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# Preparation of polystyrene–poly(styrene-*g*-*N*-isopropylacrylamide) core–shell particles: copolymerization of oligo(*N*-isopropylacrylamide) macromonomers and styrene onto polystyrene seed particles and stability of the resultant particles

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Core–shell particles were prepared in which crosslinked polystyrene formed the core and the shells were of poly(styrene-*g*-*N*-isopropylacrylamide). The particles were successfully prepared by copolymerizing styrene with an *N*-isopropylacrylamide macromonomer in the presence of crosslinked polystyrene latices. Two series of core–shell particles have been prepared. In the first series the core and shell polymerizations were affected by the hydrogen peroxide/$FeCl_2$ redox couple. Thus these particles are free from surface charges. Another series of particles was prepared with potassium persulfate as initiator so that these particles possessed sulfate surface end-groups. After purification, the sulfate functional particles were colloidally stable. Particles without surface charge were less stable. This was reflected in the larger particle sizes of the non-charged particles. Lightly grafted non-charged particles coagulated on removal of surfactant. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: core–shell particles; polystyrene; poly(styrene-*g*-NIPAAM))**

## INTRODUCTION

The temperature-responsive behaviour of poly(*N*-isopropylacrylamide) (PNIPAAM) has been well documented[1–4]. Aqueous solutions of this polymer exhibit a lower critical solution temperature (*LCST*) at 32°C[1]. Several authors have studied the behaviour of aqueous colloidal dispersions formed from PNIPAAM[5–12]. Core–shell particles have been prepared by sequential monomer addition and emulsion polymerization. In some of these preparations[11,12], the polystyrene (PS) core was coated with a PNIPAAM network by radical polymerization. Another approach to core–shell particles was adopted by Napper *et al.*[13–15]. These authors synthesized PNIPAAM, which they grafted with PS. This graft copolymer was then used to stabilize a PS soap-free emulsion polymerization. They observed that the presence of surface charges, that is sulfate end-groups from the persulfate initiator, had a profound effect on colloidal stability above the *LCST*. A colloid prepared without surface charge flocculated above the *LCST*, whilst a colloid prepared with sulfate surface charge was stable. Furthermore, negation of this negative charge by addition of a cationic surfactant (dodecyl trimethylammonium bromide) caused flocculation above the *LCST*. Similarly the particles prepared by Kawaguchi *et al.*[12], which contained sulfate surface end-groups, also gave stable colloids above the *LCST*.

Kitano *et al.*[6,16] prepared carboxylic acid end-functional NIPAAM oligomers (CONA) by radical polymerization in the presence of functional mercaptams. These materials have then been used to prepare microspheres. In the first of these publications[6] they reacted a CONA with polyallylamine to yield poly(allylamine-*g*-NIPAAM). This graft copolymer was then crosslinked, as a water-in-oil emulsion, by reaction with glutaraldehyde. Also an amino functional oligomer (AONA)[16] was reacted with *N*-succiminido acrylate to yield a macromonomer. This macromonomer was then emulsion copolymerized with styrene in water. CONA has also been used to impart thermal-responsive behaviour to enzymes[17–19].

In this work we report the synthesis of core–shell particles, in which the core is formed from crosslinked PS and the shell is poly(S-*g*-NIPAAM). The preparation is similar to that of Kitano *et al.*[16]. In the current work, however, a macromonomer (ONAA) was prepared by reaction of CONA with hydroxyethyl acrylate. These materials thus contain a hydrophobic end-group, which

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**Table 1** Feed compositions for preparation of carboxylic acid functional O(NIPAAM)

| Oligomer ref. | MPA (g) |
|---|---|
| O1 | 0.6 |
| O2 | 1.2 |
| O3 | 2.4 |

**Table 2** Recipes for batch emulsion polymerizations

| (a) Non-charged | ($P^{NC}$) particles |
|---|---|
| Styrene | 120.0 g |
| Divinylbenzene | 12.0 g |
| Hydrogen peroxide (30 wt% aq. solution) | 0.1 g |
| EDTA | 0.2 g |
| Sodium bicarbonate | 0.1 g |
| Iron (II) chloride | 0.2 g |
| Sodium dodecyl sulfate | 2.5 g |
| Water | 450.0 g |
| **(b) Charged** | **($P^{C}$) particles** |
| Styrene | 120.0 g |
| Divinylbenzene | 12.0 g |
| Potassium persulfate | 1.0 g |
| Potassium hydrogenphosphate | 0.3 g |
| Sodium dodecyl sulfate | 2.5 g |
| Water | 450.0 g |

should be soluble in styrene and easily adsorbed onto the PS core. The macromonomers were adsorbed onto the PS cores in the presence of styrene. Polymerization yields PS–P(S-*g*-NIPAAM) core–shell particles. For our purposes the sequential monomer addition procedure is preferable to the one-shot process of Kitano *et al.*[16], since it allows control of the particle size of the resultant latices.

## EXPERIMENTAL

### *Materials*

The inhibitor was removed from styrene and divinylbenze (DVB) (Aldrich) by passing the monomers through an inhibitor remover column (Aldrich). Divinylbenzene from this source contains approximately 40% ethylstyrene; no attempt was made to remove this impurity. The masses of DVB quoted further in this paper refer to this mixture. Water was doubly distilled. NIPAAM (Aldrich) was used as supplied. All other materials were used as supplied.

### *Spectroscopy*

$^{13}$C and $^{1}$H n.m.r. analyses were performed on a JEOL GSX 400 spectrometer using deuterated acetone as solvent. The *FT* i.r. spectra were obtained with a Perkin-Elmer 1720X instrument on thin films of polymers and oligomers cast on rock-salt plates from chloroform.

### *Synthesis of CONA*

The methodology of Kitano *et al.*[6] was used to prepare CONA. Thus, NIPAAM (30 g) was polymerized, in ethanol (60 cm$^3$) free-radically, at 50°C for 24 h, in the presence of mercaptoacetic acid (MPA). Azobisisobutyronitrile (0.10 g) was used as the initiator. The polymerizations were carried out in sealed ampoules under vacuum. The end-group functionality of these materials was confirmed by n.m.r. spectroscopy. The $^{1}$H and $^{13}$C resonances of the $\alpha,\alpha$-carboxy thioether methylene of the end-group were seen at 3.3 and 65.8 ppm respectively, while the carbonyl of the acid group is observed at 172.0 ppm in the $^{13}$C spectrum. The number-average molecular weight was determined by acid/base titration against 0.01 mol cm$^{-3}$ KOH. *Table 1* gives the feed compositions for these preparations.

### *Synthesis of oligo(NIPAAM) acrylates (ONAA)*

The CONA were further functionalized by esterification with hydroxyethyl acrylate (HEA). The reaction was mediated with dicyclohexylcarbodiimide (DCC). Thus each of the CONA (4 g) was dissolved in chloroform (45 ml). An equimolar amount of DCC was dissolved in chloroform (5 ml). The CONA solution was cooled with ice. The DCC solution was then added with stirring. The reaction was allowed to warm to room temperature and was allowed to react for a further 24 h. The products of these reactions were purified by precipitation from chloroform into diethyl ether. Acid/base titration of these macromonomers showed negligible acid content. The vinyl groups were seen in the $^{1}$H n.m.r. spectrum at 5.7 and 6.1 ppm and in the $^{13}$C n.m.r. spectrum at 128 and 131 ppm.

### *Synthesis of non-charged ($P^{NC}$) and charged ($P^{C}$) polystyrene particles*

Particles were prepared by batch emulsion polymerization, at 65°C for 24 h, using the recipes shown in *Table 2*. Each of the latices, $P^{NC}$ and $P^{C}$, was purified by dialysis with visking tubing for 24 h (average pore radius = 24 Å).

**Table 3** Compositions of latices

| Sample ref. | Core latex | Macromonomer $M_n$ (g mol$^{-1}$) | Shell feed, styrene/macromonomer (g/g) |
|---|---|---|---|
| C1 | $P^{C}$ | 1800 | 0.5/0.5 |
| C2 | $P^{C}$ | 3100 | 0.5/0.5 |
| C3 | $P^{C}$ | 5000 | 0.5/0.5 |
| C4 | $P^{C}$ | 1800 | 0.75/0.25 |
| C5 | $P^{C}$ | 3100 | 0.75/0.25 |
| C6 | $P^{C}$ | 5000 | 0.75/0.25 |
| N1 | $P^{NC}$ | 1800 | 0.25/0.75 |
| N2 | $P^{NC}$ | 3100 | 0.25/0.75 |
| N3 | $P^{NC}$ | 5000 | 0.25/0.75 |
| N4 | $P^{NC}$ | 1800 | 0.5/0.5 |
| N5 | $P^{NC}$ | 3100 | 0.5/0.5 |
| N6 | $P^{NC}$ | 5000 | 0.5/0.5 |
| N7 | $P^{NC}$ | 1800 | 0.75/0.25 |
| N8 | $P^{NC}$ | 3100 | 0.75/0.25 |
| N9 | $P^{NC}$ | 5000 | 0.75/0.25 |
| N10 | $P^{NC}$ | 1800 | 1.5/0.5 |
| N11 | $P^{NC}$ | 3100 | 1.5/0.5 |
| N12 | $P^{NC}$ | 5000 | 1.5/0.5 |

**Talbe 4** Initiators used in shell formation

| | N series (g) | C series (g) |
|---|---|---|
| Hydrogen peroxide (30% aq. solution) | 0.01 | 0 |
| Sodium bicarbonate | 0.012 | 0 |
| EDTA | 0.02 | 0 |
| Fe(II)Cl$_2$·4H$_2$O | 0.01 | 0 |
| Potassium persulfate | 0 | 0.05 |

### *Synthesis of ONAA-grafted particles*

The latex (45 g) (either $P^{NC}$ or $P^{C}$) was agitated along with styrene and one of the ONAAs. The feed compositions are given in *Table 3*. This mixture was agitated vigorously for 60 min at 50°C. Initiators (see *Table 4*) were then added and the polymerization carried out for 24 h under a nitrogen blanket. Each of these latices was purified by dialysis for 24 h, followed by shaking with Amberlyst IRA 420 ($Cl^-$) for 24 h and then dialysis for a further 24 h. The non-grafted latices were also treated to this purification regime. A note was made of any compositions that coagulated during purification.

### *Particle size measurements*

Particle size measurements of all the latices were obtained by photon correlation spectroscopy using a Coultier N4 submicrometre particle size analyser.

### *Soxhlet extractions*

The latices C1, C2 and C3 were dried. The resultant polymer (approximately 1.5000 g) was accurately weighed into a Soxhlet thimble and extracted with chloroform for 24 h. The solvent was removed from the extract. The residue was weighed and analysed by *FT* i.r. and $^1$H n.m.r. spectroscopy.

## RESULTS AND DISCUSSION

### *Synthesis of macromonomers*

*Table 5* shows the results of the preparations of CONA materials. Thus a range of CONA materials of varying molecular weight were prepared. Kitano *et al.*[16] prepared a macromonomer by reacting CONA with acrylic acid that had been previously activated by formation of the *N*-succiminido derivative. Whilst this procedure was successful, the synthesis of the *N*-succiminido derivative adds an unnecessary step to the preparation. Thus we prepared CONA ethoxyacrylate (ONAA) in one step by reaction of CONA with HEA. The reaction proceeded to give essentially quantitative yield of CONAA. *FT* i.r. absorbances due to the carboxylic acid O–H stretch (broad band 3100–2700 cm$^{-1}$) were absent from spectra of the macromonomers. Also acid/base titration showed that the carboxylic acid content of these materials was negligible.

### *Preparation of the latices*

The synthetic strategy used is illustrated in *Figure 1*. The particle sizes of non-grafted latices $P^{C}$ and $P^{NC}$ were 75 and 80 nm respectively. The shell formation proceeded without significant production of coagulum. Dialysis of the initially prepared latices removed excess salts. All the non-grafted and the core–shell latices were stable to this treatment. In order to remove surfactant from these systems, they were ion-exchanged with the chloride form of a strongly basic gel-type ion-exchange resin (Amberlyst IRA 420 ($Cl^-$)). The non-grafted latices coagulated when exposed to this treatment. In order to remove salts liberated as a result of ion exchange, the latices that did not coagulate were dialysed.

In order to confirm that the shells of these core–shell particles were composed of PS grafted with PNIPAAM,

**Table 5** Yields and molecular weights of carboxylic acid functional ONAA

| Sample ref. | Conversion (%) | $M_n$ (g mol$^{-1}$) |
|---|---|---|
| O1 | 31 | 5000 |
| O2 | 35 | 3100 |
| O3 | 35 | 1800 |

**Table 6** Yields of material extracted from a selection of dried latices, after Soxhlet extraction with chloroform

| Sample ref. | Yield (mass%) | Mole fraction of styrene in extract |
|---|---|---|
| C1 | 13 | 0.57 |
| C2 | 6 | 0.50 |
| C3 | 12 | 0.51 |

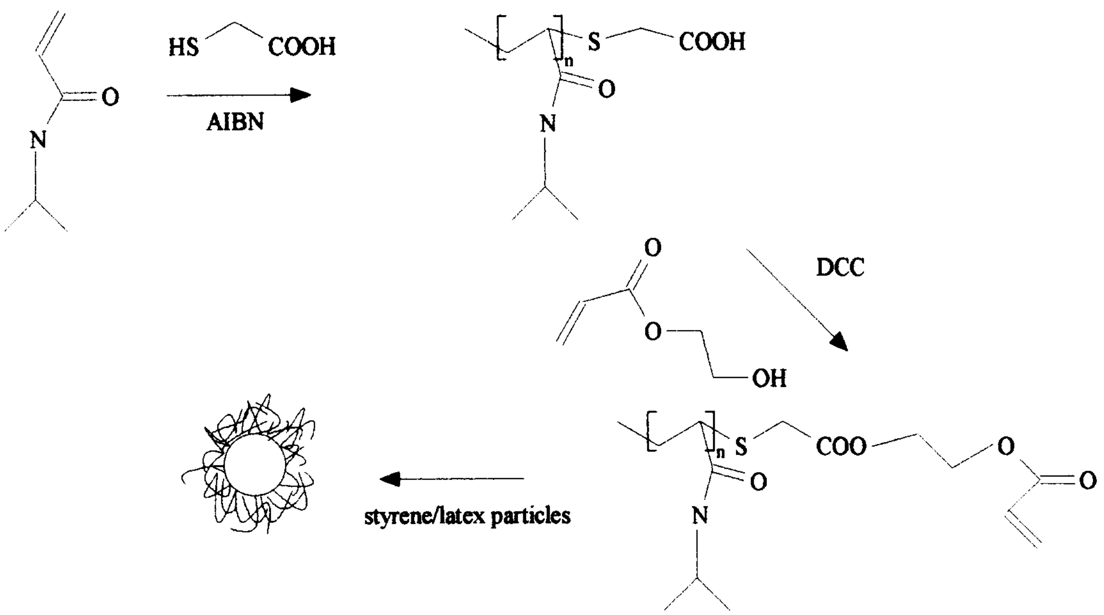

**Figure 1** Preparation of ONA-grafted particles

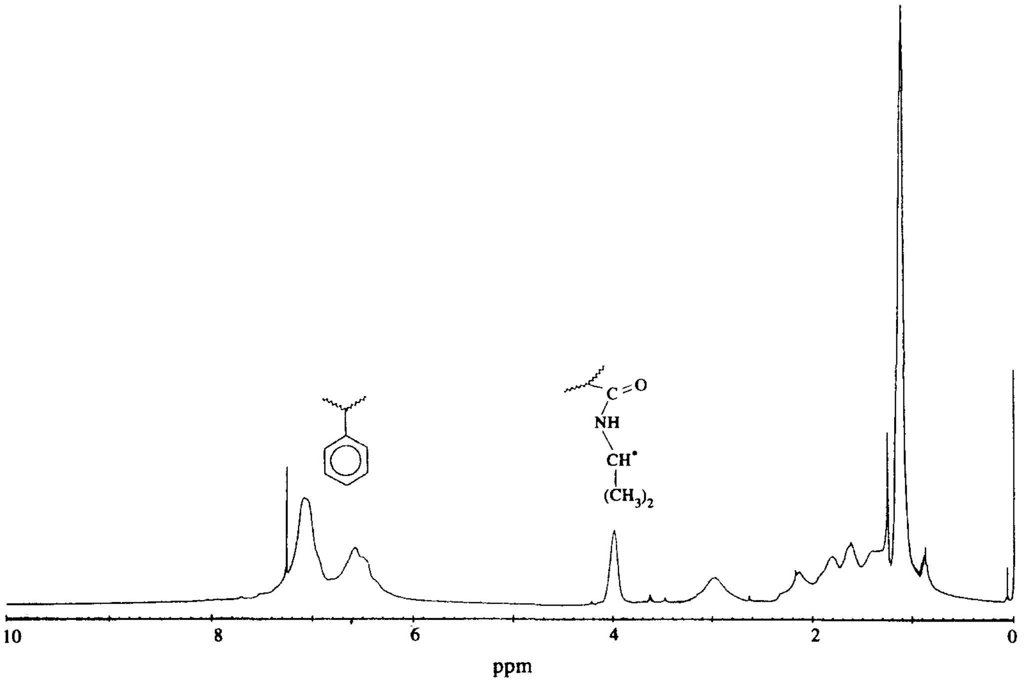

**Figure 2** $^1H$ n.m.r. spectrum of the extract from latex C1

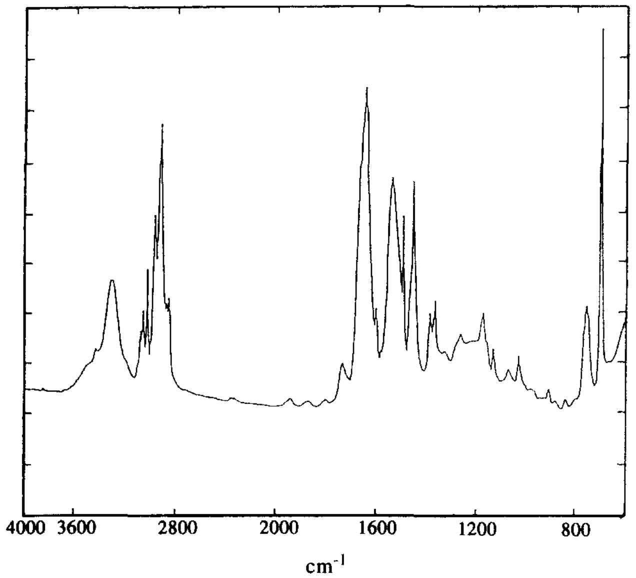

**Figure 3** *FT* i.r. spectrum of the extract from latex C1

the dried latices were extracted with chloroform. Since the central cores of these particles are crosslinked, the soluble fraction from these extractions will be shell material only. *Table 6* shows the results of Soxhlet extraction of a selection of dried latices. If one assumes that all of the shell material is non-crosslinked and therefore soluble in chloroform, then the theoretical yields should be around 10%. The results are not self-consistent but do appear to agree approximately with this theoretical value.

*Figures 2* and *3* show examples of the $^1H$ n.m.r. and *FT* i.r. spectra obtained from the extracts. Clearly, the $^1H$ n.m.r. spectrum shows the resonances of both PS and PNIPAAM. Polymerization of the macromonomer is also indicated by the absence of resonances attributable to the acrylate end-group of the macromonomer. *Table 6* gives the composition of the graft copolymer extracts. The values were calculated by comparing the integrations of the peaks corresponding to the phenyl ring (PS) resonances and those from the *N*-methine (NIPAAM). The theoretical value calculated from the feed ratios is 0.50. Clearly, the results are in very good agreement with this value. Further evidence can be gained from *FT* i.r. spectroscopy. *Figure 3* shows an example spectrum of the extracts. Clearly this spectrum also shows features indicative of both the PS backbone and the PNIPAAM side chains. G.p.c. measurements were also attempted. Unfortunately the amphilic nature of these graft copolymers made useful interpretation of the results difficult.

### *Colloidal stability*

Particle size measurements provide some insight into the factors affecting colloid stability in these systems. *Table 7* shows the results. All the latices prepared were stable when freshly prepared, that is when the system contained surfactant. Ion exchange removed the sulfate surfactant. The core latices were also ion-exchanged. Both of these non-grafted colloids coagulated on exposure to the ion-exchange resin. From examination of the results presented in *Table 7*, it is clear that the charged particles are intrinsically more stable than the non-charged particles. This is to be expected since sulfate polymer end-groups provide electrostatic stabilization to the system. Thus, all of the charged particles are seen to give stable colloids. Furthermore, the particle sizes do not increase dramatically on removal of surfactant. These observations contrast strongly with the results from the non-charged latices. In these systems we can observe two trends. First, as the mass fraction of NIPAAM increases, at constant ONAA chain length, colloidal stability increases. This can be seen by comparing the stability of latices N9, N6 and N3, of latices N8, N5 and N2, or of latices N7, N4 and N1.

**Table 7** Particle sizes of grafted latices

| Sample ref. | Stability[a] | Particle size prior to ion exchange (nm) | Particle size after ion exchange (nm) |
|---|---|---|---|
| C1 | Y | 78 | 114 |
| C2 | Y | 79 | 101 |
| C3 | Y | 77 | 77 |
| C4 | Y | 80 | 80 |
| C5 | Y | 80 | 80 |
| C6 | Y | 78 | 80 |
| N1 | Y | 90 | 96/1520[b] |
| N2 | Y | 95 | 43/1580[b] |
| N3 | Y | 94 | 1740 |
| N4 | N | 90 | – |
| N5 | Y | 100 | 82/1340[b] |
| N6 | Y | 105 | 40/1340[b] |
| N7 | N | 94 | – |
| N8 | N | 94 | – |
| N9 | N | 90 | – |
| N10 | N | 100 | – |
| N11 | N | 99 | – |
| N12 | N | 105 | – |

[a] Y indicates that the dispersion did not contain visible coagulum after ion exchange. N indicates that all or part of the latex coagulated on ion exchange

[b] In these latices particle size distribution was bimodal. The two values are the averages of these two distributions. In all cases the major distribution (approximately 90% of the particles) had the larger average particle size

Secondly, in the latices that are stabilized by the ONAA grafts, the particle size distribution becomes bimodal. All of the non-charged particles have particle sizes that are over an order of magnitude above the surfactant-stabilized particles. The series N4 to N6 may be used to examine the effect of changing ONAA chain length at constant mass composition. In this system the lowest-molecular-weight oligomer does not impart stability to the system. This latter observation fits the expected trend for sterically stabilized colloids.

It was thought that increasing the amount of NIPAAM present in the shell may improve colloidal stability. We therefore prepared latices N10, N11 and N12, which have the same fraction of NIPAAM in the shell as N7, N8 and N9, but the total quantity of NIPAAM is twice that in the latter series. Reference to *Table 7* shows that no changes in stability were observed.

The thermal behaviour of these systems was also qualitatively examined. On heating to 50°C, the charged latices partially flocculated. Cooling to 10°C allowed the fraction of particles that had flocculated to be redispersed with agitation. However, on prolonged heating (50°C for 14 days) the flocculated fraction could not be redispersed easily. The non-charged particles flocculated to a greater extent. These particles could also be redispersed with cooling and agitation. However, it was noted that a fraction of these heat-treated latices eventually settled on standing (one month at room temperature).

## CONCLUSION

We have shown that it is possible to prepare PS–P(S-*g*-NIPAAM) core–shell particles by modifying the macromonomer approach of Kitano *et al.*[16]. If the particles possess surface charge, it is possible to control the resultant particle size by choosing the correct particle size for the core. We have also observed similar effects of surface charge on stability to those previously reported by Napper *et al.*[13–15]. That is, surface charge is necessary to impart stability on very lightly grafted particles. All of the prepared particles displayed thermally responsive flocculation behaviour. The extent of flocculation was dependent on the presence of surface charge. Future publications will address the thermal behaviour of these and similar particles.

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