

# Synthesis, solution rheology and interfacial behaviour of sulphonated rigid rod polymers

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Sulphonated poly(*p*-phenylene terephthalamide) copolymers (S-PPTA) spanning a wide range of sulphonation were synthesized from their nonionic precursor through a metalation reaction. Sulphonation was accomplished with butane sultone. Solution behaviour was examined. For example, it was shown that the copolymers were water soluble at sulphonate levels greater than approximately 40 mol%. Rheological measurements show that although the molecular weight of these rigid rods are low, inter-chain hydrophobic-type associations have a profound influence on solution properties. The level of hydrophobicity is controlled directly by the sulphonate content. Preliminary observations of concentrated solutions indicate the absence of ordered structures. However, thin, bulk films are highly birefringent indicating the presence of large ordered structures. Finally, thermal measurements of these films shows a high degree of thermal stability which is in marked contrast with the deterioration in solution properties at substantially lower temperatures. The latter phenomenon can be ascribed to the hydrolysis of the amide linkages.

(Keywords: rigid rod copolymers; ionomer; polyelectrolyte; viscosity; surface tension)

## INTRODUCTION

It is well known that low levels of functionalization will, in general, produce polymeric materials which have markedly different physical properties than their unfunctionalized counterparts<sup>1-11</sup>. For example, low levels of ionic groups have been introduced into a rather large variety of polymers resulting in materials possessing unique solution and bulk properties. These property changes are due to the microphase separation of the ionic moieties containing multiplet or higher order aggregates. The driving force for this mechanism is the very low compatibility of the ionic groups, which possess a high dielectric constant, with a continuous organic phase (i.e. chain or solvent backbone) of low dielectric constant. A direct consequence of these strong ionic interactions is scientifically interesting and technologically useful rheological behaviour, including high viscosification efficiency, shear thickening, and enhanced viscosity-temperature characteristics, as compared to its unfunctionalized precursor. Recently<sup>12</sup>, a family of styrene copolymers containing a broad compositional range of sulphonate groups were synthesized. At low sulphonate contents, these copolymers have typical ionomeric solution properties. That is, associative and polyelectrolyte characteristics dominate solution behaviour in low and high dielectric solvents, respectively. Copolymers containing intermediate sulphonation levels are quite surface active in aqueous solutions, while water soluble polyelectrolyte behaviour is observed at very high levels of charge. In general, a majority of these and other ionomeric and polyelectrolyte-type polymers are best described as flexible chains. It is of interest, however, to compare these materials with those composed of more rigid segments.

A significant amount of effort has focused on the preparation of wholly aromatic polyamides because these materials possess remarkably high modulus and tensile strength with a corresponding high thermal stability<sup>13-17</sup>. These properties can be correlated to a highly rigid and oriented molecular structure. This intrinsic rigidity is a direct result of the aromatic group linkages with amide groups and the significant amount of inter-chain hydrogen-bonding between the amide moieties. As a result of this intrinsic rigidity, these rod-like polymers do not melt and do not dissolve in typical organic solvents. This problem can be overcome if the chains are appropriately functionalized.

Takayanagi *et al.*<sup>18</sup> formed homogeneously *N*-substituted poly(*p*-phenylene terephthalamide) having good solubility in common organic solvents and thermoplastic processability. This was achieved via the chemical substitution of the hydrogen of the amide groups with a variety of functionalities, such as aralkyl, alkyl, and carboxymethyl units under special conditions. This chemistry has since led to the formation of a number of graft and block copolymers containing a rigid chain backbone or grafted pendent groups.

In this study, we present results of the synthesis, solution, and interface behaviour of a family of sulphonated PPTA copolymers (S-PPTA) spanning a broad range of anionic charge. For these rigid-rod type copolymers, it is anticipated that both the bulk mechanical properties and the solubility might be improved as a result of the combined influence of the rigid backbone and the strongly interacting sulphonate groups.

## EXPERIMENTAL

The sulphonated copolymers of poly(*p*-phenylene tere-

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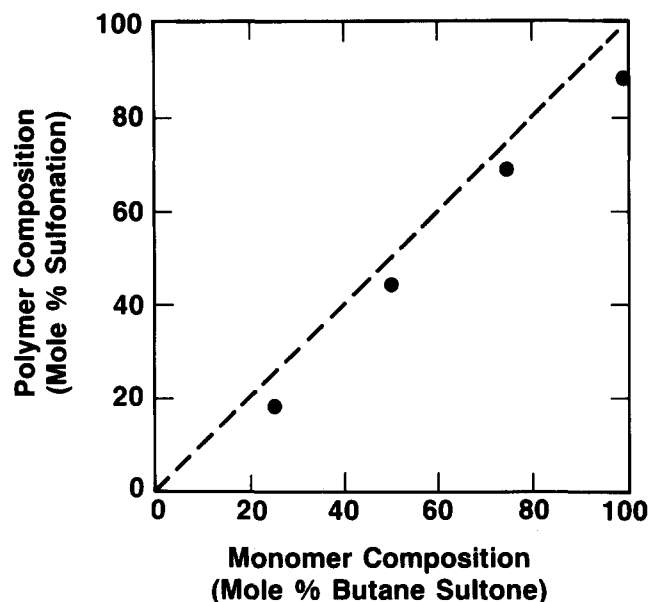


Figure 1 Copolymer composition as a function of butane sultone concentration for the sulphonation of PPTA

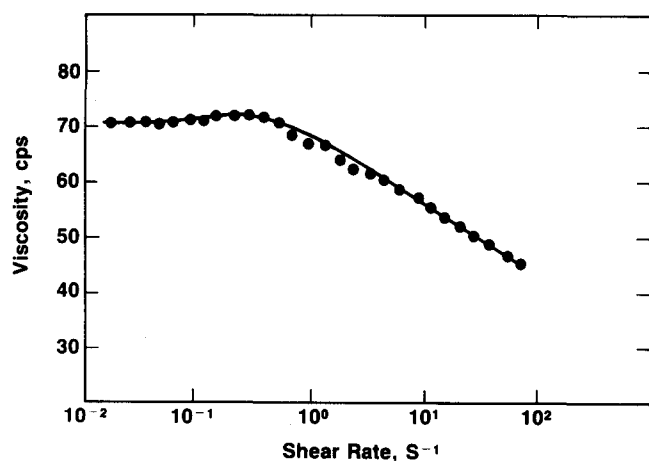


Figure 2 Viscosity–shear rate profile of the 45 mol% S-PPTA copolymer

phthalamide) were prepared by the direct functionalization of the preformed polymer (kindly provided by the DuPont Company). The sulphonation of PPTA is carried out via a metalation reaction performed in a solution of sodium methylsulphinylocarbanion in dimethylsulphoxide (DMSO). This latter compound is formed from the reaction of clean sodium hydride in a large excess of thoroughly dried DMSO. Dimethylsulphoxide is used as a solvent because of its large dielectric constant, giving enhanced solubility to the *N*-metalated PPTA. Sodium hydride is used as a strong base to abstract the proton from the amide linkage. Subsequent nucleophilic substitution by a specific amount of butane sultone (or propane sultone) produces rigid-rod copolymers containing various levels of sulphonation. A representative example of this procedure is described as follows.

A 500 ml round bottom flask equipped with condenser, drying tube, nitrogen inlet, and glass thermometer was used. An oil bath was used to maintain a constant temperature. A 200 ml aliquot of dried DMSO was added to the flask followed by 2.0 g of sodium hydride (NaH). The original oil suspension of NaH was cleaned of oil

with toluene, filtered and the solid subsequently added to the dried DMSO. This mixture was stirred for approximately 2 h at 55–60°C. The PPTA fibres (2.0 g), previously soaked in dried DMSO, were added to the flask. In a relatively short time, (10 h) the fibres dissolved forming a brilliantly red, viscous solution. The stepwise addition of butane sultone (11.5 g) resulted in a dramatic reduction in both colour and viscosity. The product was isolated at room temperature with acetone and immediately redissolved into 200 ml of fresh water containing 3.4 g of sodium hydroxide. The solution was filtered and again the polymer was isolated with an excess of acetone. The product was dried in a vacuum oven for 24 h at 45°C. Conversion is typically between 85 and 90%.

Sulphur content was determined by Dietert sulphur analysis and was used to calculate the sulphonation content. In this specific procedure, the sulphonate content was 88 mol%. The compositions of the sulphonation PPTA used in this study are presented in Figure 1.

Low shear rate viscosity measurements (25°C) were performed on a Contraves Low Shear 30 instrument with the low shear rate data extrapolated to zero-shear-rate conditions (see Figure 2, for example) or on a standard Ubbelohde viscometer in a temperature-controlled water bath (25°C). The solutions were thermally equilibrated for approximately 20 min prior to the appropriate flow-rate measurements.

Surface tension was measured with a Fisher model 215 Autotensiomat surface-tension analyser, which is based on the du Nuoy ring principle. The surface-tension analyser employs a strain-sensitive wire that is fixed at one end to a balance beam and at the other end to a transducer, which provides a force proportional to the surface tension as the ring is pulled out of the liquid. The typical output of the analyser is the pulling force on the ring as a function of the ring displacement from the liquid surface.

## RESULTS AND DISCUSSION

### Rheological behaviour

In the course of our studies on flexible chain polymers spanning a wide sulphonation range, it was observed that water soluble polystyrene copolymers were formed at sulphonation levels approaching 40 mol% (ref. 12). This amount of anionic charge is sufficient to overcome the inherent hydrophobicity of the styrene units. Similar solubility observations are noted in S-PPTA. The rheological properties (and corresponding water solubility) of these materials in fresh water are presented in Figure 3. The data show several interesting features of these solutions.

In a range of sulphonate content of less than about 40 mol%, S-PPTA is insoluble in water, presumably due to a high hydrophobic character of the copolymer. Above this sulphonation level, water solubility is exhibited. It is noteworthy that the viscosity values are inversely proportional to the sulphonation level. Because the level of sulphonation is inversely proportional to the hydrophobicity level within the chain, it is anticipated that these intra-chain hydrophobes are capable of aggregating forming larger structures possessing an enhanced apparent molecular weight. It is well known that this results in a substantial rise in the viscosity of flexible chains containing

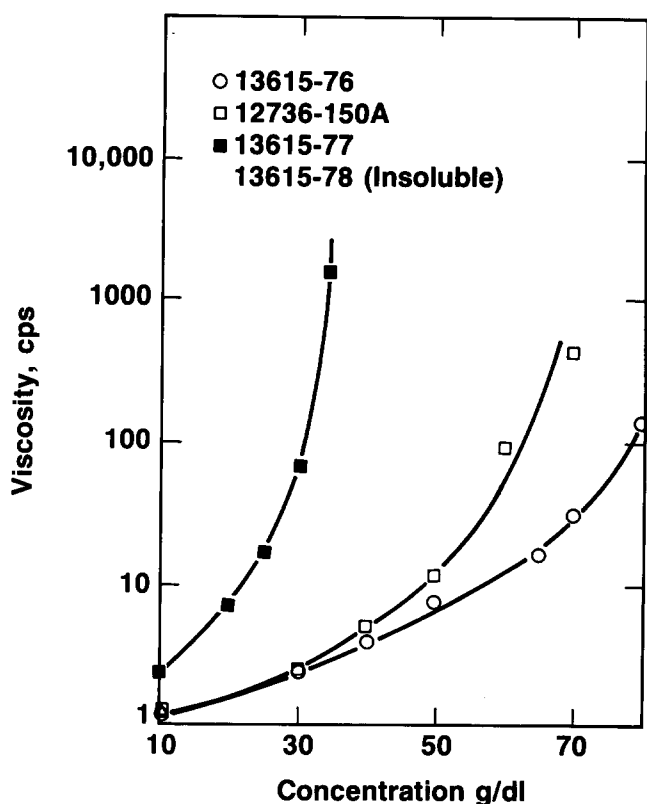


Figure 3 Viscosity–polymer concentration of various S–PPTA copolymers. Sulphonation content (mol %): 13 615-78(18), ■ (45), □ (71) and ○ (88)

low levels of pendent hydrophobic units<sup>19,20</sup>. However, because the hydrophobic units are stiff and intra-chain, the efficiency of forming large aggregate structures may be less restrictive than flexible chains. Although it is uncertain whether this is a correct assumption, it is certain that these relatively low molecular rods would not interact intramolecularly in any substantial manner. As a result, all hydrophobe units are available to form inter-chain type associations. The impact this phenomenon has on the viscosification efficiency is clearly exhibited at the 45 mol% sulphonation level (see Figure 3).

As the sulphonation content is increased, less hydrophobic character is present within the chain structure and a corresponding decrease in the inter-chain associations results. Again a decrease in viscosity is observed. The rheological characteristics of these solutions is controlled, to a first approximation, by the axial ratio parameters of the individual rods and their mutual interaction, which are substantially reduced in this instance.

An increase in the ionic strength of typical flexible chain polyelectrolytes produces a loss in viscosity. The detailed mechanism for this behaviour is complex but the charge–charge repulsions diminish because of shielding effects by the dissolved low molecular weight salts. An ‘anti-polyelectrolyte effect’ is observed, however, if long alkyl-type groups, i.e. hydrophobically associating monomer units, are chemically attached to the chain backbone. As described previously, this is attributed to the aggregation of these units in order to avoid any significant exposure to the aqueous solvent environment. The chains themselves, for the most part, have a relatively favourable polymer–solvent interaction parameter, but

are forced into a swollen multichain structure. As the ionic strength is increased, the hydrophobe units increasingly dominate solution behaviour. Somewhat similar behaviour is found in S–PPTA solutions.

Figure 4 shows the viscosity–salt concentration characteristics of the water soluble S–PPTA copolymers. At the high sulphonation level, typical polyelectrolyte behaviour is observed. That is, the viscosity is markedly diminished with increasing amounts of dissolved salt. At high ionic strength, the viscosity does begin to rise in a similar fashion as a nonionic polymer. As the level of sulphonation is decreased hydrophobic associations again dominate solution rheology in a systematic manner. At the 71 mol% level, the shielding of the anionic charge produces a substantial reduction in viscosity followed by a very large enhancement. A two-order magnitude continual viscosity rise is noted at the 45 mol% level and at about one half the polymer concentration.

#### Thermal stability

The thermal stability of these copolymers was followed by measuring the loss, if any, in viscosity as a function of heating time. Because amide units are well known to be highly sensitive to hydrolysis, chain length deterioration would be the anticipated mechanism for any substantial viscosity loss. Typical results are presented in Figure 5 in which it is confirmed that these materials are highly susceptible to hydrolysis. It is not clear whether the weakest link within the chain is at the hydrophilic sulphonated amide group or the ‘hydrophobically shielded’ unsulphonated amide links. It is noteworthy, however, that the hydrolysis rate is reduced somewhat at lower sulphonate levels.

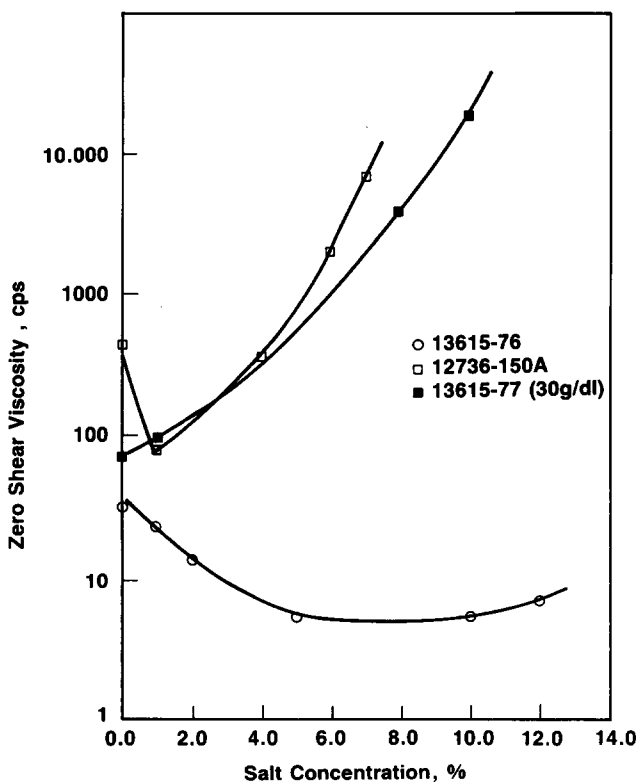


Figure 4 Zero shear viscosity as a function of salt concentration (sodium chloride) for a series of S–PPTA copolymers. (Polymer concentration is 70 g dl<sup>-1</sup> except for 13615-77 as noted)

*Air-water interface behaviour*

Substantial reduction in the surface tension of water by surfactants and diblock copolymers is very common and plays an important role in many fields<sup>21-23</sup>. The utilization of surfactants is well documented, but an area of considerable research activity pertains to polymeric-type materials. In the most general case, these higher

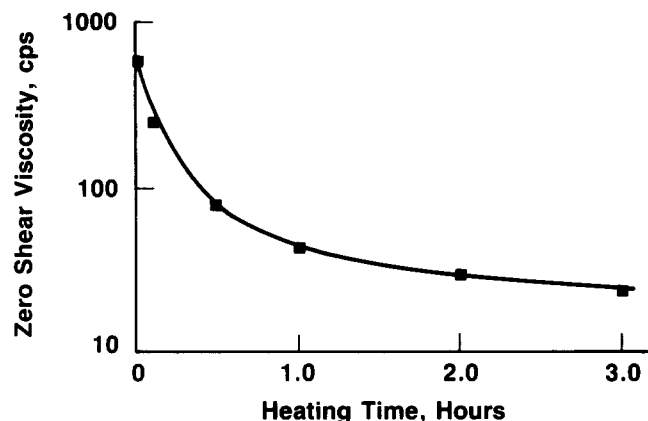


Figure 5 Zero shear viscosity as a function of heating time (50°C, pH = 11) of the 71 mol% S-PPTA

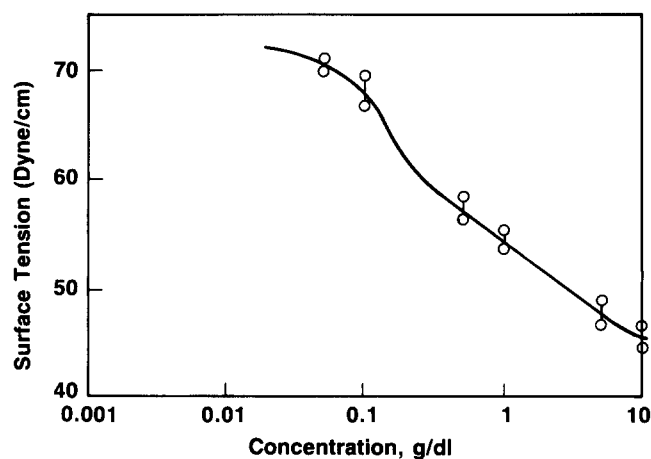


Figure 6 Surface tension as a function of polymer concentration (71 mol% S-PPTA) in water

molecular-weight species possess different water solubility characteristics with the same molecule. Typically, these structures include diblock-type copolymers or chains containing surfactant moieties, i.e., polysoaps. Recently<sup>12</sup>, it was observed that styrene copolymers containing a specific amount of sulphonate groups exhibit substantial surface activity. In essence, the styrene and sulphonate units are the lipophilic and hydrophilic regions of the chain, respectively.

Figure 6 shows the surface tension in fresh water of the 71 mol% S-PPTA copolymer as a function of copolymer composition. The data shows that the surface tension reduction is significant and comparable to the above described copolymers. This confirms that this polymer is quite surface active with a behaviour that closely parallels more flexible chains. The detailed mechanism for this observation is not clear but it is certain that the rigid hydrophobic segments within the chain are able to re-orient themselves at the interface.

*Solid state measurements*

Preliminary polarized light microscopy observations were obtained on thoroughly dried thin films of the 88 mol% S-PPTA copolymer (Figure 7). This result is compared with a flexible sulphonate polystyrene copolymer (sample 13615-63P of reference 12). The films were formed into thin layers from concentrated, non-sheared aqueous solutions. The rigid-rod copolymer shows strong birefringent colour (and striations which are oriented along the stress direction, which are not shown). Under stress, this morphology resembles aggregated fibrous structures. Therefore, these rigid-rod copolymers have a tendency to form ordered structures in the bulk phase, while no discernible birefringence is noted in semi-dilute aqueous solutions. Flexible chains of high sulphonate content do not form ordered structures in the solid state, as anticipated.

Finally, it should be noted that although these copolymers are unstable with regard to hydrolysis, the opposite is true in the solid state. Typical differential scanning calorimetry measurements on the 45 mol% S-PPTA are presented in Figure 8. The data shows under an anhydrous nitrogen atmosphere, these copolymers are reasonably thermally stable with very little change up

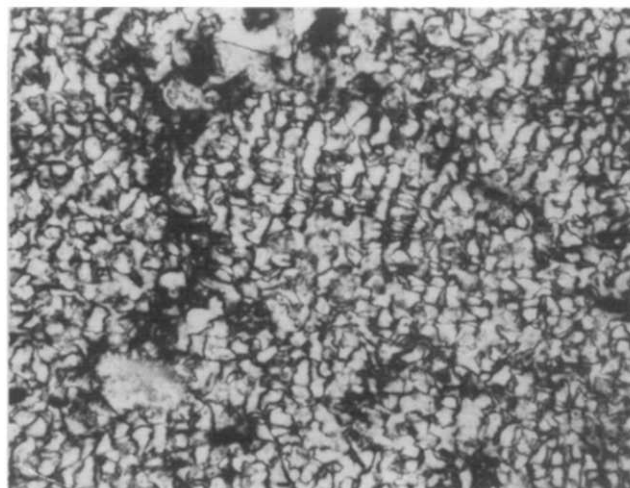
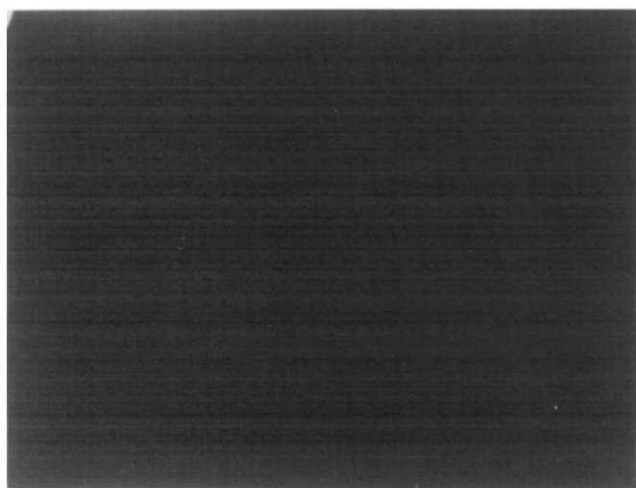


Figure 7 Polarized light microscopy observations on a thoroughly dried film of a flexible chain (66.7 mol%) water soluble copolymer (left) and a rigid rod (45 mol% S-PPTA) water soluble copolymer (right)

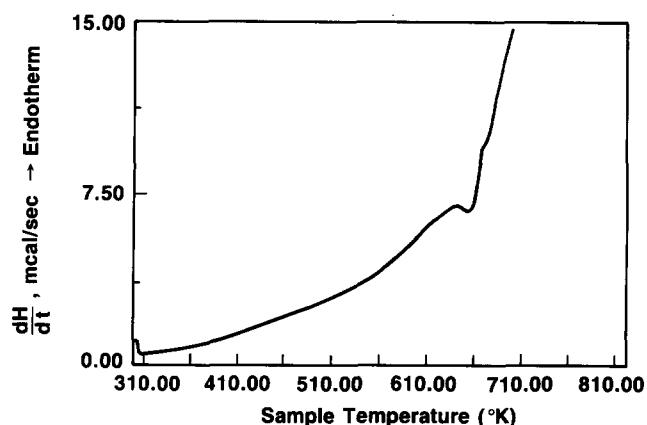


Figure 8 Typical d.s.c. scan of the 45 mol% S-PPTA copolymer

to approximately 600 K. This observation compares favourably with the unmodified PPTA precursor<sup>17</sup>.

### CONCLUSIONS

Sulphonated poly(*p*-phenylene terephthalamide) copolymers spanning a broad range of anionic charge were synthesized from the nonfunctionalized polymeric precursor through a metalation reaction. The level of sulphonation was controlled with the appropriate level of butane sultone.

Solubility and solution measurements were performed on these rigid-rod polymers in order to ascertain the extent of interaction between chains, in a qualitative sense. The results show that intra-chain hydrophobically-associating monomer units, i.e. monomer units containing nonsulphonated amide linkages, profoundly influence the viscosity-concentration-ionic strength profiles. As the level of sulphonation is decreased, the hydrophobic associations increasingly dominate behaviour. Even though these moieties are located within the chain backbone, they are quite effective associating entities due to the rigidity of the chain itself. This behaviour is reminiscent of the solution rheology of water soluble flexible chains containing pendent associating groups. A distinguishing characteristic of these rigid-rod polymers is that they undoubtedly have a substantially higher level of inter-chain association due again to their inherent inflexibility.

Preliminary studies of the aqueous solution cast as dried films confirm that these copolymers formed ordered structures in the bulk and also possess substantial thermal stability under anhydrous and oxygen-free conditions. These copolymers are, however, very susceptible to hydrolysis of the amide linkages resulting in marked deterioration in solution properties.

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