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# Synthesis and solution rheology of poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)]

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## ABSTRACT

Poly[(stearyl methacrylate)-*stat*-[2-(dimethylamino) ethyl methacrylate]] was synthesised through radical polymerisation using 1,1-diphenyl ethylene (DPE) as a molecular weight controlling agent. The amino groups were further quaternised into a cationic form in order to increase water solubility. Solubility of the polymers in water and a mixed solvent was studied with rotational rheometry. The resulting poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)] was soluble in water when the amount of stearyl methacrylate (SMA) in the polymer was less than 17 mol%. At higher SMA content, solubility strongly decreased but could be improved by using an organic co-solvent. Viscosity of the SMA-based statistical co-polymers is strongly dependent on polymer composition but solvent quality also has an influence, and the fluidic character can be either Newtonian or shear-thinning, or a weak gel can be formed. Concentration dependence behaviour deviates from that of typical polyelectrolytes. SMA polymers retain low viscosity up to rather high concentrations, but above a certain limiting concentration, the viscosity rapidly increases. This phenomenon is stronger with a higher amount of hydrophobic side-chain. At high co-polymer concentrations no entanglement formation was observed, and rheological behaviour indicates that SMA segments form aggregates in water solution.

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## 1. Introduction

Polymers with an amphiphilic character can have interesting properties. Amphiphilic polymers containing poly[2-(dimethylamino) ethyl methacrylate] (PDM) have been reported to effectively hydrophobise surfaces [1]. They have been shown to be effective as modifiers of paper surfaces [2]. Stearyl methacrylate has also been used to stabilise liposome emulsions [3]. Block co-polymers from stearyl methacrylate and DMAEMA exhibit self-organising behaviour in different organic solvents [4]. Water soluble polymers containing long aliphatic side chains have the potential to be used as dispersing agents for strongly hydrophobic materials such as polyethylene in water [5]. In water solution, amphiphilic polymers form aggregates and these can be identified with rheometry [6].

The rheological properties of polymer solutions are strongly dependent on chain architecture [7]. Typically, the viscosity of a polymer solution decreases when the solubility of the polymer in the solvent decreases, and the reduction in viscosity is caused by a decrease in the hydrodynamic radius [8]. The rheological behaviour of amphiphilic polymers deviates from that of more homogeneous polymers [9]. The most typical difference is concentration dependence [10], where a sharp increase in viscosity is observed above a certain concentration [11]. This atypically strong concen-

tration dependence [12] is observed when the length of the hydrophobic segment is long enough [13] that the polymer aggregates in solution [11].

Polymers containing long aliphatic hydrocarbon segment are poorly water soluble. However, co-polymers containing hydrophobic segments become water soluble when strongly hydrophilic segments are co-polymerised into the hydrophobic polymer. Hydrophilicity is often achieved by introducing anionic [5] or cationic groups into the polymer [1]. The solubility of the polymer is also strongly dependent on molecular weight. Polymethacrylates with controlled molecular weights can be prepared by group transfer polymerisation [14], atom transfer radical polymerisation [15], reversible addition-fragmentation chain transfer polymerisation [4,16], ring opening polymerisation, etc. SMA can also be polymerised through photopolymerisation [17]. Uncontrolled radical formation, which can cause the final molecular weight to be too high or lead to formation of a cross-linked structure, can be prevented by using DPE as a molecular weight controlling agent [18].

In the work reported in this paper, statistical co-polymers containing both strongly hydrophobic and strongly hydrophilic segments were synthesised through bulk polymerisation followed by post-modification. A set of poly(stearyl methacrylate-*stat*-DMAEMA) (PSMA) polymers was synthesised through free radical polymerisation with DPE as a molecular weight controlling agent. Melt properties of the polymers were measured with rotational rheometry. The PDM sequence in the resulting polymer was

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further modified to give a cationic form [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) in order to obtain a completely water soluble polymer (Fig. 1). Solution studies of the resulting polymers were done, with the focus on the rheological properties, and the effects of hydrophobic groups on rheological properties are discussed.

## 2. Experimental

### 2.1. Materials

The chemicals used and their suppliers were: 2-(dimethylamino) ethyl methacrylate (DMAEMA), diphenyl ethylene (DPE), deuterated chloroform, D<sub>2</sub>O and deuterated acetone, Aldrich; basic alumina, methylene iodide (MeI), acrylo isobutyro nitrile (AIBN), and tetraethylene glycol dimethyl ether (TEG), Fluka; stearyl methacrylate (SMA), tetrahydrofuran (THF), hexane and acetone, BHD Prolabo; iso-octane, Rathburn. DMAEMA was purified to remove inhibitor by filtration through basic alumina. Other chemicals were used without further purification. All chemicals were of reagent grade.

### 2.2. Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were analysed with a 300-MHz Varian Gemini 2000 in deuterated chloroform (CDCl<sub>3</sub>). Conversion during synthesis was followed with <sup>1</sup>H NMR spectroscopy as decrease in height of vinyl peaks, and the structure was confirmed with <sup>13</sup>C NMR. Formation of cationic segments through post-modification was measured in D<sub>2</sub>O and in deuterated acetone by <sup>1</sup>H NMR.

### 2.3. Size exclusion chromatography (SEC)

Purified polymers were analysed with size exclusion chromatography (SEC) using chloroform with 2% triethylamine (TEA) as eluent. Elution speed was 1 ml/min through the following column system: PLgel pre-column and PLgel 10<sup>4</sup> Å, 10<sup>5</sup> Å, 10<sup>3</sup> Å and 10<sup>2</sup> Å columns supplied by Polymer laboratories. Relative changes in molecular weight were determined with a Waters RI-detector (refractive index) against polystyrene standards and number average molecular weight (*M<sub>n</sub>*) and polydispersity (PD) were reported.

### 2.4. Synthesis of methacrylate co-polymers

Synthesis of methacrylate co-polymers was performed with radical polymerisation using AIBN as an initiator. Monomer to initiator ratio in polymerisations was 140 and initiator to DPE ratio was 10:3. The monomers SMA and DMAEMA, and DPE and the initiator were weighed in a reaction vessel. A dry atmosphere was obtained with three vacuum-argon cycles at room temperature, after which the temperature was increased to the reaction temperature of 80 °C. Monomer conversion was followed with <sup>1</sup>H NMR. Poly-

merisation was carried out for 3 h until the conversion was over 90%. The resulting polymer was precipitated in a mixture of hexane and iso-octane, where the amount of iso-octane was increased with increasing amounts of stearyl segment in the co-polymer.

### 2.5. Cationisation of PDM sub-units

Cationic species were introduced into the polymer with methyl iodide according to a method slightly modified from that presented in the literature [14,19]. A dilute solution (1 g/100 ml) of methacrylate co-polymer and tetrahydrofuran was prepared at ambient temperature. Three equivalents of methyl iodide for each equivalent of DMAEMA were added while stirring in a cool water bath. The reaction mixture was stirred overnight at ambient temperature. Cationic polymer was precipitated from the reaction mixture when the conversion was high enough. The remaining solution was filtered and washed with acetone. The quantitative reaction of cationic sub-units could be confirmed by a peak at 3.2 ppm in <sup>1</sup>H NMR.

### 2.6. Differential scanning calorimetry

Melting temperatures (*T<sub>m</sub>*) and glass transition temperatures (*T<sub>g</sub>*) were determined with a Mettler Toledo DSC 821e differential scanning calorimeter with a heating rate of 10 °C/min and a cooling rate of 20 °C/min. The measured temperature range was between –100 °C and 100 °C, and the sample size was 6–10 mg. Thermal histories of the samples were equalised by one heating cycle followed by a cooling cycle.

### 2.7. Rotational rheometry

#### 2.7.1. Polymer melt studies

Thermal transitions of the polymers were measured with an Anton Paar Physica MRC 301 dynamic rotational rheometer operated in strain-controlled mode. Temperature was controlled at the lower plate using a Peltier heating element and water circulator. Twenty-five millimeter plate geometry was used. Gap size was controlled with a TruGap induction sensor. The gap size was adjusted to an optimum of 150 μm to minimise any possible temperature gradient. The temperature ramp used for measurements was cooling from 100 °C to –30 °C at 5 °C/min followed by heating up to 100 °C at 5 °C/min. Oscillatory measurements were done at 0.1% strain within the linear viscoelastic region at 10 Hz frequency. Storage and loss moduli and viscosities were determined.

#### 2.7.2. Polymer solution studies

Rheology of the polymer solutions was measured with a stress-controlled rotational rheometer (TA Instruments AR-G2) with a Peltier heating element and water circulation cooling bath.

Solubility of the polymer in water was determined with a 20 mm steel plate and plate geometry with a 500 μm gap size. A 1% water solution was mixed using a magnetic stirring bar and placed into the measuring head. A temperature ramp was performed from 20 °C to 80 °C with a rate of 3 °C/min followed by a similar cooling ramp. Oscillatory data was measured using 1% strain at an angular frequency of 1 rad/s.

Rheological measurements at 1% mass concentration in water and in mixtures of water and tetraethylene glycol dimethyl ether (TEG) were performed using a recessed end cylinder geometry with 14 mm and 15 mm rotor and stator radii according to the following procedure: first the polymer was mixed in solvent using a magnetic stirring bar, resulting in an unstable mixture of small particles. Solutions were heated using a Peltier heating element at 5 °C/min followed by a corresponding cooling ramp. The water solutions were heated up to 80 °C and the solutions containing

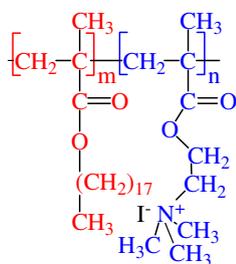


Fig. 1. Repeating units of poly[(stearyl methacrylate)-stat-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)] (PSMAQ).

TEG up to 100 °C. Oscillatory data was measured using 5% strain at 1 Hz frequency. After the cooling ramp the sample was stabilised for 15 min, after which a strain sweep from 0.1% to 1000% was done at 1 rad/s. The sample was then stabilised for 30 min, whereafter a frequency sweep with 0.2% strain from 300 rad/s to 0.05 rad/s was done. After that, shear viscosity was measured from 0.002 s<sup>-1</sup> to 1000 s<sup>-1</sup>.

Concentration studies were done with 60 mm cone and plate geometry with a 1° cone angle. Samples for concentration studies were heated up while stirring with a magnetic stirring bar. After dilution the solutions were reheated while stirring. After this treatment no visual precipitation was observed and the solutions were clear. Strain sweep was measured at 1 rad/s from 0.1% to 1000%. After a stabilisation time of 30 min, frequency sweep measurements were made with 0.2% strain from 300 to 0.05 rad/s. After that, shear viscosity of the polymer solutions was measured from 0.002 s<sup>-1</sup> to 1000 s<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Synthesis and characterisation of the polymers before ionisation

The polymers produced and their properties are listed in Table 1. Molecular weights of all other polymers except PSMA100 were less than 100,000 g/mol. Stearyl methacrylate homopolymer had a higher molecular weight, partly because the molar mass of the repeating unit of SMA is higher. It is also possible that self-initiation of DMAEMA monomer reduces molar mass. It must also be mentioned that this conventional SEC is only a relative method. The conversion obtained was similar with all SMA contents, which was to be expected because DMAEMA and methacrylate with aliphatic side chains have rather similar reactivity in the absence of a polar solvent [15].

DSC measurements indicate that stearyl groups formed crystalline segments. Crystallinity can clearly be seen in DSC when the molar percent of SMA is 50% or higher. Even at lower levels of SMA there is a slightly crystalline character. Phase transition behaviour is consistent with results reported in the literature, where the  $T_m$  of SMA homopolymer was reported to be 34 °C [20]. Because the presence of SMA segments confers a strongly crystalline character on the polymer, it can be debated whether the polymer has long segments of SMA or if the SMA is randomly distributed. The melting temperature of the stearyl methacrylate polymers decreased much more rapidly than was reported for block co-polymers of SMA and styrene [21].  $T_m$  strongly decreases with increasing amount of DMAEMA and  $T_g$  decreases. The polymerisation is statistical and reactivity of the monomers is about the same, so a random distribution of SMA is most likely. If SMA formed long segments, stronger crystallinity of the polymer would be expected [20].

Thermal transition temperatures can also be confirmed with rotational rheometry. Reliable  $T_g$  values of amorphous polymers

could not be measured with rotational rheometry because the stiffness of the polymers is outside of the operating range of the instrument [22]. Thermal transition behaviour can be seen in Fig. 2. Melt viscosity increased with increasing content of PDM. PDM also increased the complex viscosity's dependence on temperature.

#### 3.2. Synthesis and characterisation of poly(SMA-stat-META)

P(SMA-stat-DMAEMA) was methylated with methyl iodide, giving poly(SMA-stat-META) (Fig. 1). The conversion of the post-modification reaction was quantified with <sup>1</sup>H NMR and no signs of residual di-methyl groups were found in cationic polymers. After cationisation,  $T_g$  of the polymers was strongly increased by the ionic salt RN(Me<sub>3</sub>)<sup>+</sup>Cl<sup>-</sup> species formed. However, ammonium salt affected the thermal properties of the samples so that reliable DSC data could not be obtained. There was no sign that SMA would cause any softening in the polymer and no  $T_g$  could be found with rheometry. Therefore we only report thermomechanical characterisation of the samples before cationisation.

#### 3.3. Solubility of the polymers

Prepared non-quaternary SMA co-polymers were soluble in several organic solvents. After modification with methyl iodide, the polymers became cationic, whereafter their solubility in organic solvents was strongly reduced, so that the polymers precipitated from the reaction solvent [23]. Typically polymers with an amphiphilic character can be dissolved in water by first dissolving them in a solvent mixture followed by evaporation of the co-solvent [16]. In this study homogeneous solutions were achieved by heating to above the solubility temperature after careful homogenisation of water and the polymer. Solubility temperature can be seen with rotational rheometry in an oscillatory temperature scan as a sharp increase in storage and loss moduli, as shown in Fig. 3.

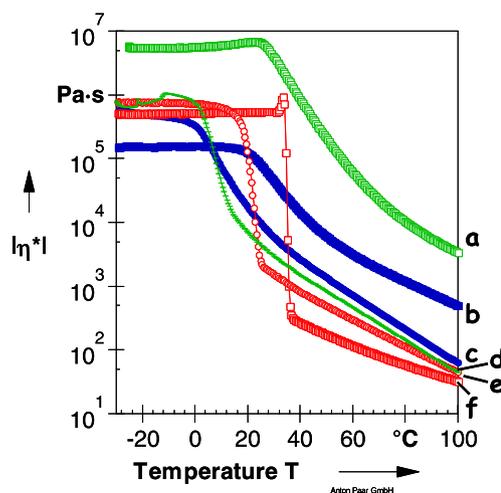
Solubility characteristics of the resulting cationic co-polymers are listed in Table 2. Solubility of the PSMA co-polymer in water rapidly decreases when the amount of hydrophobic moieties is increased. This is consistent with what has previously been reported in the literature [14], where solubilisation of poly(alkyl methacrylates) in water demanded a more than 80 mol% PDM molar ratio. Solubility can be improved by adding a suitable co-solvent. In this study, TEG was used as a co-solvent. Normally, lipophilic ethers of low molecular weight poly(ethylene glycol) are known to be non-ionic surfactants [5], but low molecular weight polymers are not

**Table 1**  
Characterisation of non-ionic pre-polymers.

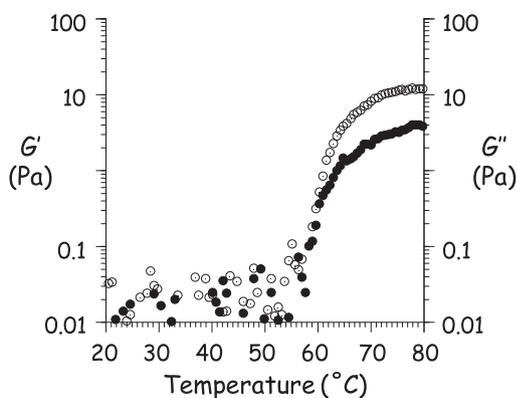
Polymer	SMA <sup>*</sup> Mol%	$M_n$ <sup>**</sup> kg/mol	PD <sup>**</sup>	DSC		Rheometer
				$T_g$ (°C)	$T_m$ (°C)	$T_m$ (°C)
PSMA100	100	195	3.2	–	36	34
PSMA50	50	75.6	2.7	–	24	14
PSMA34	34	41.7	2.0	–15	9	–
PSMA17	17	24.7	1.8	2	7	–
PSMA13	13	50.6	1.4	2	–	–
PDM	0	62.6	2.2	15	–	–

\* In feed.

\*\* Size exclusion chromatography against polystyrene standards.



**Fig. 2.** Effect of polymer composition on melt viscosity of poly(SMA-stat-DMAEMA): (a) PDM, (b) PSMA13, (c) PSMA17, (d) PSMA34, (e) PSMA50, (f) PSMA100.



**Fig. 3.** Solubility temperature of PSMA17Q seen as increase in moduli in 1% water solution ( $G'$  = open bullets and  $G''$  = closed bullets).

**Table 2**  
Solubility of SMAQ polymers.

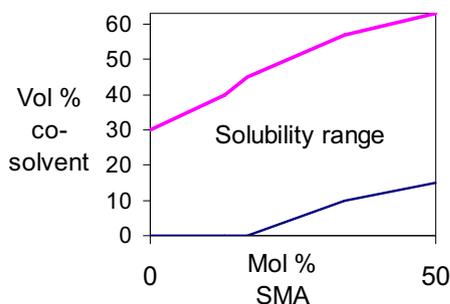
Polymer	SMA Mol%	Solubility	
		In water	Co-solvent (%)
PDMQ	0	Soluble	–
PSMA13Q	13	<21%	–
PSMA17Q	17	<5%	–
PSMA34Q	34	Insoluble	10
PSMA50Q	50	Insoluble	15
PSMA100	100	Insoluble	100

highly water soluble. Instead, TEG was chosen as co-solvent because, due to its high boiling point, it is not volatile, and it has low viscosity. TEG is also miscible in water, unlike many other ethyl ethers with a short hydrocarbon chain.

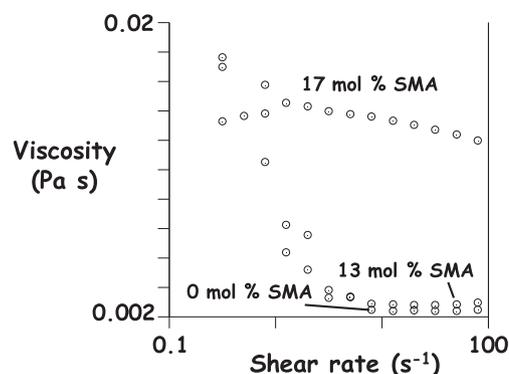
The solubility range of the cationic SMA co-polymers in the water–TEG mixture is reported in Fig. 4. It can be seen that SMA co-polymers are water soluble up to a relatively low amount of hydrophobic monomer, 17 mol%. Co-solvent improves the solubility of SMA co-polymers in water. SMA34Q was soluble in water containing 10% TEG, whereas SMA50Q dissolves in water with a 15% volume ratio of TEG. The maximum amount of organic co-solvent that could be added to water and still dissolve the polymer was also determined and the solubility limits are presented in Fig. 4. All polymers are soluble in solvent mixtures containing 30% organic co-solvent, and the amount of organic co-solvent increases almost linearly with increasing amounts of SMA segments.

### 3.4. Viscosity of the polymers in water and in solvent mixtures

The effect of SMA on solution viscosity was studied with rotational rheometry. In Fig. 5, flow viscosities of 1% water solutions



**Fig. 4.** Solubility of PSMAQ in solvent mixtures containing water and TEG.



**Fig. 5.** The effect of SMA content on the shear viscosity of poly(stearyl methacrylate-co-dimethylaminoethyl methacrylate) in 1% water solution. The scale is logarithmic.

are presented with increasing content of SMA. It can be seen that viscosity strongly increases with increasing SMA content in water solution. Typically, the viscosity of a polymer solution decreases when the solubility of the polymer is reduced, because the hydrodynamic size or radius of gyration of the polymer is reduced [7]. However, the behaviour observed with SMA co-polymers is in agreement with a phenomenon observed for amphiphilic polymers [9], where increasing amounts of hydrophobic segments in polymers increase the viscosity of their water solutions [11]. There can be number of reasons for increased viscosity with an increasing amount of SMA but one explanation is association formation. That can also explain a slight change in the rheological nature of the polymer solution, changing the behaviour of the polymer solution from Newtonian to weakly shear-thinning.

Solution viscosity is strongly dependent on the nature of the polymer, but solvent plays an important role as well [7] since it affects the hydrodynamic size of the polymer. Hydrodynamic size can decrease due to polymer structure, e.g. branching [7], or it can decrease due to a solvent in which the polymer has limited solubility, i.e. not all segments are completely dissolved [10]. Therefore viscosity of the polymers in a solvent mixture containing 15% organic co-solvent was studied and compared with viscosities obtained in water solution. The effect of viscosity of the solvent was removed by calculating the specific viscosity according to the following equation

$$\eta_{sp} = \frac{\eta_0 - \eta_{\text{solvent}}}{\eta_{\text{solvent}}} \quad (1)$$

$\eta_0$  is the zero shear viscosity determined according to Cross [24] or the Newtonian model.

Changes in solution viscosity in different solvents can be seen in Table 3, where specific viscosities are reported with different SMA contents in the polymer. Specific viscosity of the homopolymer PDMQ is not changed markedly with solvent change, and the Newtonian character of the homopolymer PDMQ is also maintained

**Table 3**

Zero shear rate specific viscosities of 1% polymer solutions in water and in solvent mixtures containing 15 vol.% TEG.

Polymer	SMA Mol%	Water		Solvent mixture	
		$\eta_s^a$	Fluid character	$\eta_s^a$	Fluid character
PDMQ	0	1.2	Newtonian	1.4	Newtonian
PSMA13Q	13	1.3	Newtonian	216	Shear-thinning
PSMA17Q	17	11	Shear-thinning	0.9	Shear-thinning
PSMA34Q	34	–	–	132	Weak gel
PSMA50Q	50	–	–	0.11	Newtonian

<sup>a</sup>  $\eta_s$  = zero shear rate specific viscosity.

when 15 vol.% organic co-solvent is added. Viscosity changes in polymers containing SMA are more notable. The viscosity of PSMA13Q increases whereas the viscosity of PSMA17Q decreases compared to viscosity in water. The viscosity of PSMA50Q in a solvent mixture containing 15% TEG is very low. In this solvent mixture, this polymer is at its solubility limit (see Fig. 4) and low viscosity can be expected [7]. Water is a good solvent for PDMQ and it adopts an extended conformation in water solution, whereas PSMA is not soluble in water at all. This solvent mixture is considered a better solvent for polymers containing higher amounts of SMA, resulting in increased viscosity.

It is not only zero shear viscosity but also the fluidic nature that is of interest when polymers containing hydrophobic and hydrophilic segments are studied. In a solvent mixture containing 15% TGDME, PSMA34Q and PSMA13Q gave zero shear rate viscosity at the same level, but the natures of the fluids are somewhat different from each other. PSMA34Q forms a gel-like structure, as can be seen in Fig. 6, whereas PSMA13Q is clearly a shear-thinning fluid instead of a gel. It is clear that polymer–solvent interactions play a key role in the viscosity of polymer solutions, and small changes in solvent composition have a significant effect on viscosity of the polymer solution.

### 3.5. Scaling effects – zero shear viscosity dependence on concentration

Aggregation behaviour was further examined by studying the concentration dependence of viscosity for the polymers. Typically, the specific viscosity of a polymer solution increases according to the scaling law [12]. Critical concentrations for each region were determined from specific viscosities according to the theory of entanglement viscosity [25]. Concentration dependence of specific viscosity for polyelectrolyte solutions typically can be determined according to following scaling relationship:

$$\begin{aligned} \text{Semidilute unentangled } \eta_{sp} &\sim c^a, c < c^* \\ \text{Semidilute entangled } \eta_{sp} &\sim c^b, c^* < c < c^{**} \\ \text{Concentrated regime } \eta_{sp} &\sim c^c, c > c^{**} \end{aligned}$$

Specific viscosities in water of two water soluble SMA co-polymers, PSMA13Q and PSMA17Q, are presented in Fig. 7. Concentration dependence in the low concentration region is similar for both of the polymers independent of the amount of SMA. However, a strong increase in viscosity is seen at higher concentrations. There are two likely reasons for such an increase in viscosity, namely entanglement of the polymer chain or associations between non-soluble SMA groups [11].

Transition concentrations and coefficients for concentration dependencies are listed in Table 4. From concentration curves of PSMA13Q, three different regions can be identified with different

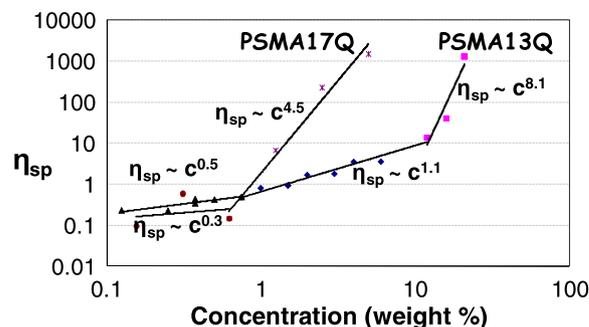


Fig. 7. Specific viscosity as mass concentration in water solution.

**Table 4**  
Scaling relationships of polymers in water solution.

	Scaling coefficient			Transition concentration (%)	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>c</i> <sup>*</sup>	<i>c</i> <sup>**</sup>
Theoretical [12]	0.5	1.5	3.75	–	–
SMA13Q	0.5	1.1	8.1	0.8	12
SMA17Q	0.3	–	4.5	–	0.7

concentration dependencies, whereas only two regions for PSMA17Q can be identified. First the viscosity of PSMA13Q increases by a factor of  $c^{0.5}$  and it follows the polyelectrolyte scaling law, [12] whereas the viscosity of PSMA17Q increases more slowly, by a factor of  $c^{0.3}$ . After a certain point, the behaviours diverge markedly.

After the unentanglement region, a separate region showing typical behaviour for an entanglement concentration of polyelectrolyte solutions was found when PSMA13Q with a lower content of SMA was studied, having a concentration dependence of  $c^{1.1}$ . A similar region with a moderate concentration dependence could not be found for PSMA17Q. In PSMA17Q, a rapid increase in viscosity occurs after the unentanglement region, and no entanglement concentration typical for polyelectrolyte solutions was found. A similarly rapid increase in viscosity with concentration was also found when PSMA13Q was studied, and in both cases the concentration dependence was atypically strong. Transition concentrations deviated significantly from each other. A concentration of  $c^{**}$  for PSMA17Q was already reached at 0.7% mass concentration, whereas PSMA13Q reached  $c^{**}$  at the relatively high mass concentration of 12%.

#### 3.5.1. Effect of polymer concentration on viscoelastic character of solutions

At low concentrations, a polymer solution is typically Newtonian [24], whereas polymer solutions at high concentrations are generally shear-thinning fluids. For many polymers a behaviour typical of polymer melts is seen when the polymer concentration is high enough [26]. In these SMA co-polymers, viscosity increases much more rapidly than in polyelectrolytes normally. Therefore it can be speculated that the polymers may exhibit melt-like behaviour [7] caused by entanglement formation in concentrated regions. In order to study the fluidic character in detail, shear and dynamic rheology were compared at high polymer concentrations. In Fig. 8 fluid strength at different concentrations can be seen in shear stress–shear rate curves for PSMA17Q. Fluid strength clearly increases with increasing concentration, as is to be expected [24].

The fluidic character of these polymers was studied by comparing elastic and viscous responses of SMA17Q solutions. Strain sweeps at various concentrations are presented in Fig. 9, and it can be seen that polymer solution becomes a shear-thinning fluid

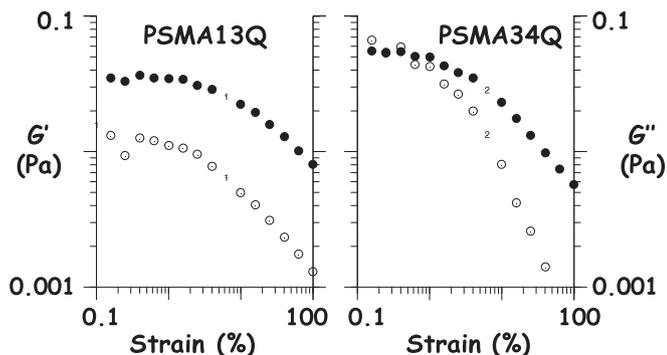


Fig. 6. Fluidic character of PSMA34Q and PSMA13Q in solvent mixtures containing 15% TEG and 85% water ( $G'$  = open bullets and  $G''$  = closed bullets).

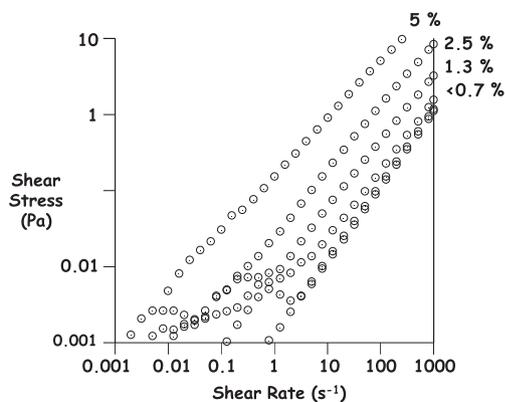


Fig. 8. Fluid strength dependence of PSMA17Q on polymer concentration in water solution.

at high concentrations. It can also be seen that the fluid strength increases with increasing polymer concentration, as can also be

seen in the flow curves in Fig. 8. Strain sweeps in Fig. 9 indicate that PSMA17Q would exhibit yield stress at the highest concentration. Yield stress is not a typical characteristic of polymer fluids [24] and indicates that PSMA17Q would form a weak gel at the highest concentration, 5%. Gel-like formation can be confirmed with frequency sweeps, as shown in Fig. 10, where the storage modulus  $G'$  exhibits a slope of 0.2. Also,  $G'$  seems to be higher than the loss modulus at low frequencies and no entanglement frequency typical of polymer melts was found. This is an indication that even at high concentrations no melt-like behaviour occurs, and the increase in viscosity of PSMA17Q is caused by interactions between polymer molecules.

Huge differences in elastic character were also found in frequency sweeps done at concentrations  $c < c^{**}$  (Fig. 10). Within this concentration region the polymer solution changed from Newtonian to shear-thinning. A slope of two for the storage modulus  $G'$  was found at the lowest concentration. When the concentration was further increased, the polymer solution formed a gel having a slope of 0 for  $G'$ . A gel forms at concentrations of 0.3% and 0.6% when the polymer solution is below the concentrated region.

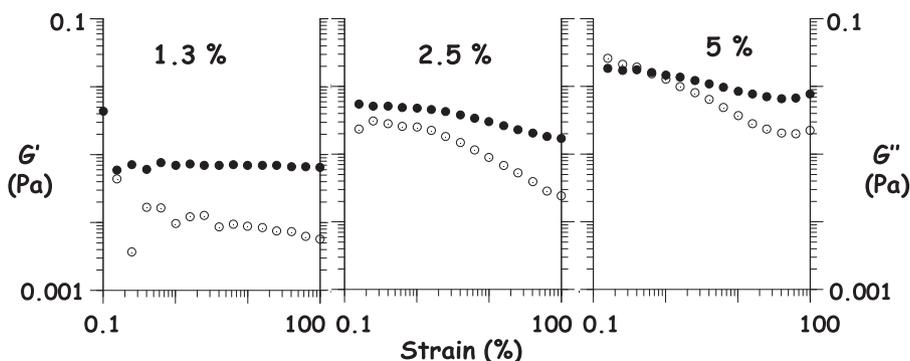


Fig. 9. Strain dependence of PSMA17Q in water solution: storage and loss moduli at concentrations  $c > c^{**}$  ( $G'$  = open bullets and  $G''$  = closed bullets).

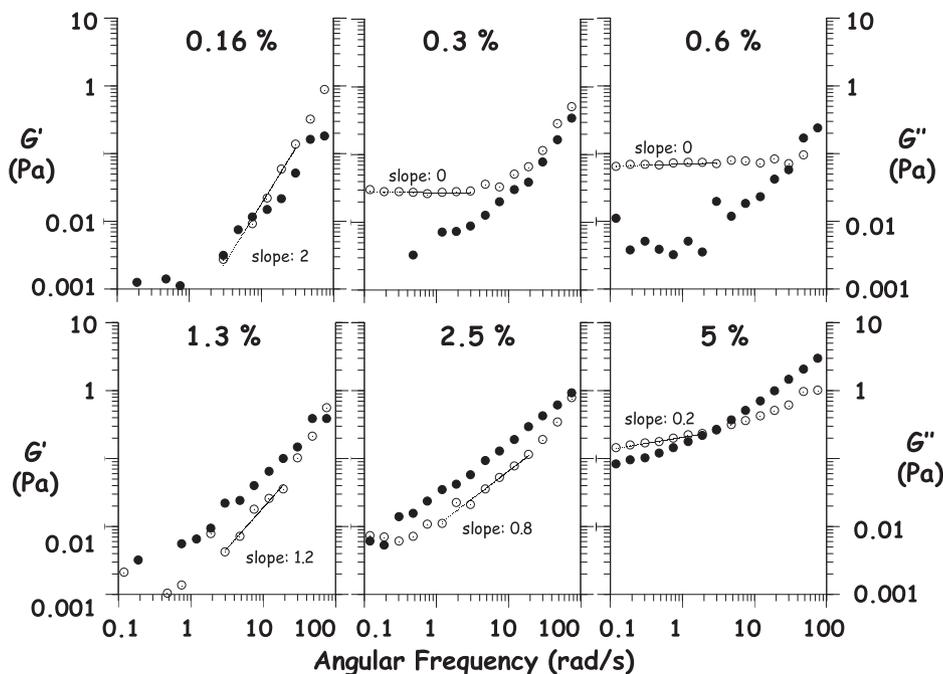


Fig. 10. Frequency dependence of PSMA17Q in water solution: storage and loss moduli at concentrations  $c < c^{**}$  (above) and  $c > c^{**}$  (below) ( $G'$  = open bullets and  $G''$  = closed bullets).

When polymer concentration is further increased into the concentrated region,  $c > c^{**}$ , a gel is not formed any more and a higher slope and lower  $G'$  is obtained again.

Rheological properties are strongly affected by polymer composition, solvent quality, and polymer concentration. We can speculate as to the reasons for such huge changes in rheological properties. There are two main effects interfering with polymer behaviour in water solution; they are hydrodynamic radius and molecular interactions. These are strongly affected by solvent but also by polymer concentration. Molecular interactions can cause aggregation resulting in low viscosity, but they can also cause intermolecular association, resulting in higher viscosity. The kind of structure formed is strongly dependent on polymer concentration as well as the amount of hydrophobic segments.

#### 4. Conclusion

Hydrophobically modified water soluble methacrylate co-polymers were synthesised with radical polymerisation followed by post-modification. Water solubility rapidly decreased with increasing amounts of hydrophobic segments, but solubility could be improved with an organic co-solvent. Proper tailoring of stearyl methacrylate co-polymers enables us to tune their properties so that the viscoelastic characteristics would be suitable for different applications. Solution viscosity of polymers containing hydrophobic and hydrophilic structures is strongly dependent on polymer composition and polymer concentration, but solvent quality also plays an important role, and solution viscosity can easily be modified by changing the solvent mixture.

These polymers exhibit stronger concentration dependence than is typical for polyelectrolytes. At low concentration the polymers exhibit low viscosity, but a rapid increase in viscosity is seen at a certain concentration. Concentration dependence is stronger with the polymer containing more SMA. At low concentration the polymers exhibit Newtonian behaviour and at high concentration they behave as shear-thinning fluids. However, even though concentrated polymer solutions exhibit high viscosity, the polymers do not form the entanglements typical of concentrated polymer solutions. The rheological behaviour indicates that the SMA segment is strong enough to form both inter and intra molecular association in water solution.

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