Partial phase diagrams of poly(p-phenylene terephthalamide) copolymers in sulfuric acid

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Copolyaramides with 2,5-di-n-hexyl terephthalic acid residues as comonomers were synthesized. Partial phase diagrams were measured for mixtures with concentrated sulfuric acid in the range between 8 and 20% w/w of polymer. Lyotropic phases were observed, but in comparison to homopoly(p-phenylene terephthalamide) the clearing temperatures are lower and the critical concentrations for the formation of the lyotropic nematic phase are increased. The existence of a master curve for the clearing temperature as it depends on the concentration of the components of both homo- and copolymers illustrates that the side chains act mainly as an 'attached solvent' to the rigid main chains.

(Keywords: phase diagram; copolymers; synthesis)

INTRODUCTION

The observation of anisotropy and/or the coexistence of isotropic and anisotropic solutions (lyotropic liquid crystals) as a function of concentration and temperature is an essential feature of mixtures of a rigid chain polymer and a suitable solvent. As a consequence the phase diagrams are more complicated than in the case of solutions of flexible polymers. Furthermore, high viscosities of the solutions make experimental investigations difficult. Therefore the literature concerning lyotropic behaviour of polymers, especially that of polyaramides, is very limited.

The system of poly(p-phenylene terephthalamide) (PPTA) in concentrated sulfuric acid has attracted considerable interest because of its importance in industry. High-strength fibres are manufactured making use of the lyotropic phase of PPTA in concentrated sulfuric acid[1]. Results from the literature[2-5] concerning the phase diagram of this system can be summarized schematically, as shown in *Figure 1*. Five phases are seen: crystallized sulfuric acid ($C_{H_2SO_4}$), isotropic solution (IS), liquid crystalline (LC), crystal solvate (CS) and crystalline PPTA (C_{PPTA}). Some special situations are marked by coordinates: T_1, w_1 indicate the eutectic temperature and composition of crystalline H_2SO_4 and its crystal solvate. Crystal solvate is the name of a particular crystalline composition of a defined number of solvent molecules (H_2SO_4) per repeat unit of the polymer incorporated into the lattice of the solid polymer. At T_2, w_2 three phases are in equilibrium: IS, CS and LC. Pure LC phase is realized when the composition exceeds w_3. At T_3, w_4 C_{PPTA} separates from the LC phase. T_{max}^{CS} and w_{cs} are the conditions under which the maximum melting temperature of CS is observed, if incongruent melting does not take place; w_{cs} determines the ratio of polymer to sulfuric acid in the crystal solvate. Finally, T_4 indicates

the onset of the temperature range (hatched area) in which the decomposition of the sulfuric acid solution of the polymer takes place.

In the context of our general studies[6-9] on modifying rigid chain macromolecules by attaching flexible side chains we became interested in the phase behaviour of copolyterephthalamides where the comonomers are derived from p-2,5-di-n-hexylterephthalic acid. The aim of such work is to maintain the overall chain stiffness of the parent polymer (PPTA) but to frustrate the direct chain–chain interactions by the presence of the flexible and voluminous side-chain segments[10,11]. The presence of side-chain segments consisting of a few monomer units was also expected to decrease the perfection of the crystallites in the fibres obtained from lyotropic solutions while maintaining the overall extended form of the individual macromolecules. Other concepts developed with the aim of decreasing the crystal perfection and enhancing the solubility and processability of polyaramides consist of introducing comonomers which could create a defect in the main chains in terms of either flexible units or kink-forming segments[12,13]. Since the production of fibres is the final goal under all circumstances, the copolymer must be processed by the usual wet-spinning process of solutions in concentrated sulfuric acid. The copolymer must therefore be inert against sulfuric acid at the spinning temperature. For this reason we selected di-n-alkylterephthalic acid as the comonomer.

Attaching side chains to stiff macromolecules initiates variations of the thermodynamic properties with respect to the underivatized chains[10,11]. Consequently changes in the phase diagram of the mixture with concentrated sulfuric acid were expected.

In this paper, regions of the phase diagrams in the IS/LC equilibrium range of interest are presented for three such copolymers which contained 4.3, 9.6 and 17.6 mol% p-2,5-di-n-hexylterephthalamide comonomer units. For the sake of comparison and to prove the

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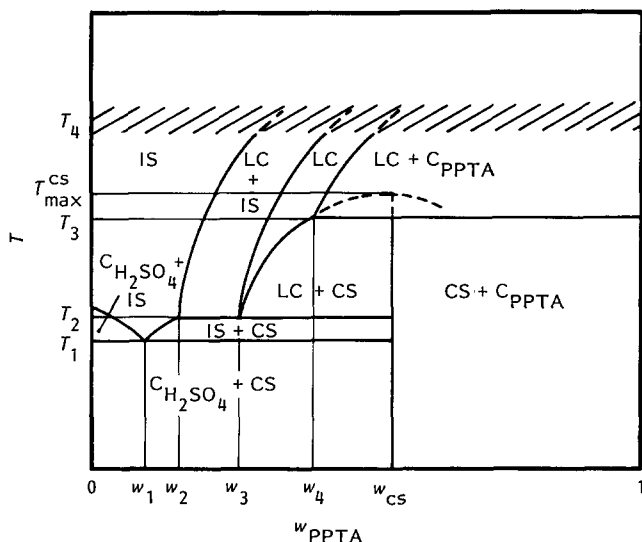
Figure 1 Schematic phase diagram in coordinates of temperature, T, and weight fraction of the polymer, w, for the system composed of poly(p-phenylene terephthalamide) (PPTA) and sulfuric acid. See text for explanation

influence of chain length, homopolymer samples of two different molecular masses have also been studied.

SYNTHESIS AND CHARACTERIZATION OF THE COPOLYMERS

2,5-Di-n-hexylterephthaloylchloride, **1**, was synthesized following the route of Rehahn et al.[9].

1
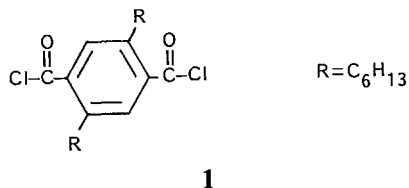
The polycondensation was performed in analogy to the low temperature polycondensation of terephthaloylchloride and p-phenylene diamine in an oversaturated solution of $CaCl_2$ in N-methylpyrrolidone (NMP)[14]. *Table 1* summarizes the copolymers of different comonomer content obtained in this work. Two homopolymers (PPTA) were also synthesized in order to obtain reference material. The composition of the copolymers in terms of comonomer content was determined quantitatively by gas chromatography after complete hydrolysis of the copolymer. This particular way of analysis was worked out by Peeters[15] and will be published elsewhere. Molecular weight characteristics were determined by g.p.c. measurements of the polymers in concentrated H_2SO_4[16]. Since calibration curves for the copolymers are not available, the data of these materials are interpreted in terms of the homopolymer as a first approach. The data in *Table 1* indicate a much larger $\bar{P}_n$ for the homopolymer synthesized under the same conditions as the copolymers; also, the polydispersity of the copolymers is substantially larger, as can be seen directly from the g.p.c. curves displayed in *Figure 2*. This effect may be a consequence of steric hindrance of the polycondensation step when the substituted diamine is either at the chain end or has to react with the activated carboxylic groups. The same steric hindrance may also cause a certain

blockiness of the copolymers, with comonomer-rich sequences being formed in the later stages of the conversion. Direct proof of this is not available, however, and therefore we assume that effects of sequence distribution do not play a significant role.

RESULTS AND DISCUSSION

Figure 3 displays the measured partial phase diagram of homopolymer 1 (*Table 1*) in concentrated sulfuric acid. It covers the section between w_2 and w_4 for temperatures exceeding T_2 (c.f. *Figure 1*). Curve 2 describes the transition from the biphasic region LC+CS to the monophasic LC state, and curve 1' from this state to the coexistence region IS+LC; finally, curve 1 marks the transition to the IS state as a function of temperature. The data of curve 2 are derived from d.s.c. measurements (peak temperature of the d.s.c. curves) and all other data come from visual observation by polarizing microscopy. The monophasic LC region between curves 1' and 2 is the most interesting for industrial practice because the molecules can be oriented to a high degree from this state

Table 1 Characterization of the copolymers

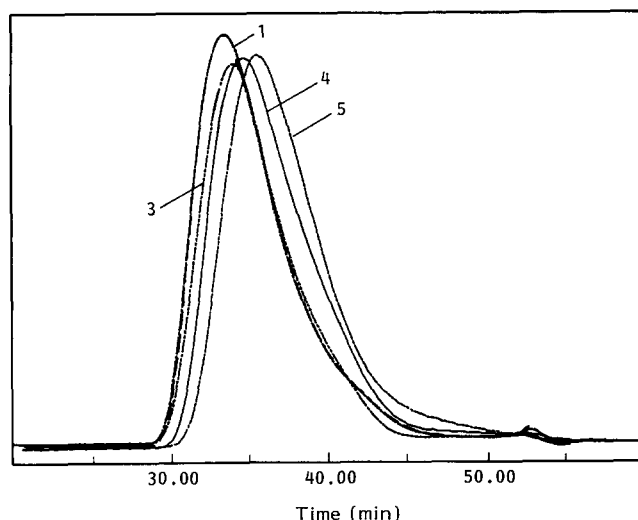| Polymer no.	Comonomer[a] content (mol%)		$[\eta]^d$ (dl g^{-1})	$\bar{P}_n^e$	$\bar{P}_w/\bar{P}_n^e$
	A[b]	B[c]			
1	0	0	5.6	70	2.0
2	0	0	1.9	–	–
3	4.3	4.3	4.5	34	2.6
4	9.6	8.6	4.2	34	2.9
5	17.6	16.0	3.1	26	3.0

[a] Comonomer unit:
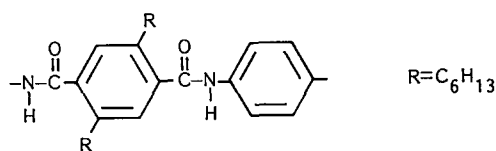
[b] In the reaction mixture
[c] Determined after hydrolysis of the copolymer
[d] In concentrated H_2SO_4
[e] From g.p.c. (c.f. *Figure 2*); $\bar{P}_n$ and $\bar{P}_w$ are the number- and weight-average degrees of polymerization

Figure 2 G.p.c. elution curves for PPTA homopolymer 1 and copolymers 3–5 (see *Table 1*) with attached n-hexyl side chains
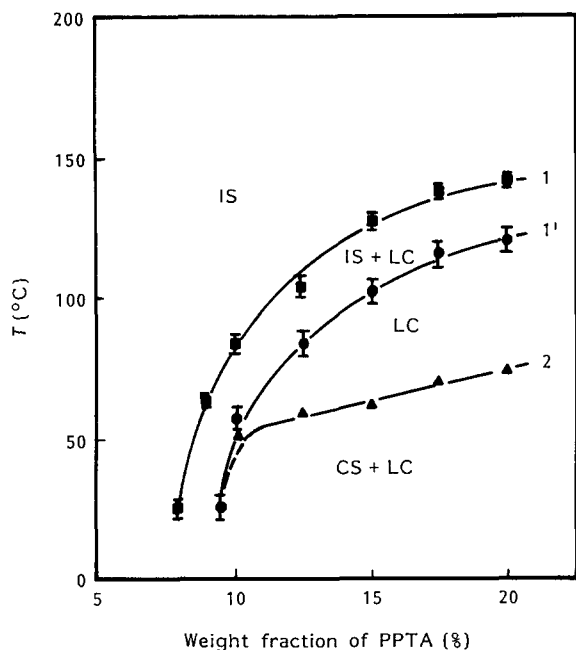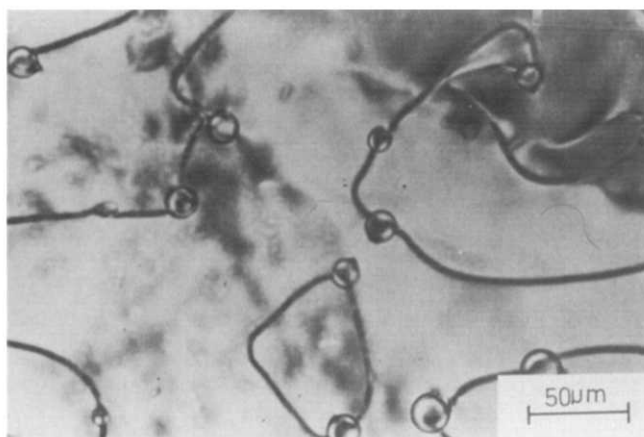
Figure 3 Partial phase diagram of homopolymer 1 (*Table 1*) in H_2SO_4. Data for curve 1 (■) and curve 1' (●) from polarizing microscopy, the error bars giving the limits in which the change of texture can be observed visually; data for curve 2 (▲) from d.s.c. measurements giving the temperature of the d.s.c. peak
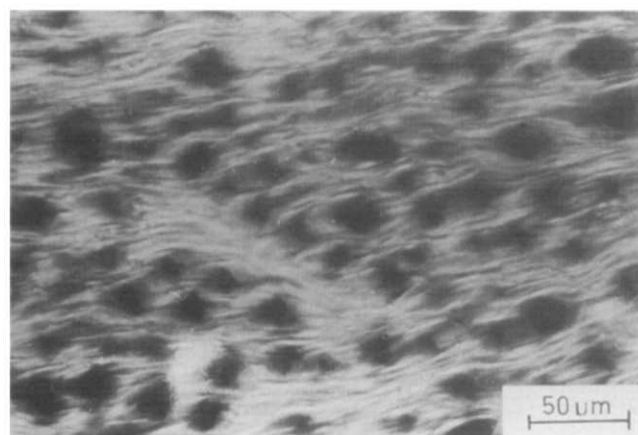
the sake of clarity the curves that separate the monophasic from the biphasic region (corresponding to curve 1' in *Figure 3*) are omitted. It is obvious that neither molecular weight nor attached side chains have an influence on the transition from the CS to the LC phase within the limits of experimental error. Also, they do not match a T^{-1} law as suggested recently by Picken[19]. Both an increase of side-chain concentration and a decrease of chain length
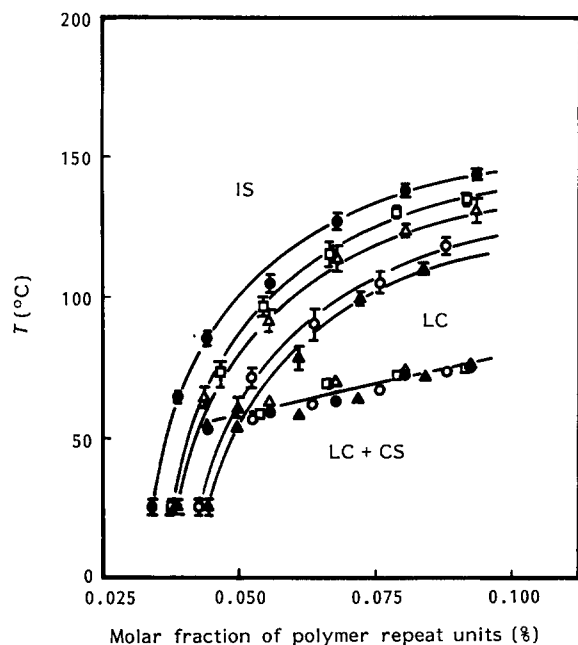

Figure 4 Optical micrograph (crossed polarizers) of the typical texture of the nematic mesophase, taken in the LC area of the phase diagram shown in *Figure 3*. The concentration of the solution was 17.5% w/w

when passing a spinneret. An optical micrograph of a sample from this region at a concentration of 17.5% w/w is shown in *Figure 4*. Under crossed polarizers a typical nematic texture is seen. It changes significantly when the temperature is lowered into the CS region. This is shown in *Figure 5*, where hedritic branching is the dominant feature of the observed texture. Similar pictures have been reported in the literature[17,18]. Due to the high viscosity of the solution the formation of hedrites is slow and thermodynamic equilibrium is reached only after a long time. This is why observation by light microscopy is unsuitable for determining transition temperatures[3]. Towards higher temperatures the monophasic LC region will change to a biphasic region where LC and IS phases coexist. *Figure 6* originates from the same sample in that temperature regime.

Curves 1 and 1' demonstrate the rather strong dependence of the LC to IS transition temperature on the concentration. The transition from the CS to the LC phase, i.e. the melting point, depends much less on concentration. However, an experimental difficulty occurs at low concentrations. Curve 2 seems to intersect curve 1' which would be contradictory to the phase rule. It is not possible to measure precisely in this region in part due to the limits of accuracy by which curve 1' can be measured as a consequence of polydispersity of the sample. We therefore suggest that the LC phase extends in the form of a small wedge towards lower temperatures.

Figure 7 displays corresponding experimental results for the two homopolymers 1 and 2 (*Table 1*), differing in molecular mass, and the three copolymers 3–5. The copolymers have only about half the degree of polymerization as the homopolymer 1. In order to compensate for the variation of molecular structure due to the attached side chains, temperatures are plotted *versus* molar composition of the mixture with H_2SO_4. In other words the composition given is normalized with regard to the number of repeat units in the system. For

Figure 5 Optical micrograph (crossed polarizers) of the texture of the crystal solvate in the LC + CS region of *Figure 3*

Figure 6 Optical micrograph (crossed polarizers) of the texture observed in the biphasic coexistence region. The dark areas show the isotropic and the bright areas the anisotropic solution in coexistence

Figure 7 Partial phase diagrams of five polyaramide–H_2SO_4 solutions. The biphasic regions (isotropic and anisotropic solution) are not shown. ●, homopolymer 1; ▲, homopolymer 2; □, copolymer 3; ○, copolymer 4; △, copolymer 5. Data relating to the LC to IS transition are from polarizing microscopy; data for the CS to LC transition are from d.s.c.
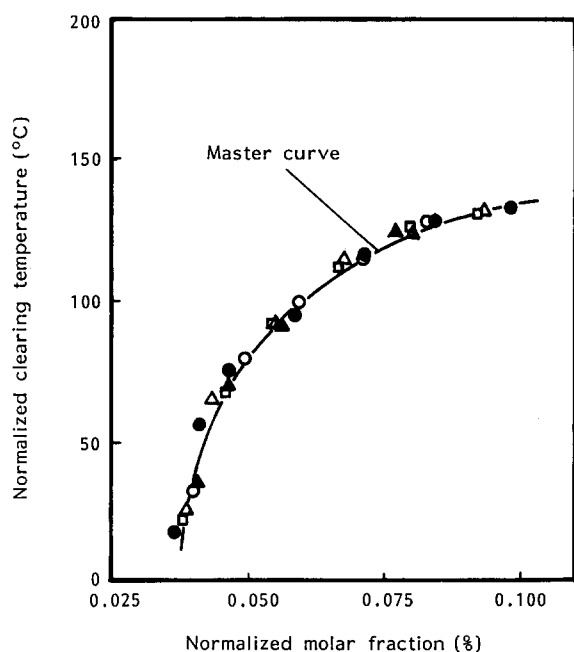
Figure 8 Master curve of normalized clearing temperatures *versus* normalized composition of five polyaramide–H_2SO_4 solutions. ●, homopolymer 1; ▲, homopolymer 2; □, copolymer 3; ○, copolymer 4; △, copolymer 5

reduce the clearing temperature and increase the critical concentration at which the anisotropic LC phase is formed at fixed temperature.

The clearing point curves can be shifted in a specific manner to give a master curve, as seen in *Figure 8*. The shift factors used to normalize temperature and concentration axes are:

$$\log a_T = T/T_r$$

and

$$\log a_x = x/x_r$$

where T_r and x_r are reference temperature and concentration, respectively. Numerical values are given in *Table 2*.

The existence of a single master curve for both homo- and copolymers is an essential result and illustrates that the molecular mechanisms responsible for establishing the equilibrium between isotropic and anisotropic solutions of stiff macromolecules are not influenced by attached side chains. This is particularly noteworthy in view of the fact that the side chains are attached in irregular sequence along the backbone and are expected to disturb the packing in the solid state. However, the critical concentration at which the anisotropic phase is formed at fixed temperature increases with increasing side-chain content as can be derived from the shift factors a_x. This observation shows clearly that flexible side chains behave like an 'attached solvent' for molecules with a rigid backbone[10,11,20,21]. Due to the side chains the rigid macromolecules are apparently in higher dilution and the transition temperature from the nematic to the isotropic state is reduced. Unfortunately the data presently at hand do not enable discrimination between the influence of chain length and of side-chain concentration.

The empirical relation between chain length and critical concentration was found by Bair *et al.*[22]. *Figure 9* shows a graph of the critical concentration at

Table 2 Shift factors used for the construction of the master curve in *Figure 8*

Polymer no.	Log a_T	Log a_x
1	0.975	1.050
2	1.000	1.000
3	0.992	1.010
4	1.025	0.935
5	1.035	0.925
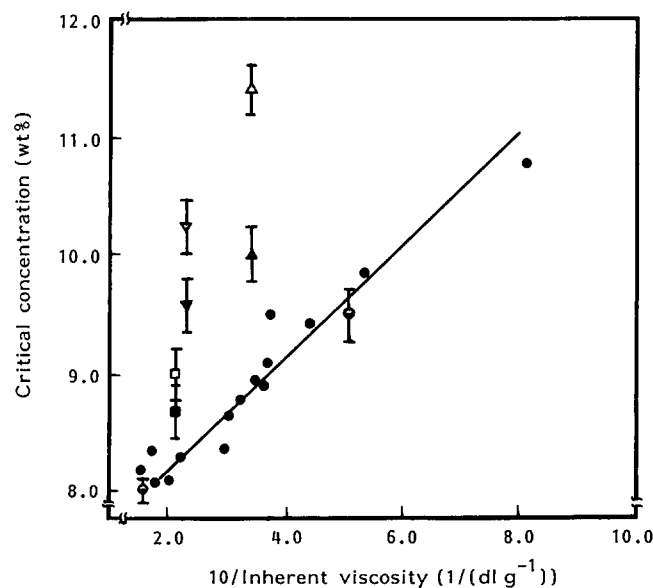
Figure 9 Plot showing the effect of side chains on the relation between the critical concentration at which the LC phase is formed at room temperature and the inverse inherent viscosities. ○, Measurements by Bair *et al.*[22]; ◓, this work for PPTA–H_2SO_4 systems. △, ▽, □ and ▲, ▼, ■, show the critical concentrations of the copolymer 3, 4, and 5 before and after deduction of the weight concentration of side chains, respectively

room temperature *versus* the inverse of the inherent viscosity of various polymers in sulfuric acid. Measurements for homopolymers in concentrated sulfuric acid which show a linear relation are taken from ref. 22. Our own measurements of homopolymers with inherent viscosities of 1.9 and 5.6 dl g^{-1} match the straight line. The values for the copolymers, however, do not fit at all (open symbols).

Considering the side chains simply as 'attached solvent' molecules, a correction to these data can be attempted. It is based on an assumed additivity of the weight concentrations of solvent and side chains, i.e.

$$w_x = w_p - w_s$$

where w_p is the apparent polymer concentration, and w_x and w_s are the concentrations of main and side chains, respectively. Applying this correction, the critical concentrations approach the straight line, but they do not fit in a satisfactory manner (solid symbols), showing that the idea of a simple additivity of the effect of the side chains is not justified.

EXPERIMENTAL

The sulfuric acid used for the polymer solutions was prepared by mixing concentrated H_2SO_4 (96%) with oleum containing 30% of free SO_3. The strength of the acid was determined by titrating a quantity of the mixture against an aqueous NaOH in order to determine the content of SO_3. The concentration of H_2SO_4 used in the investigation of phase diagrams was $99.5 \pm 0.5\%$.

Polymer solutions were prepared in a glove box under nitrogen atmosphere in order to avoid contact of the sulfuric acid with water from moist air. Polymer concentrations ranged from 8 to 20% w/w. Homogeneous solutions were obtained by intense mechanical stirring of the mixture contained in a glass vessel at 80°C for at least 4 h. Under these conditions the polymer dissolved only slowly due to the high viscosity of the solution.

The melting behaviour, i.e. the transition from crystalline to liquid crystalline state, was studied by d.s.c. measurements in a Mettler DSC 30 apparatus. Samples of the solution (10–30 mg) were sealed in stainless steel pans in the glove box under nitrogen atmosphere. The samples were first cooled to $-100°C$ at a rate of 10 K min^{-1}, then heated to $+120°C$ at a rate of 20 K min^{-1}. Solutions of low concentration were allowed to crystallize at room temperature for 1 week before measurement.

Clearing temperatures, i.e. the transition between the liquid crystalline and the isotropic state, were determined by means of a polarizing microscope (Zeiss Photomikroskop III) equipped with a heating stage (Leitz Mikroskopheiztisch 350 modified by a temperature control device). The solutions were sealed in the glove box between two glass slides by epoxy resin. Heating rates were 4 K min^{-1}. Repeated heating and cooling cycles yielded the same values of clearing temperature unless the final solution temperature exceeded 150°C, where chemical decomposition of the polymer was observed to proceed.

REFERENCES

1   Northolt, M. G. and Sikkema, D. J. *Adv. Polym. Sci.* 1991, **98**, 140
2   Gardner, K. H., Matheson, R. R., Avakian, P., Chia, Y. T. and Guerke, T. D. in 'Polymer for Fibers and Elastomers', American Chemical Society, Washington, DC, 1984, p. 91
3   Jingsheng, B., Anji, Z., Shengging, Y. and Chang, H. *J. Appl. Polym. Sci.* 1981, **20**, 1211
4   Weeyland, H. G. *Polym. Bull.* 1980, **3**, 331
5   Kulichokhin, V. G., Vasil'eva, N. V., Serova, L. D., Platonov, V. A., Mil'kova, L. P., Ardreyeva, L. N., Volokhina, A. V., Kudryavesev, G. I. and Papkov, S. P. *Polym. Sci., USSR* 1976, **18**, 672
6   Rodriguez-Parada, J. M., Duran, R. and Wegner, G. *Macromolecules* 1989, **22**, 2507
7   Schrauwen, C., Pakula, T. and Wegner, G. *Makromol. Chem.* 1992, **193**, 11
8   Stern, R., Ballauff, M., Lieser, G. and Wegner, G. *Polymer* 1991, **32**, 2096
9   Rehahn, M., Schlüter, A.-D. and Feast, W. J. *Synthesis* 1988, **5**, 386
10 Ballauff, M. *Angew. Chem.* 1989, **101**, 261
11 Ballauff, M. *Angew. Chem. Int. Edn* 1989, **28**, 253
12 Preston, J., Krigbaum, W. R. and Kotek, R. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 3241
13 Khan, A. H., McIntyre, J. E. and Milurm, A. H. *Polymer* 1985, **24**, 291
14 Vollbracht, L. and Veermann, T. J. US Patent 4 308 374, 1980
15 Peeters, J. AKZO research, Arnhem, The Netherlands, personal communication
16 Chu, B., Ying, Q., Wu, C., Ford, J. R. and Dhadal, H. S. *Polymer* 1985, **26**, 1408
17 Shouxi Chen and Yongze Jin *Polym. Commun.* 1989, **30**, 292
18 Roche, E. J., Allen, S. R., Gabara, V. and Cox, B. *Polymer* 1989, **30**, 1776
19 Picken, S. *Macromolecules* 1989, **22**, 1766
20 Ballauff, M. *Macromolecules* 1986, **19**, 1366
21 Ballauff, M. *Liq. Cryst.* 1987, **2**, 519
22 Bair, T. I., Morgan, P. W. and Killian, F. L. *Macromolecules* 1977, **10**, 1396