

## **“Liquid-crystalline” gels of polyamide networks with stiff segments and flexible junctions**

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### **Summary**

The preparation of a novel family of "liquid-crystalline" polyamide network gels is described. In these networks, the segments are stiff and longer than the critical axial ratio for mesomorphic behavior. The junctions are trifunctional and flexible. The gels are intensely birefringent in the relaxed nascent state, unlike fully rigid or fully flexible gels. The birefringence of the present gels is clearly associated with the coexistence in them of both long, stiff mesogenic segments and flexible trifurcated junctions. Thermal studies of the gels indicate very strong attractive interactions between the networks and the solvent.

### **Introduction**

The literature is replete with experimental and theoretical studies of flexible networks and gels, their swelling behavior and mechanical properties. Until recently, rigid networks and gels consisting of stiff segments and rigid branchpoints (SR-systems) were barely reported. In the past few years, experimental studies of rigid polyamide networks and gels appeared, describing their synthesis, characteristics, swelling and de-swelling behavior, and mechanical properties (1-9). To the best of our knowledge, there exists only one theoretical treatment of rigid polyamide 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 wormlike chains. We know of no literature publication describing the synthesis, characterization and properties of polyamide SF-networks and gels. In the present paper we hope to fill part of the gap. Further details and discussion will appear in a forthcoming paper (16).

### **Experimental**

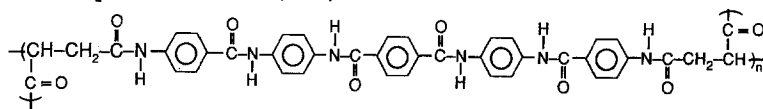
SF-gels of polyamide networks with stiff aromatic segments and trifunctional flexible junctions were prepared in a single step from the appropriate monomer mixture in solution. Therefore, the segments described below are characteristic and are not all of identical length. Details of the synthetic procedures, gel purification and characterization were described in great detail in previous publications (3-6). In the present work the trifunctional flexible joints all originate from tricarballylic acid residues. For the purpose of comparison, two gelled networks with trifunctional flexible junctions and flexible segments (FF-gels) were prepared under similar conditions. Previously synthesized trifunctional network gels having

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stiff segments with rigid branchpoints (SR-networks) and flexible segments with rigid junctions (FR-networks) were used for comparison with the SF-networks. All the above gels were studied by hot-stage cross-polarized light microscopy and DSC in the "as-prepared" state and after purification and equilibration in pure *N,N*-dimethylacetamide (DMAc). Further details of all experimental procedures will appear in ref. (16).

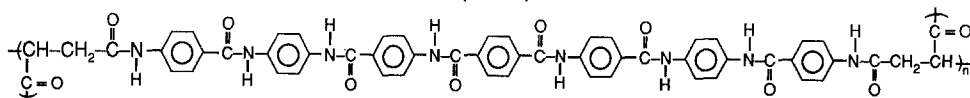
## Results

Five SF-networks were prepared in one-step Yamazaki reaction (3-6,17) in solution at polymer concentration  $C_0 = 10.0\%$ . Two of the networks had, on the average, five aromatic rings between the flexible junctions, obtained by the use of 2:1 ratio of 4,4'-diaminobenzanilide (DABA) and terephthalic acid (TPA):



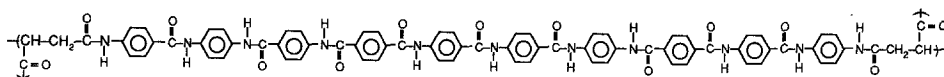
### Networks SF-62B, SF-62B2

The average length of these segments is  $37\text{\AA}$  and their axial ratio is about 5. Two additional networks with segments containing 7 rings on the average were prepared by using for the aromatic component 2:2:1 ratio of DABA, 4-aminobenzoic acid (PABA) and TPA:



### Networks SF-62A, SF-66A

Their segment length is about  $50\text{\AA}$  and their axial ratio about 7. One network, SF-62D, was prepared with an axial ratio of 10 and segment length of  $70\text{\AA}$  between flexible joints:



### Network SF-62D

In this case the average segment contained 3 DABA residues, 2 TPA residues and 2 PABA residues.

The clear nascent SF- gels were studied on the microscope stage and by DSC covering the temperature interval from  $-75^\circ\text{C}$  to  $180^\circ\text{C}$ . They were then purified and allowed to swell and reach equilibrium in DMAc. Room temperature cross-polarized light microscopy of the nascent gels with axial ratio of 10 and 7 revealed intense rainbow colored birefringence for the relaxed as well as sheared samples. The gels with axial ratio of 5 exhibited monochromatic birefringence of lesser intensity. Upon heating the birefringence was retained until around  $130^\circ\text{C}$ . The results of two typical microscopy scans, showing cross-polarized light intensity passing through the SF-gel samples as function of temperature, are shown in Figure 1. Upon swelling to equilibrium the SF-gels lost their birefringence, but it was recovered by heating the equilibrated SF-gels to less than  $120^\circ\text{C}$  and then cooling.

None of all other polyamide gels, including several members of each SR-, FR- and FF-networks, showed any birefringence under similar conditions.

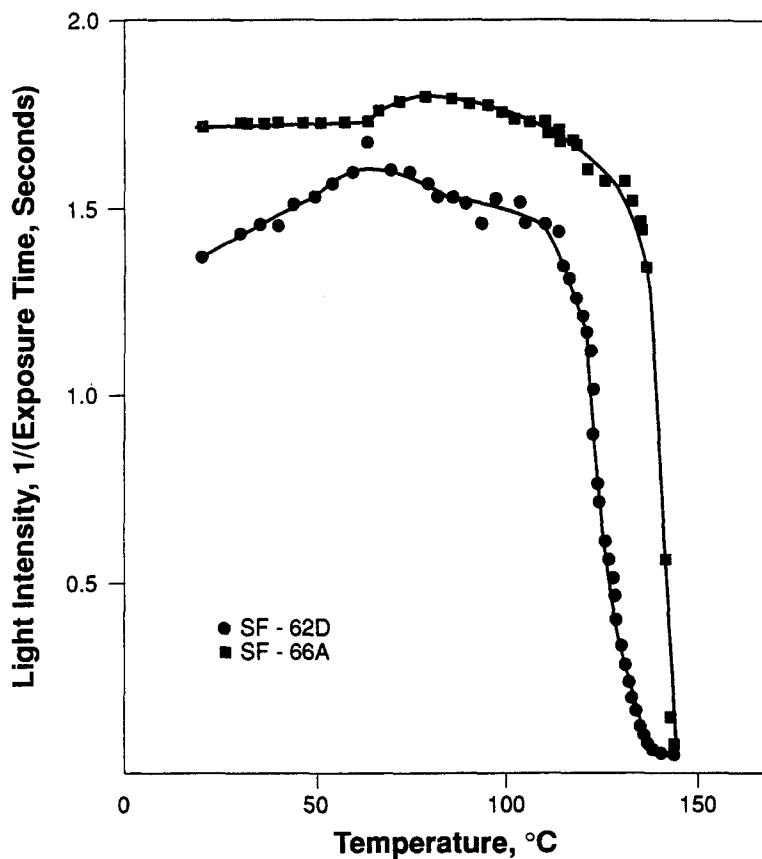


Figure 1. Intensity of cross-polarized light passing through two birefringent gels, as function of temperature.

The DSC scans reveal very strong interactions between DMAc and all polyamide networks investigated in this study. DSC scan of neat DMAc, in Figure 2, shows its melting point at about  $-20^{\circ}\text{C}$  and the onset of weight loss due to evaporation as low as  $50^{\circ}\text{C}$ . A major weight loss takes place below  $140^{\circ}\text{C}$ . In Figure 3 the DSC of a typical nascent gel is shown, containing 90% DMAc. Here the melting point is invisible and the solvent is retained in the gel up to above  $150^{\circ}\text{C}$ . In agreement with literature (18), the melting and freezing points of the solvent in the gel were depressed to below  $-50^{\circ}\text{C}$ .

Computer molecular simulation and space-filling molecular models both reveal that the tricarballic acid residue is very flexible and its preferred configuration leads the attached stiff segments to be aligned more or less in parallel to one another, as is shown in Figure 4. This alignment creates the "liquid-crystalline" birefringence observed in the SF-gels. Upon swelling the alignment changes to trigonal pyramide in order for the gel to contain as much as possible solvent. When this happens the birefringence vanishes. The mechanism for the regeneration of the birefringence upon heating and cooling of the

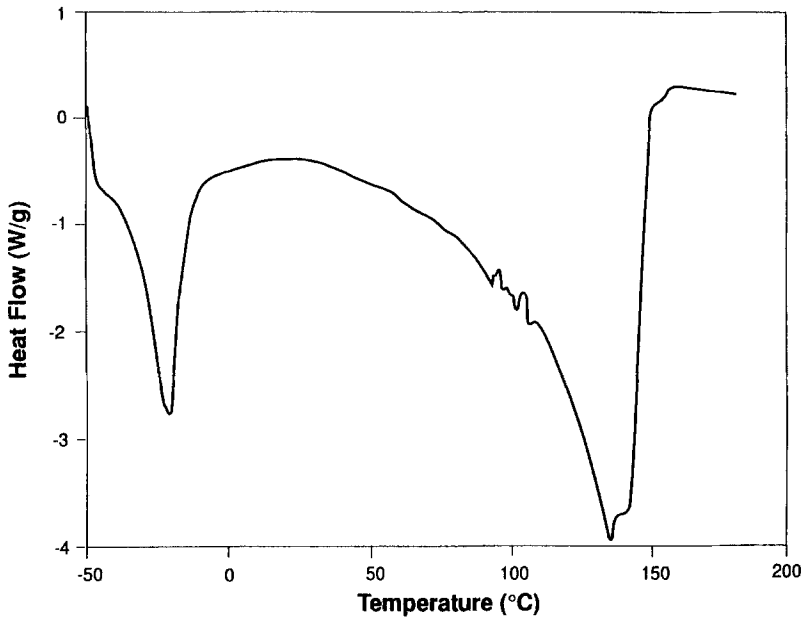


Figure 2. DSC scan of pure DMAC, indicating early onset of weight loss. Note solvent melting point at about  $-25^{\circ}\text{C}$ .

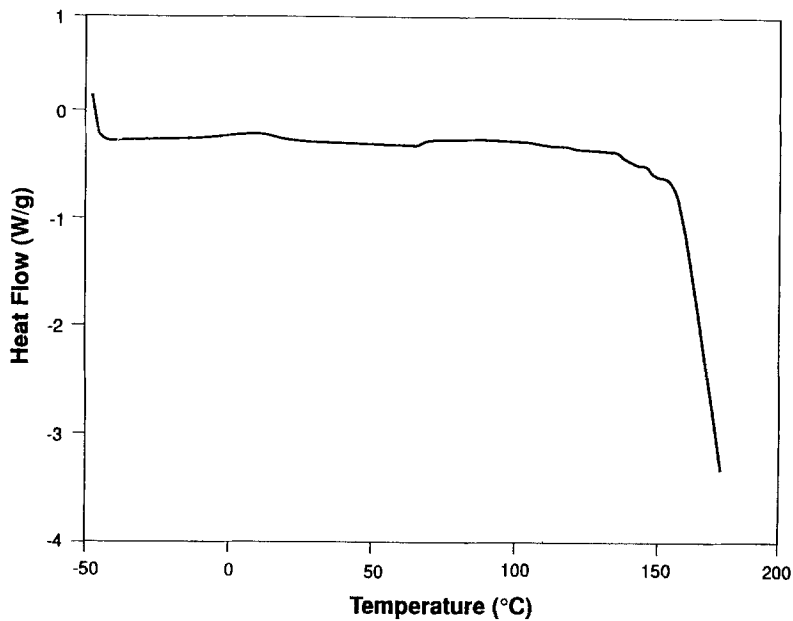


Figure 3. DSC scan of typical SF-gel indicating total solvent retention until over  $150^{\circ}\text{C}$ . Note absence of melting point down to  $-50^{\circ}\text{C}$ .

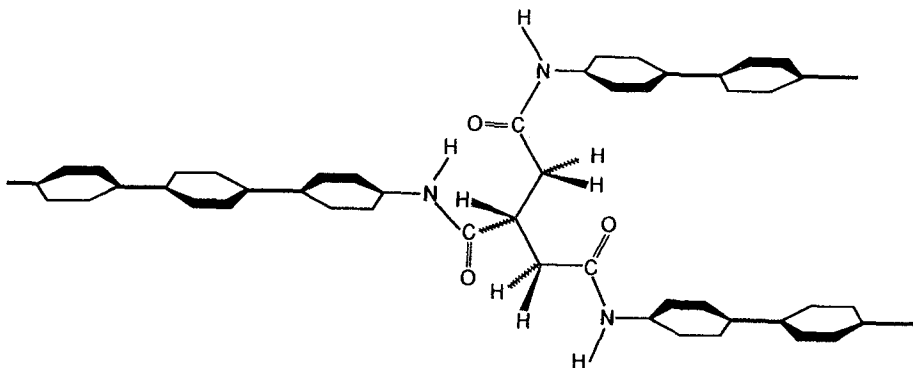


Figure 4. Low energy conformation of flexible trifurcated junction made from tricarballic acid residue. Note parallel alignment of stiff aromatic segments.

equilibrated SF-gels is not understood by us at present. In SR-gels, the branchpoint rigidity prevents parallel alignment of mesogenic segments, and no birefringence is observed. In FR- and FF-gels, no mesogenic segments are present and no birefringence exists.

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