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Synthesis and rheological properties of an associative star polymer in aqueous solutions

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Abstract

Rheological properties of aqueous solutions and hydrogels formed by an amphiphilic star block copolymer, poly(acrylic acid)-*block*-polystyrene $(PAA_{54}\text{-}b\text{-}PS_6)_4$, were investigated as a function of the polymer concentration (C_p), temperature, and added salt concentration. The water-soluble polymer synthesised by atom transfer radical polymerization (ATRP) was found to form hydrogels at room temperature at polymer concentrations, C_p, over 22 g/L due to the interpolymer hydrophobic association of the PS blocks. Increasing C_p leads to stronger elastic networks at room temperature that show a gel-to-solution transition with increasing temperature. Increase of ionic strength decreases the moduli compared with the pure hydrogel but did not affect the gel–sol transition temperature significantly. Small-angle X-ray experiments showed two distinct scattering correlation peaks for samples above the gelling C_p, which indicates the aggregates formed due to hydrophobic association. Upon heating the intensity of the scattering correlation peaks was found to decrease indicating the loss of the network structure due to thermal motion.

Keywords: Star polymer; Water-soluble; Rheology

1. Introduction

Associative polymers are of great industrial importance owing to their adjustable rheological properties, for example in oil recovery, paints, cosmetics formulations and pharmaceutical as well as medical applications such as drug delivery and tissue engineering [1]. Particularly interesting are the stimuli-responsive systems of associating polymers in which free-standing gels transform to free-flowing liquids or vice versa. To obtain such systems water-soluble polymers modified with a small number of hydrophobic groups are often used [2–32]. Enhanced viscosity and reversible gelling behaviour originate from transient intermolecular associations between the hydrophobic groups.

Responsive properties in aqueous solutions are attained by using either neutral (i.e. non-ionizable) water-soluble polymers [4–7,21,30–32] or polyelectrolytes [8–20,22–29]. The self-assembly of block polyelectrolytes gives additional versatility with regards to the responsiveness and polyelectrolytes may create strong elastic gels at lower concentrations than neutral polymers [2]. By changing the polymer concentration [4,6–11,13,14,16–19,26,27], temperature [5,6,15,17,18,21–26], ionic strength [10,27,28], pH [19,29] or by adding analytes [12,23] the solution interactions and the rheological properties may be varied significantly. The characteristics of the polymers may be tuned for example by varying the molar mass of the polymer or the mass ratios of the comonomers, but also by the topology of the polymers, using structures such as

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diblocks [2,3,10,14,23,24], triblocks [2,3,6,15–19,25,29] or stars [20,21].

In this work, we have synthesised a relatively monodisperse water-soluble associating starlike polyelectrolyte, four-armed poly(acrylic acid)-*block*-polystyrene, and investigated the stimuli-responsive behaviour of its hydrogels by rheological methods. The starlike topology of the polymer represents a special case of a branched architecture, in which all polymer chains have the same branching point. Compared with linear diblock and triblock polymers the four-armed topology may enable more effective association. Indeed, according to Lin and Cheng [31], four-arm amphiphilic stars based on poly(ethylene oxide) inner blocks and poly(*N*-isopropyl acryl amide) outer blocks are able to form gels that have higher strength than stars with higher number of arms, due to the low intramolecular aggregation in the former case. Another advantage over linear polymer systems is the existence of the central core of the star polymer. Due to the multifunctionality, and often to the hydrophobic nature of the core such polymers have been proposed as carriers for example for fragrance molecules [33], dyes [34] or catalysts [35,36]. The polyelectrolyte core in the present case may also be suitable for encapsulation of ionizable compounds and additionally the polyelectrolyte is sensitive to changes in environmental conditions. Thus in addition to polymer concentration, we have examined the effects of ionic strength and temperature on the rheological properties of the aqueous polymer solutions. Furthermore, small-angle X-ray scattering (SAXS) was used to study the structure of the non-saline polymer solutions at different temperatures.

2. Experimental

2.1. Materials

The synthesis of a tetrafunctional initiator (diTMP–Br) by acylation of di(trimethylolpropane) (diTMP) with 2-bromoisobutyrylbromide is described elsewhere [37]. *tert*-Butyl acrylate and styrene were distilled from CaH_2 prior to use. CuBr, *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (PMDETA), trifluoroacetic acid (all from Aldrich) were used without further purification.

2.2. Synthesis of starlike poly(tert-butyl acrylate), (P(tBA)$_4$)

tert-Butyl acrylate (15.34 g, 0.12 mol), CuBr (0.26 g, 1.81 mmol) and diTMP–Br (0.32 g, 0.38 mmol) were placed in a dry Schlenk tube. After dissolving of the initiator (diTMP–Br) the system was degassed by two freeze–thaw cycles under vacuum. PMDETA (0.32 g, 1.85 mmol) was added and three more freeze–thaw cycles were performed. The polymerization was conducted under nitrogen atmosphere at 70 °C for 37 min, after which it was terminated by immersing the tube into liquid nitrogen. The polymer was precipitated in 1:1 water–methanol solution and dried under vacuum at room temperature. The gravimetrically determined conversion was 64%, giving theoretical molar mass M_n(theor) = 26,200 g/mol. The molar mass determined by SEC, M_n(SEC), was 27,000 g/mol, and the corresponding polydispersity was 1.19. The molar mass determined by ^{1}H NMR from the signals of the endgroup, the initiator and the polymer, M_n(NMR), was 27,700 g/mol, and the number of arms was 4. The molar mass determined by static light scattering, M_w(SLS), 65,800 g/mol indicated that some star–star coupling has occurred during the polymerization.

^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 4.06 (br, 4H) and 3.93 (br, 8H, $-CH_2-$, initiator), 3.25 (br, 4H, $-CH_2O-$, initiator), 2.23 (1H, $-CH-$), 1.80 and 1.75 (2H, $-CH_2-$), 1.75, 1.49 and 1.20 (9H, $-C(CH_3)_3$), 1.11 (9H, $-C(CH_3)$, endgroup), 0.84.

^{13}C NMR (200 MHz, $CDCl_3$) δ ppm: 174.29 (1C, $>C{=}O$), 80.46 (1C, $-C(CH_3)_3$), 42.43 and 42.02 (1C, $-CH_2-$), 37.48 and 36.08 (1C, $-CH-$), 28.18 (3C, $-C(CH_3)_3$).

FT-IR (solid, ATR) cm^{-1}: 2997 (w), 2977 (w, $-CH_3$), 2932 (w), 2875 (w, $-CH_3$), 1723 (s, $>C{=}O$), 1479 (w, $-CH_3$), 1448 (w), 1392 (m), 1366 (m, $-CH_3$), 1335 (w), 1254 (m, $>C{=}O$), 1142 (s, $-COOR$), 1034 (w), 909 (w), 844 (m), 811 (w), 751 (w).

2.3. Synthesis of starlike poly(tert-butyl acrylate)-block-polystyrene, (ptBA-b-PS)$_4$

Starlike poly(*tert*-butyl acrylate) macroinitiator (8.00 g, 0.30 mmol) was dissolved in styrene monomer (50 mL, 45.5 g, 0.45 mol) in a dry Schlenk tube. CuBr (0.18 g, 1.3 mmol) and PMDETA (265 μL, 0.22 g, 1.3 mmol) were added and the solution was degassed by three freeze–thaw cycles under high vacuum. The polymerization was conducted under nitrogen atmosphere at 110 °C for 17 min, after which it was terminated by immersing the tube into liquid nitrogen. The polymer was precipitated in 1:1 water–methanol solution and dried under vacuum at room temperature. The molar mass of the block copolymer M_n(SEC) = 29,000 g/mol and the polydispersity was 1.16. The block copolymer was further purified by fractionation in MeOH at −18 °C, in which the soluble fractions were collected. The molar mass of the combined fractions determined by SEC was 30,300 g/mol and the polydispersity was 1.15. The polystyrene content of the combined fractions was 8.1 mol%, giving M_n(NMR) = 30,100 g/mol.

^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 7.11 and 6.63 (5H, Ar), 3.94 (br, 8H, $-CH_2-$, initiator), 3.25 (br, 4H, $-CH_2O-$, initiator), 2.24 (1H, $-CH-$, p*t*BA), 1.81 and 1.75 (1H, $-CH-$, PS, and 4H, $-CH_2-$, p*t*BA and PS), 1.49 and 1.25 (9H, $-C(CH_3)_3$), 1.11 (9H, $-C(CH_3)_3$, endgroup), 0.85.

^{13}C NMR (200 MHz, $CDCl_3$) δ ppm: 172.29 (1C, $>C{=}O$), 145.32 (1C, Ar), 128.10 (2C, Ar), 125.78 (1C, Ar), 80.46 (1C, $-C(CH_3)_3$), 42.44 and 42.00 (2C, $-CH_2-$, p*t*BA and PS), 40.56 (1C, $-CH-$, PS), 37.50 and 36.07 (1C, $-CH-$, p*t*BA), 28.18 (3C, $-C(CH_3)_3$).

FT-IR (solid, ATR) cm^{-1}: 3002 (w), 2977 (w, $-CH_3$), 2932 (w), 2875 (w, $-CH_3$), 1724 (s, $>C{=}O$), 1479 (w, $-CH_3$), 1451 (w), 1392 (m), 1366 (m, $-CH_3$), 1335 (w), 1255 (m, $>C{=}O$), 1144 (s, $-COOR$), 1032 (w), 908 (w), 845 (m), 802 (w), 751 (w), 700 (w, Ar).