Effects of nanoconfinement on the morphology and reactivity of organic materials

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When organic materials are placed in environments which physically confine the materials at the nanometre scale, interfacial effects and confinement-induced loss of entropy can significantly alter materials' properties such as the glass transition temperature as well as the nanoscale morphology as compared to a 'free' system. In block copolymers, nanoconfinement leads to a range of unusual self-organized nanoscale morphologies. In this article, attempts to induce nanoconfinement effects in new polymer systems as well as at interfaces will be highlighted and some possible future implications for organic synthesis and biology will be discussed.

Introduction

It is well known that nanoparticles of inorganic semiconductors exhibit new properties as a result of the quantum confinement of electrons. For example, CdSe nanoparticles show different emission colours depending on their size (the smaller the particles the larger the blue shift in the fluorescence). Organic materials are not expected to show a similar size dependence. All properties are defined by the molecular structure, or, as is the case for polymers, properties are determined by monomer structure, molecular weight and backbone architecture (linear, branched, block, *etc.*). To illustrate this with an example of practical importance, the optical properties of semiconducting polymers are determined by the chain conjugation length.[1] An interesting situation occurs when scaling material dimensions down to the nanometre level ($\ll$100 nm), where the dimensions of the material begin to overlap with the molecular lengthscales of polymers or even small molecules. In the case of semiconducting polymers, Kim and Swager have demonstrated how manipulation of the polymer backbones using liquid crystal environments leads to changes in the conjugation length and hence spectral properties.[2] The lowering of the glass transition temperature (T_g) by tens of degrees in ultrathin polymer films (tens of nanometres) is another now classic example of the effect of nanoconfinement on 'standard' polymer properties.[3,4] It is believed that the origin of the effect lies in the increased mobility of polymer chains near the interface, possibly as a result of trapping the chains in a higher entropic state. The surface effect is surprisingly long-ranged, with significant suppression of T_g still observable 30 nm away from the free surface. The question that arises is whether small molecules could be manipulated in a similar way by confining them to sufficiently small geometries. This not too difficult to achieve in practice by, for example, using self-assembled monolayers to confine molecules at interfaces, or by encapsulating reactants in container molecules. However, it is not immediately clear what new properties would arise from such confinement. In this review, a number of strategies to induce nanoconfinement in polymer systems and small molecules will be discussed. The effects on the physical properties of a range of polymers will be illustrated, before highlighting intriguing recent findings on changes in the reactivity of small molecules confined to interfaces and nanoscale volumes. Of particular interest are the scientific and technological implications if nanoscale confinement could be harnessed as a 'synthetic tool' to modify materials' properties.

Polymer brushes

Polymer brushes are thin polymer films formed from tethered polymer chains. These brushes can be prepared *via* a 'grafting to' approach, but recent advances in the area of surface-initiated polymerisations have resulted in a large number of new studies into very dense and chemically complex brushes.[5] On inorganic substrates, the graft density can be as high as 0.7 chains nm^{-2} for common polymers such as poly(methyl methacrylate) (PMMA) and polystyrene. This density is about one order of magnitude higher than those of the semi-dilute brushes obtainable by other techniques, and the graft systems in this density regime may be termed high-density brushes. To reduce excluded volume interactions between neighbouring chains, the chains will stretch, until the free energy gain no

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longer outweighs the entropic penalty associated with stretching chains away from a more favourable random walk configuration.[6] Even in a dry state, the polymer chains are stretched away from the surface forming a highly anisotropic film. As a result, the confinement is not only induced by the thickness of the film (which can be as thick as several microns), but also by the strong interactions between neighbouring chains. The resulting films are hence quite different from 'normal' thin films, and, remarkably, the T_g dramatically increases for short brushes (Fig. 1).[7]

Increasing the brush length leads to a decrease in T_g, but even for thick films, the T_g never quite equals the T_g of spincoated films or the bulk T_g. It is thought that even for long brushes, the brushes are sufficiently dense and in a hindered environment for the mobility to be affected. At the same time, the brushes are strongly resistant to mechanical compression and indentation, offering new insights into nanoscale property changes. The low compressibility of the brushes is interpreted on the basis of rubber elasticity of an entangled network in the stretched state and is mainly attributed to a strain-hardening effect of the highly stretched, entangled chains.[8]

Block copolymers

Moving away from thin films, the confinement can be controlled at the nanometre lengthscale in three dimensions (3D) by using block copolymers. When the blocks are incompatible, the blocks will demix (micro phase-separate) into well-defined domains, typically in the 10–100 nm regime. Depending on the length, connectivity, and mutual interaction of the different components, the microdomains form spheres, cylinders, lamellae, or more complex shapes (Fig. 2).[9]

Nanoconfinement within nanostructured self-assembled block copolymers directly influences the crystallization and melting of the minor, crystallizable copolymer component.[10,11] The microphase separation of block copolymer/amphiphile self-assembled systems has been exploited to confine blocks within small, periodic structures, leading to hierachical self-assembly and a rich variety of morphologies.[12,13] Stucky and co-workers recently published a detailed study which greatly expands the alignment and manipulation of block copolymers.[14] Nanoporous anodic alumina membranes, with precisely tailored channel diameters ranging from 18 nm to 80 nm, were used to confine the polymers. Unprecedented, and very complex structures spontaneously formed inside the nanochannels (Fig. 3). Self-consistent field calculations were carried out to account for the striking mesostructures observed using TEM and SEM. This study has opened the way to an as yet unexplored field where numerous functional polymers could be confined in nanoscale 3D environments, leading to unique new materials.

In the bulk, mesoscale structure formation is dependent on molecular parameters, but in thin films, the confinement effects mentioned for thin films above, will again play an important role. First of all, one of the blocks will generally preferentially wet the substrate, thereby distorting the 'natural' phase separation. Furthermore, the thickness (or lateral pattern, see below) can be a non-integer multiple of the bulk repetition length of the nanoscale morphology, which forces the formation of new structures. Different alignment strategies have been reported to force the microphase separation of

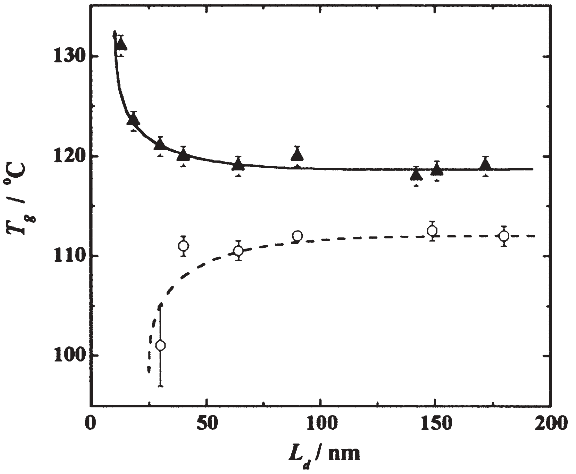

Fig. 1 Plots of T_g *vs.* thickness of a PMMA film (L_d). The solid triangles and open circles represent the data for brushes and cast films, respectively. Reproduced with permission from ref. 7.

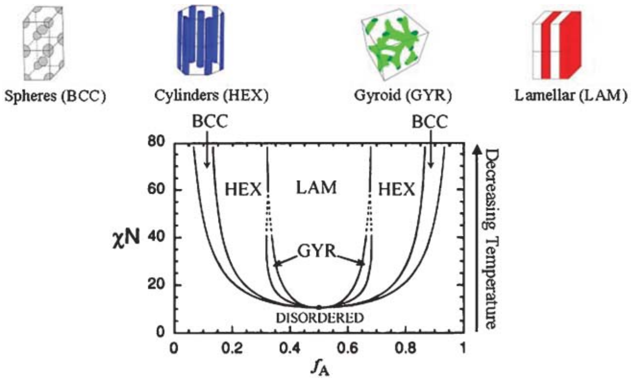

Fig. 2 Phase diagram of block copolymers as a function of the volume fraction f of each component *vs.* the interaction parameter χ times the degree of polymerisation N.

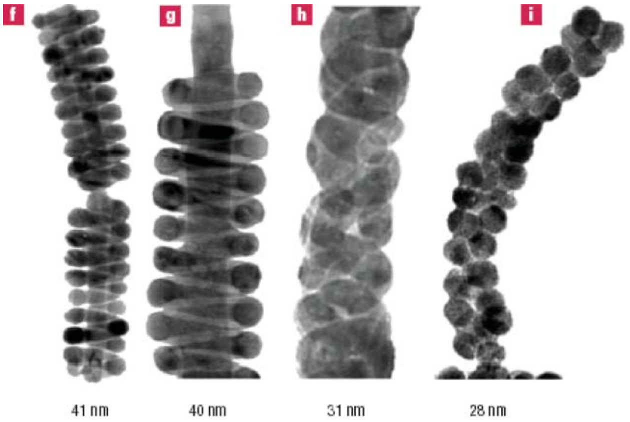

Fig. 3 TEM images of silver nano-replicas formed from microphase separated $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) triblock copolymers inside a range of different nanoprous alumina nanochannels. Reproduced with permission from ref. 14.

block copolymers into highly ordered nanoscale arrays. These include annealing in a strong electric field,[15] but nanoconfinement effects can be used as well. The presence of a free polymer–air interface in combination with the influence of the bottom surface directs the phase-separation into a preferred direction. For example, poly(styrene)-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer with a molecular weight of 46 100 for the PS block and 21 000 for the PMMA forms cylindrical PMMA phases in a PS matrix. The orientation of PMMA cylinders can be aligned normal to the surface by controlling the film thickness and the surface energy.[16,17] The PMMA blocks can be selectively removed with UV exposure and acetic acid etching. The porous PS matrix can then be used as a physical mask for etching and metal evaporation.[18,19] Alternatively, the matrix could be used as an assembly of zeptolitre reaction vessels for (in)organic synthesis.[20] If it would be possible to confine reactants to the nanopores, the effects of confined geometries on chemical reactivity could be explored.

The long range order of these nanoporous templates is generally rather low because there is no additional driving force to align the hexagonal domains (although there have been a number of recent breakthroughs in this area).[21] Additional nanoconfinement in lateral dimensions can vastly improve this ordering. Chemical nanopatterning to guide both blocks has been demonstrated[22] but requires access to very expensive lithographic technology. Several groups have exploited graphoepitaxy to impose lateral boundary conditions on the microphase separation,[23,24] forcing the block copolymers to phase-separate following the underlying pattern.[25,26] Instead of relying on prepatterned surfaces, nanoimprint lithography can be used to align phase-separated domains into 100 nm wide lines.[25]

Strikingly, the number of columns or lamellae which will fit between two vertical walls is quantized, *i.e.* only integer numbers of rows of columns will fit between two lines and when these lines are incommensurate with the natural repeat length of the block copolymers, the phase-separation will be distorted (Fig. 4).[26,27] This effect has also been described in great detail for lamellar-phase forming PS-*b*-PEP (poly-ethylene-*alt*-propylene) block copolymers.[28] The ability to position nanoscale patterns on surfaces not only has important applications in nanotechnology (for example for new memory devices) but could also open up interesting possibilities for chemistry. As discussed above, the phase-separated domains can be used to confine reagents into zeptolitre volumes and these 'nanoscale reaction flasks' can also be positioned with high precision. If, at some point in the future, the wells or domains could be addressed individually, a great number of different reactions (under different reaction conditions) could be performed on a very small surface.

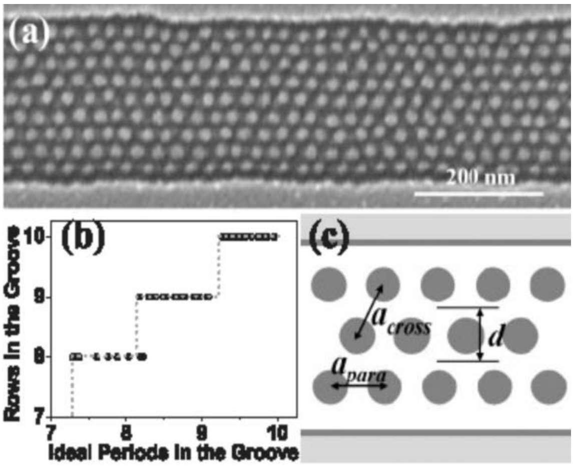

Fig. 4 Phase separation of a PS-*b*-PFP block copolymer inside lithographically prepared tracks. The width of the track controls the number of columns that can be formed between the vertical walls. The polyferrocenyldimethylsilane (PFS) blocks remain, after etching the PS in an oxygen plasma. Reproduced with permission from ref. 27.

Nanoparticles

Nanoparticles are another effective way to confine polymers in a small volume. Such particles can be prepared in different ways, including emulsion polymerisation,[29] inkjet-printing,[30] electrospraying, and the miniemulsion technique.[31] It is expected that the T_g of the polymers will be depressed, for similar reasons as discussed above in the case of thin films. More importantly, it provides a route to forcing immiscible polymers into close proximity. Due to confinement effects and the rapid evaporation of solvents, it should be possible to avoid phase-separation, leading to homogenous blends which would be impossible to prepare otherwise. Landfester and co-workers have shown that a wide variety of nanoparticles containing blends of (im)miscible functional polymers can be prepared using the miniemulsion technique,[32] and explored their use in optoelectronic devices.[33] We recently reported nanoparticles from main chain liquid crystalline polymers, with particle sizes smaller than the domain size of the liquid crystalline polymer.[34] Samples of polymeric materials generally have no intrinsic shape; rather their external form is determined by external forces such as surface tension and memory of shear (*e.g.* during extrusion, moulding or embossing). Hence, in the molten state, the thermodynamically most stable form for polymer (nano)particles is spherical. In our work, the nanoparticles have an *intrinsic*, high aspect ratio, ellipsoidal shape (Fig. 5), as a direct result of the interplay between the liquid crystalline ordering of the polymers (leading to prolate ellipsoids) and the surface tension which tries to deform the particles into a sphere.

The particles adopt a spherical shape when the temperature is raised above the clearing transition for the liquid crystalline material, thereby removing the driving force for anisotropic shapes. Anisotropic particles are only observed when the particle size is sufficiently small to allow only a single liquid crystalline domain inside. As such it is a first example on how confinement in particles could change properties of functional polymers. With recent progress in fabrication and characterisation techniques for polymers in confined geometries, rapid progress in this area can be expected, leading to new insights in polymer behaviour but also to new strategies for control over chemical functionality at the nanoscale.

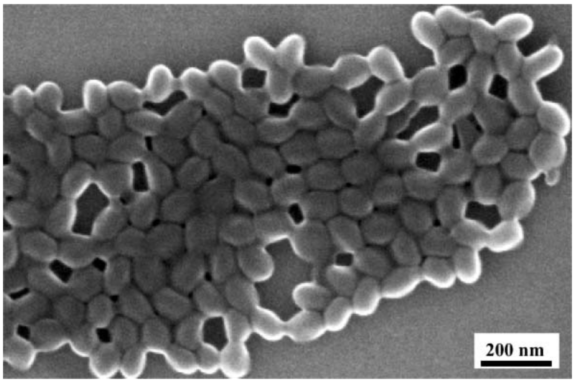

Fig. 5 Ellipsoidal nanoparticles from main chain liquid crystalline polymers, prepared *via* the miniemulsion technique. SEM image taken by Z. Yang, University of Cambridge.

Small molecules on surfaces

Thus far, we have considered the effects of nanoconfinement in polymer systems. Although the effects are more generally recognized and can easily be studied, nanoconfinement effects are not only observed in polymer science. In principle, the properties (and reactivity) of small molecules should be different in confined geometries, but it is of course much more difficult to achieve control at molecular lengthscales (0.1–10 nm) as compared to polymer lengthscales (10–100 nm). The experimentally most straightforward way to confine molecules is to study them at interfaces. When simple fluids such as the cyclic siloxane octamethylcyclotetrasiloxane (OMCTS) are confined to a few monolayers between smooth solid surfaces, they undergo an abrupt liquid-to-solid transition.[35] Measurements using a surface force balance show that the OMCTS film remains fluid from large thicknesses down to a few molecular layers, but abruptly becomes like a solid (in the sense of being able to sustain a shear stress) when its thickness is reduced from seven to six monolayers. Its effective viscosity increases by at least seven orders of magnitude at the transition at this critical thickness. The physical origin of such a transition may lie in the progressively reduced space that is available to the confined molecules in the gap. From an organic chemist point of view, an interesting question would be how this nanoconfinement can be exploited to change the chemical reactivity of the molecules involved. In the remainder of this paper, I will explore some recent findings where specific attention has been paid to the organic chemistry of nanoconfined reagents.

Reactions on self-assembled monolayers

Molecules can be confined to monolayers on surfaces using self-assembly of suitable molecules (self-assembled monolayers, SAMs). It has been shown that the reactivity of molecules in SAMs is slow compared to those in solution (with a few exceptions).[36,37] This is attributed to steric crowding at the surface of a SAM.[38] Chechik *et al.* recently reviewed how reactivity in SAMs is affected by solvents, the local environment such as altered polarity, hindered access of solution reactant to the reactive group of the SAM, and reduced conformational flexibility.[39]

Schönherr *et al.* showed that the reaction rate of alkaline hydrolysis of *N*-hydroxysuccinimide (NHS) ester present in SAMs and ultrathin polymer films of poly(*N*-hydroxysuccinimidyl methacrylate) (PNHSMA) were affected by confinement effects.[40,41] The reactions were analysed by contact angle goniometry and grazing incidence reflectance (GIR) FTIR spectroscopy to monitor the quantitative surface coverage of unreacted NHS ester. They found that the rate constant for the SAMs was five times smaller than that of the surface polymer films, but was reduced by up to 3 orders of magnitude compared to those for similar reactions in solution. The activation energies were found to be E_a (NHS–SAM) = 30 kJ mol^{-1} and E_a (PNHSMA) = 61 kJ mol^{-1}. The entropies calculated according to transition state theory were $\Delta S^\ddagger$ (NHS–SAM) = -176 J mol^{-1} and $\Delta S^\ddagger$ (PNHSMA) = -59 J mol^{-1}. The authors conclude that the strongly negative value of -176 J mol^{-1} for NHS–SAM indicates a very tight transition state (steric crowding) in the rate-determining step of the hydrolysis and accounts for the low reactivity of the SAMs.

In our research on patterned self-assembled monolayers, we were intrigued by the rapid and efficient formation of self-assembled monolayers (SAMs) on gold or Si/SiO$_2$ using microcontact printing (μCP).[42] When an elastomeric stamp, inked with trichloroalkyl silanes, is placed on a clean Si/SiO$_2$ surface, the formation of the polysiloxane network is essentially complete in minutes, while this process could take hours in solution. When placed on a self-assembled monolayer the ‘ink’ concentration at the interface between stamp and SAM becomes very high, while the SAM provides the correct orientation for reactions to occur. Microcontact printing has previously been used to couple molecules to a reactive surface, but in all these cases a catalyst or activated substrate was used to induce covalent bond formation.[43] We recently reported the formation of new bonds solely as a result of the nanoscale confinement of molecules between stamp and surface.[44] As a first reaction, we investigated the coupling of Boc-protected amino acids with amine terminated self-assembled monolayers on Au. This reaction is a suitable model system, as amide bond formation in solution requires catalysts or elevated temperatures, and long reaction times. In a typical reaction, we prepared a clean amine terminated SAM surface on gold. A flat hydrophilic stamp (treated for 30 s with an oxygen plasma and stored under Millipore water), was inked with a 1 mM ethanolic solution of an appropriate Boc-protected amino acid and placed on this surface. If required, the sample plus stamp was heated on a hotplate (to approx. 40 °C). After a certain reaction time, the stamp was lifted off and the substrate washed with ethanol and water to remove all non-covalently bound molecules (Fig. 6).

FT-IR measurements clearly showed the presence of carbonyl groups on the surface, even after deprotecting the *t*-Boc groups and extensive rinsing. We investigated different amino acids and found significant differences in their reactivity, with proline derivatives reaching a maximum thickness increase (which we correlate with coupling to the surface) within 10 s at room temperature. An alanine

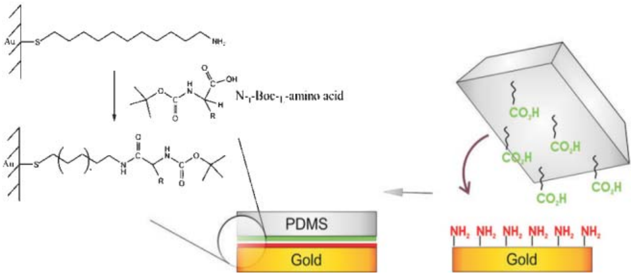

Fig. 6 Printing molecules onto reactive monolayers, resulting in unusually fast bond formation. Reproduced with permission from ref. 44.

derivative was also reactive at room temperature but a time of 30 mins was required to reach a maximum thickness. However, Boc-tyrosine required a reaction temperature of 40 °C and a printing time of 30 min. To further support our hypothesis we synthesised the tripeptide arginine–glycine–aspartate (RGD) on the surface *via* multiple stamping steps. The first step involved printing a linker onto an amine SAM on silicon. Subsequent removal of the protecting group was followed by printing Boc-aspartate (D), Boc-glycine (G) and Boc-arginine (R) (to allow for the correct N–C coupling direction). The resulting RGD tripeptide is a well-known epitope which provides attachment sites for fibroblast cells. Accordingly, cell attachment was evident on the printed surfaces indicating that the RGD was present on the surface and a multistep sequence can be carried out by repetitive stamping.

Molecular cages and containers

Molecules confined at interfaces or between a stamp and a surface, bear some analogy to molecules confined in 'cage-compounds' or 'molecular containers'.[45,46] A classic example of how pre-organization and confinement (leading to a very high local concentration) can result in dramatically altered reactivities was shown by Sanders and co-workers.[47] In their, work, a diene and dienophile were held in close proximity inside a cage-like compound by metal–ligand interactions, leading to a 6000-fold increase in the rate of the Diels–Alder reaction, while exclusively giving the *exo* product. Nanoscale hosts (or 'containers') based on resorcinarenes have been explored widely[48] and Rebek and co-workers have recently shown that it is even possible to regulate rotation of encapsulated molecules. The guest molecules are confined to such small volumes that their rotational freedom is greatly hindered. The inclusion of co-guests quite literally 'puts the brakes on' and rotation becomes slow at the NMR timescale (Fig. 7).[49]

This is a fundamentally important step towards 'molecular machines' where control over molecular motion is a prime requirement to controlling chemical reactivity and device operation. It also brings us to the final question:

Is 'mechanosynthesis' possible?

An elastomeric stamp (used in the experiments described above) comes into conformal (*i.e.* van der Waals) contact with the surface,[42] forcing 'ink' molecules very close to the surface.

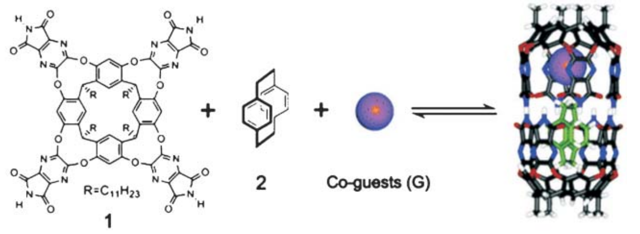

Fig. 7 Encapsulation of small molecules in resorcinarene-based self-assembling containers. Reproduced with permission from ref. 49.

We therefore speculate that the nanoscale confinement of the ink at the interface between the stamp and the SAM, in combination with preorganization of the reactants, influences the formation of covalent bonds. It is very difficult to precisely identify the factors that influence the reactivity of molecules trapped between stamp and surface, and obviously much more experimental work is required (and is in progress). Theoretical work suggests that chemical reactions in nanodroplets and nanoparticles are strongly affected by confinement.[50] The small diameter (and hence high curvature and surface tension) leads to high internal pressures, which influence the kinetics and equilibrium constants. However, in the system described above, the reaction takes places at a planar surface, and in the absences of solvents (although small amounts of solvent present in the stamp cannot be completely excluded). An alternative view is that the molecules are somehow 'pushed together'. It is therefore interesting to draw attention to the 'open debate' in *Chemical & Engineering News* between Smalley and Drexler on mechanochemistry.[51] The key argument seems to revolve around whether it is possible to build 'machines' that hold molecules in place and react them with each other with atomic precision, either in water, or in the dry state. Excluding enzymes or ribozomes, such a chemical entity is currently unknown. Walch and Merkle presented theoretical considerations on the mechanosynthesis of diamond,[52] but again, the formation of large organic molecules (or structures made out of metals) are quite difficult to even consider theoretically. However interesting these ideas may be, most experimentalists will argue that it is simply impossible to carry out mechanosynthesis at this level. Could it be however, that our findings of reactions between molecules on a stamp and an aligned monolayer could offer some route towards mechanosynthesis? Further work on determining the precise nature and the yield of the reactions, as well as the general applicability in different types of chemical reactions, will be needed to provide an answer to this question. On a much more practical level, Sijbesma and co-worker have demonstrated convincingly that mechanically induced metal–ligand bond disruption can be a very elegant way of changing materials' properties (by altering the chain length of coordination polymers), while at the same time generating catalytically active sites.[53]

Conclusions

The confinement of polymers in thin films, brushes, nanosized pores, domains of microphase separated block copolymers, or in nanoparticles are promising strategies to study the effect of confinement in one, two, or three dimensions. Thus far, the emphasis has been on investigating changes in physical properties, such as the glass transition temperature and crystallization. The stage is set, however, to start looking into changes in properties (photoluminescence, conductivity, chemical reactivity) of, for example, (semi)conducting or other functional polymers. Pushing nanoconfinement to the small molecule regime is significantly more difficult to achieve using lithographic techniques. However, as shown by the work of Klein and Kumecheva[35] and others, the confinement leads to important changes in the properties of, for example, lubricant molecules that are squeezed into a thin layer. The chemistry occurring in such confined spaces is an area that is still largely unexplored, but there are clear links with biology, where most chemistry takes place in very small volumes. The use of self-assembled monolayers and supramolecular chemistry, in combination with some of the strategies mentioned above, should allow the analysis of any nanoconfinement effects on chemical reactions.

Notes and references

1 A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Köhler, R. H. Friend and A. B. Holmes, *J. Am. Chem. Soc.*, 2004, **126**, 7041.
2 J. Kim and T. M. Swager, *Nature*, 2001, **411**, 1030.
3 J. L. Keddie, R. A. L. Jones and R. A. Cory, *Europhys. Lett.*, 1994, **27**, 59.
4 C. J. Ellison and J. M. Torkelson, *Nat. Mater.*, 2003, **2**, 695.
5 S. Edmondson, V. L. Osborne and W. T. S. Huck, *Chem. Soc. Rev.*, 2004, **33**, 14.
6 R. A. L. Jones and R. W. Richard, *Polymers at surfaces and interfaces*, Cambridge University Press, Cambridge, 1999.
7 S. Yamamoto, Y. Tsujii and T. Fukuda, *Macromolecules*, 2002, **35**, 6077.
8 K. Urayama, S. Yamamoto, Y. Tsujii, T. Fukuda and D. Neher, *Macromolecules*, 2002, **35**, 9459.
9 *Developments in block copolymer science and technology*, ed. I. W. Hamley, John Wiley & Sons, 2004.
10 L. Zhu, S. Z. D. Cheng, P. Huang, Q. Ge, R. P. Quirk, E. L. Thomas, B. Lotz, B. S. Hsiao, F. Yeh and L. Liu, *Adv. Mater.*, 2002, **14**, 31.
11 C. Vasilev, H. Heinzelmann and G. Reiter, *J. Polym. Sci. Part B: Polym. Phys.*, 2004, **42**, 1312.
12 O. Ikkala and G. ten Brinke, *Chem. Commun.*, 2004, 2131.
13 J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke and O. Ikkala, *Science*, 1998, **280**, 557.
14 Y. Wu, G. Cheng, K. Katsov, S. W. Sides, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits and G. D. Stucky, *Nat. Mater.*, 2004, **3**, 816.
15 T. Thurn-Albrecht, J. Schotter, G. A. Küstle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell, *Science*, 2000, **290**, 2126.
16 K. W. Guarini, C. T. Black, K. R. Milkove and R. L. Sandstrom, *J. Vac. Sci. Technol., B*, 2001, **19**, 2784.
17 T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky and T. P. Russell, *Science*, 1996, **273**, 931.
18 R. R. Li, P. D. Dapkus, M. E. Thompson, W. G. Jeong, C. Harrison, P. M. Chaikin, R. A. Register and D. H. Adamson, *Appl. Phys. Lett.*, 2000, **76**, 1689.
19 K. Shin, K. A. Leach, J. T. Goldbach, D. H. Kim, J. Y. Jho, M. Tuominen, C. J. Hawker and T. P. Russell, *Nano Lett.*, 2002, **2**, 933.
20 J. E. Barton and T. W. Odom, *Nano Lett.*, 2004, **4**, 1525.
21 S. H. Kim, M. J. Misner, T. Xu, M. Kimura and T. P. Russell, *Adv. Mater.*, 2004, **16**, 226.
22 S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo and P. F. Nealey, *Nature*, 2003, **424**, 411.
23 C. de Rosa, C. Park, E. L. Thomas and B. Lotz, *Nature*, 2000, **405**, 433.
24 R. Segalman, A. Hexemer and E. L. Thomas, *Macromolecules*, 2003, **36**, 6831.
25 H. W. Li and W. T. S. Huck, *Nano Lett.*, 2004, **4**, 1633.
26 J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith and G. J. Vancso, *Appl. Phys. Lett.*, 2002, **81**, 3657.
27 J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith and G. J. Vancso, *Adv. Mater.*, 2003, **15**, 1599.
28 D. Sundrani, S. B. Darling and S. J. Sibener, *Langmuir*, 2004, **20**, 5091.
29 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693.
30 B. G. Sumpter, D. W. Noid and M. D. Barnes, *Polymer*, 2003, **44**, 4389.
31 K. Landfester, N. Bechthold, F. Tiarks and M. Antonietti, *Macromolecules*, 1999, **32**, 2679.
32 T. Kietzke, D. Neher, K. Landfester, R. Montenegro, R. Güntner and U. Scherf, *Nat. Mater.*, 2003, **3**, 408.
33 T. Piok, S. Gamerith, C. Gadermaier, H. Plank, F. P. Wenzl, S. Patil, R. Montenegro, T. Kietzke, D. Neher, U. Scherf, K. Landfester and E. J. W. List, *Adv. Mater.*, 2003, **15**, 800.
34 Z. Yang, W. T. S. Huck, S. Clarke, A. R. Tajbakhsh and E. M. Terentjev, *Nat. Mater.*, 2005, **4**, 486.
35 J. Klein and E. Kumacheva, *Science*, 1995, **269**, 816.
36 J. Wang, J. R. Kenseth, V. W. Hones, J.-B. Green, M. T. McDermott and M. D. Porter, *J. Am. Chem. Soc.*, 1997, **119**, 12796.
37 T. P. Sullivan and W. T. S. Huck, *Eur. J. Org. Chem.*, 2003, 17.
38 P. Neogi, S. Neogi and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, 1993, 1134.
39 V. Chechik, R. M. Crooks and C. J. M. Stirling, *Adv Mater.*, 2000, **12**, 1161.
40 H. Schönherr, C. Feng and A. Shovsky, *Langmuir*, 2003, **19**, 10843.
41 B. Dordi, H. Schönherr and G. Vancso, *Langmuir*, **19**, 5780.
42 Y. Xia and G. M. Whitesides, *Angew. Chem.. Int. Ed.*, 1998, **37**, 551.
43 L. Yan, W. T. S. Huck, X.-M. Zhao and G. M. Whitesides, *Langmuir*, 1999, **15**, 1208.
44 T. P. Sullivan, M. L. Van Poll, P. Y. W. Dankers and W. T. S. Huck, *Angew. Chem., Int. Ed.*, 2004, **43**, 4190.
45 P. Timmerman, W. Verboom, F. C. J. M. van Veggel, W. P. van Hoorn and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1292.
46 M. M. Conn and J. Rebek, Jr., *Chem. Rev.*, 1997, **97**, 1647.
47 C. J. Walter, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1993, 458.
48 T. Heinz, D. M. Rudkevich and J. Rebek, Jr., *Nature*, 1998, **394**, 764.
49 A. Scarso, H. Onagi and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 12728.
50 A. Sanfeld and A. Steinchen, *C. R. Biol.*, 2003, **326**, 141.
51 *Chem. Eng. News*, 2003, **81**, 37, http://pubs.acs.org/cen/coverstory/8148/8148counterpoint.html.
52 S. P. Walch and R. C. Merkle, *Nanotechnology*, 1998, **9**, 265.
53 J. M. J. Paulusse and R. P. Sijbesma, *Angew. Chem., Int. Ed.*, 2004, **43**, 4460.