Colloid Polym Sci 276:1131–1139 (1998)

ORIGINAL CONTRIBUTION

G. Zhou
A. Elaïssari
T. Delair
C. Pichot

Synthesis and characterization of surface-cyanofunctionalized poly (*N*-isopropylacrylamide) latexes

Received: 25 February 1998
Accepted: 23 June 1998

G. Zhou · A. Elaïssari · T. Delair
C. Pichot (✉)
Ecole Normale Supérieure de Lyon
CNRS-bioMérieux
46 allée d'Italie
F-69364 Lyon
France
e-mail: Christian.Pichot@ens-bma.cnrs.fr

Abstract A series of *P*[*N*-isopropylacrylamide (NIPAM)] latexes with different contents of cyano groups were successfully prepared by either seeded or shot-growth polymerizations of an aqueous solution containing acrylonitrile (AN) onto a seed *P*[NIPAM] latex, respectively, and further characterized by FT-IR, ^{1}H-NMR, elemental analysis, as well as by quasielastic light scattering (QELS) and scanning electron microscopy (SEM). All prepared surface-cyanofunctionalized *P*[NIPAM] latexes exhibited the same range of lower critical solution temperature (LCST) as a pure *P*[NIPAM] latex. The shot polymerization process proved more efficient at yielding cyano derivatized latexes than the seeded polymerization technique. The amount of incorporated cyano groups onto the particles was determined with a good correlation both by ^{1}H-NMR and elemental analysis. The higher the amount of initially introduced AN monomer in the reaction mixture, the more cyano groups were incorporated onto the particles. The surface of the particles with high content of cyano groups appeared quite rough by SEM in comparison with that of the pure *P*[NIPAM] particles.

Key words *P*(*N*-isopropylacrylamide) latex – acrylonitrile – cyano groups – seeded and shot-growth polymerizations

Introduction

In recent years, hydrophilic poly[*N*-isopropylacrylamide] (*P*[NIPAM]) latexes have been extensively studied because of thermal sensitivity of *P*[NIPAM] [1]. So far such stimuli-responsive particles received a variety of applications, especially in the biomedical field for diagnostic tests [2], drug delivery system [3–5], etc. Biomolecules can be tethered onto polymer particles either by covalent coupling or physical adsorption. A series of *P*[NIPAM]-based core–shell particles, particularly with carboxylic [6] and amino groups [7] have been prepared and used as suitable solid-phase supports to immobilize biomolecules (proteins and enzymes, for example). Immobilization of biologically active molecules can only be useful if the specific activities of the biomolecules are maintained after the grafting step. Standard chemical immobilization techniques or more specific adsorption do not allow one to address the final activity issue, as these methods have no control on the orientation of biomolecules on the support.

One alternative way to avoid such a disadvantage is to perform the immobilization process via regio-selective interactions which can take place at a well-defined site of the biomolecule, not involved in the molecular recognition properties. Dipole–dipole interactions can be considered as a promising approach because some biomolecules bear polar groups at a specific position which could interact with polarizable groups borne by the supports. So far, cyano groups have been recognized to specifically interact

with sugar moieties located in antibodies [8] and this motivated us to prepare cyano-functionalized latexes.

Two main processes can be used for the syntheses of functionalized particles by copolymerization of a main monomer in the presence of a monomer bearing a chemical or functional group. The simplest process is the batch one in which all the comonomers are loaded and polymerized in one single step [9–11], however in many cases, most of the functional comonomer is wasted (buried or as water-soluble polymers) in relation with its physicochemical properties). A two-stage process, the so-called core–shell process, can also be performed for producing functional particles: it consists in the polymerization of a mixture of the functional monomer and basic monomer at the surface of either performed particles (seeded polymerization) or by adding the monomer mixture at high conversion during an initial batch polymerization (Shot-growth polymerization) [12–13]. To favor the immobilization of biomolecules on the particles, functional groups should be present at the surface of the particles. Therefore, seeded and shot polymerization were used here to prepare *P*[NIPAM] latexes bearing cyano groups by polymerization of an aqueous solution containing acrylonitrile and using potassium persulfate (KPS) as a initiator on basis of a seed *P*[NIPAM] latex. Final particles were characterized by FT-IR, ^{1}H-NMR elemental analysis in order the quantify the incorporated amount of acrylonitrile monomer. Scanning electron microscopy (SEM) and quasielastic light scattering (QELS) were used for particle size determination.

Experimental

Materials

N-isopropylacrylamide (NIPAM) from Kodak was purified by recrystallization from a mixture of hexane and toluene (v/v: 60/40). Acrylonitrile (AN) was purified by distillation under reduced pressure. *N*,*N*′-methylenebisacrylamide (MBA) from Aldrich was used as a crosslinking agent without further purification. Potassium persulfate (KPS) from Prolabo was used as an anionic initiator without further purification. Water purified by a Millipore Q-TM system was further deoxygenated by boiling under nitrogen for 2 h before use.

Methods

Infrared spectra (IR) were recorded on a Nicolet 5 PC FT-IR spectrometer using KBr pellets. ^{1}H-NMR spectra, 500 MHz, were recorded on a Varian spectrometer using D_2O and deuterated pyridine as solvents and tetramethylsilane as internal standard. Elemental analysis were performed by the "Service Central d'Analyse du CNRS" (Vernaison, France). Particle size was measured by quasielastic scattering (QELS) (N4MD from Coultronics). Scanning electron microscopy (SEM) was carried out on a Hitachi S 800, CMEABG in Claude Bernard University, Lyon I, France. Samples for SEM were prepared by putting a drop of the dispersion directly onto an aluminium sample holder and drying the latex at room temperature. All specimens for SEM were sputtered with gold using at fixed conditions (time 150 s, current 20 mA, voltage 2 kV). A standard voltage 10 kV was used for SEM experiments.

Preparation of *P*[NIPAM] latexes bearing cyano groups

Seeded polymerization

Preparation of *P*[NIPAM] seed latex: A mixture of NIPAM and MBA was dissolved in oxygen-free deionized water in a 500 ml batch reactor equipped with a mechanical stirring paddle, condensor, thermocouple and nitrogen inlet. To further remove oxygen from the aqueous phase, nitrogen was bubbled into the solution at the stirring rate of 220 rpm. Polymerization was initiated by adding 20 ml of an aqueous solution containing KPS at 70 °C, and totally carried out for 2 h at 70 °C with a stirring rate of 300 rpm. Crude *P*[NIPAM] latexes were purified by repetitive centrifugation and redispersion. A typical polymerization recipe is given in Table 1.

Preparation of *P*[NIPAM] latex bearing cyano groups: The seed latex was placed into a 100 ml batch reactor as described above and deoxygenated at room temperature by purging nitrogen for 1 h, then temperature was raised up to 60 °C. In order to prevent the evaporation of acrylonitrile, the nitrogen flow was stopped and the reactor was sealed. An aqueous solution of NIPAM, MBA an AN was injected into the reactor. After 10 min starting from the addition of the aqueous solution containing AN, an aqueous solution of the initiator KPS was also fed into the reactor. The seeded polymerization was carried out at 60 °C for an additional 2 h. The purification of the

Table 1 Recipe for preparation of seed particles

Ingredients	Quantities [g]
NIPAM	10.80
MBA	0.80
KPS	0.40
Water	550

Table 2 Polymerization recipe for the preparation of *P*[NIPAM] latexes bearing cyano groups using seed particles

Latex code	AN/NIPAM [w/w]	AN [g]	NIPAM [g]	MBA [g]	KPS [g]	Seed latex[a)] [g]	Water [g]
LW-1	10/90	0.0290	0.2683	0.0220	0.0107	40	10.0
LW-2	25/75	0.0745	0.2235	0.0220	0.0107	40	10.0
LW-3	50/50	0.1490	0.1490	0.0220	0.0107	40	10.0

[a)] Latex comprises 4% particles.

Table 3 Shot polymerization recipe for the preparation of *P*[NIPAM] latexes bearing cyano groups

First stage				Second stage			
Latex code	MBA [g]	KPS [g]	NIPAM [g]	Water [g]	AN/NIPAM [w/w]	AN [g]	NIPAM [g]
LW-4	0.08	0.04	0.54	55.0	0/100	0	0.54
LW-5	0.08	0.04	0.54	55.0	50/50	0.27	0.27
LW-6	0.08	0.04	0.54	55.0	75/25	0.405	0.135

resulting latex was performed as the procedure described above for the purification of seed *P*[NIPAM] latex. Several *P*[NIPAM] latexes bearing different content of cyano group were presented according to the experimental conditions shown in Table 2.

Shot polymerization

A mixture of NIPAM and MBA was dissolved in prepared oxygen-free deionized water in a 100 ml batch reactor as described above. To further remove oxygen from the aqueous phase, nitrogen was bubbled into the solution at the stirring rate of 220 rpm. Polymerization was initiated by adding an aqueous solution containing the initiator KPS at 70 °C. After 15 min starting from the addition of the aqueous solution of initiator, an aqueous solution containing both AN and NIPAM was injected into the presealed reactor without nitrogen supply. The polymerization was carried out for 3 h at 70 °C at a stirring rate of 220 rpm. The crude functionalized *P*[NIPAM] latex was similarly purified by repetitive centrifugation and redispersion. Three *P*[NIPAM] latexes bearing different contents of cyano groups were prepared according to the polymerization recipe shown in Table 3.

Conversion

A given volume of the crude synthesized latex was separated by centrifugation. The corresponding purified latex and water-soluble polymers were obtained and dried, so the conversion was calculated according to the weights of the separated purified latex and water-soluble polymers.

Results and discussion

Our purpose was to prepare latexes bearing surface functional cyano groups. A preliminary seed *P*[NIPAM] latex was obtained by batch polymerization. The solid content of the purified seed latex was determined and adjusted to 4.0% by adding deionized water. Two different polymerization procedures were preformed to get functionalized *P*[NIPAM] with various contents of cyano groups. Seeded polymerization was first carried out with a monomer mixture containing different AN to NIPAM weight ratios, then shot-growth process was considered upon increasing significantly the overall amount of AN.

Conversion and particle size analysis

Final conversion of the various latex preparations are given in Table 4. It was found that the overall conversion slightly increased upon increasing the amount of AN initially used in the polymerization recipe no matter whether seeded or shot polymerizations. Although reactivity ratios for NIPAM(1)/AN(2) radical-initiated copolymerizations are both close to 1 ($r_1 = 0.81$ and $r_2 = 0.863$) [14], the presence of AN in the aqueous phase (which exhibits a water solubility around 80 g/l) seems to have some effect. Particle sizes of all synthesized purified latexes as determined by quasielastic light scattering (QELS) at 45 °C are also reported in the same Table. It appears that particle diameter of the various latexes are slightly lower than that of pure *P*[NIPAM] latex (220 nm) but, due to the uncertainty of QELS measurements, no clear tendency can be evidenced as a function of the polymerization process

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Table 4 Characteristics of *P*[NIPAM] latexes bearing cyano groups

Latex code	Polymerization recipe		Overall conversion [%]	Particle size (QELS) at 45 °C [nm]	WSP[d] [%]
	AN/NIPAM [w/w]	AN [g]			
LW-1[a]	10/90	0.029	86.4	185	13
LW-2[a]	25/75	0.075	88.7	170	17
LW-3[a]	50/50	0.149	90.2	184	20
LW-4[b]	0/100	0	77.9	182	22
LW-5[b]	50/50	0.27	86.1	205	14
LW-6[b]	75/25	0.40	87.8	166	15

[a] Seeded polymerization.
[b] Shot polymerization.
[c] For the seed *P*[NIPAM] latex LW-0: 220 nm.
[d] WSP: water soluble polymer (wt%).

and the AN to NIPAM weight ratio used for the synthesis. This effect will be discussed later on in the paper. Finally, the proportion of water-soluble polymers recovered by centrifugation of the crude latexes was roughly in the same range (13–22 wt%), regardless of the process and amount of AN.

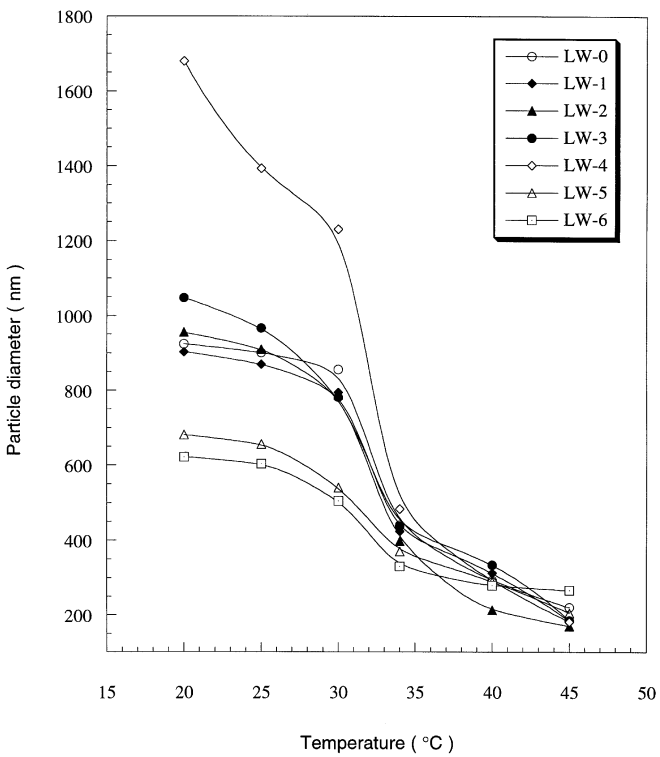
Effect of temperature on particle size

The change in particle diameter as a function of temperature was studied using QELS. As expected, the particle size decreases in a broad range of temperature (25–35 °C) due to the thermal sensitivity of the *P*[NIPAM]-rich particles. It is well known that such an effect shows the coil-to-globule transition for these latexes, but as reported by Zhu et al. [15] for *P*[NIPAM]-coated polystyrene particles, the conformational change spans over a much broader temperature range than for *P*[NIPAM] in free solution. Such a difference was attributed to the presence of electrical charges which would affect the transition of interfacial chains [15]. In the case of the actual latexes, this behavior might be enhanced because of the existence, first of a concentration gradient of crosslinked chains within the particles, second of a distribution both in the molecular weight and composition of the copolymer chains.

In addition, it is worth noting that both series of functionalized latexes exhibit a trend different to that of the pure *P*[NIPAM] seed latexes (LW-0 and LW-4 as well) for which the transitions take place in a slightly narrower temperature range, close to the LCST of *P*[NIPAM] (32 °C). The copolymerization of AN with both NIPAM and MBA in the shell layer could explain the broader transition range observed with cyanofunctionalized particles. First, the distribution of AN units along the copolymer chains constituting the shell layer should enhance the shrinking of *P*[NIPAM] chains. Second, the concentration profile of the crosslinker within the shell layer could be different from what it is in the case of pure *P*[NIPAM].

Moreover, as shown in Fig. 1, it appears that copolymerizing AN with NIPAM and MBA onto *P*[NIPAM] seed particles would also affect the particle

Fig. 1 QELS particle diameter in 0.001 mol/l NaCl solution as a function of temperature for the various functionalized *P*[NIPAM] latexes



size measured at 20 °C. This is especially well illustrated in the case of shot-functionalized latexes for which the particle size dramatically drops from 1600 nm (for LW-4 sample where the shot monomer mixture was 100% NIPAM) to 680 and 620 nm (for LW-5 and LW-6 samples where the AN to NIPAM weight ratio was 50/50 and 75/25, respectively). This phenomenon can be explained by the relative hydrophobicity of the acrylonitrile moieties which makes the *P*(AN-co-NIPAM) chains of the particle shell to shrink in aqueous solution even below the LCST. As a result, the sizes of the shot-functionalized particles become smaller below the LCST than that of the pure *P*[NIPAM] latex. The effect is not so obvious with the seeded-functionalized latexes for two reasons: (i) the shell-to-core weight ratio is indeed much smaller than in the shot ones; (ii) the uncertainty of the QELS data in the investigated size range.

Characterization of cyano groups

FT-IR was used to characterize the functionalized latexes in order to provide evidence of the presence of the cyano group on the particle. The absorption bands at 2244 cm corresponding to the cyano groups was observed in the spectra of the purified shot-functionalized latexes (LW-5, and LW6) as shown in Fig. 2. In addition, the lower the initial AN concentration in the polymerization recipe, the smaller the band in the IR spectra. Interestingly, it was very difficult to detect the presence of CN groups onto particles obtained by seeded polymerization (latexes LW-1–LW-3).

In order to further confirm the existence of cyano groups and to determine quantitatively the content of cyano groups in the particle, an ^{1}H-NMR study was performed at room temperature to characterize the functionalized particles. Since the core of the particle was crosslinked and not soluble in the solvent mixture, composed of deuterium oxide and water, the protons in the core should not be detected under solution NMR conditions. Therefore, only protons of the solvated shell were observed. However, no characteristic peak corresponding to the methine group α of nitrile moiety, at 3.6 ppm, was detected in the ^{1}H-NMR spectrum (D_2O) of the purified latex LW-3 which was synthesized with the highest AN content in the polymerization mixture. Then, assuming deuterated water was not a good enough solvent for the polyacrylonitrile segments of the shell, deuterated pyridine (C_5D_5N) was used. A close comparison of the spectra for the seed (LW-0) and functionalized latexes (LW-3) (Fig. 3a and b) allows the detection of a very small peak at 3.6 ppm corresponding to cyano groups only in the spectrum of the LW-3 sample. This further confirmed that the synthesized

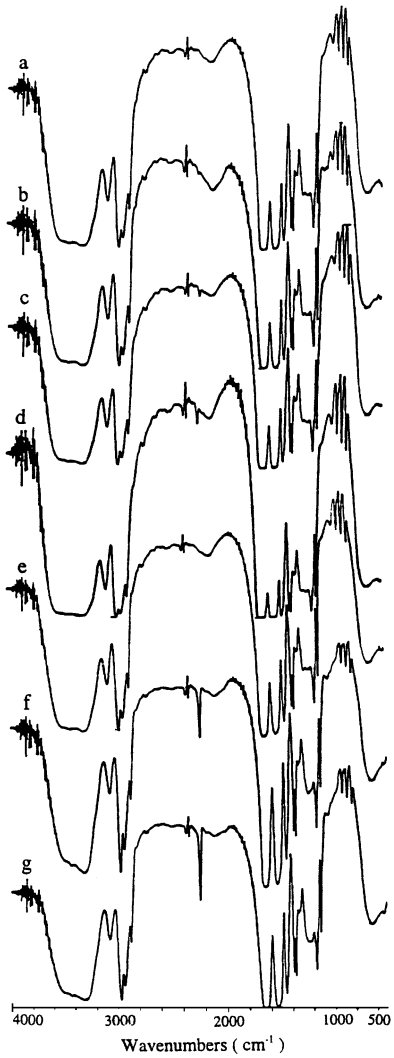


Fig. 2 FT-IR spectra (KBr plate) of the seed *P*[NIPAM] latex LW-0 (a), the purified seeded polymerization-prepared functionalized *P*[NIPAM] latex LW-1 (b), latex LW-2 (c), latex LW-3 (d) and the purified shot-polymerization-prepared pure *P*[NIPAM] latex LW-4 (e), functionalized *P*[NIPAM] latex LW-5 (f) and LW-6 (g)

functionalized latex LW-3 contained low amounts of cyano groups in relation to the overall AN composition in the recipe (order of 7 wt%). Furthermore, indirect measurement of the content of cyano groups on the particle via ^{1}H-NMR analysis of the water-soluble residues recovered from the latex sera in deuterated pyridine was unsuccessful, since no peak corresponding to AN could have been detected by this method.

Due to the larger overall amount of AN used for their synthesis, the contents of cyano groups in the particles prepared by shot-growth polymerization were expected to be higher than in the seeded polymerization process. ^{1}H-NMR spectra of the two dried and purified shot-growth

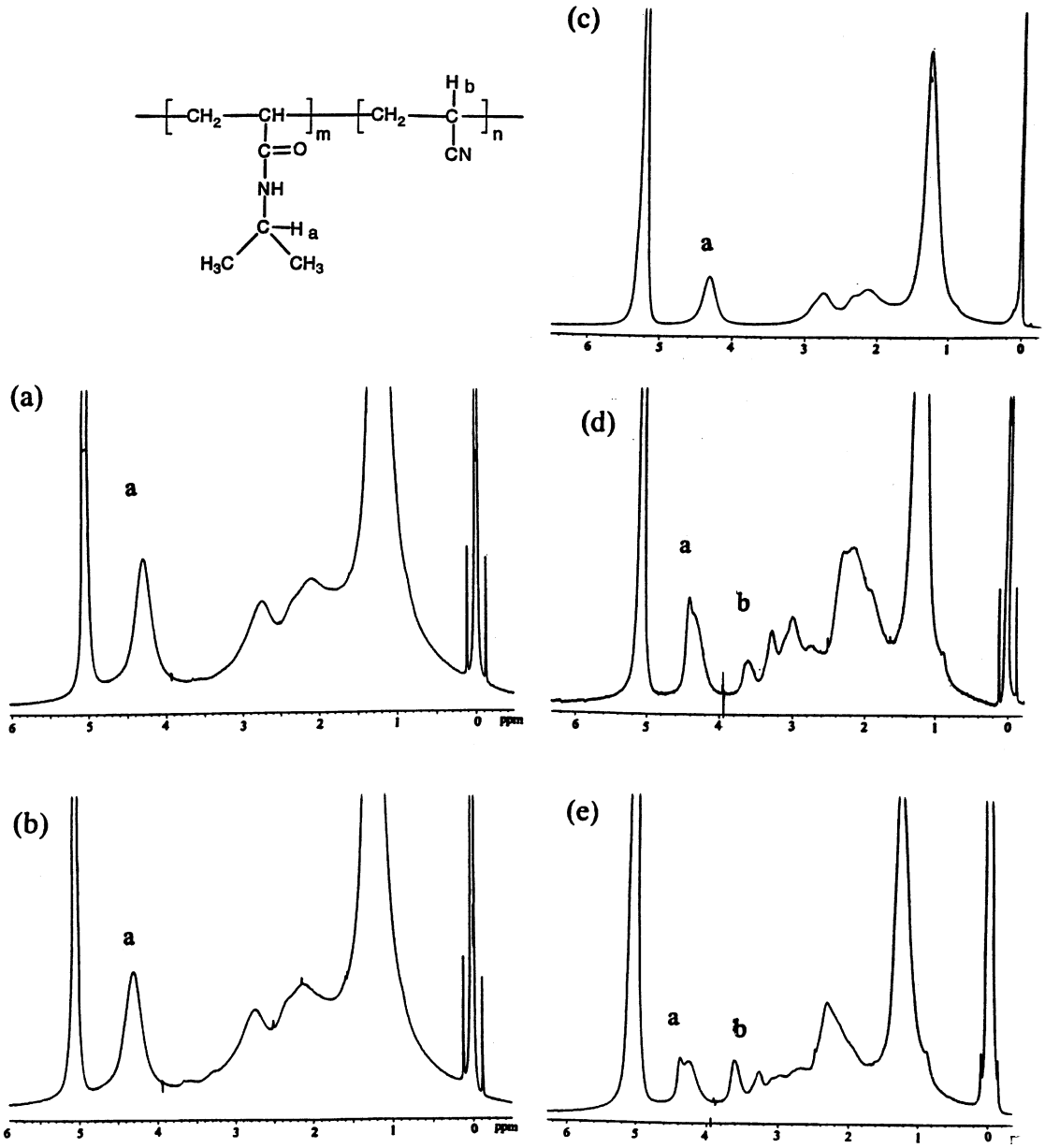
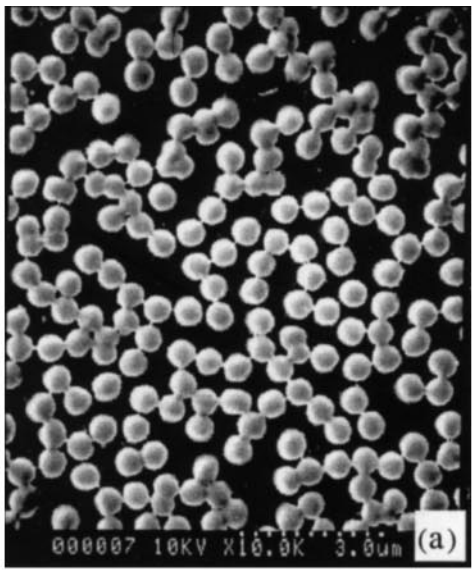
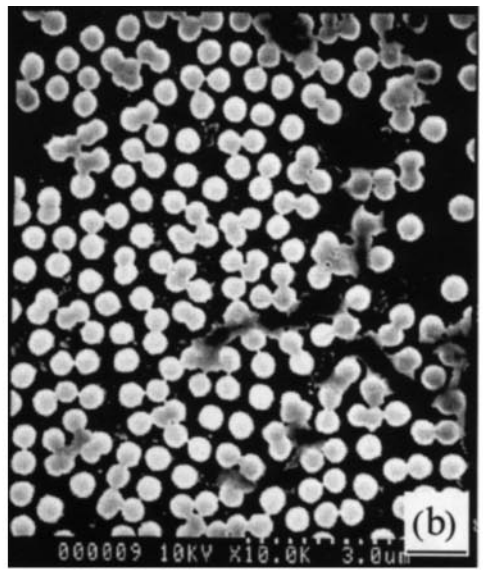


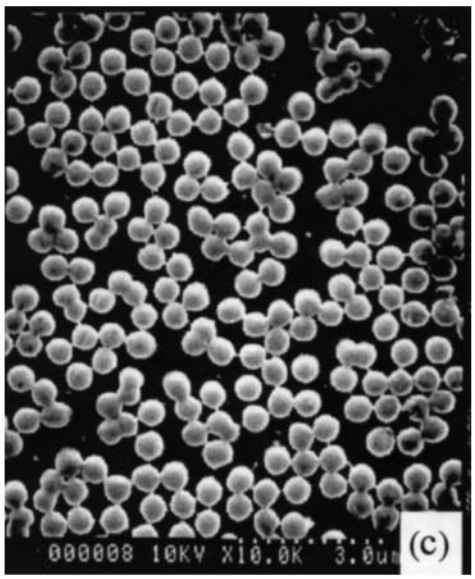
Fig. 3 ^{1}H-NMR spectra (C_5D_5N) of the seed latex *P*[NIPAM] latex LW-0 (a), purified seeded polymerization-prepared latex LW-3 (b), pure *P*[NIPAM] latex LW-4 (c), purified shot polymerization-prepared latex LW-5 (d) and latex LW-6 (e)

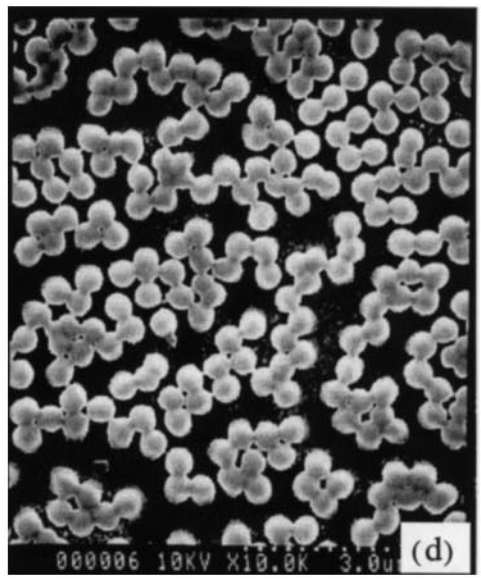
functionalized particles in d_5-pyridine (Fig. 3c–e), respectively, show a resonance of methine (CH) at 3.6 ppm for *P*[AN] in comparison with that observed in the case of the pure *P*[NIPAM] latex (LW-4). In addition, the overall content of the cyano groups in each latex was calculated according to their respective ^{1}H-NMR spectrum, as reported in Table 5. The reported data confirmed that shot-functionalized latexes indeed contained more cyano groups than seed ones. However, the content of the cyano groups located in the shell of the particle could not be determined because the particles completely dissolved in deuterated pyridine.

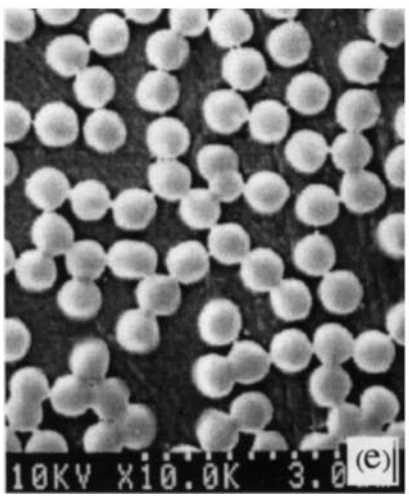
Fig. 4 SEM micrographs of various functionalized *P*[NIPAM] particles (a) seed latex LW-0, (b) LW-1, (c) LW-2, (d) LW-3, (e) LW-4, (f) LW-5 and (g) LW-6

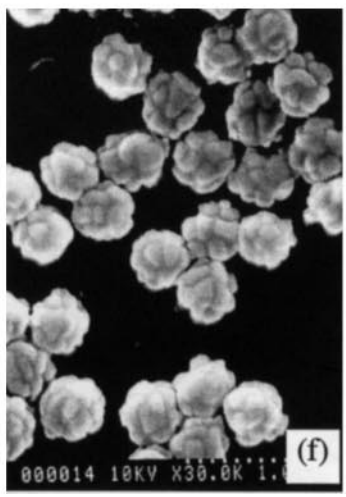

000007 10KV X10.0K 3.0um
(a)


000009 10KV X10.0K 3.0um
(b)


000008 10KV X10.0K 3.0um
(c)


000006 10KV X10.0K 3.0u
(d)


10KV X10.0K 3.0
(e)


000014 10KV X30.0K
(f)

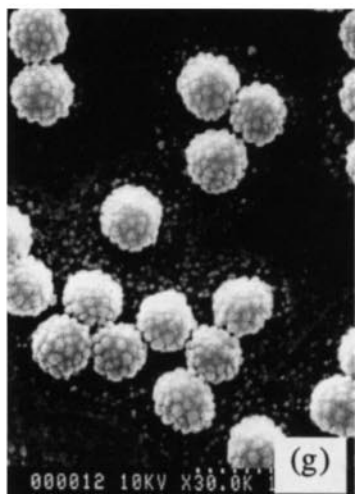

000012 10KV X30.0K
(g)

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Table 5 Amount of cyano groups in the various *P*[NIPAM/AN] shot-growth latexes

Latex code	Elemental analysis			Content of cyano groups in the particle [mol%]	
	C [%]	N [%]	S [%]	Elemental analysis	^{1}H-NMR
LW-4	59.90	12.20	<0.30	0	0
LW-5	60.00	14.60	0.35	28.70%	26.00%
LW-6	59.90	15.20	0.40	35.00%	35.70%

Finally, as reported in Table 5, it is worth mentioning that elemental analyses of the purified latexes show an overall content of cyano groups in the particle in quite good agreement with the results obtained from ^{1}H-NMR.

Particle surface SEM analysis

It was previously shown that SEM proved to be a powerful tool for examining the surface morphology of *P*[NIPAM]-based particles [16], therefore, such an analysis was also performed on these cyano-functionalized particles. From SEM micrographs reported in Fig. 4, two main features can be pointed out:

(i) all latexes are highly monodisperse which corroborates a short nucleation step during the synthesis without a secondary nucleation, especially when seeded or shot polymerization procedures were used.

(ii) on the contrary, it is clearly seen that the particle surface morphology depends upon the mode of polymerization. As already reported [14], *P*[NIPAM] particles (LW-0 and LW-4 samples) exhibit quite smooth surfaces, whereas those corresponding to shot-polymerized *P*[NIPAM/AN] (LW-5 and LW-6 samples) with high content of cyano groups show raspberry-like surface structures. The three seeded *P*[NIPAM/AN] particles (LW-1, LW-2 and LW-3 samples) with low content of cyano groups, displayed a relatively smooth surface, similarly to that of pure *P*[NIPAM] particles.

Such a particle morphology can be correlated with the mechanism of particle growth as a function of the process used to synthesize the various latexes. It seems obvious that the presence of AN plays a major role in the development of the uneven particle structure, especially in the case of shot-growth polymerization. When the shot addition of acrylonitrile together with NIPAM and MBA onto latex seed is carried out, partitioning of the monomer mixture takes place between the aqueous phase and polymer particles. Simultaneously, polymerization also operates through capture of oligoradicals originated by seed particles in water and subsequent propagation in the particles. The critical chain length for capture of these (co)oligomers is probably small since in the case of *P*[NIPAM], phase separation was reported to occur with only three repeat units [17]. As mentioned above, the *P*[AN]-rich segments incorporated in the shell of the functionalized particles can easily shrink toward the core of the particles. In addition, due to poor compatibility between *P*[AN] and *P*[NIPAM], a phase separation may occur during the synthesis, resulting in the formation of small globular structures responsible for the rough surface in the case of functionalized particles obtained with largest amount of AN. Due to the low solids content, the formation of small *P*[AN]-rich particles by homogeneous nucleation may not be discarded but most of them would heterocoagulate onto preformed particles, then also contributing to the observed morphology. However, the presence of these small particles by QELS was never evidenced during the polymerization or in the final latex sera.

Finally, surface roughness of the functionalized *P*[NIPAM] latexes can indirectly reflect the degree of the incorporation of cyano groups in the shell layer of the particles. Because the observed surface of the shot functionalized latexes (LW-5 and LW-6 samples) from SEM is quite rough, the content of cyano groups in the shell of the two functionalized particles should be high. On the contrary, unexpectedly, this does not hold in the case of seed functionalized since a smooth surface was observed. In that case, too, the analysis of the corresponding latex sera did not show the presence of *P*[AN]-rich particles.

Nevertheless, several important questions are still open such as for instance the actual copolymer composition distribution in the shell layer and globules, the precise location of *P*[AN] segments within the particle, etc. The complexity of the particle structure in these systems together with the absence of accurate kinetic data preclude any more speculation.

Conclusion

Core–shell *P*(*N*-isopropylacrylamide) latexes with surface cyano groups were successfully prepared by seeded or shot-growth polymerizations. At first, QELS size data vs. temperature of all cyano-functionalized latexes reflected that thermal sensitivity of particles was maintained with no significant change in the LCST as compared to that of

pure *P*[NIPAM] latex, however the transition definitely takes place in a broader range of temperature. The existence of cyano groups in or on the particle was clearly confirmed by FT-IR and ^{1}H-NMR. The content of cyano groups in the particle can be controlled by the initial amount of acrylonitrile monomer used in the polymerization and this amount, as determined both by ^{1}H-NMR and elemental analysis, was higher in shot-functionalized latexes than those obtained by seeded polymerization. The particle size (at 20 °C) of the shot-functionalized latexes was much smaller than that of pure *P*[NIPAM] latex, which was attributed to the more hydrophobic *P*[AN] segments causing more shrinkage of the polymer chains toward the core of the particle. Polymerization of acrylonitrile was also found to affect the surface morphology of the seed latex particles as pointed out by SEM imaging. Indeed, the surface of the particle bearing a high content of cyano groups was quite uneven compared to that of the pure *P*[NIPAM] latex. The observed phenomenon was explained either by the formation of acrylonitrile rich-polymer chains which phase-separated or by hetero-coagulation of *P*[AN]-rich small particles onto the seed latex particles. In addition, due to the narrow size dispersity of the prepared *P*[NIPAM] particles with various contents of cyano groups, such latexes were currently used for immobilizing biomolecules and results will be addressed in a next paper.

Acknowledgements The authors would like to express their sincere appreciation for their help to Laurent Véron for the ^{1}H-NMR and FT-IR analyses, David Duracher for the SEM examination and finally CNRS-K.C. Wong Foundation for providing G. Zhou a post-doctoral fellowship.

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