Synthesis of poly(acrylamide-*co*-[2-acryloyloxy ethyl]trimethyl ammonium chloride) star-shaped polymers by inverse microemulsion polymerization

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ABSTRACT

A series of star–shaped poly(acrylamide–co–[2–(acryloyloxy)ethyl] trimethyl ammonium chloride) were prepared by inverse microemulsion polymerization. The growth of side chains in the arms of the precursor has been carried out using different compositions of the comonomers acrylamide and [2–(acryloyloxy)ethyl] trimethyl ammonium chloride) (Q9). The characterization and star structure were determined by nuclear magnetic resonance, FTIR, MALDI–TOF and DSC. The dimensions of the particles were determined by quasielastic light scattering and transmission electron microscopy. Quasi–spherical particles of star polymers in the nanozise range were obtained which might be useful for the controlled transport and release of several biologically active drugs. Copyright © 2013 VBRI Press.

Keywords: Hyperbranched polymers; star–shaped polymers; microemulsion polymerization; structure–property relations; [2–(acryloyloxy)ethyl] trimethyl ammonium chloride).

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Introduction

Star polymers are built from linear polymer chains joint covalently to a common center. Because of its unique structure and physical and chemical properties [1], the synthesis of hyperbranched polymers and star–shaped polymers are receiving increasing attention in recent years [2, 3]. Star polymers can be synthesized using the arm–first method which permits to obtain star polymers with different arm composition [4–6]. At present the simplest star–shaped polymers are made by connecting various arms at a common core [7–9]. The synthesis of star–shaped polymers by emulsion and microemulsion polymerization (direct or inverse) [7], allows the control of their structure and chemical composition.

There are many potential uses for star polymers: as flocculants [8, 9], as superabsorbents [10], for capturing metal ions in waste water [11] and coating technologies to contact lenses and biomedical devices [12-14] as well as the cosmetic development industry.

In the present work we present the synthesis and properties of star–shaped poly(acrylamide–co–[2–(acryloyloxy)ethyl] trimethyl ammonium chloride). The synthesized materials were further subjected for the evaluation of their physico-chemical properties.
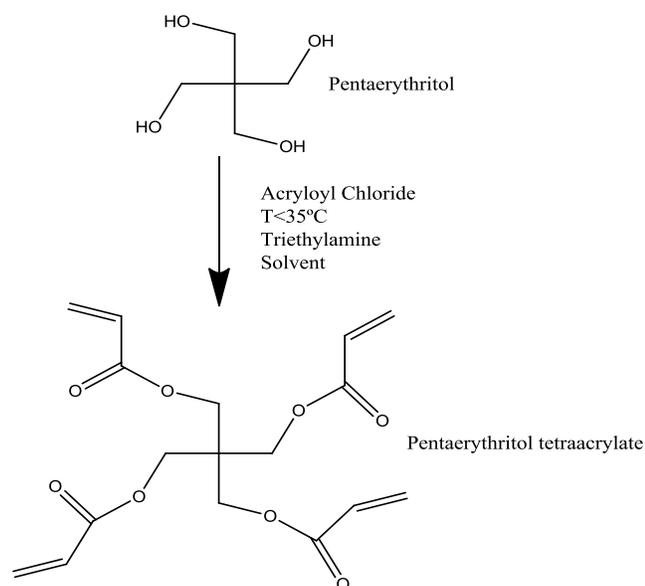
Fig. 1. Scheme of the synthesis of four Arm multifunctional initiator pentaerythritol tetra–acrylate (PETA).

Experimental

Materials

Acrylamide (AM ≥ 98%) was purchased from Across Organics and was used as received. Pentaeritrytrol (≥ 99%), [2–(acryloyloxy) ethyl] trimethyl ammonium chloride) (purity ≥ 96%), sorbitan sesquiolate (ARLACEL–83), polyoxythylene sorbitol hexaoleate (ATLAS G–1086), and chloroform (PCR reagent ≥ 99%) were purchased from Sigma Aldrich and used as received. Triethylamine (TEA) and sodium metabisulfite ($Na_2S_2O_5$, ≥ 95%) were purchased from Merck and used without

further purification. [2–(acryloyloxy)ethyl] trimethyl ammonium chloride) (Q9, 80% in water) and isoparaffinic oil (Isopar M, Esso Chemie) were supplied by Esso Chemie and used as received. Diethyl ether was purchased from Panreac and used as received. Milli–Q water was obtained using a Milli–Q purificator system under controlled conditions.
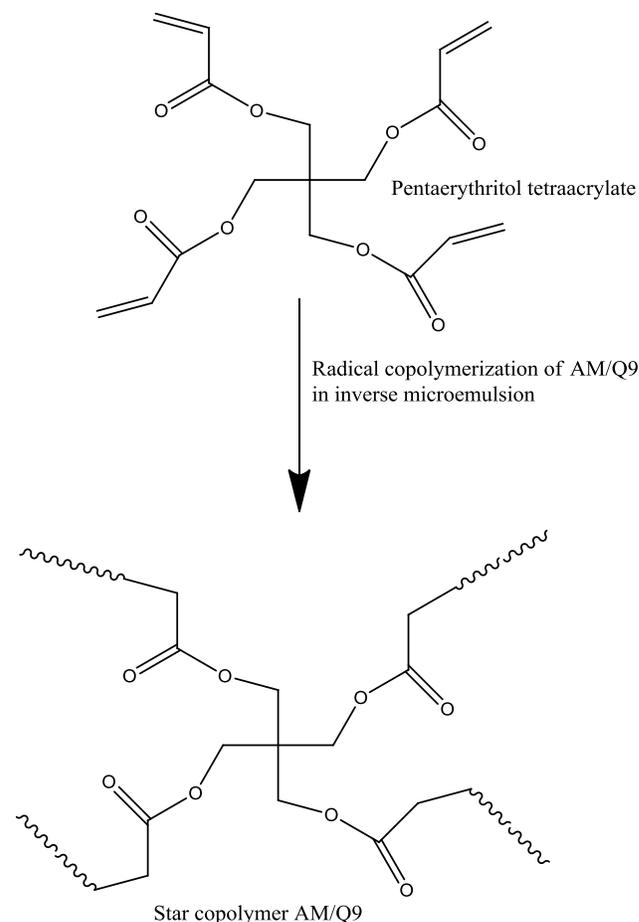
Fig. 2. Four arm star shaped AM/Q9 copolymer.

Synthesis of the multifunctional initiator

The multifunctional initiator [2–(acryloyloxy)ethyl] trimethyl ammonium chloride) (PETA) was synthesized in our laboratory following a previously reported method by Ochoa–Gómez et al. [15]. **Fig. 1** shows the general scheme for the synthesis of PETA. Pentaerythritol (5 g), triethylamine (TEA) (5 mL) and solvent (dichloromethane) (25 mL), were added into a three–necked flask The mixture was heated at 30 °C. After reaching this temperature, [2–(acryloyloxy) ethyl] trimethyl ammonium chloride) (2 mL) was added dropwise and when the addition was completed the reaction was kept under agitation at room temperature for 6 hours. The product of the reaction was washed with dichloromethane, dried at 40 °C and washed with water to remove triethylamine and unreacted acryloyl chloride (reaction with water gives rise to acrylic acid and HCl which dissolve in the aqueous phase). The organic phase

was dried with anhydrous sodium sulfate, filtering and removing the solvent by using a rotary evaporator, at 35 °C. The residue (PETA) was dried at 110 °C.

Synthesis of star–shaped polymers by inverse microemulsion polymerization

Four–arm stars were prepared by inverse microemulsion polymerizations, at 28 ℃, using as surfactant a mixture of Atlas G–1086 and Arlacel–83 (90:10); the aqueous phase consisted of the monomers, Q9 and acrylamide 58%), and sodium metabisulfite (1.6% wt) which were dissolved in MilliQ grade water (42% by total weight of the microemulsion); the Isoparaffinic oil (Isopar–M) was the organic phase (20.7%). Before copolymerization the system was a true inverse microemulsion as it was visually observed by the transparency of dispersions as well as by their stability after centrifuging at 5,000 rpm for 30 min. No phase separation was observed. Nitrogen purge (4 mL·min^{-1} at 25 ℃ and 1 bar) was kept during all reaction time and sodium metabisulfite aqueous solution was continuously added at constant flow (0.9 mL·min^{-1}) using a Methrom Dosino 700 dosing unit. Reaction mixture was cooled by a water bath kept at constant temperature (27 ℃). Reaction was considered to be completed when temperature was back to its initial value. Reaction was very fast and peak temperature was reached in less than 1 min and reaction time was 6 min. Then, the pH of the aqueous phase was adjusted to 5.0, using nitric acid. **Fig. 2** shows reaction mechanism. The polymer was obtained by destabilizing the microlatex by adding chloroform and pouring the mixture into diethyl ether. The precipitate was washed with diethyl ether for three times. Star–shaped polymers with different composition were prepared by using different monomers ratios: 100% AM, 90% AM–10% Q9, 80% AM–20%Q9 and 50% AM– 50% Q9.

Measurements procedures and characterization

Nuclear Magnetic Resonance Spectroscopy (NMR): all nuclear magnetic resonance spectroscopy spectra were recorded on a Bruker Avance 500 MHz operated in the Fourier transform mode. Deuterated water was used as the solvent.

FTIR spectra: FTIR spectra of the samples were obtained by attenuated total reflectance (ATR) using the Smart Orbit accessory coupled to a Fourier transform infrared spectrophotometer (Nicolet 6700). All spectra were obtained by averaging 100 scans.

Thermal behavior of hydrogel: The glass transition temperature of the samples (T_g) was measured using a differential scanning calorimeter (DSC), TA Instruments (DSC 2920). For calibration, Indium (T_f = 156.68 ℃) and zinc (T_f = 419.58 ℃) standards were used. The calorimetric analysis of the star polymers was carried out in the temperature range of 0 – 200 °C at a heating rate of

10 °C/min under nitrogen flow (50 mL·min^{-1}). The T_g was calculated following the midpoint criterion.

Viscosity properties: Rheological measurements of the microlattices were performed using different speeds and temperatures using a Brookfield Rheometer LVDV–II with spindle S18 Ultra at 30 rpm and thermostatic cell (25 ℃). Viscosity is expressed as relative viscosity, η_{rel}.

Morphological studies: to realize transmission electron microscopy (TEM), two microliters of each sample were deposited on 300 mesh carbon coated grids, which had been previously turned hydrophilic by glow discharge treatment. Samples were visualized using a transmission electron microscope (Philips CM120) operated at 120 kV, and images were captured with an Olympus SIS Morada digital camera. Particle size and particle size distribution were determined using quasielastic light scattering technique with a QLS AMTEC apparatus. The measurements of the intensity correlation were obtained in a Brookhaven BI–9000AT552, equipped with an argon ion laser (wavelength of 514.5 nm) water–cooled. Lattices were diluted up to 50 times with water before QLS measurements to minimize particle–particle interaction and to remove dust particles. The samples were dispersed in water. All measurements were done at 25 °C. CONTIN analysis was used to obtain particle size distribution.

MALDI–TOF spectroscopy: The matrix–assisted laser desorption/ionization time of flight (MALDI–TOF) was recorded in the linear mode on a Bruker Microflex LT System with software and platform technology AnchorChip Compass. For calibration the Bruker standard protein was used (0.5 mL). Once the apparatus was calibrated, 3 mg of the sample were dissolved in 3 mg of a matrix–solution methanol:water:trifluoracetic acid (50:50:0.05). The sample was placed on a steel plate *Ground Steel Massive 384.* Scanning was carried out between 4,500 and 3,200 Th.

Swelling behavior: equilibrium swelling measurements were carried out by introducing the star–shaped synthesized copolymers in water and at given times taking them out, blotting them with a paper filter and weighing this procedure was carried out until constant weight. The percent of water uptake of the materials (H_P) at equilibrium was calculated as:

$$\mathbf{H_p} = 100 \cdot \frac{\mathbf{w}_f - \mathbf{w}_o}{\mathbf{w}_o}$$

W_f and W_0 represent the weight of the star–shaped copolymer at the swelling equilibrium and of the dried material, respectively.

The percent of water in the star–shaped material by weight (W_p) is:

$$\mathbf{W_p} = 100 \cdot \frac{\mathbf{w}_f - \mathbf{w}_o}{\mathbf{w}_f}$$

Results and discussion

After the synthesis of multifunctional initiator, an inverse microemulsion with the monomers and multifunctional initiator was prepared. This microemulsion was initiated using free radical polymerization [16]. When copolymerization was finished the nanoparticles were obtained destabilizing the microlatex. The result was a white powder which was precipitated and purificate to obtain the star–shaped nanoparticles.
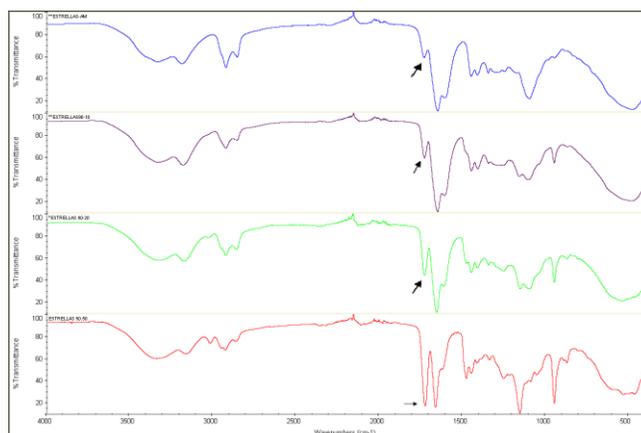
Fig. 3. FTIR spectra for the different obtained compositions.

Fig. 3 shows the FTIR spectra of the copolymers synthesized here. The spectra show at 3344.9 cm^{-1} a broad band of medium to high intensity due to the –N–H stretching band of AM (at 1664.2 cm^{-1} the characteristic vibration band of –CO–NH bond shows, and at 1726.9 cm^{-1} appears a band that corresponds to the vibration mode of the carbonyl group. **Fig. 3** also shows that the band of the carbonyl group of the Q9 (1720 cm^{-1}) becomes more pronounced when increasing the ratio of Q9 in the polymer. The band 950 cm^{-1} which corresponds to the Q9 also increases as the polymer composition is enriched in Q9.

Fig. 4 shows the glass transition temperature, T$_g$, as a function of polymer composition. All the samples showed a single glass transition temperature which indicates that polymer with homogeneous composition was obtained. First, glass transition temperature decreases when the proportion of Q9 increases and then a further increase on Q9, causes that glass transition temperature increases. The complexity of this polymer where intermolecular interactions depend on composition because of the mobility of the different chain ends groups makes it very difficult to make an analysis of the variation of glass transition temperature with composition. However, the decrease when Q9 increases can be explained by the presence of the – O – bond in the Q9 that increases the mobility of the arms. However, at higher Q9 ratio the ionic forces predominate and cause the increase in glass transition temperature.

MALDI–TOF spectra from 4,500 to 3,200 Th were taken to two of the star–shaped polymers AM–Q9 (80/20) and AM–Q9 (90/10). The samples show only one peak at around 10,000 Th. These peaks were amplified (9,950 to 10,050 g/mol) and shown in **Fig. 5**; where both samples

have similar peaks pattern and several peaks are observed which results in a polydispersity index of about 1.02 (**see Table 2**).
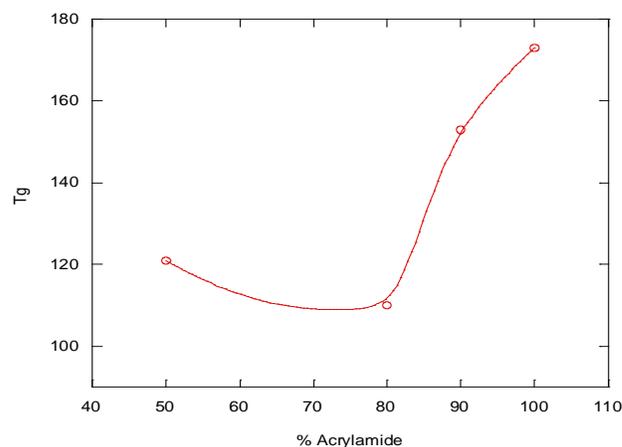
Fig. 4. Plot of the glass transition temperature against sample composition
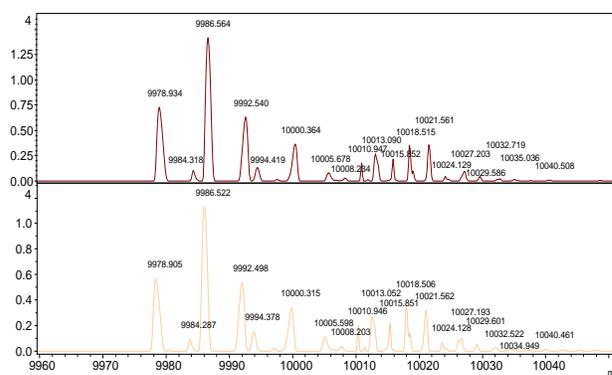
Fig. 5. Maldi–TOF mass spectra obtained for a) AM/Q9 (80/20) and b) AM/Q9 (90/10).

Table 1. Values of H$_p$ and W$_p$ as a function of AM content.

Sample	Ratio AM/Q9	H$_p$	W$_p$
AMQ50	50/50	11,844	99.2
AMQ80	80/20	3,301	97
AMQ90	90/10	1,833	93.7
AMQ100	100/0	828	89

Equilibrium swelling

All the polymers absorbed large amounts of water and reached equilibrium swelling in very short time (less than one hour). The results for H$_p$ and W$_p$ as a function of AM content are shown in **Table 1**. There is a great difference in the amount of absorbed water among samples; as the proportion of Q9 increases in the copolymer the amount of water absorbed increases because the Q9 being a salt, is more hydrophilic than the AM.

TEM microscopy

Fig. 6 shows a micrography of one of the synthetized samples (AM/Q9 80/20) where it can be seen that particle size is small (less than 100 nm) and that the particles have

quasi–spherical shape, although the departure of the spherical shape can be due to compression or deformation caused in the preparation of the sample. Similar results were obtained for the other compositions.
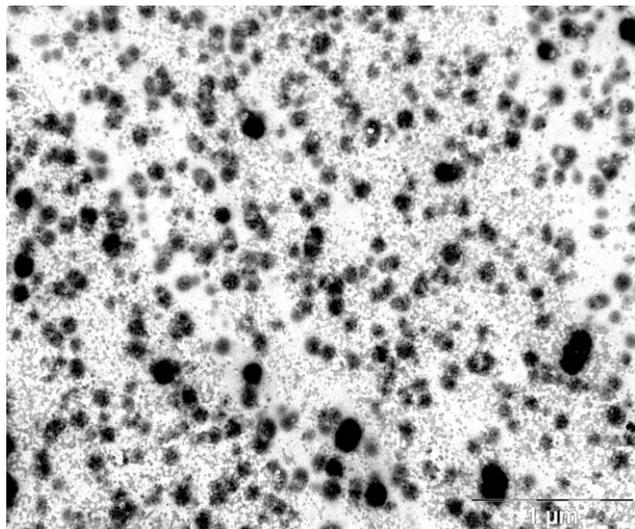
Fig. 6. TEM micrography of star polymer simple AM/Q9 (80/20).

Average particle size measured by quasielastic light scattering (QLS) ranged between (60–145 nm) and the polydispersity was small (1.02–1.03). **Table 2** shows that particle size increased when increasing the Q9 content and that slightly larger average particle sizes were obtained by QLS than with TEM indicating instead of TEM.
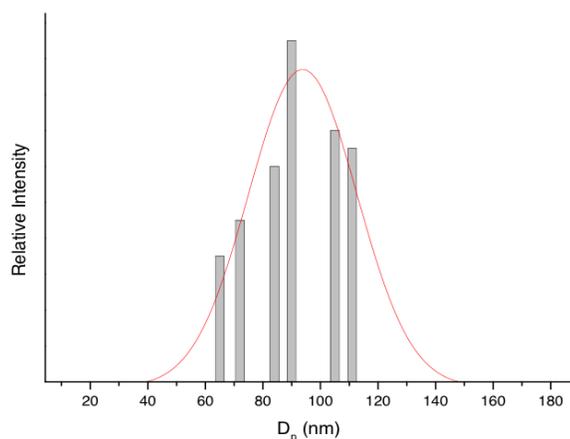
Fig. 7. Particle size distribution of the star polymer AM/Q9 (80/20) obtained by QLS technique.

Table 2. Average Particle size obtained by TEM and QLS, and polydispersity index obtained by MALDI–TOF.

Sample (AM/Q9)	Average particle size (TEM) nm	Average particle size (QLS NNLS) nm	Polydispersity Index Maldi-Tof
100/0	60	71	1.03
90/10	68	83	1.02
80/20	75	90	1.02
50/50	95	145	1.03

Fig. 7 shows the particle size distribution obtained by QLS technique of the star polymer particles of sample AM/Q9 (80/20) where can be observed that polydispersity was small since particle size was in the range 65–112 nm. **Table 2** shows that in all cases small particle size polydispersity was obtained.
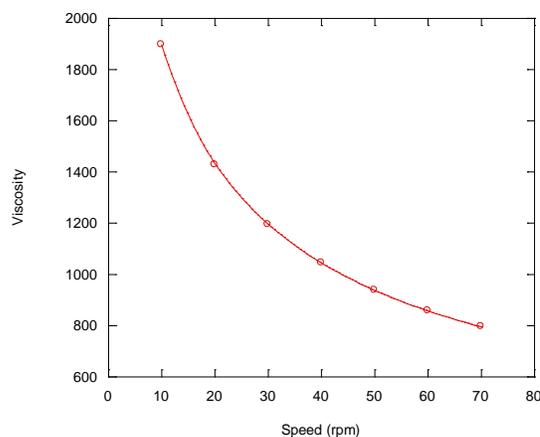
Fig. 8. Plot of the curve of viscosity versus shear rate.

Fig. 8 shows the curve of viscosity versus shear rate of the final microlatex of the sample (80/20) at 25 ºC. Viscosity decreases as the deformation rate increases which indicates that it is a *non-newtonian pseudoplastic fluid*. This type of behavior is typical when there is the presence of colloids or micelles. Similar results were obtained at 35 ºC.

Conclusion

Star polymers were synthesized using the method of inverse microemulsion. These polymers have been characterized using different experimental techniques. The FTIR has provided evidence that the copolymers had different AM/Q9 ratios. Glass transition temperature first decreased when increasing Q9 content up to 20% of Q9 and then increased with further increase of Q9. The star–shaped polymers obtained here have a narrow molecular weight distribution ($M_w / M_n \approx 1.02$) and molar mass around 10,000 g/mol. Quasi–spherical nanoparticles were obtained with low particle dispersity. Viscosity measurements indicate that the microemulsions have a pseudoplastic behavior. Inverse microemulsion polymerization starting with a four–armed multifunctional precursor is a good method of synthesis of nanoparticles of star polymers and copolymers.

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