retained their bounce and some mechanical resilience. Upon further cooling to temperatures lower than −60°C, the gels turned fully opaque and rather brittle. No transition or solvent freezing were noted around −21 and −49°C, the melting and freezing points of pure DMAc. Upon heating up to room temperature, the gels first lost their opacity and then regained their initial appearance and mechanical consistency. No measurable secretion of solvent was noted during the cooling and heating cycles.

D.s.c. scans covering the range from −50 to 175°C were obtained first from 'as-prepared' and DMAc-equilibrated SF, SR and FF gels. A general observation is that in all these systems the melting point of DMAc is missing. Scan B in *Figure 4* is typical. In it the scan of SR-45XD is shown after the network was purified and reswollen in pure DMAc from the dry state to $C = 10.0\%$.

The DMAc-equilibrated SF-66A was used to search for the missing melting point of the solvent. From *Table 1* we recall that the DMAc-equilibrated SF-66A contains only 1.87% polymer. Upon cooling with acetone/'dry ice' slush, a very abrupt freezing of the gel occurs at −60.3°C, as is seen from the sharp freezing exotherm in *Figure 5*. This is about 11.2 K below the freezing point of pure DMAc in the d.s.c. pan. Upon warming up from −75°C, in *Figure 6*, a broad melting of the solvent in the gel takes place with its peak at −28.6°C, about 7.5 K lower than the melting point of bulk DMAc in *Figure 4* (scan A). All other systems in this study had a polymer concentration in the nascent and DMAc-equilibrated states higher than the DMAc-equilibrated SF-66A, pushing the freezing point of the DMAc in the gels to temperatures substantially lower than −50°C. Because the DMAc in the gels did not freeze when 'dry ice' alone was used to cool the cell of the d.s.c.

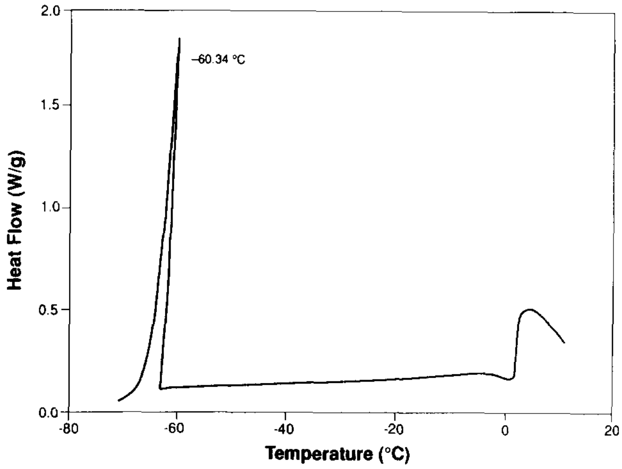


Figure 5 D.s.c. cooling curve of DMAc-equilibrated SF-66A

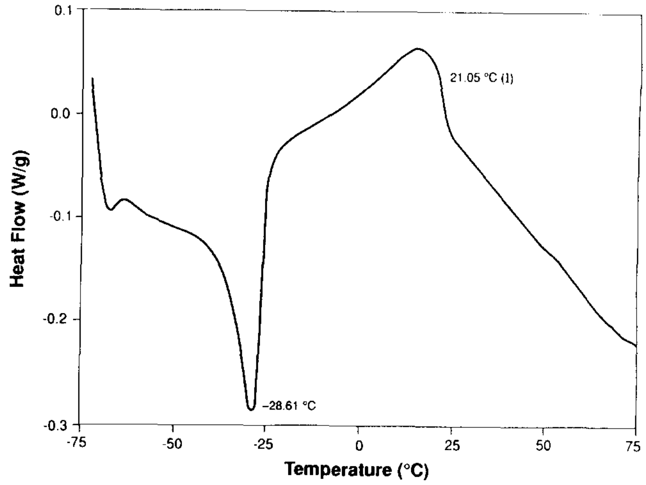


Figure 6 D.s.c. reheating curve of DMAc-equilibrated SF-66A

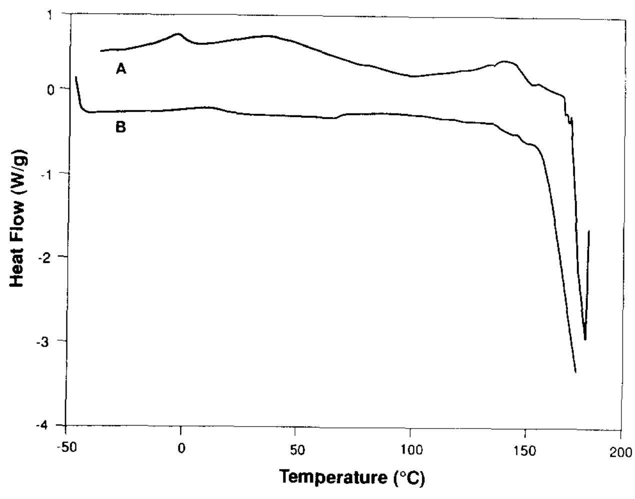


Figure 7 (A) D.s.c. trace of 'as-prepared' flexible FF-66M network gel. (B) D.s.c. scan of rigid SR-45XC in DMAc at 10% concentration

instrument, no melting point was visible in the gels even though the heating scans as a rule started at about −55°C.

Another important observation is the replacement of the gradual slope in the d.s.c. trace (A) of pure DMAc in *Figure 4* by a flat or almost flat plateau spanning the 25 to 135°C temperature interval. Scan B in *Figure 4* is typical of such plateaux. The same behaviour appears in scan A in *Figure 7* for the nascent state of the fully flexible FF-66M ($l_0 = 60$ Å, $C_0 = 10.0\%$). The flatness of the d.s.c. traces and the extension of the flat plateaux to higher and higher temperatures appear to depend on the polymer concentration in the gels: the higher C, the higher is the temperature at which the plateau terminates and the curve abruptly plunges down. In scan B in *Figure 7*, for the rigid SR-45XC in DMAc at $C = 10.0\%$, the break in the curve occurs at 150°C, similar to scan A in *Figure 7* for flexible gel in identical concentration. This temperature is significantly above the onset of the bubbling and then boiling process in pure DMAc in the bulk, as seen in scan A in *Figure 4*. A similar extension of the plateau to much higher temperature was also observed in the case of DMAc-swollen SR-74E at $C = 10.0\%$ (scan not shown here).

All the above d.s.c. results may be explained in terms of the strong attractive interactions between the solvent DMAc and the aromatic polyamide network segments in the gels. It is well known in the literature that polyamides have a strong tendency to interact strongly with solvents sufficiently strong to break intersegmental H bonds and solubilize the polymer by forming segment–solvent H bonds instead[9,25–30]. Such strong attractive interactions between DMAc and stiff aromatic polyamide segments were previously demonstrated by n.m.r. studies[9] to be present in SR gels. In the present and in previous unpublished studies, the d.s.c. scans confirm their existence in FF, SR and SF gels. We believe these interactions to be part contributors to the interesting behaviour of the DMAc in the gels during thermal cycling.

The system we studied most in this respect is DMAc-equilibrated SF-66A. It contains only 1.87% polymer with flexible trifurcated junctions and stiff segments with average length of 50 Å. In this system the freezing point of DMAc was depressed by 11.2 K and the melting point by 7.5 K relative to their temperatures for pure DMAc in the bulk. The heat of fusion was reduced from 32.62 J g^{-1} for pure DMAc to 20.54 J g^{-1} for the DMAc in the equilibrated SF-66A gel. After corrections for the weight of the polymer network in the gel, these values indicate that from the DMAc in the gel 62% could crystallize and 38% could not. We believe that the fraction of the solvent that cannot crystallize is greatly influenced by the intensity of the attractive segment–solvent interactions. Similar lowering of both freezing and melting points of DMAc and *N*-methyl-2-pyrrolidinone (NMP) were previously observed by us in fully rigid SR gels and in fully flexible FF gels. We believe the same or very similar segment–solvent interactions are operating in all such systems. The strongest from among these are, most likely, solvent–segment H bond type interactions.

Lowering of both freezing and melting points of organic solvents in permanent and thermoreversible gels was reported previously in the literature, in addition to similar behaviour of aqueous gels. The reductions in transition temperatures for organic systems containing networks in concentrations comparable with our systems were much smaller[31–33] than in the gels described in the present work. In addition to solvent–segment interactions, the reduction in the transition temperatures of solvents in gels is, to a large extent, due to the greatly reduced size of solvent crystallites forming in the polymer network upon crystallization, to their highly irregular surfaces and to the very large increase in the surface/volume ratio of such crystallites[31,33]. In our case the very large reduction in freezing and melting points may be due to both effects: large crystallite-size reduction and strong solvent–polymer attractive interactions. The magnitudes of these interactions may be appreciated from our qualitative observations of dramatic heat evolution upon mixing the comminuted dry networks with either DMAc or NMP[34,35]. Such exothermic mixing reflects negative polymer–solvent interaction parameter[36]. The conditions for very intense attractive interactions between DMAc molecules and the aromatic polyamide segments and branch-points are, hence, present in the SF, SR and FF networks described in the present and previous studies[3–6,9,34].

FINAL REMARK

The recent literature is replete with descriptions of LCP networks[37–46]. Most of these contain stiff mesogenic groups attached by flexible tethers to flexible main chains. Others contain mesogenic units alternating with flexible spacers in the main chain. In either case, the mesogenic groups are usually rather short, about three *para*-substituted aromatic rings, and the highly mobile flexible spacers, tethers and chains are relatively long, and allow the decoupling of each mesogenic group from the others. All these are fundamentally different from the system described in the present paper, where long, stiff main-chain mesogenic groups are connected by short junctions endowed with only modest flexibility and mobility.

ACKNOWLEDGEMENT

An illuminating discussion with Professor Sam Krimm is gratefully acknowledged.

REFERENCES

1 Aharoni, S. M. *Macromolecules* 1982, **15**, 1311
2 Aharoni, S. M. and Wertz, D. H. *J. Macromol. Sci., Phys. (B)* 1983, **22**, 129
3 Aharoni, S. M. and Edwards, S. F. *Macromolecules* 1989, **22**, 3361
4 Aharoni, S. M., Murthy, N. S., Zero, K. and Edwards, S. F. *Macromolecules* 1990, **23**, 2533
5 Aharoni, S. M. *Macromolecules* 1991, **24**, 235
6 Aharoni, S. M. *Macromolecules* 1991, **24**, 4286
7 Aharoni, S. M., Hatfield, G. R. and O'Brien, K. P. *Macromolecules* 1990, **23**, 1330
8 Aharoni, S. M. *Int. J. Polym. Mater.* 1992, **17**, 35
9 Curran, S. A., LaClair, C. P. and Aharoni, S. M. *Macromolecules* 1991, **24**, 5903
10 Jones, J. L. and Marques, C. M. *J. Phys. Fr.* 1990, **51**, 1113
11 Boue, F., Edwards, S. F. and Vilgis, T. A. *J. Phys. Fr.* 1988, **49**, 1635
12 Erman, B., Bahar, I., Kloczkowski, A. and Mark, J. E. *Macromolecules* 1990, **23**, 5335
13 Bahar, I., Erman, B., Kloczkowski, A. and Mark, J. E. *Macromolecules* 1990, **23**, 5341
14 Warner, M. and Wang, X. J. *Macromolecules* 1991, **24**, 4932
15 Abramchuk, S. S. and Khokhlov, A. R. *Dokl. Phys. Chem.* 1988, **297**, 1069

16 Yamazaki, N., Matsumoto, M. and Higashi, F. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 1373

17 Finkelman, H. and Rehage, G. *Adv. Polym. Sci.* 1984, **60/61**, 99

18 Aharoni, S. M. *J. Macromol. Sci., Phys. (B)* 1982, **21**, 105

19 Flory, P. J. and Ronca, G. *Mol. Cryst. Liq. Cryst.* 1979, **54**, 289, 311

20 Flory, P. J. in 'Polymer Liquid Crystals' (Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982, pp. 103–13

21 Flory, P. J. *Adv. Polym. Sci.* 1984, **59**, 1

22 Aharoni, S. M. *J. Appl. Polym. Sci.* 1980, **25**, 2891

23 Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 281

24 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Clarendon, Oxford, 1958, Ch. X, pp. 197–234

25 Aharoni, S. M. *Macromolecules* 1987, **20**, 2010

26 Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1827

27 Aharoni, S. M. and Wasserman, E. *Macromolecules* 1981, **14**, 454

28 Aharoni, S. M. and Wasserman, E. *Macromolecules* 1982, **15**, 20

29 Aharoni, S. M. *Macromolecules* 1988, **21**, 185

30 Papkov, S. P. *Adv. Polym. Sci.* 1984, **59**, 75

31 Ubbelohde, A. R. 'The Molten State of Matter', Wiley-Interscience, Chichester, 1978, pp. 30–9

32 Boonstra, B. B., Heckman, F. A. and Taylor, G. L. *J. Appl. Polym. Sci.* 1968, **12**, 223

33 Perez, E., Vanderhart, D. L. and McKenna, G. B. *Macromolecules* 1988, **21**, 2418

34 Aharoni, S. M. *J. Appl. Polym. Sci.* 1992, **45**, 813

35 Aharoni, S. M. and Edwards, S. F. *Polym. Bull.* 1992, **29**, 675

36 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, Ch. XII and XIII

37 Strzelecki, L. and Liebert, L. *Bull. Soc. Chim. Fr.* 1973, **597**, 603

38 Strzelecki, L. and Liebert, L. *Eur. Polym. J.* 1981, **17**, 1271

39 Clough, S. B., Blumstein, A. and Hsu, E. C. *Macromolecules* 1976, **9**, 123

40 Finkelmann, H., Kock, H.-J. and Rehage, G. *Makromol. Chem. Rapid Commun.* 1981, **2**, 317

41 Hirschmann, H., Meier, W. and Finkelmann, H. *Makromol. Chem. Rapid Commun.* 1992, **13**, 385

42 Reck, B. and Ringsdorf, H. *Makromol. Chem. Rapid Commun.* 1985, **6**, 291

43 Zentel, R. and Reckert, G. *Makromol. Chem.* 1986, **187**, 1915

44 Peter, K. and Ratzsch, M. *Makromol. Chem.* 1990, **191**, 1021

45 Zentel, R. *Angew. Chem. Adv. Mater.* 1989, **101**, 1437

46 Caruso, U., Centore, R., Roviello, A. and Sirigu, A. *Macromolecules* 1992, **25**, 129