Synergistic enhancement of microbubble formation in ultrasound irradiated H_2O–CH_3OH mixtures probed by dynamic light scattering

Mrinal R. Pai, Puthusserickal A. Hassan, Shyamala R. Bharadwaj* and Shailendra K. Kulshreshtha

Received (in Montpellier, France) 26th July 2007, Accepted 22nd October 2007
First published as an Advance Article on the web 5th November 2007
DOI: 10.1039/b711397h

This report investigates the formation of microbubbles in water–methanol mixtures upon ultrasound irradiation and its correlation with the yield of H_2 obtained as a result of sonochemical splitting of water. The yield of hydrogen produced by sonochemical reaction is monitored at different compositions of water–methanol mixtures. The evidence for the formation of microbubbles upon ultrasound irradiation is obtained by the dynamic light scattering technique. Microbubble formation during ultrasound irradiation of water–methanol mixtures, their stability and size distribution, has been quantitatively estimated. The effect of composition of the water–methanol mixture and duration of irradiation on the extent of bubble formation has been inferred from the changes in the light scattering intensity and its time correlation function. Exceptional stability of microbubbles without any additives is observed at a certain composition of the water–methanol mixture (4 : 3, v/v). The extent of microbubbles formed in the mixture correlates well with the yield of hydrogen detected.

1 Introduction

Water decomposition using sonochemical method has been the subject of many investigations. The generation of hydrogen from liquid water as a result of ultrasound irradiation is well reported.[1] The dissociation of water into free radicals and subsequent recombination to produce hydrogen is attributed to cavitation effects.[2] The effects of suspended particles on sonochemical reaction have been reported by several workers:[3–5] for example, Yasuda *et al.*[3] reported the effects of insoluble particles, such as silica (SiO_2) and alumina (Al_2O_3), on the sonochemical reaction and demonstrated that the reaction rate constant depended on particle properties such as particle size and number density of the particles. Harada[5] reported the stoichiometric decomposition of water to hydrogen and oxygen by irradiations of light and ultrasound with particulate photocatalysts. A recent report indicates that the addition of methanol and other additives to water significantly affects the yields of hydrogen production from sonochemical splitting of liquid water.[4] It is reported that dispersed particles of different types such as metallic, semiconductor photocatalysts, transition metal oxides, mixed oxides or insulator materials enhances the yield of hydrogen upon sonochemical decomposition of water at ambient conditions. This increase in the yield of hydrogen has been attributed to the enhancement of cavitations, though no direct evidence has been given. The increased yield of H_2 in the presence of methanol is attributed to the efficient scavenging of OH radicals by methanol and thereby preventing the recombination of H and OH radicals formed due to sonication. Apart from this, other properties of the liquid mixtures can also help in determining the yield of hydrogen from the sono-decomposition of water. At certain mole fractions of H_2O and methanol, the yield of H_2 is exceptionally higher than that obtained by either of the pure components or other mole fractions under similar experimental conditions.[4] Hence a synergistic enhancement of H_2 generation is observed in H_2O–CH_3OH mixtures.

Cavitation in liquid mixtures can also play a role in deciding the yield of hydrogen from the sonochemical splitting of water. The sonication induced cavitation and its effects were demonstrated and summarized by Suslick *et al.* and others.[5–7] Various attempts on exploring the process of cavitations and estimating the maximum temperatures and pressures achieved by the collapsing bubbles have been reported.[8–12] So far, evidences for microbubbles have been obtained from the emission spectra of transient bubbles (sonoluminescence)[8–10] and by increase of acoustic streaming.[12] Analysis of the emitted spectral lines indicates that the temperature and pressures reached inside these bubbles is around 5000 K and 1000 atm, respectively.[7] Moreover, there has been considerable interest in the stabilization of microbubbles for use in ultrasound imaging. Compressible gas bubbles scatter ultrasound by several orders of magnitude and hence act as ultrasound contrast agents.[13–17] Several strategies have been reported for the stabilization of microbubbles in ultrasound contrast agents. Perfluorocarbon-stabilized microbubbles are now also being investigated as oxygen delivery systems (blood substitutes).[18,19] Polymeric shells, polyelectrolytes, phospholipids, block copolymers *etc.* have been employed as stabilizing agents,[14–17,20–22] for microbubbles. Biologically inert perfluorocarbons (PFC) gases, when used as part of the filling gas, enhance the stability of micron bubbles and retard bubble dissolution very effectively, due to very low water

---

Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India. E-mail: shyamala@barc.gov.in

solubility.[13–17,23] Alcohol induced formation of stable micro/nanobubbles on solid surfaces has also been studied using atomic force microscopy.[24,25] Yang *et al.*[24] reported nanobubble formation on solid–liquid interfaces under varying conditions of temperature, gas type, concentration, surfactant *etc.* Their studies reveal that flushing water over alcohol covered surfaces strongly enhances the formation of surface nanobubbles. Lou *et al.*[25] reported formation of stable nanobubbles on atomically smooth solid surfaces by flowing ethanol and water intermittently.

The objective of the present study is to investigate the effect of cavitations on hydrogen yield obtained as a result of sonochemical splitting of water–methanol mixtures. The influence of solvent composition on the extent of formation of microbubbles during ultrasound irradiation was investigated and is compared with the yield of hydrogen formation. The evidence for formation of microbubbles, their stability and size distribution, has been monitored using dynamic light scattering experiments. Since methanol is known to be used as a sacrificial agent in water splitting reaction through photocatalytic or sonocatalytic means, the effect of only methanol was investigated.

1.2 Theory

Dynamic light scattering measures the time dependence of light scattered from a suspension of colloids and computes the intensity correlation function. For colloids undergoing random Brownian motion, the scattering intensity fluctuates as a function of time with a characteristic time scale that is related to the diffusion coefficient of scatterers.[26] This characteristic time of fluctuations can be obtained from the decay of the autocorrelations of scattered intensity, $c(\tau)$, defined as eqn (1):

$$C(\tau) = \frac{1}{2T}\int_{-T}^{T} I(t)I(t+\tau)\,\mathrm{d}t \qquad (1)$$

where $I(t)$ is the scattered light intensity at any time, and t and $I(t + \tau)$ is the scattered light intensity at a later time $(t + \tau)$, and T = time.

For spherical scatterers undergoing random Brownian motion, the unnormalized correlation function can be written as eqn (2)

$$C(\tau) = A + B\exp(-2Dq^2\tau) \qquad (2)$$

where A is the baseline that is equivalent to $\langle I(t)\rangle^2$, B is the amplitude of the correlation function, D is the diffusion coefficient of the scatterers and q is the magnitude of the scattering vector given by $q = (4\pi\eta/\lambda)\sin(\theta/2)$; θ being the scattering angle, n is the refractive index of the liquid and λ is the wavelength of the radiation. In the present study, $C(\tau)$ is plotted without any normalization so that the sum of baseline and amplitude $(A + B)$ can be used as a measure of the intensity of light scattered and hence the number density of scatterers when there is no significant change in the size distribution.

By fitting the correlation function with an exponential decay, the diffusion coefficient, D, of the scatterers can be obtained that is related to the diameter (d) of spherical scatterers by the Stokes–Einstein's relationship as shown by eqn (3).

$$d = \frac{kT}{3\pi\eta D} \qquad (3)$$

Here k is Boltzmann's constant, T is the absolute temperature and η is the viscosity of solvent. When a distribution of diffusion coefficients is present, the size distribution can be obtained from $C(\tau)$ by an inverse Laplace transformation and this is performed using a commercial algorithm, CONTIN.[27]

2 Experimental

2.1 Sonochemical reaction

Mixtures of distilled water and methanol of AR grade supplied by M/s S.D. fine chemicals Ltd., Mumbai, in varying ratios (pure water, 5 : 2, 4 : 3, 3 : 4, 2 : 5 v/v water–methanol and pure methanol) were used for sonochemical reactions. Sonochemical reactions were studied in a tubular reactor of 40 cm^3 capacity having two ports serving as inlets and outlets for purged gas. A septum was attached to one of the ports for withdrawing gaseous or liquid samples for analysis. Prior to sonication the liquid mixture was purged with Ar for 45 min in order to expel the air. The ultrasonic irradiator was of Toshniwal, India make with frequency of 50 kHz and power 200 W.

2.2 Dynamic light scattering (DLS)

The formation of cavities upon ultrasound irradiation was monitored by a DLS using Malvern 4800 Autosizer employing an Ar ion laser (λ = 514.5 nm) and a digital correlator. The scattered light intensity was monitored at a scattering angle of 90° and the intensity correlation function over a time range of 10^{-6} to 1 s was computed.

2.3 Evaluation of hydrogen yield

The yield of hydrogen generated in different samples was evaluated using gas chromatography (Netel India Ltd). For each experiment, 100 μl of effluent gaseous products were sampled and were injected in the molecular sieve column, and detected on a thermal conductivity detector on a gas chromatograph.

3 Results and discussion

3.1 Dynamic light scattering (DLS)

Fig. 1 shows the volume of H_2 generated per ml of liquid mixture in sonochemical water splitting when different compositions of methanol and water mixtures were subjected to ultrasound irradiation at different durations of irradiation. For pure methanol, as shown in Fig. 1, no detectable amount of hydrogen was generated upon irradiation up to 1600 s. Similarly, from pure water, only a small amount of H_2 was detected ($\sim$0.4 μl ml^{-1} of water). However, a combination of water and methanol generates a substantial amount of hydrogen upon irradiation and the yield of hydrogen increases with the duration of irradiation. Moreover, this is very substantial with a water–methanol mixture of composition 4 : 3 (v/v). It

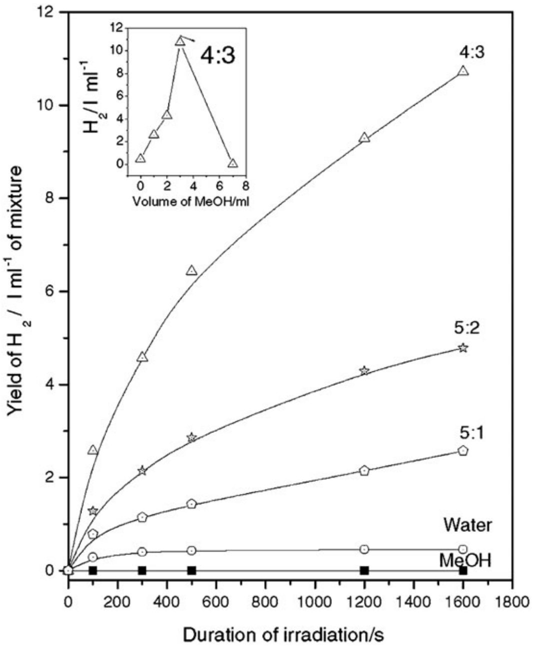

Fig. 1 The yield of hydrogen* generated in sonochemical water splitting reaction as a function of sonication irradiation time for different compositions of water–methanol mixtures (v_{water} : $v_{methanol}$). *Inset shows the comparative yield of H_2 obtained for the different mixtures when sonicated for 1600 s (the total volume of the mixture is kept constant, being equal to 7 ml).

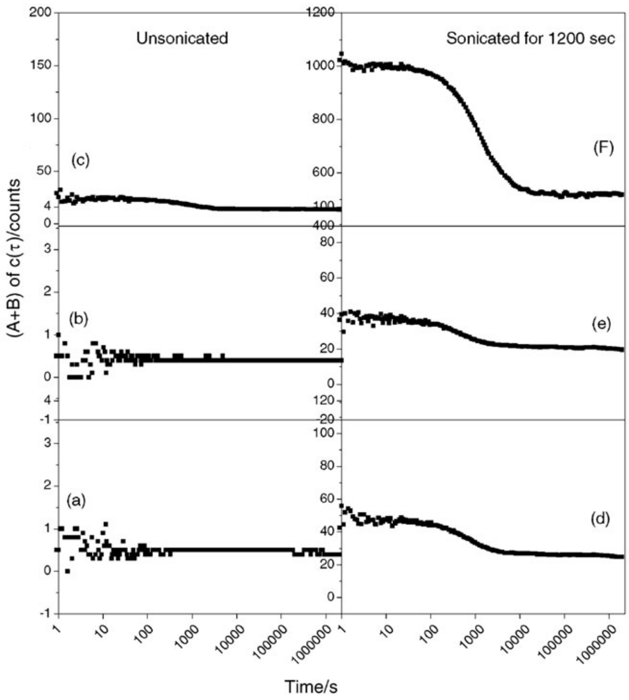

Fig. 2 Plot of correlation function of scattered light *vs.* time for different samples before (a–c) and after (d–f) ultrasound irradiation. All samples were irradiated for 1200 s: (a, d) water; (b, e) methanol; and (c, f) water–methanol (4 : 3).

can be seen that up to ~11 μl of H_2 per ml of mixture was produced by irradiating for 1600 s as opposed to less than ~0.5 μl of H_2 produced for pure water or methanol. The yield of H_2 per ml of the liquid mixture after 1600 s of irradiation as a function of the composition of the mixture is shown as an inset in Fig. 1. The amount of hydrogen generated sonochemically under similar conditions from different samples having methanol and water in varying ratios is in following order: H_2O–CH_3OH (4 : 3) > H_2O–CH_3OH (5 : 2) > H_2O–CH_3OH (5 : 1) > H_2O (trace level) > CH_3OH (nil). Sonication of water in the presence of a wetting agent such as PluronicF68 is known to produce stable microbubbles.[13] Such microbubbles can scatter light from the curved interfaces of the bubbles and the changes in the intensity of the light scattered can be used to obtain information regarding the size and relative number density of bubbles. Thus, dynamic light scattering measurements were performed on different water–methanol mixtures before and after ultrasound irradiation. From the time dependence of the scattered light intensity, the intensity correlation function $C(\tau)$ is computed and the characteristic decay time of the correlation function is a measure of the diffusion coefficient of the scatterers.

Fig. 2 shows the variation of $C(\tau)$ from pure water, pure methanol and water–methanol (4 : 3 v/v) after sonicating the liquids for 1200 s (curves (d), (e) and (f), respectively). The correlation function is plotted without any normalization, unlike traditional measurements, so that the changes in the amplitudes of the $C(\tau)$ are retained for comparison. Curves (a)–(c) show $C(\tau)$ under similar conditions for the same samples without sonication, for comparison. No correlation of scattered intensity is observed for pure water or methanol in the absence of sonication. However, the water–methanol mixture shows a correlation of intensity with small amplitude (~80 counts) even in the absence of sonication. This is probably due to the formation of microbubbles during the purging of the solution. However, purging of all the samples having different compositions were carried out under identical conditions prior to ultrasound irradiation. This implies that the composition plays a role in determining the yield of cavitations. Upon sonication, all samples showed a characteristic decay of $C(\tau)$ indicating the formation of stable microbubbles in the liquid. The scattered intensity increases due to formation of bubbles and is reflected as an increase in the amplitude of the correlation function. One important point to note here is that the amplitude of $C(\tau)$ is much larger for water–methanol mixtures than that for either water or methanol. This indicates that stable microbubbles are formed in water–methanol mixtures upon sonication and the number density of bubbles is much larger in the mixtures than in either of the pure components under the same experimental conditions. Thus, the presence of methanol in water results in synergistic enhancement of formation of microbubbles. This is consistent with the increase in sonochemical yield of hydrogen as observed in water–methanol mixtures as compared to the pure components as shown in Fig. 1.

The effect of varying amounts of methanol in the mixture on the total amplitude of the intensity correlation function ($A + B$) is shown in Fig. 3. In Fig. 3 and 4, the sum of amplitude and baseline ($A + B$) is plotted which is proportional to $\langle I\rangle^2$ and hence is a measure of the scattered intensity. It may be noted

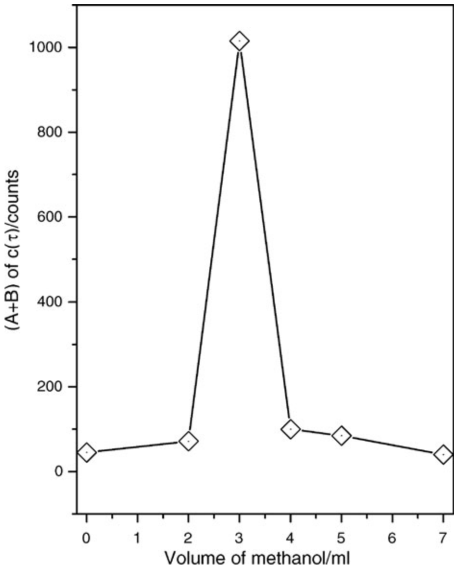

Fig. 3 Variation of the amplitude of the correlation function with volume of methanol in sonicated water–methanol mixtures (the total volume of the mixture is kept constant (7 ml)).

that in the present set up, *A* and *B* are approximately equal, and hence $A + B = 2\langle I\rangle^2$. Also, the scattering intensity depends on the number density, volume and form factor of the scatterers. However, the volume and form factor of the scatterers depends on the size and shape. Since the observed size distribution was independent of irradiation time, the volume and the form factor of the scatterers are assumed to be the same for all the experiments. Thus, the net change in intensity is ascribed to the changes in the number density of the scatterers. As evident from Fig. 3, among the various mixtures investigated, the mixture with water and methanol in 4 : 3 (v/v) composition, showed the maximum amplitude as compared to other compositions investigated. This suggests that water and methanol in the 4 : 3 (v/v) composition, results in an enhanced amount of cavitations relative to the 3 : 4 composition. Thus, for the maximum cavitations, the amount of methanol is very critical in the mixture, with water as a major component being favored. The effect of sonication time on the relative number density of bubbles for a 4 : 3 mixture of water–methanol is also inferred from correlation function measurements.

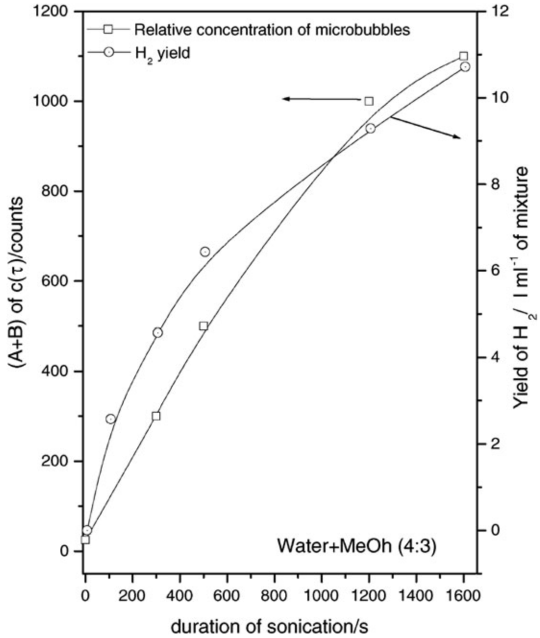

Fig. 4 Changes in the amplitude of the correlation function of the water–methanol mixture (4 : 3 v/v) with duration of ultrasound irradiation.

Fig. 4 shows the variation in the total amplitude of $C(\tau)$ for the 4 : 3 mixture along with the yield of hydrogen obtained at different durations of sonication. It is observed that the number density increases with increase in the time of sonication. Also, the yield of hydrogen for the same mixture correlates well with the increasing number density of the bubbles as shown in Fig. 4. The amplitude increases linearly with duration of irradiation and reaches a saturation value at around 1600 s beyond which no further increase is observed. No significant changes in the relaxation time of correlation function are observed after different periods of sonication. This suggests that the size distribution of the bubbles is not altered significantly with irradiation time. Here, we present the data obtained for the same sample when sonicated for different time durations in Fig. 4. However, this has been repeated and verified by taking an independent sample which was also directly sonicated for 1200 s and showed nearly the same result. Analysis of the decay of $C(\tau)$ using the CONTIN algorithm indicates the presence of bubbles with a wide distribution in sizes ranging from a few hundred nanometers to a few microns.

Fig. 5 shows the particle size distribution of cavities formed subsequent to ultrasound irradiation of the water–methanol (4 : 3, v/v) mixture. Among the various mixtures with different compositions investigated, the mixture with composition 4 : 3

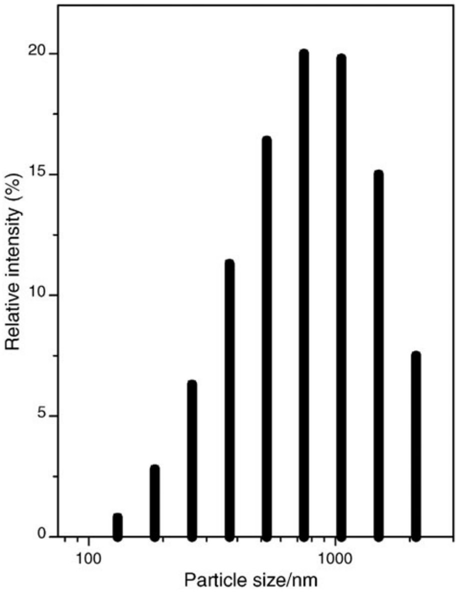

Fig. 5 The intensity weighted size distribution of bubbles formed upon ultrasound irradiation of a water–methanol mixture (4 : 3 v/v) as obtained by CONTIN analysis of the correlation function.

showed the maximum intensity for light scattering. This is probably due to the extra stability of the bubbles formed after sonication in this mixture. The role of liquid mixture in stabilizing the microbubbles is still not clear. The liquid–air interfacial tension of the bubbles plays a major role in stabilizing the microcavities. However, a similar mixture of acetone and water that has comparable interfacial tension as that of water–methanol did not lend any extra stability to the bubbles and no correlation function is observed for such a mixture. This negates the sole role of interfacial tension and it is likely that other factors are responsible for the stabilization of the bubbles. The creation and stabilization of microbubbles by acoustic waves is of immense importance for various applications involving ultrasound. For example, contrast enhancement agents in ultrasound imaging consist of gas microbubbles that scatter ultrasound by several orders of magnitude.[14–16] Formation of microbubbles with exceptionally long shelf life has been reported recently in a formulation comprising of fluorinated phospholipids and block copolymer amphiphiles as stabilizing agents.[13] In the present investigation no additives were used for the stabilization of bubbles. From the scattered light intensity, it was noticed that the microbubbles remain stable up to 48 h for the 4 : 3 mixture of H_2O–MeOH which was sonicated for 1200 s. The time evolution of intensity was monitored intermittently up to 48 h and it was noticed that the intensity remains constant up to 3 h and then decreases in a non-linear manner. Sufficient scattering was noticed even after 48 h and the intensity was about 50% of the original value.

Conclusions

Sonication-induced microbubble formation in water–methanol mixtures were analyzed quantitatively. Dynamic light scattering studies indicate the enhanced formation of microbubbles in water–methanol mixtures as opposed to pure water or methanol. Similar behavior has been noticed in the yield of hydrogen formed upon sonochemical splitting of water–methanol mixtures. The relative number of microbubbles in H_2O–CH_3OH mixtures compares well with the yield of H_2 generation and found to follow the order: H_2O–CH_3OH (4 : 3) > H_2O–CH_3OH (3 : 4) > H_2O–CH_3OH (5 : 2) = H_2O–CH_3OH (2 : 5) > H_2O > CH_3OH. Hence a synergistic enhancement of microbubble formation is observed in H_2O–CH_3OH mixtures with a maximum yield at 4 : 3 (v/v) water–methanol. The stability of the microbubbles has been monitored using light scattering and it was found that they are stable up to ∼48 h for certain compositions of the mixture.

Acknowledgements

We thank Dr G. Venkateshwaran, Head, Reactor Water Chemistry Section, of Water and Steam Chemistry Division, BARC, for providing the ultrasound irradiator.

References

1 *Photocatalysis Science and Technology*, ed. M. Kaneko and I. Okura, Springer Publications, Berlin, 2002, p. 203.
2 E. L. Mead, R. G. Sutherland and R. E. Verrall, *Can. J. Chem.*, 1976, **54**, 1114.
3 Y. Yasuda, R. Tanigawa, M. Oga, K. Uehara, M. Tachi, Y. Bando and M. Nakamura, *Proc. 8th Ann. Meeting Jpn. Soc. Sonochem., Kyoto*, 1999, p. 38 (in Japanese).
4 R. Sasikala, O. D. Jayakumar and S. K. Kulshreshtha, *Ultrason. Sonochem.*, 2007, **14**, 153.
5 H. Harada, *Ultrason. Sonochem.*, 2001, **8**, 55.
6 A. Hernim, *Ultrason. Sonochem.*, 1995, **2**, S115.
7 K. S. Suslick, Y. Didenko, M. M. Fang, T. Hyeon, K. J. Kolbeck, W. B. Mcnamara, M. M. Mdleleni and M. Wong, *Philos. Trans. R. Soc. London, Ser. A*, 1999, **357**, 335.
8 D. J. Flannigan and K. S. Suslick, *Nature*, 1999, **434**, 52.
9 D. Lohse, *Nature*, 2005, **434**, 33.
10 D. Lohse, *Nature*, 1998, **392**, 21.
11 T. Kubo, M. Kuwabara and J. Yang, *J. Appl. Phys.*, 2005, **44**, 4647.
12 S. Sakamoto and Y. Watanabe, *Jpn. J. Appl. Phys.*, 1999, **38**, 3050.
13 F. Gerber, M. P. Kraft, G. Waton and T. F. Vandamme, *New J. Chem.*, 2006, **30**, 524.
14 E. G. Schutt, D. H. Klein, R. M. Mattrey and J. G. Riess, *Angew. Chem., Int. Ed.*, 2003, **42**, 3218.
15 J. G. Riess, *Curr. Opin. Colloid Interface Sci.*, 2003, **8**, 259.
16 J. R. Lindner, *Nat. Rev. Drug Discovery*, 2004, **3**, 527.
17 E. C. Unger, T. Porter, W. Culp, R. Labell, T. Matsunaga and R. Zutshi, *Adv. Drug Delivery Rev.*, 2004, **56**, 1291.
18 J. G. Riess, *Chem. Rev.*, 2001, **101**, 2797.
19 C. E. Lundgren, G. W. Bergoe and I. Tyssebotn, *Undersea Hyperb. Med.*, 2004, **31**, 105.
20 D. G. Shchukin, K. Kohler, H. Möhwald and G. B. Sukhorukov, *Angew. Chem., Int. Ed.*, 2005, **44**, 3310.
21 M. A. Borden and M. L. Longo, *Langmuir*, 2002, **18**, 9225.
22 G. Pu, M. L. Longo and M. A. Borden, *J. Am. Chem. Soc.*, 2005, **167**, 6524.
23 A. Kabalnov, J. Bradley, S. Flaim, D. Klein, T. Pelura, B. Peters, S. Otto, J. Reynolds, E. Schutt and J. Weers, *Ultrasound Med. Biol.*, 1998, **24**, 751.
24 S. Yang, S. M. Dammer, N. Bremond, H. J. W. Zandvliet, E. S. Kooij and D. Lohse, *Langmuir*, 2007, **23**, 7072.
25 S. T. Lou, Z. Q. Ouyang, Y. Zhang, X. J. Li, J. Hu, M. Q. Li and F. J. Yang, *J. Vac. Sci. Technol., B*, 2000, **18**, 2573.
26 R. Pecora, in *Dynamic Light Scattering: Application of Photon Correlation Spectroscopy*, Plenum Press, New York, 1985.
27 S. W. Provencher, *Comput. Phys. Commun.*, 1982, **27**, 213.