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SOLUBILISATION OF HOMOPOLYSTYRENES BY MICELLES FORMED BY A POLYSTYRENE -*b*-POLY(ETHYLENE/PROPYLENE) COPOLYMER IN A BASE LUBRICATING OIL

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ABSTRACT

A study was made of the solubilisation of some polystyrene homopolymers in a paraffinic base oil containing polystyrene-*b*-poly(ethylene/propylene) copolymer micelles. The solubility was found to be dependent on the molecular weight of the polystyrene homopolymer and on the amount of the copolymer in solution. There was no significant solubilisation of a polystyrene homopolymer ($\overline{M}_n$ = 63,000 g mol^{-1}) having a molecular weight greater than that of the polystyrene blocks ($\overline{M}_n$ = 35,000 g mol^{-1}).

KEY WORDS

Micelles; block copolymers; solubilisation; viscosity index improvers.

INTRODUCTION

Studies have shown that polystyrene-*b*-poly(ethylene/propylene) block copolymers associate in paraffins and paraffinic base oils to form micelles (1). Since these liquids are selectively bad solvents for polystyrene, the micelles consist of a core composed of polystyrene blocks surrounded by a flexible fringe of poly(ethylene/propylene) blocks. A range of techniques has been used to characterise the micelles including Rayleigh light scattering (2), photon correlation spectroscopy (3), nuclear magnetic resonance spectroscopy (1), gel permeation chromatography and electron microscopy (4). Because of their ability to form micelles, the block copolymers are able to usefully modify the viscosity behaviour of base lubricating oils and are used at concentrations up to approximately 2% w/w as viscosity index improvers.

Tuzar and Kratochvil (5) reported some years ago that block copolymer micelles can solubilise homopolymers in their cores. Tuzar et al. (6) solubilised polybutadiene with micelles formed by a polystyrene-*b*-polybutadiene-*b*-polystyrene copolymer. There is a need however for more detailed and wide ranging studies of the solubilisation characteristics of organic micelles. The information gained would be particularly useful in the development of new oil additives.

In our laboratory we have undertaken a study of the ability of polystyrene-*b*-poly(ethylene/propylene) micelles to solubilise polymeric and low molecular weight substances in organic liquids. We report at this time an investigation of the solubilisation of five polystyrene homopolymers in a highly paraffinic base oil.

EXPERIMENTAL

Materials

The polystyrene-b-poly(ethylene/propylene) copolymer and the base lubricating oil were kindly supplied by Shell Research. The copolymer had been synthesised by hydrogenating a polystyrene-b-polyisoprene copolymer. It contained 34 ± 4% by weight of polystyrene and had an $\overline{M}_n$ = (1.03 ± 0.06) x 10^5 g mol^{-1} and $\overline{M}_w/\overline{M}_n$ = 1.14. The base lubricating oil was a highly paraffinic XHVI oil derived from an Iranian crude. Its viscosity was 31.12 cSt at 40°C and 5.91 cSt at 100°C.

An electron micrograph of micelles isolated from a solution of the block copolymer in the base oil using a procedure described earlier (4) indicated the micelles were spherical in shape and had a narrow size distribution. Rayleigh light scattering gave $\overline{M}_w$ = 2.2 x 10^7 g mol^{-1} for the micelles in the base oil at 50°C.

The polystyrene homopolymers used in the study had the following values of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ (a) 2100, <1.1 (b) 4000, <1.1 (c) 7300, 1.09 (d) 12000, 1.06 (e) 63000, 1.06.

Solubilisation

It was not possible to solubilise the polystyrene homopolymers in the micelles simply by heating them together in the base oil. This was because solubilisation in such systems only occurs at a significant rate in the vicinity of the critical micelle temperature and the latter was very high for all the solutions of interest in this study. For a copolymer solution of concentration 0.014 g cm^{-3} the micelles showed no significant dissociation to chains until 180°C (as indicated by viscometry) and the critical micelle temperature was estimated to be in the region of 200°C. Heating the solutions to these temperatures for the times required for solubilisation would undoubtedly have caused permanent chemical changes in the system. An alternative procedure was therefore adopted.

The polystyrene homopolymers were first dissolved in chloroform and volumes of these solutions, which were of concentration 0.01 g cm^{-3}, were added to micellar solutions of the copolymer in the base oil at 20°C. The temperature was then raised over a period of four hours to 120°C and the chloroform allowed to distil off. The temperature was maintained at 120°C, whilst purging with dry N_2, until all traces of solvent had been eliminated from the system. The temperature of the solutions was then lowered to 25°C. The added homopolystyrene was judged to have been completely solubilised in solutions which remained clear on standing at this lower temperature for three days. Solutions which became turbid were judged to contain some homopolymer which had not been taken up in the micellar cores. A set of preliminary experiments was carried out to establish the region in which the solubility boundary occurred, and then further solutions were studied to define the boundary more precisely (± 0.1% of the ratio by weight of homopolystyrene/oil).

RESULTS AND DISCUSSION

Results obtained in the solubilisation studies for four of the homopolystyrenes ($\overline{M}_n$ = (a) 2100, (b) 4000, (c) 7300 and (d) 12000 g mol^{-1}) are plotted in Figure 1. In each case the weight of homopolystyrene solubilised increases approximately linearly with the weight of copolymer in the oil. The solubility is strongly dependent on molecular weight, the higher the molecular weight the lower the solubility.

It was not possible to solubilise measurable amounts of the homopolystyrene ($\overline{M}_n$ = 63000 g mol^{-1}) with molecular weight greater than that of the polystyrene block in the copolymer ($\overline{M}_n$ = 35000 g mol^{-1}). The latter result is consistent with the findings of Morton (7) for bulk state mixtures of homopolystyrene with polystyrene-b-polybutadiene-b-polystyrene and with polystyrene-*b*-polyisoprene-*b*-polystyrene thermoplastic elastomers. The homopolystyrenes were shown by opacity and property studies to be incompatible with the polystyrene domains of the elastomers when their molecular weights were significantly greater than that of the polystyrene blocks.

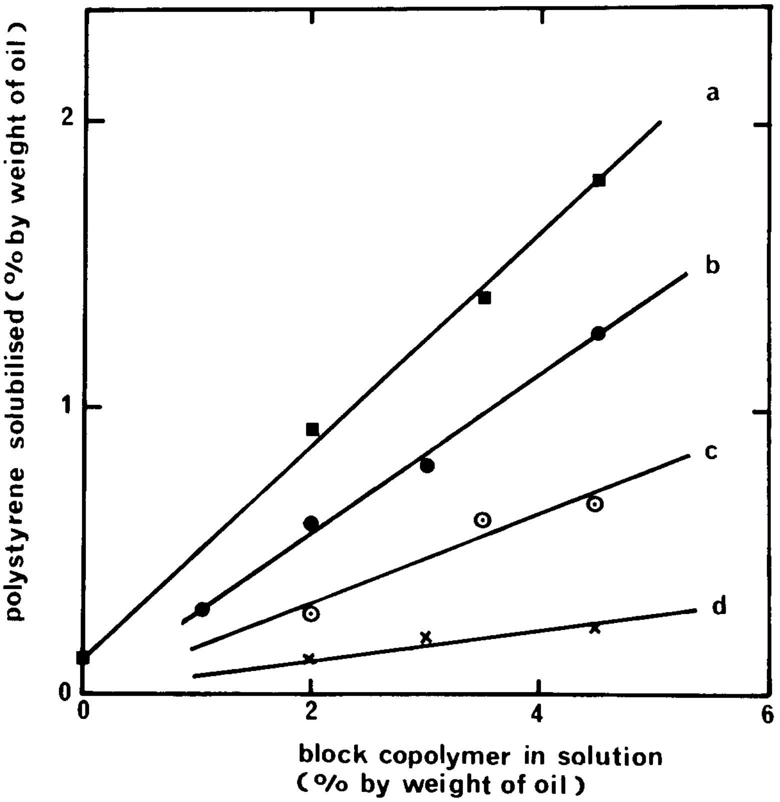

Figure 1. Solubilisation of homopolystyrenes by a polystyrene-*b*-poly(ethylene/propylene) copolymer in a paraffinic base lubricating oil. Plots are for homopolystyrenes of number-average molecular weights of (a) 2100, (b) 4000, (c) 7300 and (d) 12000 g mol^{-1}.

Electron microscopy studies now in progress show that on solubilising the homopolystyrenes the shape of the micellar particles remains spherical. Results from these studies, together with investigations of solubilisation by gel permeation chromatography, will be reported later.

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REFERENCES

(1) F.Candau, F.Heatley, C.Price and R.B.Stubbersfield, *Europ. Polym. J.*, **20**, 685 (1984).

(2) C.Price, A.L.Hudd and B.Wright, *Polymer*, **23**, 170 (1982).

(3) C.Price, A.L.Hudd, R.B.Stubbersfield and B.Wright, *Polymer*, **21**, 9 (1980).

(4) C.Price, A.L.Hudd and B.Wright, *Polymer*, **23**, 650 (1982).

(5) Z.Tuzar and P.Kratochvil, *Advan. Colloid Interface Sci.*, **6**,201 (1976).

(6) Z.Tuzar and P.Kratochvil, *Makromol. Chem.*, **170**, 177 (1973) and Z.Tuzar, P.Bahadur and P.Kratochvil, *Makromol. Chem.*, **182**, 1751 (1981).

(7) M.Morton, 4th. International Synthetic Rubber Symposium, London, page 70 (1970).