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Ultrasonic production of block copolymers as *in situ* compatibilizers for polymer mixtures

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The use of high-intensity ultrasound for forming copolymers by sonication of mixtures of homopolymers is discussed. It is shown that the block copolymers formed *in situ* by this method can be used to compatibilize blends of immiscible polymers. The mixtures used in this preliminary study were polystyrene with either poly(*cis*-butadiene) or poly(methyl phenyl silane). The sonochemical method was found to be convenient and easy to use compared with the usual procedure of adding preformed block copolymers as compatibilizing agents. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer blends; compatibilization; sonication)

Introduction

There is considerable current interest in the production and characterization of polymer blends[1]. Most polymer mixtures are thermodynamically incompatible although, in general, better mechanical and material performance can be obtained with compatible blends[2]. The number of miscible systems known remains quite small, such systems generally involving components between which some positive interaction can take place to overcome the very low entropy change on mixing. An alternative approach to improving miscibility is to add a compatibilizing agent such as a copolymer containing sequences of the two polymers. The copolymer acts as an 'emulsifier' by dissolving in both domains, reducing the interfacial energy and leading to miscibility. Synthetic methods for the production of block copolymers include[3] sequential monomer addition during living anionic or group transfer polymerization and the reaction of α,ω-functionalized oligomers. However, these are complex and relatively expensive procedures, particularly on a large scale.

Previous work in the authors' laboratory has involved characterization of the degradation of polymer chains caused by exposure to high-intensity ultrasound[4–6]. Here, the rapid movement of solvent molecules and intense shock waves around cavitation bubbles set up large shear gradients which stretch out and break chains in a non-random cleavage that occurs preferentially near the centre of the chain. Variation of the experimental conditions such as solvent, concentration and temperature allows considerable control over the resulting polymer. The primary product of the sonochemical cleavage of organic polymers is a macromolecular radical. A number of workers[7,8] have sonicated mixtures of two polymers, the macroradicals from which combine to form a block copolymer. Problems with this approach include control of the two block lengths and the difficulty of recovering the copolymer from the remaining homopolymers. A more controllable method[9], which has been used in our work[10], involves using the macroradical to initiate polymerization of a second monomer in solution, where varying the concentration can modify and control the block lengths.

For use as a compatibilizer, precise control of the block lengths is unimportant as long as they remain large enough to enter the homopolymer domains. Also, recovery of the copolymer from the parent homopolymers is not necessary, so that the limitations of the sonochemical method for preparing block copolymers do not arise. The possibility of using ultrasound to compatibilize normally immiscible polymers has therefore been examined in this work. Two systems have been studied for this preliminary report. Polystyrene–butadiene blends are important in the production of 'high impact', rubber-modified polystyrenes[11,12]. The second system includes a class of materials, all-silicon backbone polymers, which has attracted considerable attention recently. Poly(organosilanes) are becoming important for a number of reasons due to their interesting photo- and electroactivity[13]. The first report of a block copolymer used to compatibilize poly(methyl phenyl silane) with polystyrene in an effort to improve its mechanical properties, appeared recently[14]. This employed a multistep process where a carefully produced α,ω-dichloropolysilane was coupled with an anionically produced polystyryl lithium. This report was rapidly followed by descriptions of the structure and morphology in these and similar blends[15,16].

This communication demonstrates the potential of the ultrasonic method, advantages of which include the speed and convenience of a single-step process.

Experimental

Materials. The polystyrene (PS) was a secondary standard with a number-average molecular weight of 120000 and polydispersity of 2.4. It was supplied by Aldrich Chemical Co. as was the poly(*cis*-butadiene), the specification for which was 98% *cis* and molecular

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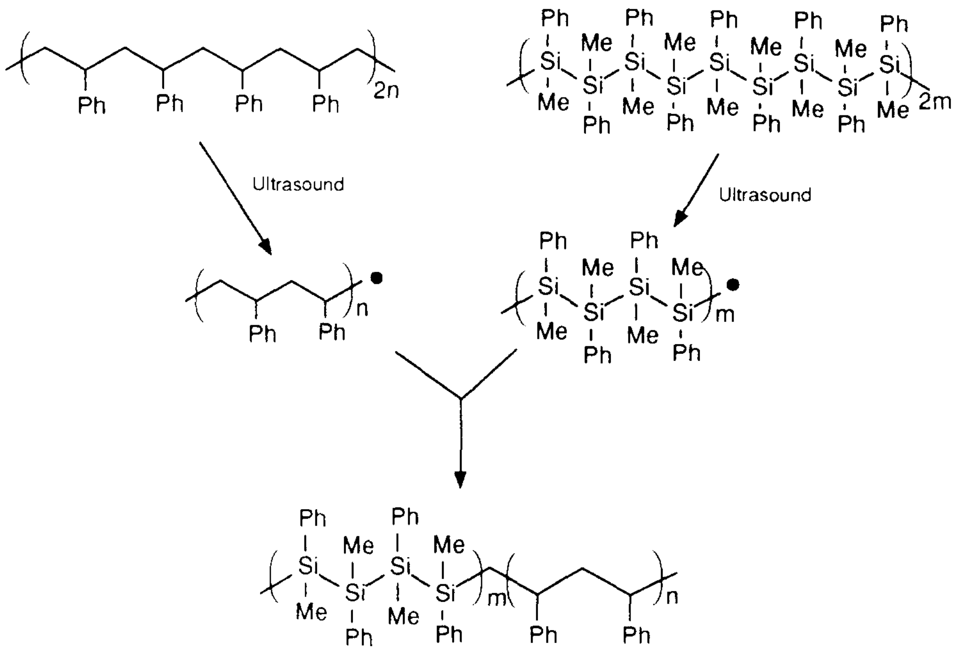

Scheme 1

weight > 2 000 000. The poly(methyl phenyl silane) (PMPS) was prepared in our laboratory by the usual Wurtz coupling method[13,17]; it had a polystyrene equivalent molecular weight and polydispersity, measured by gel permeation chromatography, of 31 000 and 5.1, respectively. Solvents were of reagent grade or better and were also supplied by Aldrich Chemical Co.

Sonication procedure. Sonications were carried out in a cell with a capacity of 100 cm^3 similar to that described previously[4]. The polymers were dissolved in toluene to make 1% solutions by weight containing 80% polystyrene and 20% of the other component. The solutions were deoxygenated by bubbling oxygen-free nitrogen through for 30 min and a flow of gas over the solution was maintained during sonication. Sonication was carried out for 1 h at a calorimetrically determined intensity of $37.5 \pm 3.5\,W\,cm^{-2}$.

Material analysis. Portions of the sonicated solutions were coated onto aluminium pans and the solvent removed in a vacuum oven at 120°C. The pans were sputter-coated with gold and micrographs recorded in the usual manner[18] on a Jeol T-330 scanning electron microscope (SEM).

Results and discussion

The primary product of sonochemical degradation in all the carbon-based polymers studied to date has been a macromolecular radical, confirmed both by trapping experiments and the use of electron spin resonance spectroscopy[4,7]. This is also the case in poly(methyl phenyl silane)[19]. The basic requirement is that the polymer molecular weight is larger than the limiting value for the degradation, as is the case in all the materials used here. Hence, the process can be represented as shown in *Scheme 1*.

An additional mechanism is possible in the case of poly(*cis*-butadiene). A macroradical arising from the degradation of polystyrene could attack a double bond along the chain to give a graft copolymer which could also, in principle, act as a compatibilizer.

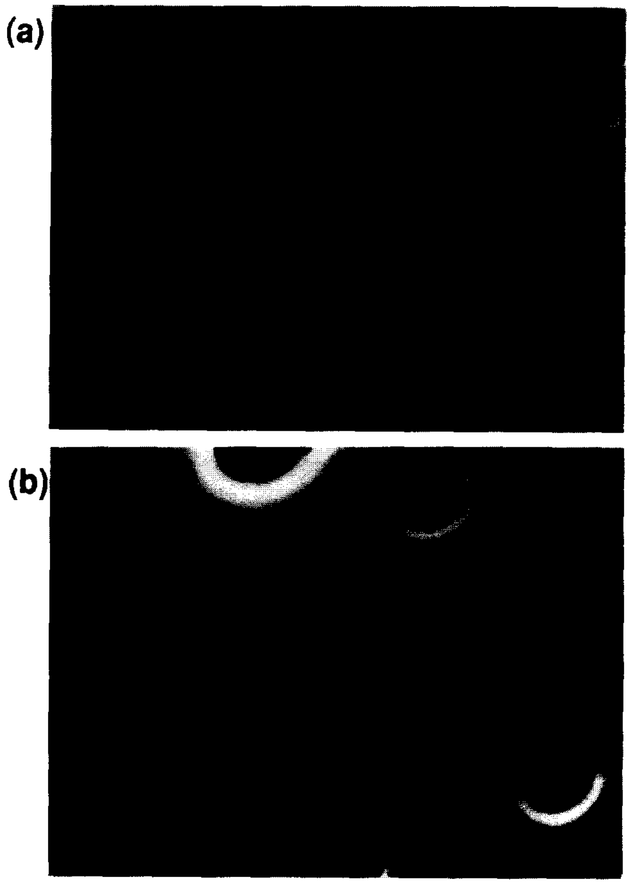

Figure 1 Electron micrographs of polystyrene-poly(*cis*-butadiene) mixture prior to sonication: (a) magnification × 1000; (b) magnification × 10 000

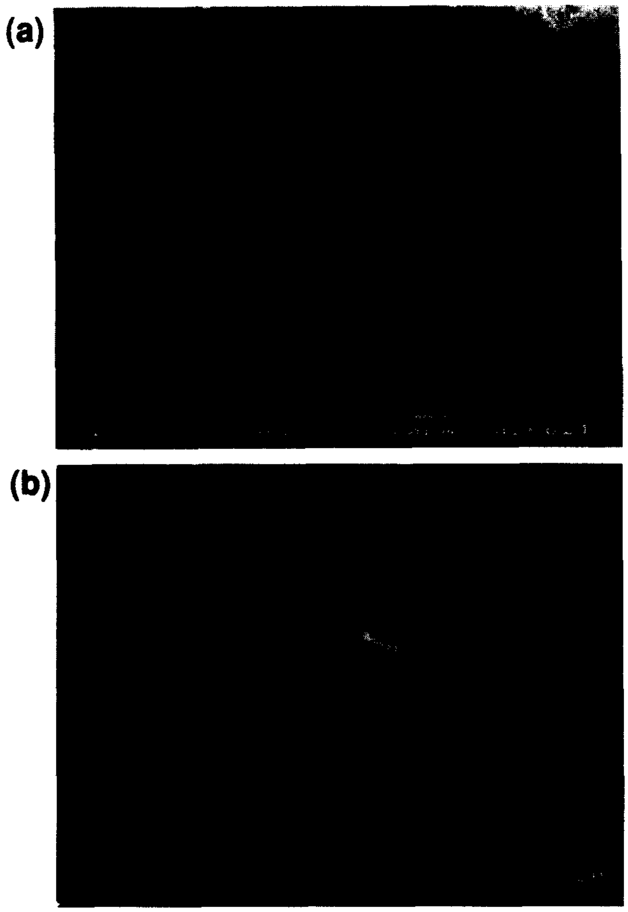

Figure 2 Electron micrographs of polystyrene–poly(*cis*-butadiene) mixture after sonicating separately for 1 h and mixing: (a) magnification × 1000; (b) magnification × 10 000

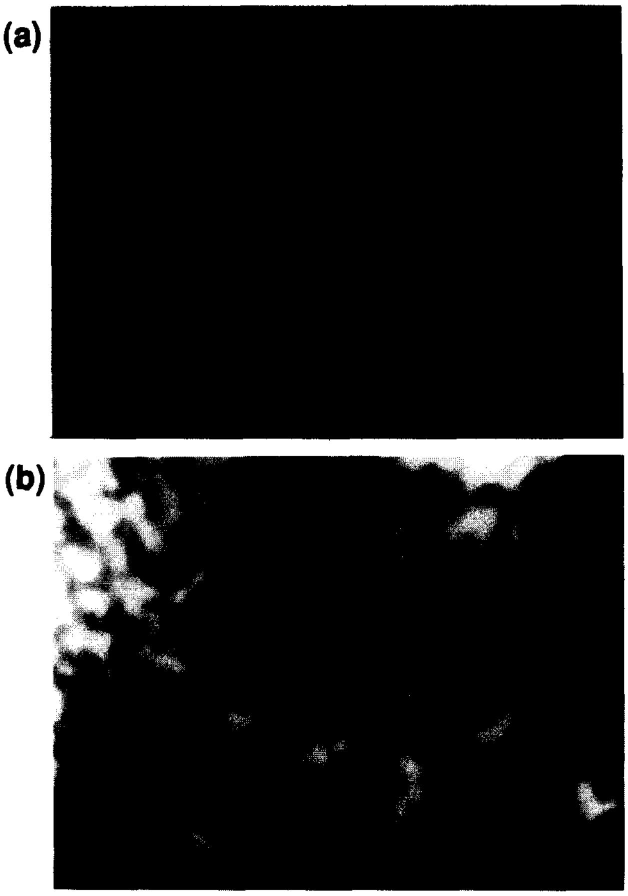

Figure 3 Electron micrographs of polystyrene–poly(*cis*-butadiene) mixture after sonication for 1 h: (a) magnification × 1000; (b) magnification × 10 000

*Poly(styrene-*b*-butadiene).* The electron micrographs recorded for films cast from this mixture prior to sonication are shown in *Figure 1*. There is clear two-phase behaviour, with the polybutadiene dispersed in the polystyrene matrix in domains approximately 2–5 μm in size. To discount the possibility that a simple reduction in molecular weight caused by sonication could be responsible for any effects, solutions of the polymers were sonicated separately under the same conditions and then mixed. SEM micrographs of the resulting films are shown in *Figure 2*. While the appearance is somewhat different to *Figure 1*, the two-phase behaviour is still apparent and the domain size rather larger. The effect of sonication is shown in *Figure 3*. While some small domains remain, the high-magnification micrograph indicates that there is a much larger degree of homogeneity in the sonicated blend.

*Poly(styrene-*b*-methyl phenyl silane).* The SEM micrographs from this system are shown in *Figure 4*. While the effect is less pronounced here, the texture of the blend after sonication is considerably modified and there are no well-defined biphasic regions shown in *Figure 4a*. Again, the blend after sonication clearly displays a much greater degree of compatibility as seen in the higher magnification pictures.

Further discussion. Tessié and co-workers showed that inclusion of 10% by weight of a block copolymer into a blend of PS and PMPS led to better dispersion of the components and a reduced domain size from 5–10 μm to < 1 μm, so that the results obtained here mirror their studies. However, in this work, it was achieved in a much shorter process time and avoided the complexity of reaction conditions needed for the anionic polymerization. Clearly, conventional procedures relying on ionic or group transfer type mechanisms are superior to the ultrasonic method in that they yield recoverable, characterizable copolymers. However, if the aim is simply to obtain a compatible blend, then the avoidance of the rigorous reaction conditions required could be a considerable advantage. Apparatus is now coming on the market which will allow operation of sonochemical processes at reasonably large, commercially viable, scales. Before widespread adoption, the process must be optimized in terms of the ultrasound intensity and treatment time. For example, the process described here was performed for only 1 h. Longer times should lead to a greater degree of compatibilization. Suitable manipulation of the time and ultrasound intensity may allow tuning of the compatibility, giving a further parameter to control the structure and morphology in blends and mixtures. Operation at much higher concentrations than those used here would be necessary and study of these factors in a wider range of systems will be the next phase of our work.

Conclusion

We have shown that irradiation of mixtures of polymers dissolved in a common solvent can lead to

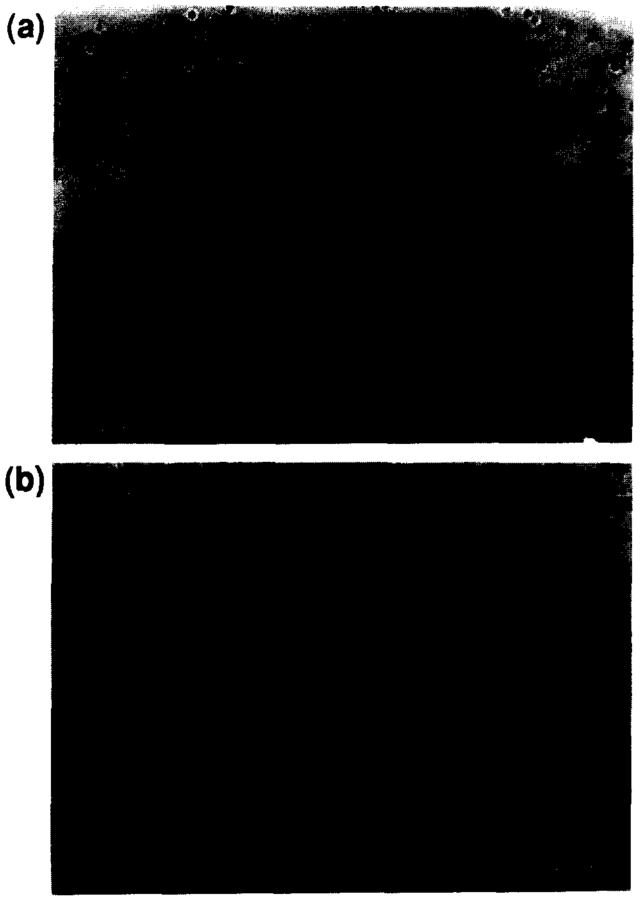

Figure 4 Electron micrographs (magnification × 1000) of PS–PMPS mixtures: (a) before sonication; (b) after sonication

compatibilization of otherwise immiscible polymer mixtures through the formation of block copolymers. The resulting blends appear by electron microscopy to be more homogeneous. Although the methodology has limitations in the control of the structure of the copolymer and its recovery, it has great potential for *in situ* mixing of polymers at the molecular level.

Acknowledgements

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