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Thermally induced gelation of an oil-in-water emulsion stabilised by a graft copolymer

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Oil-in-water (O/W) emulsions exhibiting reversible thermally induced gelation have been prepared using a graft (comb) copolymer containing poly(*N*-isopropylacrylamide) [poly(NIPAM)] as the backbone and poly(ethylene glycol) methacrylate as the side chains.

Emulsions are dispersions of one immiscible liquid in another. They occupy a significant position in colloid science and occur as products (or during processing stages) in a number of areas including the paint, food and agrochemical industries.[1] The majority of emulsions studied or produced commercially are prepared using short-chain surfactants. The properties of these systems are reasonably well understood.[1,2] In recent years copolymers have been employed as macrosurfactants to prepare emulsions.[3,4] One of the advantages of using macrosurfactants for emulsion preparation is the large degree of architectural control that can be exerted in order to explore and optimise copolymer structure—emulsion property relationships. Water-soluble copolymers can be prepared which exhibit solvent–polymer interactions that are thermally responsive. This compositional control thus allows fine control over the lower critical solution temperature of the copolymer.[5] The preparation of emulsions using thermally responsive copolymers is a new area of research and is the subject of this communication.

The objective of the present study was to prepare emulsions with stabilities which are responsive to environmental conditions (*e.g.* temperature). We reasoned that the use of copolymers based on poly(*N*-isopropylacrylamide) [poly(NIPAM)] would provide gross conformational changes at the oil-in-water (O/W) interface at temperatures lower than the cloud point of short-chain ethylene-oxide based surfactants. Perrin *et al.*[3,6] have used hydrophobically modified poly(sodium acrylate) copolymers in order to prepare emulsions the stability of which are sensitive to pH and ionic strength. Mathur *et al.*[7] employed pH sensitive poly(acrylic acid)-g-poly(ethyleneoxide) copolymers in order to break emulsions. Our interest in the use of poly(NIPAM) copolymers to prepare emulsions follows from our earlier work involving swellable poly(NIPAM) microgel particles,[8] linear poly(NIPAM) chains adsorbed at latex particle interfaces[9] and depletion flocculation of emulsions.[10,11] The use of copolymers based on poly(NIPAM) to prepare emulsions was expected to provide large and reversible changes in emulsion properties (*e.g.* viscosity) as the temperature approaches the lower critical solution temperature (LCST). The results presented below show that this is indeed the case.

The copolymer comprised of poly(NIPAM) and poly(ethylene glycol methacrylate) (PEGMa); the latter having a number average molecular weight of 360. AIBN and *tert*-butyl alcohol were used, as the initiator and solvent, respectively, during the free radical copolymerisation stage.[12] Proton NMR data revealed that there was on average one PEGMa group per six NIPAM units in the copolymer. Fig. 1 shows how the turbidity and viscosity vary with temperature for poly(NIPAM–PEGMa) in water. The LCST of the copolymer is taken as *ca.* 34 °C from the turbidity data. This is *ca.* 2 °C higher than that of poly(NIPAM) homopolymer, which is attributed to the hydrophilic nature of the PEGMa in the copolymer.[13] The O/W emulsions were prepared by first dissolving the copolymer in water (5 wt%). 1-bromohexadecane was then added to the copolymer solution, before the mixture was sheared using a Silverson SL2T laboratory mixer operating at *ca.* 7500 rpm. A control emulsion was prepared using the short-chain surfactant $Me(CH_2)_8(OCH_2CH_2)_6OH$, ($C_9E_6$) for comparison.

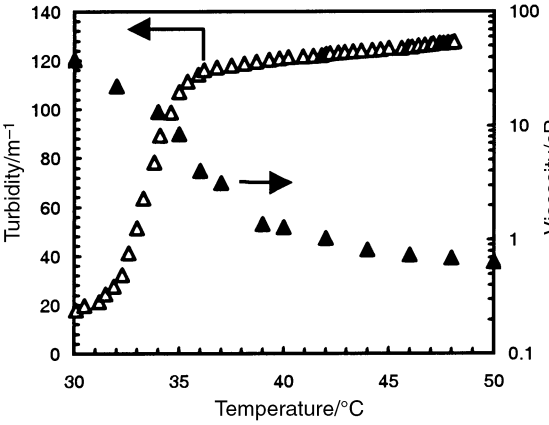

Fig. 1 Variation of the turbidity (Δ) and viscosity (▲) of poly(NIPAM–MPEGMa) solution as a function of temperature. The concentration of copolymer used was 2.5 wt%.

Fig. 2 shows the variation of viscosity with temperature for the emulsions prepared using poly(NIPAM–PEGMa) and C_9E_6. The viscosity data were measured using an Ostwald capillary viscometer. The viscosity for the emulsion prepared using poly(NIPAM–PEGMa) decreases with increasing temperature and reaches a minimum at 44 °C. A dramatic increase in viscosity occurs above 48 °C. The viscosity increased to such an extent that gelation of the emulsion occurred (see Fig. 3). As

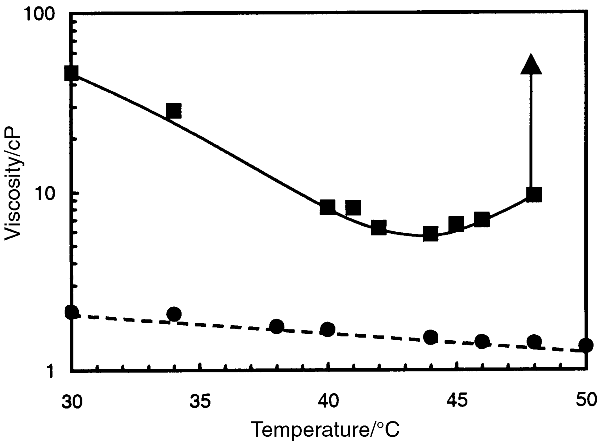

Fig. 2. Effect of temperature on the viscosity of emulsions prepared using poly(NIPAM–MPEGMa) (■) and C_9E_6 (●). The volume average diameters were 9.6 and 4.9 μm, respectively. The volume fraction of the dispersed phase was 0.30. The concentration of copolymer or C_9E_6 present was 2.5 wt% with respect to the total emulsion.

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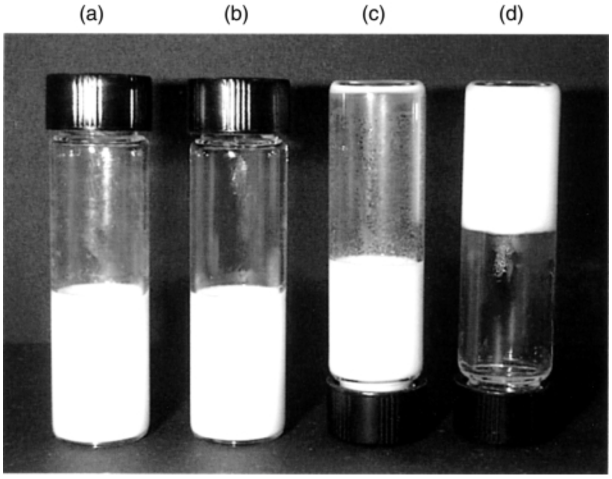

Fig. 3 Emulsions prepared using C_9E_6 (a) at RT and (c) at 50 °C and poly(NIPAM–MPEGMa) (b) at RT and (d) at 50 °C. Note that tubes (c) and (d) have been inverted.

expected, the emulsion prepared using C_9E_6 exhibited a slight decrease in viscosity over the whole experimental temperature range. It should be noted that the rheological behaviour observed for the emulsion prepared using the copolymer is opposite to what is observed for concentrated poly(NIPAM) microgel dispersions, which form gels at room temperature and flow when the temperature exceeds the LCST. It was found that emulsion gelation could be reversed by agitation at 50 °C or cooling to room temperature in the absence of agitation. The emulsions did not break as a result of gelation reversal, although there was evidence of a slight increase in droplet size. Optical microscopy revealed residual flocs were present in the emulsions after one heating/cooling cycle. The emulsion viscosity measured at 30 °C increased by *ca.* 5% as a result of one heating/cooling cycle.

The data shown here demonstrate that it is possible to reversibly gel our O/W emulsion using temperature variation alone. The mechanism by which this occurs is of interest to both the polymer and emulsion science communities. The fact that the gelation temperature is significantly greater than the LCST of the copolymer in solution suggests that the onset of gelation is not solely due to the collapse of the copolymer in the aqueous phase. The viscosity data for the copolymer (Fig. 1) show a decrease in viscosity with increasing temperature and rules out any contribution from temperature-induced continuous phase thickening (*e.g.* associated with the copolymer chains in solution) to emulsion gelation. The zeta potential for the droplets was measured at *ca.* 5 mV, which indicates that electrostatic stabilisation of the emulsions is not significant. The LCST of poly(NIPAM) chains adsorbed at highly charged surfaces is known to increase to values above that for the solution polymer.[14] However, this effect is not likely to occur in the present system due to the low charge of the droplets.

The stability of the emulsions arises primarily from steric stabilisation afforded by the adsorbed copolymer. The mechanism tentatively suggested for emulsion gelation involves thermally induced flocculation due to collapse of the adsorbed poly(NIPAM–PEGMa) layer at temperatures greater than the solution LCST. The depth of the secondary minimum would increase with increasing temperature (decreasing copolymer layer thickness) leading to stronger flocculation at higher temperatures. At 45 °C the minimum is sufficiently greater than kT to provide strong gelation *via* adhesive droplets. The collapse of the adsorbed layer presumably results in a rigid interface which opposes coalescence of flocculated droplets. It is likely that interpenetration and entanglement of interfacial copolymer chains contributes to the limits of residual flocculation observed upon cooling. Note that this good degree of reversibility for the copolymer stabilised emulsions is distinctly different to the behaviour of emulsions stabilised by short-chain ethylene oxide surfactants (*e.g.* C_9E_6) when heated to above the phase inversion temperature. For the latter emulsion breaking results from heating to the phase inversion temperature in absence of shear.

The work described above has shown that the use of poly(NIPAM–MPEGMa) graft copolymers allows the reversible gelation of O/W emulsions. This could have significant technological importance in the field of emulsion stability as the thermally induced gelation results in reversible transformation of a liquid emulsion into a highly viscous gel within a short period of time upon application of modest heating. Copolymers based on NIPAM can be prepared that have a range of LCST values. These ratios can be carefully controlled *via* copolymer architecture modification during synthesis. This versatility should allow the gelation temperature to be finely tuned to suit specific applications. The mechanism by which gelation occurs will be further investigated using light scattering, rheological and small-angle neutron scattering measurements and the results of these stuides will be published in due course.

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Notes and references

1 B. Binks, in *Modern Aspects of Emulsion Science*, ed. B. P. Binks, RSC, Cambridge, 1998.
2 T. F. Tadros and B. Vincent, in *Encylopedia of Emulsion Technology*, ed. P. Becher, Marcel Dekker, New York, 1983.
3 P. Perrin, *Langmuir*, 2000, **16**, 881.
4 A. E. Cárdenas-Valera and A. I. Bailey, *Colloids Surf. A*, 1995, **97**, 1.
5 M. Hahn, E. Görnitz and H. Dautzenberg, *Macromolecules*, 1998, **31**, 5616.
6 P. Perrin, N. Monfreux, A. L. Dufour and F. Lafuma, *Colloid Polym. Sci.*, 1998, **276**, 945.
7 A. M. Mathur, B. Drescher, A. B. Scranton and J. Klier, *Nature*, 1998, **392**, 367.
8 B. R. Saunders and B. Vincent, *Adv. Colloid Interface Sci.*, 1999, **80**, 1.
9 B. R. Saunders, J. M. Saunders, J. Mrkic and E. H. Dunlop, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1562.
10 A. Koh, G. Gillies, J. Gore and B. R. Saunders, *J. Colloid Interf. Sci.*, 2000, **227**, 390.
11 M. Shields and B. R. Saunders, *Colloids Surf. A*, in press.
12 A. Koh and B. R. Saunders, manuscript in preparation.
13 J. Virtanen and H. Tenhu, *Macromolecules*, 2000, **33**, 5970.
14 P. W. Zhu and D. H. Napper, *J. Colloid Interf. Sci.*, 1994, **164**, 489.