

Electrostatic self-assembly of thermally responsive zwitterionic poly(*N*-isopropylacrylamide) and poly(ethylene oxide) modified with ionic groups

Ana N. Nedelcheva^a, Christo P. Novakov^a, Stojan M. Miloshev^b, Iliyana V. Berlinova^{a,*}

^a*Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

^b*University of Chemical Technology and Metallurgy, Sofia 1700, Bulgaria*

Received 16 August 2004; received in revised form 10 December 2004; accepted 10 January 2005

Available online 25 January 2005

Abstract

The electrostatic self-assembly of thermally responsive copolymers of *N*-isopropylacrylamide (NIPAM) containing up to 10 mol% of the sulfobetaine monomer 3-[*N*-(3-methacrylamidopropyl)-*N,N*-dimethyl]ammonio propane sulfonate (SPP) and poly(ethylene oxide) modified with terminal cationic or anionic groups (IMPEO) was studied in methanol and aqueous solutions by static light scattering, turbidimetry, viscometry, and rheological measurements. The formation of graft-like complexes at stoichiometric dipole–ion ratio and their self-association was detected in the dilute and semidilute regime at temperatures below and above the lower critical solution temperature (LCST). The ability of the graft-like complexes to associate below the LCST depended on the sulfobetaine content of the copolymers, the functionality of IMPEO, and the polymer concentration. The effect of the IMPEO terminal group on the solution behavior of the graft-like complexes was less pronounced. With increasing temperature their semidilute aqueous solutions form gels, stable over a wide temperature range.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Thermally responsive sulfobetaine copolymers; Electrostatic self-assembly; Graft-like complexes

1. Introduction

An ongoing challenge in polymer chemistry is the construction of advanced polymer architectures. The approaches to the creation of novel structures are distinguished by the modes of binding the components, either through covalent fixation, or by means of hydrophobic, hydrogen bonding, or electrostatic self-assembly. Instead of performing complicated chemical modifications, attractive intermolecular interactions have been triggered by changes in temperature, pH, ionic strength, or by addition of surfactants and functional polymers to yield systems stable under certain conditions [1–3]. The continuing interest in such environmentally responsive structures, also known as smart systems, stems from their potential application as

drug delivery systems, chemical separators, sensors, and catalysts.

One of the most studied responsive polymers, used as a component of smart systems, is the thermally responsive poly(*N*-isopropylacrylamide) (PNIPAM). PNIPAM exhibits a well-defined LCST in water at about 32 °C [4,5]. It is commonly accepted that the phase transition is a result of changes in the balance between the hydrophobic interactions and hydrogen bonding [6]. This is a two-stage process involving an intramolecular coil collapse followed by aggregation and precipitation from solution [7]. To prevent aggregation of the polymer chains during the coil-to-globule transition a small amount of surfactant that interacts with the polymer chain can be added [8]. The surfactant binding is associated with the hydrophobic nature of the polymer that changes with temperature. The pronounced hydrophobic character of PNIPAM even at 25 °C made possible the formation of mixed aggregates between PNIPAM and hydrophobically modified

* Corresponding author. Tel.: +359 2 979 6335; fax: +359 2 870 0309.
E-mail address: ivberlin@polymer.bas.bg (I.V. Berlinova).

poly(sodium acrylate) [9]. In our previous paper, we have shown that in semi-dilute aqueous mixtures of PNIPAM and fluorocarbon modified PEO the increase in temperature induces hydrogel formation due to hydrophobic interactions between the fluorocarbon groups and PNIPAM at temperatures close to its LCST [10]. Increasing temperature stabilizes hydrogen-bonding complexes between PNIPAM and poly(acrylic acid) also due to hydrophobic interaction [11].

PNIPAM self-assembly can be modulated by synthesis of copolymers containing functional groups or blocks prone to specific interactions. Depending on their nature multi-responsive systems that show complex phase transition behavior can be created. The introduction of charged groups into the PNIPAM chain affects its LCST and prevents the coagulation of the colloidal particles formed above the LCST [12–14]. At 6–7 mol% incorporation, a cationic monomer does not affect the LCST of PNIPAM, a carboxybetaine monomer raises it to 43 °C, while the negatively charged copolymer does not exhibit phase transition up to 90 °C [15]. The structure of the aggregated species depends on the degree of ionization of the comonomer [16]. Positively or negatively charged copolymers based on PNIPAM can interact with surfactants or hydrophobically modified polyelectrolytes both through electrostatic attraction and hydrophobic association [17–19].

An interesting class of multi-responsive systems is based on polymers containing zwitterionic moieties. While polymers containing cationic or anionic groups exhibit an electrostatic repulsion, those with zwitterionic groups exhibit electrostatic dipole–dipole association [20–22]. Common properties of poly(sulfobetaines) are the upper critical solution temperature (UCST), the preferential binding of the zwitterionic groups to ‘soft’ cations and anions, and the increase in viscosity with increasing salt concentration, known as ‘antipolyelectrolyte’ effect [20,22–25]. In aqueous salt solutions, used for screening the electrostatic interactions, diblock copolymers comprising polymethacrylate and polysulfobetaine blocks formed micelles stabilized by hydrophilic polybetaine chains [26]. Thermosensitive hydrogels prepared from NIPAM and sulfobetaine monomers revealed antipolyelectrolyte swelling in concentrated salt solutions [27,28]. Laschewsky et al. prepared block copolymers from NIPAM and SPP that reveal double thermoresponsivity [29]. Since the blocks exhibit LCST and UCST, respectively, and opposite response to salt addition it was possible to switch from one type of self-assembly to another by changing either the temperature or the ionic strength [29,30].

The alternative approach to the development of polymer architectures similar to those of block and graft copolymers by employing specific interactions between unlike polymer chains has been explored both in blends and solutions [31–34]. In selective solvents these complexes form micelle-like

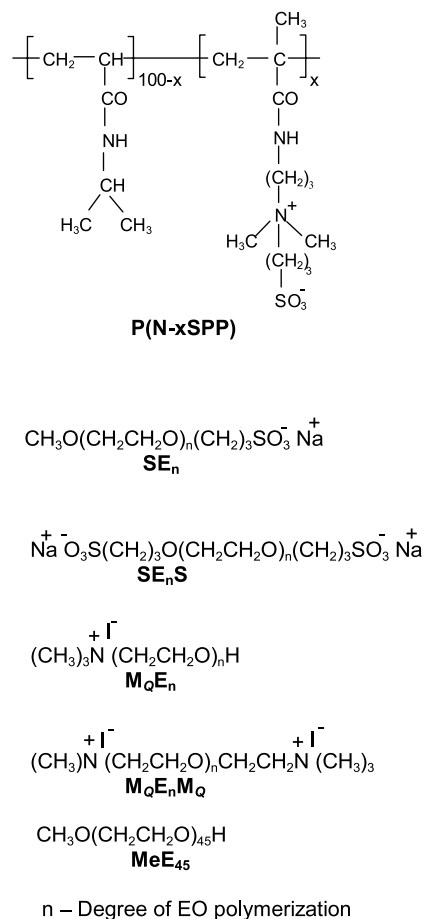
structures, which core and corona are linked by specific interactions rather than by covalent bonds [35].

The aim of the work was to study the ability of PNIPAM copolymers containing up to 10 mol% sulfobetaine groups to form graft-like complexes with PEO bearing terminal charged groups. The structure and abbreviations of the polymers used in this work are shown in Scheme 1. The attractive interactions between the zwitterionic groups of the main chain and the terminal cationic or anionic groups of PEO can yield charged complexes of highly variable structure, namely the number and nature of the charged groups per chain. They were characterized in terms of their behavior in methanol and aqueous solutions in the dilute and semidilute regime, and the phase transition upon heating.

2. Experimental

2.1. Materials

The reagents were purchased from Aldrich. NIPAM was recrystallized from a 65:35 (v/v) mixture of hexane and benzene. Ethylene oxide (EO) and methyl iodide were distilled. *N,N*-dimethylaminoethanol was distilled under



Scheme 1. Polymers structure and abbreviations.

reduced pressure. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Tetrahydrofuran (THF) was refluxed over sodium–potassium alloy and distilled. All other reagents and α -methoxypoly(oxyethylene) 2000 (MeE₄₅) were used as received.

2.2. Synthesis of monomers and polymers

2.2.1. 3-[N-(3-Methacrylamidopropyl)-N,N-dimethyl]ammoniopropane sulfonate (SPP)

SPP was obtained from N-[3-(Dimethylamino)propyl]-methacrylamide and 1,3-propane sultone in acetonitrile according to the procedure given by Lee et al. [36].

2.2.2. Poly(N-xSPP)

Copolymers of NIPAM and SPP were prepared by radical polymerization in methanol by varying the mole fraction of SPP in the feed. The NIPAM concentration was 1.5 mol l⁻¹ and the SPP feed content (x) was 1, 3, 5, or 10 mol%. The initiator was AIBN (0.1 or 0.2 mol%). The copolymerization was performed at 50 °C for 2 days in ampoules sealed under vacuum after utilization of freeze-thaw technique. The solution was precipitated into diethyl ether. The composition of the copolymers was estimated by ¹H NMR in D₂O from the relative peak area of the methine proton resonance of the isopropyl groups at δ =3.78 ppm and that of (CH₃)₂N⁺ proton resonance of the sulfobetaine unit at δ =3.04 ppm. The content of SPP in the copolymer, determined by ¹H NMR, was equal to its content in the feed.

2.2.3. Poly(ethylene oxide) modified with ionic groups (IMPEO)

2.2.3.1. α -(2-Trimethylammonioethyl)poly(oxyethylene) (M_QE_n). The synthesis was performed in two successive steps: anionic polymerization of EO initiated by potassium alkoxide of dimethylaminoethanol to obtain α -(2-dimethylaminoethyl)poly(oxyethylene), and its quaternization with methyl iodide as previously described [37].

2.2.3.2. α -(2-Trimethylammonioethyl)- ω -trimethylammonio poly(oxyethylene) (M_QE_nM_Q). M_QE_nM_Q was prepared by quaternization of trimethylamine with α -(2-bromoethyl)- ω -bromopoly(oxyethylene) according to the procedure given by Bückmann et al. [38]. The process was monitored by ¹H NMR in D₂O by the disappearance of the signal due to -CH₂Br protons at δ =3.74 ppm and appearance of a signal at δ =3.04 ppm due to (CH₃)₃N⁺ protons.

2.2.3.3. 3-[N-[2-(α -Hydroxypoly(oxyethylene)ethyl]-N,N-dimethyl]ammoniopropane sulfonate (SBE_n). The synthetic procedure was the same as the one for M_QE_n, except that the quaternizing agent was 1,3-propane sultone.

2.2.3.4. 3-[α -Methoxypoly(oxyethylene)propane sulfonate sodium salt (SE₄₅). MeE₄₅ (10 g, 5 mmol OH) was dried by

azeotropic distillation with toluene and dissolved in 55 ml of THF. NaH (0.19 g, 7.5 mmol) was added to the stirred polymer solution under nitrogen and the mixture was maintained at 60 °C overnight. 1,3-Propane sultone (1.0 g, 8.2 mmol) was added and the mixture was stirred at 60 °C for 3 days. The mixture was filtered, concentrated and precipitated into diethyl ether. The completeness of the reaction was evidenced by the ¹H NMR spectrum of the product in D₂O. The ratio of the intensities of CH₃O protons at δ =3.3 ppm and CH₂-SO₃⁻ protons at δ =2.83 ppm was 3:2.

2.2.3.5. 3-[α -(3-Sulfonatopropyl)oxypoly(oxyethylene)]propane sulfonate disodium salt (SE_nS). The synthetic procedure was the same as the one for SE_n, except that bifunctional PEG-2000 or PEG-4000 were modified with 1,3-propane sultone. The completeness of the reaction was evidenced by the ¹H NMR spectra of the products in D₂O. The ratio of the intensities of the oxyethylene protons at δ =3.51 ppm and CH₂-SO₃⁻ protons at δ =2.83 ppm was equal to the predicted one.

2.3. Complexes between poly(N-xSPP) and IMPEO

All complexes were prepared at stoichiometric ion–dipole ratio. The solutions of the complexes were kept at room temperature for 2 days before measurements.

2.4. Measurements

2.4.1. Measurement of the LCST

The LCST was determined by UV–Vis spectroscopy. The copolymer solutions were poured into 1 cm cell. The cell holder was heated at a rate of 0.1 °C min⁻¹. The phase transition temperature was determined by monitoring the transmittance at 500 nm. The LCST was defined as the temperature at which the transmittance becomes 50% of its initial value at 20 °C.

2.4.2. SEC measurements

SEC measurements were performed on a system (Waters) consisting of M510 pump, U6K injector, refractometer 410, and a set of CATSEC Å (Eprogen Inc. and Eichrom Techn. Inc. USA) columns 100 and 300. The mobile phase was 0.2 M CH₃COONa, 0.4 M CH₃COOH, and 2% ethylene glycol eluting at a flow rate of 0.5 ml min⁻¹ at 30 °C.

2.4.3. Light scattering measurements

Static light scattering measurements (SLS) were carried out on a multi-angle laser light scattering detector DAWN DSP Laser Photometer (Wyatt Technology Corp.) equipped with an argon laser emitting at a wavelength of 632.8 nm. Analyses were performed in a microbatch mode at 25 °C. The weight average molar mass, the radius of gyration, R_g, and the second virial coefficient, A₂, were obtained from the

Berry plots processed with Astra (Wyatt Corp.) software. The specific refractive index increments at 25 °C were measured on an Optilab 903 Wyatt interferometric refractometer and determined by the Wyatt dn/dc software. The dn/dc values for the copolymers and for the complexes are listed in Tables 1–3.

The stock solutions for the light scattering measurements of P(N-*x*SPP) were prepared at concentration of $1 \times 10^{-3} \text{ g ml}^{-1}$, while those of the complexes at total concentration of $1 \times 10^{-2} \text{ g ml}^{-1}$. They were purified of dust using filter of 0.2 μm pore size (PVDF filter) and diluted with filtered solvent.

2.4.4. Viscosity measurements

Solution viscosities of the individual polymers and of polymer mixtures were determined with an Ubbelohde viscometer at 25 °C. The total polymer concentration ranged from 0.2 to 1 g dl^{-1} .

2.4.5. Rheology measurements

Rheology measurements were performed on a Rheometer RheoStress 600 (Thermo Electron Corp.) in the plate/plate geometry (diameter 60 mm). The viscoelastic properties of P(N-*x*SPP) and their complexes with IMPEO were measured in both steady state and dynamic mode in the temperature range from 25 to 70 °C. The storage modulus (G') and the loss modulus (G'') were measured as a function of the angular frequency, ω ranging from 0.1 to 100 rad s^{-1} . The strain was 0.01.

For the rheological measurements the aqueous solutions of the complexes were prepared at a constant concentration of P(N-*x*SPP) equal to 5 wt%.

3. Results and discussion

3.1. Characterization of the copolymers P(N-*x*SPP)

The incorporation of sulfobetaine units into the PNIPAM chain affects its properties, which can be readily found by viscosity, optical and light scattering measurements. P(N-*x*SPP) copolymers are soluble in methanol and water at room temperature. However, the aqueous solutions become

turbid when heated above their LCST. Copolymerization of NIPAM with SPP shifts the LCST to higher temperatures in line with the more hydrophilic nature of the SPP units (Table 1).

It is well known that zwitterionic groups associate intra- or intermolecularly depending on the concentration and the copolymer composition. Salt addition has been shown to disrupt the ionic cross-links and promote chain expansion [24,39]. Studying the effect of the composition on the solution behavior of water-soluble sulfobetaine containing polymers McCormick and Salazar observed a decrease in the second virial coefficient with increasing sulfobetaine content [40]. In pure aqueous solutions, the polysulfobetaines exhibit negative A_2 values, which increase and change to positive values upon addition of salt [20].

The dilute solution properties of P(N-*x*SPP) were studied by SLS measurements on water and methanol solutions in the concentration range from 5×10^{-5} to $1.0 \times 10^{-3} \text{ g ml}^{-1}$. Methanol is a better solvent for PNIPAM than water. Although A_2 for PNIPAM in both methanol and water is positive, its value is larger in methanol [41].

Tables 1 and 2 show the apparent molecular weights, M_{app} , and the second virial coefficients for P(N-*x*SPP) in water and methanol at 25 °C as determined by Berry plots [Fig. 1(a)]. The values of M_{app} for the copolymers in aqueous solution are larger than those in methanol. The values for A_2 differ in sign being negative in water and positive in methanol. Large R_g values were determined in aqueous solutions. These results suggest that in aqueous solutions attractive intermolecular interactions result in the formation of large aggregates. It is plausible that the values for M_{app} and A_2 listed in Table 1 indicate the contribution from both individual chains and multichain aggregates.

Viscosity measurements are usually used to discriminate inter—from intra-molecular interactions. The data for the intrinsic viscosities of P(N-*x*SPP) in salt-free and 0.5 M KSCN solutions at 25 °C (shown in Table 1) can be rationalized in terms of simultaneous disruption of intra- and inter-chain electrostatic interactions upon salt addition. P(N-5SPP) and P(N-10SPP) display a substantial viscosity decrease with the addition of KSCN. This indicates that the likelihood for intermolecular interactions increases with the increase in the SPP content.

Table 1
Characteristics of P(N-*x*SPP) in aqueous solutions

Code	LCST °C	[η] (dl g^{-1}) ^a		SLS ^b			
		Salt-free	0.5 M KSCN	dn/dc	$M_{\text{app}} \times 10^{-5}$ (g mol^{-1})	$A_2 \times 10^3$ (mol ml g^{-2})	R_g (nm)
P(N-1SPP)	32.3	0.851	0.831				
P(N-2SPP)	34.8	0.96	0.95	0.201	3.0	−1.1	27
P(N-3SPP)	36.2	0.834	0.854	0.207	2.4	−1.4	56
P(N-5SPP)	52.1	0.98	0.74	0.207	2.5	−1.1	71
P(N-10SPP)	70.1	1.11	0.85	0.204	3.8	−1.8	94

^a Determined at 25 °C.

^b In the concentration range of 2×10^{-4} to $1 \times 10^{-3} \text{ g ml}^{-1}$ at 25 °C.

Table 2
Characteristics of P(N-xSPP) and their complexes with SE₄₅ in methanol at 25 °C

Code	Copolymer SLS			Complex SLS ^a			
	dn/dc	$M_{\text{app}} \times 10^{-5}$ (g mol ⁻¹)	$A_2 \times 10^3$ (mol ml g ⁻²)	dn/dc	$M_{\text{app}} \times 10^{-5}$ (g mol ⁻¹)	A_2 (mol ml g ⁻²)	R_g (nm)
P(N-2SPP)	0.24	0.7 ^b	1.3 ^b				
P(N-3SPP)	0.225	0.9 ^b	1.2 ^b	0.155	4.0	9.7×10^{-5}	54
P(N-5SPP)	0.187	2.9 ^c	1.2 ^c	0.143	6.0	1.0×10^{-4}	56
P(N-10SPP)	0.166	1.2 ^c	4.3 ^c	0.142	11.0	7.0×10^{-5}	77

^a In the concentration range of 1.0×10^{-3} to 1.0×10^{-2} g ml⁻¹.

^b In the concentration range of 1.0×10^{-4} to 1.0×10^{-3} g ml⁻¹.

^c In the concentration range of 5.0×10^{-5} to 4.0×10^{-4} g ml⁻¹.

The rheological behavior of P(N-xSPP) copolymers was compared with that of PNIPAM with molecular weight 1.5×10^5 . At temperatures below the LCST the 5 wt% aqueous solution of PNIPAM is a viscoelastic fluid exhibiting $G' < G''$. The dynamic moduli sharply increase close to the LCST and G' becomes larger than G'' . Further increase in temperature causes precipitation of the aggregated species.

The behavior of the copolymers at temperatures below the LCST depends on their sulfobetaine content. The solution properties of P(N-2SPP) are similar to those of PNIPAM below the LCST but quite different above the LCST. The increase in temperature above the LCST does not cause precipitation and the system exhibits storage modulus larger than the loss modulus.

Quite distinct is the behavior of P(N-xSPP) copolymers with SPP content $x \geq 3$ at temperatures below the LCST (Fig. 2). The value of the storage modulus is above that of the loss modulus indicating the formation of a temporary network due to dipole–dipole interactions. The increase in temperature induces shrinkage and aggregation of the PNIPAM entities which causes sharp increase in the dynamic moduli. In contrast to the case of the PNIPAM solution no phase separation occurs at temperatures above the LCST probably due to the stabilization of the aggregates by the hydrophilic sulfobetaine units located on their surface.

3.2. Complex formation between P(N-xSPP) and IMPEO

In mixtures of P(N-xSPP) with IMPEO dipole–ion interactions between the zwitterionic groups randomly distributed along the PNIPAM chain and the terminal ionic groups of IMPEO can form positively or negatively

charged graft-like complexes. The design of such structures is a novel approach to the development of associative polymers that respond to environmental stimuli.

3.2.1. Thermal phase transition

Fig. 3(a) shows the light transmittance versus the temperature plots for 1 wt% aqueous solution of P(N-2SPP) as well as for its mixtures either with IMPEOs or with MeE₄₅. The phase transition temperatures of the aqueous mixtures are higher than that of the pure P(N-2SPP) solution. The increase in the LCST when P(N-2SPP) is mixed with the nonionic MeE₄₅ suggests an interaction between the polymers that makes the sulfobetaine containing polymer more hydrophilic. The enhancement of the LCST is more pronounced when P(N-2SPP) is mixed with IMPEO. In such mixtures, the formation of graft-like complexes due to dipole–ion interactions can be proposed. Actually, similar shift of the LCST to higher temperatures has been observed upon grafting of PEO chains onto PNIPAM backbone [42].

The effect of concentration on the phase transition temperature of the graft-like complexes is presented in Fig. 3(b). 1 or 5 wt% solutions of P(N-3SPP) were mixed with SE₄₅ at 1:1 dipole/ion ratio. No shifting of the LCST of P(N-3SPP) was observed in this concentration range. On the contrary, the phase transition temperature of the mixture is concentration-dependent and shifts to lower temperatures with increasing concentration. Actually, the same phenomenon has been observed in the case of PNIPAM-g-PEO copolymers [42]. It has been argued that in concentrated solutions of PNIPAM-g-PEO large core-shell particles are formed at temperatures below the LCST and the high density of PNIPAM in the core facilitates its thermally-induced transition.

Table 3
Light scattering data of complexes between P(N-5SPP) and IMPEO in water at 28 °C

Polymers		SLS ^a			
Copolymer	IMPEO	dn/dc	$M_{\text{app}} \times 10^{-6}$ (g mol ⁻¹)	A_2 (mol ml g ⁻²)	R_g (nm)
P(N-5SPP)	M _Q E ₉₀ M _Q	0.186	6.0	-1.0×10^{-5}	140
P(N-5SPP)	SE ₉₀ S	0.188	4.6	6.1×10^{-4}	144

^a In the concentration range of 2.0×10^{-4} to 3.0×10^{-3} g ml⁻¹.

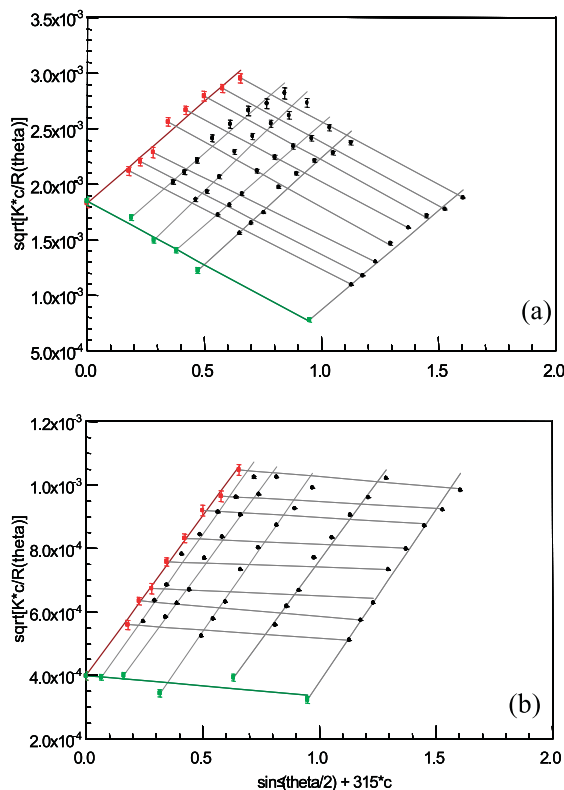


Fig. 1. Berry plot for P(N-5SPP): (a) in pure aqueous solution in the concentration range of 2.0×10^{-4} to 1.0×10^{-3} g ml $^{-1}$ and (b) in aqueous mixture with $M_QE_{90}M_Q$ at 1:1 dipole/ion ratio in the concentration range of 2.0×10^{-4} to 3.0×10^{-3} g ml $^{-1}$.

3.2.2. Static light scattering measurements

SLS measurements of methanol and aqueous mixtures of P(N-xSPP) with IMPEO provide evidence for complex formation at temperatures below the LCST (Tables 2 and 3).

The SLS data for the complexes formed in aqueous mixtures of P(N-5SPP) with either $SE_{90}S$ or $M_QE_{90}M_Q$ [(Fig. 1(b))] are summarized in Table 3. The square reciprocal reduced scattered intensity at zero angle, (Kc/R_0)

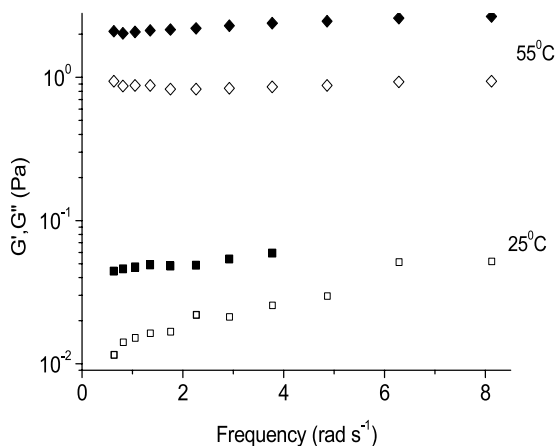


Fig. 2. Frequency dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) for 5 wt% aqueous solution of P(N-3SPP) at 25 and 55 °C.

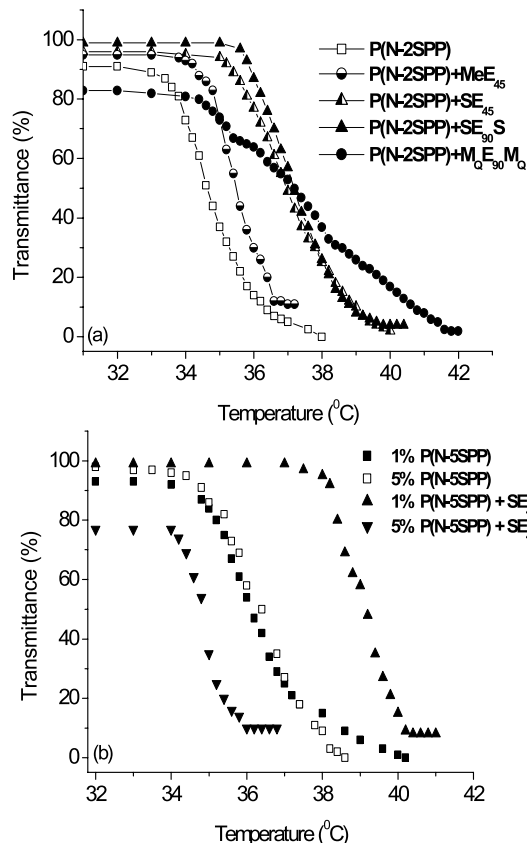


Fig. 3. Temperature dependence of the transmittance at 500 nm for: (a) 1 wt% P(N-2SPP) aqueous solution, and its mixtures with the nonionic MeE_{45} , and with IMPEO, and (b) 1 and 5 wt% P(N-5SPP) aqueous solutions and their mixtures with SE_{45} at 1:1 dipole/ion ratio.

$R_0)^{1/2}$, varied linearly with concentration, which implies that the complexes are stable on dilution. The complexation of P(N-5SPP) with telechelic IMPEOs could be either intra- or interchain. It is the interchain complexation that yields large nanoparticles stabilized by both PEO chains and charged groups located on their surface.

3.2.3. Viscometric studies and SEC analysis

Viscometry is an effective method to establish complexation in mixed polymer solutions. The effect of the intermolecular interactions on the solution viscosities of mixtures of P(N-xSPP) with IMPEO was studied with respect to the nature of the PEO terminal groups. The total polymer concentration of the mixed solutions was 1 g dl $^{-1}$, which was lower than the overlap concentration of P(N-xSPP) ($c^* \approx 1/[\eta]$). In this regime, if there were no specific interactions between the unlike polymer chains, the viscosity of the solution would follow the additivity law.

Fig. 4 shows the concentration dependence of the reduced viscosity of the aqueous mixture of P(N-5SPP) with M_QE_{45} . The viscosities of the pure components and those calculated for a mixture, which obeys the additivity law, are also included. The reduced viscosities of the mixture highly deviate from the calculated ones. This

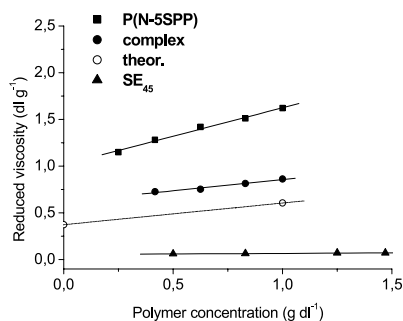


Fig. 4. Concentration dependence of the reduced viscosity in deionized water at 25 °C of P(N-5SPP), $M_{QE_{45}}$, mixture of P(N-5SPP) with $M_{QE_{45}}$, and a theoretical curve for the mixture calculated according to the additivity law.

behavior is common for most of our systems, whatever the nature of the PEO terminal group. It can be considered as an indication that intermolecular specific interactions result in the formation of graft-like complexes, which hydrodynamic volume differs from those of the component polymers.

The complex formation in an aqueous mixture of P(N-5SPP) with $M_{QE_{45}}$ was monitored by SEC analysis under conditions suitable for elution of cationic polymers. Fig. 5(a) shows the SEC traces of the component polymers while Fig. 5(b) illustrates the elution of the complex formed in the mixture kept for 24 h at room temperature. The complex has a larger elution volume than that of the parent P(N-5SPP). Since in SEC experiments the factor determining the retention of the macromolecules is their hydrodynamic volume, one can assume that the graft-like complex exhibits a compact conformation. This suggestion is in agreement with the viscosity data for the same complex shown in Fig. 4. Recently, Virtanen and Tenhu have also established that increasing the number of PEO grafts makes the conformation of PNIPAM-*g*-PEO copolymers more compact [43].

3.2.4. Rheological properties of the complexes in semidilute regime

Rheological measurements performed on aqueous

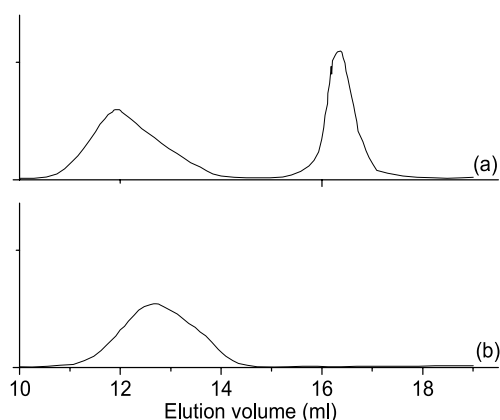


Fig. 5. SEC curves of: (a) P(N-5SPP) and $M_{QE_{45}}$ and (b) mixture of P(N-5SPP) and $M_{QE_{45}}$ kept for 24 h at room temperature.

mixtures of P(N-3SPP) or P(N-5SPP) with IMPEO provide evidence for complex formation between the component polymers.

Fig. 6 depicts the temperature dependence of the storage and loss moduli at 0.5 Hz for 5 wt% aqueous solution of P(N-3SPP) and for its mixture with SE_{45} . In the case of P(N-3SPP), the value of the storage modulus is always above that of the loss modulus indicating the formation of temporary networks at temperatures below and above the LCST. The addition of SE_{45} to the solution of the same copolymer changes its rheological properties. At temperatures lower than 40 °C the value of the storage modulus for the mixture is below that of the loss modulus. The dynamic moduli, especially G' , sharply increase at about 45 °C, and G' exceeds G'' . This observation indicates that in the mixture of P(N-3SPP) with SE_{45} the formation of a network occurs just above the LCST. Such behavior appeared to be common for the complexes between P(N-*x*SPP) and IMPEO bearing one terminal ionic group. Measurements were also performed on mixtures of P(N-3SPP) or P(N-5SPP) with PEO bearing a terminal sulfobetaine group (SBE_{45}). Although the interacting groups were zwitterionic the temperature dependence of the dynamic moduli was similar to that of the complexes formed between P(N-*x*SPP) and semitelechelic IMPEOs. The results suggest that the rheological properties of these complexes are governed rather by the presence of grafted PEO chains than of charged groups. The fact that at temperatures below the LCST the value of G' for the mixture is smaller than that of G'' can be explained by disruption of the intermolecular dipole–dipole cross-links upon complex formation.

Substituting the telechelic SE_{90S} for the semitelechelic SE_{45} has a pronounced effect on the rheological behavior of its mixture with P(N-5SPP). Fig. 7(b) shows that at temperatures below the LCST the value of G' for the complex is above that of G'' and much larger than the value of G' for the pure copolymer solution [shown in Fig. 7(a)]. This fact can be rationalized by the assumption that the

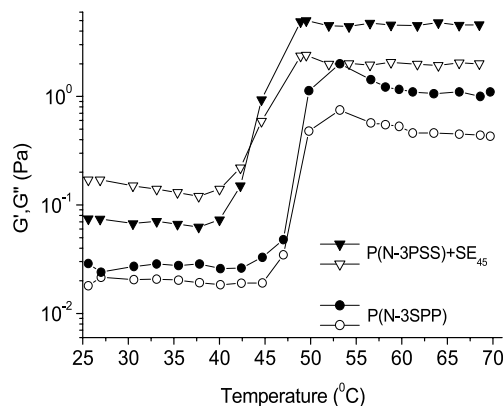


Fig. 6. Temperature dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) at 0.5 Hz for 5 wt% aqueous solutions of: P(N-3SPP), and mixture of P(N-3SPP) with SE_{45} .

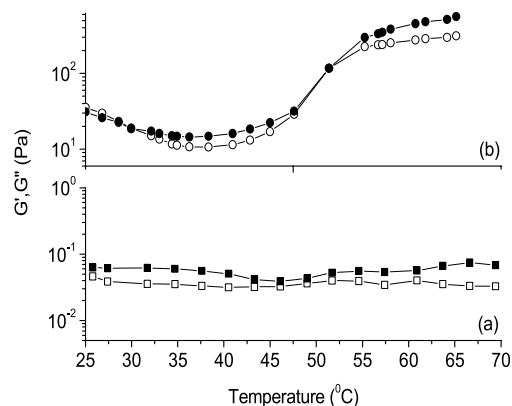


Fig. 7. Temperature dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) at 0.5 Hz for 5 wt% aqueous solutions of: (a) P(N-5SPP) and (b) mixture of P(N-5SPP) with SE₉₀S.

complex formation between P(N-5SPP) and SE₉₀S results in an increase in the number density of the elastically effective chains.

The temperature-induced changes in the dynamic moduli are in line with changes in the steady shear viscosity of the respective mixed solutions. The viscosity of 5 wt% mixtures of P(N-5SPP) either with SE₄₅ or with SE₉₀S indicates a pronounced shear thickening at temperatures below 50 °C. Fig. 8(a) shows that the mixture of P(N-5SPP) with SE₉₀S exhibits a strong shear thickening at a low shear rate followed by shear thinning. The shear thickening is usually considered as a result of shear-induced modification of the sizes of the aggregates existing at rest. At a certain shear rate, the shear forces are strong enough to extend the aggregated structures and to cause a disruption of intra-chain cross-links. The associating groups released can form intermolecular associations, leading to viscosity increase.

At high temperatures the collapsed and aggregated species are stabilized not only by the grafted PEO chains but also by the charges located on their surface. Their repulsion prevents further aggregation and precipitation does not occur over broad temperature range.

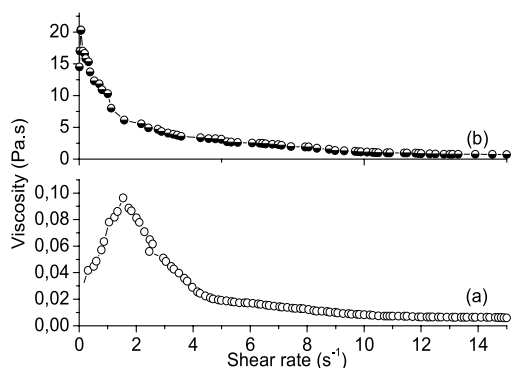


Fig. 8. Shear rate dependence of viscosity for 5 wt% aqueous mixture of P(N-5SPP) with SE₉₀S at temperatures: (a) 45 °C, and (b) 60 °C.

4. Conclusions

A new approach for the preparation of graft-like complexes consisting of a thermosensitive backbone and PEO side chains was described. The complexes were formed by dipole–ion interactions between sulfobetaine containing PNIPAM copolymers and PEO bearing either cationic or anionic terminal groups. Optical, static light scattering, viscosity, and rheological measurements gave evidence for complex formation in the dilute and semidilute regime.

In semidilute aqueous solutions of sulfobetaine containing PNIPAM copolymers, the addition of PEO bearing terminal cationic or anionic groups caused rupture of the zwitterionic dipole–dipole cross-links. The rheological properties of the complexes between P(N-*x*SPP) and IMPEOs at temperatures below the LCST depended on the functionality of IMPEO. At temperatures above the LCST the complexes formed gels stable over a wide temperature range.

Acknowledgements

Support of this research by the National Science Fund, Bulgarian Ministry of Education and Science through Project X-1303 is gratefully acknowledged. We would like kindly to acknowledge Wyatt Technology Corporation (Santa Barbara, CA, USA) for the generous loan of the DAWN-DSP/Optilab light scattering system. We also acknowledge Alexander von Humboldt Foundation for the financial support for purchasing Rheometer RheoStress 600.

References

- [1] Hashidzume A, Noda T, Morishima Y. In: McCormick CL, editor. Stimuli-responsive water soluble and amphiphilic polymers. ACS symposium series 780. Washington, DC: American Chemical Society; 2000. p. 14–37.
- [2] Hoffman AS. *Macromol Symp* 1996;98:645–64.
- [3] Tezuka Y. *J Polym Sci, Part A: Polym Chem* 2003;41:2905–17.
- [4] Heskins M, Guillet JE. *J Macromol Sci Chem* 1968;A2:1441–5.
- [5] Fudjishige S, Kubota K, Ando I. *J Phys Chem* 1989;93:3311–3.
- [6] Winnik FM. *Macromolecules* 1990;23:233–42.
- [7] Wang X, Qiu X, Wu C. *Macromolecules* 1998;31:2972–6.
- [8] Meewes M, Rička J, de Silva M, Nyffenegger R, Binkert Th. *Macromoleculen* 1991;24:5811–6.
- [9] Bokias G, Hourdet D, Iliopoulos I, Staikos G, Audebert R. *Macromolecules* 1997;30:8293–7.
- [10] Berlinova IV, Nedelcheva AN, Samichkov V, Ivanov Ya. *Polymer* 2002;43:7243–50.
- [11] Staikos G, Karayanni K, Mylonas Y. *Macromol Chem Phys* 1997;198: 2905–15.
- [12] Feil H, Bae YH, Feijen J, Kim SW. *Macromolecules* 1993;26: 2496–500.
- [13] Deng Y, Pelton R. *Macromolecules* 1995;28:4617–21.
- [14] Qiu X, Kwan CMS, Wu C. *Macromolecules* 1997;30:6090–4.

- [15] Hahn M, Görnitz E, Dautzenberg H. *Macromolecules* 1998;31:5616–23.
- [16] Jean B, Bokias G, Lee LT, Iliopoulos I, Cabane B. *Colloid Polym Sci* 2002;280:908–14.
- [17] Matsukata M, Hirata M, Gong JP, Osada Y, Sakurai Y, Okano T. *Colloid Polym Sci* 1998;276:11–18.
- [18] Bokias G, Mylonas Y. *Macromolecules* 2001;34:885–9.
- [19] Liaw D-J, Huang C-C, Wang T-S. *Polymer* 2002;43:6221–9.
- [20] Schulz DN, Peiffer DG, Agarwal PK, Larabee J, Kaladas JJ, Soni L, Handwerker B, Garner RT. *Polymer* 1986;27:1734–42.
- [21] Koňák Č, Rathi RC, Kopečková P, Kopeček J. *Macromolecules* 1994;27:1992–6.
- [22] McCormick CL, Salazar LC. *Polymer* 1992;33:4617–24.
- [23] Salamone JC, Volksen W, Israel SC, Olson AP, Raia DC. *Polymer* 1977;18:1058–62.
- [24] Monroy Soto VM, Galin JC. *Polymer* 1984;25:254–62.
- [25] Lee WF, Tsai CC. *Polymer* 1995;36:357–64.
- [26] Lowe AB, Billingham NC, Armes SP. *Macromolecules* 1999;32:2141–8.
- [27] Lee WF, Yeh PL. *J Appl Polym Sci* 1999;74:2170–80.
- [28] Xue W, Champ S, Huglin MB. *Eur Polym J* 2001;37:869–75.
- [29] Arotçaréna M, Heise B, Ishaya S, Laschewsky A. *J Am Chem Soc* 2002;124:3787–93.
- [30] Virtanen J, Arotçaréna M, Heise B, Ishaya S, Laschewsky A, Tenhu H. *Langmuir* 2002;18:5360–5.
- [31] Horion J, Jérôme R, Teyssié Ph. *J Polym Sci, Part C* 1986;24:69–76.
- [32] Pispas S, Floudas G, Pakula T, Lieser G, Sakellariou S, Hadjichristidis N. *Macromolecules* 2003;36:759–63.
- [33] Weiss RA, Sasongko S, Jérôme R. *Macromolecules* 1991;24:2271–7.
- [34] Liu S, Zhang G, Jiang M. *Polymer* 1999;40:5449–53.
- [35] Liu S, Jiang M, Liang H, Wu C. *Polymer* 2000;41:8697–702.
- [36] Lee WF, Tsai CC. *Polymer* 1994;35:2210–7.
- [37] Berlinova IV, Dimitrov IV, Vladimirov NG. *Polymer* 2000;41:6431–8.
- [38] Bückmann AF, Morr M, Johansson G. *Makromol Chem* 1981;182:1379–84.
- [39] Itoh Y, Abe K, Senoh S. *Makromol Chem* 1986;187:1691–7.
- [40] McCormick CL, Salazar LC. *Polymer* 1992;33:4617–24.
- [41] Chiantore O, Guaita M, Trossarelli L. *Makromol Chem* 1979;180:969–73.
- [42] Virtanen J, Baron C, Tenhu H. *Macromolecules* 2000;33:336–41.
- [43] Virtanen J, Tenhu H. *Macromolecules* 2000;33:5970–5.