Heteromeric liquid-crystalline association chain polymers: structure and properties*

C.-M. Lee, C. P. Jariwala and A. C. Griffin†
Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, UK

Liquid-crystalline association chain polymers involving hydrogen-bond connectivities between pyridyls and carboxylic acids have been synthesized and characterized by optical, thermal, infra-red, solid-state nuclear magnetic resonance and rheological analysis. For one system a chemical reaction occurs during its preparation, which alters its primary (covalent) structure. The liquid-crystalline thermal stability is increased by this modification, wherein it has greatly diminished crystallinity. Variable-temperature infra-red spectroscopy was used to follow the extent of hydrogen bonding as a function of temperature. At the melting transition a discontinuous decrease in hydrogen bonding is seen. Rheological data on complexes with varying degree of polymerization show similar values of *G'*, with gradually increasing *G'* on cooling through the mesophase, as would be expected for increased hydrogen bonding at lower temperatures.

(Keywords: LC association chain polymers; synthesis; characterization)

INTRODUCTION

The incorporation of design concepts from supramolecular chemistry into macromolecular systems is of great current interest[1–3]. Stadler[4] has described association chain polymers in which the polymer chain is held together only by hydrogen-bond interactions, and Lillya[5] has shown that mechanical behaviour in association chain polymers is related to chain length, which, owing to the dependence of hydrogen-bond association on temperature, is temperature-dependent. Lenz *et al.*[6] have reported chain extension by dimerization of α,ω-diaromatic acids connected by oligomeric ethylene oxide spacers. These diacids formed liquid-crystalline mesophases.

We[7] have described recently a chemically simple system which, through molecular recognition of complementary components, can self-assemble into a chain-extended, i.e. polymeric, liquid-crystalline structure. Both the linear chain extension and the liquid-crystalline (mesomorphic) behaviour derive from this self-assembly process, which relies only on a single hydrogen-bonding interaction between dissimilar components. In this study we report both spectroscopic and mechanical characterization for such systems, and also on an intriguing chemical reaction that, for one system, occurs during complexation and significantly alters the behaviour of the polymer.

EXPERIMENTAL

General

Melting temperatures were determined on a Gallenkamp MFB-595 capillary melting-point apparatus. Infra-red spectra were recorded on a Nicolet 510 FTIR. Variable-temperature infra-red spectra were taken on a Perkin–Elmer 1600 FTIR equipped with an Omega 019 hot stage. Proton and carbon spectra were recorded on a Bruker 250 MHz Fourier Transform NMR spectrometer with tetramethylsilane (TMS) as internal reference. Elemental analyses were performed by the Department of Chemistry, University of Cambridge. Mesophase transition temperatures were determined using a Zeiss Axioskop polarizing light microscope equipped with a Linkam TMS 91/THMS 600 heating stage or with a Leitz Laborlux S polarizing microscope fitted with a Mettler FP 80HT/FP 82HT microfurnace. A Perkin–Elmer model Delta DSC-7 was used for differential scanning calorimetry. Heating and cooling rates of 10°C min^{-1} were employed for d.s.c. studies. Dynamic mechanical studies were performed on a Rheometrics Dynamic Strain Rheometer II (Rheometrics Inc.) in parallel-plate geometry operating between 100 and 175°C at a frequency of 20 rad s^{-1} and a strain of 1%. The 25 mm disc samples used for the measurement were prepared by compression moulding. The complexes were heated in the mould to a temperature 15°C lower than the melting temperature for 5 min while under an applied load of 20 ton m^{-2} and were kept under this load for 2 h after cooling to room temperature. Solid-state n.m.r. spectra were obtained on a Bruker MSL-200 NMR spectrometer at the University of Southern Mississippi. Silica gel was used for thin-layer chromatography. The eluant was typically ethyl acetate/n-hexane/methanol (1:2:2 v/v/v).

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[†] To whom correspondence should be addressed. Present address: Departments of Chemistry and Polymer Science, The University of Southern Mississippi, Box 5043, Hattiesburg, MS 39406-5043, USA

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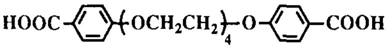
Synthesis

The reactants used for association polymerization in this study are shown below. In this group compounds **1** and **4** have been described previously[7] while compound **3** is available from Aldrich Chemical Co.

Pentaethyleneglycoxy bis-(4-benzoic acid) (*2*). A 250 ml round-bottomed flask was charged with 10.00 g (18.3 mmol) of pentaethyleneglycol di-*p*-tosylate (Aldrich), 6.08 g (36.6 mmol) of ethyl *p*-hydroxybenzoate, 1.61 g (40.3 mmol) of sodium hydroxide and 120 ml of 2-propanol. The mixture was stirred and refluxed for 10 h. A white precipitate formed during refluxing. After cooling, the precipitate was filtered and washed with 2-propanol. From the filtrate an oily liquid was collected after removal of the solvent by rotary evaporation. This liquid was then refluxed with 150 ml of 10% sodium hydroxide (w/v) in 95% ethanol for 1 h. The solvent was removed *in vacuo* and the solid residue was dissolved in 300 ml of water. The solution was made strongly acidic with hydrochloric acid. The precipitate that resulted was filtered, dried and recrystallized from ethanol, yielding 4.41 g of white product. Yield, 50.4%; m.p., 173.5°C.



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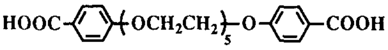

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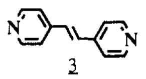

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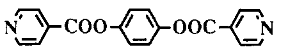


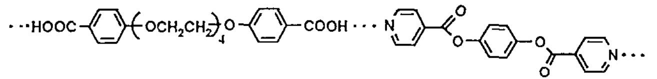
4

I.r. (KBr) ($\mathrm{cm^{-1}}$): broad OH centred at 3000; 2880, 2666, 1682, 1605, 1578, 1430, 1321, 1254, 1113, 774. ^{1}H n.m.r. (DMSO-d_6) (ppm): 12.63 (2H, s, $-\mathrm{COO\underline{H}}$), 7.87 (4H, d, Ar), 7.01 (4H, d, Ar), 4.14 (4H, t, $-\mathrm{Ph{-}OC\underline{H}_2CH_2{-}}$), 3.78 (4H, t, $-\mathrm{Ph{-}OCH_2C\underline{H}_2{-}}$), 3.36–3.68 (12H, envelope, $\mathrm{OC\underline{H}_2C\underline{H}_2{-}OC\underline{H}_2C\underline{H}_2{-}OC\underline{H}_2C\underline{H}_2{-}}$). ^{13}C n.m.r. (DMSO-$d_6$) (ppm): 167.9 (carbonyl), 163.0, 132.2, 123.9, 115.1, 70.8, 70.7, 69.6, 68.3. Anal. calc. for $\mathrm{C_{24}H_{30}O_{10}}$: C, 60.24; H, 6.32. Found: C, 60.10; H, 6.30.

Preparation of the 1:1 acid/pyridyl polymer followed a melt method that has been described previously[7]. The symbol L refers to long (10 min) polymerization times and S refers to short (≤2 min) times.

RESULTS AND DISCUSSION

In our initial study[7] we described the thermal properties of hydrogen-bonded, liquid-crystalline association chain polymers; one was the complex formed by reacting **1** with **4** (**1/4S**). This material exhibits an enantiotropic nematic phase between 174 and 183°C and a monotropic smectic phase (which was not identified in the previous study). The complex was prepared from an equimolar mixture of **1** and **4** by short melt polymerization, i.e. reaction in the isotropic phase for 2 min. We have now found that the resulting species shows unusual features upon repeated thermal cycling as revealed by d.s.c. (*Figure 1*) and optical microscopy. After each repeated heating, a decrease in the melting transition (solid→nematic) and also an increase in the clearing transition (nematic→isotropic), 2 and 1.5°C increase on second and third heating respectively, were observed. On cooling cycles a decrease both in the nematic→smectic transition (5°C initially) and in the crystallization transition (6°C initially) were observed.



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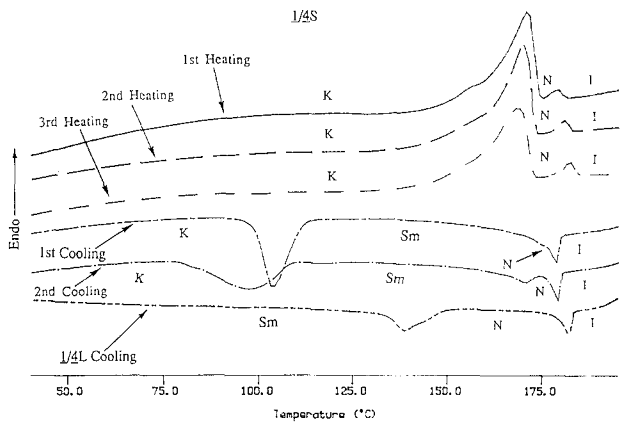
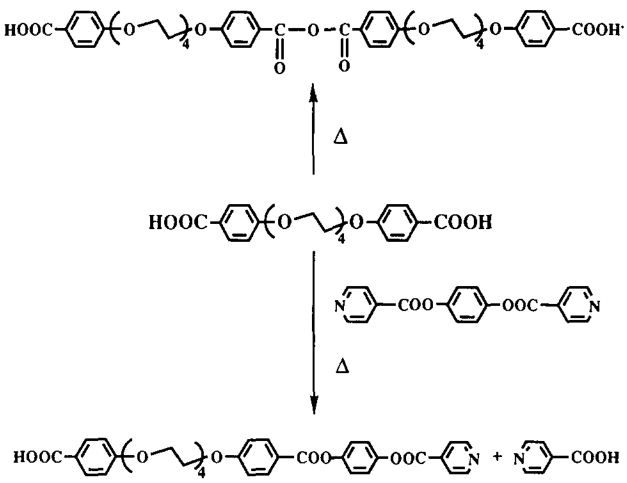


Figure 1 Thermal cycling (d.s.c.) of complex **1/4S** and cooling curve for **1/4L**

The above results imply that the chemistry of self-association between **1** and **4** may be changing with repeated heating. In order to examine this effect of thermal cycling, an additional complex of the same components, **1/4L**, was prepared by reaction in the isotropic phase for 10 min. This complex was examined by optical microscopy and by d.s.c. (*Figure 1*). On cooling, broader-range nematic and smectic phases were exhibited compared to the analogous **1/4S**. The sequence of transitions for **1/4L** on cooling is I182N139Sm. The smectic texture is retained on cooling to room temperature, i.e. a glassy smectic phase at low temperatures. In *Figure 1* the cooling curves are instructive, showing that complex **1/4S** can be transformed by repeated thermal cycling into **1/4L**. The key feature, hinted at in **1/4S** on initial cycling and realized in **1/4L**, is that the N–I temperature rises with a decrease in the N–$\mathrm{S_A}$ temperature and the decreased (or eliminated) crystallinity of the complex. The origin of these phenomena has proven to be attributable to a cross-reaction between **1** and **4** with the resulting formation of a new primary (covalent) structure. To investigate this high-temperature reaction between the two components of the complex, an experiment was performed using preparative thin-layer chromatography to separate the cross-reaction products of **1/4L**. Several groups of mixtures were found in addition to small amounts of **1** and **4**. The top fraction (highest R_f) showed aliphatic C–H, hydroxyl and ester functional groups by infra-red spectroscopy. Another fraction also contained the same functional groups and is likely to be cross-reaction products between **1** and **4**. Examination of the n.m.r. spectrum revealed proton absorptions from both components. In addition, the acid and pyridyl t.l.c. spots were broadened, indicating chemical modification of these original components.

Possible high-temperature reactions of **1** and **4** are shown in *Scheme 1*. An anhydride may be formed from



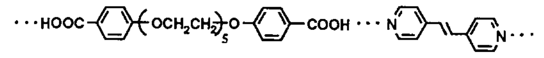
Scheme 1 Potential reactions of diacid at elevated temperature

the diacid. We have not observed evidence for this reaction, however. Another possibility is cross-reaction between **1** and **4**, which could give isonicotinic acid as a product. We have, for long-time preparations, identified isonicotinic acid by thin-layer chromatography. By this type of acid–ester exchange process, a number of related structures could subsequently form. It is also possible that mixed anhydrides could form, releasing a phenolic group. The infra-red spectrum of **1/4L** is dominated by the characteristic bands[8–13] resulting from self-association of pyridyl and acid through intermolecular hydrogen bonding: two O–H frequencies observed at 1910 and 2512 cm^{-1} (these are stronger than those for **1/4S**), and the carbonyl band of the diacid shifted from 1686 to 1701 cm^{-1}. Cross-reaction products of the type shown would maintain pyridyl and acid groups at the molecular ends, which would also be able to participate in associations leading to chain extension. These new covalent structures would then be incorporated into the polymer chain. One would expect that this 'randomization' of the rigid segment in the chain would lead to lowered T_m, and this is indeed found. The more randomized rigid segments explain as well the decrease in the N–S_A temperature on cycling, random structures decreasing smectic thermal stability. A lowered T_m is also seen upon thermal cycling of the **1/4S** complex, which we feel reflects cross-reaction on cycling. The formation of longer rigid segments between spacer groups from the cross-reaction explains also the elevated N–I temperatures seen.

This high-temperature cross-reaction was further examined by solid-state carbon n.m.r. The formation of hydrogen bonds between pyridyls and acids modifies electron density around the nuclei. Strong hydrogen bonding should cause changes in the carbon chemical shifts of those resonances involved in the interaction. The carboxyl carbon of the acid is known to shift upfield when a hydrogen bond between the acid and a pyridyl is formed[14]. This chemical shift change is due to an increase in electron density at the carboxyl carbon of the complex relative to that in the acid dimer.

A set of complexes, **1/4S** and **1/4L**, were examined by solid-state carbon n.m.r. The spectra of **1**, **4**, **1/4S** and **1/4L** are shown in *Figure 2*. The carboxyl carbon of diacid **1** absorbs at 172.5 ppm and is shifted to 171 ppm upon formation of the complex **1/4S**. This upfield shift is consistent with hydrogen-bond formation. In contrast, **1/4L** is likely a mixture containing some of the original components, but primarily cross-reaction products (esters, new pyridyls, new acids). All the absorptions of **1/4L** are broadened. The carboxyl carbon in **1/4L** is shifted to 167.5 ppm. This could be due to the formation of new acids and esters (and possibly mixed anhydrides) when **1** and **4** are cross-reacted. Strong hydrogen bonding is evident from infra-red spectroscopy in this chemically modified complex. Although other ester-based pyridyls have been examined, only this hydroquinone diester shows this strong tendency for covalent reaction.

In contrast to the hydroquinone-based pyridyl ester **4**, the bispyridyl **3** is incapable of cross-reaction and is more easily studied. The thermal behaviour of the **2/3** complex is given in *Table 1*. The phase transition temperatures were recorded by differential scanning calorimetry (d.s.c.) and optical microscopy. The 1:1 complex showed an 'enantiotropic' smectic A phase on second and subsequent heatings in place of the monotropic smectic A phase



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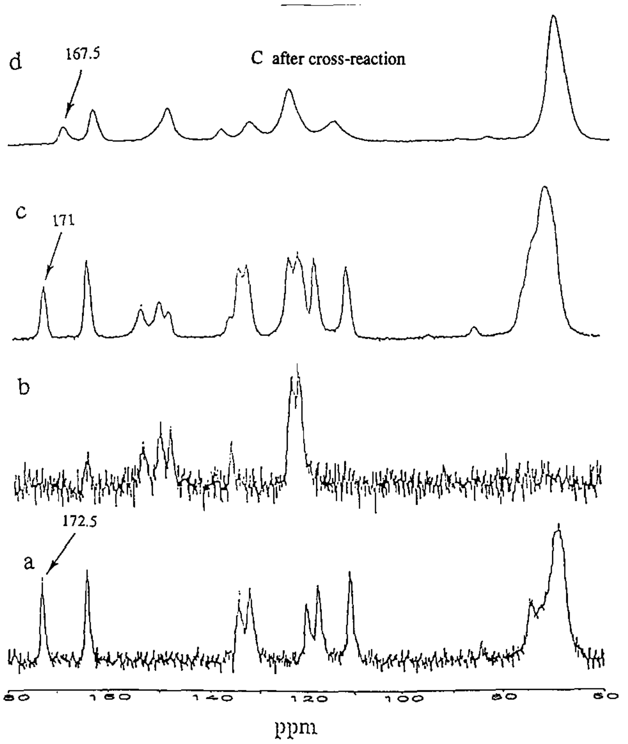

Figure 2 Solid-state carbon n.m.r. of (a) **1**, (b) **4**, (c) **1/4S**, (d) **1/4L**. All spectra taken at room temperature

Table 1 Thermal behaviour of polymeric complex **2/3** (microscopy)

Thermal cycle	Transitions (°C)[a]
1st heating	K $\xrightarrow{168.5}$ I
1st cooling	K $\xrightarrow{134.5}$ S_A $\xrightarrow{162.5}$ I
2nd heating	K $\xrightarrow{160}$ S_A $\xrightarrow{164}$ I

[a] K Crystalline or semicrystalline solid
N Nematic
S_A Smectic A
I Isotropic

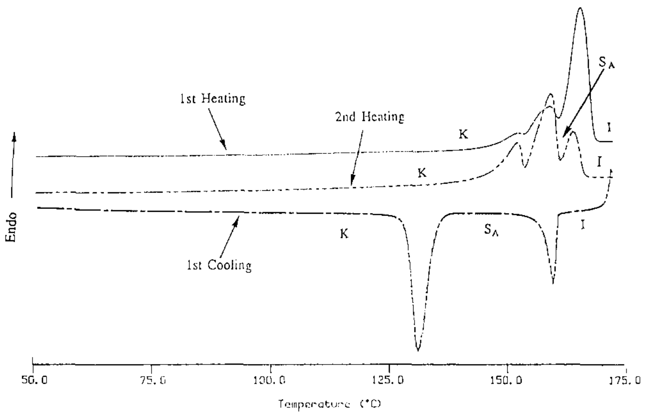

Figure 3 D.s.c. curves for **2/3**

exhibited on first heating. The d.s.c. thermogram in *Figure 3* shows this behaviour. The presence of a smectic A phase is confirmed by optical microscopy (characteristic focal conic fan texture). Neither **2** or **3** exhibit liquid crystallinity, and the formation of a mesophase from the mixture arises through molecular recognition between the pyridyl and carboxylic acid groups, leading to self-assembly via intermolecular hydrogen bonding into a chain-extended mesogenic complex.

Infra-red spectroscopy of this type of complex has two main features: a pair of O–H absorptions around 1900 and 2500 cm^{-1} due to hydrogen bonding between acid and pyridyl groups, and the shift of acid carboxyl absorption from 1686 to 1701 cm^{-1} upon complexation. Correspondingly upon complexation the analogous absorptions from the acid dimer virtually disappear[8,12,13]. The temperature dependence of these absorptions has been examined for the complex **2/3**. *Figure 4* shows i.r. spectra taken at 140, 165 and 170°C. The sample undergoes isotropization from the crystalline phase at 168.5°C. At both 140 and 165°C, in the solid state, the hydrogen-bonding absorptions are strong, relative to methylene absorptions, with no evidence of acid dimer being present, i.e. complete or near-complete complexation even immediately below the melting temperature. However, at 170°C, above the isotropization temperature, these hydrogen-bonding absorptions are significantly reduced. In addition there is evidence for some acid dimer — broad OH centred around 3000 cm^{-1}. It appears that upon isotropization the equilibrium

$$\text{acid} + \text{base} \overset{K_{eq}}{\rightleftharpoons} \text{complex}$$

shifts to produce greater amounts of acid and base. Kato[13] has reported temperature-dependent i.r. data for low-molar-mass complexes similar to these and notes increasing amounts of uncomplexed species at elevated temperatures. We[15] have examined theoretically the effect of mesophase ordering on the extent of hydrogen bonding in such systems and found a significant coupling between the two.

Rheological properties of association chain polymers should be influenced by the effective number of associated units, i.e. the chain length. A series of complexes, **2/3**, having differing molar ratios were examined by rheological dynamic spectroscopy. In each case except 1:1 the bispyridyl is in excess. Since the pyridyls do not self-associate, it is possible to obtain for each molar ratio an average oligomer degree of polymerization (*DP*) by assuming the complexation between acid and pyridyl is complete. For example at a **2/3** molar ratio of 2/1, the $DP=2$; for 3/2, $DP=3$; for 4/3, $DP=4$; etc. At 1/1 the DP is in principle very large. In *Figure 5* the storage modulus G' is presented as a function of temperature, on cooling from the isotropic phase, and the molar ratio. It can be seen that there is an abrupt increase in G' (elasticity) at the isotropic–smectic A transition for each molar ratio, followed at lower temperature by crystallization, leading to another rapid increase in G'. As the molar ratio becomes nearer unity, increasing *DP*, the higher the temperature at which elastic response becomes significant. It is worth noting that the G' values in the mesophase for all of the molar ratios are approximately the same. This is at first surprising in that a strong dependence of G' on *DP* might be expected. However, the dynamics of hydrogen-bond formation and breaking in fluid phases at elevated temperatures might be too rapid to permit a coherent mechanical response

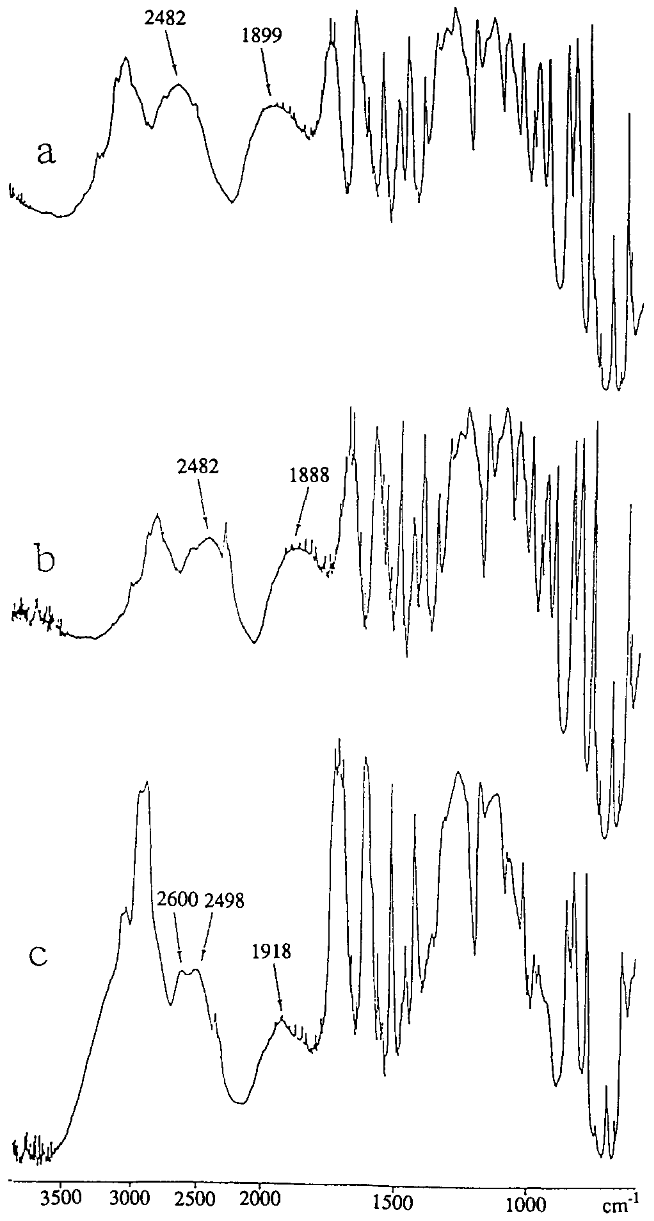

Figure 4 Variable-temperature infra-red spectra of **2/3** at (a) 140°C, (b) 165°C, (c) 170°C

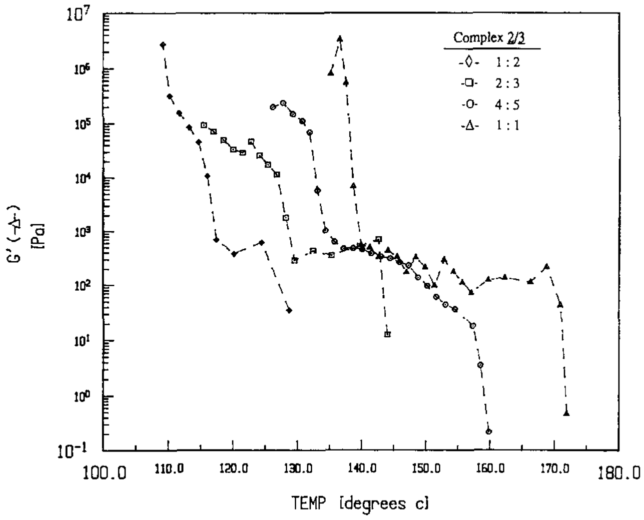

Figure 5 Rheology of **2**/**3** at different molar ratios and temperatures; G' = storage modulus

of these systems under these conditions irrespective of *DP*. However, there is an increasing slope as the temperature decreases for the larger *DP* complexes, reflecting increased elastic response as the chain length becomes effectively longer through increased hydrogen bonding as the temperature decreases throughout the mesophase range.

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