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Associative graft copolymers comprising a poly(*N*-isopropylacrylamide) backbone and end-functionalized polyoxyethylene side chains. Synthesis and aqueous solution properties

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Abstract

Novel, water-soluble associative graft copolymers were prepared by radical copolymerization of *N*-isopropylacrylamide (NIPAAm) and polyoxyethylene (PEO) macromonomer bearing a terminal perfluorooctyl, sulfobetaine or trimethylammonium group. The macromonomer contents ranged from 0.04 to 0.2 mol%. Associative properties in dilute and semidilute regime were studied by viscosity, static light scattering and rheology measurements. Below the lower critical solution temperature (LCST) the aqueous solution behaviour of the graft copolymers was determined by the balance between intra- and intermolecular side group interactions, which depended on the type of the associative group, the length and degree of grafting of the PEO chains and on external parameters: concentration and temperature. In dilute solution, the polymers containing perfluorooctyl or sulfobetaine groups form aggregates with molar masses depending on the type and the content of the associative group. In semidilute solution, the graft copolymers revealed a shear thinning behaviour. The copolymer with 0.1 mol% PEO chains bearing perfluorooctyl groups showed the greatest viscosity enhancement at low shear rate. Above the phase transition temperature the same copolymer formed an elastic gel. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Associative graft copolymers; Polyoxyethylene modification; Thermoassociative behaviour

1. Introduction

In recent years studies on associative water-soluble polymers have become an attractive field owing to their unique solution properties. Uncharged and ionic polymers bearing groups or segments prone to attractive interactions reveal stimuli sensitivities and their behaviour changes drastically with environmental pH, temperature, solvent composition and ionic strength [1]. They have found application as rheology modifiers, additives in enhanced oil recovery or water treatment, for immobilization of enzymes, controlled drug release and microencapsulation [2,3].

The modification of a hydrophilic polymer with a low amount of hydrophobic groups is now a routine procedure for controlling the rheological properties of aqueous fluids. The most thoroughly studied associative polymers are the derivatives of polysaccharides [4–6], polyoxyethylene (PEO) [7–11] and acrylamides [12–18] bearing alkyl, aralkyl, fluoroalkyl groups or steroids. The preference of the hydrophobic groups for intra- or intermolecular interactions depends on their nature, content and distribution along the polymer chain. Hydrophobic domains of intermolecular type appear above a critical aggregation concentration, which may be substantially lower than the overlap concentration [18]. At sufficiently high concentration the attractive interactions between the hydrophobic segments create a transient network, which results in a considerable viscosity enhancement of the solution at low shear rates [8,16,17].

Further enhancement of the thickening performance of water-soluble copolymers is expected from hydrophilic chains possessing inherent hydrophobicity. Poly(*N*-isopropylacrylamide) (PNIPAAm) is a polymer that reveals remarkable properties when dissolved in water. It exhibits a lower critical solution temperature (LCST) ca. 32°C [19,20]. The sharp coil-to-globule transition at the LCST has been attributed to an abrupt change of the delicate hydrophilic–hydrophobic balance within a narrow temperature range. There is no aggregation between the PNIPAAm

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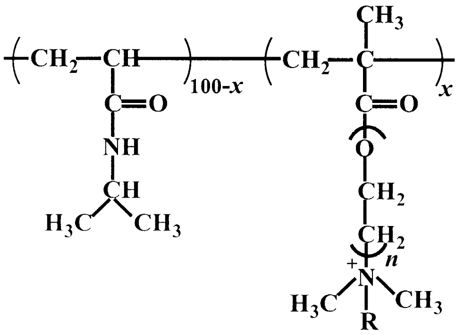
coils below the LCST [21]. A concentrated solution of high molar mass ($>10^6$) PNIPAAm shrinks above the LCST without forming a gel but the introduction of acrylic acid comonomer units in the thermosensitive chain gives rise to a reversible gel formation [22]. On the contrary, hydrophobically modified PNIPAAm which associates below its LCST phase separates on heating due to the rupture of the micellar-type domains and the formation of mixed aggregates of collapsed PNIPAAm chains and hydrophobic alkyl groups [23–25].

The architecture of PNIPAAm based copolymers is the factor determining their response to temperature changes in aqueous media. Block and graft copolymers containing PNIPAAm chains belong to the family of the so-called thermoassociative polymers [26–29]. The exciting property of such copolymers is that above the LCST their semidilute solutions reversibly gel and the transition to the solid-like state is characterized by storage modulus (G') much higher than the loss modulus (G'') [26,29,30]. This behaviour is due to the formation of a network from collapsed thermosensitive blocks interconnected by soluble chains.

The possibilities of creating self-associating polymers are widened by varying the nature of the associating-type functionality. Ionic and zwitterionic groups located at different places along the polymer chains may give rise to specific interactions that greatly affect their behaviour in aqueous media [31,32].

The present article deals with the synthesis of water-soluble graft copolymers comprising a PNIPAAm backbone and a low level of end-functionalized PEO side chains (Scheme 1 — structures of the associative water-soluble graft copolymers: x refers to the molar percent of the PEO macromonomer; $n = 22$ or 45). Their aqueous solution behaviour has been studied in the dilute and semidilute state. The aim has been to create structures able to associate through non-covalent interactions below and above the phase transition of the thermosensitive backbone. The PEO end-functionalities may give rise to the following interactions:

(a) hydrophobic interactions arising from the end-standing perfluoroalkyl groups and the hydrophobic character of PNIPAAm above a certain temperature;
(b) dipole–dipole interactions between end-standing zwitterionic groups;
(c) donor–acceptor interactions in case of end-standing trimethylammonium groups.



xGR$_n$

xGF$_n$ $R = C_8F_{17}$
xGSB$_n$ $R = (CH_2)_3SO_3^-$
xGTM$_n$ $R = CH_3$

Scheme 1.

2. Experimental

2.1. Materials

The reagents were purchased from Aldrich. NIPAAm was recrystallized from a 65:35 (vol/vol) mixture of hexane and benzene. Methyl iodide was distilled. Azobisisobutironitrile (AIBN) was purified by recrystallization from methanol. Perfluorooctyl iodide (PFOI) and 1,3-propanesultone (PS) were used as received. Benzene and tetrahydrofuran (THF) were refluxed over sodium–potassium alloy and distilled. *N*,*N*-dimethylformamide (DMF) was dried over P_2O_5 and distilled under vacuum.

2.2. Synthesis of end-functionalized PEO macromonomers

2.2.1. α-Dimethylaminoethylpolyoxyethylene (NPEO)

NPEO of general formula $(CH_3)_2NCH_2CH_2(OCH_2CH_2)_n$-OH with $n = 22$ or 45 was prepared by anionic polymerization of ethylene oxide in THF initiated by potassium alkoxide of *N*,*N*-dimethylethanolamine. The molar masses were determined by ^1H NMR in $CDCl_3$ from the relative intensities of $-O-CH_2CH_2-O-$ protons at $\delta = 3.64$ ppm and CH_3-N protons at $\delta = 2.32$ ppm. Molar mass data were also obtained from MALDI-TOF mass spectrum of NPEO using 2,5-dihydroxybenzoic acid as a matrix.

2.2.2. PEO bearing a quaternary ammonium group (QPEO)

QPEO was obtained through quaternization of NPEO with methyl iodide, PS or PFOI. The quaternization reactions with methyl iodide or PS were carried out in THF as previously described [33], whereas the quaternization with PFOI was run in DMF at 85°C for 7 days. The quaternization was complete as evidenced by the lack of CH_3-N protons and the relative intensities of $-O-CH_2CH_2-O-$ protons at $\delta = 3.64$ ppm and CH_3-N^+ protons at $\delta = 3.44$ ppm.

2.2.3. QPEO methacrylate (QPEOMA)

QPEOMA was obtained by carbodiimide esterification of methacrylic acid with QPEO according to the procedure

Table 1
Molecular characteristics and aqueous solution properties of associative graft copolymers

Sample	AG[a] content (mol%)	N[b]	LCST (°C)	$[\eta]$ (dl g^{-1})		k_H	
				20°C	25°C	20°C	25°C
$0.04GF_{45}$	0.037	16	31.6	2.37	2.06	0.62	0.79
$0.1GF_{45}$	0.085	42	31.9	2.35	2.05	0.77	0.87
$0.1GF_{45}$				2.13[c]	–	0.42[c]	–
$0.2GF_{45}$	0.150	83	32.7	1.87	1.74	0.55	0.50
$0.2GSB_{45}$		83		1.91	1.80	0.65	0.67
$0.2GSB_{22}$		83		2.20	–	0.70	–
$0.05GTM_{45}$		21	32.0	1.63	–	0.58	–
$0.3GTM_{22}$		125		2.49	–	0.65	–
$0.44GTM_{22}$		183		2.35	–	0.59	–
$1.13GTM_{22}$		470	31.4	2.29	–	0.54	–
PNIPAAm			31.6	2.30	2.07	0.61	0.57
PNIPAAm				1.92[c]	–	0.52[c]	–

[a] Associative group.

[b] Number of associative groups per main chain.

[c] Viscosity measurements in DMF.

described by Gnanou and Rempp [34]. The functionalization was quantitative as estimated from ^{1}H NMR spectra in $CDCl_3$ from the peak intensity ratio of the terminal groups CH_3N^+ at $\delta = 3.44$ ppm and $CH_3–C=C$ at $\delta = 1.9$ ppm.

2.3. Synthesis of graft copolymers

In a typical reaction a proper amount of QPEOMA was added to a NIPAAm (1.7 g, 15 mmol) solution in 20 ml of benzene. Then AIBN (0.5 mol%) was added. The copolymerizations were carried out in sealed ampoules under vacuum at 50°C for 2 days. The solvent was evaporated, the residue was dissolved in H_2O and dialyzed against distilled water for two weeks. A dialysis membrane (Spectrapor, Spectrum Medical Industries Inc., USA) with a cut-off value of 12,000-14,000 was used.

The samples were designated as $x\mathrm{GR}_n$, where x refers to the mol% of incorporated PEO macromonomer with degree of polymerization n.

The compositions of the graft copolymers were determined by ^{1}H NMR in $CDCl_3$ from the relative intensities of the methine protons of the isopropyl groups at $\delta = 4.00$ ppm and the oxyethylene protons at $\delta = 3.64$ ppm applying Eq. (1).

$$\frac{\text{area of methine protons at } \delta = 4.00\text{ ppm}}{\text{area of oxyethylene protons at } \delta = 3.64\text{ ppm}} = \frac{100 - x}{4nx} \quad (1)$$

The actual content of the associative groups is lower than x since PEO chains act as diluent (Table 1).

An uncharged graft copolymer and PNIPAAm, used for comparative studies, were also prepared under conditions identical to those for the preparation of the associative graft copolymers. The graft copolymer designated as $0.2GN_{45}$ was obtained by copolymerization of methoxy-capped poly(oxyethylene) methacrylate and NIPAAm. The intrinsic viscosity of PNIPAAm determined in THF at 27°C was 202.49 ml g^{-1}. Using the relationship $[\eta] = 9.59 \times 10^{-3} M^{0.65}$ [35] the viscosity-average molar mass of PNIPAAm was determined to be $M_v = 4.5 \times 10^6$.

3. Characterization

3.1. Measurement of the LCST

The LCST was determined by UV–Vis spectroscopy. The polymer was dissolved in distilled water to give a 1 wt% solution and 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 by heating the solution at a temperature rate of 0.1°C $\min^{-1}$. The LCST was defined as the temperature corresponding to a 50% reduction in the initial value of transmittance at 500 nm.

3.2. Viscosity measurements

Solution viscosities were determined with an Ubbelohde viscometer at 25°C. Solvent flow time exceeded 200 s. Viscosity data were analyzed using the Huggins equation [36]:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \quad (2)$$

3.3. Light scattering measurements

Static light scattering measurements 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 488 nm.

Analyses were performed in a microbatch mode at 25 and 50°C. The specific refractive index increment was measured at 25 and 50°C on an Optilab DSP Wyatt interferometric refractometer and determined with the Wyatt d*n*/d*c* software; d*n*/d*c* (ml g^{-1}) = −0.1703, −0.1873, −0.1394 and −0.2196 for $0.04GF_{45}$, $0.1GF_{45}$, $0.2GF_{45}$ and $0.2GSB_{45}$ in water at 25°C, respectively; −0.1835, 0.2122, −0.1445 and −0.1331 for $0.04GF_{45}$, $0.1GF_{45}$, $0.2GF_{45}$ and $0.2GSB_{45}$ in water at 50°C, respectively. The weight-average molar mass, M_w, the radius of gyration, R_g, and the second virial coefficient, A_2, were obtained from the scattering data and calculated using ASTRA (Wyatt Corp.) software.

3.4. 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. The dynamic storage and loss moduli, G' and G'', were examined as a function of temperature in the range of 20–40°C.

4. Results and discussion

Recently we have synthesized amphiphilic graft copolymers with cationic groups in the PEO side chains [33]. In low-polarity and polar solvents they exhibit a complex association behaviour that depends on the charge location and the grafting degree. In the present work our interest is in the preparation of double hydrophilic graft copolymers that turn out to be amphiphilic upon heating due to the thermosensitivity of the PNIPAAm backbone. The terminal functionality in the PEO side chains may give rise to interactions that are concentration and temperature dependent.

4.1. Synthesis of associative graft copolymers

There are two approaches to the synthesis of graft copolymers consisting of a PNIPAAm backbone and PEO side chains: grafting of amino-functionalized PEO onto a copolymer of NIPAAm with acryloxysuccinimide [26,37] and radical copolymerization of NIPAAm with PEO macromonomers [28,38]. The “grafting onto” method enables the preparation of copolymers with high degree of grafting. On the contrary, the macromonomer method is suitable for the synthesis of copolymers with low levels of grafted chains since a higher concentration of PEO chains brings about gelation of the copolymer solution [39].

The synthesis of graft copolymers with low levels of PEO grafts bearing terminal functionality was attempted applying the macromonomer method. Its advantage is that we have controlled the functionality of the PEO chain at each stage of its modification and each side chain of the graft copolymers obtained is modified with an associative group.

4.2. Solution properties

4.2.1. Thermal phase transition

Fig. 1 shows the effect of temperature on the transmittance of 1 wt% solutions of xGF_{45} and $0.05GTM_{45}$. A slight increase of the LCST is observed with increasing the molar fraction of the PEO macromonomer, *x*.

The phase transition of a thermosensitive polymer is a result of the change in its hydrophilic–hydrophobic balance. Below the LCST the hydrogen-bonding interactions of the polymer with water molecules determine its solubility. When raising the temperature these interactions are weakened and above the LCST the hydrophobic interactions become predominant [40]. Changes in the structure of the polymer chain that increase its overall hydrophilicity result in an increase of the LCST of the polymer solution [41]. Such a tendency was observed in the xGR_n solutions (Table 1).

The incorporation of associative groups at the end of the PEO side chains may affect the polymer–solvent interactions. At the same low molar fraction of PEO macromonomer the LCST of $0.05GTM_{45}$ solution is equal to that of $0.1GF_{45}$. One can assume that specific interactions of the $(CH_3)_3N^+$ groups with the backbone carbonyl groups as proposed by Hamid and Sherrington [42] affect the solvation of the copolymer chain.

The terminal associative groups in xGF_{45} affect the shape of the phase transition curves. The transmittance of a xGF_{45} solution slightly decreases in the range of 24–30°C while that of PNIPAAm and $0.05GTM_{45}$ solutions is kept nearly constant (Fig. 1). This suggests increased hydrophobic interactions below the phase transition of the backbone. Since PNIPAAm is quite hydrophobic at 25°C [43] one can

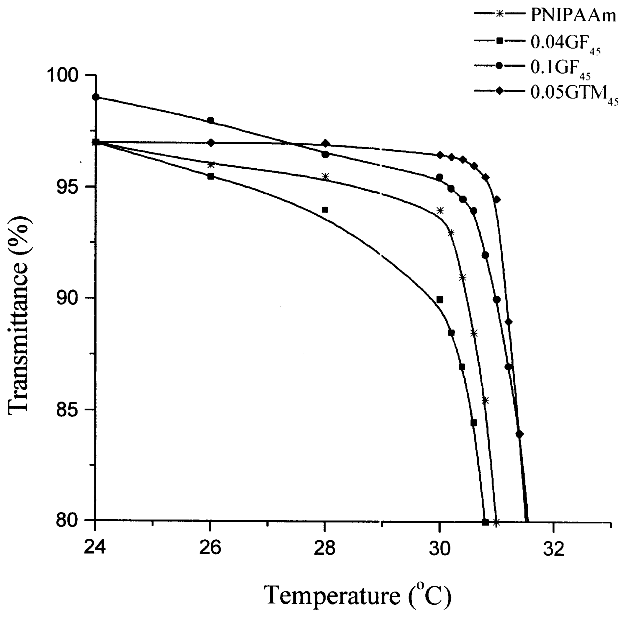


Fig. 1. Temperature dependent transmittance at 500 nm of 1 wt% aqueous solutions of xGR_{45} copolymers and PNIPAAm.

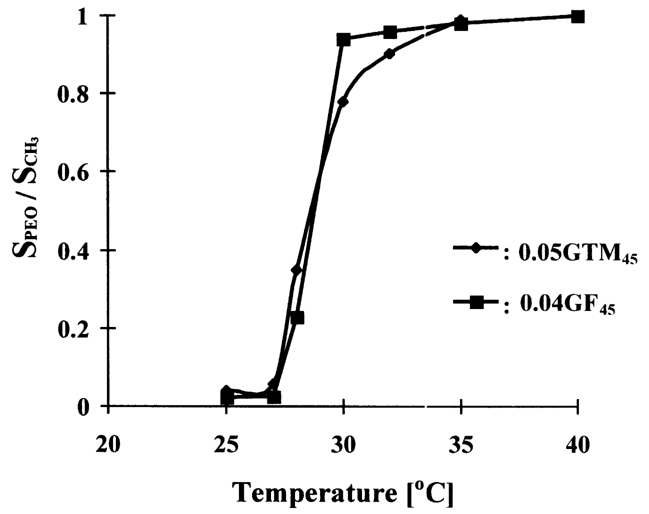


Fig. 2. Effect of temperature on the relative intensities of the oxyethylene side chain protons and the methyl protons of the PNIPAAm backbone.

assume that it interacts with the perfluoroalkyl groups creating mixed hydrophobic microdomains.

The phase transition of the graft copolymers is accompanied by a decrease of the PNIPAAm chain mobility. This process can be monitored by ^{1}H NMR. In Fig. 2 the ratio of the integrated peak intensities of the oxyethylene protons at 3.68 ppm and of methyl protons at 1.18 ppm is plotted vs. temperature. Contrary to the abrupt loss of the mobility of the backbone in 0.04GF$_{45}$ that in 0.05GTM$_{45}$ proceeds in a wider temperature range. This observation is in favor of the proposed interaction between the cationic groups and the NIPAAm units that affect the phase transition of 0.05GTM$_{45}$.

4.2.2. Viscosity measurements

Plots of reduced viscosity versus polymer concentration for xGR$_n$ copolymers and for 0.2GN$_{45}$ and PNIPAAm in water at 20°C are given in Fig. 3. The viscosities of all copolymers with terminal graft functionality are less than those of 0.2GN$_{45}$. The figure illustrates the effect of the end-group, the degree of grafting and the length of the side chain on the viscosity behaviour of the graft copolymers. The intrinsic viscosities and the Huggins coefficients in water at 20°C and 25°C, determined by Eq. (2), are listed in Table 1. Included are data for the viscosity of 0.1GF$_{45}$ and PNIPAAm in DMF.

At a constant length of PEO grafts ($n = 45$ or 22) the increase in x brought about a decrease in the reduced and intrinsic viscosities. The viscosity change is more pronounced in the case of copolymers with longer grafts. Despite its low grafting degree ($x = 0.05$) the graft copolymer with terminal trimethylammonium groups shows the lowest viscosity among the copolymers studied. The observations suggest different types of interactions arising from the presence of associative groups.

Recently we have shown that, in a good solvent, graft copolymers bearing cationic groups at the end of PEO side chains show a preference for intramolecular side chain interactions when the degree of grafting is increased [33]. This phenomenon is common for a variety of non-ionic amphiphilic graft copolymers and has been attributed to specific interactions between PEO side chains [44,45]. The aqueous solution behaviour of the double hydrophilic graft copolymers with modified PEO side chains suggests that hydrophobic, cationic and zwitterionic terminal groups exert a pronounced effect on the side chain interactions. In fact the viscosity data give more information about the intramolecular interactions since associates formed through non-covalent interactions are unstable under the shear applied in the viscometric tube.

It is well established that perfluorocarbon groups reveal a great tendency to associative interactions in aqueous media. The hydrophobic nature of the side group interactions in case of 0.1GF$_{45}$ was confirmed by performing viscosity measurements in H$_2$O and DMF at 20°C. The higher values of viscosity and Huggins coefficient in H$_2$O than in DMF (Fig. 4 and Table 1) suggest increased polymer–polymer

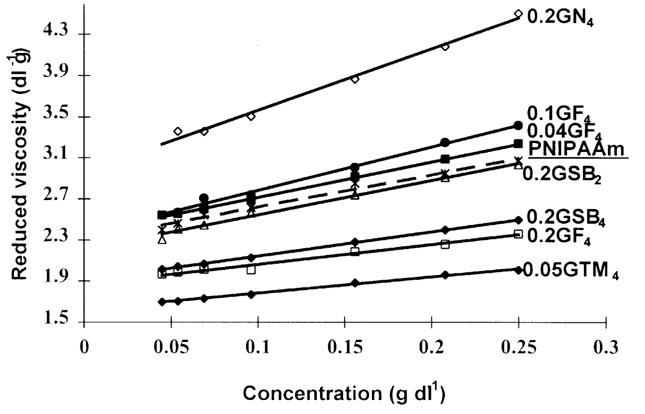


Fig. 3. Concentration dependence of reduced viscosity for graft copolymers, xGR$_{45}$, 0.2GN$_{45}$ and PNIPAAm in H$_2$O at 20°C.

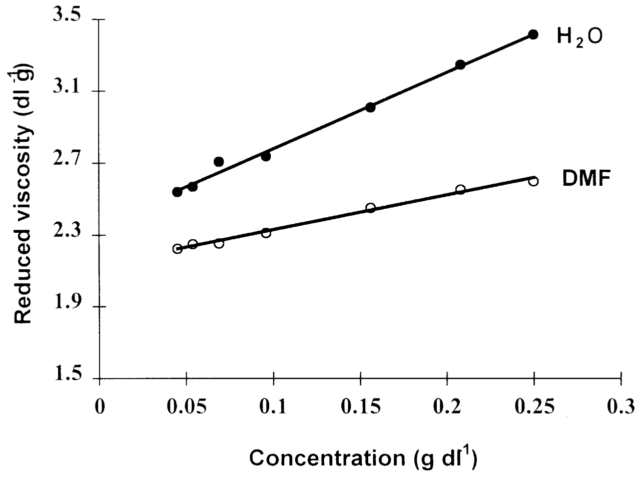


Fig. 4. Concentration dependence of reduced viscosity for 0.1GF$_{45}$ in H$_2$O and DMF at 20°C.

interactions due to the presence of hydrophobic C_8F_{17} groups.

Chains containing zwitterionic groups characterized by a permanent dipole are prone to intra- and intermolecular interactions [32]. The lower viscosities of $0.2GSB_{45}$ compared to those of the uncharged copolymer, $0.2GN_{45}$, are in favour of the assumption that the terminal zwitterionic groups affect the associative behaviour of the PEO grafts.

The considerable decrease in viscosity of the graft copolymers bearing terminal trimethylammonium groups might be due to the intramolecular interaction of the cationic groups with the abundance of main-chain carbonyl groups. The high flexibility of the PEO chain enables such interactions resulting in a shrinkage of the polymer coil. In cases of $x\mathrm{GF}_n$ and $x\mathrm{GSB}_n$ such interactions are hindered by the more bulky substituents and the hydrophobic or electrostatic interactions become prevalent.

The probability for intramolecular side group interactions increases with the lengthening of the PEO grafts. At the same level of grafted chains the copolymers with longer chains reveal lower viscosities. The viscosity data suggest that the decrease of the reduced viscosity due to side group interactions follows the order:

$$N^+(CH_2)_3SO_3^- < C_8F_{17} < (CH_3)_3N^+.$$

4.2.3. Static light scattering

Static light scattering measurements were performed in the concentration range from 5.0×10^{-5} to 1.6×10^{-4} g ml^{-1}. Data for M_w, R_g and A_2 are listed in Table 2.

The data in Table 2 suggest that in the series of $x\mathrm{GF}_{45}$ copolymers $0.04GF_{45}$ and $0.1GF_{45}$ aggregate in the concentration range under study at 25°C. In spite of the low grafting degree the number of grafts per backbone ($N = 15$–42, Table 1) is enough to promote intermolecular interactions. On the contrary, the copolymer with higher level of grafted chains ($0.2GF_{45}$) reveals intramolecular associative behaviour; its molar mass is close to M_w of individual PNIPAAm chains.

The values of M_w and R_g for $0.2GSB_{45}$ indicate that at $x = 0.2$ the copolymer with terminal zwitterionic groups associates intermolecularly contrary to the case of the perfluoroalkyl containing copolymer. One can assume that at a constant degree of grafting the balance between the inter- and intramolecular interactions depends on the nature of the terminal associative group.

Considering the A_2 values for the polymers listed in Table 2 we can assert that, at 25°C, water is a good solvent for the graft copolymers that show a preference for intermolecular interactions. The change in the sign of A_2 for $0.2GF_{45}$ indicates a change in the quality of the solvent for the copolymer which is not aggregated below the LCST. This may be rationalized by the assumption that in the intermolecularly associated chains, the unfavourable contacts of the associative groups with water are hindered. In the intramolecularly associated side chains of $0.2GF_{45}$ the hydrophobic groups remain exposed to water thus, decreasing the value of A_2.

From light scattering measurements Qui and Wu [38] inferred that, at room temperature, PNIPAAm grafted with methoxy-PEO exists as non-associated chains at concentrations ranging from 1×10^{-5} to 2×10^{-4} g ml^{-1}. Above the LCST micelle-like nanoparticles are formed with core made of collapsed and aggregated PNIPAAm chains and corona of soluble PEO.

The data included in Table 2 suggest that at 50°C PNIPAAm grafted with a low level of end-functionalized PEO chains forms large species. The molar mass of the aggregated species decreases with increasing x, which might be due to the greater stabilization of the insoluble core by the more densely grafted chains.

4.2.4. Rheological behaviour

The rheological properties of the graft copolymers have been studied at polymer concentration of 5 wt%, which is above the overlap concentration of the polymers ($c^* \approx 1/[\eta] \approx 0.5$ g dl^{-1}).

Fig. 5 shows the dependence of viscosity on the shear rate for 5 wt% solutions of $x\mathrm{GF}_{45}$, $0.2GSB_{45}$ and PNIPAAm at 20°C. At low shear rate the viscosity of the graft copolymers is higher than the viscosity of PNIPAAm. All solutions appear to be pseudoplastic. We should note that the type of the associative group and its content affect the flow curve. The copolymer $0.1GR_{45}$, which reveals the greatest viscosity enhancement at low shear rates, exhibits viscosities in the whole shear-rate range under study higher than those of PNIPAAm.

Table 2
Light scattering results of $x\mathrm{GF}_{45}$, $0.2GSB_{45}$ and PNIPAAm in water at 25 and 50°C

Sample	$T = 25$°C			$T = 50$°C		
	$M_w \times 10^{-6}$ (g mol^{-1})	*RMS* (nm)	$A_2 \times 10^4$ (mol ml g^{-2})	$M_w \times 10^{-6}$ (g mol^{-1})	R_g (nm)	$A_2 \times 10^4$ (mol ml g^{-2})
$0.04GF_{45}$	62.0	294	4.3	133.0	133	1.5
$0.1GF_{45}$	44.0	182	1.7	95.0	143	1.6
$0.2GF_{45}$	6.5	125	−5.1	7.3	77	6.8
$0.2GSB_{45}$	17.0	267	5.7	38.0	134	1.1
PNIPAAm	5.6	145	8.1	7.4	102	−7.4

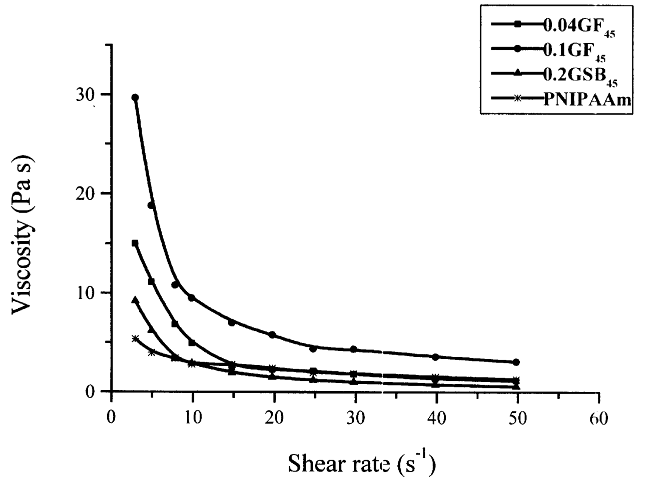


Fig. 5. Dependence of viscosity on shear rate for 5 wt% solutions of xGR$_{45}$ and PNIPAAm at 20°C.

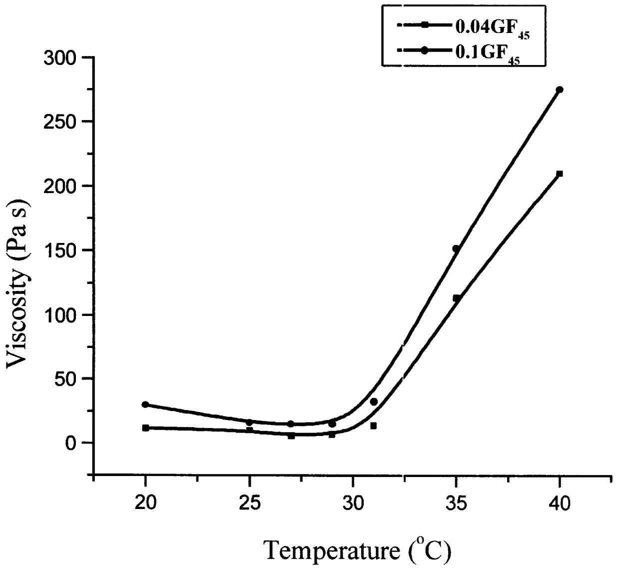


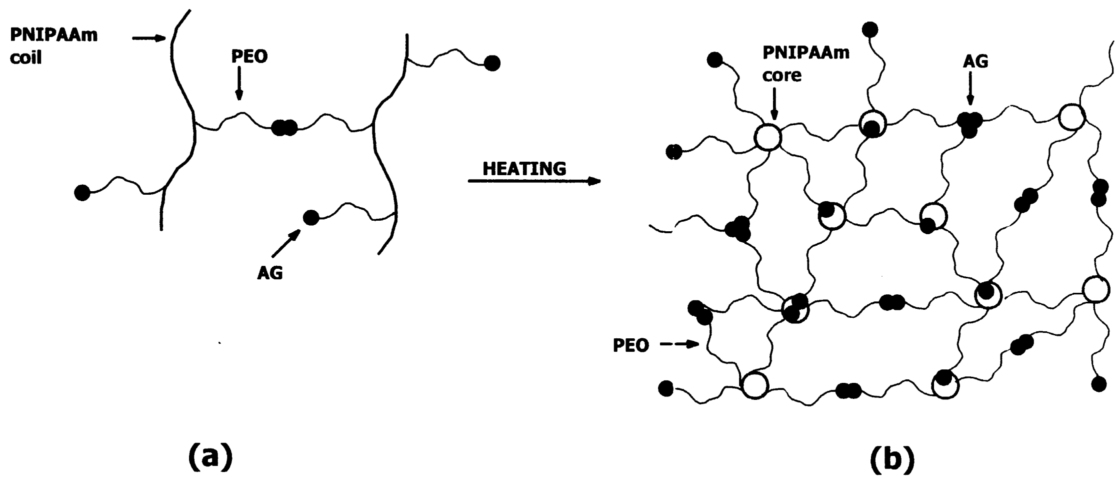
Fig. 6. Temperature dependence of viscosity of 5 wt% solutions of xGF$_{45}$ at shear rate = 3 s^{-1}.

In the series of graft copolymers containing perfluorooctyl groups at the end of PEO side chains there is a pronounced dependence of the viscosity on the macromonomer content. A maximum appears at 0.1 mol% grafted chains and the increase in the macromonomer content results in a decrease of the viscosity at low shear rate. The viscosity of 0.2GF$_{45}$ is even lower than that of 0.2GSB$_{45}$.

In the semidilute regime, whose onset is above the overlap concentration, chain entanglements result in a viscosity enhancement. On the other hand the functional groups are brought to close proximity and their inter- or intramolecular interactions will play a dominant role in the viscosification effect. A dependence of viscosity on shear rate is typical of solutions of associating polymers [18,46].

The behaviour of the functionalized graft copolymers may be interpreted in terms of the formation of microdomains through hydrophobic or dipole–dipole interactions. They act as physical cross-links of a transient network (Scheme 2a — a schematic illustration of the associative behaviour of 0.1GF$_{45}$ below the LCST) whose strength varies with the type and the number of the functional groups per chain. The greatest viscosifying ability of 0.1GR$_{45}$ suggests that in this case, the intermolecular hydrophobic interactions prevail over the intramolecular ones. Since the cross-links are formed by non-covalent binding of the perfluoroalkyl or the zwitterionic groups, the increase in shear rate brings about a breakdown of the network. The viscosities for the 0.1GF$_{45}$ solution are higher than those for PNIPAAm solution at higher shear rates suggesting an incomplete rupture of the hydrophobic microdomains.

The effect of temperature on the viscosity for 5 wt% solutions of xGF$_{45}$ at low shear rate (3 s^{-1}) is shown in Fig. 6.



Scheme 2.

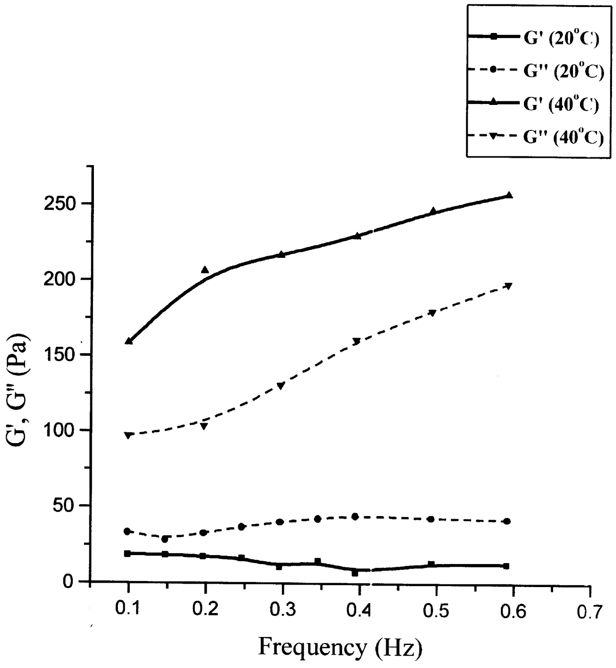


Fig. 7. Frequency dependencies of the dynamic moduli of 5 wt% solution of $0.1GF_{45}$ at 20 and 40°C.

The increase of temperature above 30°C brings about a sharp increase in viscosity. Such thermothickening behaviour is an inherent characteristic of PNIPAAm systems. It is due to the collapse of the PNIPAAm chains followed by their aggregation. At higher temperature the phase separation of the PNIPAAm phase results in a viscosity decrease.

The attachment of end-functionalized PEO chains to PNIPAAm backbone affects both the viscosity and the viscoelastic behaviour of the graft copolymers. The viscoelastic properties of unmodified polymers are governed by chain entanglements. In the case of copolymers grafted with modified PEO chains the viscoelastic behaviour depends on the side group associative interactions.

Fig. 7 shows the frequency dependence of the dynamic moduli for $0.1GF_{45}$ at 20 and 40°C. At 20°C, the loss modulus G'' is larger than the storage modulus G' in the frequency range under study. At 40°C, G' is higher than G''. Such behaviour is typical of a system that undergoes a temperature-induced transition from a viscoelastic fluid to an elastic solid. The temperature dependence of G' and G'' at constant frequency, 0.6 Hz, is shown in Fig. 8. The intersection point corresponds to the phase transition temperature.

Such a transition to an elastic gel does not occur in the solution of the uncharged ($0.2GN_{45}$) polymer and in that of the copolymer bearing sulfobetaine groups.

The behaviour of the graft copolymers xGF$_{45}$ above the phase transition temperature is due to their unique structure and to the high propensity of the C_8F_{17} groups to hydrophobic interactions. The micelle-like aggregates with a core of collapsed PNIPAAm chains might be bridged either by PEO chains already associated through the fluoroalkyl groups or by the participation of the PEO terminal groups in other PNIPAAm cores (Scheme 2b — a schematic illustration of the associative behaviour of $0.1GF_{45}$ above the LCST).

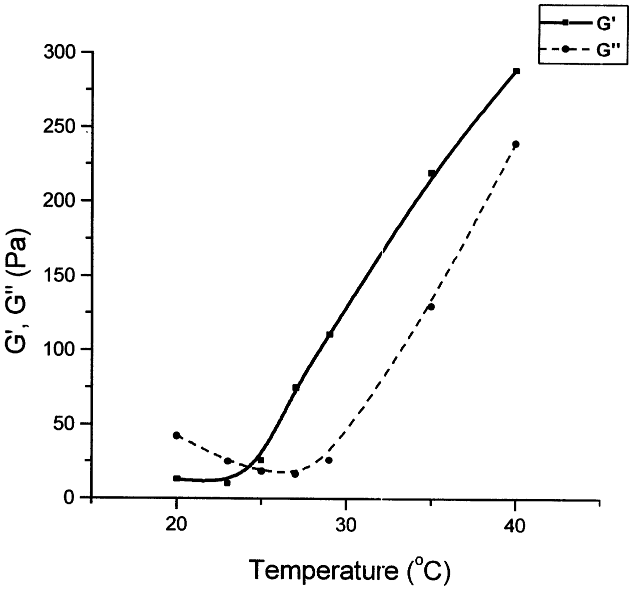


Fig. 8. Temperature dependence of the dynamic moduli of 5 wt% solution of $0.1GF_{45}$ at frequency = 0.6 Hz.

5. Conclusions

Novel associative graft copolymers consisting of a PNIPAAm backbone and a low level of PEO side chains bearing terminal perfluorooctyl, sulfobetaine or trimethylammonium groups have been prepared by applying the macromonomer approach. In aqueous solution the PEO terminal groups give rise to hydrophobic, dipole–dipole or donor–acceptor interactions. The balance between intra- and intermolecular side group interactions can be controlled by varying the length of the side chains, the degree of grafting and the polymer concentration. In dilute regime, the copolymers bearing terminal perfluoroalkyl or sulfobetaine groups form aggregated species even at concentration as low as 5×10^{-5} g ml^{-1}. Below the phase transition temperature the semidilute solutions of the graft copolymers exhibit shear-dependent rheological properties. The highest viscosity enhancement at low shear rate shows PNIPAAm grafted with 0.1 mol% PEO bearing perfluorooctyl groups. Above the phase transition temperature the same copolymer gives a gel with an elastic modulus higher than the loss modulus. The results are consistent with the formation of transient networks of soluble or collapsed PNIPAAm chains bridged by soluble PEO chains.

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