NORMAL AND UNUSUAL MORPHOLOGIES IN BLENDS OF AB-CROSSLINKED POLYMERS

G.C. Eastmond and D.G. Phillips†
Department of Inorganic, Physical and Industrial Chemistry, Liverpool University, Liverpool L69 3BX, U.K.

INTRODUCTION

The majority of recent studies of multicomponent polymers can be divided into two main categories; those based on well-defined and well-characterised AB and ABA block copolymers and those involving complex mixtures of relatively ill-defined multicomponent species and homopolymers, such as are encountered in impact-resistant materials. The former are the more amenable to scientific investigation in the sense that their morphologies and properties can be related to detailed molecular structures. However, since block copolymers are usually prepared anionically, the range of components which can be incorporated into such well-defined materials is somewhat limited. The AB-crosslinked polymers (ABCPs), with which this paper is concerned, are prepared by free-radical processes and are a class of materials into which a wider variety of components can be incorporated. While ABCPs are structurally related to conventional AB and ABA block copolymers they are more complex but, when prepared under controlled conditions, their structural parameters can be determined. Thus, the formulation of structure-property relations is permitted and extensions of the relations developed for simpler systems to more complex situations can be considered.

Before proceeding with a discussion of the morphologies of ABCPs it will be useful to summarise some pertinent results of previous morphological studies of linear block copolymers.

† Present address: CSIRO, Department of Textile Industries, Belmont, Victoria, Australia.
Morphologies of Block Copolymers and their Blends

The morphologies of AB and ABA block copolymers have been studied by many workers. It is now recognised that in bulk polymers the three basic morphologies identified by Matsuo et al. can exist; namely, spherical or cylindrical domains of the minor component within a matrix of the other or alternate lamellae of the two components (1). Under equilibrium conditions the morphologies are determined by the relative sizes of the A and B blocks and in carefully prepared samples very uniform morphologies with a high degree of long-range order have been obtained (2).

From theoretical calculations Meier predicted that characteristic dimensions $D$ of morphological features, i.e. domain radii and lamellar thicknesses, would be given by the equation

$$D = kC\alpha M^\frac{1}{4}$$  \hspace{1cm} (1)

in which $k$ is a constant determined by the domain shape and molecular architecture, $C$ is the constant relating unperturbed root-mean-square end-to-end chain dimensions to the molecular weight $M$ of the domain-forming chain and $\alpha$ is an expansion parameter (3,4).

Relatively few morphological studies of block copolymer blends have been undertaken. Hoffmann et al. blended two styrene-butadiene diblock copolymers with different block sizes (5). They reported that in cast films two sizes of styrene domains were observed corresponding to those of the individual polymers, implying that fractionation by molecular weight accompanied microphase separation.

Inoue et al. investigated the effects of simultaneously adding homopolymers of both components to styrene-isoprene diblock copolymers (6). These workers demonstrated that while homopolymers of molecular weights smaller than those of the corresponding blocks in the copolymer were solubilised within the microphase of that component, high-molecular-weight homopolymers were incompatible with the chemically identical blocks in the copolymer and macroscopic phase separation was observed. Inclusion of compatible homopolymers into a styrene-isoprene block copolymer containing 40% styrene caused a disruption of the long-range order of the lamellar structure of the pure block copolymer.

During an investigation into the liquid crystalline structures present in solutions of block copolymers, Douy and Gallot dissolved styrene-butadiene block copolymers in styrene monomer (7). Subsequent polymerization of the solvent produced blends of block copolymer and polystyrene. It was observed that a regular lamellar morphology was retained when up to 45% of polystyrene was