



## APPLICATION OF A NEW CHROMATOGRAPHIC METHOD, LC CAP, IN THE CHARACTERIZATION OF POLYSTYRENE-GRAFT-POLY(ETHYLENE OXIDE) COPOLYMERS

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**Abstract**—The application of liquid chromatography at the critical adsorption point (LC CAP) to a graft copolymer analysis is presented. This procedure is based on the coupling of size exclusion and adsorption chromatographic mechanisms. The data obtained by LC CAP (the apparent molecular weights of the polystyrene backbone, the number of the grafts per unit backbone and the amount of poly(ethylene oxide) in the graft copolymers) were compared with results of static light scattering (SLS), differential refractometry and conventional SEC. SLS measurement were performed in toluene as an isorefractive solvent for polyethylene oxide side chains. Good agreement was found among the data obtained with all the above methods and it can be concluded that the LC CAP method can also be applied to graft copolymers with not very long side chains. © 1998 Elsevier Science Ltd. All rights reserved

### INTRODUCTION

Copolymerization using macromonomers has recently received much attention as a powerful method for obtaining graft copolymers with various side chains and thus widely different properties. Most studies have been concerned with understanding the copolymerization procedure [1–5]. However, only a few studies concerning the characterization of copolymers prepared from macromonomers have been published [6–8].

Liquid chromatography at the critical adsorption point (LC CAP) seems to possess good potential for solving the problem of molecular characterization of graft copolymers. The method is based on the coupling of size exclusion and adsorption chromatographic mechanisms. The experimental conditions such as column packing, mixed eluent composition and temperature can be identified for a given polymer under which the above separation mechanisms fully compensate [9]. As a result, macromolecules with different molecular weights leave the LC column at the same retention volume that roughly corresponds to the total volume of liquid in the system ( $V_m$ ).

So far LC CAP has been applied to the discrimination of polymer mixtures [10] where one constituent elutes under the critical point of adsorption while another one is conventionally separated in the size exclusion (SEC) mode, and also to the characterization of diblock copolymers [11] when one block is under CAP conditions while another block is SEC separated, and finally to

functionalized oligomers [12] where the main chain is eluted under CAP conditions and functionalities such as end groups are separated in the liquid adsorption mode. In all of the above-mentioned cases, one kind of polymer chain is “chromatographically invisible” and does not influence the separation of other polymer chains.

In this study we tested the LC CAP approach in the characterization of graft copolymers with the polystyrene backbone and grafts formed by poly(ethylene oxide) side chains (see Scheme 1). We expected that when the side chain of a graft copolymer eluted at CAP the main polystyrene chain could be characterized on the basis of the SEC mechanism. The data obtained by LC CAP were compared with results of static light scattering (SLS), differential refractometry and conventional SEC.

### EXPERIMENTAL

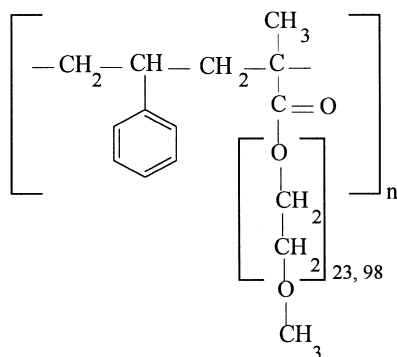
#### Preparation of graft copolymers

**Materials.** Commercially available styrene monomer and dibenzoyl peroxide initiator (DBP) were purified by the usual methods. Twice-distilled water and ethanol were used as a polymerization medium. Methacryloyl-terminated polyoxyethylene (PEO-MA,  $M_n = 1000$  g/mol and 4250 g/mol) was supplied by NOF Corp., Ltd, Japan.

**Polymerization procedure.** Batch dispersion copolymerizations of PEO-MA macromonomers and styrene were carried out at 60°C. All runs involved 5 ml of an ethanol/water (4/1, v/v) mixture, 1.11 g of styrene and 0.3 g of PEO-MA macromonomer. For preparation of samples 1, 2, 3 and 4 the macromonomer with  $M_n = 1000$  g/mol and for the sample 5 the macromonomer with  $M_n = 4520$  g/mol was used. The amounts of DBP varied as shown in Table 1. Unreacted polymers were separated from the product by dialysis.

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Scheme 1.

### Characterization

**SEC.** A size exclusion chromatographic system was used that consisted of a Waters 510 pump, a Knauer injection valve with a 20  $\mu\text{m}$  loop and a refractive index detector (RI) (Philips, PU 4026). Chromatographic measurements were made with a styrene/divinylbenzene gel/PL-gel (mixed B,  $d_p = 10 \mu\text{m}$ ,  $7.5 \times 300 \text{ mm}$ ) and PL-gel (pore size = 500  $\text{\AA}$ ,  $d_p = 10 \mu\text{m}$ ,  $7.5 \times 300 \text{ mm}$ ) columns. Narrow polystyrene (PS) and poly(ethylene oxide) (PEO) standards were obtained from Pressure Chemicals Co., U.S.A. The injected concentration was 1.0 mg/ml. Analytical grade THF (Merck, Darmstadt, Germany), purified by distillation, was used as mobile phase at a flow rate of 1 mL/min. All SEC experiments were performed at ambient temperature. The data were collected on-line using a Waters PC-based data acquisition system.

**LC CAP.** Liquid chromatography at the critical adsorption point was performed with the system consisting of a Waters 510 pump, a Knauer injection valve with a 20  $\mu\text{m}$  loop and a Model DDL-21 evaporative light-scattering detector (Cunow, Cergy Pointoise, France). A chromatographic phenogel (linear,  $d_p = 10 \mu\text{m}$ ,  $7.8 \times 300 \text{ mm}$ ) column was packed with the styrene/divinylbenzene gel.

Narrow polystyrene (PS) standards were used as above. The injected sample concentration was 0.5 mg/ml. Mixtures of analytical grade THF (Merck, Darmstadt, Germany) and *n*-hexane (Lachema, Brno, Czech Republic), both purified by distillation, were used as mobile phases at a flow rate of 1 mL/min. The temperature during all experiments was maintained at 30°C with a Knauer column oven. The data were collected on-line using a Waters PC-based data acquisition system.

**Light scattering measurements.** All light scattering experiments were performed using a laser light scattering goniometer (Brookhaven Instruments Co., New York, U.S.A.). Static light scattering measurements were carried out in analytical grade THF (Merck, Darmstadt, Germany) and toluene (Lachema, Brno, Czech Republic). Sample solutions were filtered through Whatman filters (Maidstone,

Table 2. Apparent (SEC) molecular weights and molecular weight distribution data of the PEO-MA macromonomers

Macromonomer no.	$M_n$	$M_w$	$M_w/M_n$
1	4250	4335	1.02
2	1750	1785	1.02
3	1009	1030	1.03
4	953	982	1.03

Column: PL gel (pore size = 500  $\text{\AA}$ ,  $d_p = 10 \mu\text{m}$ ,  $7.5 \times 600 \text{ mm}$ ); detector: RI; eluent: THF; standards: PEO; temperature: ambient; flow rate: 1 mL/min.

U.K.) into the light scattering cells. The light scattering cell was designed with an Ar-laser (wavelength 514 nm) as the light source, using the photon-counting method. The excess Rayleigh ratio ( $R_{ex}$ ) was extrapolated to zero concentration and zero angle by Zimm or Berry plots to determine the apparent molecular weight ( $M_w$ ).

**Differential refractometry.** The refractive index increments were determined for PS, PEO-MA and the graft copolymers using a Brice-Phoenix, BP-2000 differential refractometer (Philadelphia, U.S.A.). All measurements were made at 25°C.

### RESULTS AND DISCUSSION

The overall copolymer compositions were calculated using the equation [13]:

$$v = w_A v_A + w_B v_B, \quad (1)$$

where  $w_A$ ,  $w_B$  are weight ratios of monomers A and B and  $v$ ,  $v_A$ ,  $v_B$  are the specific refractive index increments of copolymer and monomers A and B, respectively. When  $v_A$  and  $v_B$  differ appreciably in a given solvent, equation (1) affords a convenient means to estimate the copolymer composition from the measured value of  $v$ . This is the case here, because  $v_{PS} = 0.182 \text{ mL/g}$  and  $v_{PEO} = 0.045 \text{ mL/g}$  in THF and at a wavelength  $\lambda_0 = 514 \text{ nm}$ . The results obtained are given in Table 1.

The values of molecular weights for PEO-MA macromonomers determined by conventional SEC are shown in Table 2. The SEC measurements confirmed the purity of the graft copolymers. No peaks corresponding to the free PEO-MA macromonomers or the poly(macromonomer)s were observed on the chromatograms of the polystyrene-graft-poly(ethylene oxide) copolymers.

The critical diagram of copolymer mass vs retention volume for PEO-MA macromonomers is shown in Fig. 1. At hexane concentrations less than 29% by weight in the solvent mixture the retention volume decreases as the molar mass increases. The reverse behaviour is observed at hexane concentrations higher than 29% by weight, where retention volume increases with increasing molar mass. At a solvent composition of THF/hexane = 71:29% by weight, the retention volume does not change with molar mass.

Figure 2 shows the chromatograms of polystyrene-graft-poly(ethylene oxide) copolymers in the different chromatographic modes. The solid line represents the chromatograms of the polystyrene-graft-poly(ethylene oxide) copolymers eluted in SEC mode. The mobile phase was THF. The dashed line shows the "critical" composition of eluent for which

Table 1. PEO content of polystyrene-graft-poly(ethylene oxide) copolymer obtained by differential refractometry at  $\lambda_0 = 514 \text{ nm}$  in THF

Sample no.	$[\text{DBP}] \times 10^{-2}$ (mol/dm)	$v^{514} = dn/dc$ (mL/g)	PEO (wt%) <sup>a</sup>
1	0.23	0.1710	17.5
2	0.56	0.1715	17.2
3	1.13	0.1719	16.9
4	2.25	0.1703	17.9
5	2.25	0.1399	37.8

<sup>a</sup>Evaluated from equation (1).

CAP of PEO-MA macromonomers was reached (see Fig. 1). Under these conditions the retention volumes of eluted copolymers are shifted to higher values. It means that under this "critical adsorption point" separation is accomplished exclusively with respect to molar mass of PS backbones regardless of the molar mass of PEO-MA macromonomers. In other words, under CAP conditions, the chromatographic column "does not see" PEO-MA chains. At the same time the PS backbone chains that are not at their CAP are separated by the SEC mechanism. Moreover, as can be seen from these chromatograms, under CAP conditions the peaks became sharper.

Apparent (SEC and LC CAP) molecular weights, molecular weight distribution data, polystyrene-graft-poly(ethylene oxide) copolymer compositions and number of grafts per unit backbone are shown in Table 3. The number of graft chains per backbone chain was calculated (from Table 3) as follows:

$$M_w^{\text{TOTAL}} - M_w^{\text{PS}} = M_w^{\text{PEO}}, \quad (2)$$

where  $M_w^{\text{TOTAL}}$  is the apparent weight-average molecular weight of copolymer determined by SEC,  $M_w^{\text{PS}}$  is the apparent weight-average molecular weight of PS backbone determined by LC CAP, and  $M_w^{\text{PEO}}$  is the apparent weight-average molecular weight of PEO grafts. Then the average number of graft chains per unit backbone chain will be  $M_w^{\text{PEO}}/M_w^{\text{MACR}}$ , where  $M_w^{\text{MACR}}$  is the apparent weight-average molecular weight of the macromonomers used for the preparation of the copolymers (see polymerization procedure).

Independent light scattering measurements did not show formation of the spherical micelles of block copolymers in THF within the concentration range used in the chromatographic measurements. The experimental data obtained by SLS are listed in Table 4. Toluene was chosen as an isorefractive solvent for poly(ethylene oxide) grafts ( $n^D = 1.498$ ). Under these conditions the molar mass of the polystyrene backbone could be assessed.

If we compare weight percentages of PEO in the polystyrene-graft-poly(ethylene oxide) copolymer obtained by different independent methods (see Tables 1, 3 and 4), one can see fair agreement between them. Moreover, the numbers of grafts per unit backbone were found to be similar in all cases. Of course, we have to take into account errors which are specific for each of the methods used. For instance, it is well known [14] that the apparent molecular weights based on the SEC calibration with linear standard polymers are severely underestimated, particularly at higher molecular weights, i.e. for comb polymers with a longer and/or higher number of side chains. In our case, since our samples contain relatively short PEO side chains, the differences between apparent molecular weights measured by SEC and SLS methods are not so large.

Sample 5 is an exception to this rule. As can be seen from Tables 3 and 4, apparent weight-average molecular weights measured by SEC and SLS differ appreciably. Almost half the value of molecular weight measured by the SLS method can be explained by intercoil interactions between PEO chains inside the column. At higher concentrations, intermolecular

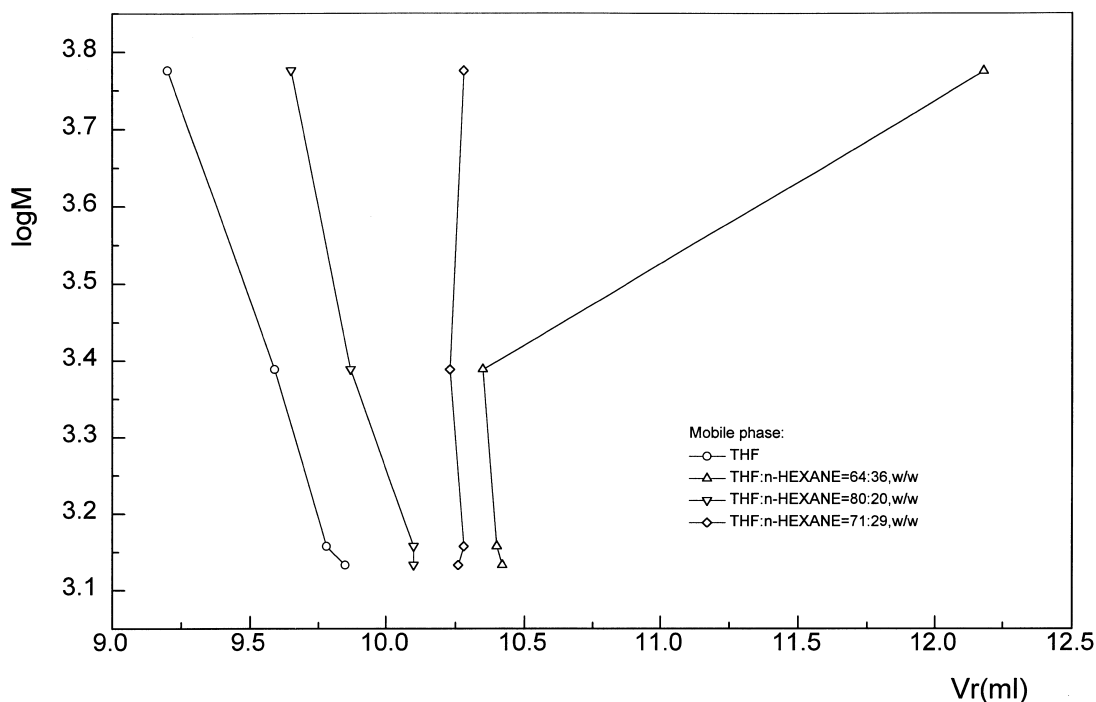


Fig. 1. Plot of the logarithm of molar mass ( $\log M$ , in g/mol) as a function of retention volume ( $V_r$ , in mL). The curves are for PEO-MA macromonomers in a mixed eluent (THF/hexane) at various compositions. The sorbent was styrene/divinylbenzene gel.

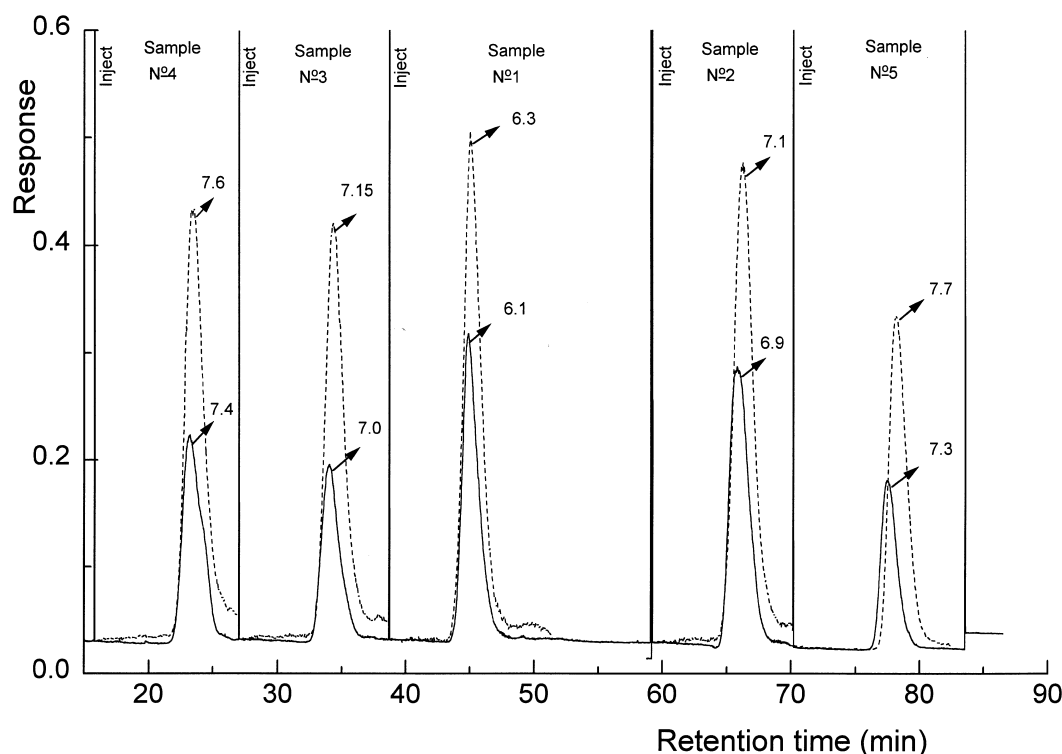


Fig. 2. Chromatograms of polystyrene-graft-poly(ethylene oxide) copolymers. Column: phenogel (linear,  $d_p = 10 \mu\text{m}$ ,  $7.8 \times 300 \text{ mm}$ ); eluent: (---) THF/hexane (71:29 wt%), (—) THF; detector: ELSD; flow rate: 1 mL/min; temperature: 30°C.

interactions became appreciable and phase separation could occur. The solution behaviour of these amphiphilic graft copolymers was studied by quasi-elastic light scattering and viscometry. We plan to publish these results in the near future.

By themselves, these results do not provide definitive proof of the versatility of the LC CAP method, since our experiments were done on graft copolymers with relatively short side chains. On the other hand, our experimental results agree with the theoretical predictions of Guttman *et al.* [15]. They varied the length of the backbone and the length of the arms of graft copolymers and calculated the influence of these parameters on the partition coefficient  $K_d$ . The largest change in  $K_d$  which Guttman *et al.* reported for the graft copolymers (with similar architecture to those we studied) was less than 7%.

## CONCLUSIONS

Several independent methods were used for the characterization and the determination of PEO content in the polystyrene-graft-poly(ethylene oxide) copolymers with various molecular weights of backbone and with different lengths of side chains; namely SEC and LC CAP methods, a light scattering method and differential refractometry.

Concerning the PEO content in the graft copolymers, all these methods give very similar results. As to the number of PEO grafts per unit PS backbone, the data obtained are close enough and in good agreement with theoretical predictions.

It seems that LC CAP, operating between SEC and adsorption chromatography, can be used not only for determination of the functionality type distribution of telechelic oligomers and characterization of the molecular weight distribution of blocks in block

Table 3. Apparent (SEC and LC CAP) molecular weights, molecular weight distribution data and polystyrene-graft-poly(ethylene oxide) copolymer composition

Sample no.	SEC (total)		LC CAP(PS backbone)		SEC $M_w/M_n$	LC CAP $M_w/M_n$	PEO (wt%) evaluated from $M_w$	No. of grafts <sup>a</sup> per unit backbone
	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$				
1	286	807	240	644	2.8	2.7	20	158.2
2	134	357	119	293	2.7	2.5	17.9	62.1
3	73	185	67	156	2.5	2.3	15.7	28.1
4	49	126	45	105	2.5	2.3	16.7	20.3
5	63	140	39	92	2.2	2.3	34.4	11.3

Column: phenogel (linear,  $d_p = 10 \mu\text{m}$ ,  $7.8 \times 300 \text{ mm}$ ); detector: ELSD; eluent: SEC = THF, LC CAP = THF/*n*-hexane = 71:29 wt%; standards: PS; temperature: 30°C; flow rate: 1 mL/min.

<sup>a</sup>Evaluated from  $M_w$ .

Table 4. Apparent weight-average molecular weight of polystyrene-graft-poly(ethylene oxide) copolymers determined by SLS method in THF and toluene (isorefractive solvent for PEO)

Sample no.	$M_w$ (total) $\times 10^{-3}$ in THF	$M_w$ (PS backbone) $\times 10^{-3}$ in toluene	PEO (wt%)	No. of grafts per unit backbone
3	220	182	17.3	36.4
5	71	41	42.1	7.0

copolymers, but also for the investigation of graft copolymers. Results generated by this method are believed to be quite reliable and will enhance future studies of the internal structure of copolymers.

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