

Synthesis and characterization of polystyrene-poly(ethylene oxide) graft copolymers

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Amphiphilic graft copolymers have been synthesized. The grafting reaction proceeds by anionic deactivation of a 'living' monofunctional poly(ethylene oxide) onto a partly chloromethylated polystyrene backbone. The copolymers are well-defined compounds (molecular weight of the backbone, number and length of the grafts are known), which exhibit narrow molecular weight distribution and are shown to be homogeneous in composition. The degree of grafting is high. Light scattering, vapour pressure osmometry, ultra-violet spectroscopy, nuclear magnetic resonance, differential refractometry and gel permeation chromatography were used for an accurate characterization of the structure of these copolymers.

INTRODUCTION

Much interest has been devoted in the past few years to amphiphilic block copolymers¹⁻³ owing to the interesting properties they exhibit when dissolved in solvent-non-solvent mixtures. However very few studies have appeared in the literature concerning graft copolymers containing water compatible grafts attached to a hydrophobic backbone, because of the difficulty in synthesizing well-defined copolymers of this type with narrow molecular weight distribution.

Among water soluble non-ionic polymers, poly(ethylene oxide) (PEO) is very convenient to study since it can be polymerized anionically to yield samples of well-defined molecular weight and of low polydispersity. The PEO chains are linear and have a high tendency to crystallize when unsolvated.

Grafting poly(ethylene oxide) onto polyvinyl backbones has been attempted by various methods. Some of them proceed by carbanionic initiation, using a backbone fitted with organometallic sites as polyfunctional initiator for the polymerization of ethylene oxide monomer⁴. This type of procedure does not allow a precise characterization of the obtained graft copolymer. The number of carbanionic sites on the backbone, which is not easily accessible in most cases, may be higher than the number of grafts formed, because of incomplete initiation. Furthermore, the grafts may be of quite different lengths.

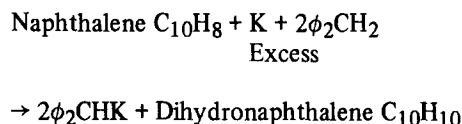
Grafting of poly(ethylene oxide) was also attempted by alkaline transesterification on to poly(methyl methacrylate)^{5,6}. Though satisfactory results were obtained, this reaction is slow and requires high temperatures and long reaction times.

We have attempted to apply the general scheme of anionic deactivation to the grafting of 'living' monofunctional poly(ethylene oxide) on to a polystyrene (PS) backbone fitted with a known number of electrophilic deactivation sites. We report here the method used to achieve this goal, and the characterization procedure employed to determine the structure of the graft copolymers.

EXPERIMENTAL

Solvents [tetrahydrofuran (THF), benzene] and monomers (styrene, ethylene oxide) were purified according to well known procedures⁷.

The diphenylmethylpotassium used as an initiator for the polymerization of ethylene oxide was prepared under argon atmosphere by the indirect metallation method described by Normant and Angelo⁸. However, instead of using equimolecular quantities of potassium, naphthalene and diphenylmethane, we have added only half of the naphthalene, together with an excess of potassium. The equation can thus be written:



This method has the advantage of consuming the whole of the naphthalene. The concentration of the initiator solution was determined by titration with acetanilide.

Preparation of the polystyrene backbone

Styrene was polymerized anionically in benzene solution using *sec*-butyl-Li as initiator. The reaction was carried out at 45°C in a 2 l flask, at an overall concentration of 10%, under a slight argon overpressure to prevent entrance of air or of moisture. After protonic deactivation, the polymer was precipitated into methanol, dried *in vacuo* and characterized by various techniques. Each batch yielded approximately 100 g of polymer of known molecular weight and of low polydispersity.

Chloromethylation of polystyrene

This reaction was carried out according to a procedure described earlier^{9,10}. Dry polystyrene (25 g) was dissolved

into carbon tetrachloride (1.3 l) and chloromethyl ether (150 ml) containing 1 to 2 ml of tin tetrachloride was added at once, at room temperature. The rate of the chloromethylation reaction strongly depends upon temperature, and on the amount of SnCl_4 . The degree of chloromethylation (% of units having been chloromethylated) after 24 h of reaction was of the order of 1 to 11%, depending upon the conditions chosen. The overall concentration had to be low (<5%) to prevent coupling reactions occurring. The absence of such reactions was checked by comparative molecular weight determination before and after chloromethylation (light scattering and g.p.c.).

Grafting process

In a reactor fitted with argon inlet and magnetic stirrer, 500 ml of pure THF was treated with butyllithium (a drop of styrene being used as indicator) to remove the last traces of impurities. Less than 0.5 ml of a 0.5 N solution was necessary to achieve this goal. Next, pure ethylene oxide (50 g) was added from an ampoule fitted with a break-seal, and the mixture first cooled to -20°C . Then, the calculated amount of diphenylmethyl-K was added to the mixture and the temperature allowed to rise to 20°C – 30°C and kept at this value for several hours (6 to 24 h according to the molecular weight required). Some of the PEO was sampled out at this stage. The rest of the PEO solution was then mixed with a solution of the chloromethylated PS in highly pure benzene, the amount of backbone being calculated so as to have a slight excess of 'living' PEO with respect to the overall amount of chloromethylated sites. After completion of the grafting reaction the solution mixture was filtered to separate the KCl precipitate, and the crude graft copolymer was precipitated into cold heptane, a non-solvent of both constituents. The copolymer was then redissolved in benzene and freeze-dried.

Homopolymers and copolymers characterization

Poly(ethylene oxide)

In order to determine with accuracy the length of the PEO grafts, we used several techniques well adapted to the measurement of low molecular weights ($M < 10^4$).

Determination of M_n . Vapour pressure osmometry determinations were carried out using a vapour pressure osmometer Mecrolab 301 A. Measurements were carried out at 37°C in chloroform.

Ultra-violet spectra were taken using a Beckman Spectrophotometer Acta CV. We measured the specific absorption of the diphenylmethyl groups at 262 nm. The molar extinction coefficient of our samples was assumed to be the same as that of diphenyl-1,1-pentane; this compound was synthesized specially for this purpose and its extinction coefficient was found to be $\epsilon = 860$ at 262 nm.

By reacting an excess of phosgene the alcohol end-groups are converted into chloroformate end-groups. The excess phosgene is then eliminated and the chlorine determinations allow a satisfactory accuracy up to molecular weights of the order of $10\,000$ ¹².

Determination of M_w . Light scattering measurements were made using a Sofica Photogoniometer. Values of M_w were determined for PEO samples in methanol solution

($dn/dc = 0.150$ ml/g at $\lambda = 5460$ Å).

Gel permeation chromatography (g.p.c.) was carried out with a chromatograph Waters GPC 200. The molecular weights of samples were determined from a calibration curve obtained by g.p.c. with standard samples furnished by Hoechst Co.

Polystyrene

Weight-average molecular weights of polystyrene samples dissolved in benzene were determined by light scattering and their polydispersities were ascertained by g.p.c.

Graft copolymers

A differential Brice-Phoenix refractometer was used to measure the refractive index increment of the copolymers in THF solution (at $\lambda = 5460$ Å).

For light scattering measurements the copolymer samples were dissolved in THF, solvent for both sequences. The apparent molecular weight thus measured was converted into the true molecular weight, as will be shown in the next section.

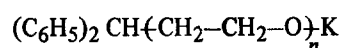
Nuclear magnetic resonance spectra were taken with a Hitachi Perkin-Elmer NMR spectrometer (R - 24 A). Copolymers were dissolved in carbon tetrachloride to give about 20–40% solutions, TMS being used as reference zero. The poly(ethylene oxide) spectra show one resonance peak at $\delta = 3.4$ ppm (internal $\text{CH}_2\text{-O}$ group) whereas the polystyrene spectra reveal 3 resonance peaks at $\delta = 1.4$ (methylene group), $\delta = 1.9$ (methine group) and $\delta = 7$ ppm (aromatic group). The ratio of areas corresponding to the peaks characteristic of PEO protons and PS protons respectively provides the molar composition of copolymer.

RESULTS AND DISCUSSION

Grafting via carbanionic deactivation on to the benzylic chloride functions of a partly chloromethylated polystyrene has already proved to be an efficient method for the synthesis of comb-like polystyrenes^{9,10}. Most side reactions can be avoided, and grafting takes place with fairly high yields.

In the present investigation, instead of the very active polystyrene carbanions, we used the terminal alcoholate functions of 'living' poly(ethylene oxides), which are far less reactive. We expected them to require longer reaction times and higher temperatures. But in practice the reaction was fast and was completed in less than 1/2 h at 40°C : two small amounts of solution sampled out, one soon after the addition of chloromethylated PS, the other 24 h later, exhibited the same g.p.c. chromatogram.

For the polymerization of ethylene oxide at room temperature (or slightly above), a monofunctional initiator was chosen, diphenylmethylpotassium, which proceeds by addition, yielding PEO chains possessing a single alcoholate function:



Molecular weight determinations on the PEO grafts were carried out by several methods: g.p.c.; light scattering; vapour pressure osmometry; chemical determination of the alcohol end-groups, and u.v. spectroscopy using the specific absorption of the diphenylmethyl group at 262 nm ($\epsilon = 860$).

The last two methods are based upon the hypothesis that one OH function and one ϕ_2 CH group are found on each of the PEO molecules formed. If either transfer or initiation by sites other than ϕ_2 CHK occurred, discrepancies between the results should be expected. Two samples of these checks are given in Table 1.

From determination of the Cl content of the backbone polymer, one can calculate the number of possible sites for the grafting process. Knowing the molecular weight of the PEO molecules, the proportions of the two constituents can be chosen so as to attain quantitative grafting. In fact, a slight excess of PEO was used in most of our experiments. To remove the ungrafted PEO in the crude polymer, it may be treated with cold water³ but care has to be taken since the copolymer may be partly soluble, depending upon the number of water soluble grafts. A most successful method was to submit the copolymer to a fractional precipitation using the solvent-non solvent system benzene-iso-octane at 34°C.

In spite of the fact that copolymers with crystallizable grafts are difficult to fractionate, we succeeded in the separation of the homo-PEO from the graft copolymer; the reason is probably the low molecular weights of the grafts ($<8 \times 10^3$) compared with that of the graft copolymer.

The first fractions did not contain any homo-PEO as can be seen on the g.p.c. chromatogram (Figure 1); they could be used without further treatment for characterization purposes. The data obtained are gathered in Table 2, and call for the following comments:

(a) The method allows an 'a priori' determination of the molecular structure of the graft copolymer. The molecular weight of the backbone, its degree of chloromethylation, and the molecular weight of the grafts can be chosen at will. The chloromethylated sites are distributed at random along the backbone (Table 2, columns 3 and 4).

Table 1 Molecular weight determinations for two homo-PEO samples

Number of sample	PEO graft of copolymer 1	PEO graft of copolymer 3
M_n (u.v. spectroscopy)	1420	4450
M_n (phosgenation)	1430	4330
M_n (vapour pressure)	1440	4660
$M_{g.p.c.}$	—	4750
M_w (light scattering)	—	4730

(b) We have indicated the average molecular weights of the PS backbone and of the PEO grafts (Table 2, columns 2 and 5). In order to determine the exact composition of the copolymers, it is necessary to know accurately the lengths of the grafts. As has been shown above, the combination of several techniques leads to a precise value of their molecular weights. In each case, the polydispersity was checked by g.p.c. (Figure 2) and it was found to be very low ($M_w/M_n \leq 1.05$).

(c) The composition of the graft copolymer has been calculated by several complementary methods:

(i) from the weight of the crude polymer it is possible to calculate the composition of the graft copolymer, provided account is taken of the amount of homo-PEO present, which can be determined by g.p.c. (Table 2, column 6).

(ii) N.m.r. spectroscopy provides the molar composition of the copolymer. Knowing the number of initially chloro-

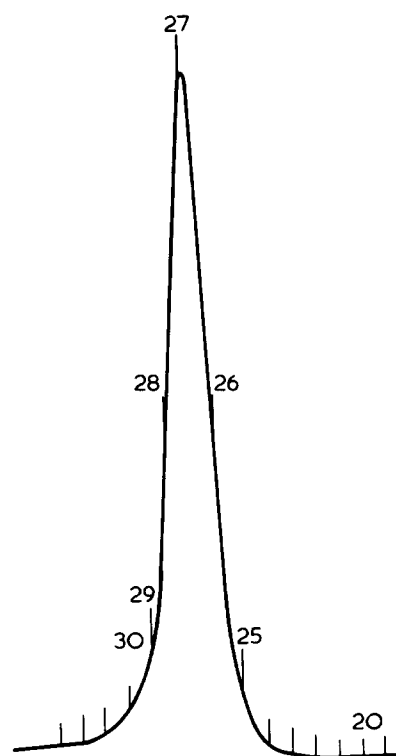


Figure 1 G.p.c. chromatogram of graft copolymer sample number 5

Table 2 Structural characteristics of graft copolymers

Copolymer sample	$M_w \times 10^{-4}$ (PS backbone)	Chlorine content (backbone) (%)	Average number of chloromethylated sites (backbone)	M_w PEO graft	Yield of grafting (%) calculated from		Average number of grafts \bar{p}	dn/dc of copolymer in THF (ml/g)		$10^{-5} M_w$ copolymer	
					Weight yield of copolymer and g.p.c.	N.m.r.		Calculated for 100% yield	Measured	Calculated for 100% yield	Measured by light scattering
1	13.5	0.5	19	1420*	—	99	19	0.174	0.168	1.62	1.61
3	13.5	1.58	61	4750	100	100	61	0.108	0.106	4.25	7.00
4	1.82	1.92	9.8	2100	90	90	9	0.132	0.134	0.388	0.384
5	1.82	1.92	9.8	3700	100	100	9.8	0.111	0.109	0.545	0.550
6	13.5	2.2	84.3	2900	95	96	82	0.114	0.118	3.80	3.87
7	1.82	1.77	8.9	7800	74	73	6.5	0.095	0.100	0.88	0.75

* Number-average molecular weight

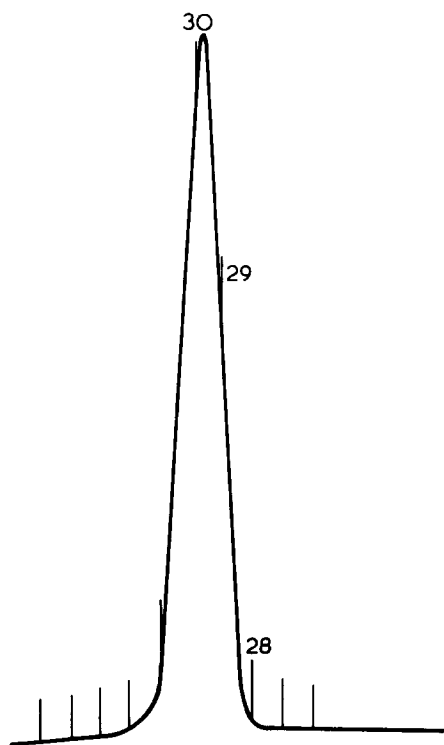


Figure 2 G.p.c. chromatogram of the PEO graft of copolymer sample number 7

methylated sites and the average length of the branches, the structural composition of the copolymer may be deduced and consequently the average number of grafts (Table 2, column 7 and Figure 3). From Table 2 it can be seen that there is a good agreement between these two methods: in all cases except the last the reaction goes to high yields. This solitary deviation may be because the reaction gets slower as the length of the grafts increases, due either to steric hindrance, or to increased incompatibility between the reacting polymers.

(iii) the composition of copolymer can also be determined from the refractive index increment of the graft copolymer in solution in a good solvent (Table 2, columns 9 and 10).

We have compared the experimental values of dn/dc of copolymers in solution in THF with those calculated using the well-known principle of additivities of refractive index increments:

$$\nu_{AB} = \nu_A x_A + (1 - x_A) \nu_B$$

where ν_{AB} , ν_A , ν_B are the refractive index increments for the copolymer and for the two homopolymers respectively and x_A is the weight fraction of component A in the overall copolymer.

The good agreement between calculated and experimental values is additional confirmation of the above results.

(d) In the last column of Table 2 the molecular weights of the graft copolymers, measured by light scattering in THF solution, are compared with the values expected under the assumption of quantitative grafting, and calculated from the molecular weight of the backbone and the number and length of the grafts.

It is however well known that when copolymers are heterogeneous in composition, conventional light scattering leads to an apparent molecular weight (M_{app}) rather than to the true average molecular weight. This problem has been

treated by Bushuk and Benoit¹¹. In the present case the high yield of grafting obtained with this method of preparation allows the fluctuations in composition within the copolymer to be neglected. The copolymer behaves as a homopolymer and $M_{app} \approx M_w$. THF was selected as solvent for this study, because of the large value of the refractive index increment of the copolymer over the whole range of compositions studied.

The good fit between experimental and calculated values gives additional evidence for the compositional homogeneity of the graft copolymers.

However, in one case, the molecular weight of the graft copolymer is much higher than it was expected. This may be due to some coupling between individual molecules by means of a few difunctional PEO molecules, which may have formed during the process, either by transfer, or by some additional potassium derivative contributing to the initiation of the EO polymerization. (This is why BuLi was chosen instead of $\phi_2\text{CHK}$ to neutralize the last protonic impurities of the solvent.)

Such bifunctional PEO molecules can establish bridges between two backbones. Clearly, the probability of such a reaction occurring is low. If it were high, a crosslinked gel would be obtained. The effect of these couplings remains quite negligible for short backbones bearing a small number of chloromethyl sites. They also remain small when an excess of PEO is used with respect to the chloromethyl sites, since the probability of difunctional PEO molecules reacting with these active sites is reduced.

CONCLUSION

The aim of the present study was to describe the synthesis and characterization of well-defined graft copolymers having side chains of predetermined molecular weight. The reaction consisted of grafting preformed monofunctional PEO onto a partly chloromethylated PS backbone. The yield of graft copolymers was generally very high and in many cases virtu-

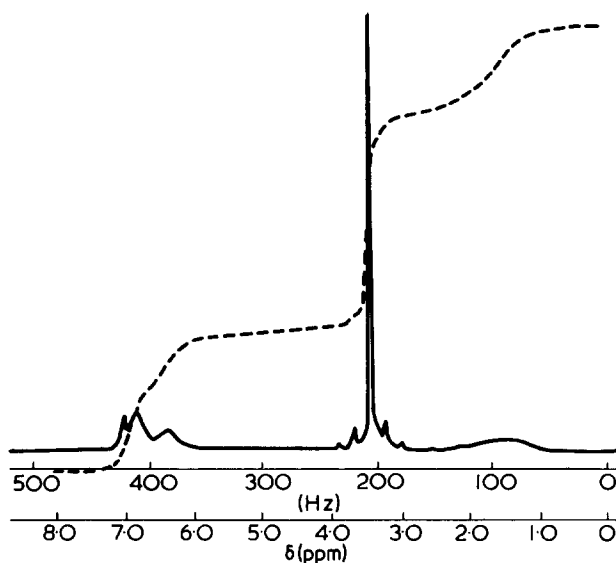


Figure 3 N.m.r. spectrum of PEO–PS graft copolymer sample number 4; . . . , represents areas of the resonance peaks of PEO and PS protons. From the ratio of the respective areas, the number of PEO grafts per PS macromolecule were calculated (9 in the case illustrated)

ally quantitative. The graft copolymers were characterized by several techniques and they are shown to be homogeneous in composition. Such copolymers having both hydrophilic and hydrophobic parts are of interest as emulsifiers; most of them are soluble in alcohols and their solubility increases when the molar ratio of PEO to PS increases. The micro-emulsifying properties of these compounds will be disclosed in a future communication.

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