A novel gel deformation technique for fabrication of ellipsoidal and discoidal polymeric microparticles

Anne-Claude Courbaron,[a] Olivier J. Cayre[ab] and Vesselin N. Paunov*[a]

Received (in Cambridge, UK) 31st July 2006, Accepted 19th October 2006
First published as an Advance Article on the web 6th November 2006
DOI: 10.1039/b610994b

A simple fabrication technique for anisotropic particles of ellipsoidal/discoidal shape has been developed, based on stretching/compressing of oil-in-water emulsion templates embedded into an elastic aqueous gel; a range of solid anisotropic microparticles have been fabricated by polymerising of the deformed oil drops in the elastic gel matrix and their shape and aspect ratios have been studied as a function of the gel deformation.

Particles of anisotropic properties due to asymmetric shape or surface charge distribution are expected to exhibit additional orientational interactions in suspensions.[1–9] Several techniques for fabrication of anisotropic metal nanoparticles have been reported over the past five years or so, based on electrochemical[10] and photochemical[11] reduction, surfactant-aided growth,[15,16] templating of porous membranes[12,13] and nanotubes.[14] Other studies report formation of Janus particles,[1,2] non-spherical shaped "acorn" particles,[3,4] and unsymmetrical 3D macromolecules of large dipolar moment.[5,6] Recently, novel methods for preparation of anisotropic colloid particles, based on microcontact printing,[17] gel trapping technique[18] and solvent attrition techniques[19] have been invented. On the nanometre scale, two main methods for the fabrication of unusual shaped particles have been developed based on growth directed syntheses such as seeded emulsion polymerisation,[20,21] and template directed syntheses such as the assembly of spherical colloids into anisotropic structures.[20,21] Preparation of inorganic ellipsoidal and needle-like microcrystals of various materials like calcium carbonate,[22] hematite[23] and lanthanide compounds[24] by precipitation of inorganic salts from aqueous solutions has been reported and the microcrystals aspect ratio has been controlled by modifying the crystalisation conditions. However, few methods have arisen for the fabrication of non-spherical polymeric microparticles. Ho *et al.*[25] reported a technique for preparation of ellipsoidal particles by stretching a thin film of polyvinyl alcohol containing spherical latex particles. Other methods based on heterocoagulation or modification of polymer particles by solvent adsorption and swelling often result in anomalous shapes without direct control over their morphology.[26–28] Most of the reported procedures[20,21,25] (except ref. 19, 22–24) for fabrication of anisotropic polymeric microparticles are carried out on a two-dimensional (2D) scale and require preparation of 2D particle monolayers or their embedding into thin films prior to their modification.

[a]*Surfactant & Colloid Group, Department of Chemistry, University of Hull, Hull, UK HU6 7RX. E-mail: V.N.Paunov@hull.ac.uk; Fax: +44 (0)1482 466410; Tel: +44 (0)1482 465660*
[b]*Department of Biomolecular and Chemical Engineering, North Carolina State University, Raleigh, NC, 27695-7905, USA*

Here we report a rapid scalable 3D method for the preparation of ellipsoidal polymeric microparticles from oil-in-water (o/w) emulsion templates. Emulsions of various polymerisable oils in water were mixed with a hot solution of two polysaccharides (Locust Bean Gum and κ-Carageenan from CP Kelco, USA, in ratio 1 : 1) and the aqueous phase was set to a gel by lowering the temperature below the gelling point of the polysaccharides solution. Thus, the continuous phase of the emulsion acquired the elastic properties of the aqueous gel and was further subjected to stretching or compressing during which the emulsion droplets of polymerisable oil were deformed due to the local strain caused by the macroscopic stress applied to the gelled emulsion.

The droplets were subsequently solidified by UV curing as the system was kept at constant temperature on a cooled stage. After that, the sample was heated to 80 °C, *i.e.* above the gel melting point to release the solid microparticles from the gel. The particles were washed and filtered while the system was kept at 80 °C to

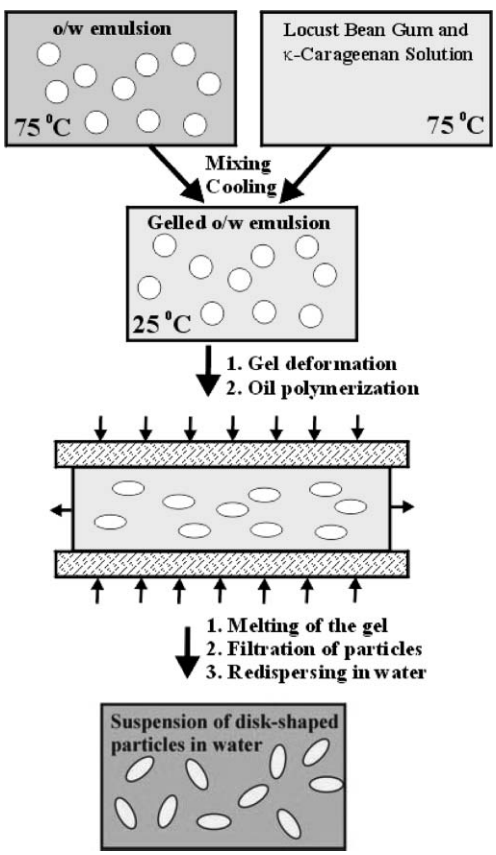

Fig. 1 Scheme for the preparation of anisotropic ellipsoidal colloid particles from a polymerisable oil-in-water emulsion template.

allow complete removal of the polysaccharides. The produced non-spherical microparticles were redispersed in milliQ water directly from the filter. In a typical experiment, an o/w emulsion (10% volume fraction of oil) was prepared in the presence of 10 mM sodium dodecyl sulfate by stirring the two phases in a beaker. The polymerisable oil phase was either an optical adhesive (NOA 72, from Norland Products Inc., USA) or 1,6-hexanediol-diacrylate, (HDDA, from Aldrich in combination with UV initiators of radical polymerisation Irgacure 819 and Irgacure 184 in a 10 : 1 ratio (1% wt of the oil phase) obtained from Ciba Speciality Chemicals, Switzerland. The emulsion was further homogenised at approximately 80 °C with the preheated solution of the polysaccharide mixture. Subsequently, the system was cooled down to room temperature to set the aqueous phase to an elastic gel. After stretching or compression of the gel fragment to the required size, polymerisation of the oil drops was induced by shining a strong UV light through the sample (UV Spot cure lamp) and was completed in 1 to 2 h depending on the oil type and the sample thickness. Redispersion of the sample was then carried out at 80 °C and followed by filtration and thorough washing of the particles before their final redispersion in milliQ water.

Fig. 2 shows two SEM images taken at different magnifications of the sample of non-spherical particles prepared from an initial HDDA-in-water emulsion. The segment of gelled emulsion was compressed so that the final height of the sample was only 2/3 of its original. This ultimately resulted in the preparation of microparticles presenting a flattened coin-like shape.

One can see that the particles appear of a similar shape although they are polydisperse due to the polydispersity of the emulsion template. We also studied how the emulsion droplet size influences the final aspect ratio. The results show that larger drops produce solid particles of slightly higher aspect ratio. We believe that this is as a result of specific visco-elastic properties of the polysaccharide mixture when deforming the gel, so that upon application of stress it produces slightly different deformation of the microdroplets depending on their size, *i.e.* at fixed applied stress, the deformation

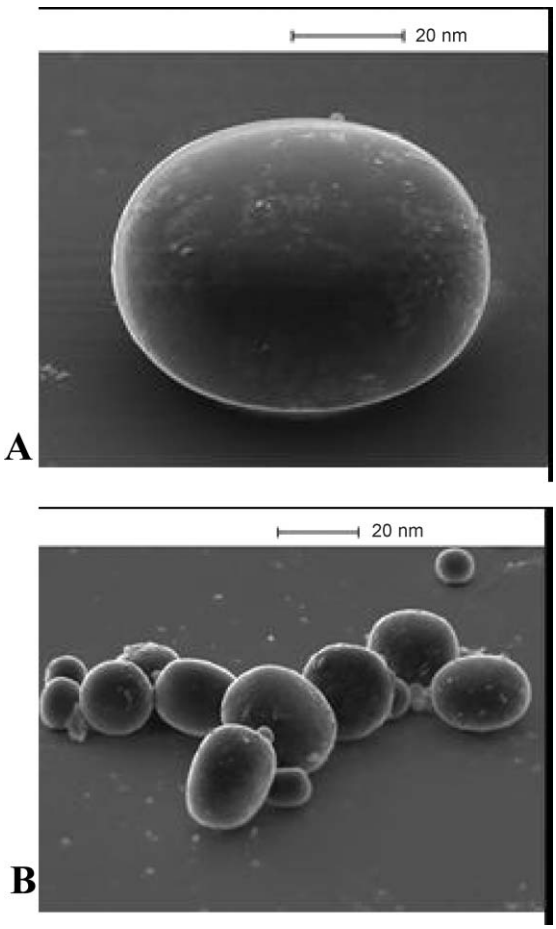

Fig. 2 SEM images of ellipsoidal particles prepared from an HDDA-in-water emulsion with a gel aqueous phase compression ratio of 0.67.

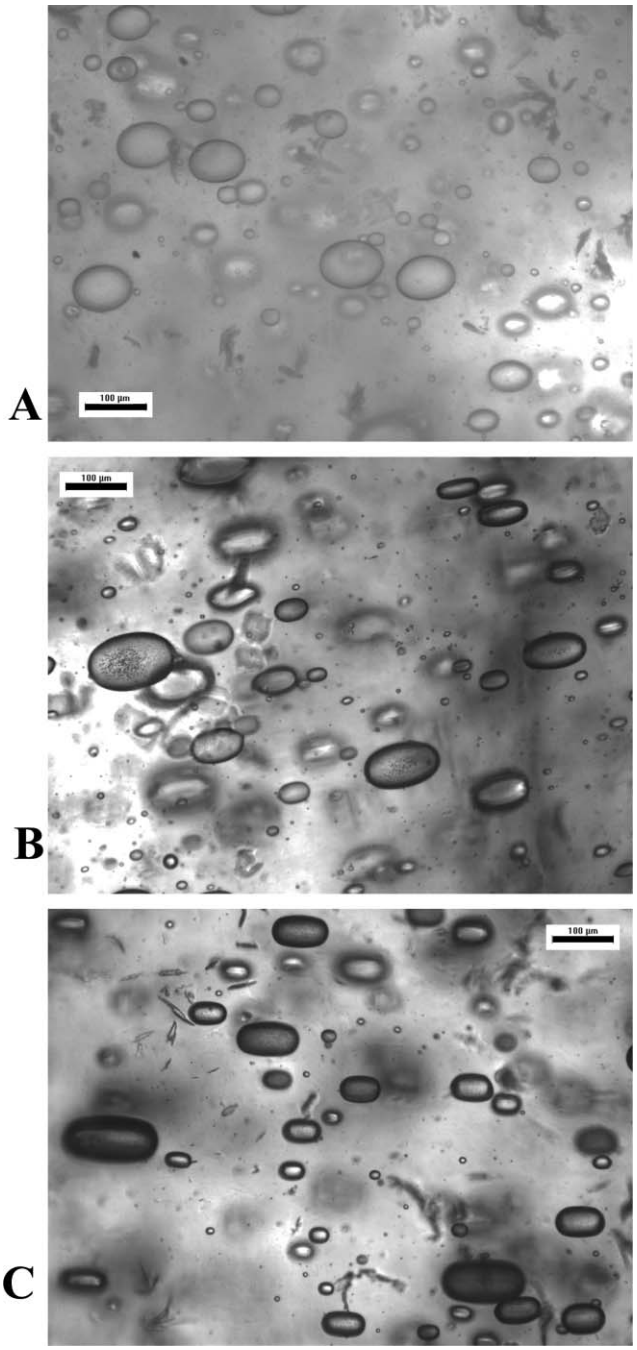

Fig. 3 Optical images of deformed NOA72 emulsion droplets after stretching of the gelled aqueous phase segment to three different aspect ratios: (a) 1.15, (b) 1.35 and (c) 1.55. Bars are 100 µm.

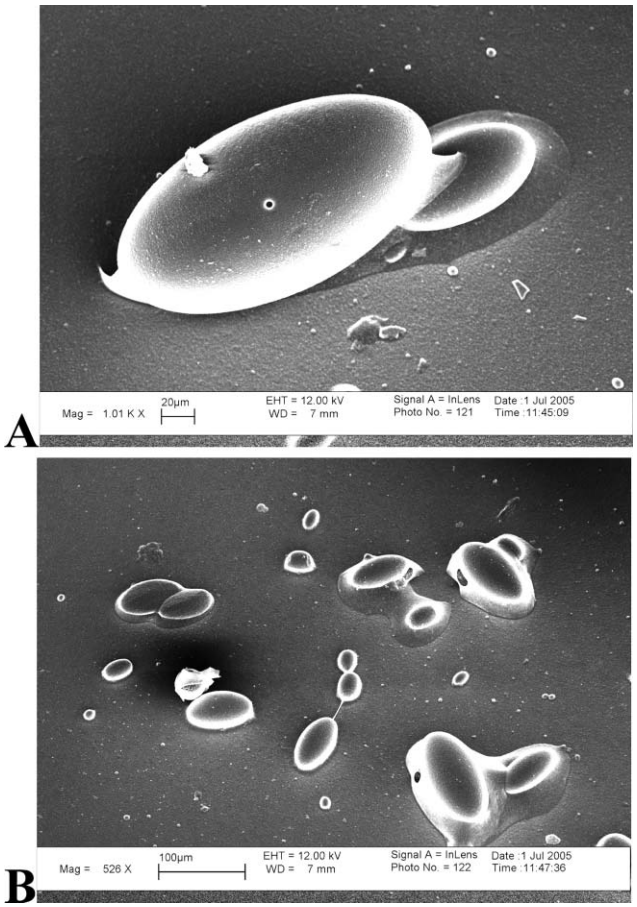

Fig. 4 (A) High and (B) low magnification SEM images of ellipsoidal polymeric particles (NOA72) obtained by stretching of the gel matrix. The solid particles have been released from the gel matrix.

that the gel "transmits" to the embedded droplets is size dependent. This assertion will be discussed further as additional studies on the different parameters controlling the deformation of the droplets in the aqueous gelled phase will be reported in a follow-up publication. Fig. 3 shows optical microscopy images of NOA72 emulsion droplets in a gelled and deformed aqueous phase. These images correspond to three different experiments where a gel segment of the same sample was stretched to different ratios before the polymerisation of the oil droplets. Solid particles of different aspect ratios were recovered from these samples, however, here we present images of the polymerised particles still embedded within the stretched gel matrix for ease of observation. As expected the higher macroscopic deformation leads to ellipsoidal particles of larger aspect ratio. This can be seen in Fig. 3 as the average shape of the particles produced shows a dramatic change from being close to spherical in the case of the lowest deformation ratio (1.15) to highly elongated structures for the highest deformation ratio (1.55). Note that, we were not able to reach a higher aspect ratio as the gelled aqueous phase ruptured easily above this elongation ratio. Fig. 4 shows the polymeric particles released from the gel matrix (after melting the gel and washing of the particles with water) at one of the highest aspect ratios we were able to achieve at this gel composition.

In summary, we have designed a rapid and easy procedure for "in bulk" preparation of non-spherical microparticles by polymerisation of deformed gelled oil-in-water emulsion templates. The droplet deformation was shown to depend on the macroscopic deformation of the gelled continuous aqueous phase, the gel strength and the viscosity of the polymerisable oil phase. This last point will be reported in a detailed follow-up paper where oils of different viscosities were studied and allowed us to fabricate particles of varying shapes at the same compression or stretching deformation. We believe that this method can be extended to produce anisotropic non-spherical nanoparticles by using gelled microemulsions following the same steps, as described in Fig. 1. It is also worth mentioning that the proposed method is not restricted to UV-polymerisable oils and the process of solidifying of the emulsion drops can also be conducted by using thermal initiators of the polymerisation. This, although much slower would eliminate the necessity to produce the gel matrix in the form of a layer. Such a study is under way.

Notes and references

1 C. Casagrande, P. Fabre, E. Rhaphaël and M. Veyssié, *Europhys. Lett.*, 1989, **9**, 251.
2 T. Ondarcuhu, P. Fabre, E. Rhaphaël and M. Veyssié, *J. Phys. (Paris)*, 1990, **51**, 1527.
3 A. T. Skjeltrop, J. Ugelstad and T. Ellingsen, *J. Colloid Interface Sci.*, 1986, **113**, 577.
4 A. Loxley and B. Vincent, *J. Colloid Interface Sci.*, 1998, **208**, 49.
5 K. L. Wooley, C. J. Hawker and J. M. Fréchet, *J. Am. Chem. Soc.*, 1993, **115**, 11505.
6 I. M. Saez and J. W. Goodby, *Chem. Commun.*, 2003, **14**, 1726.
7 H. Takei and N. Shimizu, *Langmuir*, 1997, **13**, 1867.
8 K. Fujimoto, K. Nakahama, M. Shidara and H. Kawaguchi, *Langmuir*, 1999, **15**, 4630.
9 K. Nakahama, H. Kawaguchi and K. Fujimoto, *Langmuir*, 2000, **16**, 7882.
10 Y. Y. Yu, S. S. Chang, C. L. Lee and C. R. C. Wang, *J. Phys. Chem. B*, 1997, **101**, 6661.
11 K. Esumi, K. Matsuhisa and K. Torigoe, *Langmuir*, 1995, **11**, 3285.
12 B. R. Martin, D. J. Dermody, B. D. Reiss, M. M. Fang, L. A. Lyon, M. J. Nathan and T. E. Mallouk, *Adv. Mater.*, 1999, **11**, 1021.
13 V. M. Cepak and C. R. Martin, *J. Phys. Chem. B*, 1998, **102**, 9985.
14 S. Fullam, D. Cottel, H. Rensmo and D. Fitzmauritce, *Adv. Mater.*, 2000, **12**, 1430.
15 N. R. Jana, L. Gearheart and C. J. Murphy, *Adv. Mater.*, 2001, **13**, 1389.
16 C. J. Murphy and N. R. Jana, *Adv. Mater.*, 2002, **14**, 80.
17 O. J. Cayre, V. N. Paunov and O. D. Velev, *Chem. Commun.*, 2003, 2296; O. J. Cayre, V. N. Paunov and O. D. Velev, *J. Mater. Chem.*, 2003, **13**, 2445.
18 V. N. Paunov and O. J. Cayre, *Adv. Mater.*, 2004, **16**, 778.
19 R. G. Alargova, K. H. Bhatt, V. N. Paunov and O. D. Velev, *Adv. Mater.*, 2004, **16**, 1653.
20 J. Ugelstad, P. C. Mork, K. H. Kaggerud, T. Ellingsen and A. Berge, *Adv. Colloid Interface Sci.*, 1980, **13**, 101.
21 M. Okubo, Y. Katsuta and T. Matsumoto, *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 481.
22 L. Wang, I. Sondi and E. Matijević, *J. Colloid Interface Sci.*, 1999, **218**, 545.
23 M. Ozaki, S. Kratohvil and E. Matijević, *J. Colloid Interface Sci.*, 1984, **102**, 146; M. Ozaki, T. Egami, N. Sugiyama and E. Matijević, *J. Colloid Interface Sci.*, 1988, **126**, 212; M. Ozaki, K. Nakata and E. Matijević, *J. Colloid Interface Sci.*, 1988, **131**, 233.
24 E. Matijević and W. P. Hsu, *J. Colloid Interface Sci.*, 1987, **118**, 506.
25 C. C. Ho, A. Keller, J. A. Odell and R. H. Ottewill, *Polym. Int.*, 1993, **30**, 207; *Colloid Polym. Sci.*, 1993, **271**, 469.
26 E. Matijević and Y. Kitazawa, *Colloid Polym. Sci.*, 1983, **261**, 527.
27 A. M. Islam, B. Z. Chowdhry and M. J. Snowden, *Adv. Colloid Interface Sci.*, 1995, **62**, 109.
28 M. Okubo, Y. Konishi, M. Takebe and H. Minami, *Colloid Polym. Sci.*, 2000, **278**, 919.