

Liquid-liquid phase separation in a ternary blend of polyethylenes

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Blends of linear polyethylene with two ethylene-octene copolymers of 2 and 8 mol% octene content have been prepared and their melt-phase behaviour determined by examination of quenched samples by differential scanning calorimetry and transmission electron microscopy using surface replicas. The ternary phase diagram for the system has been determined. It shows three distinct regions of liquid-liquid phase separation, all at high branch content.

(Keywords: ethylene-octene copolymers; ternary blends; liquid-liquid phase separation)

INTRODUCTION

In a series of recent publications¹⁻⁶ we have shown that liquid-liquid phase separation (LLPS) can occur in melts of linear with branched polyethylenes (LPE with BPE). In all the binary blends that we have studied (except for one where the molecular weight of the LPE was extremely low and one where the BPE was extremely branched) we have found a region of phase separation asymmetrically placed at the low-linear-content side of the phase diagram; this phase-separated region appears to be of a closed-loop nature. A schematic phase diagram showing typical behaviour is sketched in *Figure 1*. Similar behaviour has been observed in other blend systems of a linear homopolymer with a branched copolymer, in polyesters⁷ and polypropylenes⁸.

Most of these studies have used commercial polymers that are not homogeneous either in their molecular weights or in their branch content. Consequently, detailed modelling of the phase behaviour has not been possible. However, recently we have been able to study a series of specially polymerized ethylene-octene copolymers⁶. We found, to our surprise, that the width of the phase-separated region decreased as the octene content of the BPE was increased. This counter-intuitive observation, that more dissimilar polymers are more compatible, led us to devise a simple model⁹ in which it is assumed that the two components are basically compatible with very small free energies of mixing. However, we postulated that there is a further small, asymmetric, free energy of mixing for very low additions of linear to branched polymer. Such a model is able to predict phase behaviour of the type we observed.

It has been suggested^{2,3,10} that the phase separation can lead to gross morphologies (phase morphologies) which can impart advantageous properties to the polymer. In particular it has been noted that certain

very-low-density polyethylenes (VLDPE)^{11,12} and linear-low-density polyethylenes (LLDPE)³ show thermal behaviour and internal morphologies which suggest that they may have undergone phase separation in the melt prior to crystallization; some of these polymers have been fractionated into components of varying branch content^{13,14}. It has also been suggested that the high fracture toughness of these materials may arise from these 'phase morphologies'. Accordingly it would be very useful if we could begin to understand the phase behaviour of such complex, multicomponent materials.

In the present publication we report the results of an attempt to understand the behaviour of a three-component system, as a first stage to the understanding of complex, multicomponent systems. We chose to blend LPE with two of the ethylene-octene copolymers that were used in our recent work⁶. In order to understand the features of the resulting phase diagram, we attempted to produce a descriptive model of phase separation in these systems. We have adapted and extended the model developed previously (to explain the behaviour of binary copolymer blends⁹) so as to include the ternary blends of the current work.

EXPERIMENTAL

The polymers used were an LPE, and two approximately random ethylene-octene copolymers containing 2 and 8 mol% octene (O(2) and O(8), respectively). Details of the preparation of these polymers are given in ref. 6, and their molecular weights are shown in *Table 1*. The blends

Table 1 Molecular weights of the polymers

Polymer	M_w	M_n	M_w/M_n
LPE	50×10^3	17.9×10^3	2.8
O(2)	51×10^3	23.2×10^3	2.2
O(8)	43×10^3	21.5×10^3	2.0

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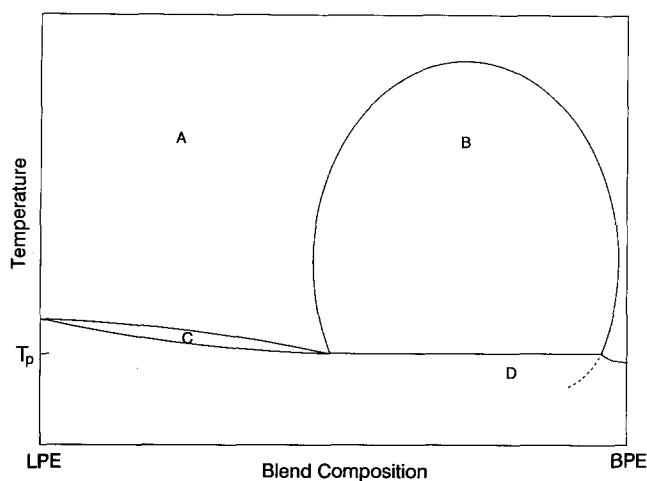


Figure 1 Generalized 'phase diagram' showing four features found for LPE/BPE binary blends. There are four regions: A, mixed melt; B, segregated melt; C, crystal plus liquid phases; D, metastable region into which the melt can be cooled prior to crystallization. The dashed line (bottom right) is a continuation of the phase boundary into the metastable region

were prepared by dissolving the polymers in xylene and precipitating into cold acetone, following the same procedures used previously for preparing binary blends¹⁻⁶. We use a simple code to describe the composition of the blends; we quote the weight percentage of each of the three polymers with the least branched first. Thus a blend coded as 60/30/10 would contain 60% of the linear polymer 30% of the 2 mol% ethylene-octene copolymer and 10% of the 8 mol% copolymer.

As previously, we used differential scanning calorimetry (d.s.c.) and transmission electron microscopy (TEM) of surface replicas. The samples were quenched from the melt into acetone at its freezing point to determine whether or not LLPS had occurred. The methods rely on the observation that if quenching from the melt is sufficiently fast, then any large-scale phase separation observed in the crystalline solid must have been present in the melt⁵. No additional large-scale phase separation occurred during crystallization. We considered that LLPS had occurred if we observed two distinct morphologies in the TEM replicas and two corresponding d.s.c. peaks on remelting; conversely we considered that no LLPS had occurred when a single morphology was found together with a single melting endotherm.

RESULTS

We began by determining the phase diagram for the binary blend of the 2 and 8 mol% copolymers; this phase diagram and those for the LPE with each of the two BPEs (taken from ref. 6) are shown in Figure 2a. Details of the experimental results for the binary octene copolymer system are shown in Figure 2b. This phase diagram for the blend of the two copolymers is quite similar in overall shape to those for the binary LPE-copolymer blends. The phase-separated region is again in the form of a closed loop asymmetrically placed towards compositions containing large amounts of the higher-octene-content copolymer. This is what we would expect on the basis of our understanding of the LPE-BPE blend systems. We should note that as we are using two copolymers, which both crystallize rather slowly and at lower temperatures than the linear polymer, we have been

able to investigate their behaviour at lower melt temperatures. Accordingly we have been able to examine, for the first time, the whole region around the lower critical temperature, and hence map out the whole closed loop region of phase separation.

The three binary phase diagrams shown in Figure 2a provide an indication of the best samples to prepare in order to investigate the ternary system. We began our survey of the ternary system by mapping out the phase diagram at 140 and 160°C, largely by d.s.c. Subsequently we used surface replicas to determine the upper critical temperatures (UCTs).

Figure 3 shows typical d.s.c. traces from two ternary blends, both quenched from 160°C; one (20/32/48) shows

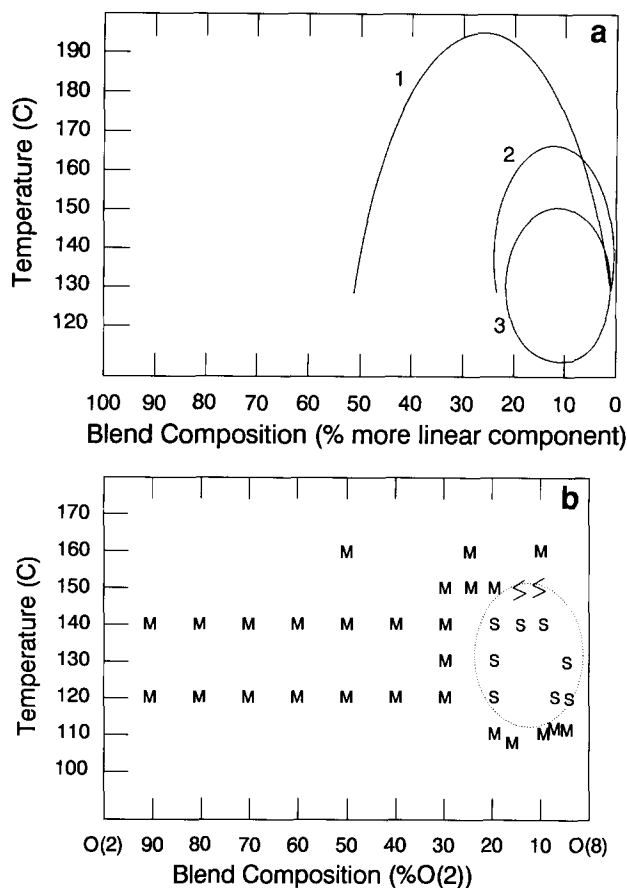


Figure 2 (a) Regions of liquid-liquid phase separation found for the three binary blends: 1, LPE-2 mol% octene; 2, LPE-8 mol% octene; 3, 2 mol%-8 mol%. (b) Experimental points recorded for binary blends of 2 mol% with 8 mol% octene copolymers; M, mixed melt; S, phase-separated melt; \lessdot , borderline cases

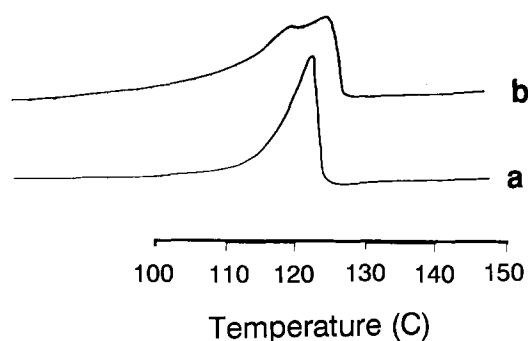


Figure 3 D.s.c. traces obtained on heating blends quenched from 160°C at 10°C min⁻¹. (a) Typical result obtained from a mixed blend (20/32/48); (b) typical result obtained from a segregated blend (40/42/18)

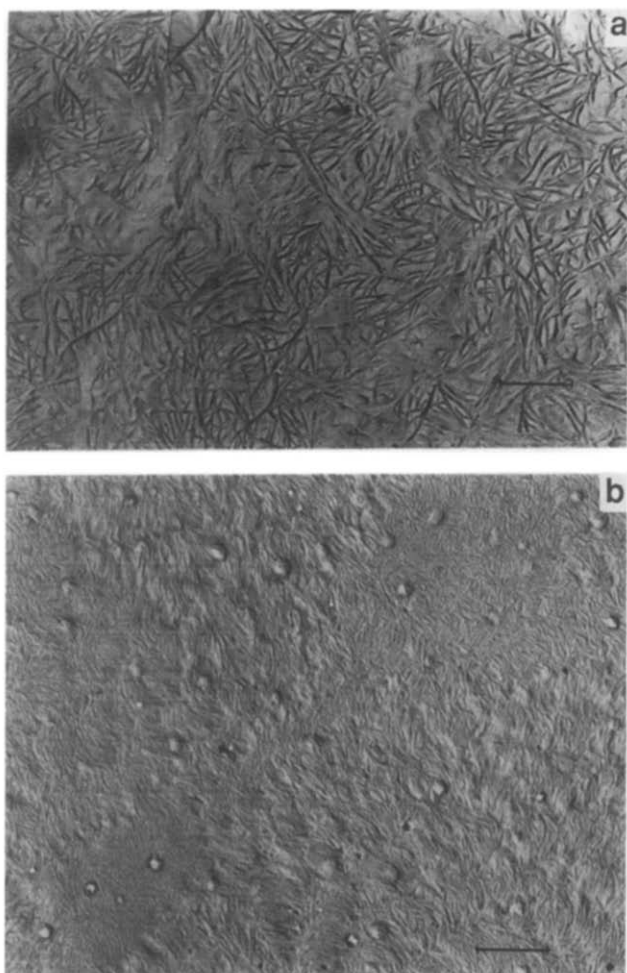


Figure 4 Transmission electron micrographs of surface replicas of blends quenched from 160°C. The blends are the same as those in *Figure 3*. The scale bar represents 1 μm

a mixed system and the other (40/42/18) shows a demixed system. The morphologies of these samples are shown in the electron micrographs of *Figure 4*. Note that in the sample with a single d.s.c. peak (*Figure 3a*) only one morphology is seen (*Figure 4a*) but in the sample showing two d.s.c. peaks (*Figure 3b*) there are two distinct morphologies present, lying in well-separated areas of the specimen (*Figure 4b*).

The ternary phase diagram deduced from these experiments is shown in *Figure 5*. *Figure 5a* shows isothermal contours (obtained by TEM) for all the LLPS regions. We may make an estimate of the likely compositions of the phase-separated regions from a consideration of the melting temperatures of the two phases. In *Figure 5b* we indicate the general directions of the tie lines deduced from such measurements. The phase diagram shows three distinct regions of LLPS. The principal features may be summarized as follows: two lobes occur with the addition of either 2 mol% copolymer to the blend of LPE and 8 mol% copolymer or 8 mol% copolymer to the blend of LPE and 2% copolymer; and a finger-like region occurs when a little LPE is added to a blend of the two copolymers.

It should be noted from *Figure 5a* that the LLPS regions all have rather flat tops with respect to temperature, as do the LLPS regions in the binary phase

diagrams previously determined. The finger-like region at low LPE content rises to just above 160°C; the peak of the lobe near the 8 mol% apex occurs at just over 180°C and the peak of the lobe near the 2 mol% apex is the highest, at about 195°C.

The UCT nature of the LLPS regions has been clearly established, as is shown in *Figure 5a*. We know that all three binary phase diagrams (obtained by blending the components in pairs) show lower critical temperature behaviour, but we have not investigated the phase behaviour at low temperatures away from the binary lines.

DISCUSSION

Descriptive interpretation of the phase separation

In our previous publication⁹ we outlined a simple qualitative scheme, involving the use of free energy diagrams, to interpret the asymmetric phase separation

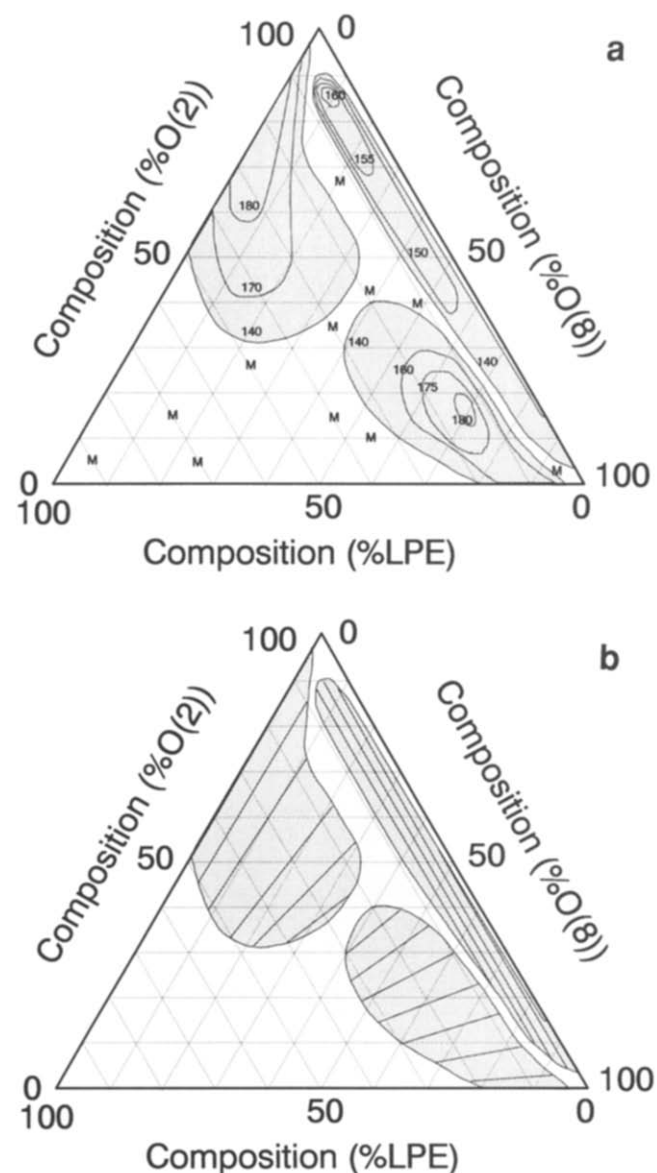


Figure 5 Ternary phase diagram for blends of LPE with 2 and 8 mol% octene copolymers. There are three regions of LLPS. (a) Isothermal contours (note that different contours are shown for the three regions); M indicates a mixed melt. (b) Direction of the tie lines in each of the regions

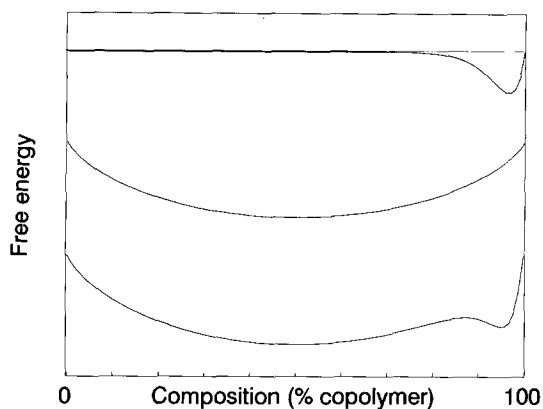


Figure 6 Free energy diagrams: top curve, extra asymmetric free energy term; middle curve, free energy diagram for a fully miscible blend; bottom curve, sum of the above two free energy curves. The free energy curve now illustrates a system that would exhibit phase separation

in binary blends of LPE with octene copolymers. The basis of this model was the assumption that the two polymers were in all cases basically miscible, and that all the free energy changes on mixing were very small. We further postulated that there was some additional, small free energy of mixing which was itself asymmetric in composition; this term may be of either an attractive or a repulsive nature. *Figure 6* shows that when such an asymmetric free energy term (top curve) is added to that for a basically miscible system (middle curve) the total free energy of mixing becomes as illustrated by the bottom curve, and asymmetric phase separation occurs.

We can extend this same simple scheme to aid in the interpretation and understanding of the ternary system. For a ternary system, the free energy diagrams of *Figure 6* become a free energy surface. If we maintain our assumption that the polymers are basically miscible then we would obtain a smooth free energy surface with a minimum near a blend composition of 33/33/33. We may extend the previous binary model by assuming that on adding a small amount of LPE to any blend of BPEs, there would be a small additional free energy term, equivalent to adding a 'trough' in the free energy near the binary line for the two branched polymers. Consideration of the binary phase diagram for the 2 and 8 mol% copolymers indicates that a further 'trough' or 'ridge' should appear on addition of a little 2 mol% polymer to a blend containing mostly 8 mol% copolymer. *Figure 7a* is a photograph of a model depicting such a free energy surface for a set of three miscible polymers. It is a relatively straightforward matter to determine regions of the phase diagram in which phase separation would occur, by finding common tangents to the free energy surface. This has been done for the model free energy surface illustrated in *Figure 7a*, to produce the regions of phase separation qualitatively indicated on the free energy surface. Examples of common tangents to the free energy surface in different regions of phase separation are illustrated in *Figures 7b* and *c*.

Relation of phase diagram to multicomponent systems

The phase diagram that we have observed and interpreted in a simple descriptive manner should lay the basis for the discussion of the possible phase behaviour

in more complex multicomponent systems such as real LLDPEs and VLDPEs. It should be apparent that in all cases where there is only a small amount of linear or lightly branched polymer present (in amounts of only a few per cent) then LLPS should be expected to occur. Further, in systems where no LLPS occurs, it should be possible to induce it, either by the addition of small amounts of linear polymer (if there is none present in the

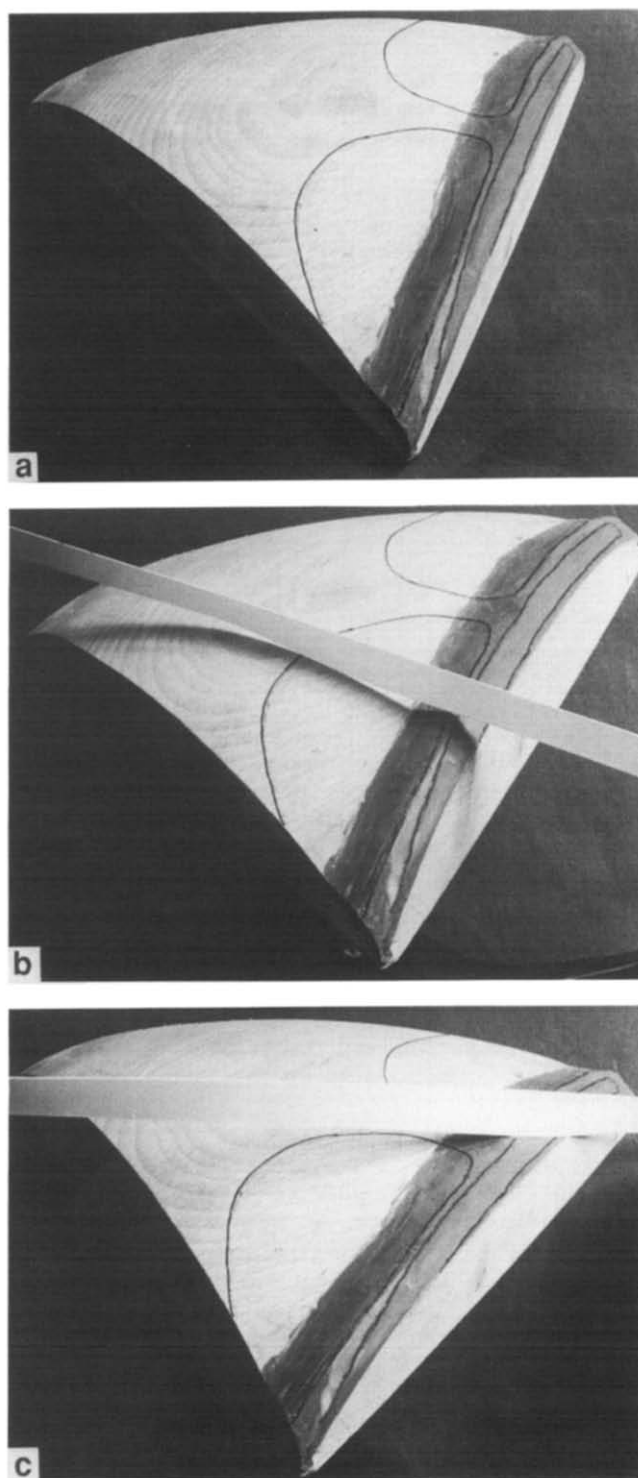


Figure 7 Photographs of a free energy surface model as envisaged for the ternary blend system: (a) general view of the free energy surface with the regions of LLPS sketched; (b) view of the free energy surface showing a common tangent in one region of phase separation; (c) same as (b) but showing a common tangent in the 'finger-like' region of phase separation

first place), or by increasing the amount of the more highly branched species (if there is already a significant quantity of linear material present). Thus, with a reasonable understanding of this (relatively) simple ternary system, it becomes immediately apparent that some straightforward rules can be formulated to aid in the preparation of LLDPEs and VLDPEs in which phase separation is required to be either suppressed or enhanced.

CONCLUSIONS

We have demonstrated that there is a quite complex phase behaviour in a ternary blend system of linear and branched polyethylenes. Further, we have shown that consideration of a simple, descriptive model allows the phase behaviour to be interpreted in terms of the free energy surfaces, leading to some understanding of the underlying physical principles involved.

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REFERENCES

- 1 Barham, P. J., Hill, M. J., Keller, A. and Rosney, C. C. A. *J. Mater. Sci. Lett.* 1988, **7**, 1271
- 2 Hill, M. J., Barham, P. J., Keller, A. and Rosney, C. C. A. *Polymer* 1991, **32**, 1384
- 3 Hill, M. J., Barham, P. J. and Keller, A. *Polymer* 1992, **33**, 2541
- 4 Hill, M. J. and Barham, P. J. *Polymer* 1992, **33**, 4094
- 5 Hill, M. J. and Barham, P. J. *Polymer* 1992, **33**, 4891
- 6 Hill, M. J., Barham, P. J. and van Ruiten, J. *Polymer* 1993, **34**, 2975
- 7 Organ, S. J. and Barham, P. J. *Polymer* 1993, **34**, 459
- 8 Puig, C. C., Hill, M. J. and Barham, P. J. *Polymer* 1993, **34**, 3117
- 9 Barham, P. J., Hill, M. J., Goldbeck-Wood, G. and van Ruiten, J. *Polymer* 1993, **34**, 2981
- 10 Mirabella, F. M., Westphal, S., Fernando, P. L., Ford, E. and Williams, J. G. *J. Polym. Sci., Polym. Chem. Edn* 1988, **26**, 1995
- 11 Deblieck, R. A. C. and Mathot, V. B. F. *J. Mater. Sci. Lett.* 1988, **7**, 1276
- 12 van Ruiten, J. and Boode, J. W. *Polymer* 1992, **33**, 2548
- 13 Wild, L., Ryle, T. and Knobloch, D. *Am. Chem. Soc. Polym. Prepr.* 1982, **23** (2), 133
- 14 Mathot, V. B. F. and Pijpers, M. F. J. *J. Appl. Polym. Sci.* 1990, **39**, 979