Liquid crystalline polyester and polysulphone mixtures: observation of phase separation and aggregation

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As a preliminary investigation, the flexibility of a wholly aromatic paralinked random copolyester is studied from measurements of the radius of gyration by small angle X-ray scattering and of the hydrodynamic radius by viscosimetry. In this way, the persistence length has also been evaluated. The ability of this polyester to be oriented by means of a magnetic field (as shown by ^{1}H n.m.r.) confirms the high flexibility of the polyester backbone. In concentrated solutions, the polyester aggregates. An indication of the aggregate size is inferred from the wide angle light scattering (WALS) study. When polysulphone is added to these mixtures, the demixing process is also preceded by aggregation. The structure of these aggregates is investigated by WALS and indicates that a state of ordering exists which is a precursor to that found in the mixtures in the solid state.

(Keywords: thermotropic polyester; composites; phase separation; aggregation; wide angle light scattering)

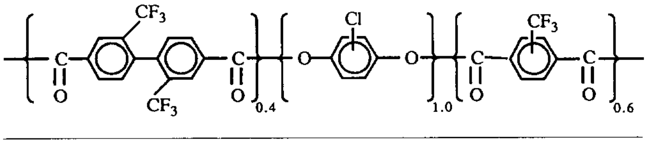
INTRODUCTION

Liquid crystalline (LC) polyesters with good solubility properties in organic solvents, as well as low transition temperatures, are now available. It is of great interest to mix them with conventional flexible polymers, the ultimate purpose being to obtain composites miscible at the molecular level. However, it is well known that most polymers, and particularly liquid crystalline polymers (LCPs) and conventional flexible polymers, are incompatible which is a major handicap to their blending. The mechanisms and kinetics of their phase separation have been studied by several authors[1–3].

The purpose of this paper is to investigate the statistical structure of systems consisting of two incompatible polymers: a LCP and a conventional polymer. It will be shown that a phase separation occurs in a system composed of a LC random copolyester mixed with polysulphone. Aggregation behaviour is observed in binary systems of LC polyester/solvent and ternary systems of LC polyester/flexible polymer/solvent, using wide angle light scattering (WALS). As a preliminary study, the chain flexibility of the copolyester is also investigated.

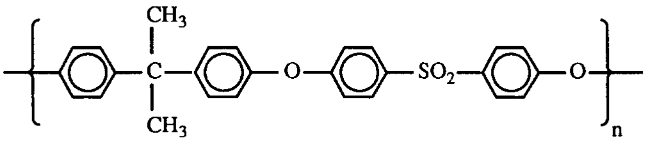
MATERIALS

The polyester used, synthesized by Polaroid[4,5], is a completely aromatic, paralinked random copolyester. Its chemical structure is



Its number-average molecular weight, $M_n = 10\,400$ g mol^{-1} with a polydispersity of 2.1 (ref. 6). The maximum solubility in tetrahydrofuran (THF) is reached at 48.5% (w/v) at room temperature. It undergoes a second order transition between the glassy and nematic states at 110°C. Neither a melting point nor a clearing point have been detected up to the degradation temperature $T = 443$°C (under air) of the pure polymer. The random copolymerization of three monomers with different structures and lengths generates a polymer whose backbone has little symmetry. Interchain interactions are further decreased by the disorder introduced along the backbone by the non-planar substituted biphenyl. These structural properties are responsible for the good solubility, the low glass transition temperature and the semi-stiffness of this polyester.

The flexible polymer used was a polysulphone ($M_w = 30\,000$ g mol^{-1}), purchased from Aldrich, chosen because of the similarity in chemical structure with the polyester. Its chemical structure is



It is also soluble in THF. This purely amorphous material undergoes a glass transition at $T_g = 185$°C, as determined by d.s.c. It was used as received.

Preparation of composite films

The composition of the blends was LCP:flexible polymer, 40:60 (wt%). Blend films were prepared according to the following methods:

1. *Polymer-coating.* A glass slide was coated with a few drops of a ternary solution containing 0.2 wt% LCP.

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It was placed above a THF bath in a dish, the top of which was covered with filter paper. The solvent was allowed to evaporate slowly for 12 h from the ternary solution. The sample was then dried under vacuum for 24 h at room temperature. The thickness of the blend layer was ~15–20 μm.

2. *Spin-casting*. These films were cast by spinning a few drops of a ternary solution containing 0.2 wt% LCP on a microscope slide. The sample thickness was ~7 μm.

With both methods, the films obtained were homogeneous and almost totally transparent.

EXPERIMENTAL

The properties of the polymer samples were investigated in several ways.

Small angle X-ray scattering

SAXS experiments were performed using a Kratky camera equipped with a Braun position-sensitive X-ray detector coupled to a Canberra multichannel analyzer. The Siemens X-ray generator operated at the copper Kα wavelength $\lambda = 1.54$ Å. The scattered intensities were measured over a q-range of 3.85×10^{-3} to 11.47×10^{-2} Å^{-1}, calibrated using a duck tendon. The solutions were placed in Lindeman capillary tubes of 1 mm diameter, which were sealed with paraffin films (parafiln M, American Can Company). The scattered intensities were corrected for the background scattering arising from the pure solvent and for the detector wire sensitivity using an Fe55 source. However, they were not corrected for the error due to the slit-focused nature of the incident beam. The concentrations ranged from $c = 2.51$–0.99% (weight of polymer per unit weight of solution). These concentrations were determined precisely by weight at $\pm 1\%$.

Viscosity

Viscosity measurements were performed with a Cannon 25 viscosimeter, placed in a thermostated bath. The temperature was kept constant at $T = 25 \pm 0.1$°C. Flow times were >100 s. The concentrations ranged from $c = 0.89 \times 10^{-2}$ to 0.090×10^{-2} g cm^{-3} (weight of polymer per unit volume of solution). Great care was taken in the preparation of the solutions in order to get high precision concentrations. These were determined with an accuracy of $\pm 1\%$. For a given concentration, the measured times were the same with a dispersion of $<1\%$.

Nuclear magnetic resonance

No sample preparation was necessary for the bulk studies. The ^{1}H n.m.r. experiments were performed using a Bruker CXP90 spectrometer operating at 90 MHz and were carried out at the CEN Grenoble (France). A sample of about 50 mg was placed in a conventional n.m.r. tube (5 mm diameter) and annealed for 12 h at 160°C under magnetic field ($B \cong 2.1$ T). The temperature was raised to 180°C for 5 min, then decreased progressively in a series of 5°C steps down to 100°C. At each step the temperature was kept constant for 5 min before recording the spectrum.

Optical microscopy

The observations were made using a Leitz microscope equipped with a camera for Polaroid 55 films. A Mettler hot stage was used for the thermal treatments.

Small angle light scattering

The light scattered from composite films was studied with a two-dimensional Optical Multichannel Analyser (OMA III, Princeton Applied Research), operating at $\lambda = 632.8$ nm. This enabled the recording of scattered intensities of u.v. as a function of the scattering and azimuthal angles. The experimental set-up is described in ref. 7. U.v. patterns were corrected for dark count.

Wide angle light scattering

WALS measurements on polymeric solutions were performed using a BI200SM light scattering goniometer (Brookhaven Instruments) at $\lambda = 632.8$ nm. These experiments were carried out at Polaroid Inc. (Cambridge, MA). Intensities were measured between 30 and 140°. They were corrected for dead time, dark count, scattering volume, refraction and absorption; (reflection and multiple scattering were neglected). The temperature was kept constant at 24°C. Absolute intensities were determined by calibration with toluene; Rayleigh ratios of toluene, refractive index increment and THF refractive index were taken as, respectively, V_v(toluene, 90°) $= 10.6 \times 10^{-6}$ cm^{-1}, H_v(toluene, 90°) $= 3.3 \times 10^{-6}$ cm^{-1} (refs 8, 9), $dn/dc = 0.1236$ ml g^{-1} (ref. 10) and $n_{\mathrm{THF}} = 1.4036$ at $\lambda = 632.8$ nm and $T = 24$°C. Solutions with different weight ratios of the polyester to the flexible polymer were studied. The concentration ranges were: (i) $c = 9.88 \times 10^{-2}$ to 0.45×10^{-2} g cm^{-3} for polyester only in solution; (ii) $c = 6.85 \times 10^{-2}$ to 0.45×10^{-2} g cm^{-3} for the ratio 7:1; (iii) $c = 5.31 \times 10^{-2}$ to 0.46×10^{-2} g cm^{-3} for the ratio 3:1 (concentrations are in gram of polyester per unit volume of solution). The demixing concentrations (at which the solution becomes optically turbid) are about 8×10^{-2} and 6×10^{-2} g cm^{-3} for the ratios 7:1 and 3:1, respectively. The more concentrated solution was filtered through a 0.45 μm Millipore filter into the cell. The following concentrations were obtained by dilution in the cell. The commercial solvent had been distilled and was further filtered through a 0.2 μm Millipore filter.

POLYESTER FLEXIBILITY

As a first step in this work, attention was focused on the chain flexibility. It was investigated by comparing the radius of gyration and the hydrodynamic radius of the chain determined by SAXS and viscosimetry respectively, to the ideal Gaussian mean end-to-end distance. The possibility of aligning this LC polyester by means of a magnetic field was also studied.

Mean chain size in dilute solution

To estimate the radius of gyration R_g of the polyester chain, the X-ray intensity $I(q)$ scattered by dilute solutions of polyester was analysed according to the Guinier formula[11]:

$$I(q) = I(0)\left(1 - \frac{R_g^2}{3} q^2 + o(q^2)\right) \tag{1}$$

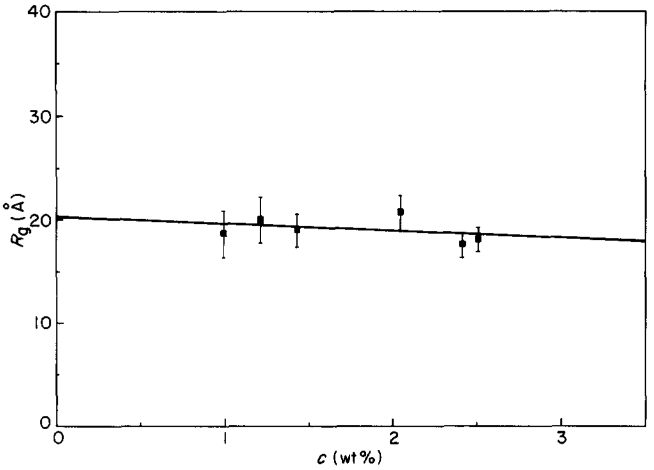

Figure 1 Dependence of the smeared radius of gyration R_g of the polyester in dilute THF solution upon the concentration c

where the wave vector $q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the angle between incident and scattered beams.

The concentration dependence of the smeared radius of gyration, derived from the slope of the Guinier plot for q between 2.80×10^{-2} and 5.62×10^{-2} Å^{-1} is shown in *Figure 1*. The extrapolation at $c = 0$ yields $R_{gc\to 0} = 20.2 \pm 2.6$ Å. Let R_{gdes} be the value of R_g obtained after desmearing. Guinier and Fournet[12] showed that $R_g^2 = 1.071 R_{gdes}^2$. Thus, the error due to the slit-smeared effect is about 4%, which is below the experimental error. An estimate of the concentration of chain overlap[13] $c^* = 3.5 \times 10^{-2}$ g cm^{-3} is derived from $R_{gc\to 0}$.

The viscosity of the same polyester solutions was represented by a power series in the concentration variable[14] as:

$$\eta = \eta_0(1 + [\eta]c + kc^2 + o(c^2)) \qquad (2)$$

The concentration c is the weight of polymer per unit volume of solution. The specific viscosity $(\eta - \eta_0)/\eta_0$ is plotted *versus* the polyester concentration in *Figure 2*. Data were found to fit a parabolic curve. The fit yields $[\eta] \cong 0.70$ dl g^{-1}.

The hydrodynamic radius[13] R_η of the polyester, considered as a hard sphere, is such that:

$$\eta = \eta_0\left(1 + 2.5 N_a n \frac{4\pi R_\eta^3}{3V}\right) \qquad (3)$$

where n is the number of moles of chains, V is the solution volume and N_a is the Avogadro number. In the case of a polydispersed sample, equation (3) becomes:

$$\eta = \eta_0\left(1 + 2.5\frac{4\pi}{3} N_a c \frac{\int n(M)R_\eta^3(M)\,\mathrm{d}M}{\int n(M)M\,\mathrm{d}M}\right) \qquad (4)$$

with $n(M)$ the number of moles of chains of molecular weight M and radius $R_\eta(M)$.

Consequently, the intrinsic viscosity is expressed as:

$$[\eta] = 2.5 N_a \frac{4\pi}{3} \frac{\int n(M)R_\eta^3(M)\,\mathrm{d}M}{\int n(M)M\,\mathrm{d}M} \qquad (5)$$

or

$$[\eta] = 2.5 N_a \frac{4\pi}{3} \frac{\langle R_\eta^3 \rangle}{M_n} \qquad (6)$$

with

$$\langle R_\eta^3 \rangle = \frac{\int n(M)R_\eta^3(M)\,\mathrm{d}M}{\int n(M)\,\mathrm{d}M} \qquad (7)$$

The numerical value of $R_\eta = \langle R_\eta^3 \rangle^{1/3}$ is about 49 Å.

The chain contour length L can be estimated from M_n, the molecular weight of each monomer, and the length of the bonds C=C, C–C, C–O. This yields ~300–350 Å for L. Therefore, the ratio R_g^2/L is too small compared to L for the chain to be considered as a Porod–Kratky chain[15]. The persistence length l can be estimated by means of the formula derived by Benoit and Doty[16] for flexible chains. This gives 3.4–4 Å for l, which is a rough value considering the random structure of the chain and the polydispersity of the system. According to this determination, l is referred to the total number of skeletal bonds, as is usual[17], and not to the number of repeat units. It is verified that $l/L \ll 1$. This indicates a high chain flexibility.

Furthermore, it is found that $R_\eta \cong 6^{1/2} R_g$ in accordance with a mean end-to-end distance of a chain that obeys Gaussian statistics. The values of R_g and $R_\eta/6^{1/2}$ are very close to each other. However, both methods do not yield the same mean value of the radius because of the sample polydispersity. From SAXS, the mean R_g is a z-average while from viscosimetry the mean R_η is given by equation (7).

In conclusion, these results suggest that the conformation of an isolated polyester chain, i.e. in dilute regime, is closer to a coil than to a rod. The small order of magnitude found for the persistence length suggests that the short bonds –CO—O– probably contribute largely to the flexibility, despite the presence of stiff elements along the chain. This is also consistent with the low transition temperature (110°C) which is observed. Usually[18], copolyesters exhibit more stiffness, which induces higher transition temperatures (300–400°C) and less solubility.

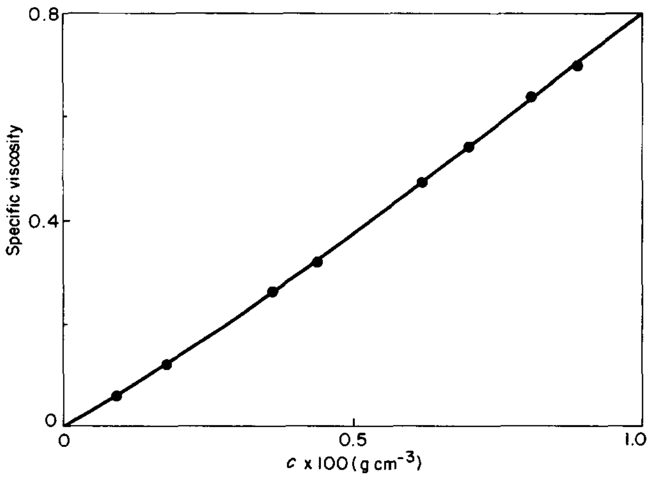

Figure 2 Dependence of the specific viscosity of polyester/THF solutions on the concentration c. A parabolic curve fits the data

Orientational property in nematic state

Another property of this polyester lies in its ability to be oriented macroscopically by means of a magnetic field. Indeed, a way of aligning polymeric chains in bulk consists of placing a molten sample in the nematic state under a magnetic field[19]. Due to the anisotropy of diamagnetic susceptibility, the molecules tend to orient cooperatively parallel to the direction of the magnetic field and a situation of equilibrium is achieved when the mean nematic director lies parallel to the applied field. A monodomain is then obtained.

A typical spectrum is represented in *Figure 3a*. The ^{1}H n.m.r. line shape is rather complicated due to the large number of proton spins in dipolar interaction. The mean feature is the existence of a doublet $\Delta\nu$, which originates essentially from the dipolar interaction between spins in *ortho*-positions on the phenyl rings. It has been shown within a good approximation, neglecting the biaxiality of the nematic order, that this splitting is nearly proportional to the order parameter S.

As can be seen in *Figure 3b*, the splitting, i.e. the order parameter, is constant over the temperature range studied and is ~17 kHz. It is worth noting that this polyester degrades at 443°C before reaching the clearing temperature. The highest studied temperature (180°C) is far from what would have been the transition temperature. The dependence of S on temperature is not unexpected for a first order transition between the nematic and isotropic states. Moreover, the broadening of the spectrum which occurs with decreasing temperature suggests, by analogy with previous studies[20], that this constant value of the order parameter results from the contribution of two competing effects: (i) an effect of ordering by decreasing the temperature which would tend to increase the n.m.r. splitting; and (ii) an increase of the average viscosity by decreasing the temperature which tends to 'freeze' the long wave orientational fluctuations of the nematic director with respect to the time scale associated with ^{1}H n.m.r. These frozen fluctuation modes appear, as seen by n.m.r., as a partial disordering resulting in the decrease of the measured n.m.r. splitting and the broadening of the n.m.r. spectrum. It is also worth noting that the macroscopic nematic order can be supercooled at least 10°C below the glass transition as derived by d.s.c. measurements.

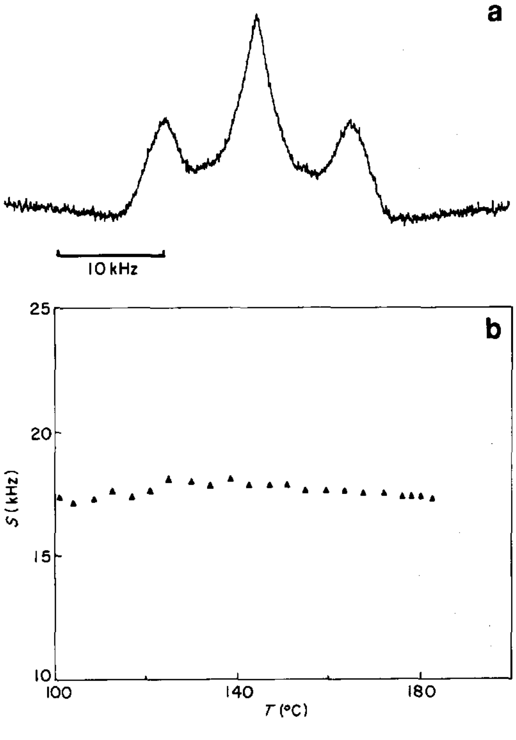

Figure 3 (a) Typical ^{1}H n.m.r. spectrum of a polyester sample in bulk nematic state ($T = 182.5$°C). (b) Dependence of the splitting order parameter S upon the temperature T in a polyester sample in bulk

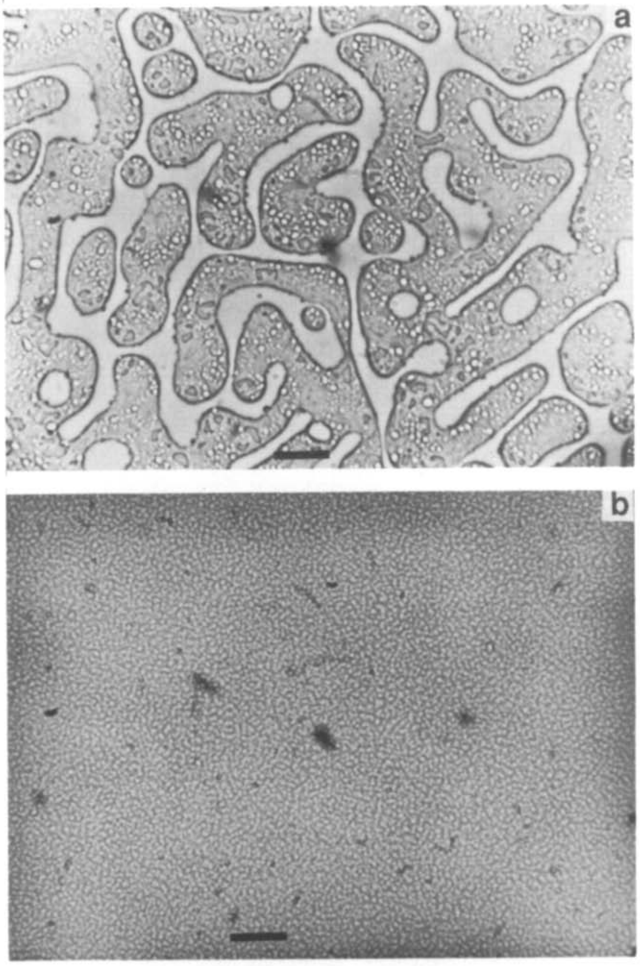

Figure 4 Textures of blend films observed under microscope between parallel polarizers: (a) film prepared by polymer coating; (b) film prepared by spin casting. Scale bar = 20 μm

Conclusion

These results show that this polyester backbone exhibits a high flexibility when there is no interaction between the chains, as in dilute solutions. However, previous results[21] have shown that, at high concentrations these chains orient themselves and their backbones become semi-stiff.

COMPOSITES OF SEMI-STIFF AND FLEXIBLE MACROMOLECULES

Our aim was to obtain thin composite films of the LC polyester mixed with flexible macromolecules, in this case polysulphone chains.

Domain size

When observed under the microscope, both kinds of film (i.e. polymer-coated and spin-cast films) appeared to be non-birefringent, despite the high content of LCP (60 wt%) which is a birefringent material. *Figure 4* shows the morphology of these films as seen between parallel polarizers. In *Figure 4a*, large domains of sizes ranging from ~10–30 μm constitute the polymer-coated film. This morphology is typical of a spinodal decomposition. A similar texture has been observed by Nakai *et al.*[2]. The SALS study of these films (with polarized incident light) reveals a u.v. pattern showing a scattering ring (no azimuthal dependence). The maximum intensity was obtained for $q_{\max} = 0.33\ \mu\mathrm{m}^{-1}$. Thus, the domain size, $d = 2\pi/q_{\max}$, is 19 μm, which is consistent with the size of the domains observed by microscopy.

Figure 4b shows the morphology of a spin-cast film. Two phases can be distinguished, but the size of the domains is much smaller in this case, ~2 μm. However, the kinetics of phase separation was again faster than that of the solvent evaporation.

Stability under temperature variations

Various thermal treatments were applied to both kinds of film: (i) heating from room temperature up to 250°C with annealing for 10 min every 10°C; or (ii) annealing for 12 h at 300°C, and subsequent quenching to room temperature on a metal block. After each of these treatments the textures remained unchanged. Neither coarsening of the textures, nor birefringence appeared. This suggests that these phase-separated states are thermodynamically stable between 25 and 300°C.

Conclusion

These composites of LC polyester and polysulphone chains are formed from domains which are isotropic and dispersed at the micrometre level. Furthermore, these composites are in a thermodynamically stable demixed state over the temperature range studied. Domains which are rich in LCP as well as those which are poor in LCP are well mixed, indicating some partial miscibility.

AGGREGATION BEHAVIOUR IN BINARY AND TERNARY SYSTEMS

The investigation was extended by studying the state of ordering as well as the demixing process in the binary system of LC polyester/THF and the ternary system of LC polyester/polysulphone/THF, the latter giving rise to blends in the solid state.

Density and orientation correlations in polymeric solutions have been studied by the light scattered intensities analysed according to the formulae of Stein and Wilson[22]:

$$H_v(q) = \frac{K}{15}\langle\delta\rangle^2 \int f(r)\frac{\sin(qr)}{qr} r^2\,\mathrm{d}r \tag{8}$$

$$V_v(q) = \frac{4}{3}H_v + K\langle\eta\rangle^2 \int \gamma(r)\frac{\sin(qr)}{qr} r^2\,\mathrm{d}r \tag{9}$$

where H_v and V_v are the scattered intensities between crossed and parallel polarizers respectively. The functions $f(r)$ and $\gamma(r)$ are the orientation and density correlation functions respectively, $\langle\delta\rangle$ is the average of the molecular anisotropy fluctuations, $\langle\eta^2\rangle$ is the mean square average of the refractive index fluctuations, q is the wave vector in the solution, and K is an optical constant. The scattered intensities are expressed as:

$$H_v(q) = \frac{K'}{15}\langle\delta\rangle^2 \frac{a_0^3}{(1 + a_0^2 q^2)^2} \tag{10}$$

and

$$V_v(q) - \frac{4}{3}H_v(q) = K'\langle\eta^2\rangle \frac{a_d^3}{(1 + a_d^2 q^2)^2} \tag{11}$$

when it is assumed that the correlation functions have a simple exponential dependence upon r (ref. 23): $\exp(-r/a_i)$, with i equal to d or o for the density or orientation correlation lengths respectively. Debye–Bueche type analysis[23] of H_v and $V_v - (4/3)H_v$ intensities yield the correlation lengths a_0 and a_d.

The V_v intensity at 90° increases linearly with the polyester concentration before sharply increasing when the concentration approaches the demixing zone. A Debye-Bueche analysis of $V_v - (4/3)H_v$ intensities seems relevant since the variation of $(V_v - (4/3)H_v)^{-1/2}$ *versus* q^2 are effectively linear.

Domain size in binary systems

The density correlation length a_d observed in binary systems is plotted *versus* polyester concentration in *Figure 5*. It varies in the range 10–20 nm. The general trend is an increase of a_d with the semi-stiff molecule concentration. Indeed, the order of magnitude found for the density correlation length is high compared to the size of one molecule ($R_g \approx 20$ Å). Thus, a_d is probably related to the size of an aggregate of chains. These aggregates become increasingly large when the concentration approaches the demixing zone. The comparison of these results with those found by Hsaio *et al.*[21] for the same kinds of solutions, leads to $a_d \gg a_0$. Thus, it is likely that an aggregate of size a_d in fact contains several subaggregates in which the molecules are oriented.

Domain size in ternary systems

Figure 5 shows that the density correlation lengths increase with the polyester concentration, for both

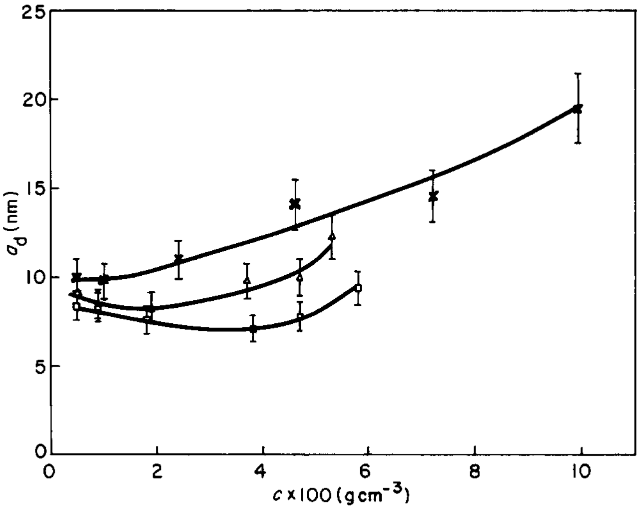

Figure 5 Variations of the density correlation lengths a_d with the polyester concentration c. Compositions of the solutions: ×, polyester in THF; □, polyester/polysulphone in THF (ratio 7:1); △, polyester/polysulphone in THF (ratio 3:1). The demixing concentrations are $48.5 \times 10^{-2}\ \mathrm{g\,cm^{-3}}$ for the polyester in THF, 8×10^{-2} and $6 \times 10^{-2}\ \mathrm{g\,cm^{-3}}$ for the ratios 7:1 and 3:1, respectively

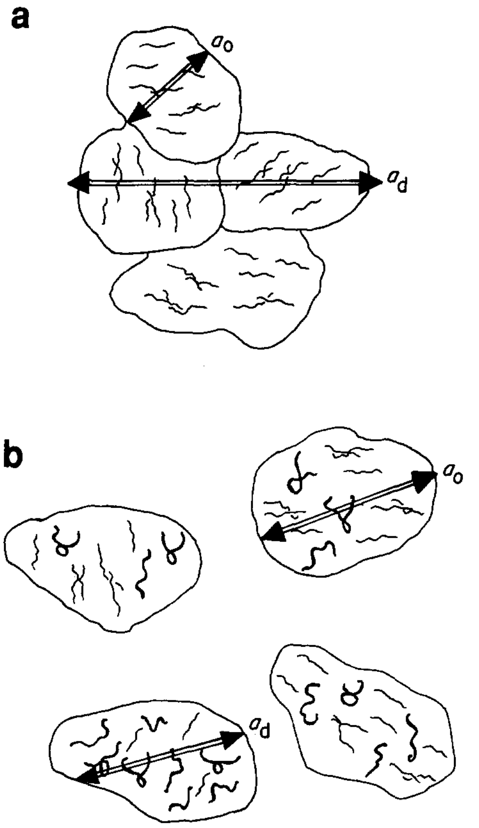

Figure 6 Diagrams showing possible aggregation behaviour in (a) binary solutions ($a_d \gg a_0$); (b) ternary solutions ($a_0 \gtrsim a_d$)

ternary systems studied. They are in the range 7–12 nm. Thus, for a given concentration, they are smaller than the length a_d found for the binary solution. However, they are still larger than the molecular dimensions; this, together with the strong growth of the density fluctuations preceding the demixing, suggests the presence of aggregates in these solutions also.

Furthermore, by comparison with previous results[21], it is noticed that $a_0 \gtrsim a_d$ in these solutions. Therefore, it is reasonable to assume that there are probably two kinds of aggregates. The first is mainly composed of semi-stiff molecules with a few coils, its size related to the extent of the orientation correlation distances of the molecules, i.e. a_0. The second kind, whose size is related to a_d, is composed mainly of coils with a few semi-stiff chains. This behaviour is a precursor to the state of ordering in the solid state, which consists of two phases: one rich in semi-stiff chains and poor in flexible molecules and vice versa for the other phase.

The scheme presented in *Figure 6* gives a possible picture of the aggregation in these binary and ternary solutions.

CONCLUSION

A SAXS investigation of a wholly aromatic paralinked random copolyester shows that it has a radius of gyration of 20 Å in dilute solution. This leads to a short mean persistence length and reveals a high backbone flexibility. Viscosity measurements yield a hydrodynamic radius of ~49 Å. In the bulk nematic state, the polyester can be oriented by a magnetic field. A monodomain is obtained, as shown by ^{1}H n.m.r.. This result confirms the flexibility of the backbone.

However, at high concentrations, these polyester chains tend to orient themselves and form aggregates. Density and orientation correlations studied from WALS yield information about the size of aggregates, measured as ~10–20 nm and consisting of oriented subaggregates.

In concentrated solutions containing polysulphone and polyester, aggregation is observed prior to the demixing process. Two kinds of aggregates are formed: one rich in polysulphone and poor in polyester, and vice versa for the other kind. This behaviour is consistent with the observations in the solid state: these polymers undergo a phase separation. Blend films (40 wt% LCP) are composed of two isotropic phases, an estimate of their size being a few micrometres. The kinetics of the phase separation is very fast compared to that of the solvent elimination from the mixture.

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