Combing out defects in block copolymer films

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Block copolymers (BCPs) comprise two linked but chemically disparate subunits. Like oil and water, they try to separate physically but can’t get very far from each other because of covalent bonding. This ‘microphase separation’ can result in nanometer-sized periodic structures, such as dense arrays of lines or dots, which could be useful for patterning nanoscale features in future generations of electronics and data storage.

It’s a neat idea, but the microstructures created so far have been far from perfect. Now researchers from the National Institute of Standards and Technology (NIST) report a novel method for annealing BCP films that results in rapid ordering with low defect density and preferential alignment [Berry et al., Nano Lett. (2007) 7, 2769].

The previous best results had been obtained using hot zone annealing. Here the thin BCP film moves slowly through a heated region that temporarily raises its temperature just above the point at which the phases become disordered. This works by melting the polymer pattern and then reforming it. Because the reforming pattern is localized in a small area, defects can rapidly diffuse away into the disordered region ahead.

“It’s like combing out the defects as the zone moves through,” explains NIST’s Ronald L. Jones. Hot zone annealing doesn’t work for all materials – such as the cylinder-forming BCP poly(styrene-b-methylmethacrylate), or PS-P MMA, used in this study – because the polymer degrades before the order–disorder transition temperature is reached.

NIST’s approach is called cold zone annealing. It is similar to the hot zone process but takes place at a temperature below the order–disorder transition yet above the glass transition temperature of the two polymer subcomponents. At this intermediate temperature, the BCP is not melted but still has enough mobility to allow defects to diffuse away. What’s more, unlike hot zone annealing, the process results in films with good orientational order, although the mechanism for this is not yet understood.

Microelectronics firms are currently evaluating the method for the fabrication of sub-30 nm features. Grain sizes of the ordered regions are about an order of magnitude smaller than would be required for commercial processing, but the researchers hope to improve on this as they gain better understanding of the fundamental mechanisms.

Pauline Rigby

Bringing order to random copolymers

POLYMERS

Researchers have developed the first simple method of controlling the sequence distribution of monomers in random copolymers [Semler et al., Adv. Mater. (2007) doi: 10.1002/adma.200602359]. The work, carried out at North Carolina State University (NCSU), the University of Houston, and Aston University in the UK, could be important in functional polymer synthesis, because copolymers with different types of ordering display different physical and chemical properties.

Some types of copolymer have ordered monomer sequences, such as alternating and block copolymers. But producing copolymers with controlled but nonrepeating sequences has proven tricky.

“Controlling the monomer sequence in random copolymers is something any polymer chemist dreams about,” says Jan Genzer of NCSU.

Genzer and colleagues work was inspired by the theoretical studies of Alexei R. Khokhlov of Moscow State University in Russia and Pavel G. Khalatur, now at the University of Ulm, Germany. Their idea was that if a polymer chain was collapsed into a dense ball, only the parts of the chain on the outer edges of the ball would be available for chemical substitution or reaction. When the ball is unraveled, the distribution of the monomer species obtained by this method will be more ‘blocky’ than if the same reaction were performed on an extended polymer chain.

Genzer’s team started with polystyrene and added bromine under dark conditions for a fixed period of time to make poly(styrene-co-4-bromostyrene). Using a good solvent produces an extended polymer configuration in solution, and so generates a random distribution of the 4-bromostyrene (4-BrS) units.

Using a poor solvent results in a collapsed polymer configuration and a blocky distribution of the 4-BrS. This reaction was selected because 4-BrS units can be used for further chemical tailoring via Suzuki coupling. Now that it’s possible to produce polymers with different degrees of randomness, a whole new raft of experimental work opens up. The researchers are studying absorption on flat substrates, and bulk thermodynamics, and how these properties depend on monomer distribution. “Not surprisingly, there is a non-negligible effect,” says Genzer.

Pauline Rigby