Copolymers of acrylamide and surfactant macromonomers: synthesis and solution properties

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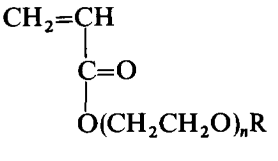
Surfactant macromonomers 'surfomers' have been copolymerized with acrylamide to form hydrophobically associating polymers. This study focuses upon the use of nonylphenoxypoly(etheroxy) acrylates of variable poly(etheroxy) chain length. Since such hydrophobic monomers have built in surfactant character, no external surfactant is needed for the preparation of high molecular weight acrylamide copolymers with 0.1–5 mol %, hydrophobe content. The acrylamide surfomer copolymers containing even small concentrations of surfomer (i.e. $\leqslant 0.5$ mol%) show interesting solution properties, e.g. enhanced viscosity above C^*, and reduced viscosity below C^*. The viscosity of such polymers is more sensitive to the surfomer level and type than to changes in $[M]/[I]^{1/2}$. Highest solution viscosities are achieved for polymers purified/isolated by a solution polymer route.

(Keywords: hydrophobically associating polymers; macromonomers; surfactants; acrylamide copolymers; conformers)

INTRODUCTION

Recently, there has been substantial interest in hydrophobically associating acrylamide polymers (e.g. copolymers of acrylamide and long chain *N*-alkyl acrylamides). Such materials are characterized by enhanced viscosity combined with brine and/or shear stability[1-8]. Since acrylamide and long chain alkyl acrylamides are mutually incompatible, specialized copolymerization techniques (e.g. alcohol[1] or surfactant homogenation[1,5]; microemulsion[3] or micellar[4] polymerization) are required. Such processes are characterized by low product molecular weights and/or large usage of external surfactant. Surfactant/hydrophobe ratios of 20–100 are not uncommon in order to solubilize the hydrophobic monomer in the aqueous phase.

To obviate the need for external surfactants and also to control the solubility of the final polymers better, we have studied the use of hydrophobic monomers with built in surfactant character [i.e. *surf*actant macromon*omers* or *surfomers*, R-PEO-Ac(I)]



$$\begin{array}{l} CH_2{=}CH \\ \quad\;\, | \\ \quad\;\, C{=}O \\ \quad\;\, | \\ \quad\;\, O(CH_2CH_2O)_nR \end{array}$$

Ia $R = \text{nonylphenyl}, \bar{n} = 10$
Ib $R = \text{nonylphenyl}, \bar{n} = 20$
Ic $R = \text{nonylphenyl}, \bar{n} = 40$

(I)
R-PEO-Ac

This report describes the synthesis and solution properties of copolymers of acrylamide and surfomers. Preliminary reports of this work can be found elsewhere[7,9-11].

EXPERIMENTAL

Materials

Potassium persulphate from Phaltz Bauer was used as received. Acrylamide (AM) monomer, reagent grade from Aldrich, was recrystallized from acetone and vacuum dried at room temperature prior to use. The surfactant macromers, e.g. nonylphenyl-, phenyl and methyl-poly(etheroxy) acrylates, were prepared according to modifications of known procedures[12] and/or obtained from Monomer-Polymer and Dajac Laboratories.

Equipment

Reduced viscosity data was obtained on a Contraves Low-Shear 30 viscometer at $1.28\,s^{-1}$ and 25°C.

Brookfield viscosity (25°C) was determined for undialysed reaction mixtures (0.3% polymer) using a Brookfield viscometer and spindles 2 or 3 at 12 rev/min ($\dot{\gamma} = 2.6$–$2.9\,s^{-1}$).

Typical polyacrylamide polymerization

Distilled water (500 ml) was added to a resin flask equipped with a water condenser, thermometer, mechanical stirrer, and a nitrogen inlet and outlet. The water was deoxygenated for 15–30 min by a nitrogen purge. The monomer (30 g) was added and the solution further purged at 50°C with nitrogen for between 45 min and 1 h. The $K_2S_2O_8$ (0.01 g) initiator was charged and the polymerization temperature maintained at 50–55°C. The polymerization was run for 18.5 h (conversion 90–100%).

Typical copolymerization of acrylamide with nonylphenoxypoly(etheroxy)ethyl acrylate

A 500 or 1000 ml quantity of distilled water was added to a resin flask equipped with a water condenser,

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thermometer, mechanical stirrer, and a nitrogen inlet and outlet. Nitrogen was bubbled through the solution for 15–30 min; the acrylamide monomer (30 g) and nonylphenoxypoly(etheroxy) acrylates R(PEO)Ac (1–5 g) were charged to the flask. The solution was heated by an oil bath under nitrogen purge at 50°C for 1 h. After this period of time, the $K_2S_2O_8$ initiator (0.01 g) was added and the temperature maintained at 50–55°C under nitrogen for 18.5 h (conversion 70–85%).

Polymer purification and isolation

Polymers were purified/isolated in one of two separate ways. In one method, the polymers were isolated as dry powders by precipitation/vacuum drying or dialysis/freeze drying (solid polymer route).

In a second method (solution polymer route), the solid polymers were never isolated; rather, the reaction mixtures were diluted to 0.3–0.6 w/w% with low conductivity water and dialysed against water to remove impurities.

Analytical characterization

The surfactant macromonomers were analysed by our newly developed h.p.l.c. technique[13]. The presence of surfomer in the copolymers was confirmed by u.v. analysis of the nonylphenoxy(polyetheroxy) acrylate chromophore at 276 nm after correction for a low level acrylamide absorbance. Absorbance vs. concentration plots followed Beer's Law[14]. Incorporation levels of surfomers in the copolymers were generally 40–50% based upon active monomer charged.

Polymer solution properties: solid polymer route

The solid dry polymers were weighed (± 0.001 g) into flasks; the solvent (doubly distilled water or doubly distilled water containing NaCl) was weighed into the same flask. The polymers were agitated by magnetic stirrer for a minimum of 48 h or until complete solubility was achieved, as determined by visual observation. The experimental polymers had a slower dissolution rate than polyarylamide. If a polymer solution displayed 'gel' particles after a lengthy dissoltuion period, the solution was centrifuged at 2000 rev/min for 2 h to separate the 'gel' from the soluble portion. A few of the more viscous solutions were subjected to an additional filtration through a 150 mesh stainless steel screen to remove any micro-gel particles. An aliquot was then removed and vacuum dried at 110°C to determine solubility and polymer concentration for all polymers. When polymer solubility did not approximate 90%, polymer concentrations were corrected. Dilutions of each polymer stock solution were prepared in water or brine and the viscosity obtained after waiting a minimum of 1 h after dilution to achieve equilibrium.

The intrinsic viscosities of the polymers were determined using standard techniques. The reduced viscosity or viscosity number $(\eta - \eta_0)/c$, where η is the polymer solution viscosity (centipoise), η_0 is the solvent viscosity and c is the polymer concentration, was used to obtain the intrinsic viscosities $(\eta_{\mathrm{red},c\to 0})$. Polymer concentration began at 3000 ppm (unless indicated) to establish an initial baseline prior to dilution. Viscosity measurements were conducted at 25°C using the Contraves viscometer. Viscosity comparisons were made on 'unaged'[15] samples because the various copolymers did not 'age' at the same rate.

Polymer solution properties: solution polymer route

The reaction mixture containing about 3.0 wt% polymer was diluted 1:1 with doubly distilled water. The Brookfield viscosity (12 rev/min, spindles 2 or 3) of this solution (~1.5% polymer) was then determined to provide an initial evaluation of synthesis and polymer quality. This 1.5 wt% solution was then diluted (to 0.3–0.6% polymer) with doubly distilled water and dialysed for two to three days to remove unreacted monomer, catalyst residues, polymerization byproducts, etc. Dialysis was conducted in a Spectrapor membrane (No. 2, *MW* cut-off = 12 000–14 000) which was previously conditioned by boiling for 1 h in 2% $NaHCO_3$ solution. In a typical dialysis run, about 500 ml of the reaction mixture was placed in about three feet of conditioned dialysis membrane. Plastic clamps from Spectrum Medical Industries were used to seal the ends of the membrane. The membrane was placed in about 4 litres of doubly distilled water contained in a 4 litre beaker. A magnetic stirrer was used to provide mixing of the system. After each dialysis period (one to two days), the conductivity of the water on the outside of the membrane was measured via a Model 31 Conductivity Bridge (YSI). The membrane containing the polymer solution was placed in fresh doubly distilled water and the process repeated until the desired conductivity was reached. The dialysis was considered complete when the conductivity of the water on the outside of the membrane reached a steady state value. A dialysis time of two to three days was usually sufficient.

Initially, the reaction mixture was diluted to 0.6% before dialysis. At this concentration, the dialysed solutions of some polymers were gel-like, had very high viscosities and were difficult to handle when diluting to the desired concentrations for viscometric analysis. For such systems, the reaction mixtures were initially diluted to about 0.2–0.3% with doubly distilled water prior to dialysis.

The dialysed solutions were diluted to the desired concentration (usually 3000, 2000 and 1000 ppm) with the appropriate quantity of a 2% NaCl solution (doubly distilled water). Initially, each concentration was prepared separately by this method. To improve precision and accuracy, it was found desirable to prepare an initial 2% NaCl solution of the highest desired polymer concentration and dilute this solution with 2% NaCl solution (double distilled water) to obtain lower concentrations. Evaluation of the viscometry of these solutions was conducted via the Contraves viscometer as previously described.

RESULTS AND DISCUSSION

Surfactant macromonomers such as alkyl(polyetheroxy) acrylates, R-PEO-Ac(I), are water soluble or water dispersible. The extent of water solubility depends upon the hydrophile–lipophile balance (HLB) of the surfactant and the temperature. In this study, we emphasize the use of surfactant macromers (I), wherein R = nonylphenyl and $\bar{n} = 10$ (Ia), 20 (Ib) and 40 (Ic).

The surfomers of this study have been analysed by our previously described reverse phase h.p.l.c. method (*Table 1*)[13]. Such macromomers show a distribution of polyether chain lengths with the surfactant macromomers and precursor alcohols being the major components detected

Table 1 Reverse phase h.p.l.c. of surfactant macromonomers[a]

Comonomer ID	Average PEO chain length, *n*	Components	Distribution of PEO chain lengths, *n*	wt%
Ia-1	10	Phenoxypoly(etheroxy) acrylate	2–18	0.48
		Phenoxyacrylate	–	0.09
		Nonylphenoxypoly(etheroxy) alcohol	2–18	49
		Nonylphenoxypoly(etheroxy) acrylate	2–18	49
Ia-2	10	Phenoxypoly(etheroxy) acrylate	2–18	–
		Phenoxyacrylate	–	–
		Nonylphenoxypoly(etheroxy) alcohol	2–18	22[a]
		Nonylphenoxypoly(etheroxy) acrylate	2–18	78[a]
Ia-3	10	Nonylphenoxypoly(etheroxy) acrylate		100[a]
Ib	20	Phenoxypoly(etheroxy) alcohol	6–20	1.2
		Phenoxyacrylate	–	0.09
		Nonylphenoxypoly(etheroxy) alcohol	6–20	62
		Nonylphenoxypoly(etheroxy) acrylate	6–20	36
Ic-1	40	Phenoxypoly(etheroxy) alcohol	>20	1.1
		Nonylphenoxypoly(etheroxy) alcohol	>20	65
		Nonylphenoxypoly(etheroxy) acrylate	>20	33
Ic-2	40	Phenoxypoly(etheroxy) alcohol	>20	–
		Nonylphenoxypoly(etheroxy) alcohol	>20	15[a]
		Nonylphenoxypoly(ethoxy) acrylate	>20	85[a]

[a] Minor (<2%) components [e.g. phenoxypoly(etheroxy) acrylate and phenoxy acrylate] not included in total

Table 2 Synthesis of P(AM-*co*-R-PEO-Ac)

AM mol	R-PEO-Ac comonomer type/level: R	(EO)$_n$	mol × 10^3	mol%	H_2O (g)	$K_2S_2O_8$ (g)	[η] in 2% NaCl (dl g^{-1})	$\bar{M}_v \times 10^{-6}$
0.42	$C_9H_{19}Ph$	40	0.042	0.10	500	0.1	5.60	2.0
0.42	$C_9H_{19}Ph$	40	1.23	0.30	1000	0.053	3.90	1.3 (7.7[b])
0.42	$C_9H_{19}Ph$	40	1.23	0.30	1000	0.013	3.83	1.2 (7.5[b])
0.42	$C_9H_{19}Ph$	20	1.30	0.30	1000	0.13	5.1	1.8
							6.0	2.2
0.42	$C_9H_{19}Ph$	10	1.30	0.30	1000	0.013		
0.42	$C_9H_{19}Ph$	40	1.20	0.30	1000	0.013	7.6	3.0
0.42	$C_9H_{19}Ph$	10	1.20	0.45	1000	0.023	7.1	2.8 (4.6[c])
0.21	$C_9H_{19}Ph$	10	6.9	3.2	500	0.005	1.6	0.4
0.42	CH_3	40	1.2	0.3	500	0.01		
0.42	Ph	30	1.2	0.3	500	0.01	6.0	2.2

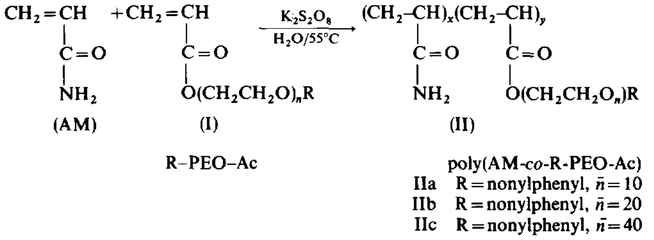
[a] Calculated from $[\eta] = 7.19 \times 10^{-3} M_v^{0.77}$ (Kulicke, W. M., Kniewski, R. and Klein, J. *Prog. Polym. Sci.* 1982, **8**, 373

[b] M_w determined by sedimentation/LALLS measurement (Holzwarth, G., Soni, L. and Schulz, D. N. *Macromolecules* 1986, **19**, 422

[c] M_w determined by static LALLS measurement

by this method. Of course, the alcohols are not polymerizable. Yet they can exert a molecular weight reducing effect via chain transfer.

Such surfomers can be easily copolymerized with acrylamide (AM) to form water soluble copolymers, i.e. poly(AM-*co*-R-PEO-Ac) (II), which contain low levels (<5 mol%) of surfactant group.



$$CH_2{=}CH(CONH_2) + CH_2{=}CH(CO\text{-}O(CH_2CH_2O)_nR) \xrightarrow[H_2O/55^\circ C]{K_2S_2O_8} (CH_2\text{-}CH(CONH_2))_x(CH_2\text{-}CH(CO\text{-}O(CH_2CH_2O_n)R))_y$$

(AM) (I) (II)

R–PEO–Ac

poly(AM-*co*-R-PEO-Ac)
IIa R = nonylphenyl, $\bar{n} = 10$
IIb R = nonylphenyl, $\bar{n} = 20$
IIc R = nonylphenyl, $\bar{n} = 40$

Unlike the copolymerization of acrylamide with other hydrophobic monomers (e.g. long chain alkylacrylamides), large amounts of external surfactant are not needed to solubilize the hydrophobic monomer[3,4]. Rather, conventional free radical solution methods can be used to form high molecular weight copolymers (*Table 2*). Copolymer molecular weights tend to decrease with increasing levels of surfomer. This result suggests some chain transfer to surfactant macromonomer or concomitant alcohol. Moreover, depending upon the HLB of the surfomer, there can be solubility problems at high levels of surfomer. Consequently, our work focused on the use of the lowest levels of surfomer necessary to achieve hydrophobic enhancements of viscosity, while minimizing molecular weight or solubility debits.

Acrylamide copolymers containing even small quantities of surfomer units (i.e. ≤0.5 mol%) exhibit interesting solution properties. For example, above the polymer overlap concentration (C^*) (i.e. >1000 ppm), these polymers show substantially higher viscosities than unsubstituted polyacrylamide; below C^*, the surfomer copolymers show lower intrinsic viscosities [η] and elevated Huggins constants, k_H (*Table 3*). Such behaviour has been demonstrated for solutions of other associating polymers[7,16,17]. Thus, above C^* the chains interact intermolecularly to form a species with larger hydrodynamic radius and viscosity than that of the unsubstituted polymer. Below C^*, the chains interact intramolecularly to collapse the coil further, lowering [η] and raising the slope of the reduced viscosity concentration plot, i.e. k_H.

Above C^*, the viscosity depends upon the level and type of surfomer, as well as conventional polymerization variables, such as the ratio of monomer concentration to the square root of the initiator concentration, $[M]/[I]^{1/2}$.

Table 3 Viscosity data[a] for PAM and P(AM-*co*-R-PEO-Ac)[c] copolymers

	PAM	IIa	IIb	IIc
Viscosity at 3000 ppm (cP)	4.50	12.9	33	11.50
Viscosity at 1000 ppm (cP)	1.70	2.30	2.00	2.50
[η] (dl g^{-1})[b]	7.6	6.4	5.1	3.8
k_H[b]	0.29	0.4	1.27	11.6

[a] In 2% NaCl solution, filtered through a 150 mesh screen and measured at 1.3 s^{-1}

[b] [η] and k_H calculated according to the Flory–Huggins relationship, $\eta_{sp/c}=[\eta]+k_H[\eta]^2C+k_H[\eta]^3C^2$

[c] 0.3 mol% (charge) surfomer, nonylphenylpoly(etheroxy) acrylate of variable poly(etheroxy) chain length

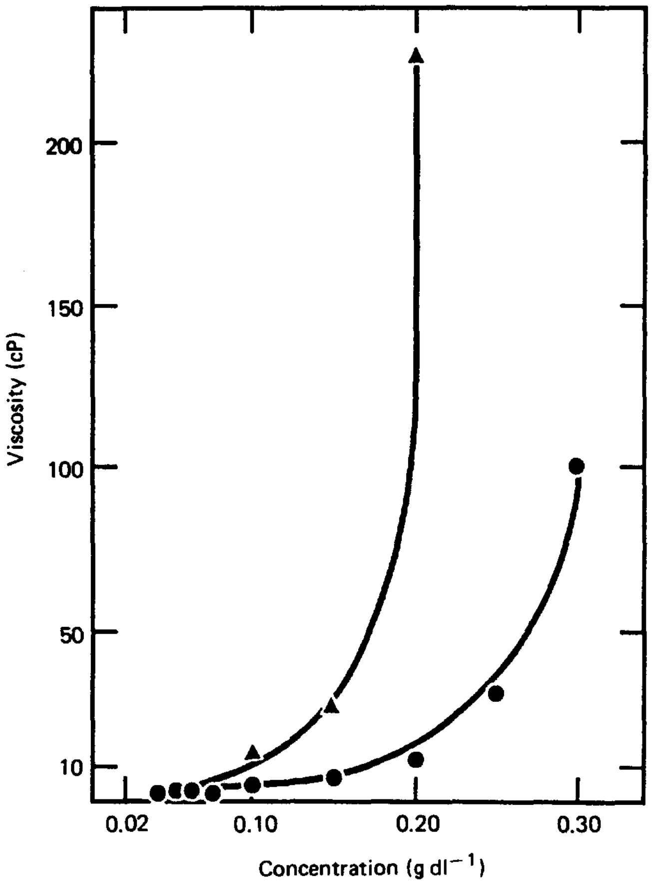


Figure 1 Comparison of the viscosities at 25°C of poly(AM-*co*-R-PEO-Ac) at two levels of P-PEO-Ac surfomer: ▲, 0.6 mol% (charge); ●, 0.3 mol% (charge). Viscosities were measured on a Contraves viscometer ($\gamma=1.3$ s^{-1}) in 2% NaCl solution for polymers isolated by the solution polymer route

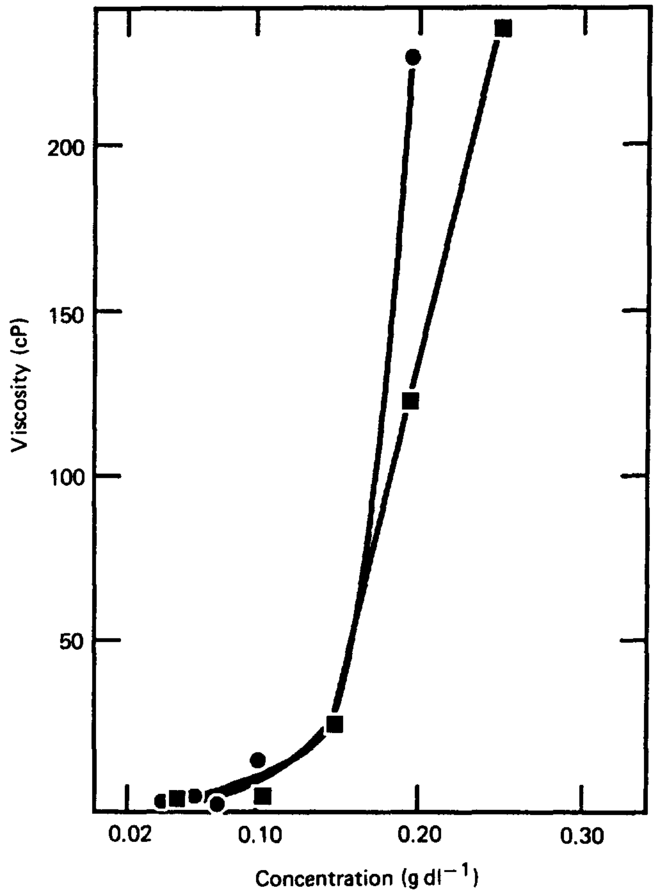


Figure 2 Comparison of the viscosities at 25°C of P(AM-*co*-R-PEOAc) polymers at two levels of $[M]/[I]^{1/2}$: ●, 60; ■, 30. Viscosities were measured on a Contraves viscometer ($\gamma=1.3$ s^{-1} in 2% NaCl solution for polymers isolated by the solution polymer route

Of course, the $[M]/[I]^{1/2}$ ratio is related to the degree of polymerization (*DP*) (or molecular weight $\bar{M}_w$) the polymer for an ideal free radical polymerization by the well known relationship:

$$\bar{M}_w \text{ or } DP=\frac{k_p[M]}{(Fk_dk_t)^{1/2}}[I]^{1/2}$$

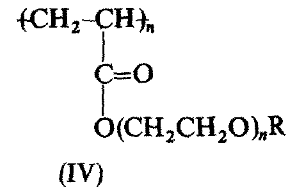
where k_p = propagation rate constant, F = frequency factor, [M] = monomer concentration, k_d = initiator decomposition constant, k_t = termination rate constant and [I] = initiator concentration.

Above C^*, the solution viscosity of the surfomer copolymers is more sensitive to changes in the level of surfactant macromonomer than to changes in $[M]/[I]^{1/2}$. For example, doubling the surfomer level from 0.3 to 0.6 mol% greatly increases the polymer solution viscosity (*Figure 1*). However, doubling the $[M]/[I]^{1/2}$ from 30 to 60 has almost no effect on the viscosity–concentration profile of the surfomer copolymer (*Figure 2*).

Proof that the enhanced viscosity above C^* for the surfomer copolymers results from the association of the surfactant groups, especially the hydrophobic tails, comes from studies of changes in surfactant structure. For example, *Figure 3* shows the effect of changes in the structure of the surfomer end group for the poly(AM-*co*-PEO-Ac) copolymers at a fixed ethylene oxide content of $\bar{n}=40$. Above C^* the more hydrophobic nonylphenoxy end group is a more potent enhancer of viscosity than phenyl, or methyl end groups.

Additional evidence that the increased viscosity of the surfomer polymers comes largely from association of the surfactant tails has been obtained by the addition of appropriate denaturing agents, e.g. nonionic and anionic surfactants, H-bond breakers etc. (*Figure 4*). The most drastic losses in viscosity occur with the addition of nonionic surfactants with structures similar to those attached to the polymer chains [e.g. Triton X-100 (III), homopolymer (IV) and monomer (I)].

$R(OCH_2CH_2)_nOH$
(Triton X-100)
(III)



$$\left(CH_2-\underset{\underset{\underset{O(CH_2CH_2O)_nR}{|}}{\underset{|}{C=O}}}{CH} \right)_n$$

(IV)

R = nonylphenyl

Addition of an ionic surfactant (e.g. sodium lauryl sulphate) also substantially decreases the polymer solution viscosity, but not as greatly as those external surfactants with structures more closely related to the bound surfactants. Presumably, the added nonionic surfactants disrupt the hydrophobic domains of the polymer-bound surfactants, and thereby reducing their effects.

Hydrogen bond breakers, e.g. urea, decrease the solution viscosity only slightly. Moreover, crown ethers show the least viscosity loss after addition. The latter molecules have polyether groups but no surfactant tails. These various results also suggest that the hydrophobic tails, rather than H-bonding via the polyether groups, are the structural features which dominate the solution properties (e.g. viscosity) of these polymers.

As with other high molecular weight, water-soluble polymers, the mode of polymer purification and isolation can also have a profound effect on polymer solution properties. Polymers purified by the solid polymer route (i.e. precipitation/vacuum drying or dialysis/freeze drying) have lower viscosities than polymers purified by the solution polymer route (i.e. dialysis followed by dilution) (see Experimental). This effect is especially pronounced at high $[M]/[I]^{1/2}$ ratios or for high molecular weight polymers, suggesting the loss or breakdown of some polymer upon precipitation and redissolution or the removal of low molecular weight impurities via dialysis (*Table 4*).

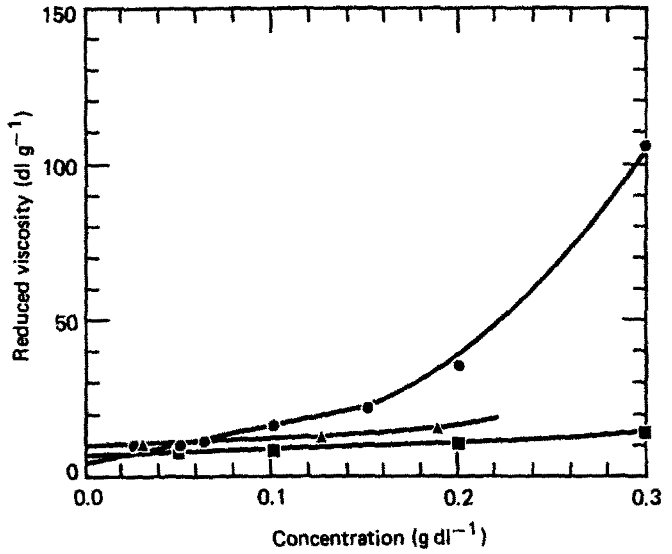


Figure 3 Effect of end-group type on the brine (2% NaCl) viscosity at 25°C of P(AM-*co*-R-PEO-Ac) copolymers (30–40 mol EO). ■, CH_3-PEO-Ac, 0.3 mol% (charge), $[\eta] = 6$ dl g^{-1}; ▲, Ph-PEO-Ac, 0.3 mol% (charge), $[\eta] = 9$ dl g^{-1}); ●, C_9H_{19}Ph-PEO-Ac, 0.3 mol% (charge), $[\eta] = 3$ dl g^{-1})

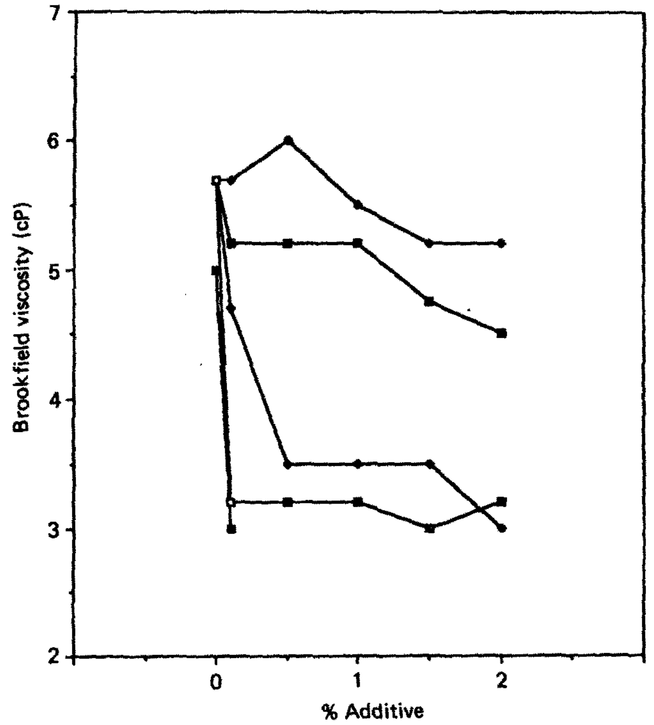


Figure 4 Effect of additives on the aqueous viscosities (cP) at 25°C of 0.3% solution of P(AM-*co*-R-PEO-Ac) with 10 mol EO and 0.3 mol (charge) R-PEO-Ac. ⊡, Triton X-100 (9–10 mol EO); □, monomer; ■, homopolymer; ◆, sodium lauryl sulphate; □, urea; ◇, 18 crown 6. Viscosities were measured on a Brookfield viscometer ($\dot{\gamma} = 2.6$–2.9 s^{-1})

Table 4 Influence of isolation methods on solution properties of P(AM-*co*-R-PEO-Ac)

	Viscosity (cP; 25°C; 0.3% polymer/2% NaCl)					
	$M/[I]^{1/2} = 30$		$M/[I]^{1/2} = 60$		$M/[I]^{1/2} = 98$	
Copolymer	Solid polymer route	Solution polymer route	Solid polymer route	Solution polymer route	Solid polymer route	Solution polymer route
IIa	9	11	11	27	18	1200
IIb	155	145	71	246	177	2800
IIc	33	305	731	2800	–	946

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