Epoxy masters for embossing nanotopographies

JOHN H. DALY*, D. HAYWARD, J. J. LIGGAT
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland
E-mail: j.h.daly@strath.ac.uk

Over the past decade there has been a continuing, growing interest in polymeric materials with structured surface topographies sized on the nanometre scale (viz. nano-topography). The implications of such topographies are important in the medical field where they have potential in the area of tissue regeneration of, e.g., tendons, ligaments, and cartilage [1]. In order to produce these nano-topographies one approach is to produce an embossing master. This typically involves the production of a metal substrate (e.g., nickel) that contains the requisite pattern produced by electron beam writing technology [2]. The master can then be utilised in a hot-pressing procedure to transfer the reverse pattern to a particular polymeric system. Another approach involves colloidal lithography [3, 4] which results in a nano-structured polymer surface. However,

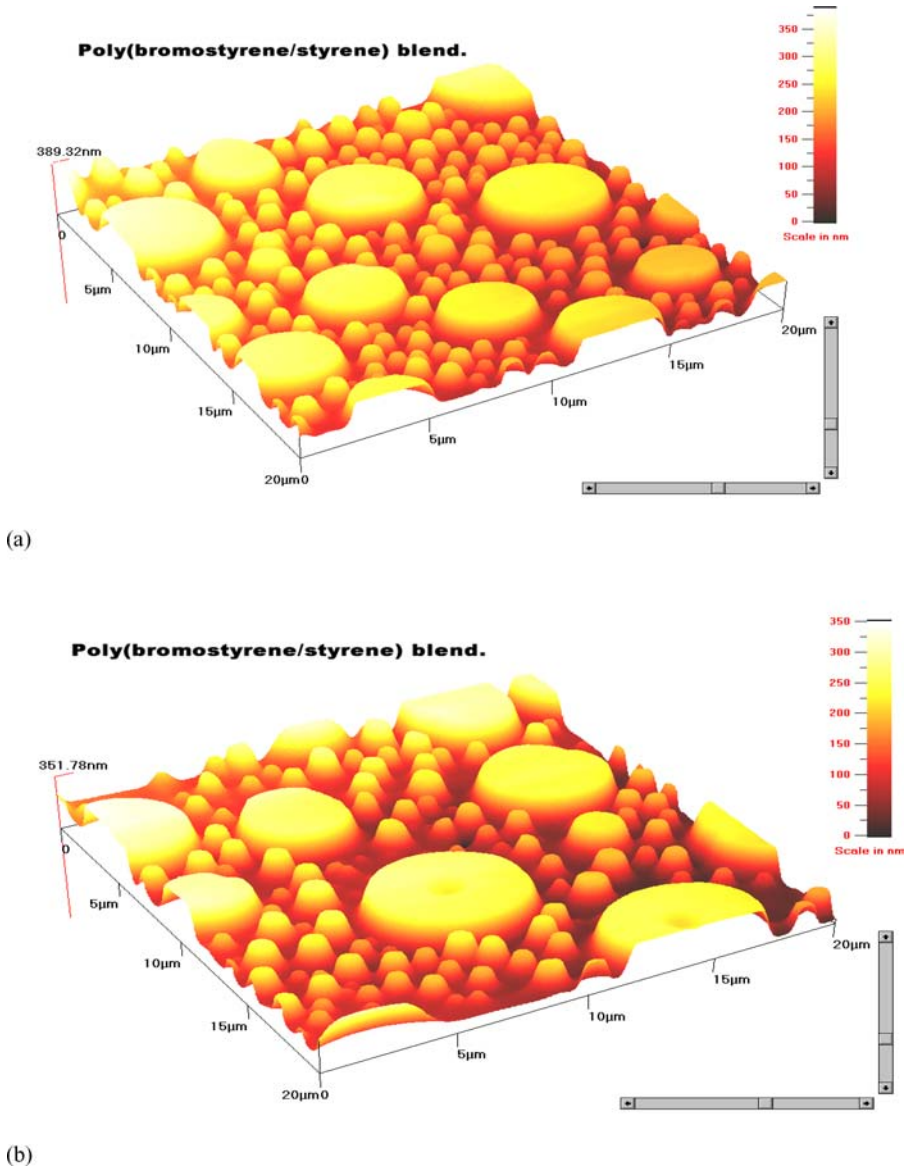

Figure 1 AFM images for poly(bromostyrene/styrene) blend for: (a) area 1, and (b) area 2.

*Author to whom all correspondence should be addressed.

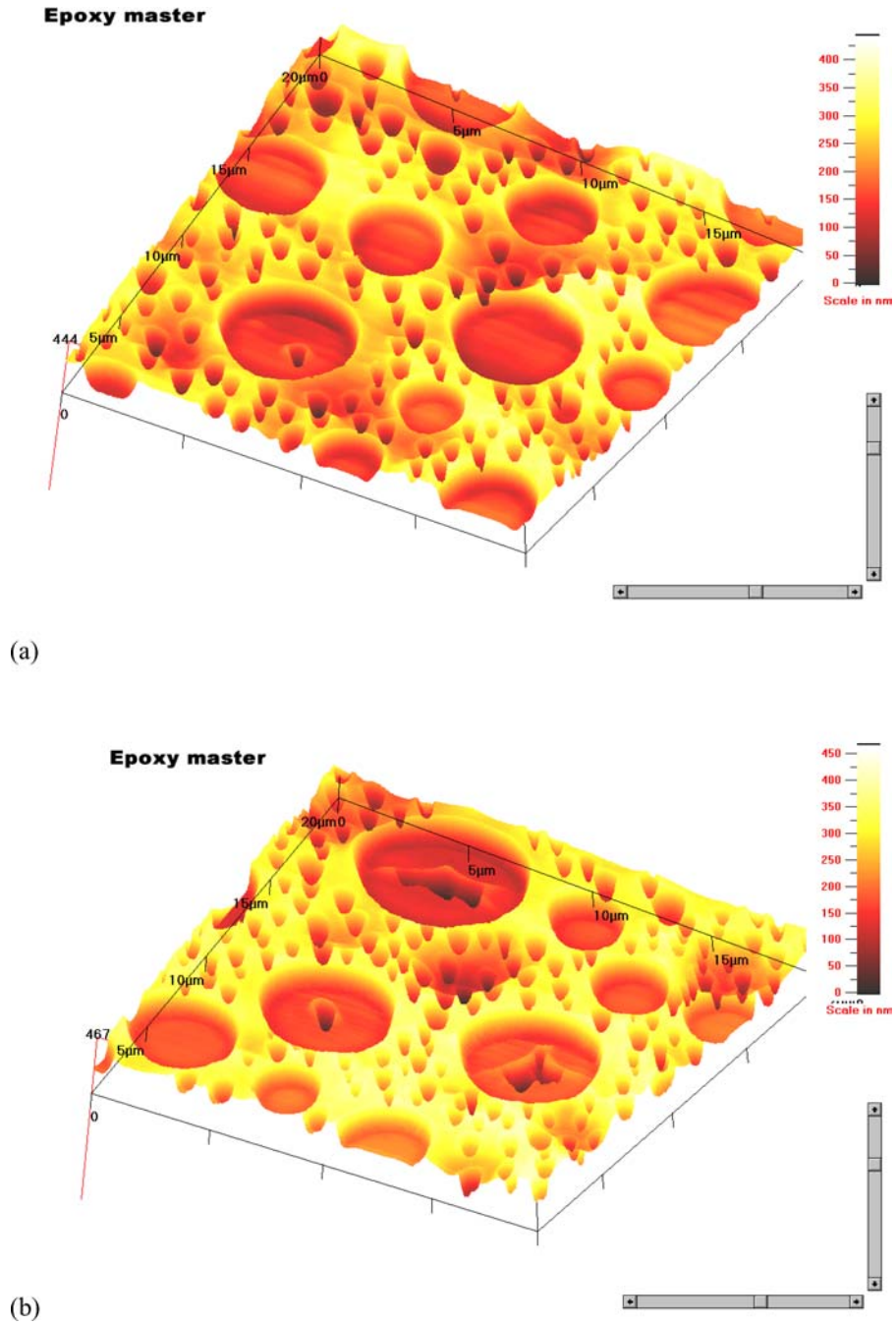

Figure 2 AFM images of the epoxy master: (a) cured and (b) postcured and silanized.

the disadvantage of this technique is that the polymer is attached to a substrate, which may be undesirable in *in vivo* applications.

There are also, however, certain disadvantages with the aforementioned embossing masters. From the point of view of a research program dealing with polymer types of varying e.g., moduli and T_g, there is a basic necessity to have a ready supply of such masters. The nickel masters are expensive to produce and easily damaged. Also, when working with low modulus and low T_g materials, there is the problem of removal of the embossed polymer from the master. Furthermore, the master produces an inverse topography on the polymer, i.e., raised structure become troughs and *vice versa*, which may not be what is required.

In this communication we describe a particular procedure in which we reproduce and transfer a complex topography produced by the phase separation of poly(bromostyrene)/poly(styrene) blends [5]. Such systems have already been assessed with regards to their interaction with human blood and tissue cell types [6, 7]. However, similar to colloidal lithography, the polymer is attached to a substrate, and is, thus, unsuitable for *in vivo* trials. Nevertheless, utilising the topography developed by such blends we are able to produce a master based on an epoxy resin. This epoxy system can then be used as a master to provide polymer films with the exact topography as the initial polymer blend.

The initial step in the preparation of an epoxy master is to prepare a system with a suitable nano-structure. To this end we have chosen a poly(bromostyrene)/poly(styrene) blend. [For brevity, we will use the designation poly(bromostyrene/styrene)

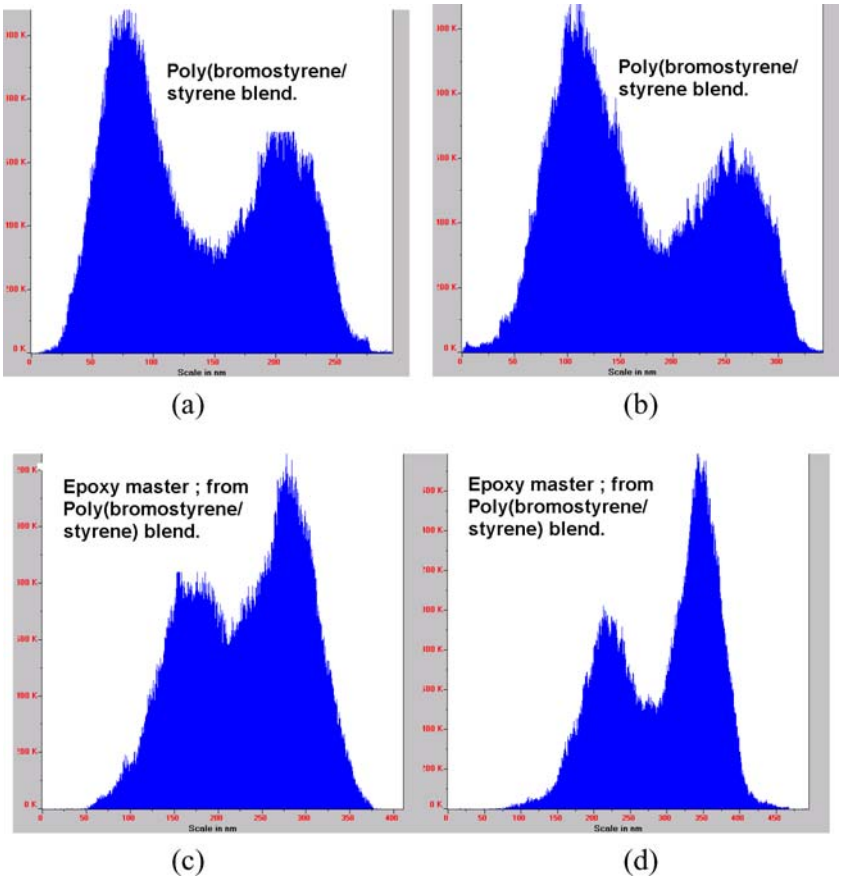

Figure 3 AFM analysis histograms for: (a) blend-area 1, (b) blend-area 2, (c) cured epoxy master, and (d) postcured and silanized epoxy master.

blend during the course of this communication]. The poly(4-bromostyrene) [ex. Aldrich, mol wt ca. 64000] and poly(styrene) [ex. Aldrich, mol wt ca. 1000000] were blended (as received) at a ratio of 60:40 w/w as a 5% solution in toluene. The blend was spin coated onto a 16 mm diameter glass cover slip, then annealed at 115 °C for 15 min. The surface topography was subsequently examined with a Quesant 250 Atomic Force Microscope. Representative structures of these blends for two different areas of the sample are highlighted in Fig. 1.

Analysis of the structures show that the topography produced from this particular blend system is essentially bimodal (Fig. 3a and b). The large diameter features are higher than their smaller diameter counterparts. Also, for this particular blend system there is significant variation with respect to the range of the heights of the features. For the features in Fig. 3a, the peak in the heights are ca. 75 and 210 nm respectively. For those of Fig. 3b, the peaks change to 110 and 250 nm respectively. Such anomalies, however, are quite understandable when you consider that we are taking a 'snapshot' of an area of the surface which is a mere 20 μm by 20 μm square, over a total nano-structured area 16 mm in diameter.

Using these blended materials the preparation of the epoxy masters was carried out as follows:

1. The glass cover slip incorporating the blend was attached to one face of a two-part stainless steel mold with adhesive strips. The mold was subsequently assembled with a 1.6 mm spacer.
2. An epoxy system based on an epoxy resin (MY 750, ex. Ciba) and a hardener (diaminodiphenyl-

TABLE I Physical properties of polymers for nano-embossing

Polymer	Molecular weight[a]	T_m [b] (°C)	T_g [c] (°C)	Modulus (MPa)
Poly(1,4 butylene succinate)co-1,6-diisocyanatohexane[d]	98200	120	−31	292[e]
Poly(cyclohexyladipate)[f]	25700	125	13	1.06[g]
Poly(cyclohexylsebacate)[f]	46200	90	−8	0.25[g]

[a]From GPC analysis.
[b]From DSC analysis.
[c]From DMTA analysis.
[d]Purchased from Sigma-Aldrich.
[e]From tensile test at ambient temperature.
[f]Synthesised according to references 11 and 12.
[g]From the method described in reference 13.

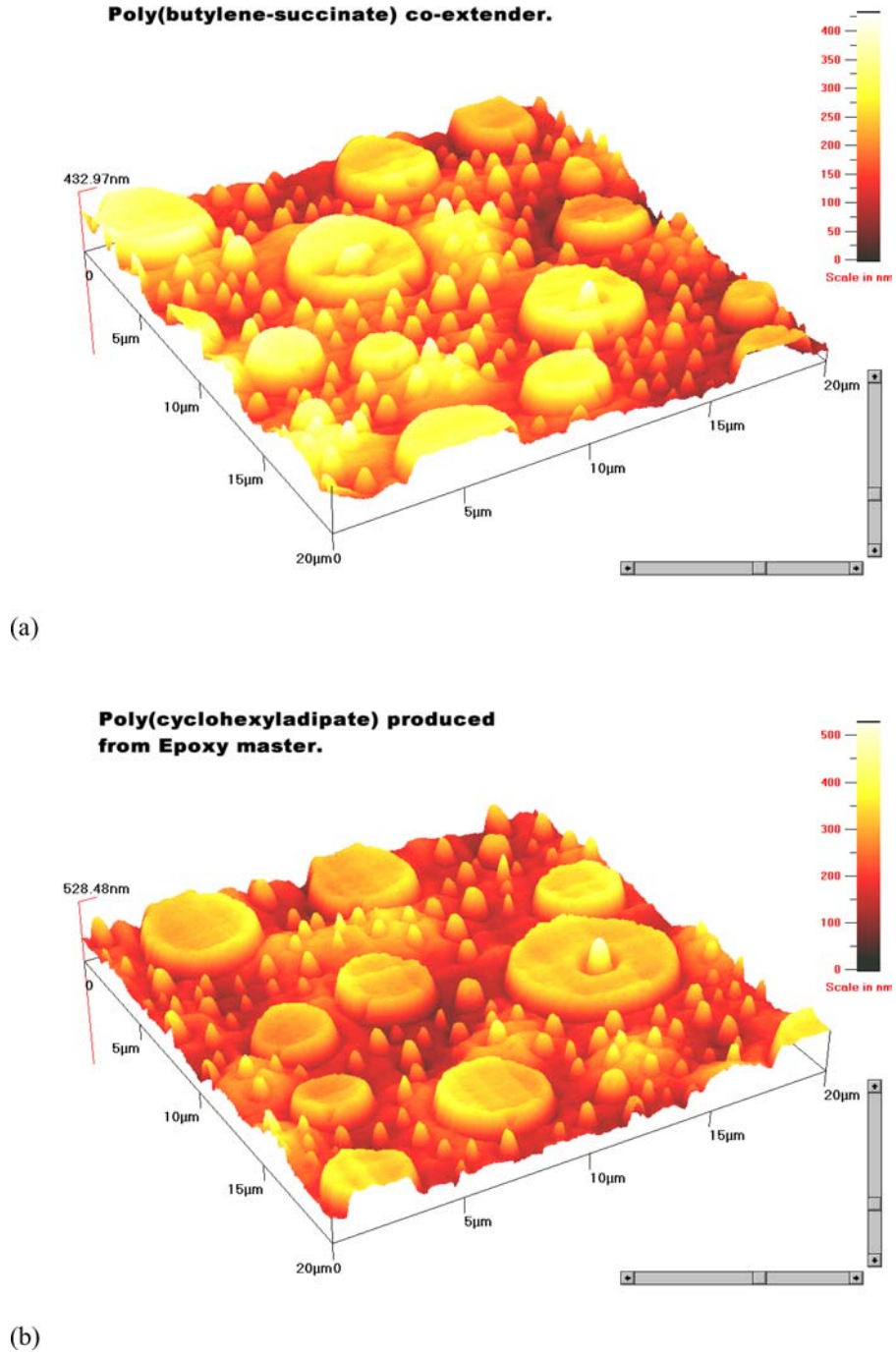

Figure 4 AFM images for: (a) poly(1,4 butylene succinate coextender), and (b) poly(cyclohexyl adipate).

methane, HT 972, ex. Ciba) was mixed at a ratio of 100:30 w/w. at 80 °C then degassed for 5 min.

3. The resin was poured into the mold and the system cured at 100 °C for 2 hr.

4. The mold was opened and removal of the glass cover slip from the cured epoxy surface was facilitated by immersion in toluene.

An example of the surface topography on the epoxy system is highlighted in Fig. 2a. We can clearly see that the topography produced is the "negative" of the blend. Also, analysis of the topography (Fig. 3c) confirms the bimodality of the structures.

The aforementioned epoxy master was cured at 100 °C, which is around the T_g of the polystyrene phase of the blend. This chosen temperature ensured that the polystyrene structures were unaffected by the curing process. However, to ensure that the epoxy system was suitable for higher temperature embossing procedures it was essential to postcure the material. Using Dynamic Mechanical Thermal Analysis (DMTA), the glass transition of the cured and postcured system was monitored. The measured T_g's were 128 °C (cured) and 153 °C (postcured) respectively. The final stage of the epoxy master preparation involved a silanization process to facilitate removal of the embossed polymer films.

As cited earlier in this communication there is a problem of sample removal from nickel masters particularly when the materials being embossed have low T_g's and moduli. Silanization of the epoxy (as with silicate glasses) results in the reaction of hydroxyl groups thus greatly reducing the polarity of the epoxy

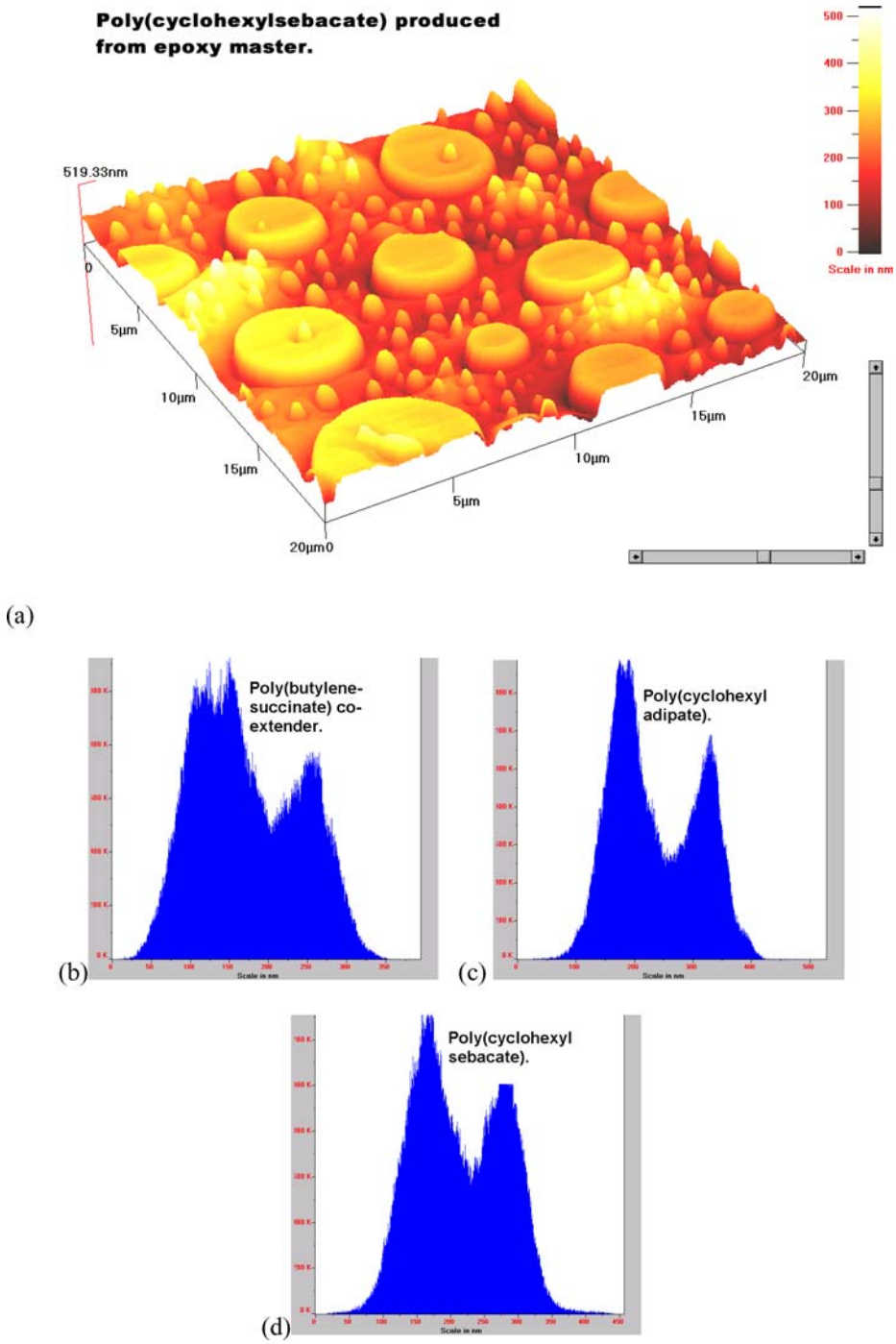

Figure 5 (a) AFM image for poly(cyclohexyl sebacate), and AFM analysis histograms for (b) poly(1,4,butylenes succinate coextender), (c) poly(cyclohexyl adipate) and (d) poly(cyclohexyl sebacate).

surface. The procedure involved placing the epoxy master in a silanization medium (viz. Silanization Solution I; 5% dimethyldichlorosilane in heptane obtained from Sigma, Aldrich) for 20 min after which the sample is thoroughly washed with methanol then subsequently baked at 120 °C for 1 h. The postcuring and silanization procedure had no detrimental effect on the surface topography as seen in Figs 2b and 3d.

Now that the epoxy master has been prepared we had to decide which polymers would be suitable for embossing. Since our major interest is in the field of materials for *in vivo* medical applications [8–10] we have chosen potentially biodegradable systems. Three materials have been identified and are listed in Table I.

The three polymers chosen have melting points that can easily be accommodated by the epoxy master, and, to demonstrate the versatility of the embossing procedure, their T_g's and moduli are significantly different. The embossed films were prepared in an in-house built facility in which a preformed film of the polymer was sandwiched between the epoxy master and a scratch free glass plate. This assembly was then subjected to a temperature ramp to a point equal to the melting temperature of each polymer at which juncture pressure was applied to the system for a period of 5 min. After cooling to ambient temperature, with pressure still maintained, the assembly was removed. It was found that by lowering the temperature of the assembly

below the T_g of the polymer (either by placing the sample in the freezer compartment of a fridge or using solid carbon dioxide) the assembly could be dismantled and the sample removed. The embossed topographical features were examined by AFM and representative examples of the three polymers are highlighted in Figs 4a, b and 5a. The three polymer films show topography consistent with the original poly(bromostyrene/styrene) blends used to produce the epoxy masters. As with the blends and the master, analysis of the topography (Fig. 5b–d) shows that the bimodality of the structures still exists.

In conclusion, we have demonstrated that epoxy masters can be produced easily and cheaply to prepare embossed polymeric materials. The embossed systems, with nano-topography identical to the poly (bromostyrene/styrene) blend, are significant since such topographies have already been assessed as potential cell growth structures. We can make use of the fact that other poly (bromostyrene/styrene) blends can be formulated to provide a range of differing topographies. Finally, the fact that 'free standing' embossed films can be made provides materials ideally suitable for *in vivo* studies.

Acknowledgements

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References

1. A. CURTIS and C. W. WILKINSON, *Biomaterials* **18** (1997) 1573.
2. N. GADEGAARD, S. THOMS, D. S. MACINTYRE, K. MCGHEE, J. GALLAGHER, B. CASEY and C. D. W. WILKINSON, *Microelectr. Engng.* **67/68** (2003) 162.
3. F. A. DENIS, P. HANARP, D. S. SUTHERLAND and Y. F. DUFRENE, *Nanoletters* **2** (2002) 1419.
4. P. HANARP, D. S. SUTHERLAND, J. GOLD and B. KASEMO, *Coll. Surf. A: Physiochem. Enging. Asp.* **214** (2003) 23.
5. S. AFFROSSMAN, S. A. O'NEILL and M. STAMM, *Macromolecules* **31** (1998) 6280.
6. M. J. DALBY, G. E. MARSHALL, H. J. H. JOHNSTONE, S. AFFROSSMAN and M. O. RIEHLE, *IEEE Trans. Nanobiosc.* **1** (2002) 18.
7. M. O. RIEHLE, M. J. DALBY, H. JOHNSTONE, A. MACINTOSH and S. AFFROSSMAN, *Mater. Sci. Engng.* C **23** (2003) 337.
8. GILLIAN GRAY, BSc Thesis, University of Strathclyde (Glasgow), "Biodegradable Polyester-Urethanes for Medical Applications" (2000).
9. G. GIAVARESI, M. TSCHON, J. H. DALY, J. J. LIGGAT, M. FINI, P. TORRICELLI and R. GIARDINO, *Intern. J. Artific. Org.* (in press).
10. G. GIAVARESI, M. TSCHON, V. BORSARI, J. H. DALY, J. J. LIGGAT, M. FINI, R. GIARDINO and A. CARPI, To be published in "Biomedicine and Pharmacotherapy."
11. D. BRAUN and P. HEMPLER, *Die Angewandte Makromol. Chemie* **210** (1993) 173.
12. E. BARRIAU, P. A. G. CORMACK, J. H. DALY, J. J. LIGGAT and A. QUINCY, *Europ. Cells Mater.* **4** (2002) 100.
13. Y. LI, H. ZHIBING and C. LI, *Jnl. Appl. Polym. Sci.* **50** (1993) 1107.

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