# Properties of polymer–nanoparticle composites

Gudrun Schmidt*, Matthew M. Malwitz

*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA*

## Abstract

An overview of properties of polymer–nanoparticle composites in bulk and in solution is presented along with a review of work performed during the last 3 years. The review is particularly focused on organic–inorganic materials such as polymer–nanospheres, tubes, rods, fibers and nanoplatelets. Fundamental studies on flow-induced structures in polymer–particle composites are emphasized. This relatively new area demands sophisticated experiments to augment pragmatic knowledge necessary to support theoretical descriptions of composite structures and properties. The complexity of this area guarantees that this will remain an active field for some time to come.
© 2003 Elsevier Science Ltd. All rights reserved.

*Keywords:* Nanoparticle; Polymer; Orientation; Shear

## 1. Introduction

In recent years, polymer–nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. Whether in solution or in bulk, these materials offer unique mechanical [1], electrical [2], optical [2,3•] and thermal properties [1,4]. Such enhancements are induced by the physical presence of the nanoparticle and by the interaction of the polymer with the particle and the state of dispersion [1,5,6].

One advantage of nanoparticles, as polymer additives appear to have is that compared to traditional additives, loading requirements are quite low. Microsized particles used as reinforcing agents scatter light, thus reducing light transmittance and optical clarity. Efficient nanoparticle dispersion combined with good polymer–particle interfacial adhesion eliminates scattering and allows the exciting possibility of developing strong yet transparent films, coatings and membranes.

Shear-induced structural changes in fluids containing anisotropic species are often encountered in polymer solutions in liquid crystalline materials, block copolymer melts and in particle solutions. A large body of literature exists on the flow behavior of inorganic particle slurries and solutions as well as polymer solutions. However, little is known about the influence of shear on combined polymer–nanoparticle systems. Here we will focus on some of the most recent results.

This review highlights recent accomplishments and trends in the field of polymer–nanoparticle composites which combine soft polymer components with rigid inorganic nanoparticles. Reviewed articles examine the unique chemical and physical aspects associated with polymer based composites and show future directions and opportunities for the development of new materials. Unraveling the structure property relationships of polymer–nanoparticle materials become a challenge and a new frontier in polymer–nanoparticle composites.

## 2. Nanotubes, fibers, rods

There has been increasing commercial interest in carbon nanotube polymer composites mainly due to their conductivity at very low loading levels. Driven in part by industrial relevance and concerns over intellectual property, fundamental scientific studies abound in the literature. Recent reviews on nanotubes and polymers cover aspects of mechanical and electrical properties of polymer composites [7,8] and survey approaches to the chemical functionalization of nanotubes to tailor the interaction with polymers [9] as well as the attachment of nanotubes to surfaces and polymer matrices [10]. Effective dispersion of nanotubes in polymer matrices

*Corresponding author. Tel.: +1-225-578-7375; fax: +1-225-578-3458.

*E-mail address:* gudrun@lsu.edu (G. Schmidt).

is being investigated as a means of deriving new and advanced engineering materials [11]. The synthesis of polymer films and fibers containing oriented single wall nanotubes employing shear orientation at the nanoscale still poses a special challenge [12,13]. Recent results show that flow induced alignment of nanotubes in a polymer matrix can lead to preferential orientation of the tubes, into either ribbons or fibers [14•]. Raman spectroscopy is able to determine the degree of shear orientation and the polarization direction of the nanotubes [15]. Studies of nanotube incorporation cover a wide range of matrices, flows and techniques. However, consistently successful approaches to production of shear-induced supramolecular structures containing inorganic nanotubes, rods or fibers remain elusive.

Films with tunable colors can be produced depending on the nature and size of a nanorod [3•]. Metal nanorods are especially interesting because they exhibit high electrical capacitance and the color of a colloid is affected by the effective charge of the particle [3•].

Solid state polymerization of molecularly oriented silica/monomer matrices lead to unique conductive composites. The architecture and extent of self assembly of conductive polymer–silica hybrids as films or fibers is suitable for integration into different kinds of devices and microsystems [16•]. The nanostructured inorganic host alters the monomer polymerization behavior, and the resulting nanocomposite exhibits unusual chromatic changes in response to thermal, mechanical and chemical stimuli. The inorganic framework serves to protect, stabilize, and orient the polymer, and to mediate its function [16•].

## 3. Polymers and nanospheres

Combining the ease of processability of an organic polymer with the improved mechanical and optical properties of an inorganic nanoparticle is of practical use for the fabrication of many new devices. For example, Brott et al. developed a method for creating an ordered array of silica spheres on a polymer substrate. To obtain this nanostructure they incorporated a peptide into a polymer hologram. When the nanopatterned structure is exposed to silicic acid, an ordered array of biocatalytically formed silica nanospheres is deposited onto the polymer substrate [17••]. Other studies describe well structured silica nanospheres with incorporated polymer [18], gold nanospheres coated with polymer brushes [19], or nanoparticle formation within a dendrimer matrix [20]. Many different structures can be prepared by using superstructures in organogels as a template. The synthesis of polymer coated silica nanoparticles and the strength of interactions and aggregation in solution was studied by Fong et al. They contrast the weakness of physical polymer–silica interactions which can be 'washed away' vs. the covalently attached or strongly adsorbed polymers [21]. The effect of physical adsorption of polymers on the viscosity of concentrated dispersions of charged silica particles has been found to be an interplay between rheology, adsorption and surface charge [22]. Adsorption studies provide information on the polymer layer density and conformation, that is whether the polymer is pancake-like or brush-like adsorbed to the silica particles [22]. Shear disruption processes of fractal polydisperse silica clusters can be monitored via online ultrasonic measurements [23].

There is also extensive interest in morphological features of films and membranes provided from composites of hard inorganic particles and soft polymeric materials. Enhancing membrane separation processes are attractive because they contribute to low cost, energy efficient, green technology where nanoparticles enhance the selectivity and permeability in glassy amorphous membranes [24].

A recent study on latex–silica nanocomposite films has shown that structure and morphology can be controlled by systematically varying synthetic parameters in solution. The authors suggest that a competition between silica aggregation and the solidification of the film is responsible for the aggregation kinetics [25]. These films show considerable reinforcement when subjected to small deformations, whereas at high elongations, the rheology approaches that of the pure nanolatex film [26].

Measurements by Kobayashi et al. on polymer–colloidal silica films show that the polymer interdiffusion depends on the silica filler size. The high surface of the silica raises the effective glass transition temperature of the polymer matrix [27]. Either small particles can act as obstacles to increase the tortuosity of the diffusion path or the silica surface can make the adjacent polymer matrix more rigid, which is the traditional 'filler effect'. The authors suggest that the polymer adsorption onto the silicate surface plays an important role in affecting the diffusion rate of the polymer [27]. Nanoparticles may not only raise the glass transition of polymers [27] but also change the phase behavior of nanocomposite blends [28], nanoparticles enhance the selectivity and permeability in glassy amorphous membranes [24], or lead to new electro-optical properties in polymer films [2].

Recent theoretical studies deal with chain dimensions in nanosphere-filled polymers [29], while molecular dynamic simulations cover the polymer–nanoparticle interactions and the structure and dynamics of the polymer melt containing nanoparticles [30]. Investigation on the flow dichroism of colloidal particle systems suggests that the polymer induces depletion attractions, which give rise to a 'gas liquid critical point'. Dichroic behavior is used to test theoretical predictions (mean field) on microstructural order under shear conditions [31].

## 4. Polymer–platelet interactions

The colloidal and rheological properties of polymer–nanoplatelet composites in bulk and in solution have received considerable attention, and good reviews are available [6,32••,33]. One recent focus has been on the supramolecular organization of polymers and nanoparticles. A transition from a liquid crystalline hexagonal to a lamellar phase has been observed in an aqueous mixture of Pluronic type block copolymer and clay. The adsorption of polymer to clay was important to structure formation [34]. A small angle neutron scattering (SANS) study by Lal and Auvray described the adsorption of PEO polymer chains to Laponite clay platelets at low concentrations [35,36]. It was observed that gelation of clay was prevented or extremely retarded, depending on the polymer weight, and the polymer and clay concentration. For low concentrations Lal and Auvray have been able to separate the SANS contributions from bulk and adsorbed polymer chains using contrast variation methods [35,36]. While their results were not sensitive to the shape of the polymer concentration profile, Smalley et al. and Swenson et al. use neutron diffraction to address the interlayer and ordered structure around each clay platelet as well as the mechanism of bridging flocculation [37,38••].

Below the threshold for complete saturation of clay particles by polymer, 'shake gels' can be generated with the consistency of 'a half cooled gelatine dessert'. Zebrowski et al. observe these suspensions to undergo a dramatic change in shear thickening when subjected to vigorous shaking [39]. The shake gels are reversible, relaxing back to a fluid with a relaxation time that depends on the PEO concentration. Shear induces a bridging between the colloidal particles resulting in some kind of temporary gel network that spans the system. For the same polymer–clay system, however, at slightly higher concentrations and higher polymer molecular weight, polymer chains were found to be in dynamic adsorption–desorption equilibrium with the clay particles to form a permanent network [40–42]. These highly elastic networks behave more like a soft 'chewing gum' than gelatin. In this case SANS contrast matching methods cannot distinguish between the intensity contribution of network active PEO, adsorbed PEO or excess PEO inside the network [40–42].

Despite all the obvious differences between gelatin desserts and chewing gums, the interactions between polymer and clay are intriguing and a clearer understanding of polymer–particle interactions as well as more quantitative knowledge is necessary for proper interpretation of the experimental results. Theoretical approaches by Nowicki look at the structure and entropy of polymer chains in the presence of colloidal particles and may aid in understanding systems discussed above [43]. There also has been some recent theoretical interest in poly-

mer–clay composites by Balazs and Ginzburg, who combined self-consistent field theory with density functional theory to calculate the equilibrium behavior of nanocomposites [44,45]. Their theory models the phase behavior for a mixture of polymers and solid, thin discs and takes into account the possible nematic ordering of the discs within the polymer matrix. Recent computer simulation studies by Hackett et al. use Monte Carlo and molecular dynamics to explore the atomic scale structure of intercalated polymer–nanoplatelet composites. Particular attention is paid to the configuration of the polymer within confinement [46].

## 5. Flow effects in polymer–platelet systems

Understanding polymer solutions, liquid crystalline materials, block copolymer melts and nanoparticle-containing composite materials is complicated by shear-induced structural changes. Industrial processes involve non-equilibrium as well as equilibrium states, where shear affects both preparation and product application. Real-time investigations are quite relevant to such processing applications. On-line scattering studies of flowing systems provide insight into the real-time states of matter.

Ordering platelets at the nanometer length scale is a challenging and active research area in materials science. Approaches developed so far, range from manipulation of individual particles to exploitation of self assembly in colloids [47]. The large aspect ratio of platelets promotes a supramolecular organization similar to other mesoscopic systems such as liquid crystalline polymers, surfactants or block copolymers. Multicomponent systems may generate new structures with hybrid properties. Here we focus on the shear orientation of polymer–nanoplatelet systems in solution as well as the bulk.

A two-dimensional object can align under flow along three primary directions, often referred as a, b, and c orientation in the literature (Fig. 1). In the perpendicular, or 'a' orientation, the surface normals align parallel to the vorticity direction so that the particles lie in the flow shear gradient plane. In the transverse, or 'b' orientation, the surface normals align parallel to the flow direction so that the particles lie in the vorticity shear gradient plane. Finally, in the parallel or 'c' direction, the surface normals align parallel to the shear gradient direction and the particles lie in the flow vorticity plane [48].

The general or intuitive response of clay platelets in a polymer matrix or network is to align in the parallel or 'c' orientation. This is nicely described by early studies on nylon based nanocomposites as reviewed by Krishnamoorti and Yurekli [32••]. Recent studies such as by Lele et al. [49] using in situ X-ray diffraction experiments provide a direct evidence for rheology-microstructure linkages in polypropylene nanocomposites.
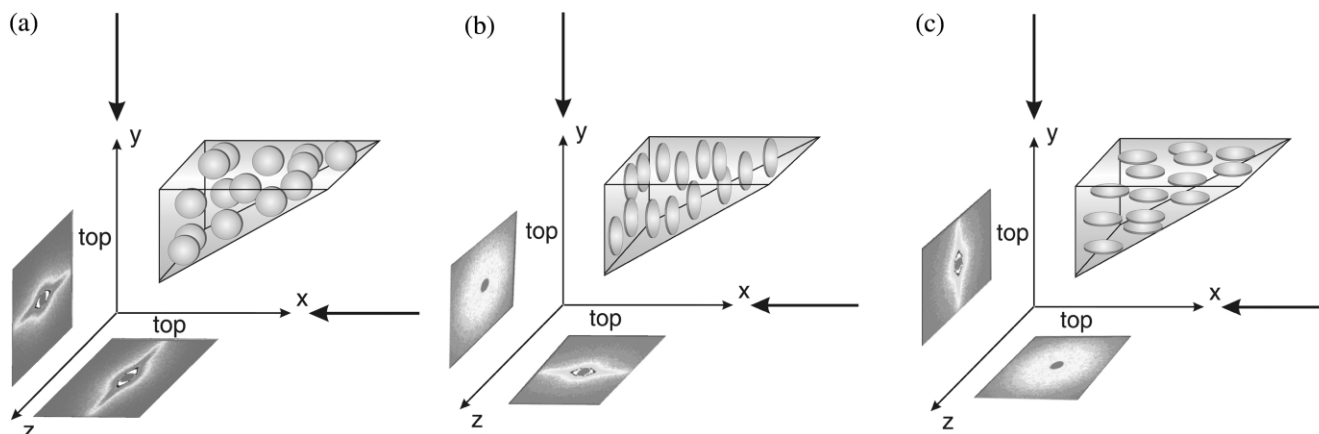
Fig. 1. SANS detection of possible shear-orientation of clay platelets. (a) Assume plates align with surface normal along neutral direction: vertical streak in radial pattern (y) and vertical streak in tangential pattern (x). (b) Assume plates align with surface normal in shear plane: horizontal streak in radial SANS pattern (y direction) and isotropic tangential pattern (x direction). (c) Assume plates align with surface normal along velocity direction: isotropic radial pattern (y) and horizontal streak in tangential pattern (x). An imperfect orientation of platelets is assumed.

An unexpected case of 'a' orientation was observed by Schmidt et al. [40,41] for aqueous polymer–clay solutions containing poly(ethyleneoxide) and Laponite clay. The polymer and the clay interact in a dynamic adsorption–desorption equilibrium to form a network [42]. SANS on samples in $D_2O$ measured the shear-induced orientation of polymer and platelets. SANS on contrast matched samples detected the orientation of the polymer alone. With increasing shear rate clay particles orient first then polymer chains start to stretch. As the shear distorts and ruptures the transient gel, coupling between composition and shear stress leads to the formation of spatially modulated macrodomains [50•]. Lin-Gibson et al. suggested that the clay orients in response to the biaxial stress arising from the shear and elastic forces [50•].

Recent TEM analysis by Okamoto et al. [51••] has revealed a house of cards structure in polypropylene/clay nanocomposite melts under elongational flow. Strong strain induced hardening and rheopexy features at higher deformation originated from the perpendicular alignment of the silicate to the stretching direction ('b' orientation). Although TEM is not an in situ technique it did reveal the difference in the shear flow induced vs. elongational internal structures of the nanocomposite melt. Similar to the polymer–clay solutions discussed by Lin-Gibson, Okamoto's nanocomposites do have strong interactions between the polymer matrix and the silicate layers.

A dispersion of nickel hydroxide platelets stabilized with a polymer was studied by Brown and Rennie [52]. Their main aim was to look at flow of dispersions rather than polymer–particle interactions. Adsorption of low molecular weight charged polyacrylate onto the platelets provided steric repulsion. They found direct evidence for a shear-induced phase transition with a change in alignment of the particles. At low shear rates the discs aligned with the normals in flow direction ('c' orientation) while at higher shear rates the discs aligned with their normals in the gradient direction ('a' orientation). At intermediate shear rates, they observed a phase transition from a columnar to a smectic phase. This system appears to use its finite two-dimensional size to arrange itself so that it can respond to low shear as a system of uniaxial particles, while at high shear rates it prefers to respond like lamellar phase [48,52].

## 6. Conclusions

From the point of view of materials chemistry, fundamental studies described here should eventually lead to the discovery of a new class of oriented polymer–particle materials. We expect that in the future it will be possible to orient particles in any desired way. Nanoparticle composites contribute to the development of future data storage, optical and electro-rheological materials, or display devices.

### Acknowledgments

### References and recommended reading

• of special interest
•• of outstanding interest

[1] Krishnamoorti R, Vaia RA. Polymer nanocomposites, vol. 804. Washington, DC: ACS, 2002.

[2] Chapman R, Mulvaney P. Electro-optical shifts in silver nanoparticle films. Chem Phys Lett 2001;349:358–62.

[3] • Wilson O, Wilson GJ, Mulvaney P. Laser writing in polarized silver nanorod films. Adv Mater 2002;14:1000.

[4] Yoon PJ, Fornes TD, Paul DR. Thermal expansion behavior of nylon 6 nanocomposites. Polymer 2002;43:6727–41.

[5] Lagaly G. Introduction: from clay mineral–polymer interactions to clay mineral–polymer nanocomposites. Appl Clay Sci 1999;15:1–9.

[6] Luckham PF, Rossi S. The colloidal and rheological properties of bentonite suspensions. Adv Coll Interface Sci 1999;82:43–92.

[7] Bernholc J, Brenner D, Nardelli MB, Meunier V, Roland C. Mechanical and electrical properties of nanotubes. Ann Rev Mater Res 2002;32:347–75.

[8] Safadi B, Andrews R, Grulke EA. Multiwalled carbon nanotube polymer composites: synthesis and characterization of thin films. J Appl Polymer Sci 2002;84:2660–9.

[9] Sinnott SB. Chemical functionalization of carbon nanotubes. J Nanosci Nanotechnol 2002;2:113–23.

[10] Bahr JL, Tour JM. Covalent chemistry of single-wall carbon nanotubes. J Mater Chem 2002;12:1952–8.

[11] Andrews R, Jacques D, Minot M, Rantell T. Fabrication of carbon multiwall nanotube/polymer composites by shear mixing. Macromol Mater Eng 2002;287:395–403.

[12] Poulin P, Vigolo B, Launois P. Films and fibers of oriented single wall nanotubes. Carbon 2002;40:1741–9.

[13] Vigolo B, Poulin P, Lucas M, Launois P, Bernier P. Improved structure and properties of single-wall carbon nanotube spun fibers. Appl Phys Lett 2002;81:1210–2.

[14] • Vigolo B, Penicaud A, Coulon C, et al. Macroscopic fibers and ribbons of oriented carbon nanotubes. Science 2000;290:1331–4.

[15] Frogley MD, Zhao Q, Wagner HD. Polarized resonance Raman spectroscopy of single-wall carbon nanotubes within a polymer under strain. Phys Rev B 2002;65: (art. no.-113413).

[16] • Lu YF, Yang Y, Sellinger A, et al. Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites. Nature 2001;410:913–7.

[17] •• Brott LL, Naik RR, Pikas DJ, et al. Ultrafast holographic nanopatterning of biocatalytically formed silica. Nature 2001;413:291–3.

[18] Patwardhan SV, Clarson SJ. Silicification and biosilicification—Part 1. Formation of silica structures utilizing a cationically charged synthetic polymer at neutral pH and under ambient conditions. Polymer Bull 2002;48:367–71.

[19] Ohno K, Koh K, Tsujii Y, Fukuda T. Synthesis of gold nanoparticles coated with well-defined, high density polymer brushes by surface-initiated living radical polymerization. Macromolecules 2002;35:8989–93.

[20] Grohn F, Kim G, Bauer AJ, Amis EJ. Nanoparticle formation within dendrimer-containing polymer networks: route to new organic–inorganic hybrid materials. Macromolecules 2001;34:2179–85.

[21] Fong B, Stryjewski W, Russo PS. On the use of pattern fluorescence photobleaching recovery with modulation detection to obtain colloidal size distributions. J Coll Interface Sci 2001;239:374–9.

[22] Zaman AA. Effect of polyethylene oxide on the viscosity of dispersions of charged silica particles: interplay between rheology, adsorption, and surface charge. Coll Polymer Sci 2000;278:1187–97.
Systematic investigation on the adsorption of PEO onto 'large nanoparticles' (two hundred nm) and viscosity behavior at high concentrations.

[23] Haider L, Tatibouet J, Lafaurie A, Ferry L. In-line ultrasonic characterization of shear dispersion processes of polydisperse fillers in polymer melts. J Phys-Condens Matter 2002;14:4943–61.

[24] Merkel TC, Freeman BD, Spontak RJ, et al. Ultrapermeable, reverse-selective nanocomposite membranes. Science 2002;296:519–22.

[25] Oberdisse J, Deme B. Structure of latex–silica nanocomposite films: a small-angle neutron scattering study. Macromolecules 2002;35:4397–405.

[26] Oberdisse J. Structure and rheological properties of latex–silica nanocomposite films: stress–strain isotherms. Macromolecules 2002;35:9441–50.

[27] Kobayashi M, Rharbi Y, Brauge L, Cao L, Winnik MA. Effect of silica as fillers on polymer interdiffusion in poly(butylmethacrylate) latex films. Macromolecules 2002;35:7387–99.

[28] Karim A, Yurkeli K, Meredith C, Amis E, Krishnamoorti R. Combinatorial methods for polymer materials science: phase behavior of nanocomposite blend films. Polymer Eng Sci 2002;42:1836–40.

[29] Vacatello M. Chain dimensions in filled polymers: an intriguing problem. Macromolecules 2002;35:8191–3.

[30] Starr FW, Schroder TB, Glotzer SC. Molecular dynamics simulation of a polymer melt with a nanoscopic particle. Macromolecules 2002;35:4481–92.

[31] Lenstra TAJ, Dhont JKG. Flow dichroism in critical colloidal fluids. Phys Rev E 2001;6306: (art. no.-061401).

[32] •• Krishnamoorti R, Yurekli K. Rheology of polymer layered silicate nanocomposites. Curr Opin Coll Interface Sci 2001;6:464–70.

[33] Vaia RA, Gianellis EP. Polymer nanocomposites: status and applications. MRS Bull 2001;62:394–401.

[34] Castelletto V, Ansari IA, Hamley IW. The influence of added clay particles on the structure and rheology of a hexagonal phase formed by an amphiphilic block copolymer in aqueous solution, Macromolecules, 2003; in press.

[35] Lal J, Auvray L. Interaction of polymer with clays. J Appl Crystallography 2000;33:673–6.

[36] Lal J, Auvray L. Interaction of polymer with discotic clay particles. Mol Crystals Liq Crystals 2001;356:503–15.

[37] Swenson J, Smalley MV, Hatharasinghe HLM, Fragneto G. Interlayer structure of a clay polymer salt water system. Langmuir 2001;17:3813–8.

[38] •• Smalley MV, Hatharasinghe HLM, Osborne I, Swenson J, King SM. Bridging flocculation in vermiculite–PEO mixtures. Langmuir 2001;17:3800–12.

[39] Zebrowski J, Prasad V, Zhang W, Walker LM, Weitz DA. Shake gels: shear-induced gelation of laponite–PEO mixtures'. Coll Surf A 2003;213:189–97.

[40] Schmidt G, Nakatani AI, Butler PD, Han CC. Small-angle neutron scattering from viscoelastic polymer–clay solutions. Macromolecules 2002;35:4725–32.

[41] Schmidt G, Nakatani AI, Butler PD, Karim A, Han CC. Shear orientation of viscoelastic polymer–clay solutions probed by flow birefringence and SANS. Macromolecules 2000;33:7219–22.

[42] Schmidt G, Nakatani AI, Han CC. Rheology and flow-birefringence from viscoelastic polymer–clay solutions. Rheol Acta 2002;41:45–54.

[43] Nowicki W. Structure and entropy of a long polymer chain in the presence of nanoparticles. Macromolecules 2002;35:1424–36.

[44] Ginzburg VV, Ba C. Calculating phase diagrams for nano-

composites: the effect of adding end functionalized chains to polymer clay mixtures. Adv Mater 2000;12:1805–9.

[45] Ginzburg VV, Singh C, Balazs AC. Theoretical phase diagrams of polymer clay composites: the role of grafted organic modifiers. Macromolecules 2000;33:1089–99.

[46] Hackett E, Manias E, Gianellis EP. Computer simulation studies of PEO-layer silicate nanocomposites. Chem Mater 2000;12:2161–7.

[47] Gabriel JCP, Camerel F, Lemaire BJ, Desvaux H, Davidson P, Batail P. Swollen liquid-crystalline lamellar phase based on extended solid-like sheets. Nature 2001;413:504–8.

[48] Butler P. Shear induced structures and transformations in complex fluids. Curr Opin Coll Interface Sci 1999;4:214–21.

[49] Lele A, Mackley M, Galgali G, Ramesh C. In-situ rheo-X-ray investigation of flow-induced orientation in layered silicate syndiotactic polypropylene nanocomposite melt. J Rheol 2002;46:1091–110.

[50] Lin-Gibson S, Schmidt G, Kim H, Han CC, Hobbie EK.
●    Shear-induced mesostructures in nanoplatelet–polymer networks, Phys Rev Lett, submitted for publication.

[51] Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N,
●●   Usuki A. A house of cards structure in polypropylene/clay nanocompocites under elongational flow. Nano Lett 2001;1:295–8.

[52] Brown ABD, Rennie AR. Images of shear-induced phase separation in a dispersion of hard nanoscale discs. Chem Eng Sci 2001;56:2999–3004.