Eur. Polym. J. Vol. 27, No. 7, pp. 687–693, 1991
Printed in Great Britain. All rights reserved

0014-3057/91 $3.00 + 0.00

INTERACTIONS IN SOLUTIONS OF LIQUID-CRYSTALLINE POLYMERS—2. EXPERIMENTAL EVIDENCE FOR INTERMACROMOLECULAR AGGREGATION*

KONRAD WITKOWSKI and LESZEK WOLIŃSKI†
Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Wita Stwosza 57, Poland

(Received 13 August 1990)

Abstract—The results of investigations carried out by the methods of elastic and quasi-elastic light scattering are reported for three liquid-crystalline polymer samples in solution in tetrachloroethane. In polyester solutions with mesogenic groups in the backbone chain and in polyolefinosulphone solutions with polar side-groups, strong effects of macromolecular aggregation were observed. The effect of the polarity of mesogenic groups on the aggregation and internal arrangement in the aggregates is discussed.

INTRODUCTION

The phenomenon of metastable association of macromolecules has been extensively investigated [1–4]. In recent years, the processes of macromolecular association in polymer solutions containing rigid mesogenic groups have been of particular interest. Under such conditions, the associates can be considered as the origins of an ordered mesophase formed in dilute solution [5, 6]. In certain cases, an enhanced mesogenic group arrangement inside the aggregate can be observed because of change in the environmental conditions such as the solvent temperature or thermodynamic quality [7, 8]. Such phase transitions related to the arrangement variations inside the aggregates were predicted in Flory's theory [9].

In our previous paper [10], the problem of possible formation of domains within a single macromolecular with mesogenic groups in dilute solutions was discussed. Such considerations can be applied directly to associated macromolecules where the ordered domains embrace a greater number of macromolecules constituting a single aggregate.

Light scattering methods [1] are particularly useful for the investigation of macromolecular association phenomena, enabling the variations in the aggregate dimensions and molecular weight to be studied in great detail.

In the present paper, preliminary results of investigations of solutions of polymers with mesogenic groups by the method of elastic and quasi-elastic light scattering are reported. The compounds examined, were two polyolefinosulphone polymers with mesogenic side-groups [11] and a polyester [12] with a rigid mesogenic group in the backbone chain; they were synthesized in the Institute of Plastics in Darmstadt (Germany). Two of these polymers exhibit distinct macromolecular association even in dilute solutions.

THEORY

The angular distribution of the scattered light intensity in dilute macromolecular solutions, where macromolecular association is likely to occur, is described by modified Zimm's equation [1]:

$$\frac{K^*c}{\Delta R} = \frac{1}{\bar{M}_w^* P(\Theta)} + 2\bar{A}_2 c + 3\bar{A}\,\bar{M}_w^* c^2 + \cdots \quad (1)$$

where $K^* = [2\pi\tilde{n}(\partial\tilde{n}/\partial c)]^2/\lambda_0^4 N_A$ is the optical constant depending on the light wavelength, λ_0, the solvent refraction index, $\tilde{n}$, and the increment of the refraction index, $\partial\tilde{n}/\partial c$, N_A is the Avogadro number, and c is the concentration in g/cm^3. ΔR denotes the difference between the reduced intensities of light scattered in the solution and in pure solvent. The left-hand side of equation (1) can be determined experimentally, whereas the right-hand side comprises macromolecular parameters characteristic of the scattering centres, i.e. of macromolecules or associates. $\bar{M}_w^*$ denotes the concentration-dependent "apparent" molecular weight which, for a polydispersive sample, represents the weighted average molecular mass of associates, and becomes the actual weight-average molecular mass, $\bar{M}_w$, of the solute macromolecules for infinitesimally dilute solutions. The light scattering function, $P(\Theta)$, depends on the dimensions and shapes of the scattering centres. The gyration radius, $\bar{R}_g$, of the scattering centres can be obtained from the run of this function when condition $\bar{R}_g \approx \lambda_0$ is satisfied. Otherwise, $P(\Theta) \approx 1$ can be assumed. The virial coefficients, $\bar{A}_2$ and $\bar{A}_3$, in equation (1) describe the polymer–solvent interactions and the excluded volume effects.

The apparent molecular mass, $\bar{M}_w^*$, can be expressed as a function of the molecular mass, $\bar{M}_w$ of individual macromolecules by assuming a certain model of the association process. For instance, for the "open" association model, when an equilibrium exists between the associates with all possible degrees

---

*Carried out under Research Project 01.12.8 of the Polish Academy of Sciences.

†To whom all correspondence should be addressed.

of association from $N = 1$ to $N \to \infty$, the following relationship is obtained [1]:

$$(\bar{M}_w^*)^2 = (\bar{M}_w)^2 + 4 \times 10^3 c\, K_0 \bar{M}_w (U + 1) \quad (2)$$

where K_0 is the equilibrium constant for the formation and disaggregation of associates, and $U = \bar{M}_w / \bar{M}_n$ represents the heterogeneity of the molecular mass distribution in the polymer sample examined in the nonassociated state.

In quasi-elastic light scattering experiments, the autocorrelation function is usually measured [13]:

$$C(q, c, t) = \langle n(0)\, n(t) \rangle \quad (3)$$

where $n(0)$ and $n(t)$ are the numbers of photons reaching the detector during time intervals from 0 to Δt or from t to $t + \Delta t$, respectively, Δt being the sampling time fixed for a given experiment. The scattering parameter, $q = 4\pi\tilde{n}/\lambda_0 \sin(\Theta/1)$, expresses the dependence of the measured function upon the light wavelength, λ_0, and the scattering angle, Θ. For $q \to 0$, the autocorrelation function can be given by the relation [14]:

$$\lim_{q \to 0} C(q, c, t) = \left(A \int_0^\infty w(D)\, e^{-q^2 D \alpha D} \right)^2 + B \quad (4)$$

where D is the translational diffusion coefficient of macromolecules and $w(D)$ is the diffusion coefficient distribution function in which the polydispersity of macromolecular shape and dimensions has been taken into account.

Equation (4) can be solved and the distribution function, $w(D)$, determined by the use of appropriate approximation methods [10, 14]. The diffusion coefficient distribution function can be converted into macromolecular dimension distribution function, $w(R_H)$, by use of the Stokes–Einstein function:

$$R_H = \frac{kT}{6\pi\eta_0 D_0} \quad (5)$$

where R_H is the equivalent hydrodynamic radius of a macromolecule; η_0, the solvent viscosity; k, the Boltzmann constant; and T, temperature.

For a system of associates, the diffusion coefficient and associate dimension distribution functions, and not the distribution function of individual macromolecules, are obtained from the measurements of quasi-elastic light scattering.

The hydrodynamic radius of macromolecules, R_H, can be expressed by the parameters of the theoretical model describing macromolecular conformation in solution. For the description of conformation of macromolecules with rigid groups in the chain, a wormlike chain model [15] seem particularly suitable in which the hydrodynamic radius is expressed by the approximate relations:

$$R_H = \tfrac{1}{2} L \left(\ln \frac{L}{a} + 0.083 \frac{L}{\rho} - 1 + \frac{a}{b} \right)^{-1} \quad (6)$$

for rigid macromolecules ($\tfrac{1}{2}\rho \ll 1, L/a \gg 1$), and

$$R_H = \tfrac{1}{2} L \left(1.303 \sqrt{\frac{L}{\rho}} - \ln \frac{a}{2\rho} - 2.431 - \frac{a}{b} \right)^{-1} \quad (7)$$

for flexible macromolecules ($L/2\rho \gg 1$).

In the above formulae, L denotes the "geometrical" length of a stretched polymer chain, ρ is the persistence length determining the polymer chain rigidity, a is the geometrical diameter of the chain, and b is the chain hydrodynamic diameter within which possible rinsing and solvation effects are taken into account.

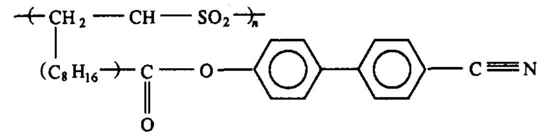
The persistence length can be obtained from the above formulae when the molecular mass and chemical composition of the chain are known, thus enabling the geometric chain dimensions to be determined.

EXPERIMENTAL PROCEDURES

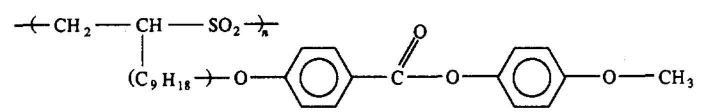
Samples

Three polymer samples with liquid-crystalline properties, synthesized in the Institute of Plastics in Darmstadt (Germany), were investigated. The particulars of the polymer synthesis and the results of calorimetric and spectroscopic measurements were reported by Braun and co-workers [11, 12].

The chemical structures of two polyolefinosulphone samples, denoted 1POS and 2POS, are shown below:

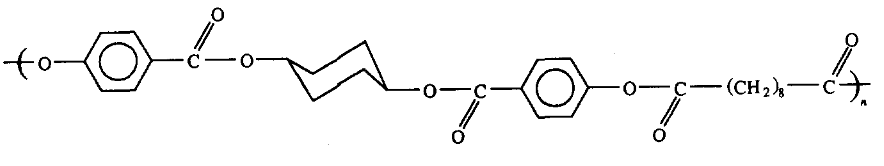


1POS



2POS

The sample denoted CO8 is a polyester with mesogenic groups in the backbone chain, having the following molecular structure:



CO8

As known from calorimetric measurements [11, 12], 1POS occurs as a S_A type smectic phase at temperatures from 63 to 152°; 2POS occurs in a liquid-crystalline phase of unidentified type in range 62 to 139°, whereas polyester CO8 occurs in a nematic phase at temperatures from 228 to 264°.

In the present paper, the results of the investgations these three polymer samples in dilute solutions in 1,1,2,2-tetrachloroethane at 25° are reported. The solvent, passed through a 0.22 μm Millipore filter, was spectroscopically pure.

Seven solutions with concentrations from 10^{-4} to 10^{-3} g/cm^3 were prepared for each sample. Measurements at higher concentrations up to 10^{-2} g/cm^3, and at 5×10^{-5} g/cm^3 were carried out also for CO8 and 1POS. The light scattering measurements were carried out after 3–4 days following the solution preparation, when the scattered light intensity variations occurring during 24 hr did not exceed 2%.

Light scattering measurements

The apparatus for simultaneous measurement of elastic and quasi-elastic light scattering, as well as the procedures employed for treatment of experimental data, have been described [10, 14, 16, 17]. A 35 mV He–Ne laser was used as the light source; the measurements of the elastic light scattering were carried out by the photon-counting technique. In the quasi-elastic scattering experiment, the values of the clipped autocorrelation function were determined by means of a 64-channel digital correlator.

The data obtained from the elastic scattering were analysed by Zimm's method of double extrapolation based on equation (1) [1, 15]. The mean diffusion coefficients, $\bar{D}_z(c)$, were determined from the quasi-elastic scattering measurements by the cumulant method [18], and next the mean hydrodynamic radius $\langle R_H^{-1} \rangle_z^{-1}$, was calculated by use of relation (5). The hydrodynamic radii distribution function, $w(R_H)$, was also determined by the solution of equation (4), using the modified Provencher regularization method [14, 19].

RESULTS AND DISCUSSION

The results of the light scattering measurements are shown in Figs 1–6 and Table 1. Zimm's diagrams for the three polymer samples are shown in Fig. 1. Figure 2 shows the dependence of inverse apparent weighted average of the molecular mass, $\bar{M}_w^*(c)$, upon the solution concentration, c, for all samples under investigation. These relations were obtained from the measurements of elastic light scattering carried out for these systems in the broader concentration range, from 5×10^{-5} to 10^{-2} g/cm^3, by extrapolation of the experimentally determined side of equation (1) to zero scattering angle:

$$\frac{1}{\bar{M}_w^*(c)} = \lim_{\Theta \to 0} \frac{K^* c}{\Delta R(\Theta, c)}. \tag{8}$$

The distributions of linear dimensions of the scattering centres are shown in Fig. 3 for the same polymer–solvent systems. More precisely, these are the distribution functions, $w(R_H)$, of the hydrodynamic radii of the scattering centres (molecules or aggregates) obtained from the quasi-elastic light scattering measurements on solutions at a concentration of 10^{-3} g/cm^3. These distributions were obtained by solving the integral equation (4) by the modified method [12] of Provencher's constrained regularization [19].

Figure 4 shows the concentration dependence of the mean hydrodynamic radius, $\bar{R}_H(c)$, of the scattering centres, obtained by determining the mean value of the translational diffusion coefficient, $\bar{D}_{oz}(c)$, from quasi-elastic light scattering by the cumulative method [18], and next by calculating the mean value of the hydrodynamic radius, $\bar{R}_H(c)$, from formula (5).

The dependence of the depolarized component of the scattered light reduced intensity, $R_{HV}(c)$, on the sample concentration, the former measured in the systems studied at a scattering angle $\Theta = 90°$, is shown in Fig. 5.

The values of individual molecular parameters obtained from the QELS and ELS measurements at a zero-concentration limit are summarized in Table 1.

The experimental results have been discussed briefly based on the analysis of the shape of Zimm's diagrams shown in Fig. 1 and on the values of the molecular parameters. The horizontal run of line $c \to 0$ in all diagrams indicates that the linear dimensions of the scattering centres were in all solutions examined considerably smaller than the incident light wavelength ($\langle R_G^2 \rangle_z^{1/2} < 0.05\lambda \approx 22$ nm). Determination of the mean gyration radius, $\langle R_G^2 \rangle_z^{1/2}$, of the scattering centres based on the angular scattered light intensity distribution was therefore impossible.

The curvature (concavity) of line $\Theta \to 0$ in Zimm's diagrams for the CO8 and 1POS solutions [Fig. 1(c) and (b)] indicates the occurrence of aggregation in these solutions [1], this being confirmed by the strong

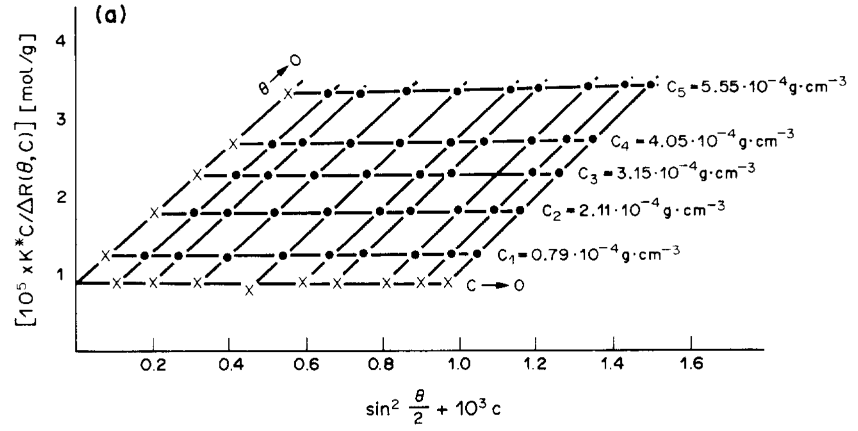
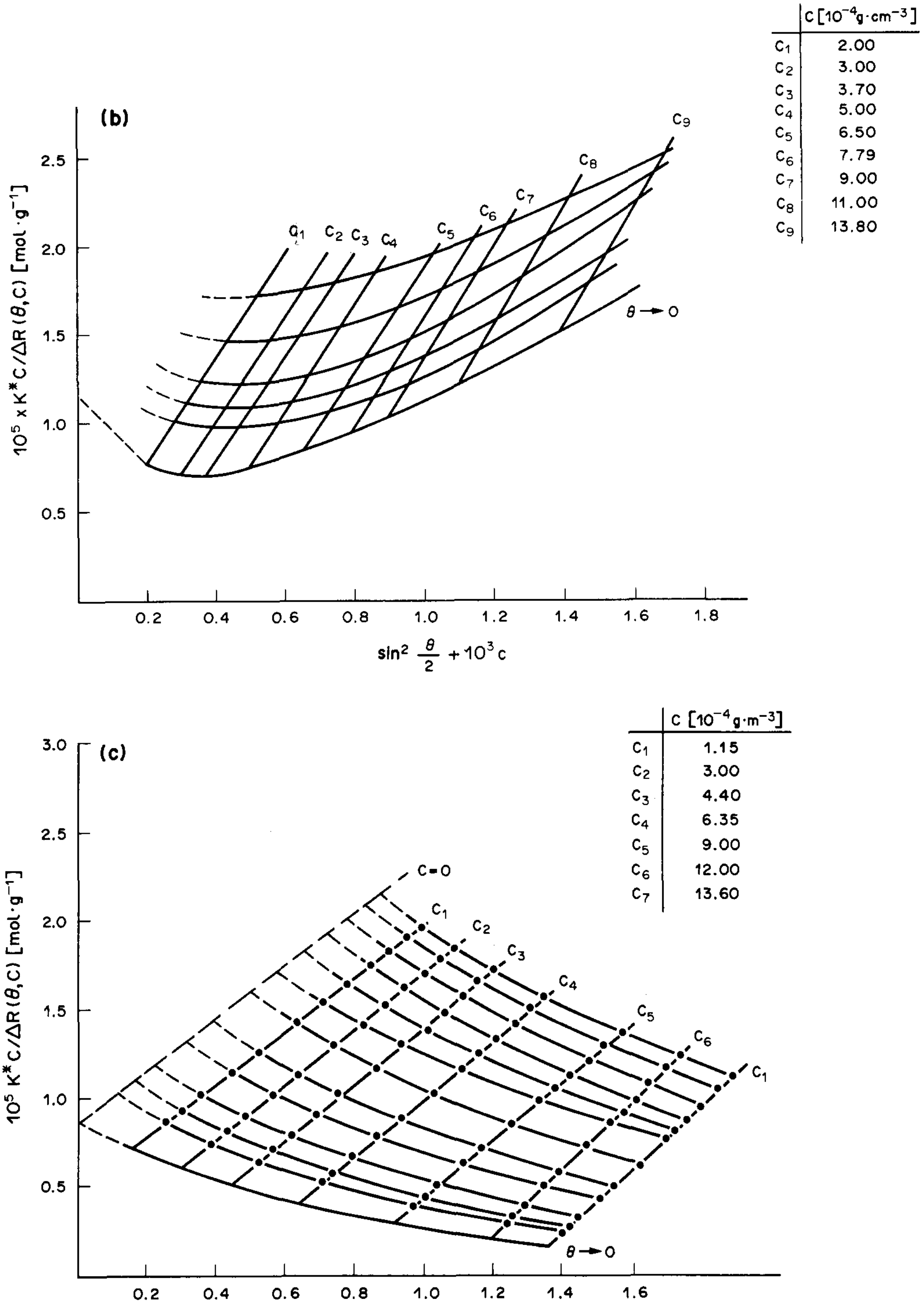


Fig. 1—*continued overleaf.*



	c [10^{-4}g·cm^{-3}]
c_1	2.00
c_2	3.00
c_3	3.70
c_4	5.00
c_5	6.50
c_6	7.79
c_7	9.00
c_8	11.00
c_9	13.80

	c [10^{-4}g·m^{-3}]
c_1	1.15
c_2	3.00
c_3	4.40
c_4	6.35
c_5	9.00
c_6	12.00
c_7	13.60

Fig. 1. Zimm's diagrams for the polymer sample solutions investigated in tetrachloroethane at 298 K. (a) 2POS, (b) 1POS, (c) CO8.

dependence of $\bar{M}_w^*$ on c, shown in Fig. 2, as well as by the enlargement of the linear macromolecular dimensions of the scattering centres, which in this case should be regarded as macromolecular associates, growing with increase in concentration (Fig. 4).

For polysulphone 2POS, Zimm's diagram [Fig. 1(a)] does not reveal these peculiarities. It can therefore be supposed that in this case the solutions were of molecular dilution, while the molecular parameters given in Table 1 can be attributed to single

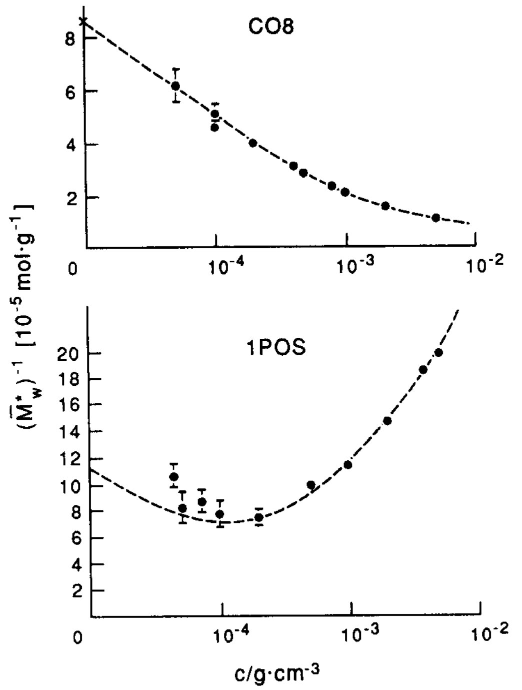


Fig. 2. Concentration dependence of apparent weighted average molecular mass, $(\bar{M}_w^*)^{-1}(c)$, determined for the polymer–solvent systems investigated by the elastic light scattering measurements.

molecules of this polymer in solution in tetrachloroethane. Slight curvature of line $c \to \Theta$ in Zimm's diagram for this polymer can be accounted for a quite high polydispersity of the 2POS sample, this being also confirmed by Figs 3 and 4; the dimension distribution, $w(R_H)$, obtained is fairly broad and typical of a polydisperse sample, whereas the weak dependence of the hydrodynamic dimensions of sample 2POS on concentration (see Fig. 4) indicates that the solution is of molecular dilution with negligible aggregation.

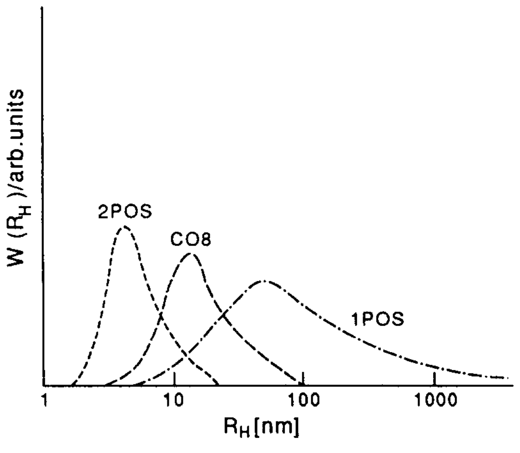


Fig. 3. Dimension distributions of the scattering centres obtained for the systems examined by quasi-elastic light scattering, using Provencher's regularization method for solution concentration $c = 10^{-3}$ g/cm^3. R_H, Hydrodynamic radius of the scattering centres (macromolecules or aggregates); $w(R_H)$, weight distribution functions of hydrodynamic radii.

Thus, the results of the light scattering measurements demonstrate that the association processes in polymer 2POS are negligible, whereas in the 1POS and CO8 polymer solutions macromolecular aggregation plays a key role.

Analysis of relation $\bar{M}_w^*(c)$ for those latter polymers (Fig. 2) enables at least two conclusions to be drawn. First, no characteristic bend of the plot $(\bar{M}_w^*)^{-1}(c)$, which could have been attributed to the occurrence of the critical micellization concentration (CMC) [1], was observed. It should rather be inferred that the value of CMC does not exist for the systems investigated and that it is the open type association that is dealt with, in which the associates of all possible dimensions with aggregation degrees from 0 to ∞ coexist in dynamical equilibrium. The existence of this type of association also seems to be indicated by the dimensions of the scattering centres (associates) increasing smoothly with concentration for the two polymers considered (see Fig. 4). Second, the increase of function $(\bar{M}_w^*)^{-1}(c)$, approximately linear, at higher concentrations suggests that the systems are characterized by positive values of the second virial coefficient, $\bar{A}_2$, i.e. thermodynamically tetrachloroethane seems to be a good solvent for the polymers.

In the case of the open type aggregations in thermodynamically favourable solvents, the complex form of relations $(\bar{M}_w^*)^{-1}(c)$ shown in Fig. 2 is described by equations (1) and (2) (under certain simplifying assumptions—*cf* Ref. [1]). The values of the parameters describing both the individual macromolecules, such as weighted average molecular mass $\bar{M}_w$, virial coefficient $\bar{A}_2$, and the aggregates, the equilibrium constant K_0, describing the open association processes, can be determined by iteration which fits the numerical values of these parameters in equations (1) and (2) to the relation obtained experimentally. This procedure yields reliable results if the experimental data are available for a sufficiently broad concentration range.

In solutions of CO8, the aggregation degree grows so slowly with increase of concentration that it was possible to use this procedure for reliable determination of the parameters named above by employ-

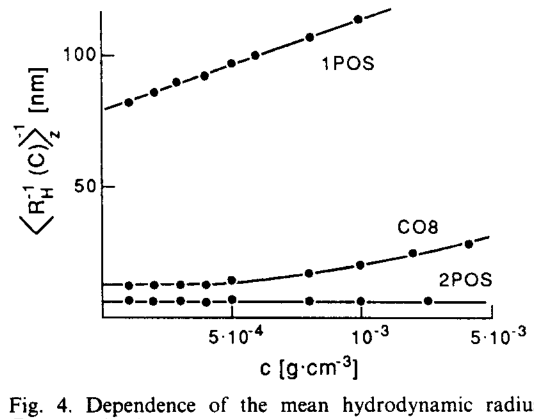
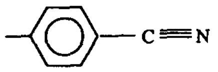


Fig. 4. Dependence of the mean hydrodynamic radius, $\bar{R}_H \equiv \langle R_H^{-1}\rangle_z^{-1}$, on concentration for the samples investigated in tetrachloroethane.

ment of the light scattering results for concentrations from 5×10^{-5} to 10^{-2} g/cm^3. The values of these parameters are given in Table 1.

For 1POS sample, quite strong aggregation has already been observed at the lowest concentrations permitting the light scattering experiment to be carried out. As a consequence, it was not possible to find precisely the values of parameters occurring in equations (1) and (2). The values of $\bar{M}_w$ and $\bar{A}_2$ given in Table 1 for 1POS cannot be therefore regarded as referring to individual macromolecules. They most probably describe the aggregates of unknown aggregation degree.

The mechanism of interactions responsible for the intermolecular aggregate formation in polymer solutions of types considered here has not yet been elucidated. Nevertheless, the differences in the structure of side-groups in the polysulphones should be pointed out. The side-group in 1POS carries a strongly polar



group, whereas the side-groups in the nonassociating 2POS polymer do not include such highly polar group, whereas the side-groups in the nonassociating 2POS polymer do not include such highly polar bonds. For polymers with mesogenic groups in the backbone, including the CO8 polyester, the association capability has frequently been observed [6, 7]. It seems possible that, with enhanced chain rigidity, the weaker interactions between the phenyl rings and the ester groups —COO— are sufficient to cause this phenomenon.

The arrangement of mesogenic groups within aggregates constitutes a separate problem. The molecular arrangement within aggregates has been dealt with in numerous theoretical studies which, however, were concerned mainly with simple systems markedly different from those considered here. Aggregates built of low molecular mass compounds were in most cases investigated [20]. Macromolecular aggregation induced by the presence of strongly polar terminal groups in polymer chains was recently observed by Wang *et al.* [21] and Bug *et al.* [3]. The reported results indicate the existence of essential differences in the internal arangement of the aggregates, as well as in the mechanism of formation between aggregates of low molecular mass substances and those of macromolecules. These differences are due to strong excluded volume effects in polymer solutions and to the tendency, typical of macromolecules, of adopting conformations with maximum entropy. However, unlike systems considered in Refs [21, 3], the characteristic of the polymers with liquid-crystalline properties dealt with in the present paper is the occurrence of numerous polar centres distributed along the backbone chain or in side-groups. Therefore, the direct employment of the results of model calculations reported in the cited papers is not possible. It should, however, be anticipated that also in the cases considered here the degree of the arrangement of whole macromolecules and of the mesogenic groups alone within the aggregates would be determined by the conditions of the equilibrium between the free energy of the mesogenic groups, decreasing in the ordered state, and the entropy term, increasing with the enhancing arrangement, which reflects the tendency of the polymer chains to adopt unordered conformations. This theoretical approach is to a great extent analogous to that applied in Refs [22, 23] for the description of phase transitions in polymer liquid crystals.

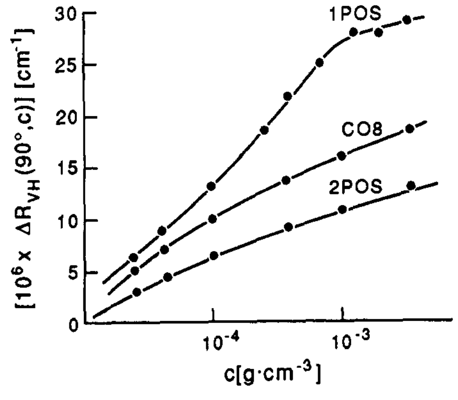


Fig. 5. Concentration dependence of the anisotropic component of excessive reduced scattered light intensity for the polymer sample solutions in tetrachloroethane.

Table 1. Molecular parameters determined for polyester CO8 and polysulphones 1POS and 2POS in tetrachloroethane at $T = 298$ K

	$C_2H_2Cl_4$		
$\tilde{n}$[a]	1.546		
$\eta_0[10^{-3}$ N sec m$^{-2}]$	0.539		
	CO8	1POS[h]	2POS
$\frac{\partial \tilde{n}}{\partial c}$ [cm^3 g^{-1}][b]	0.152	0.159	0.146
$\bar{M}_w \times 10^{-3}$ [g mol^{-1}][c]	11.6	89.0	18.6
$A_2 \times 10^4$ [g^{-2} cm^3 mol][c]	2.6	0.42	0.83
$\bar{D}_{oz} \times 10^7$ [cm^2 sec^{-1}][d]	3.11	0.506	6.32
$\bar{R}_H$ [nm][e]	13	80	6.4
$\bar{R}_{Hn} : \bar{R}_{Hw} : \bar{R}_{Hz}$[f]	1:4:7.5	1:8:24	1:2.7:3.5
K_0[g]	10^5	3×10^7	—

[a] Refraction index for light wavelength 633 nm.

[b] Measured by means of an R-401 (Waters) differential refractometer for $\lambda_0 = 633$ nm.

[c] Obtained by the method of double Zimm extrapolation from elastic light scattering measurements.

[d] Obtained by the method of cumulants from quasi-elastic light scattering measurements.

[e] Determined from equation (5).

[f] Parameters describing the polydispersion of hydrodynamic radii, $w(\bar{R}_H)$, determined from quasi-elastic light scattering measurements by the solution of equation (4) with the use of equation (5).

[g] Molecular association equilibrium constant determined from elastic light scattering measurements according to equations (1) and (2).

[h] Values referring to the aggregates—the extrapolation to $c \to 0$ was not possible because of strong aggregation even at the lowest concentrations.

This would suggest the possibility to observe phase transitions related with the changes in the internal arrangement of aggregates while changing the thermodynamic conditions (temperature or solvent quality). It seems that such a possibility exists also for the solutions considered here, the observations being, however, complicated by polydispersive effects.

The data on the internal arrangement of aggregates can only be indirectly obtained from the light scattering experiment [7]. For example, the high anisotropic component of the scattered light intensity, ΔR_{HV}, increasing quite strongly with concentration (Fig. 5) for the CO8 solutions, indicates fairly good arrangement of the mesogenic groups—hence, also the whole chains—in the aggregates of this polymer.

On the other hand, in the solutions of 1POS, considerably weaker increase in the anisotropic component intensity has been observed with rising concentration, with simultaneous faster enlargement of the aggregate dimensions as compared to the CO8 solutions [according to the data in Fig. 4, $\bar{R}_H(c) \sim c^{0.5}$ for CO8, and $\bar{R}_H(c) \sim c^{0.61}$ for 1POS solutions]. This difference might indicate a lower degree of the mesogenic groups arrangement in the solutions of this polymer compared to the CO8 solutions. It would, however, be possible to draw quantitative conclusions in this regard when comparing the experimental data with results of precise model calculation.

Concluding, the results indicate the occurrence of intermolecular aggregation in solutions of the polyester with mesogenic groups in the backbone chain, and in one of the two polysulphones with side-groups including strongly polar —C≡N bonds.

Several molecular parameters describing both the single macromolecules in solution and the macromolecular aggregation processes in the CO8 and 1POS solutions have been determined.

The data referring to the dependence of the hydrodynamical dimensions of aggregates on concentration, when compared to the concentration dependence of the anisotropic component of the scattered light intensity, suggest a higher degree of arrangement of the mesogenic groups within CO8 polyester aggregates as compared to that within 1POS polysulphone aggregates.

Acknowledgement—The authors thank Professor Dietrich Braun (Deutsches Kunststoff-Institut in Darmstadt, Germany) for kindly putting at our disposal the polymer samples with liquid-crystalline properties.

REFERENCES

1. H. G. Elias. Study of the association and aggregation of polymers via light scattering. In *Light Scattering from Polymer Solutions* (edited by M. B. Huglin). Academic Press, New York (1972).
2. H. G. Elias. *J. Polym. Sci.* **11,** 137 (1973).
3. A. L. R. Bug, M. E. Cates, S. A. Safran and T. A. Witten. *J. chem. Phys.* **87,** 1824 (1987).
4. M. E. Cates and T. A. Witten. *Macromolecules* **19,** 732 (1986).
5. C. C. Lee, S. G. Chu and G. C. Berry. *J. Polym. Sci.* **B21,** 1573 (1983).
6. G. C. Berry. *J. Polym. Sci.; Polym. Symp.* **65,** 143 (1978).
7. G. C. Berry, C. C. Wei-Berk and R. Fumakawa. *Polym. Prepr. Am. chem. Soc.* **27,** 228 (1986).
8. G. Wenz, M. A. Muller, M. Schmidt and G. Wegner. *Macromolecules* **17,** 837 (1984).
9. P. J. Flory. *Adv. Polym. Sci.* **59,** 1 (1984).
10. L. Woliński, K. Witkowski and Z. Turzyński. *Eur. Polym. J.* **26,** 521 (1990).
11. D. Braun, R.-P. Herr and N. Arnold. *Makromolek. Chem. Rapid Commun.* **8,** 359 (1977).
12. D. Braun and U. Schülke. *Makromolek. Chem.* **187,** 1145 (1986).
13. B. J. Berne and R. Pecora. *Dynamic Light Scattering.* Wiley, New York (1976).
14. L. Woliński and K. Witkowski. *Makromolek. Chem.* **188,** 2203 (1987).
15. H. Yamakawa. *Modern Theory of Polymer Solutions.* Harper & Row, New York (1971).
16. K. Witkowski and L. Woliński. *Optik (Stuttgart)* **73,** 3 and 45 (1986).
17. K. Witkowski. *Optik (Stuttgart)* **73,** 91 (1986).
18. D. E. Koppel. *J. chem. Phys.* **57,** 4814 (1972).
19. S. W. Provencher. *Makromolek. Chem.* **180,** 201 (1979).
20. Th. F. Tadras (Ed.). *Surfactants.* Academic Press, London (1984).
21. Z. G. Wang and S. A. Safran. *J. chem. Phys.* **89,** 5323 (1988).
22. X. J. Wang and M. Warner. *J. Phys.* **A19,** 2215 (1986).
23. X. J. Wang and M. Warner. *J. Phys.* **A20,** 713 (1987).