The anionic synthesis and characterization of poly(styrene-*g*-ethylene oxide) copolymers

M. H. George*, M. A. Majid†, J. A. Barrie and I. Rezaian‡
The Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, UK
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The synthesis of poly(styrene-*g*-ethylene oxide)s is reported, involving the coupling of living polyethylene oxide chains, with potassium counterions, and chloromethylated polystyrene, in tetrahydrofuran solution at 50°C. The graft copolymers were purified by a liquid extraction method and characterized with respect to molecular weight and composition. The viscosity behaviour of one graft copolymer was studied in toluene–methanol mixtures at 30°C with variation in both composition and temperature, and also with variation of temperature in solution in toluene. No dramatic variations in limiting viscosity number occurred, in contrast to results for many other graft copolymer systems. Dynamical mechanical results suggested partial phase separation in the graft copolymer.

(Keywords: grafting; poly(styrene-*g*-ethylene oxide); anionic grafting; styrene–oxirane graft copolymers; chloromethylated polystyrene)

INTRODUCTION

The association of non-polymeric amphiphilic molecules, each containing hydrophilic and hydrophobic parts, to form micellar aggregates in solution is well established[1], and the structures of many amphiphilic micellar aggregates has been reviewed[2]. Stable aggregates of block and graft copolymers have also been observed in selective solvents which interact preferentially, in a thermodynamic sense, with particular components of the copolymer molecules[3,4].

There has always been considerable interest in the colloidal properties of block and graft copolymers composed of polystyrene (PS) and polyethylene oxide or polyoxirane (PEO) owing to their potential industrial importance. There have been many studies of the properties of poly(styrene-*b*-ethylene oxide)s (P(S-*b*-EO)s) since their first synthesis by Richards and Szwarc[5]. For example, investigations have been made of the structures existing in concentrated solutions using X-rays[6], of the surface properties of solutions[7], of the structures existing in dilute solutions using viscosity and high-resolution ^{1}H nuclear magnetic resonance[8,9], of solution–surfactant interactions[10], and of the solution properties of star-shaped block copolymers using a Du Nouy tensiometer[11]. Some of the other physical methods for studying block copolymers, with particular reference to poly(styrene-*b*-butadiene)s, have been reviewed[12].

Fewer studies have been made of graft copolymers of PS and PEO, and apart from early references concerning the synthesis of poly(ethylene oxide-*g*-styrene) (P(EO-*g*-S))[13,14], attention has been focused on poly(styrene-*g*-ethylene oxides)s (P(S-*g*-EO)s). The synthesis and characterization of P(S-*g*-EO)s has been described[15,16], as well as structural studies of colloidal particles and solubilization characteristics[17–21], while the properties of some hydrophilic networks have also been reported[22].

This paper reports the synthesis of P(S-*g*-EO)s by coupling living poly(ethylene oxide) chains, each with a potassium counterion, PEO$^-$K$^+$, with chloromethylated polystyrene (PSCH$_2$Cl) in tetrahydrofuran (THF) solution at 50°C. The graft polymers were purified by a liquid–liquid extraction method, similar to that originally used for another system by Stannett and coworkers[23], and subsequently characterized with respect to molecular weight and composition. Some solution and bulk properties for one graft copolymer sample were investigated and are described in this paper.

EXPERIMENTAL AND RESULTS

Synthesis and characterization of graft copolymers

Polystyrene, prepared anionically using n-butyllithium and of predetermined molecular weight, was chloromethylated in CCl$_4$ solution at 0°C using chloromethyl methyl ether, catalysed by SnCl$_4$, according to the procedure described elsewhere[24]. Using the appropriate reaction conditions, chloromethylation was controlled to keep the chlorine content of the polymers below 10% w/w. The chloromethylated polymer was purified by precipitation from a toluene solution into methanol and dried to a constant weight in a vacuum oven. The molecular weight of each chloromethylated polystyrene was determined by membrane osmometry and gel permeation chromatography and its chlorine content was found by microanalysis. A weighed amount of the chloromethylated polymer was freeze-dried from benzene solution, and then dissolved in purified THF in a vacuum sealed flask joined by a break-seal to a second flask which was used for the anionic polymerization of ethylene oxide, and subsequently for the coupling reaction. Ethylene oxide (from BDH) was dried by stirring for 3 h at 0°C over calcium hydride, degassed, distilled into a flask containing a sodium mirror, stirred for 2 h at 0°C, and finally distilled into the polymerization vessel.

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* To whom correspondence should be addressed
† Currently at The Chemistry Department, University of Chittagong, Bangladesh
‡ Currently in The Faculty of Engineering, Tehran University, Iran

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The purified ethylene oxide, dissolved in THF, was anionically polymerized, initiated by cumylpotassium initiator, under high vacuum at a temperature of 40°C for 24 h. The colour of the polymer solution gradually turned from a pale yellow to a golden yellow and the viscosity of the solution gradually increased during the course of the reaction. A portion of this polymer was drawn off in an ampoule joined to the polymerization flask, terminated by 0.1 M HCl, purified and characterized separately.

To the major portion of this polymer solution, now cooled to room temperature, chloromethylated polystyrene solution in THF was added dropwise under vacuum. The mixed solution was heated to 50°C and the coupling reaction was carried out at this temperature for 72 h with efficient magnetic stirring. The coupling reaction was accompanied by a change of colour from golden yellow to pale yellow and an increase in viscosity of the solution. After the specified reaction time, the uncoupled living PEO was terminated by adding 0.1 M HCl to the reaction mixture cooled to room temperature. The polymer mixture was twice precipitated from approximately 5% w/v toluene into 10-fold v/v methanol and dried to a constant weight in a vacuum oven at room temperature.

The graft copolymer P(S-*g*-EO) was purified and freed from uncoupled PEO, using the following extraction procedure. A 2% w/v solution of the polymer in benzene was made up and several aliquots of diethyl ether, a non-solvent for poly(ethylene oxide), were then added. The two liquid phases obtained after each addition of diethyl ether were equilibrated using heating and cooling cycles and the clear upper ethereal layer containing successive fractions of graft in ether were isolated by syphoning off. The graft copolymer and the component homopolymer were characterized as described below.

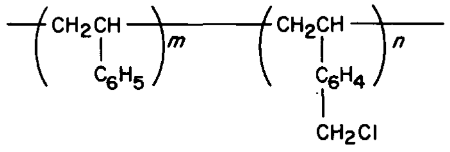
The number-average molecular weights of the polymers, $\bar{M}_n$, were obtained by g.p.c. measurements carried out by the Polymer Supply and Characterisation Centre, RAPRA, Shawbury, Shrewsbury, using 0.2% w/v solutions of the polymers in THF at 20°C. The number-average molecular weight of the graft copolymer sample was also determined by membrane osmometry using a Mecrolab Recording Osmometer model CSM-2 with the graft polymer dissolved in toluene at 37°C.

I.r. spectra of the polymer samples were recorded using a Perkin–Elmer 157-G Grating Spectrophometer, using KBr discs. Most features of the spectrum of an individual graft copolymer were found to be equivalent to the sum of those of the two separate components, chloromethylated polystyrene and ungrafted polyethylene oxide.

Elemental microanalysis of $PSCH_2Cl$, PEO and P(S-*g*-EO) were carried out, and the graft frequency in the copolymer was estimated using the chlorine content values of $PSCH_2Cl$ and the graft copolymer.

Composition, structure and predicted molecular weights of graft copolymers

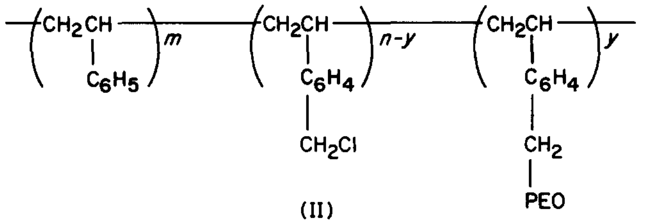
The molecular formula for chloromethylated PS may be expressed:



$$-\left(CH_2CH(C_6H_5)\right)_m-\left(CH_2CH(C_6H_4CH_2Cl)\right)_n-$$

(I)

and that of the graft copolymer:



$$-\left(CH_2CH(C_6H_5)\right)_m-\left(CH_2CH(C_6H_4CH_2Cl)\right)_{n-y}-\left(CH_2CH(C_6H_4CH_2PEO)\right)_y-$$

(II)

where *n* is the number of Cl atoms in chloromethylated polystyrene and *y* is the graft frequency.

From formula I and the $\bar{M}_n$ of $PSCH_2Cl$, $\bar{M}_n(PSCH_2Cl)$, we obtain

$$\text{Per cent Cl in } PSCH_2Cl = \frac{n \times 35.5 \times 100}{(m \times 104.1) + (n \times 152.6)} \qquad (1)$$

$$104.1m + 152.6n = \bar{M}_n(PSCH_2Cl) \qquad (2)$$

From formula II and the $\bar{M}_n$ of PEO, $\bar{M}_n$(PEO), we obtain

$$\text{Per cent Cl in P(S-}g\text{-EO)} = \frac{(n-y) \times 35.5 \times 100}{(m \times 104.1) + [(n-y) \times 152.6] + [(117.1 + \bar{M}_n(\text{PEO})] \times y} \qquad (3)$$

Using these equations, the values of *n* and *y* were calculated from per cent chlorine contents and number-average molecular weights. These values, for the one sample of graft copolymer whose properties were studied further, are presented below.

Estimated number-average molecular weights, $\bar{M}_n$(calc., graft), of graft copolymers was calculated from the equation:

$$\bar{M}_n(\text{calc., graft}) = (104.1 \times m) + [152.6 \times (n-y)] + [117.1 + \bar{M}_n(\text{PEO})] \times y \qquad (4)$$

Dynamic mechanical testing of the graft copolymer samples and the component homopolymers was performed using a 'Rheovibron' instrument. Films of polystyrene and graft copolymers were prepared by moulding at 140°C using a hydraulic press and the samples were annealed at 80°C under 0.1 mmHg pressure for 24 h. Films of PEO were cast from benzene solution and dried. Tan δ measurements were made at 5°C intervals after sufficient time had been allowed for thermal equilibrium to be reached.

Characterization of graft copolymer PG1

For the preparation of the sample of graft copolymer, poly(S-*g*-EO), designated PG1, the number-average molecular weight of the initial $PSCH_2Cl$ was 18 440 and the initial chlorine content was 4.74%. The number-average molecular weight of the PEO grafts was 38 490, as determined by g.p.c. The residual chlorine content in the graft copolymer PG1 was 1.06%, indicating that the anionic grafting procedure process was not very efficient under the experimental conditions employed.

Using equations (1)–(3), the values of *m*, *n*, *y* and $(n-y)$ for PG1 were 141.05, 24.62, 1.53 and 23.09, respectively. Using these values, and equation (4), the value of $\bar{M}_n$(calc., graft) was 77 276, which compared well with the value of 73 900 obtained by osmometry. An apparent number-average molecular weight for the graft copolymer of 40 790 was determined by g.p.c. This low value reflects the general behaviour of such graft copolymers in solution in g.p.c. measurements.

Some properties of graft copolymer PG1

Limiting viscosity numbers of one sample of the graft copolymer PG1 and the hompolymers, PS and PEO, were measured as a function of varying solvent composition in toluene–methanol mixed solvent systems, at 30°C (*Figure 1*), at three different temperatures (*Figure 2*) and as a function of temperature in pure toluene (*Figure 3*).

For a number of graft copolymers, it has previously been observed[25,26] that $[\eta]$ increased in mixed solvent systems as the solvent became more selective for one of the graft copolymer components and a poorer solvent for the other component, until the latter component collapsed. Monomolecular micelles were then produced, resulting in a sharp fall in $[\eta]$. The initial increase in $[\eta]$ is due to an increase in molecular dimensions concurrent with increased repulsion between unlike chain segments and is solvent dependent[25].

In other studies[27,28], however, the limiting viscosity number was found to decrease progressively as the solvent became more selective for one of the components. This decrease in $[\eta]$ is due to a collapse of one of the components, which is usually the backbone. Precipitation of the graft copolymer does not necessarily occur, due to monomolecular micelle formation. However, the formation of polymolecular micelles, especially in concentrated solutions, may eventually lead to precipitation. As indicated in *Figure 1*, curve A, as the proportion of methanol, a non-solvent for the PS backbone, was increased in the liquid mixture, the graft copolymer showed a sharp increase in $[\eta]$. This increase was more pronounced than in the case of a PEO homopolymer, *Figure 1*, curve B, and is clearly an indication of repulsion between the two unlike graft copolymer segments. This interpretation is supported since for homopolymer, polystyrene, the molecular dimensions progressively decrease causing a gradual decrease in $[\eta]$, as shown in *Figure 1*, curve C. Again at about 31–32% v/v methanol, the PS homopolymer solution became turbid, ultimately resulting in liquid–liquid phase separation. The P(S-*g*-EO) copolymer, however, remained in solution up to a solvent composition of 35–36% v/v methanol and was then precipitated. The increased solubility of the graft copolymer may be due in part to the formation of monomolecular micelles.

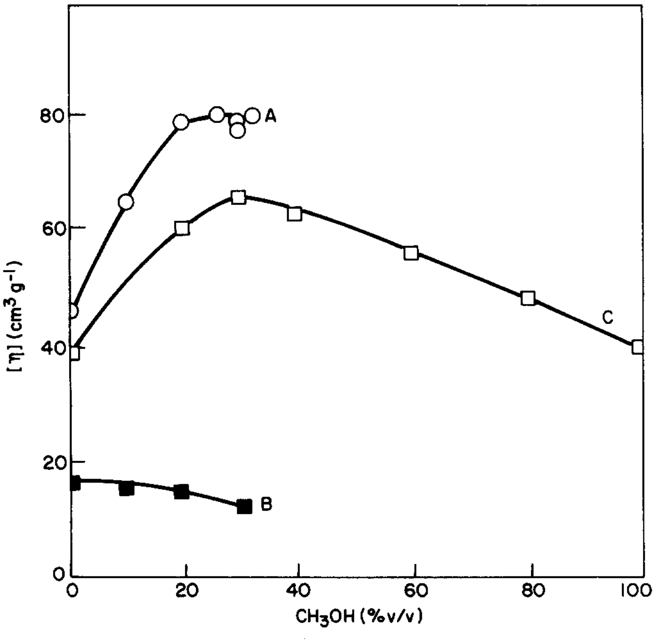


Figure 1 Dependence of limiting viscosity number, $[\eta]$, on solvent composition in toluene/methanol mixtures at 30°C: ○, poly(styrene-*g*-ethylene oxide), curve A; ■, chloromethylated polystyrene, curve B; □, poly(ethylene oxide), curve C

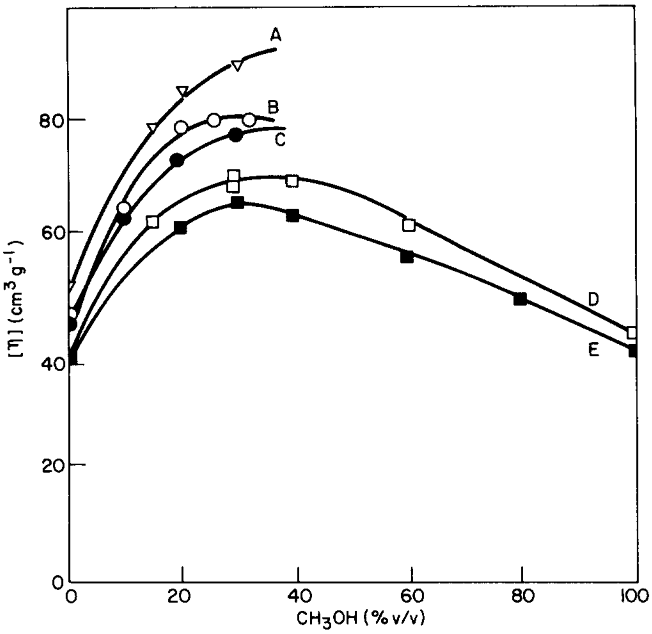


Figure 2 Dependence of limiting viscosity number, $[\eta]$, on methanol content in a toluene/methanol mixture, at different temperatures: ▽, poly(styrene-*g*-ethylene oxide) at 10°C, curve A; ○, poly(styrene-*g*-ethylene oxide) at 30°C, curve B; ●, poly(styrene-*g*-ethylene oxide) at 46°C, curve C; □, poly(ethylene oxide) at 15°C, curve D; ■, poly(ethylene oxide) at 30°C, curve E

In toluene–methanol mixed solvents, as the temperature was increased, the limiting viscosity number of the graft copolymer was found to decrease in a solvent mixture of the same composition, *Figure 2*, curves A–C. A similar trend was observed for the PEO homopolymer in mixed solvents and in methanol, *Figure 2*, curves D and E. The behaviour of both the graft copolymer and PEO homopolymer is somewhat unexpected in view of the positive temperature coefficients of the unperturbed chain dimensions of both PS and PEO, separately[29]. As shown in *Figure 3*, the limiting viscosity numbers of the P(S-*g*-EO) copolymer and those of the corresponding homopolymers in toluene, a good solvent for both the backbone and the grafts, as a function of temperature, within the temperature range studied, seemed to be independent of temperature, within experimental error. These results differ from those reported for some other graft copolymers in single or mixed solvents[30–32], when the effect of temperature on $[\eta]$ was more dramatic, but are similar to results of some studies carried out in this laboratory with poly(styrene-*g*-butadiene)s[28].

Dynamic mechanical results were obtained for a sample of the graft copolymer and separate samples of the homopolymers, PEO and chloromethylated polystyrene,

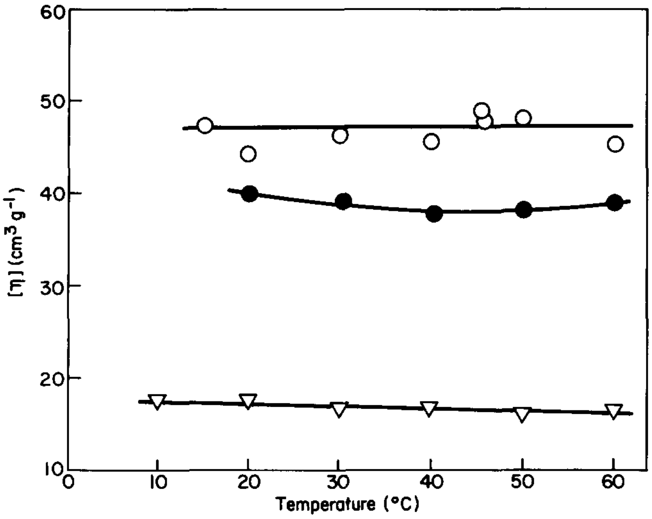


Figure 3 Dependence of limiting viscosity number, $[\eta]$, on temperature: ○, poly(styrene-*g*-ethylene oxide); ●, poly(ethylene oxide); ▽, chloromethylated polystyrene, in toluene

respectively. The tan δ peaks corresponding to the glass temperatures, T_g, for PEO and chloromethylated polystyrene, $PSCH_2Cl$, were -63°C and 94°C, respectively. These were slightly different from the corresponding values of the graft copolymer, -53°C and 86°C, respectively, which suggests that partial phase separation occurred in the graft copolymers. Differential scanning calorimetry of $PSCH_2Cl$ indicated a glass temperature of 102°C, while studies with the graft copolymer also revealed a melting temperature of PEO crystallites at 59°C, and a glass temperature of the PS segments of 97°C.

Preliminary transmission electron microscopy studies using thin films of the graft copolymer cast from ethylbenzene, and subsequently stained with osmium tetroxide, again indicated that phase separation occurred. Probably the polystyrene regions were preferentially darkened in the micrographs to provide the necessary contrast. More work, however, remains to be done.

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