Polymer 50 (2009) 6193–6197

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Microgel electrospinning: A novel tool for the fabrication of nanocomposite fibers

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ARTICLE INFO

Article history:
Received 10 July 2009
Received in revised form
26 October 2009
Accepted 3 November 2009
Available online 10 November 2009

Keywords:
Electrospinning
Microgels
Metal nanoclusters

ABSTRACT

We demonstrate for the first time herein that electrospinning of soluble crosslinked polymer particles (microgels) is feasible and that it can be used to obtain micron-sized fibers from these macromolecules. Most notably, the electrospinning approach is found to be successful also in the case of microgels bearing metal nanoclusters, and allows to prepare composite fibers containing a homogeneous dispersion of metal nanoparticles without alterations in the nanoparticle size and size distribution. Given the broad applicability of microgels as exotemplates and stabilisers for inorganic nanoparticles, the proposed preparation method stands out as a novel, general approach for the synthesis of potentially useful composite fibers containing inorganic nanoparticles.

Soluble crosslinked polymer particles (“microgels”) [1] are a class of materials with intermediate characteristics between those of linear polymers and three-dimensional networks, whose technological relevance is growing at a steady pace [2]. Current application of microgels range from more traditional ones, such as their extensive involvement as additives for coatings [3], to more advanced ones, such as their use as drug-delivery systems [4], biomimetic receptors/catalysts [5], soluble supports for low molecular weight reagents/scavenging agents/(bio) catalysts [6], and most notably as exotemplates/stabilisers in the preparation of inorganic nanoparticles, in particular metal nanoclusters [7–11].

All the above mentioned applications exploit the molecular properties of microgels in solution. On the other hand, microgels can be potentially also employed as building blocks to create macroscopic structures with peculiar properties and application possibilities. For example, microgels have excellent film forming properties, which form the basis of their application in coatings. Recently, their tendency to aggregate and to build ordered superstructures has been put to advantage in the preparation of thin films, responsive colloidal crystals or composite materials, with potential applications extending from biomedicine to photonics and chemomechanics [12,13]. Herein, we report on yet another possibility of using microgels as building blocks for the fabrication of novel material formats, in that we demonstrate for the first time that concentrated microgel solutions can be subjected to electrospinning forming fibers. Moreover, we show that the same is true for microgels containing inorganic nanoparticles, which paves the way to the development of a novel general strategy for the preparation of fibrous organic–inorganic composites.

Electrospinning is a simple and well-established technique for the preparation of submicrometer-sized organic and inorganic fibers from solutions containing suitable fiber precursors [14]. Linear organic polymers are the most widely used precursors for fiber formation. The preparation of composite nanofibers containing inorganic nanoparticles by electrospinning has already been reported in the literature in recent years, using electrospinning of solutions containing a commercial organic polymer and either preformed inorganic nanoparticles [15] or suitable precursors which give rise to inorganic nanoparticles in a subsequent step after electrospinning [16]. In comparison to these previous reports, an approach based on electrospinning of microgels containing inorganic nanoparticles presents many potential advantages, since (1) it allows to employ nanoparticles of predetermined size, which are stabilised against aggregation by the microgel; (2) it warrants a homogeneous dispersion of the nanoparticles in the fiber, since the inorganic and organic component are already intimately mixed within the microgel; (3) it is readily applicable to different kinds of inorganic nanoparticles (metals, oxides, sulfides etc.) which have all been successfully generated within microgels [7–11].

In order to test the feasibility of this approach, we have prepared two microgels, hereafter termed **MG1** and **MG2**, by radical solution polymerisation of a mixture of *N*,*N*-dimethylacrylamide (DMAA) as

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0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.11.004

the main comonomer, ethylene dimethacrylate (EDMA) as the crosslinker, and respectively 4-vinylpyridine (VP) or acrylamidoethylsulfonic acid (AMSA) as the functional, metal binding comonomer. We employed two different functional monomers in order to test the effect of the presence of functional groups of different nature (in particular, neutral or charged) on the outcome of the electrospinning procedure. The molar composition of the monomer mixture was DMAA:EDMA:functional monomer 8:1:1 in all cases, and the polymerisation conditions are reported in the Experimental Section. The microgels could be conveniently isolated by precipitation as white powders, readily redispersable in water and in many different organic solvents such as alcohols, dialkylamides, nitriles, dichloromethane, acetone and THF.

The microgels were characterised in water by asymmetrical flow field flow fractionation (AF-FFF) coupled to a MALLS detector. They were found to exhibit a bimodal size distribution, as it is commonly the case with microgels prepared by solution polymerisation [5a,17]. The size distribution peaked at values of the radius of gyration of 56.3 and 65.3 nm for microgel **MG1** and of 70.6 and 82.0 nm for **MG2**. Assuming spherical shape of the swollen microgels, these values correspond to hydrodynamic radii of 73.1 and 85.0 nm for **MG1** and of 68.9 and 84.3 nm for **MG2**.

The microgels were subsequently redispersed in solution and loaded with the metal precursor in order to reach a metal content in the microgel of 1% by weight. Microgel **MG1** was solubilised in dichloromethane and treated with a solution of $HAuCl_4$, whereby the Au^{III} centers became coordinated to pyridine groups contained in the microgel; subsequent reduction with sodium triethylborohydride afforded sample **MG1**-**Au** containing Au nanoclusters [9f]. Microgel **MG2** was instead dissolved in acetonitrile and treated with a solution of AgOAc, which reacted with the sulfonic acid groups of the microgel forming silver (I) sulfonate. The resulting Ag-containing microgel was found to undergo spontaneous metal reduction in solution, which was completed by addition of ethanol and reflux to yield sample **MG2**-**Ag** containing Ag nanoclusters.

TEM micrographs confirmed the formation of microgel-stabilised metal nanoclusters with these procedures (see below); Au nanoclusters were fairly monodisperse with an average size of 7.5 ± 2.2 nm, whereas in the case of Ag a rather broad size distribution between 5 and 50 nm was observed. This is the consequence of the uncontrolled, spontaneous reduction of the metal that takes place in this case, which according to our experience leads to comparatively large particles with broad size distribution [9a,9d].

The AF-FFF characterisation of the microgels was repeated on the newly generated nanocomposites **MG1**-**Au** and **MG2**-**Ag**. In both cases, the two peaks observed in the size distribution of the parent microgels merged into a single broad peak and a reduction of the gyration radius and consequently of the hydrodynamic radius, more marked in the case of microgel **MG2**, was observed: in particular, sample **MG1**-**Au** exhibited a gyration radius of 53.9 nm (hydrodynamic radius of 79.4 nm), whereas the observed value for sample **MG2**-**Ag** was 34.0 nm (hydrodynamic radius of 37.4 nm). This is in accordance with the fact that the metal nanoparticles do interact with the surrounding microgel polymer chains, thereby limiting microgel swelling. Similar observations were already made by one of us on core–shell microgels containing metal nanoparticles [10].

We subsequently turned to determine the suitability of these materials to undergo fiber formation through electrospinning. Electrospinning was first attempted using solutions of the pure microgels. Different organic solvents as well as water were initially employed, whereby protic solvents such as water or ethanol soon

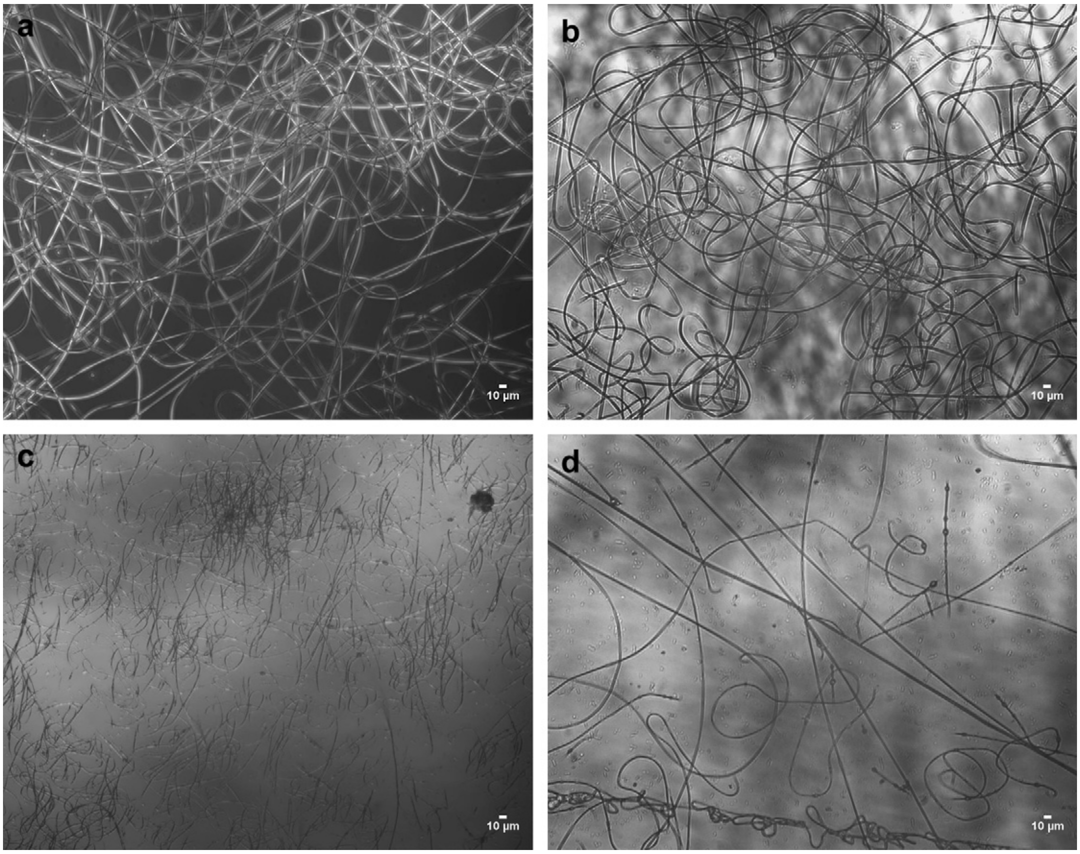

Fig. 1. Optical pictures of fibers obtained by electrospinning of (a) **MG1**, (b) **MG2**, (c) **MG1-Au**, (d) **MG2-Ag**.

emerged as the ones giving the best results. Due to their cross-linked, globular nature, microgel solutions exhibit a lower viscosity compared to solutions of linear polymers of similar molecular weight. Consequently, concentrated solutions (35–60% Wt/Vol) had to be used in order to reach viscosity values suitable for electrospinning, and the resulting fibers turned out to be rather thick. Nevertheless, using concentrated microgel solutions in ethanol we were able to obtain for the first time the formation of dense and uniform fibers (Fig. 1, above) with a diameter ranging between 0.6 and 1.5 μm.

Encouraged by this result, we set out to evaluate the spinnability of the microgel nanocomposites. We found out to our delight that the incorporation of metal nanoparticles does not change to a significant extent the spinnability of microgels. Both composites **MG1**-**Au** and **MG2**-**Ag** could be in fact efficiently electrospinned from ethanol or water/ethanol solutions, respectively, and the resulting fibers were found not to differ significantly from those of the corresponding pure microgels (Fig. 1 below).

The AFM images of the **MG1**-**Au** and **MG2**-**Ag** fibers (Fig. 2), show that the fibers in the former case are homogeneous with diameter ~1 μm, the profile on the upper right evidences the cylindrical shape of the fibers. In the latter case, the fiber are ribbon-like, with an ellipsoidal rather than perfect circular section, having longitudinal and vertical diameters measuring about 4 and 0.6 μm. The same difference is observed in the AFM images of the fibers stemming from the pure microgels (data not shown). We are currently investigating the reasons for such phenomenon, which is presumably related to the presence of charged functional groups within microgel **MG2**.

The fiber obtained by electrospinning of the composite microgels was subsequently subjected to TEM analysis. The obtained micrographs (Fig. 3) highlight the fact that in both cases the average size of the metal nanoparticles before and after the spinning process does not change. In particular, in the case of the **MG1**-**Au** fibers (Fig. 3, left) the average dimension of the nanoparticles was found to be 7.5 ± 2.3 nm, which coincides with the size observed before electrospinning. Moreover, the nanoparticles were found to be uniformly dispersed along the fiber. This behavior indicates a high stability of the microgel–metal nanocomposites, which prevents segregation or even phase separation of the metal nanoparticles in the course of the electrospinning process.

In conclusion, we have been able to demonstrate for the first time that microgels can be subjected to electrospinning forming fibers. Moreover, fibers can be formed also with microgels containing inorganic nanoparticles such as noble metal nanoclusters. In this way, composite micron-sized fibers are formed with a homogeneous distribution of the inorganic nanoparticles along the fibers and without any observable change in their size and size distribution. In particular, we have prepared fibers containing Au or Ag nanoclusters, for which interesting applications can be envisaged

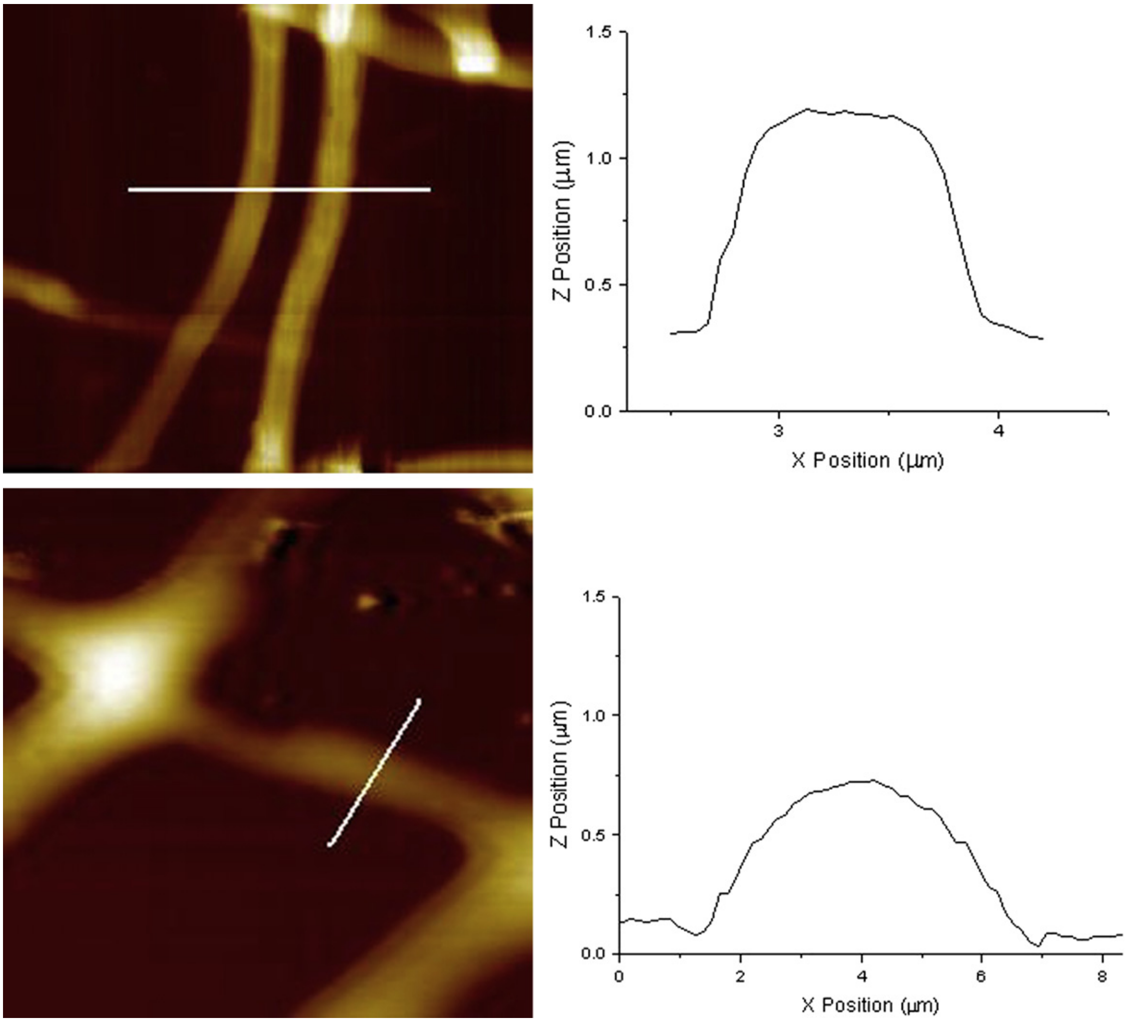

Fig. 2. Contact mode AFM image and height profile along the white line of **MG1**-**Au** (above) and **MG2**-**Ag** (below).

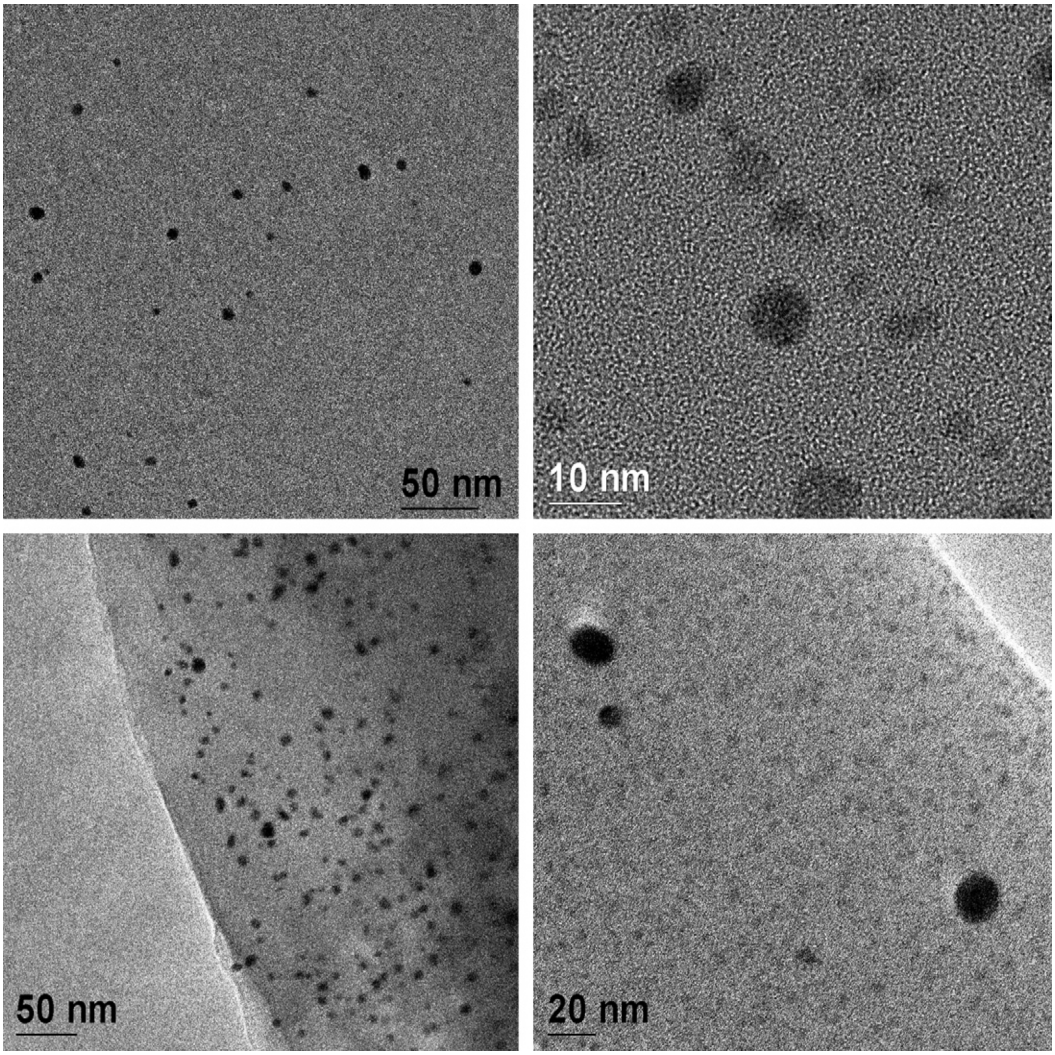

Fig. 3. TEM micrograph of **MG1-Au** (left) and of **MG2-Ag** (right) before and after electrospinning.

given e.g. the catalytic potency of gold nanoclusters [18] and the antimicrobial activity of the silver ones [19]. We are currently aiming at gaining a better control on the properties of the resulting fibers, most notably of their diameter, and at extending our investigation to different kinds and different loadings of inorganic nanoparticles.

2. Experimental section

Solvents and chemicals were of reagent grade and were used as received, apart from the monomers for microgel synthesis, which were freshly distilled to free them from inhibitors prior to use. AF-FFF data were collected on a DAWN EOS instrument equipped with a K5 cell type, with a flow rate of 1.000 mL/min. AFM measurements were performed on an AFM-NSOM nanonics (Israel). TEM analyses were carried out with JEM 3010 (JEOL) electron microscope operating at 300 kV, point-to-point resolution at a Scherzer defocus of 0.17 nm.

2.1. Microgel preparation

Monomers were mixed in the molar ratio *N,N*-dimethylacrylamide:ethylene dimethacrylate:functional monomer 8:1:1 in a round-bottomed flask. The resulting mixtures (5 g) were diluted with cyclopentanone (45 g). Azobis(isobutyronitrile) (AIBN) (0.15 g, 3% w/w with respect to the monomer mixture) was then added. The resulting solution was degassed, put under nitrogen and placed for 48 h in a thermostated oven preheated at 80 °C. The polymerisation solution was concentrated to about half of its original volume and subsequently poured into the fivefold volume of diethyl ether under efficient stirring. The precipitated solid was filtered off and dried under vacuum to constant weight. Yields were higher than 90% in all cases.

2.2. Preparation of microgel-stabilised Au nanoclusters

Microgel **MG1** (2.0 g) was dissolved in dichloromethane (120 mL) under an inert atmosphere. $HAuCl_4$ (34.6 mg, 0.10 mmol) was then added, and the resulting solution was stirred at room temperature for 24 h. Subsequently, $NaHBEt_3$ (0.88 mL 1 M solution in THF) was added and the resulting solution was stirred at room temperature for another 24 h. The solution almost immediately changed its colour from pale yellow to reddish-purple. The solution was concentrated to about half of its original volume and the nanocluster-containing microgel was subsequently precipitated by pouring the solution into the fivefold volume of diethyl ether under efficient stirring to yield a dark purple powder in 98% yield.

2.3. Preparation of microgel-stabilised Ag nanoclusters

Microgel **MG2** (1.00 g) was dissolved in acetonitrile (60 mL) under an inert atmosphere. AgOAc (15.6 mg, 0.10 mmol) was then added, and the resulting solution was stirred at room temperature for 24 h in the dark. The solution slowly changed its colour from colourless to brown. Subsequently, ethanol (20 mL) was added and the resulting solution was refluxed for another 5 h, whereby the solution colour gradually became darker. The solution was concentrated to a few mL and the nanocluster-containing microgel was subsequently precipitated by pouring the solution into 100 mL of diethyl ether under efficient stirring. The resulting sticky solid was redissolved into the minimum volume of dichloromethane and again reprecipitated from diethyl ether to yield a yellowish brown powder in 98% yield.

2.4. TEM measurements

Microgel samples for TEM measurements were prepared by placing a drop of a solution of microgel-stabilised metal nanoclusters in ethanol on a carbon-coated copper grid followed by solvent evaporation at room temperature. Fiber samples for TEM measurements were prepared by directly depositing them on a TEM grid positioned on the glass slide which made out the target of the electrospinning apparatus (see below). Average metal nanocluster sizes and size distributions were computed as the average of at least 100 particles taken from different fields.

2.5. Electrospinning procedure

Microgels **MG1**, **MG1-Au** and **MG2** were dissolved in ethanol (60%, 55% and 35% Wt/Vol, respectively). Microgel **MG2-Ag** was dissolved in a 2:1 water:ethanol mixture (60% Wt/Vol). The solutions were loaded in a 1 mL disposable syringe equipped with a 23G needle. A glass slide positioned 15 cm away from the tip of the needle was used as target. Electrospinning was performed at 18 KV using a vertical experimental setup. Under these conditions, fibers with diameters between 0.6 and 1.5 μm were obtained.

Acknowledgements

This work was supported by the European Community through the Marie Curie RTN "NASCENT" (contract no. MRTN-CT-2006-033873).

References

[1] Baker WO. Ind Eng Chem 1949;41:511–20.
[2] (a) Funke W, Okay O, Joos-Müller B. Adv Polym Sci 1998;136:139–234;
  (b) Saunders BR, Vincent B. Adv Colloid Interface Sci 1999;80:1–25;
  (c) Pelton RH. Adv Colloid Interface Sci 2000;85:1–33.
[3] Saatweber D, Vogt-Birnbrich B. Prog Org Coat 1996;28:33–41.
[4] (a) Kwon YJ, James E, Shastri N, Frechet JMJ. Proc Natl Acad Sci 2005;102:18264–8;
  (b) Das M, Mardyani S, Chan WCW, Kumacheva E. Adv Mater 2006;18:80–3 [and references cited therein].
[5] (a) Biffis A, Graham NB, Siedlaczek G, Stalberg S, Wulff G. Macromol Chem Phys 2001;202:163–71;
  (b) Maddock SC, Pasetto P, Resmini M. Chem Commun 2004:536–7;
  (c) Hunt CE, Pasetto P, Ansell RJ, Haupt K. Chem Commun 2006:1754–6;
  (d) Wulff G, Chong BO, Kolb U. Angew Chem Int Ed 2006;45:2955–8;
  (e) Chen Z, Hua Z, Wang J, Guan Y, Zhao M, Li Y. Appl Catal A Gen 2007;328:252–8;
  (f) Carboni D, Flavin K, Servant A, Gouverneur V, Resmini M. Chem Eur J 2008;14:7059–65.
[6] Selected examples:
  (a) Luthra AK, Williams A. J Mol Catal A 1995;95:83–92;
  (b) Otero C, Robledo L, Alcantara AR. J Mol Catal B Enzymatic 1995;1:23–8;
  (c) Ford WT, Lee J-J, Yu H, Ackerson BJ, Davis KA. Macromol Symp 1995;92:333–43;
  (d) Ohkubo K, Funakoshi Y, Sagawa T. Polymer 1996;37:3993–5;
  (e) Kihara N, Kanno C, Fukutomi T. J Polym Sci A 1997;35:1443–51;
  (f) Schunicht C, Biffis A, Wulff G. Tetrahedron 2000;56:1693–9;
  (g) Spanka C, Clapham B, Janda KD. J Org Chem 2002;67:3045–50;
  (h) Shimomura O, Clapham B, Spanka C, Mahajan S, Janda KD. J Comb Chem 2002;4:436–41.
[7] (a) Antonietti M, Gröhn F, Hartmann J, Bronstein L. Angew Chem Int Ed 1997;36:2080–3;
  (b) Whilton NT, Berton B, Bronstein L, Henze H, Antonietti M. Adv Mater 1999;11:1015–8;
  (c) Bronstein LM, Chernyshov DM, Karlinsey R, Zwanziger JM, Matveeva VG, Sulman ES, et al. Chem Mater 2003;15:2623–31.
[8] (a) Xu S, Zhang J, Paquet C, Lin Y, Kumacheva E. Adv Funct Mater 2003;13:468–72;
  (b) Zhang J, Xu S, Kumacheva E. J Am Chem Soc 2004;126:7908–14;
  (c) Gorelikov I, Field LM, Kumacheva E. J Am Chem Soc 2004;126:15938–9;
  (d) Zhang J, Xu S, Kumacheva E. Adv Mater 2005;17:2336–40.
[9] (a) Biffis A. J Mol Catal A Chem 2001;165:303–7;
  (b) Biffis A, Orlandi N, Corain B. Adv Mater 2003;15:1551–5;
  (c) Biffis A, Sperotto E. Langmuir 2003;19:9548–50;
  (d) Minati L, Biffis A. Chem Commun 2005:1034–6;
  (e) Biffis A, Minati L. J Catal 2005;236:405–9;
  (f) Biffis A, Cunial S, Spontoni P, Prati L. J Catal 2007;251:1–6;
  (g) Biffis A. In: Corain B, Schmid G, Toshima N, editors. Metal nanoclusters in catalysis and materials science: the issue of size-control. Amsterdam: Elsevier; 2008. p. 341–6.
[10] (a) Pich A, Bhattacharya S, Lu Y, Boyko V, Adler H-JP. Langmuir 2004;20:10706–11;
  (b) Pich A, Hain J, Lu Y, Boyko V, Prots Y, Adler H-JP. Macromolecules 2005;38:6610–9;
  (c) Pich A, Karak A, Lu Y, Ghosh AK, Adler H-JP. Macromol Rapid Commun 2006;27:344–50;
  (d) Hain J, Schrinner M, Lu Y, Pich A. Small 2008;4:2016–24;
  (e) Agrawal M, Pich A, Gupta S, Zafeiropoulos NE, Rubio-Retama J, Simon F, et al. J Mater Chem 2008;18:2581–6.
[11] (a) Palioura D, Armes SP, Anastasiadis SH, Vamvakaki M. Langmuir 2007;23:5761–8;
  (b) Suzuki D, Kawaguchi H. Langmuir 2006;22:3818–22 [and references cited therein].
[12] (a) Lyon LA, Meng Z, Singh N, Sorrell CD, St. John A. Chem Soc Rev 2009;38:865–74;
  (b) Nayak S, Lyon LA. Angew Chem Int Ed 2005;44:7686–708.
[13] Richter A, Turke A, Pich A. Adv Mater 2007;19:1109–12.
[14] Reviews:
  (a) Greiner A, Wendorff JH. Angew Chem Int Ed 2007;46:5670–703;
  (b) Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. Compos Sci Technol 2003;63:2223–53.
[15] (a) Yang QB, Li DM, Hong YL, Li ZY, Wang C, Qiu SL, et al. Synth Met 2003;137:973–4;
  (b) Wang M, Singh H, Hatton TA, Rutledge GC. Polymer 2004;45:5505–14;
  (c) Kim G-M, Wutzler A, Radusch H-J, Michler GH, Simon P, Sperling RA, et al. Chem Mater 2005;17:4949–57;
  (d) Kedem S, Schmidt J, Paz Y, Cohen Y. Langmuir 2005;21:5600–4.
  (e) Gupta P, Asmatulu R, Claus R, Wilkes G. J Appl Polym Sci 2006;100:4935–42;
  (f) Saquing CD, Manasco JL, Khan SA. Small 2009;5:944–51.
[16] (a) Son WK, Youk JH, Lee TS, Park WH. Macromol Chem Rapid Commun 2004;25:1632–7;
  (b) Demir MM, Gulgun MA, Menceloglu YZ, Erman B, Abramchuk SS, Makhaeva EE, et al. Macromolecules 2004;37:1787–92;
  (c) Melaiye A, Sun ZH, Hindi K, Milsted A, Ely D, Reneker DH, et al. J Am Chem Soc 2005;127:2285–91.
[17] (a) Sun X, Chiu YY, Lee LJ. Ind Eng Chem Res 1997;36:1343–51;
  (b) Chiu YY, Lee LJ. J Polym Sci A 1995;33:257–67.
[18] See for example the recent special issue of Chemical Society Reviews dedicated to gold catalysis: Chem Soc Rev 2008; 37(9):1745–2140.
[19] See for example Sharma VK, Yngard RA, Lin Y. Adv Colloid Interface Sci 2009;145:83–96 [and references cited therein].