Design and properties of co-continuous nanostructured polymers by reactive blending

HELENE PERNOT[1], MARTIN BAUMERT[2], FRANÇOIS COURT[2] AND LUDWIK LEIBLER*[1]

[1]Laboratoire Matière Molle et Chimie (UMR 167, CNRS/ESPCI/ATOFINA), ESPCI 10, rue Vauquelin, 75 005 Paris, France
[2]ATOFINA, CERDATO, 27 470 Serquigny, France
*e-mail: ludwik.leibler@espci.fr

Published online: 2 September 2002; doi:10.1038/nmat711

With an annual production of hundreds of millions of tons, the few commodity polymers that dominate the plastics market cannot satisfy all the applications and expectations. In this context, the fabrication of thermodynamically stable polymer blends structured on submicrometre scales raises much hope, but poses significant scientific and industrial challenges. Here, we propose and demonstrate for an industrially relevant system, polyethylene and polyamide, that hitherto inaccessible co-continuous morphologies can be produced over a wide range of compositions by reactive blending. Paradoxically, the self-assembled structures are thermodynamically stable because of the molecular polydispersity inherent in the production method. These nanostructured materials present a unique combination of properties impossible to achieve with classical blends. This versatile, low-cost and simple strategy should be widely applicable.

Most of the plastics industry market is covered by only a few commodity polymers, including polyolefins, polystyrene and polyvinylchloride. However, the increasingly demanding applications require improved or new combinations of properties, which cannot be satisfied by these few polymers alone. There has therefore been considerable scientific and industrial interest in modifying and mixing together these existing commodity polymers with a view to achieving properties currently exhibited only by more expensive engineering polymers or non-polymeric materials. Polyethylene (PE), for example, represents an annual production of more than a hundred million tons, and is used in a large field of applications ranging from packaging to adhesives and wire coatings. Yet, because of its low melting temperature, polyethylene creeps rather easily and has a relatively poor heat resistance. This limits its widespread use in the automotive and construction industries. For more than three decades, considerable effort has been devoted to the improvement of the high-temperature properties of polyethylene by blending it with a high-melting-temperature polymer such as polyamide[1]. Unfortunately, such blends naturally tend to phase separate on the macroscopic scale. Consequently, a substantial improvement of thermal and mechanical properties such as toughness, stress at break or high-temperature creep resistance can be achieved only when the polyamide phase is continuous. The challenge is to make the polyamide phase continuous while keeping polyethylene as the major component. In this context, it seems particularly desirable to be able to make materials with finely dispersed co-continuous morphologies. Here, we present a new general strategy to obtain stable co-continuous polymer materials structured at the nanometre scale, and show, for the polyethylene and polyamide pair, that the as-formed blend can exhibit a remarkable combination of properties.

So far in polymer science, two methods have been proposed to obtain co-continuous structures in polymer blends. The first consists of quenching non-equilibrium morphologies produced during intensive high-temperature mixing of blend components. The major difficulty here is to achieve submicrometre structure by mechanical mixing, and to preserve the optimized morphology during the processing stage. Added compatibilizing agents or compatibilizing agents formed *in situ* help to

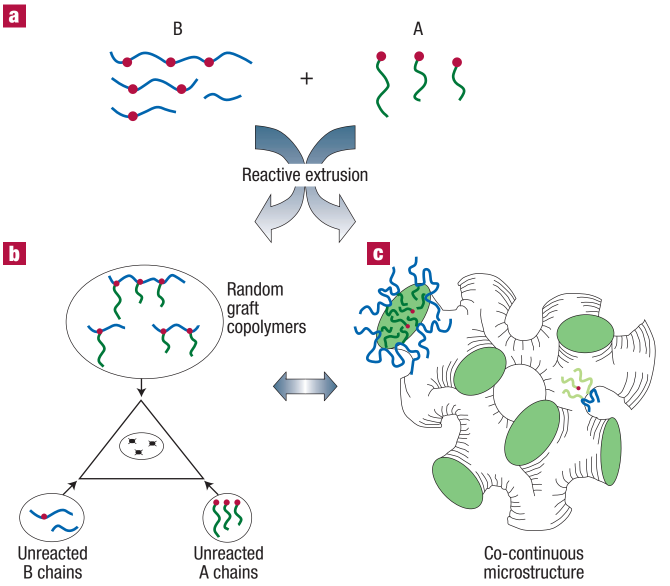

Figure 1 Reactive blending principle and strategy. a, End-reactive A chains (such as PA_6) react with B chains (such as PE-1), which bear reactive groups along the backbone. During reactive blending, random graft copolymers are formed. **b**, The mixture of random graft copolymers and unreacted backbones (B chains) and grafts (A chains) results in the thermodynamically stable microstructure in **c**.

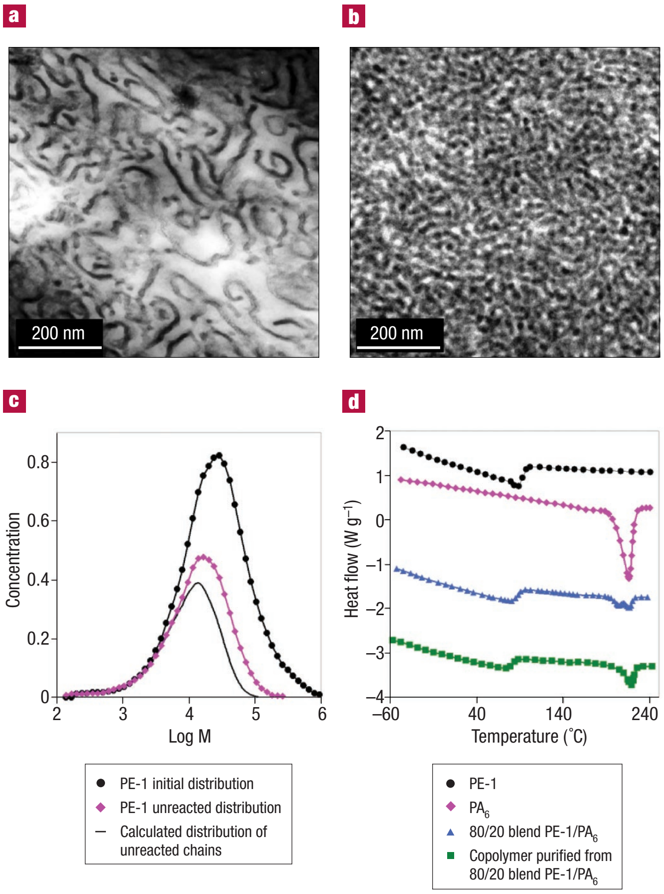

Figure 2 Co-continuous nanostructured blend. Transmission electron micrographs for: **a**, 80/20 blend PE-1/PA_6 after 1 min of extrusion (the PA_6 phase is stained in black with phosphotungstic acid). **b**, Isolated copolymer purified from 80/20 blend PE-1/PA_6. **c**, Molecular weight distribution obtained by size-exclusion chromatography. **d**, Differential scanning calorimetry heating curves at 20 °C min^{-1}.

control the coalescence and improve the adhesion between the two phases. The other method uses self-assembling and structuring properties of block copolymers: linear macromolecules consisting of two or more monomer sequences covalently linked together. In a striking analogy with surfactant molecules and microemulsions[2], A–B block copolymers with carefully controlled molecular weight and composition are expected to self-assemble when mixed with the homopolymers A and B to form, under favourable conditions, thermodynamically stable co-continuous structures at the nanometre scale. Very recently the existence of such phases has been confirmed in studies on model systems[3–7]. Unfortunately, these phases exist only in a narrow channel of composition and molecular parameters. More importantly, for many polymer pairs such as polyethylene and polyamide, it is very difficult or just impossible to synthesize linear block copolymers. In this work, we show that reactive blending may serve as a low-cost method to obtain nanostructured thermodynamically stable materials with co-continuous morphology, and demonstrate the versatility of this technique by applying it to the industrially relevant pair of polymers: polyethylene and polyamide. The co-continuous materials so produced are structured on the scale of tens of nanometres and are crystalline. In consequence, they exhibit exceptional properties inaccessible to classical blends. The main new idea is paradoxical. We rely on polydispersity and randomness introduced naturally by the production process, reactive blending, to impart microscopic organization and thermodynamic stability.

More specifically, we propose to use random graft copolymer chains synthesized by reactive blending, a process in which two polymers carrying complementary reactive groups are mixed together and react at high temperature (Fig. 1). The backbone polymers, B, carry reactive groups randomly distributed along their length, whereas the A chains, the grafts, are functionalized at one end only. The challenge is to achieve a thermodynamic self-assembly of random graft copolymers formed *in situ* without expulsion and phase separation of unreacted chains. The polydispersity of the backbone and of the grafts, as well as the randomness in graft-attachment positions paradoxically helps to stabilize disordered co-continuous structures. Indeed, it enables local fluctuations of the interface curvature, and facilitates the incorporation of homopolymers in blends. This is a unique polymeric effect. In low-molecular-weight surfactant systems, co-surfactants—slightly different surfactant molecules—are usually introduced to increase the interface flexibility and thereby stabilize a microemulsion phase[7]. Here, a well-adapted molecular weight distribution and inherent molecular disorder may naturally yield a co-surfactant-like effect.

The choice of our reactive systems heavily relies on design principles available in previous studies. First, the coupling reaction has to be fast. Recent experiments show that the reaction between maleic anhydride (MAH) and NH_2 groups satisfies this requirement[8–14].

Second, the reactive groups have to be randomly distributed along the backbone chains so that the number of reactive groups is proportional to the backbone chain length. Indeed, homopolymer expulsion is driven by entropic effects related to the stretching of copolymer chains in self-assembled organizations[15]. To avoid the phase separation, homopolymers have to be short. This is where polydispersity and random distribution of reactive groups become important. Consider a wide-molecular-weight distribution of B chains. A critical molecular weight exists below which B chains do not bear (on average) any reactive site. Therefore, only the shortest B chains are left unreacted, but they have a chance to be incorporated into the self-assembled structure formed by the graft copolymers made from the longer B chains. This natural selection does not work for the end-functionalized A chains. It is therefore important that they are as short as possible—but just long enough to preserve the capacity of crystallization. In analogy with block copolymers[16,17], we expect that both the random distribution of graft-attachment locations and the polydispersity of the graft length should reduce chain stretching in graft copolymer structures, and should facilitate incorporation of unreacted chains.

Finally, guided by some basic strong segregation models, we anticipate that the average fraction of reactive units on the backbone chains has to be chosen so that the average distance between grafts is approximately twice the average graft length. The strong asymmetry in graft copolymer composition is then avoided, and interfaces with large radii of curvature are favoured. The inherent disorder caused by polydispersity increases the flexibility of the interfaces, and can naturally stabilize disordered co-continuous structures, such as that in Fig. 1. Such structures are well adapted to accommodate unreacted homopolymers A and B without distinction, and allow the overall material composition to be tuned over a wide range.

Our experiments seem to confirm the general picture described above. We present some typical examples. The first, in which a co-continuous interconnected morphology has been realized, is shown in Fig. 2a. The grafting reaction was performed in a Leistritz co-rotating twin-screw extruder at 220 °C for 1 min (rotation rate 75 r.p.m.). The functionalized polyethylene used for the backbone chain (PE-1) is a random copolymer of ethylene, ethylacrylate and MAH. This polymer has been synthesized at high pressure and high temperature using free-radical initiators in a continuous copolymerization process. PE-1 had a number-average molecular weight of 9,300 g mol^{-1}, a polydispersity index of 5.5, an MAH weight fraction of 1.0% and an ethylacrylate weight fraction of 17%. The polyamide-6 (PA_6), synthesized by polycondensation, is terminated at one end by the reactive functional group NH_2, and at the other end by a non-reactive group CH_3. PA_6 had a number-average molecular weight of 2,500 g mol^{-1} and a polydispersity index of 2. The weight fraction of PA_6 was 20%, which corresponds to a stoichiometric ratio of 1 MAH/1 NH_2. The morphology was observed with a transmission electron microscope (TEM) on samples cryomicrotomed at –80 °C. The sections, approximately 50 to 100 nm thick, were picked up on gold grids, and the PA_6 phase was preferentially stained in a 2% aqueous solution of phosphotungstic acid for 30 min at 50 °C. All sections cut along three perpendicular axes show very similar morphologies. Clearly a macroscopically homogeneous mesophase made of interconnected sheets of PA_6 is observed with a characteristic thickness of about 20 nm (Fig. 2a). The observed structure does not depend on mixing conditions. In fact, we have obtained similar morphologies using a co-rotating twin-screw microextruder (made by DACA, Goleta, California) and varying the mixing time (1–15 min) and screw rotational speed (10–100 r.p.m.). In addition, the structure is preserved after long annealing (three weeks) above the melting point of PA_6, and after several processing operations such as injection moulding, extrusion or compression moulding. The only change brought by successive processing is an anisotropic orientation of the co-continuous morphology induced by the flow field. These observations confirm the thermodynamic character of structure formation, and indicate that when molecular parameters are well adjusted, the reactive blending is a very robust method of material preparation.

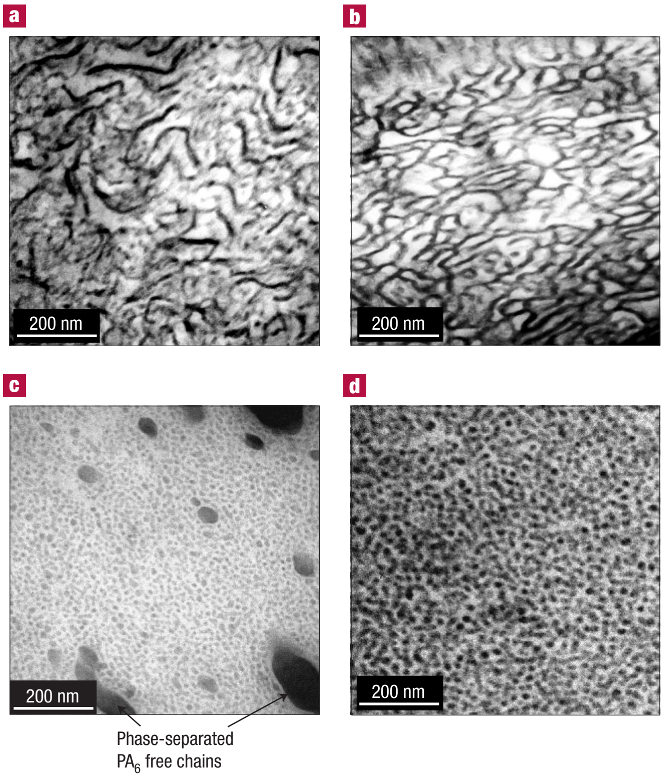

Figure 3 Co-continuous versus phase-separated blends. Transmission electron micrographs, after 1 min of extrusion, for: **a**, 70/30 blend PE-1/PA_6; **b**, 60/40 blend PE 1/PA_6; **c**, 80/20 blend PE-0.5/PA_6; **d**, Isolated copolymer purified from 80/20 blend PE 0.5/PA_6.

The as-formed material contains graft copolymers as well as unreacted PA_6 and PE-1 chains. Our hypothesis is that graft copolymers form a co-continuous structure by themselves, and that this is why they can be readily swollen by homopolymers without macroscopic phase separation. To verify this, we isolated the graft copolymers from the extruded blends by using a fractionation method based on solvent extraction. The purification method consists of two steps. In the first step, extraction of unreacted PE-1 chains was performed with a Soxhlet extractor in boiling chloroform, a selective solvent for the copolyethylene. A second extraction was then performed on the solid residue with formic acid, a selective solvent for the free chains of PA_6. At each step of the extraction, the fractionated parts were quantitatively analysed by both infrared and NMR spectroscopy. The remaining residue is composed of the purified PE-1/PA_6 grafted copolymer, and constitutes 45 wt% of the initial material. The weight fraction of PA_6 in the copolymer, measured experimentally by three techniques—mass balance, NMR and infrared spectroscopy—was 30%, 20% and 28%, respectively. The morphology of the copolymer extracted from the blend observed by TEM is shown in Fig. 2b. The copolymer spontaneously self-assembles to form a disordered bicontinous microphase-separated structure. Clearly, the PE-1 zones are thinner than in the initial blend presented in Fig. 2a, which confirms the ability of the graft copolymer to incorporate unreacted PE-1 chains.

The incorporation of the unreacted PE-1 chains is possible owing to the phenomenon of natural selection of unreacted chain length. High-temperature size-exclusion chromatographic (SEC) analysis of initial and extracted molecular weight distributions of PE-1 chains (Fig. 2c) demonstrates that indeed only the shortest PE-1 chains did not react.

The SEC results also confirm the key design principle: natural selection is possible owing to the random distribution of functional groups along the backbone PE-1 chains. Indeed, for such a random distribution, it is straightforward to show[18] that the fraction x_i of chains of i monomers that did not react should be equal to:

$$x_i = \sum_{\alpha=0}^{i} \frac{(fi)^{\alpha} e^{-fi}}{\alpha!} (1-q)^{\alpha}$$

where α denotes the number of reactive groups per chain and f and q are equal to the average (macroscopic) molar fraction of reactive groups and to the grafting probability, respectively. The calculated distribution

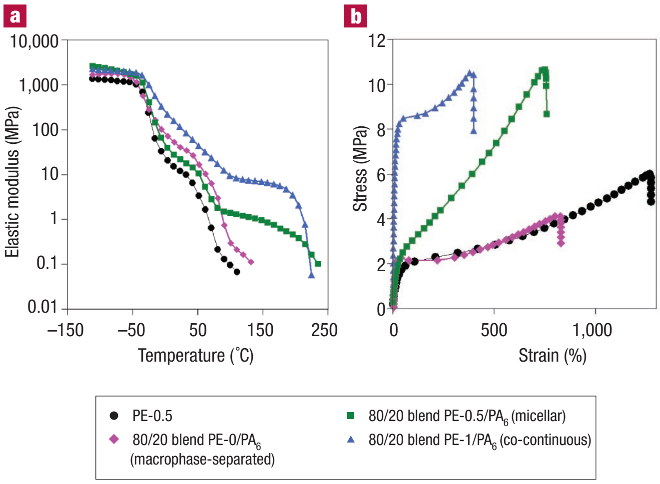

Figure 4 **Mechanical properties.** **a**, Young's elastic modulus from dynamic mechanical analyser measurements (TA Instruments) at 1 Hz, 0.1% strain and a heating rate of 3 °C min^{-1}. **b**, High-strain tensile properties.

of unreacted chain length with $f = 0.0028$ and a grafting probability of $q = 0.5$ (equal to the average fraction of reacted groups) is included in Fig. 2c. It is in good agreement with the experimental distribution, considering the precision of experiments and the total absence of fitting parameters.

Copolymers that form co-continuous morphologies are able to incorporate a large excess of unreacted PA$_6$ chains. For example, Fig. 3a and b shows that, in blends containing 30% and 40% by weight of PA$_6$ the nanostructure is conserved: the PA$_6$ free chains swell PA$_6$ microdomains without provoking macroscopic phase separation. We have verified by extraction and SEC that the graft copolymer formed by reactive extrusion is independent of the initial composition of the blend. The characteristics of the polymers, MAH concentration and grafted chain length, are thus the most relevant parameters. These observations confirm a promising opportunity of using reactive blending to prepare thermodynamically stable blends over a large range of compositions.

To test further the crucial role played by the architecture of the backbone polymer, we studied materials with smaller fractions of reactive sites. The copolymers formed are expected to be more asymmetric, and should lead to strongly curved interfaces with PA$_6$ on the concave side. As a result, a fraction of the unreacted PA$_6$ chains should be expelled from the copolymer mesophase[19]. We used a PE with a MAH weight fraction of 0.5% (PE-0.5). PE-0.5 had a number-average molecular weight of 16,000 g mol^{-1}, a polydispersity index of 5 and 30 wt% of ethylacrylate. A composition of 80/20 PE-0.5/PA$_6$ was chosen, which corresponds to a ratio of 1 MAH/2 NH$_2$. After reaction, the graft copolymer, extracted by the procedure described above, constituted 50 wt% of the blend. Its morphology is shown Fig. 3d. The weight fraction of PA$_6$ in this copolymer was about 12%. As expected, we observe a disorganized spherical morphology with PA$_6$ grafts forming spherical domains. This result shows that our polydisperse random copolymers qualitatively follow a morphology evolution similar to that of classical copolymers[20]. The asymmetric structure of the copolymer is no longer able to solubilize all the PA$_6$ free chains, most of which macrophase separate as can been seen in Fig. 3c. The matrix itself consists of graft copolymer micelles dispersed in unreacted PE-0.5 chains. Similar spherical and cylindrical structures organized at the nanometre scale have previously been reported with other polymers using the MAH/NH$_2$ coupling reaction[8–14]. In all these experiments, macroscopic phase separation has been avoided because the reaction yield was almost complete.

It is remarkable that, even when confined in self-assembled nanostructures, the two components are able to crystallize. For example, the heating curve obtained from differential scanning calorimetry of 80/20 PE-1/PA$_6$ (Fig. 2d) shows two melting points: the first one at about 90 °C corresponds to melting of PE-1 crystallites, whereas the second one at 220 °C can be assigned to the short PA$_6$ chains. The crystallization behaviour of a microphase-separated block copolymer is the result of a complex competition between thermodynamic phenomena, which favour the breakdown of microphase organization, and the kinetics of reorganization implying mass transport. The confined crystallization of block copolymers in organized structures can occur when the microphase separation process is strong enough to inhibit morphological rearrangement during the timescale of crystallization[21–23]. In our sample, the PA$_6$ phase crystallizes first from the melt in the confined nanodomains, because the phase separation and the entanglements of the PE-1 copolymer backbone allow no rearrangement during the crystallization process. When the PE-1 crystallizes, it is confined by the already crystallized PA$_6$ phase. This combination of the crystalline systems of PA$_6$ and PE-1 is also observed in the purified copolymers for both the co-continuous (Fig. 2d) and micellar morphologies.

Because both components are able to crystallize in confined nanodomains, the nanostructured materials have unique properties. One example concerns high-temperature creep resistance. In contrast to PE or classical PE/PA blends, the nanostructured materials do not creep when heated above the PE melting point. The nanostructured materials containing as much as 80 wt% of PE exhibit a nearly constant elastic modulus of 10 MPa (for PE-1/PA$_6$) and 1 MPa (for PE-0.5/PA$_6$) between 100 °C and 220 °C (Fig. 4a). They start to flow under stress only at temperatures above 220 °C when PA$_6$ crystallites melt. In contrast, a classical blend of unreactive PE (PE-0 with no MAH and 30% of ethylacrylate) and PA$_6$ flows readily when the temperature is raised above 100 °C. The remarkable strengthening at high temperatures observed in PE-1/PA$_6$ materials organized at nanometre scales results from the continuity of the PA$_6$ crystalline phase. The creep resistance of PE-0.5/PA$_6$ samples arises from PE-0.5 chain bridges linking together PA$_6$ domains. These domains act as physical crosslinks and prevent flow up to the melting temperature of PA$_6$. The existence of bridges between PA$_6$ domains is possible only because some of the PE-0.5 chains have more than one graft chain. Hence, different grafts belonging to the same PE-0.5 backbone can belong to different PA$_6$ domains. The bridging mechanism also operates in co-continuous systems.

The ultimate solid-state mechanical properties also show considerable improvements. The high-strain tensile behaviour has been tested on dog-bone tensile bars (75 × 4 × 2 mm) with an Instron tensile testing machine at a strain rate of 7×10^{-2} s^{-1} (Fig. 4b). Compared with PE 0.5 alone, the most striking feature of the nanostructured blends comes from the important increase of stress at break, without loss of ductility. The co-continuous materials show a substantial increase of the yield stress, whereas the micellar systems exhibit strong stress hardening owing to the bridging effect discussed above. Such a combination of properties, resistance at break and high ductility, is impossible to attain in classical blends with PE being the major phase. The formation of nanostructures really makes a difference.

We have found that an appropriate polymer polydispersity and random graft copolymerization by reactive blending can lead to the production of stable self-assembled nanostructured blends with properties inaccessible to classical blends. The example of PE and PA presented here is interesting in its own right. It shows that even with PE as the major component, it is possible to improve material transparency, creep and solvent resistance, and increase the stress at break while keeping ductility. Polyamides, other than PA$_6$ (for example, PA$_{11}$), can also be used as grafts, bringing an additional lever to finely tune the ultimate melting temperature. This unique combination of properties should open applications hitherto inaccessible to PE. Looking to the future, the approach developed here provides a versatile route to other new materials, which, we hope, will lead to new applications for already existing polymers.

Received 14 June 2002; accepted 29 July 2002; published 2 September 2002.

References

1. Utracki, L. A. *Polymer Alloys and Blends* (Hanser, New York, 1989).
2. de Gennes, P. G. & Taupin, C. Microemulsions and the flexibility of oil/water interfaces. *J. Phys. Chem.* **86,** 2294–2304 (1992).
3. Bates, F. S. *et al.* Polymeric co-continuous microemulsions. *Phys. Rev. Lett.* **79,** 849–852 (1997).
4. Fredrickson, G. H. & Bates, F. S. Design of co-continuous polymeric microemulsions. *J. Polym. Sci. Part B: Polym. Phys.* **35,** 2775–2786 (1995).
5. Hillmyer, M. A., Maurer, W. W., Lodge, T. P., Bates, F. S. & Almdal, K. Model co-continuous microemulsions in ternary homopolymer/block copolymer blends. *J. Phys. Chem. B* **103,** 4814–4824 (1999).
6. Washburn, N. R., Lodge, T. P. & Bates, F. S. Ternary polymer blends as model surfactant systems. *J. Phys. Chem. B* **104,** 6987–6997 (2000).
7. Fredrickson, G. H. & Bates, F. S. Stabilizing co-continuous polymer blend morphologies with ABC block copolymers. *Eur. Phys. J. B* **1,** 71–76 (1998).
8. Orr, C. A., Adedeji, A., Hirao, A., Bates, F. S. & Macosko, C. W. Flow-induced reactive self-assembly. *Macromolecules* **30,** 1243–1246 (1997).
9. Lyu, S.-P. Cernohous, J. J., Bates, F. S. & Macosko, C. W. Interfacial reaction induced roughening in polymer blends. *Macromolecules* **32,** 106–110 (1999).
10. Charoensirisomboon, P., Inoue, T. & Weber, M. Interfacial behavior of block copolymers in situ-formed in reactive blending of dissimilar polymers. *Polymer* **41,** 4483–4490 (2000).
11. Ibuki, J. *et al.* Reactive blending of polysulfone with polyamide: a potential for solvent-free preparation. *Polymer* **40,** 647–653 (1999).
12. Charoensirisomboon, P., Chiba, T., Solomko, S. I., Inoue, T. & Weber, M. Reactive blending of polysulfone and polyamide: a difference in interfacial behavior between in situ formed block and graft copolymers. *Polymer* **40,** 6803–6810 (1999).
13. Oyama, H. T., Ougizawa, T., Inoue, T., Weber, M. & Tamaru, K. Interfacial coupling between immiscible polymers: reactive interface between polysulfone and amorphous polyamide. *Macromolecules* **34,** 7017–7024 (2001).
14. Yin, Z., Koulic, C., Pagnoulle, C. & Jerome, R. Reactive blending of functional PS and PMMA: interfacial behavior of in situ formed graft copolymers. *Macromolecules* **34,** 5132–5139 (2001).
15. de Gennes, P. G. Conformations of polymers attached to an interface. *Macromolecules* **13,** 1069–1075 (1980).
16. Milner, S. T., Witten, T. A. & Cates, M. E. Effects of polydispersity in the end-grafted polymer brush. *Macromolecules* **22,** 853–861 (1989).
17. Thompson, R. B. & Matsen, M. W. Improving polymeric microemulsions with block copolymer polydispersity. *Phys. Rev. Lett.* **85,** 670–673 (2000).
18. Pernot, H. Thesis, Univ. Pierre et Marie Curie (Paris 6), in preparation.
19. Leibler, L. Emulsifying effects of block copolymers in incompatible polymer blends. *Makromol. Chem.-M. Symp.* **16,** 1–17 (1988).
20. Pochan, D. J. *et al.* Morphologies of microphase-separated A_2B simple graft copolymers. *Macromolecules* **29,** 5091–5098 (1996).
21. Loo, Y.-L., Register, R. A., Ryan, A. J. & Dee, G. T. Polymer crystallisation confined in one, two or three dimensions. *Macromolecules* **34,** 8968–8977 (2001).
22. Loo, Y.-L., Register, R. A. & Ryan, A. J. Modes of crystallisation in block copolymer microdomains: breakout, templated, and confined. *Macromolecules* **35,** 2365–2374 (2002).
23. Xu, J.-T. *et al.* Morphological confinement on crystallisation in blends of poly(oxyethylene-*block*-oxybutylene) and poly(oxybutylene). *Macromolecules* **35,** 3614–3621 (2002).

Acknowledgements

We are indebted to L. Monnerie and A.-V. Ruzette, and also to P. Robert and M. Hert from Atofina for helpful discussions on reactive blending and polymer alloys. We also thank L. Murino for technical advice, P. Coupard for TEM observations and C. Degoulet for SEC analysis. We are grateful to S. Granick for comments on the manuscript.
Correspondence and requests for materials should be addressed to L.L.

Competing financial interests

The authors declare that they have no competing financial interests.