Table 4 Other polyester preparations

Polymer	Temperature (°C)	Time (h)	$[\eta]$ (dl g^{-1})	$\bar{M}_n$
Poly(ethylene terephthalate)	110	3	0.145	3400
Poly(1,4 butylene terephthalate)	110	2	0.392	11 130
Poly(hexamethylene terephthalate)	120	2	0.660	10 650
Poly(*p*-xylylene sebacate)	100	½	0.980	–
Poly(decamethylene sebacate)	110	2	1.100	–

Reaction conditions: 5 m mol dibromo compound, 5.25 m mol caesium dicarboxylate, 4 ml NMP

prolonging the reaction time beyond 10 h leads to a fall in molecular weight.

The general applicability of this polymerization procedure has been examined for the polyesters listed in *Table 4*. Apart from poly(ethylene terephthalate), (2GT), quite satisfactory polymers were obtained which appeared to have high molecular weights as judged by solution viscosity measurements and by the ease with which fibres could be drawn from molten samples. In the case of 2 GT, discolouration was very apparent during synthesis, possibly due to the greater ease of the elimination reaction. No doubt the conditions could be modified to improve this particular polymerization.

Some structural characterization of the polymers has been made. Infra-red and n.m.r. spectra of samples of 10 GT prepared by this procedure are identical with those of a conventionally prepared sample. The d.s.c. behaviour is also very similar though the melting point of the 10 GT prepared *via* this procedure appears to be 4°–5°C lower than the conventionally prepared sample. Elemental analyses gave satisfactorily high carbon contents, but rather erratic (though low) bromine contents.

In conclusion, it is clear that the procedure outlined offers a very convenient and rapid method for preparing a variety of polyesters of reasonably high molecular weight. Stoichiometric equivalence of reagents is not necessary provided the reagent present in excess is the carboxylate salt. It seems likely that the overall rate of reaction is governed by the rate of dissolution of the carboxylate salt, so that the predominant end groups in the growing polymer are the alkyl bromide species. Whilst further studies of this reaction are in progress, it has not escaped our attention that this procedure offers a route to the hitherto unprepared poly(methylene esters) and we are at present engaged in their synthesis.

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The concentration dependence of the angular dissymmetry of light scattered by micellar solutions

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A light scattering investigation was made of micelles formed from a polystyrene-poly(ethylene/propylene) two-block copolymer in n-nexane. n-Hexane is a selectively bad solvent for polystyrene and so polystyrene blocks formed the cores of the micelles. The light scattering measurements were made at 25°C for concentrations up to 0.015 g cm^{-3}. The dissymetry ratio ($I_{45°}/I_{135°}$) was found to decrease with increase in concentration and it was below unity for measurements at $c > 4.8 \times 10^{-3}$ g cm^{-3}. The effect of concentration on the dissymmetry ratio was predicted quite well by assuming the micelle packing could be described by radial distribution functions for hard spheres.

Keywords Polystyrene; scattering; light scattering; copolymer micelles; concentration dependence; dissymmetry ratio

Introduction

When a block or graft copolymer is dissolved in a hydrocarbon solvent that is selectively bad for one of the polymer components, the copolymer molecules can associate reversibly to form micelles[1–6]. The micelles generally consist of a compact swollen core of insoluble polymer blocks surrounded by a protective fringe of soluble blocks. Gel permeation chromatography and electron microscopy studies have shown that in many cases the micelles have a very narrow size distribution[2].

In some copolymer/selective–solvent systems[2,5] the association equilibrium

$$NP_1 \rightleftarrows P_N$$

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between copolymers in the free-chain form (P_1) and in the micelle form (P_N) can overwhelmingly favour micelle formation. Since strong association of this type can occur over a wide range of temperature, the properties of micelles play an important role in the solution behaviour of block copolymers.

Here we report a light-scattering investigation of micelles formed from a polystyrene poly(ethylene/propylene) two-block copolymer in n-hexane. The n-hexane is a selectively bad solvent for polystyrene and so polystyrene blocks form the cores of the micelles. Light scattering measurements have been made at 25°C for concentrations up to 0.015 g cm^{-3}. Attention is focused on the angular dissymmetry of the scattered light which, over a limited region of concentration, is found to fall below unity.

Experimental

Material. The block copolymer was provided by Shell Research Ltd. It had been prepared by hydrogenating the polyisoprene block of a polystyrene–polyisoprene block copolymer. The copolymer contained $38.5 \pm 3.0\%$ by weight polystyrene. Its weight-average molecular weight $\bar{M}_w = 1.06 \times 10^5$ g mol^{-1} and the ratio of its weight-average to number-average molecular weight $\bar{M}_w/\bar{M}_n = 1.16$.

Electron microscopy. Specimens were isolated from solution using a technique which has been described fully elsewhere[4]. A typical electron micrograph obtained using an AEI 6G electron microscope operating at 80 kV is shown in *Figure 1*. During specimen preparation the micelles collapsed to form particles with a density similar to that of the bulk polymer. From shadowing, it was deduced that the micelles become approximately disc-shaped because they tended to flow and wet the substrate surface. The micrograph indicates that the micelles have a moderately narrow size distribution ($\bar{M}_w/\bar{M}_n \simeq 1.15$).

Light scattering. Measurements were made using a Sofica PGD 40B photogoniometer. Light scattering measurements were made with light of wavelength 546 nm. Sealed cells were used for the experiments. The instrument was calibrated using pure benzene together with a secondary glass reference standard. Solutions and pure solvent were filtered several times at 20°C using PTFE Millipore filters of nominal pore size 0.2 μm to remove dust. Tests showed that solution concentrations were not changed by filtration. A Brice-Phoenix differential refractometer was used to measure the refractive index increment.

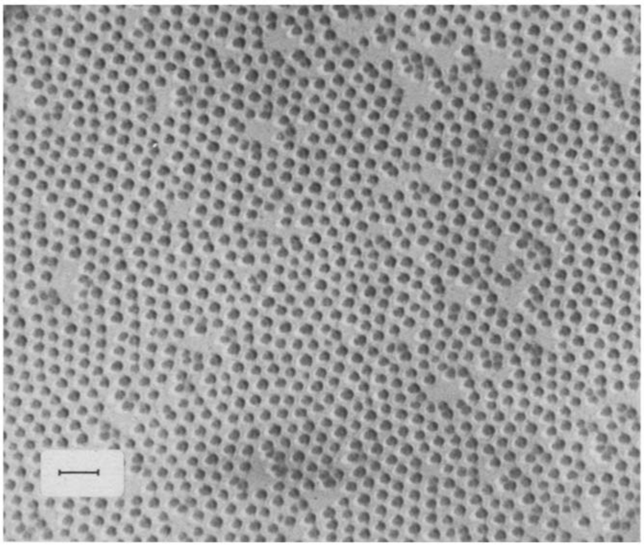

Figure 1 Electron micrograph of collapsed micelles isolated from a micellar solution of the polystyrene–poly(ethylene/propylene) block copolymer in n-hexane. The scale bar is 200 nm

Theoretical background

For a system of non-independent particles with a spherically symmetric segment distribution, the normalized intensity of scatter in the absence of multiple scattering is given by[7,8]

$$I = F^2(\theta)[1 - 4\pi(N/V)\int_0^\infty (1 - g(r))\sin kr)(kr)^{-1}r^2\mathrm{d}r] \quad (1)$$

In this expression N is the number of particles in volume V, r is the distance from the centre of any reference particle, $g(r)$ is the radial distribution function, $F^2(\theta)$ is a scattering factor for isolated particles, and $k = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ is the wavelength of the radiation in the medium and θ is the angle between the incident beam and the direction of scattering. In the limit of infinite dilution the term in square brackets becomes unity and light scattering measurements when suitably extrapolated to meet this condition provide a means of determining the form of $F^2(\theta)$. In more conventional terms we write

$$(Kc/R_\theta)_{c=0} = [\bar{M}_w P(\theta)]^{-1} \quad (2)$$

where $\bar{M}_w$ is the weight-average molecular weight of the particles, R_θ is the difference between the Rayleigh ratio of the solution and that of the pure solvent, $P(\theta) \equiv F^2(\theta)$, and K is an optical constant containing amongst other variables the square of the refractive index increment. Since at zero angle $F^2(\theta) = 1$ a double extrapolation of light scattering results to zero concentration and zero angle give a measure of the weight-average molecular weight provided the particles concerned are homogeneous in chemical composition[9]

$$(Kc/R_\theta)_{\substack{c=0\\ \theta=0}} = \bar{M}_w^{-1} \quad (3)$$

In the case of copolymers that are heterogeneous in chemical composition use of equation (3) yields an apparent molecular weight, the value of which is dependent on the refractive index of the solvent, rather than the true weight-average molecular weight[10,11]. The homogeneity of the present copolymer system was undoubtedly sufficient to render any contribution from this effect insignificant in the analysis of the results; studies of $\bar{M}_w$ by light scattering from true molecular solutions in different solvents (e.g. tetrahydrofuran, decalin) gave values in good accord.

For a solution of a homopolymer in the limit of zero concentration and at sufficiently low angles, equation (2) takes the form

$$(Kc/R_\theta)_{c=0} = \bar{M}_w^{-1}[1 + (16\pi^2/3\lambda^2)\langle\overline{s^2}\rangle_z \sin^2(\theta/2)] \quad (4)$$

The z-average root mean-square radius of gyration, $\langle\overline{s^2}\rangle_z^{1/2}$ may be calculated therefore from the limiting slope of the plot $(Kc/R_\theta)_{c=0}$ against $\sin^2(\theta/2)$. For a copolymer even where the chains are homogeneous in size and chemical composition, the method yields[12] an apparent mean-square radius of gyration, $\langle s_*^2\rangle$. For the present micellar system $\langle s_*^2\rangle<\langle \overline{s^2}\rangle_z$.

Light scattered at the limit of zero angle for solutions of finite concentration is given by

$$(Kc/R_\theta)_{\theta=0}=\bar{M}_w{}^{-1}[1-4\pi(N/V)\int_0^\infty(1-g(r))r^2\mathrm{d}r]^{-1} \qquad (5)$$

For very dilute solutions the equation reduces to

$$(Kc/R_\theta)_{\theta=0}=\bar{M}_w{}^{-1}+24_2c \qquad (6)$$

where A_2 is the second virial coefficient. The second virial coefficient, which may be determined from the limiting slope of a plot of $(Kc/R_\theta)_{\theta=0}$ against c, provides an alternative measure of particle size since if we treat the scattering particles as equivalent thermodynamic spheres[13],

$$A_2=(16/3)(N_A\pi R^3M^{-2}) \qquad (7)$$

where R is the equivalent thermodynamic radius.

For scattering by spheres of diameter D, the term in square brackets in equation (1) may be approximated by an expression derived by Fournet[14] from the theory of imperfect gases which gives

$$(Kc/R_\theta)=(Kc/R_\theta)_{c=0}[1+(4/3(N/V)\pi D^3\Phi(kD)] \qquad (8)$$

where $\Phi(kD)=3(\sin kD-kD\cos kD)(kD)^{-3}$. The dissymmetry ratio (=reduced scattering intensity at 45°/reduced scattering intensity at 135°) at a number density of spheres N/V is then given by

$$(I_{45}/I_{135})=(I_{45}/I_{135})_{c=0}\left[\frac{1+(4/3)(N/V)\pi D^3\Phi(k_{135}D)}{1+(4/3)(N/V)\pi D^3\Phi(k_{45}D)}\right] \qquad (9)$$

Unfortunately the application of equation (8) is limited since it cannot be applied to concentrations at which simultaneous interactions of more than pairs of particles need to be considered. For these higher concentrations a knowledge of $g(r)$ is required to predict the dissymmetry ratio which from equation (1) is given by

$$(I_{45}/I_{135})=(I_{45}/I_{135})_{c=0} \qquad (10)$$
$$\times\left[\frac{1-4\pi(N/V\int_0^\infty(1-g(r))\sin k_{45}r)(k_{45}r)^{-1}r^2\mathrm{d}r}{1-4\pi(N/V\int_0^\infty(1-g(r))\sin k_{135}r)(k_{135}r)^{-1}r^2\mathrm{d}r}\right]$$

Results and Discussion

In *Figure 2*, Kc/R_θ extrapolated to zero angle is plotted against c for the range $c=(1.5-10)\times10^{-4}$ g cm^{-3}. The intercept yields $\bar{M}_w=(2.1\pm0.1)\times10^7$ g mol^{-1} and the limiting slope $A_2=(9.7\pm1.2)\times10^{-6}$ g^{-2} mol cm^3. For the dilute solution region shown, the plot has a positive slope and is approximately linear. This dependence of $(Kc/R_\theta)_{\theta=0}$ on concentration provides evidence that the micelle/free-chain equilibrium is overwhelmingly in favour of micelle formation under the conditions chosen for our experiments.

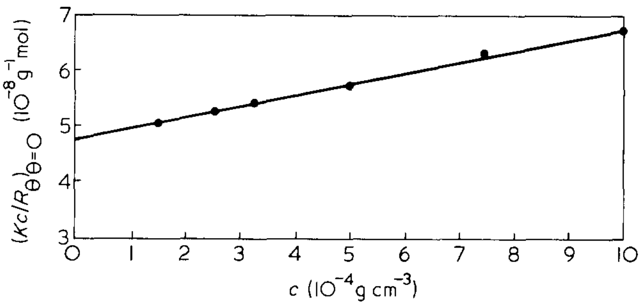

Figure 2 Plot of $(Kc/R_\theta)_{\theta=0}$ against concentration for the polystyrene–poly(ethylene/propylene) block copolymer in n-hexane at 25°C

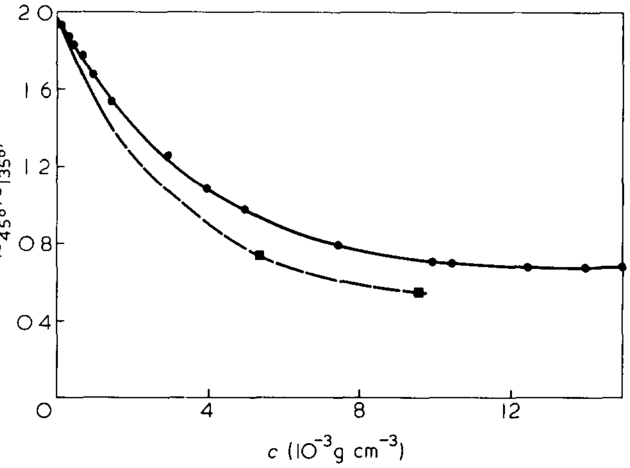

Figure 3 Dissymmetry ratio against concentration for the polystyrene–poly(ethylene/propylene) block copolymer in n-hexane at 25°C; the upper curve passes through the experimental points (●) whilst the lower curve indicates the behaviour predicted by the simple hard sphere model

A plot of dissymmetry ratio against concentration is shown in *Figure 3*. The dissymmetry ratio is seen to decrease with increase in concentration and it falls below unity at $c=4.8\times10^{-3}$ g cm^{-3}.

The effect of concentration on the dissymmetry ratio is predicted quite well if we assume the micelles behave as hard spheres. On increasing the concentration the hard spheres can be considered to pack closer together and to become ordered locally in the same manner as other condensed non-crystalline arrays (such as the molecules of a single liquid). In calculating the theoretical curve shown in *Figure 3* we assumed, as a first approximation, that the molecular weight and structure of the micelles was independent of concentration. The hard sphere diameter (=150 nm) was determined from A_2 using equation (7). The first part of the dissymmetry curve ($c<1.5\times10^{-3}$ g cm^{-3}) was established using equation (9). The dissymmetry ratio at $c=5.4\times10^{-3}$ g cm^{-3} was calculated from equation (10) using values of $g(r)$ determined for a number density of hard spheres $\rho=0.372\rho_0$ (where ρ_0 is the number density of a close packed system) by Monte Carlo machine calculations[15].

The dissymmetry at $c = 9.6 \times 10^{-3}$ g cm^{-3} was determined from $g(r)$ values derived by Kirkwood and Boggs[16] for what they termed an idealized liquid structure in which the average distance between the centre of a sphere and the centre of its nearest neighbours was 1.15D.

Better agreement between experiment and theory could undoubtedly be obtained by choosing a slightly different effective size for the micelles. The present analysis is sufficient to show that the micelles remain colloidally stable even when packed at relatively high number densities. If however we increased the concentration somewhat further, a transition from a liquid-like to a more highly ordered mesomorphic type structure would eventually occur.

Recently we found that other micellar systems show a similar dependence of angular dissymmetry on concentration to that described here. A full report on these studies will be presented later.

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Lithium doping of *cis* polyacetylene $(CH)_x$

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n-Type doping of polyacetylene $(CH)_x$ has been performed using benzophenone–lithium solutions in THF. It is shown that doped *cis*-rich films can reach the metallic level, as evidenced by e.p.r. Raman spectroscopy shows that during the doping process, isomerization from *cis* to *trans* occurs. Preliminary results show that for short doping times the distribution of the dopant in thick films is strongly inhomogeneous.

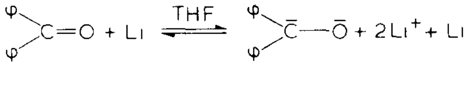
Keywords Polymer, polyacetylene, spectroscopy; Raman; doping; lithium; isomerization

A great deal of experimental work has focused on the chemical and physical properties of polyacetylene films doped with electrons acceptors such as I_2, AsF_5,[1] $NOHSO_4$,[2] $FeCl_3$,[3] etc.

Much less work has been done on the subject of doping with electron donors such as alkali metals. Interest concerning this type of doping comes from the potential ability of polyacetylene films being used as electrodes in electrochemical processes. For instance $(CH)_x$ can be electrochemically doped with Li^+ or with ClO_4^- by using a solution of $LiClO_4$ in propylene carbonate[4]. Only a few experiments have been performed using chemical doping with Li[5], Na[5-7], and K[5]. The extreme reactivity of the system with air and moisture does not permit easy handling of the samples. Nevertheless some combined e.p.r., i.r. and visible spectroscopies and conductivity measurements have shown that, by doping with Na, polyacetylene could be brought to the metallic state and that isomerization occurred during the doping process[6,7].

In this communication we present the chemistry of the Li doping using benzophenone–lithium complexes in THF, as well as preliminary e.p.r. and Raman spectroscopies experiments. A careful analysis of the results suggests that for short doping times the dopant distribution is strongly inhomogeneous and varies with time.

Polyacetylene films have been obtained using the standard procedure of Ito *et al.*[8]. A solution of benzophenone and Li in very dry and clean THF was prepared with excess Li in order to favour the following reaction:



$$\varphi_2C{=}O + Li \xrightleftharpoons{THF} \varphi_2\bar{C}{-}\bar{O} + 2Li^+ + Li$$

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