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Thermally induced hydrogel formation in aqueous solutions of poly(*N*-isopropylacrylamide) and fluorocarbon-modified poly(oxyethylene)s

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Abstract

A number of perfluorooctyl-modified poly(oxyethylene)s (F_QPEOs) of molar masses of approximately 2000 and 4000 were synthesised using a two-step procedure: (a) preparation of PEO precursors bearing tertiary amino groups (NPEOs) and (b) their quaternisation with perfluorooctyl iodide to obtain one-ended (F_QE_n), telechelic ($F_QE_nF_Q$) or PEO modified with a C_8F_{17}-group in the mid of the polyether chain ($E_nF_QE_n$). F_Q is abbreviation of the C_8F_{17}-group attached to a PEO chain (E_n) through a quaternary ammonium group. The aqueous solution properties of F_QPEOs were studied by viscosity measurements at 25 °C. The cationic charge affects the association ability of the F_Q group and the one-ended F_QE_n behaves like PEO modified with a C_6F_{13}-group through urethane linkage. Temperature induced interactions in aqueous mixtures of F_QPEOs with poly(*N*-isopropylacrylamide) (PNIPAM) were studied by turbidity and rheological measurements. In the semi-dilute regime, the aqueous polymer mixtures exhibit a large viscosity enhancement upon heating as soon as the temperature reaches 35 °C. In the range from 35 to 40 °C the mixtures of PNIPAM with F_QE_n and $E_{50}F_QE_{50}$ form gels with viscoelastic response. The solution of PNIPAM mixed with the telechelic $F_QE_{100}F_Q$ reveals shear-thickening at 35 and 40 °C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorocarbon-modified poly(oxyethylene)s; Poly(*N*-isopropylacrylamide); Thermally induced hydrophobic interaction

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1. Introduction

Specific molecular interactions, such as hydrogen bonding, hydrophobic, and ionic interactions lead to the formation of well-defined entities, known as supramolecules, that can further assemble to nanoscale structures. The supramolecular assembly, being very sensitive to external stimuli, provides access to environmentally responsive materials; able to change their properties by minute changes in temperature, light, electric field, pH, or ionic strength. Among the various types of associating structures, the hydrophobically interacting water-soluble polymers have attracted an increasing interest. Because of their unique rheological properties, they have found applications in paper manufacture, water treatment, oil production and cosmetic and pharmaceutical formulations [1–3]. Recently, a novel class of associative polymers has emerged whereby a polymer chain, which undergoes a thermally induced phase transition, acts as a hydrophobe. On this basis, Hourdet et al. [4,5] proposed the concept of the so-called thermo associative polymers. Above certain temperatures, their semi-dilute aqueous solutions can form reversible gels with significant elastic moduli.

PNIPAM is a temperature sensitive polymer, which undergoes phase transition at the lower critical solution temperature (LCST) due to changes in the balance of the hydrophobic and hydrophilic bonding states [6–9]. This is a two-stage process involving an intramolecular coil collapse upon heating followed by aggregation of the collapsed coils [8]. The ability of PNIPAM to act as a hydrophobic host above the LCST is of particular interest for its use as a carrier moiety, which releases the hydrophobic guest at lower temperatures [10]. However, such release is not complete and a part of the hydrophobic guest remains associated with the PNIPAM coils suggesting weak hydrophobic interactions below the LCST [11]. The occurance of strong hydrophobic interactions above the LCST is also evidenced by the rupture of the micellar type domains existing in the solutions of alkylated PNIPAM below the LCST and the formation of mixed aggregates of

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collapsed PNIPAM chains and hydrophobic alkyl groups [12–14].

Mixing PNIPAM with amphiphilic polymer chains is a promising approach to the design of smart PNIPAM based materials [15,16]. These materials reveal properties interesting for application in the high concentration regime, where the interparticle interactions are dominating. Even below the LCST, PNIPAM is able to associate with sodium dodecylsulfate [17,18] and hydrophobically modified poly (sodium acrylate) [15]. A remarkable viscosity enhancement and viscoelasticity are switched with temperature and they could be controlled by changes in the mixture composition and in the molecular characteristics of the interacting polymers. The thermothickening was observed close to the LCST, but it was lost when the temperature exceeded 40 °C due to phase separation. By introducing charges in the PNIPAM chain, the LCST was shifted to higher temperatures and the thickening ability of PNIPAM was observed in a wider temperature range [16].

Recently, a great attention has been paid to block and graft copolymers of PNIPAM and PEO [19–26]. These temperature responsive polymers form stable particles of core–shell structure above the phase transition temperature of the PNIPAM chain [19–21,24–26]. Their aggregation behaviour is determined by the competition between the intraparticle coil-to-globule transition and the interparticle interaction [21]. At low concentration, the intraparticle coil-to-globule transition could lead to a collapsed single chain globule stabilised by a PEO shell. At high concentrations, the interparticle aggregation may occur before the onset of the phase transition. The aggregation number and the size of the particles formed depend on the architecture of the copolymers and on the length of the blocks. Below the LCST, long PNIPAM chains densely grafted with PEO overlap and form an entangled network with uniform pores that reveal high DNA separation efficiency [23]. Concentrated solutions of PNIPAM-*b*-PEO turn into hydrogels with viscoelastic response above the LCST. In the physical network formed, the aggregated PNIPAM chains play the role of temporary network junctions [22].

We have shown [27] that graft copolymers comprising a PNIPAM backbone and PEO side chains end-functionalised with perfluorooctyl, sulfobetaine or trimethylammonium groups behave as associative polymers in dilute and semi-dilute regime. The copolymer with 0.1 mol% PEO bearing terminal perfluorooctyl groups shows the greatest viscosity enhancement at low shear rate and forms an elastic gel above the LCST. It was proposed that the soluble PEO chains bridge the mixed aggregates formed by collapsed PNIPAM chains and perfluorooctyl groups.

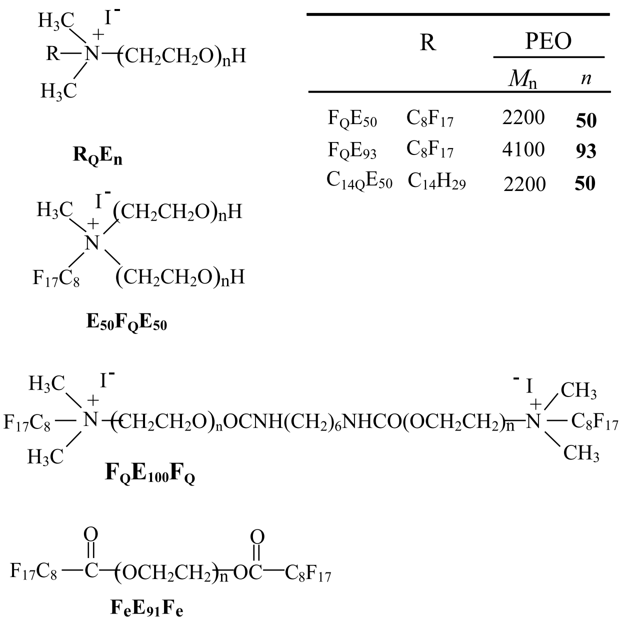
The high thickening ability of fluorocarbon modified water-soluble polymers is well established [28,29]. The hydrophobic association in fluorocarbon-modified PNIPAM is more pronounced than in the hydrocarbon substituted one and interchain association exists even in very dilute solutions [30,31]. PEOs end-capped with fluoroalkyl groups were used as model compounds to study how their associative behaviour is influenced by the length of the soluble chain and the size of the hydrophobic group [32–36]. To explain the viscosity enhancement in aqueous solutions of one-ended fluorocarbon-modified PEO, Hogen-Esch et al. [34] proposed intermolecular interactions between the fluorocarbon groups and the PEO chains. In semi-dilute regime, telechelic PEOs end-capped with fluorocarbon groups do not show shear-thickening in contrast to those bearing long alkyl hydrophobes [33,36].

In the present paper we report on the thermothickening behaviour of aqueous mixtures of PNIPAM and F_QPEOs. The objective of the work was to create networks by temperature induced hydrophobic interactions between these polymers in aqueous solution. Many parameters were varied, such as the length of the PNIPAM and the PEO chain, the location and number of the perfluorooctyl groups in the PEO chain, as well as the ratio of F_QPEO to PNIPAM chains in their mixed solutions. The solution properties of the synthesised F_QPEOs were also studied (Chart 1—structures and designation of perfluorooctyl-modified PEOs).

2. Experimental

2.1. Materials

The reagents were purchased from Aldrich. *N*-isopropylacrylamide (NIPAM) was recrystallised from a 65:35 (v/v) mixture of hexane and benzene. Ethylene oxide (EO) was distilled. *N*,*N*-dimethylethanolamine, *N*-methyldiethanolamine and hexamethylene diisocyanate (HMDI) were distilled under reduced pressure prior to use. Azobis(isobutyronitrile) (AIBN) was recrystallised from methanol.



	R	PEO	
		M_n	*n*
F_QE_{50}	C_8F_{17}	2200	**50**
F_QE_{93}	C_8F_{17}	4100	**93**
$C_{14Q}E_{50}$	$C_{14}H_{29}$	2200	**50**

Chart 1.

Perfluorooctyl iodide, tetradecyl bromide, dibutyltin dilaurate (DBTDL), dicyclohexylcarbodiimide (DCC), and dimethylaminopyridine (DMAP) were used as received. Tetrahydrofuran (THF) was distilled over sodium–potassium alloy. *N*,*N*-dimethylformamide (DMF) was dried over P_2O_5 and distilled under vacuum.

2.2. Synthesis and characterisation

2.2.1. PEO modified with one hydrophobic group at the end (F_QE_{50}, F_QE_{93} and $C_{14Q}E_{50}$) or in the mid of the chain ($E_{50}F_QE_{50}$)

The synthesis proceeded in two reaction steps:

(i) Preparation of PEO precursors by standard anionic polymerisation technique: α-dimethylaminoethylpoly(oxyethylene)s (NE_n) and PEO bearing a tertiary amino group in the mid of the PEO chain (E_nNE_n) were prepared by initiating the polymerisation of EO either with the potassium alkoxide of *N*,*N*-dimethylethanolamine or with the dialkoxide of *N*-methyldiethanolamine. The molar masses of the PEO precursors were determined by ^1H NMR in DMSO-d_6 from the relative intensities of the oxyethylene protons at $\delta = 3.5$ ppm and either the protons of the terminal OH groups at $\delta = 4.6$ ppm or the protons of the CH_3–N groups at 2.13 ppm. Molar mass data for E_nNE_n were also obtained from its MALDI-TOF mass spectrum using 2,5-dihydroxybenzoic acid as a matrix. They were close to the molar masses estimated by ^1H NMR. The molar masses of the synthesised NPEOs are summarised in Chart 1.

Size exclusion chromatography results confirmed the monodispersity of the products. No trace of higher molar mass fraction was observed. The measurements were conducted on a Waters equipment, consisting of a M510 solvent delivery module M717 WISP autosampler, and a M410 differential refractive index detector. The separation was achieved on a set of CATSEC (Eprogen Inc., USA and Eichrom Technologies Inc., USA) columns 4000 + 1000 + 300 + 100, 250 × 4.6 mm at 40 °C. The eluent was 0.2 M $LiNO_3$ with 0.1% trifluoroacetic acid.

(ii) Quaternisation of the PEO precursors: The quaternization of NPEOs with perfluorooctyl iodide and tetradecyl bromide was performed in DMF as previously described [27]. In all cases, the quaternization was complete as evidenced by ^1H NMR spectra in DMSO-d_6. The disappearance of the peak of the CH_3–N protons at $\delta = 2.13$ ppm and the appearance of the signal for CH_3–N^+ protons at 3.04 ppm revealed that the conversion in the quaternization reaction was 100%. In the spectrum of the polymer quaternized with $C_{14}H_{29}Br$ ($C_{14Q}E_{50}$), the ratio of the signals at $\delta = 3.04$ and 0.85 ppm, due to the $(CH_3)_2$–N^+ and CH_3 protons, being 2:1, confirmed the quantitative quaternization of the terminal dimethylamino group with tetradecyl bromide.

2.2.2. Telechelic perfluorooctyl end-capped PEO ($F_QE_{100}F_Q$)

A two-step reaction sequence was used to prepare $F_QE_{100}F_Q$

(i) Coupling of NE_{50} with HMDI to obtain a telechelic PEO precursor: NE_{50} (4.4 g, 2 mmol) was dissolved in 50 ml of toluene and dried by azeotropic distillation. HMDI (0.168 g, 1 mmol), and DBTDL (0.01 ml) were added to the stirred polymer solution under argon and the temperature maintained at 20 °C until no NCO absorption was visible in the IR spectra. The solution was concentrated and precipitated into diethyl ether. The completeness of the reaction was evidenced by the ^1H NMR spectra of the product in DMSO-d_6 and D_2O. The ratio of the intensities of CH_2–OOC and CH_3–N protons at $\delta = 4.04$ and 2.13 ppm was 1:3. In DMSO-d_6, the triplet at $\delta = 4.6$ ppm ascribable to the terminal PEO hydroxyl protons was not detected.

(ii) The product was quaternized with perfluorooctyl iodide. The quaternization was complete since in the ^1H NMR spectra of the product in DMSO-d_6 and D_2O, the signals due to CH_3–N protons disappeared and a signal for CH_3–N^+ appeared, as mentioned above.

2.2.3. Telechelic C_8F_{17}-modified-PEO synthesised through esterification ($F_eE_{91}F_e$)

$F_eE_{91}F_e$ was obtained by carbodiimide esterification of polyethylene glycol 4000 according to the procedure described by Zalipsky et al. [37]. PEG 4000 (1 g, 0.5 mmol OH) and heptadecafluorononanoic acid (0.3 g, 0.65 mmol) were dissolved in 5 ml of dichloromethane. DMAP (0.025 g, 0.2 mmol) and DCC (0.65 mmol, 0.135 g) were added to the stirred solution and the reaction mixture maintained at 20 °C for 2 days. The mixture was filtered and precipitated into diethyl ether. The product was extracted with chloroform. The solution was concentrated and precipitated into diethyl ether. Then the product was extracted with diethyl ether to remove any traces from DCC. The esterification degree determined by ^1H NMR in $CDCl_3$ from the relative intensities of $-OCH_2CH_2O-$ protons at $\delta = 3.64$ ppm and $-COOCH_2-$ protons at $\delta = 4.52$ ppm was found to be 70%.

2.2.4. PNIPAM8.8 and PNIPAM78

The number codes indicate the molar mass of the PNIPAM × 10^{-5}.

PNIPAM samples were prepared by polymerisation of NIPAM using AIBN as initiator in methanol or *tert*-butanol at 50 °C for 40 h. The NIPAM concentration was 2 mol/l. Viscosity average molar masses were determined in THF at 27 °C using the equation $[\eta] = 9.59 \times 10^{-3}\ M^{0.65}$ [38]. Typical experimental conditions for the preparation of PNIPAM were as follows: NIPAM (1.7 g) and AIBN (0.011 g, 0.45 mol%) were dissolved in 7.5 ml of *tert*-butanol. The polymerisation was carried out in ampoules sealed under vacuum. The isolated PNIPAM had $M_v = 7.8 \times 10^6$.

When the polymerisation was carried out in methanol, the amount of AIBN was 0.25 mol% relative to NIPAM. The isolated PNIPAM had $M_v = 8.8 \times 10^5$.

2.2.5. Solutions of PNIPAM mixed with F_QPEO ($x F_Q$PEO/PNIPAM; x refers to the number of F_QPEO chains per 100 NIPAM repeat units)

Weighed amount of PNIPAM was dissolved in water at 10 °C. Then desired amount of F_QPEO was added. When the polymer was completely dissolved, water was added to adjust the concentration.

2.2.5.1. Measurement of the LCST. The LCST was determined by UV–vis spectroscopy. The PNIPAM concentration was kept constant equal to 1 wt%, while the amount of added F_QPEO was varied. The solution was poured onto a 1 cm cell. The cell holder in the spectrophotometer was thermally controlled. The change of the transmittance at 500 nm was monitored upon heating the solution at a temperature rate of 0.1 °C min^{-1}. The LCST was defined as the temperature corresponding to a 10% reduction in the initial value of transmittance at 500 nm [39].

2.2.5.2. Rheological measurements. Rheological measurements were performed on a Rheotron–Brabender rheometer in the cone and plate geometry (cone angle = 0.3 °, radius = 2.5 cm). Both the steady shear and oscillatory experiments were carried out in the temperature range between 20 and 40 °C.

For the rheological measurements the concentrations of PNIPAM8.8 and PNIPAM78 were kept constant equal to 5 wt%. Prepared solutions were kept at least 1 day before rheological measurements.

3. Results and discussion

3.1. Synthesis of hydrophobically modified PEO

In the literature, two methods are employed for the synthesis of fluorocarbon-modified PEOs. The first is based on the interaction of perfluorooctylpropanoyl chloride with PEO [32], while the other one-on the attachment of a fluorocarbon alcohol to PEO via isophorone diurethane unit [33–35].

Our strategy for the synthesis of F_QPEO was based on the quaternization of PEO bearing tertiary amino groups [27]. The quaternization with perfluorooctyl iodide proceeded quantitatively and enabled the preparation of not only end-functionalised PEO, but also of PEO with a hydrophobic group in the mid of the polyether chain. Since the precursors were obtained by anionic polymerisation of EO initiated with alkoxides of tertiary amino alcohols, they were monodispersed and the initiator/monomer ratio determined the length of the PEO chain.

F_QPEOs synthesised through quaternization of PEO precursors contain equal number of fluorocarbon groups and cationic charges located at the junction points. This is the difference between the present fluorocarbon-modified PEOs and those studied so far, which contained a hydrocarbon spacer between the fluorocarbon group and the PEO chain [33–35].

3.2. Aqueous solution behaviour of F_QPEOs (viscosity measurements)

The aqueous solution properties of fluorocarbon-modified PEOs strongly depend on the length of the soluble chain, the fluorocarbon substituent, and of the spacer between the fluorocarbon group and the polyether chain [34,35].

The aqueous solution viscosities of the synthesised F_QPEOs were measured in the concentration range from 0.6 to 5 g/dl. The concentration dependence of the reduced viscosity for all studied polymers did not show an upward deviation (Figs. 1 and 2) contrary to that of the fluorocarbon-modified PEOs studied so far [32,34,35]. One can assume that the cationic charges at the junction points affect the aqueous solution properties of the studied PEOs.

In Fig. 1, the viscometric behaviours of one-ended F_QE_{50} and F_QE_{93} are compared with those of the respective precursors. F_QE_{93} had intrinsic viscosity almost twice larger than that of NE_{93} indicating that probably associates of two F_QE_{93} chains were formed. Similar behaviour was found with the one-ended C_6F_{13}-PEO5K studied by Hogen-Esch et al. [34]. Obviously, the cationic charge close to the C_8F_{17}-group in F_QE_n reduces its association ability and it might be compared with that of the C_6F_{13}-group attached to PEO via an isophorone diurethane unit. Considering the viscometric behaviour of F_QE_{50} (Fig. 1) and the alike one of $E_{50}F_QE_{50}$, we assume that the association of both to micelles is quite plausible. A well established fact is the increase in the

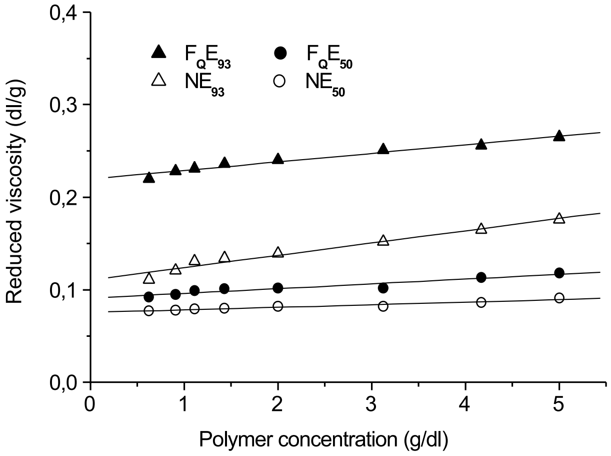


Fig. 1. Concentration dependence of reduced viscosity for F_QE_{50} and F_QE_{93} aqueous solutions (filled symbols) and for the precursor polymer solutions (open symbols) at 25 °C.

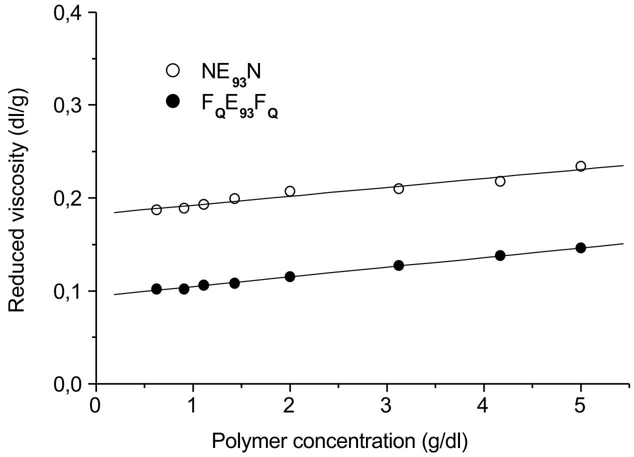


Fig. 2. Concentration dependence of reduced viscosity for $F_QE_{100}F_Q$ aqueous solution (filled symbols) and for the precursor polymer solution (open symbols) at 25 °C.

propensity of fluorocarbon-modified PEOs to aggregation with the decrease in the chain length [34].

Quite different is the behaviour of the telechelic polymer $F_QE_{100}F_Q$ (Fig. 2). It showed reduced viscosities and $[\eta]$ lower than those of the precursor polymer. Such a decrease in the hydrodynamic volume might be due to intrachain end group association followed by the formation of micelles composed of looped chains [40]. The viscosity data suggest that the aggregate molar mass stayed stable against concentration changes in the range between 0.6 and 5 wt%.

3.3. Thermally induced interactions in x F_QPEO/PNIPAM systems

3.3.1. Thermal phase transition

The values of the LCST of 1 wt% aqueous solutions of PNIPAM mixed with F_QPEOs are summarised in Table 1 and compared with that of PNIPAM mixed with $C_{14}H_{29}$-modified PEO. The aqueous solution of PNIPAM78 exhibited a steep thermal phase transition and it was practically not affected by the addition of $C_{14Q}E_{50}$. On the contrary, the LCST decreased with the increase in the number of added F_QPEO chains and the transition became broader. It was possible to monitor the gradual decrease in the optical transmittance of these mixtures and to estimate the grades at 10% reduction in transmittance at 500 nm. The results suggest that the intermolecular attractive interactions between PNIPAM and F_QPEO had taken place before the PNIPAM collapse thus endowing the thermosensitive polymer with greater hydrophobicity. It is well established that even slight increase in the hydrophobicity of PNIPAM results in a decrease of its phase transition temperature [41].

Table 1
LCST of PNIPAM mixed with hydrophobically modified PEOs. [PNIPAM] 1 g/dl

Mixture of PNIPAM with PEO-derivative		x^a	LCST (°C)
PNIPAM $M_v \times 10^{-5}$	PEO-derivative		
78	–	–	31.4
78	$C_{14Q}E_{50}$	5	31.2
78	F_QE_{50}	3	31.0
78	F_QE_{50}	5	30.5
78	F_QE_{50}	10	29.8
78	F_QE_{93}	3	30.5
78	F_QE_{93}	5	29.6
78	F_QE_{93}	10	29.4
78	$E_{50}F_QE_{50}$	3	30.4
78	$E_{50}F_QE_{50}$	5	30.1
78	$E_{50}F_QE_{50}$	10	29.6
8.8	F_QE_{50}	5	30.5
8.8	F_QE_{93}	5	30.3

[a] Number of PEO-chains per 100 NIPAM units.

3.3.2. Rheological properties

3.3.2.1. Oscillatory shear measurements. The coil-to-globule transition of PNIPAM grafted with PEO leads to the formation of core–shell nanoparticles. From light scattering measurements, Qiu and Wu [21] inferred that at higher concentrations, the aggregate formation proceeds before the PNIPAM collapse. Since the soluble PEO chains prevent PNIPAM from collapse, the sizes of the aggregates are large. Koňák et al. [42] also reported the formation of large particles when the aqueous solution of the block copolymer PNIPAM-*b*-poly[*N*-(2-hydroxypropyl)methacrylamide)] was heated to its cloud point. Further increase in temperature causes the PNIPAM shrinkage inside the core [24].

We believe that in F_QPEO/PNIPAM systems, the increase in temperature induces mixed aggregate formation through interchain hydrophobic interactions. Each PNIPAM chain links several bound micelles at temperatures close to the LCST that stabilise the partially shrunken PNIPAM coil. In the semi-dilute regime, the mixed aggregates can serve as building blocks for a temporary network formation (Chart 2—a schematic representation of temperature induced network formation).

The formation of a transient network is usually evidenced by oscillatory rheological measurements. It is established that in solutions of polymers forming a transient network, the curves of the frequency dependences of the storage modulus (G') and the loss modulus (G'') intersect at a critical point, which depends on the junction density and the relaxation time. While G' reflects the junction density, G'' reflects the effective volume occupied by the temporary network [43,44].

The oscillatory studies in the temperature range between 20 and 40 °C showed that in 5 wt% PNIPAM8.8 solutions containing F_QPEO of different composition, dynamic moduli can be measured only when the temperature reaches 35 °C. The reference mixtures of PNIPAM8.8 with α-CH_3O-E_{50} or $C_{14Q}E_{50}$ did not show viscoelastic response in the frequency range under study.

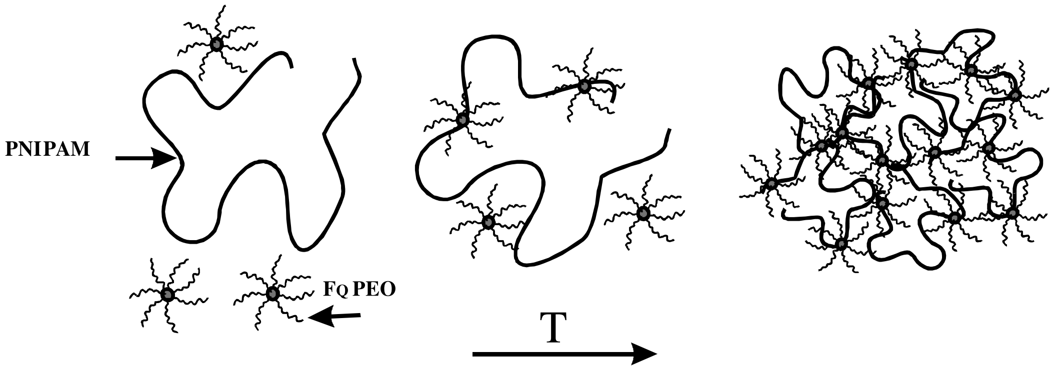


Chart 2.

Figs. 3 and 4 compare the effect of the structure and concentration of F_QPEO on the rheological behaviour of $x F_Q$PEO/PNIPAM systems at 35 °C. While the PNIPAM concentration was kept constant at 5 g/dl, x was varied. The figures show that at frequencies lower than 0.1 Hz, G' is smaller than G'' for the studied solutions. With increase in the frequency, a crossover of G' and G'' is observed and a clear plateau exists in the range between 0.1 and 0.8 Hz. At still higher frequencies, the storage modulus decreases while the loss modulus increases.

The effect of the increase in the relative F_Q-PEO/PNIPAM composition on the G' and G'' values is shown in Fig. 3. In mixtures of PNIPAM8.8 with different amounts of F_QE_{50}, the plateau modulus increases with increasing x and the crossover shifts to lower frequency. Since G' is a measure of the density of the network junctions it is reasonable to assume that the increase in x increases the probability of mixed aggregate formation and hence the number of the physical cross-links becomes larger.

There is a slight difference in the plateau modulus values for the systems $3F_QE_{50}$/PNIPAM and $3E_{50}F_QE_{50}$/PNIPAM (Figs. 3 and 4). It is reasonable to assume that both F_QE_{50} and $E_{50}F_QE_{50}$ form mixed aggregates of different aggregation number. Hence, the properties of the transient network should be different.

The values of the dynamic moduli for the system $x F_QE_n$/PNIPAM depend on the length of the polyether chain (Fig. 3). The lower values of the dynamic moduli for the system $2F_QE_{93}$/PNIPAM compared to those for $2F_QE_{50}$/PNIPAM suggest a lower density of the transient network formed. This might be due to the decreased association ability of F_QE_n when having a longer polyether chain.

The mixtures of PNIPAM8.8 with the telechelic $F_QE_{100}F_Q$, whose functionality is equal to 2, did not show an elastic response in the frequency range under study. Since chains in looped conformation are elastically inactive, the interaction of $F_QE_{100}F_Q$ with the PNIPAM coils will not result in elastic gel. However, the mixture of PNIPAM with the incompletely modified $F_eE_{91}F_e$ (Fig. 4) exhibited elasticity. This might be due to the presence of micelles formed by looped and dangled chains. The entanglement of

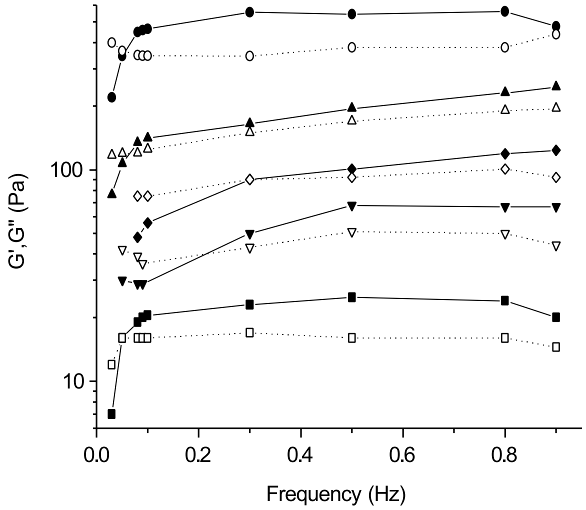


Fig. 3. Frequency dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) for mixtures of PNIPAM8.8 (5 g/dl) with F_QE_{50} and F_QE_{93} at 35 °C. (■,□) $2F_QE_{93}$/PNIPAM; (▼,▽) $0.5F_QE_{50}$/PNIPAM; (◆,◇) $1F_QE_{50}$/PNIPAM; (▲,△) $2F_QE_{50}$/PNIPAM; (●,○) $3F_QE_{50}$/PNIPAM.

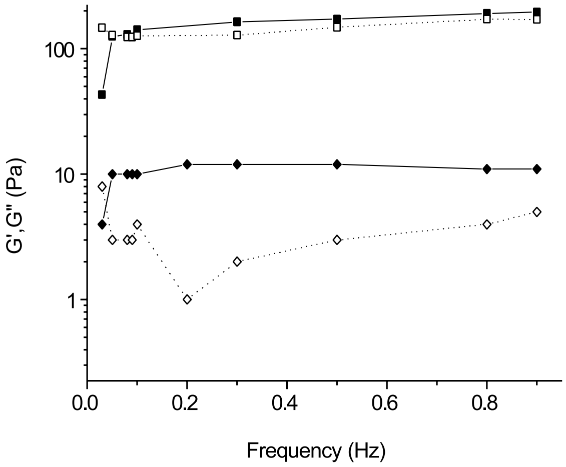


Fig. 4. Frequency dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) for mixtures of PNIPAM8.8 (5 g/dl) with $E_{50}F_QE_{50}$ and $F_eE_{91}F_e$ at 35 °C. (◆,◇) $3F_eE_{91}F_e$/PNIPAM; (■,□) $3E_{50}F_QE_{50}$/PNIPAM.

the dangled chains can promote a network with a slight elastic response.

The molar mass of the PNIPAM chain did not affect the viscoelastic response of the mixed solutions. Changing PNIPAM with molar mass 7.8×10^6 for PNIPAM with molar mass 8.8×10^5 at the same polymer concentrations resulted in the formation of a gel with practically the same values for the dynamic moduli. Obviously, the density of the network formed did not depend on the length of the PNIPAM chain.

The effect of temperature on the G' and G'' values is shown in Fig. 5. The temperature raise to 40 °C causes an increase in the dynamic moduli, which reflects the increased interaction between PNIPAM and F_QPEO. At still higher temperatures a phase separation occurs.

3.3.2.2. Steady-shear measurements. Steady shear viscosity measurements of $x\,F_Q$PEO/PNIPAM systems of different composition support the above suggestions.

Figs. 6 and 7 show the shear rate dependence of viscosity for 5 wt% solution of PNIPAM and for its mixtures with one-ended or telechelic F_QPEO at 35 and 40 °C. All solutions appeared to be pseudo plastic. The viscosity of any mixed solution at low shear rate was higher than that of pure PNIPAM solution. The viscosity increase was larger at higher values of x suggesting the formation of transient network with larger number of physical cross-links.

At the same x value, the viscosity of $3F_QE_{50}$/PNIPAM solution was higher than that of $3F_QE_{93}$/PNIPAM and $3E_{50}F_QE_{50}$/PNIPAM. The results are in accordance with the oscillatory measurements of the same systems and reflect the greater density of the network formed by the association of F_QE_{50} with PNIPAM.

It turned out that, depending on the relative amount of the components in the $x\,F_QE_{50}$/PNIPAM system, the semi-dilute solutions exhibited different rheological properties, displaying shear-thinning behaviour in cases of $x < 3$ but shear-thickening at $\gamma \approx 25\ \mathrm{s}^{-1}$ in the case of $x = 3$ (Fig. 6). The $3F_QE_{50}$/PNIPAM system showed the largest viscosity enhancement, which reflected the formation of the densest network. It is the structural reorganisation of the network under shear that may cause the shear thickening at moderate shear rates.

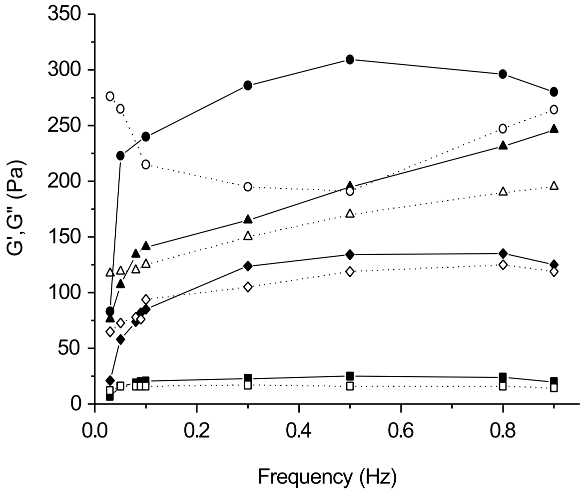


Fig. 5. Effect of temperature on the frequency dependence of the storage modulus G' (filled symbols) and the loss modulus G'' (open symbols) for mixtures of PNIPAM8.8 (5 g/dl) with F_QE_{50} or F_QE_{93}. (–■--□–) $2F_QE_{93}$/PNIPAM at 35 °C; (–◆—◇–) $2F_QE_{93}$/PNIPAM at 40 °C; (–▲--△–) $2F_QE_{50}$/PNIPAM at 35 °C; (–●—○–) $2F_QE_{50}$/PNIPAM at 40 °C.

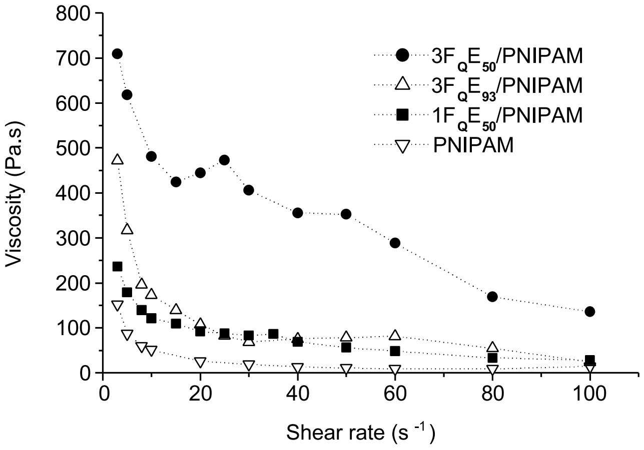


Fig. 6. Shear rate dependence of viscosity for 5 wt% PNIPAM solution and for its mixtures with F_QPEO at 35 °C.

A pronounced shear-thickening in the γ range between 20 and 50 s^{-1} took place in the 5 wt% solution of PNIPAM mixed with the telechelic $F_QE_{93}F_Q$ at 35 and 40 °C (Fig. 7). The lack of elastic response during the oscillatory measurements indicated that only elastically inactive chains existed in the system, probably loops, free chains, or insignificant amount of dangling chains. Kaczmarski et al. [45] stated that the shear-thickening in aqueous solutions of hydrophobically modified ethoxylated urethanes might be related to a transition from intra- to interhydrophobic

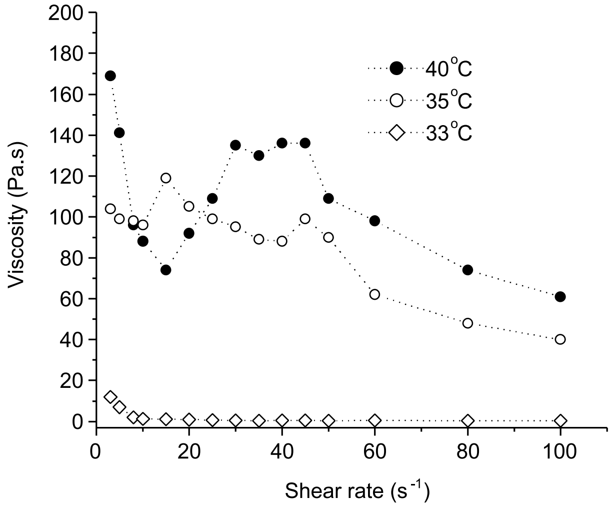


Fig. 7. Shear rate dependence of viscosity for the system $2F_QE_{100}F_Q$/-PNIPAM at 33 and 40 °C.

associations as the shear rate is increased. A similar process has been proposed to account for the shear-thickening behaviour of C_8F_{17}-modified PNIPAM when the fluorocarbon content was 0.4 mol% or higher [46]. The shear-thickening in the $3F_QE_{93}F_Q$/PNIPAM system can be rationalised on the basis of the increase in the number of the dangling chains with increasing shear rate. In addition to their entanglement, a bridging of the aggregates by the telechelic PEO chains can be proposed.

4. Conclusions

The key conclusion derived from this study is that in aqueous solution, PNIPAM interacts with perfluorooctyl-modified PEOs close to the LCST.

The quaternization of PEO precursors bearing tertiary amino groups at the end or in the mid of the polyether chain turned out to be an efficient method for the synthesis of fluorocarbon-modified PEOs. The self-association ability of F_QPEO in aqueous solutions depends on the length of the PEO chain, and the number and placement of the fluorocarbon group in the chain.

The LCST of PNIPAM slightly decreases in the presence of F_QPEO. Hydrophobic interactions were proposed between PNIPAM and the perfluorooctyl groups at temperatures close to the LCST.

Strong interactions between PNIPAM and F_QPEO close to the LCST were evidenced by the rheological properties of their semi-dilute mixed solutions. The oscillatory measurements of mixtures of PNIPAM with PEO bearing one perfluorooctyl group showed that at 35 and 40 °C, the increase in frequency causes an increase in the dynamic moduli and at a critical value, the storage modulus G' becomes larger than the loss modulus G''. The results were rationalised on the bases of entangled network formation and on the association ability of the F_QPEOs. The mixtures of PNIPAM with the telechelic $F_QE_{93}F_Q$ did not show a viscoelastic response. The formation of aggregates with looped elastically inactive PEO chains was proposed. The peculiarity of this system is that it exhibits shear-thickening behaviour at 35 and 40 °C, which was related to the transformation of the looped chains into dangling ones, which can entangle or even bridge the aggregates.

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