Synthesis and characterization of poly(acrylamide)-*graft*-poly(ethylene oxide-*co*-propylene oxide)*

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The synthesis and first experiments on the rheological behaviour of poly(acrylamide) (PAAm) grafted with poly(ethylene oxide-*co*-propylene oxide) are presented. Well-defined, water-soluble graft copolymers were prepared in high yields by grafting poly(oxyalkylene) monoamines onto partly hydrolysed PAAm. Reversible gelation of aqueous graft copolymer solutions ($c > c^* = 1/[\eta]$) was observed in 0.5 M K_2CO_3 at elevated temperatures, accompanied by viscosity changes of almost three orders of magnitude between 80 and 85°C at low shear rates. The observed phenomena are explained in terms of the formation of secondary bonds or association between the grafts.

(Keywords: PAAm-*g*-PEO/PPO; reversible gelation; rheology)

INTRODUCTION

Poly(acrylamide) (PAAm) with a molecular weight of $10\text{–}20 \times 10^6\,\mathrm{g\,mol^{-1}}$ is a water-soluble polymer which is frequently used as a viscosity modifier, e.g. for polymer flooding in enhanced oil recovery[1,2]. Like most solutions of linear polymers, PAAm in water shows a shear-thinning flow behaviour and a decrease in the viscosity upon raising the temperature, which can be a disadvantage for particular applications[1-3].

The present work was directed towards the modification of PAAm in order to achieve the following solution properties[2]:

1. a low viscosity at room temperature and a high viscosity ($\geqslant 100$ mPa s) at elevated temperatures ($\geqslant 60$°C);
2. high viscosities at low concentrations with relatively low molecular weight polymers so that the primary structure is little sensitive to shear degradation; and
3. constant or even increasing viscosity with increasing shear rate, in particular at the higher temperatures.

The strategy which has been developed to achieve such unusual properties exploits the introduction of molecular units that can undergo temperature dependent reversible interactions. If the interaction is favoured on raising the temperature, the macromolecules can associate or even, when the concentration is high enough, form a physical network. At high stress, such a structure will break at its weakest links, i.e. at the secondary bonds. Thus, shear degradation of the primary molecules is unlikely and the physical network can recover when the system is left at rest.

The secondary bonds should be distinguished from entanglements between polymer molecules. The latter are sliding contacts, whereas the former are bonds between localized points on the polymer chains. A more important difference is that entanglements arise as a result of an excluded volume type interaction, and consequently are little dependent on temperature or solvent quality[4]. Contrary to this, the bonds we are thinking of are the result of an association reaction whose equilibrium will depend not only on temperature but also on solvent quality. Factors of the water-based systems which affect the solvent quality can be the pH and the type and concentration of an added electrolyte. The influence of these factors depends on the chemical structure of the molecules and can thus be tailored as required.

In solutions of polymer molecules equipped with temporarily interacting sites there will be an equilibrium between the bonds between sites on one and the same macromolecule (intramolecular bonds) and those connecting different macromolecules (intermolecular bonds). Upon increasing the number of intermolecular bonds a long-range network can eventually be formed. However, the system remains a liquid because intermolecular bonds exist temporarily only, and one may speak of a 'transient network'[5] or of a 'dynamic network'[6].

In the limit of zero shear rate, the viscosity is determined by the dynamic equilibrium at rest. Three

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processes may happen simultaneously upon increasing the shear rate.

1. The stretching of the supermolecular structures, owing to their deformation in the imposed shear, will cause intermolecular bonds to 'break' (accelerated kinetics[6] of the disappearance of bonds), by which the spatial dimensions of the structures, and the viscosity inherent in this dimension, will decrease.
2. The polymer molecules forming a supermolecular structure might be compelled to move relative to each other, resulting in an increasing number of encounters between reactive sites on different molecules. This will promote the formation of intermolecular bonds, eventually at the expense of intramolecular bonds.
3. The polymer molecules forming the supermolecular structures being stretched, see (1), may be extended so far that non-linear equations are required to describe the relations between the forces on and the relative positions of the secondary bonds connecting one polymer molecule to the supermolecular structure.

Because in general structures with smaller spatial dimensions have lower intrinsic viscosity values, process (1) promotes a shear stress increasing less than linearly as a function of shear rate. On the other hand, process (2) promotes a shear stress increasing more than linearly as a function of shear rate for the very same reason.

Process (3) does the same as process (2), but the underlying mechanism is completely different. Here the individual polymer molecules are extended more and more when shear rate is increased, and the forces on the secondary bonds become greater and greater. The shear stress, mainly being the result of an averaging process over the forces exerted on the secondary bonds, reflects the non-linear force relations of the individual polymer molecules in a more than linear increase as a function of shear rate.

In case all three processes are present, process (1), or one or both of processes (2) and (3), may dominate in a restricted range of shear rates. When process (1) dominates, this will be observed as *shear-thinning*, whereas domination of processes (2) and/or (3) will be observed as *shear-thickening*

Shear thinning is the more usual phenomenon on polymer solutions or polymer melts[7]. On the other hand, shear thickening has been observed[4,8–12] in solutions of certain surfactants and block and graft copolymers[13,14]. A very striking example of shear thickening is that of aqueous solutions of poly(methacrylic acid) in water[15]. This behaviour was explained[16] in terms of the second of the mechanisms already described. Shear thickening followed by shear thinning has been observed for sulfonated polystyrene ionomers in non-polar solvents[17] and was described recently for solutions of poly(styrene-*block*-isoprene-*block*-styrene) in n-tetradecane, a non-solvent for poly(styrene)[6,12]. In the case of the polystyrene ionomers the viscosity behaviour was suggested to be caused by the mechanism described in (2), whereas the viscosity behaviour of the triblock copolymer was explained by the mechanism described in (3)[6]. In the latter case the Lodge transient network model[5] was extended to allow for a non-linear relation between the force on and the strain of a polymer chain, and the chance of breakage of intermolecular bonds was, on using physical arguments, taken to be force dependent. This resulted, on taking the total number of molecules participating in the supermolecular structures to be constant, in shear-thinning preceded by shear-thickening behaviour that matched the experimental results quite well. We wish to mention that the triblock copolymer solutions thermoreversibly gelate on lowering the temperature.

As an attempt to design a water-soluble polymer with comparable macroscopic properties, we describe the synthesis and the viscosity of aqueous solutions of PAAm polymers grafted with poly(ethylene oxide-*co*-propylene oxide). Owing to the decreasing solvation of the polyether grafts, particularly in salty solutions, these water-soluble polymers are expected to associate at elevated temperatures, the intermolecular interaction being a function of the polymer concentration, the temperature and the amount of added salt. A higher molecular weight, a higher propylene oxide content and a greater salt concentration, especially with bivalent anions (CO_3^{2-}, SO_4^{2-}), are essential factors that promote association of the grafts at lower temperatures[13,14,18].

EXPERIMENTAL

Materials and solvents

High molecular weight poly(acrylamide) and partly hydrolysed poly(acrylamide) were used as received from Aldrich. *N*-hydroxysuccinimide (NHS), *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), 1 M HCl solution, THF of analytical quality and MeOH were obtained from Merck and used without further purification. Jeffamine® M-600 and M-2070 (poly(oxyalkylene)monoamines) were kindly provided by Texaco Chemical Belgium. Jeffamine® M-600 has an M_w of 597 g mol^{-1} and the structure $H_3COCH_2CH_2O(CH_2CH(CH_3)O)_8CH_2CH(CH_3)NH_2$. Jeffamine® M-2070 has an M_n of $\sim$2000 g mol^{-1} and is a random copolymer of ethylene oxide with 30% propylene oxide, i.e. $H_3COCH_2CH_2O(CH_2CH(R)O)_nCH_2CH(CH_3)NH_2$ where R is H or CH_3.

Synthesis of the graft copolymers

Around 250 ml of a 2–3 wt% solution of poly(acrylamide) (PAAm) in water were delivered into a 500 ml three-necked flask equipped with two dropping funnels, a pH electrode and a magnetic stirrer. Based on the assumption that the PAAm contained 5 mol% of COOH groups, a double molar quantity (relative to the carboxy content of the PAAm) of poly(oxyalkylene) monoamine was added. About 50 ml of an aqueous solution containing 0.6 wt% EDC and 2.6 wt% NHS were prepared separately and poured into the polymer solution. The quantities of EDC and NHS were chosen to obtain a molar ratio[19] of EDC:NHS:COOH equal to 5:2:1. The initial pH of the prepolymer solution was 9.0–9.2 and this decreased to 7–8 upon addition of the EDC/NHS solution. The pH of the mixture was adjusted to the optimum range of 5–5.5 by adding 1 M HCl from the dropping funnel[19]. In the initial stage of the reaction ($t \leqslant 30$ min), the reaction consumed H^+ and the pH increased slowly. After stirring the mixture overnight at room temperature, the pH had decreased to 4. The mixture was neutralized with a 0.1 M NaOH solution added via the second dropping funnel and then precipitated in THF. Graft copolymer with a high molecular weight backbone precipitated in MeOH and was filtered over a Büchner funnel and dried under vacuum at 50°C. Lower molecular weight polymers were obtained after decanting the THF and drying overnight under vacuum at 50°C. Residual salts from the coupling reaction were removed by dialysis after dissolving the graft copolymers in water. As the purified graft copolymers could not be precipitated in MeOH or THF, the aqueous solutions were freeze dried. The yield of the reactions was 85–95 wt% relative to the initial amount of PAAm. The loss of some PAAm is probably caused by fractionation during the purification steps.

^{1}H n.m.r. spectra

^{1}H n.m.r. spectra were recorded on a Bruker AC250 spectrometer at 250 MHz with D_2O as the solvent. Chemical shifts refer to tetramethylsilane (TMS).

Gel permeation chromatography (g.p.c.)

Experiments were performed in 0.1 M NaCl at room temperature using a TSK-PWXL guard column in series with a TSK-GMPWXL mixed bed column with a pore size >1000 Å and a TSK G-DNA-PW column with a pore size >4000 Å (Toyo Soda). Elution was detected by means of a Waters 411 differential refractometer and a Viscotek H502 viscosity detector. Calibration was done with broad molecular weight distribution PAAm samples (Polymer Standard Service). The resolution of the g.p.c. columns was at its limit for the high molecular weight ($>10^6\,\mathrm{g\,mol^{-1}}$) fractions, and as a result the peaks of the high molecular weight polymers were non-symmetrical.

Intrinsic viscosities

Viscosities in 0.1 M NaCl and in 0.5 M K_2CO_3 at 25°C were measured with Ubbelohde capillaries using an automated set-up from Schott (AVS 350).

Rheological measurements

Measurements were performed on graft copolymer solutions in water and in 0.5 M K_2CO_3. The salt solution was chosen based on turbidity experiments with poly(ethylene glycol)s ($MW=750$, 2000 and $5000\,\mathrm{g\,mol^{-1}}$), which showed that cloud points below 60°C could be obtained in 0.5 M K_2CO_3, dependent on the polymer concentration and molecular weight. Flow curves, showing the shear stress (τ in Pa) as a function of the shear rate (γ' in $\mathrm{s^{-1}}$), were obtained with a Carri-Med® controlled stress rheometer[6,20]. A cone and plate set-up (DIN 53018) with a diameter of 60 mm and an angle of 0.98° between the cone and plate was used with a vapour lock to prevent evaporation of water from the polymer solution at elevated temperatures (up to 85°C).

RESULTS AND DISCUSSION

Preparation of the graft copolymers

Poly(acrylamide)-*graft*-poly(ethylene oxide-*co*-propylene oxide) samples have been prepared either by copolymerization of acrylamide with monomethoxypoly(ethylene oxide) methacrylates (MePEOMA) or by grafting poly(oxyalkylene) monoamines onto partly hydrolysed PAAm[21]. The first, so-called 'macromer', method has the advantage that it yields the graft copolymer in only one step. However, this method also has several drawbacks[22–25], i.e.

1. the molecular weights of the graft copolymers are rather polydisperse and little defined owing to chain transfer reactions, which may even lead to crosslinked, insoluble polymers[22];
2. the copolymerization parameters of acrylamide with MePEOMA are not known and can be expected to vary with the molecular weight of the macromers and the growing graft copolymer[24]; and
3. a satisfactory characterization of the graft copolymers by g.p.c. and viscometry will be difficult owing to association of the grafts and shrinkage of the polymer coils.

For the present approach, it was therefore chosen to synthesize poly(acrylamide)-*graft*-poly(ethylene oxide-*co*-propylene oxide) by the 'grafting onto' method. Monoamine-terminated ethylene oxide/propylene oxide copolymers were coupled to the carboxy groups in PAAm by a carbodiimide-activated reaction[19,26,27] (*Scheme 1*).

The water-soluble *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide **1** adds rapidly to the nucleophilic carboxylate groups in partly hydrolysed PAAm. However, the resulting *O*-acylisourea can hydrolyse or rearrange to the much less reactive *N*-acylurea **3** by an intramolecular *N*-acyl shift[26]. Both side reactions can be suppressed by the addition of *N*-hydroxysuccinimide (NHS)[19], which reacts with **2** to give the NHS ester **4** which is then converted to the graft copolymer **5**. Hydrolysis of **4** is very slow compared to its reaction with the amine-terminated ethylene oxide/propylene oxide (EO/PO) copolymer.

The reaction gives easy access to any desired combination of hydrolysed PAAm with monoamine-terminated EO/PO copolymers or with other monoamine-terminated (co)polymers. Backbone and grafts can be characterized prior to the coupling and can serve as a reference for the characterization of the graft copolymers. Thus, rather well-defined 'model' graft copolymers can be obtained

Table 1 Graft copolymers synthesized by the 'grafting onto' method

	Backbone		Graft		Graft copolymers	
Sample	M_w[a] ($\mathrm{g\,mol^{-1}}$)	$[\eta]$[b] ($\mathrm{ml\,g^{-1}}$)	M_w[a] ($\mathrm{g\,mol^{-1}}$)	$[\eta]$[b] ($\mathrm{ml\,g^{-1}}$)	N_{grafts}[c]	$[\eta]$[d] ($\mathrm{ml\,g^{-1}}$)
P(A-*g*-M-600)	4.0×10^5	150	597	4.9	4.3	–
P(A-*g*-M-2070)-I	4.0×10^5	150	2000	9.2	5.6	174
P(A-*g*-M-2070)-II	2.6×10^6	612	2000	9.2	1–2[e]	582

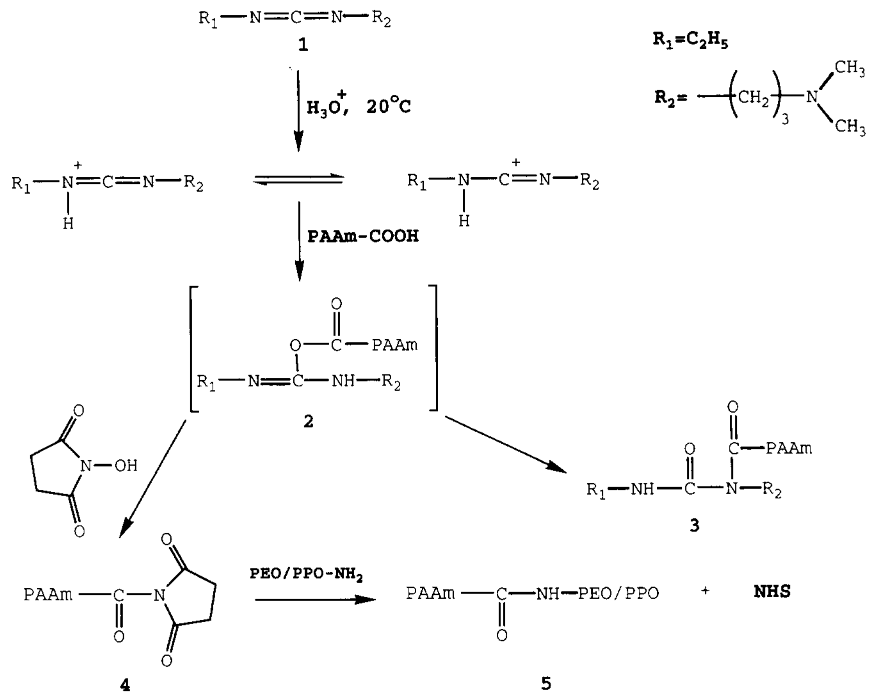
[a] M_w was calculated from $[\eta]$ in 0.1 M NaCl at 25°C from the Mark–Houwink relation[28]: $[\eta]=(9.33\times10^{-3})M_w^{0.75}$

[b] Intrinsic viscosities were measured in 0.1 M NaCl at 25°C with an Ubbelohde capillary

[c] Average numbers of grafts per 100 monomer units as calculated from the signal intensities in the ^{1}H n.m.r. spectra

[d] Intrinsic viscosities were measured in 0.5 M K_2CO_3 at 25°C with an Ubbelohde capillary

[e] Estimated from the signal intensities in the ^{1}H n.m.r. spectrum



Scheme 1

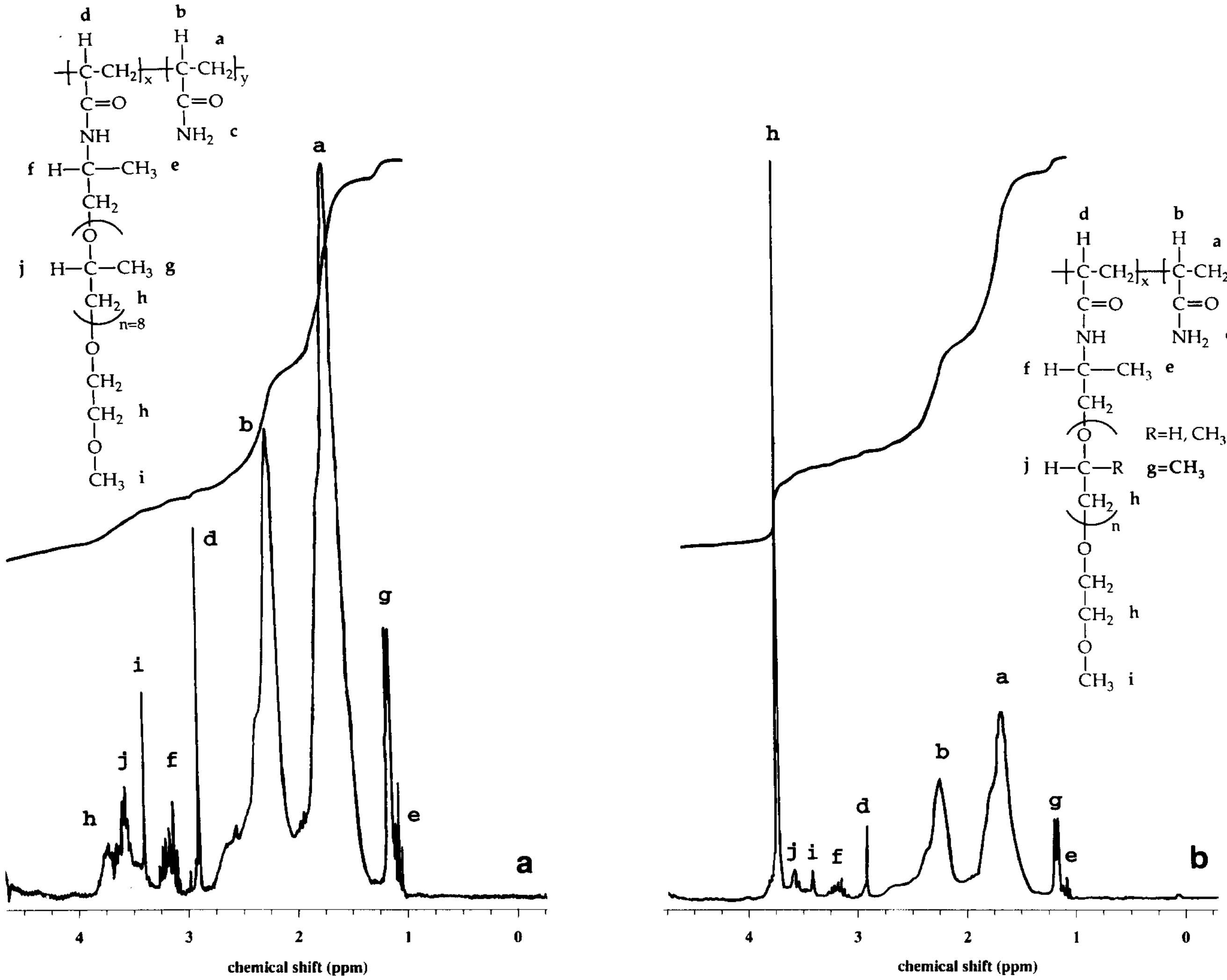


Figure 1 ^{1}H n.m.r. spectra of (a) P(A-*g*-M-600) and (b) P(A-*g*-M-2070)-I, both measured in D_2O

which can also be used to characterize graft copolymers synthesized by the 'macromer' method[21,22].

An overview of the prepared graft copolymers is given in *Table 1*. Samples P(A-*g*-M-600) and P(A-*g*-M-2070)-I were prepared from a partly hydrolysed PAAm with an M_w of approximately 400 g mol^{-1} as calculated from the intrinsic viscosity in 0.1 M NaCl. Sample P(A-*g*-M-2070)-II was prepared from a high molecular weight PAAm with a small content ($\leqslant$5 mol%) of carboxy groups, as is commonly present in commercial PAAm.

The parent PAAm, the poly(oxyalkylene) monoamines and the synthesized graft copolymers were characterized by ^{1}H n.m.r. spectroscopy, gel permeation chromatography (g.p.c.) and viscometry. The ^{1}H n.m.r. spectra of P(A-*g*-M-600) and P(A-*g*-M-2070)-I (*Figure 1*) clearly confirm the coupling of the grafts to the backbone.

The signal for the methine protons (d) of the grafted acrylamide units is shifted towards lower field (2.9 ppm) compared to the signal for the corresponding protons (b) of the ($CH_2CHCONH_2$) units. The number of grafts per 100 monomer units could be calculated from the signal intensities (see *Table 1*) using the following expression

$$N_{\text{grafts}}=\left(\frac{I_d}{I_d+I_b}\right)\times 100\ [100\ \text{monomer units}]^{-1} \quad (1)$$

where I_d and I_b are the integrals of the ^{1}H n.m.r. signals for the two different types of methine proton in the graft copolymers.

Figure 2 shows the g.p.c. traces of the graft copolymers and their constituent building blocks as measured at room temperature. In 0.1 M NaCl there was no significant difference between the elution volumes of the non-grafted poly(acrylamide)s (backbone) and the graft copolymers, which is in accordance with the g.p.c. results in 0.1 M NaCl. The intrinsic viscosity of P(A-*g*-M-2070)-I was found to be equal to the intrinsic viscosity of the backbone polymer ($[\eta]=150$ ml g^{-1}). Also, in 0.5 M K_2CO_3 the intrinsic viscosity of P(A-*g*-M-2070)-II was practically the same as that of the precursor polymer in 0.1 M NaCl (see *Table 1*). Only when the molecular weight of the backbone precursor was relatively small, i.e. P(A-*g*-M-2070)-I, was the intrinsic viscosity in 0.5 M K_2CO_3 slightly higher than that of the backbone precursor in 0.1 M NaCl (see *Table 1*).

Rheological measurements

Flow curves of a solution of 10.15 mg ml^{-1} P(A-*g*-M-2070)-I in pure water (solution 1) were measured at temperatures from 30 to 80°C at shear rates from approximately 100 to 2700 s^{-1}. At these shear rates, the viscosity of the solution was independent of the shear rate and decreased with temperature. This behaviour is expected for a polymer solution where no specific interactions between the macromolecules take place.

Flow curves of a dilute solution of P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 ($c=1.54$ mg m^{-1}, $c^*=1.7$ mg ml^{-1}; solution 2) showed a similar viscosity behaviour to that observed for pure water solutions. The rather low viscosities decreased again with increasing temperature. However, association of the ether grafts can be expected if the macromolecules are not dissolved in pure water but in a K_2CO_3 solution. Therefore the viscosity measurements indicate that associations of the polyether grafts in the dilute solution 2 are predominantly intramolecular. *Figure 3* shows the initial slope, i.e. the viscosity at low shear rate η_{init}, as a function of temperature for both solutions as compared to the viscosity of water[29].

Figure 4 shows the flow curves of a semiconcentrated solution of P(A-*g*-M-2070)-II in 0.5 M K_2CO_3, i.e. 2.97 mg ml^{-1} corresponding to $c=1.7c^*$. Up to about

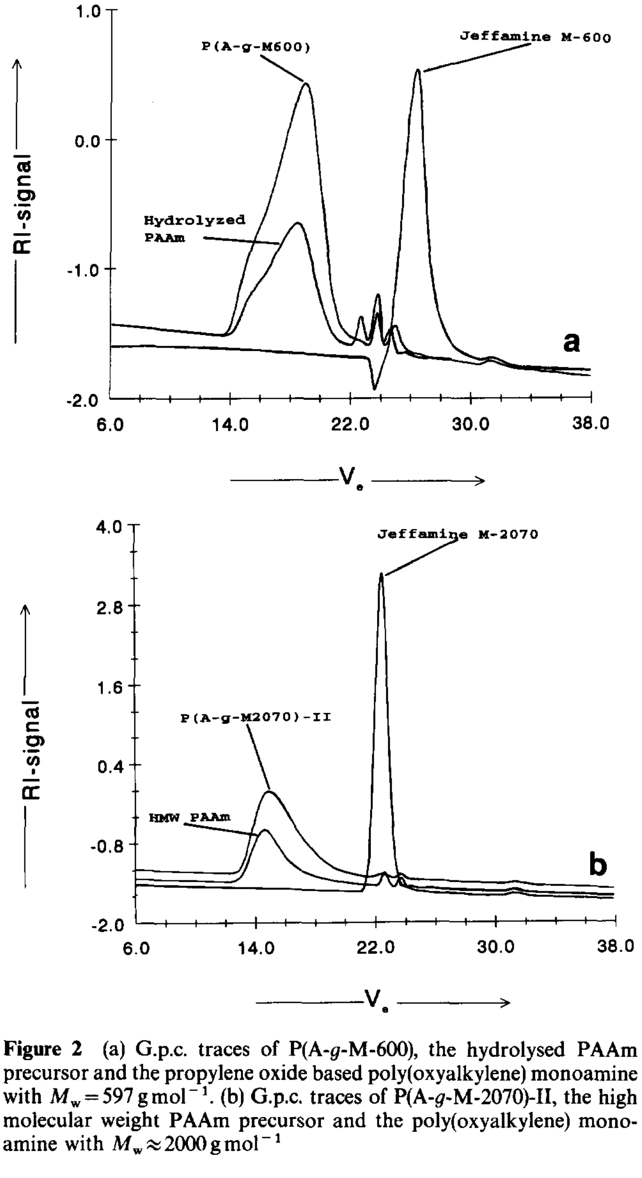


Figure 2 (a) G.p.c. traces of P(A-*g*-M-600), the hydrolysed PAAm precursor and the propylene oxide based poly(oxyalkylene) monoamine with $M_w=597$ g mol^{-1}. (b) G.p.c. traces of P(A-*g*-M-2070)-II, the high molecular weight PAAm precursor and the poly(oxyalkylene) monoamine with $M_w\approx 2000$ g mol^{-1}

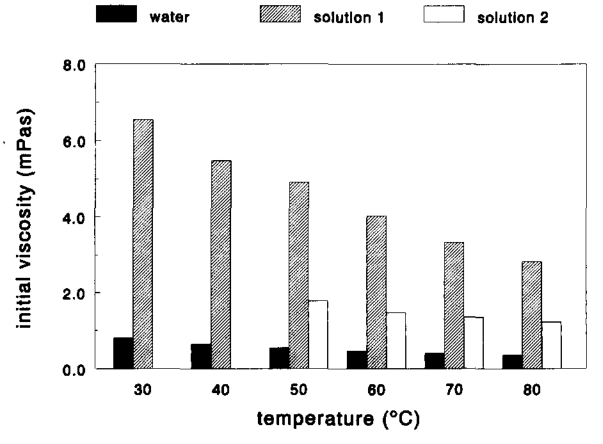


Figure 3 Initial viscosities (η_{init}) for solutions of 10.15 mg ml^{-1} P(A-*g*-M-2070)-I in water (solution 1) and 1.54 mg ml^{-1} P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 (solution 2) and the viscosity of water at different temperatures

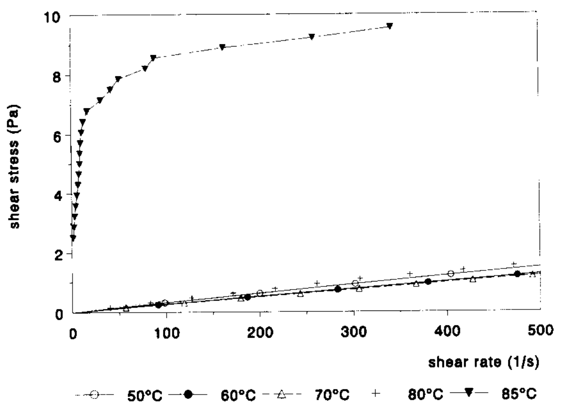


Figure 4 Flow curves for 2.97 mg ml^{-1} P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 at different temperatures. Initial viscosities were obtained by extrapolating the viscosity to zero shear rate: $\eta_{init}(50°C) = 3.15$ mPa s; $\eta_{init}(60°C) = 2.74$ mPa s; $\eta_{init}(70°C) = 2.66$ mPa s; $\eta_{init}(80°C) = 3.83$ mPa s; $\eta_{init}(85°C) = 1.88$ Pa s

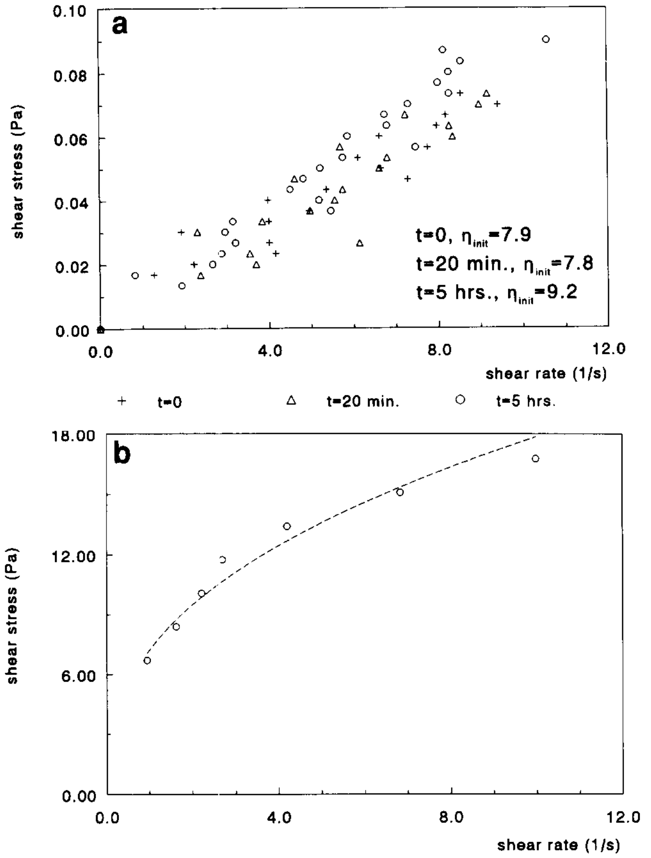


Figure 5 Flow curves for 6.67 mg ml^{-1} P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 at (a) 50°C and (b) 80°C. Initial viscosities are in mPa s and are average values over the shear rate range listed in *Table 2*

Table 2 Averaged initial viscosities as a function of temperature for a solution of P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 ($c = 6.67$ mg ml^{-1})

Time (h)	Temperature (°C)	Shear rate range (s^{-1})	Initial viscosity η_{init} (mPa s)
0.0	50	2–10	7.9
0.3	50	2–10	7.8
2.5	80	<1	$\sim 1.5 \times 10^4$
3.5	70	2–9	12 ± 4
3.5	70	4–21	8.9 ± 1.7
4.5	60	0.5–5	18 ± 6
4.5	60	0.5–10	13 ± 3
4.5	60	1–15	14 ± 3
5.0	50	2–10	11.2 ± 2.6

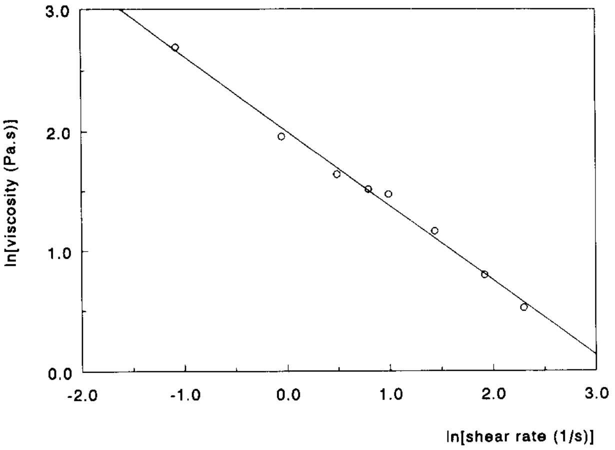


Figure 6 Viscosity *versus* shear rate for 6.67 mg ml^{-1} P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 at 80°C

70°C, the initial slope, i.e. the viscosity at low shear rate η_{init}, decreases with temperature. However, η_{init} increases strongly between 80 and 85°C. The data show not only an increase in η_{init} of almost three orders of magnitude, but also a strong dependence of the viscosity on the shear rate. At 85°C the viscosity decreases from 1.88 Pa s at a shear rate of 1.3 s^{-1} to 0.5 Pa s at a shear rate of 12.9 s^{-1}. The occurrence of a very high initial viscosity at 85°C (*Figure 4*) indicates the formation of a reversible gel, which is destroyed at shear rates above 10 s^{-1}.

In order to demonstrate the reversibility of the observed viscosity phenomena and to determine whether evaporation of solvent at high temperatures influenced the measurements, flow curves of a solution of 6.67 mg ml^{-1} P(A-*g*-M-2070)-II in 0.5 M K_2CO_3 were also recorded in the sequence 50°C, 80°C, 70°C, 60°C, 50°C.

Figure 5a shows that after 5 h the viscosity at 50°C has only increased from initially 7.8–7.9 mPa s to 9.2 mPa s*. The data show some scattering, because the measurements were performed just above the lower limit of the measuring range of the rheometer used. Nevertheless, it was concluded that evaporation of water from the polymer solution can be neglected. The averaged values of η_{init} measured at the different temperatures are listed in *Table 2*.

The flow curve in *Figure 5b* at 80°C shows a viscosity of approximately 15 Pa s at a shear rate of 0.3 s^{-1}, followed by a steep decrease in the viscosity up to a shear rate of 3 s^{-1}. The viscosity at shear rates higher than 10.0 s^{-1} is less than 1 Pa s. At low shear rates, the measurements indicate the shear rate dependent reorganization of the dynamic associate structure by a steep decrease in the viscosity as a function of shear rate. This steep decrease of the viscosity with shear rate is also shown in *Figure 6*, where the logarithm of the viscosity (as calculated point by point) is plotted against the logarithm of the shear rate. The data fit the power-law: $\ln(\eta) = 1.997 - 0.62\ln(\gamma')$.

More detailed measurements, particularly at shear rates of less than 1 s^{-1}, have to be performed in order to determine whether the apparent stepwise change

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* The system is not expected to have a yield stress, because the measured viscosities were very low ($\eta < 10$ mPa s). Thus, the initial viscosities were determined by fitting the data to the linear equation $\tau = \eta_{init} * \gamma'$, which goes through the origin

in the viscosity function indicated in *Figure 5b* might be correlated with particular stress dependent transitions of the associated structure.

CONCLUSIONS

Water-soluble poly(acrylamide)-*graft*-poly(ethylene oxide-*co*-propylene oxide)s can be tailor-made in high yields by the 'grafting onto' method described above. Defined graft copolymers resulted when defined PAAm and monoamine-terminated ethylene oxide/propylene oxide copolymers were coupled. These can be helpful in characterizing the corresponding poorly defined macromer copolymers.

The rheological behaviour of the 'model' graft copolymers in aqueous solution was studied with a stress-controlled cone and plate rheometer. The viscosities of solutions of the graft copolymers in pure water and dilute solutions ($c<1/[\eta]$) of the graft copolymers in 0.5 M K_2CO_3 decreased with temperature. However, at higher concentrations ($c>c^*$) the viscosity increased from 10–20 mPa s between 20 and 70°C to almost 15 Pa s at 85°C. The observed phenomena can be explained in terms of the formation of secondary bonds or association between the polyether side chains, causing reversible network formation in the liquid (temperature thickening).

The flow behaviour at shear rates lower than 2 s^{-1} indicated reversible gelation through the occurrence of relatively high initial shear stresses. At shear rates higher than 2–5 s^{-1} all solutions clearly showed shear thinning. Above the lower limit of the shear rate of the rheometer used no shear thickening was observed. Corresponding studies at lower shear rates and on the optimization of the graft copolymer structure are presently being performed and will be the subject of a future report.

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