**polymer**

# Polystyrene-graft-poly(ethylene oxide) copolymers prepared by macromonomer technique in dispersion. 2. Mechanism of dispersion copolymerization

I. Capek[*], S.H. Nguyen, D. Berek

*Polymer Institute of the Slovak Academy of Sciences, 842 36 Bratislava, Slovakia*

## Abstract

The reaction mechanism of dispersion copolymerization of methacryloyl-terminated poly(ethylene oxide) macromonomer and styrene in the polar media is discussed. The copolymerization products were analyzed by means of liquid chromatography. This analysis revealed presence of rather large amount of polystyrene in the final polymer product. It is assumed that the system undergoes phase separation in the course of copolymerization. The graft copolymer created in the first stage of polymerization acts as a detergent (amphiphile). The hydrophobic phase is hardly accessible for hydrophilic macromonomer but well dissolves styrene and benzoylperoxide initiator. Therefore, polystyrene homopolymer is intensively formed in this reaction locus. Its molar mass is rather low because of high initiator and low monomer concentration at the reaction loci. We suppose existence of at least two different polymerization loci; the continuous phase and the particle core. The existence of third polymerization locus, viz. particle surface layer cannot be excluded, either. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Graft copolymer; SEC and FAD approaches; Polymerization loci

## 1. Introduction

Amphiphilic graft copolymers are conveniently prepared in solution or disperse media by the radical copolymerization of a hydrophilic macromonomer and hydrophobic comonomer and vice versa [1]. These materials are of great interest because of their surface-active properties. For example, amphiphilic graft copolymers synthesized from PEO macromonomer and hydrophobic comonomers [2–5] were found to form micellar aggregates in polar medium such as water, water/alcohol, alcohol, dimethylformamide. These phase separation processes take place also during polymerization and supposedly affect not only the polymerization kinetics but also properties of resulting copolymers. So far unanswered remains the question of molecular characteristics of reaction products including homopolymers from macromonomer or comonomer formed under both the homogeneous and heterogeneous (micellar) reaction conditions.

Modern liquid chromatographic techniques allow discrimination of polymeric constituents differing in their chemical structure and/or physical architecture. Subsequently the molar mass and molar mass distribution of constituents can be assessed.

We have recently analyzed the products of dispersion copolymerization of polyethylene oxide methacrylate macromonomer with styrene and found rather large amount of polystyrene homopolymer [6]. The mechanism of polystyrene formation in the latex particles is discussed in present paper.

## 2. Experimental

### 2.1. Materials

Commercially available monomer (styrene, S), initiator (dibenzoyl peroxide, DBP) solvents (water, ethanol, toluene, dichlorethane (DCE), tetrahydrofuran (THF), dimethylformamide (DMF)) were purified by usual methods (distillation prior to use) [7,8]. Methacroyl terminated polyoxyethylene [PEO–MA, $M_n = 1000$ ($M_{n,1000}$), 2000 ($M_{n,2000}$), and 4300 ($M_{n,4300}$)] was supplied by NOF Corp., Ltd., Japan. Polystyrene (PS) standards were bought from Pressure Chemicals (Pittsburgh, PA, USA). Linear size

---

* Corresponding author. Fax: + 42-7-375923.
  *E-mail address:* upolign@savba.sk (I. Capek).

Table 1
Kinetic and colloidal parameters of dispersion copolymerization of PEO–MA macromonomer and styrene (recipe: 5 ml of ethanol/water (4/1, v/v) (runs C1–C4) or 5 ml THF (runs C5 and C6) and 0.3 g of PEO–MA)

| Sample | $[DBP] \times 10^2$ (mol/dm$^3$) | Feed$_{st}$ (wt%) | Conv. (%) | $D$ (nm) | $N \times 10^7$ (/dm$^3$) |
|--------|--------|--------|--------|--------|--------|
| C1 | 0.23 | 20 | 42 | 130 | 1.34 |
| C2 | 0.56 | 20 | 50 | 125 | 1.6 |
| C3 | 1.13 | 20 | 56 | 112 | 1.9 |
| C4 | 2.23 | 20 | 60 | 107 | 2.4 |
| C5 | 1.98 | 5 | 60 | Homog. | |
| C6 | 1.98 | 20 | 70 | Homog. | |

exclusion chromatographic column $300 \times 7.5$ mm was bought from Polymer Laboratories (Church Stretton, UK) and full adsorption–desorption columns were packed with bare nonporous silica particles [6].

## 2.2. Polymerization procedure

The graft copolymers (polystyrene-*graft*-polyoxyethylene) (PS-*graft*-PEO) were prepared by the dispersion copolymerization of PEO–MA macromonomer and styrene initiated by dibenzoyl peroxide (DBP). The polymerization technique used to prepare the graft copolymers has been described in detail earlier in [8,9]. Monomer and macromonomer were dissolved in ethanol/water (4:1) mixture together with different DBP concentrations and polymerized at 60°C (Samples C1–C4). The feed weight ratios of S/PEO–MA together with DBP concentration of four samples are given in Table 1. Samples C5 and C6 were prepared by the solution polymerization in THF using DBP (Table 1) at 70°C. Unreacted macromonomer and other low molecular substances were removed from polymer dispersion (Samples C1–C4) by dialysis and then by precipitation in methanol. The polymer products obtained by the solution polymerization (samples C5 and C6) were twice precipitated from THF by methanol.

Conversion of monomer was determined by gravimetry. Particle size measurements of dialyzed latexes were done using light scattering techniques. Other conditions of particle characterization and estimation of the particle number were described in detail elsewhere [10].

## 2.3. Liquid chromatography

The most popular liquid chromatographic technique for polymer characterization is size exclusion chromatography (SEC). As known, SEC separates macromolecules according to their size in solution. Size of copolymer species depends on their molar mass, chemical structure and architecture. Consequently, SEC can produce precise molar mass values for copolymers only under favorable conditions, which are rather rare. Further, SEC cannot discriminate between chemically different polymeric species such as copolymer and its parent homopolymers if their sizes do not differ substantially. A very powerful method for char-

acterization of graft copolymers seems to be liquid chromatography at the critical adsorption point (LC CAP) [11–13]. LC CAP works under conditions when one kind of polymer chains elutes at constant retention volume irrespectively of its size "chromatogaphically invisibility" [14]). In this case, the observed retention volume of graft copolymer corresponds solely to the SEC retention of second kind of chains (graft or main chain). Unfortunately, LC CAP suffers from many experimental problems [15] and it also cannot discriminate the "visible" parent homopolymer from their copolymers if molecular sizes of both are similar.

Therefore, we applied two novel approaches that were recently developed for separation and characterization of complex polymer systems such as graft copolymer containing parent homopolymers. Gradient-elution liquid adsorption chromatography (LAC) is a technique that is based on coupling of adsorption and exclusion of separated macromolecules in one single chromatographic system [16]. LAC separates statistical- and graft-copolymers possessing molar mass higher than few tens of thousands of dalton exclusively according to their composition while molar mass of sample does not influence its retention volumes. LAC separation is very selective and allows readily separate parent homopolymers from the copolymers. LAC can be on line followed with SEC ("two dimentional liquid chromatography") which separates particular LAC fractions according to the molar mass of constituents.

Full adsorption–desorption (FAD) method is known to easily separate multicomponent polymer blends [17,18]. FAD is a chromatography-like on-and-off approach based on the complete adsorption/retention of whole sample on its part in a minicolumn packed with appropriate adsorbent. Next, the constituents of polymer sample are stepwise desorbed according to their molar mass and/or chemical composition using a series of appropriate displacers. Macromolecules released from the FAD column can be directly transported into an SEC column for determination of their molar masses.

The above series of PEO-*graft*-PS copolymers was characterized by means of all four methods [7,12,13]. LAC and FAD/SEC methods revealed presence of rather large amounts of homoPS in the samples and FAD/SEC method could assess also its molecular characteristics. These latter

Table 2
(Effective) molar mass and polydispersity values of homo-PSt and graft copolymer fractions. Homo-PS content in each sample was calculated from ELSD peak area

| Sample | Nonadsorbed (PS) fraction | | | Absorbed (PSt-g-PEO) fraction | | PSt-g-PEO[a] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $M_w \times 10^{-3}$ | MWD | (wt%) | $M_w \times 10^{-3}$ | MWD | $M_w \times 10^{-3}$ | | MWD | |
| | | | | | | (1) | (2) | (1) | (2) |
| C1 | 371 | 2.63 | 22 | 851 | 4.15 | 745 | 807 | 3.8 | 2.8 |
| C2 | 218 | 2.61 | 30 | 377 | 3.94 | 329 | 357 | 3.5 | 2.7 |
| C3 | 145 | 2.84 | 62 | 170 | 3.46 | 154 | 185 | 3.1 | 2.5 |
| C4 | 79 | 2.82 | 61 | 92.0 | 3.08 | 84 | 126 | 2.9 | 2.5 |
| C5 | 12.1 | 2.73 | 42 | 13.5 | 1.82 | | | | |
| C6 | 7.26 | 2.36 | 13 | 15.4 | 1.95 | | | | |

[a] The whole reaction product (graft copolymer plus PSt homopolymer), (1) FAD/SEC, in THF; (2) SEC, in THF.

results are discussed in present paper and form a base for tentative explanation of processes taking part during dispersion copolymerization PEO macromonomer with styrene.

## 3. Results and discussion

### 3.1. Aggregation of graft copolymers

In the polar reaction medium, the amphiphiles aggregate in such a way that the non-polar (hydrophobic) chains form core surrounded by a corona of hydrophilic soluble chains [1–4]. In the oil (nonpolar-chromatographic eluent) medium, the amphiphiles aggregate in the reverse way, i.e. the hydrophilic chains form core surrounded by hydrophobic chains. The organized aggregates can serve as reaction loci. Due to aggregation, molar masses determined in solution are often overestimated. We have observed aggregation of PS-graft-PEO copolymer in DMF eluent [6], which is a poor solvent for copolymer. Shoulders appeared on SEC chromatograms of graft copolymers in the region of low retention volumes indicating presence of aggregates. THF is a good solvent for both PS main chain and PEO grafts and aggregation should be suppressed. Unfortunately, PEO chains are strongly retained within SEC column used due to adsorption. Therefore a mixed eluent DMF/THF 15:85 wt/wt was applied to suppress both aggregation and adsorption. Furthermore, shoulders on SEC chromatograms in DMF eluent disappeared at higher temperatures (close to 100°C).

### 3.2. Kinetic and mechanistic approach

The FAD and LAC data [6] indicate that besides the graft copolymer also PS homopolymer is formed in the course of dispersion copolymerization of PEO–MA macromonomer and styrene. The homopolymer has already appeared at about 10% conversion when the polymer particles begin to grow by propagation. Before polymerization, PEO–MA, styrene, and initiator dissolve completely in the solvent. Surface active graft copolymers are produced by copolymerization in the continuous phase. The solubility of these copolymers is a function of their molecular weight and the composition. Polymers with a molecular weight larger than a certain critical value precipitate and begin to coagulate on contact, and the coagulation between them is continuous until sterically stabilized particles form. This point is referred as the critical point, at which styrene can penetrate into the polymer particle core take part in homo-propagation. At about 40% conversion (run C1) the wt% of PS is 22% while at ca. 60% conversion (run C4) the amount of PS increased up to 61 wt% (Table 1). The presence of PEO polymacromonomer formed during the dispersion copolymerization of PEO macromonomer with hydrophobic comonomers was confirmed by Lacroix-Demazes and Guyot [19]. These findings indicate that the chain growth proceeds in both the continuous phase and polymer particles. The hydrophilic polymacromonomer is formed in the continuous phase when the main fraction of hydrophobic comonomer (styrene) is consumed or the unreacted fraction is mainly located in the monomer/polymer particles. This can happen at very high conversion. On the contrary, PS appears as soon as the compact core of monomer/polymer particles is formed and partitioning of hydrophobic and hydrophilic monomers occurs.

Table 2 summarizes the overall molar masses of final polymer products (graft copolymer and PS homopolymer) determined by the (two step) FAD/SEC method and those estimated earlier by (one step) SEC method (in THF) [12]. In the former case, the real molar masses of PS and apparent molar masses of graft copolymer were determined separately in the FAD fractions by an on-line SEC. In the latter case, the molar masses of the copolymerization products were determined by the one step SEC. These polymer products consisted of both homo-PS and graft copolymer and the molar masses were directly calculated from the PS calibration curve. For both reasons the obtained values can be considered only apparent.

Table 2 indicates that the molar masses of both PS and graft copolymer decrease with increasing initiator

concentration. The molar masses of PS are much lower than that of graft copolymers and unusually low for the polymerization in the polymer particles. PS in samples C1–C4 is expected to be formed under the restricted termination (the compartmentalization of growing radicals [20]), while the graft copolymer is created under increased termination which is governed by the kinetics of solution polymerization [21]. Therefore macromolecules of PS should be larger than that of graft copolymer. The results show that the reverse is true. Under similar conditions but using a water-soluble initiator, the molar masses of PS should be close to $10^6$ [20–23]. Our result can be understood considering accumulation of DBP in the styrene saturated polymer particles. The alcohol/water continuous phase favors the predominant location of DBP in the monomer-swollen polymer particles. The low level of oil-soluble (DBP) initiator in the continuous phase disfavors bimolecular termination and therefore large macromolecules might appear.

As expected, the molar mass of PS decreases with increasing DBP concentration and decreasing particle size (Table 1). The volume fraction of thick interfacial layer formed by PEO chains decreases with increasing particle size. The larger particles the larger monomer saturated particle core and higher polymer growth rate. The relatively low molar mass PS in the polymer particles can be taken as a direct evidence for the reaction mechanism earlier proposed by Capek et al. [9] for the dispersion copolymerization of PEO macromonomer and styrene initiated by DBP characterized by the limiting conversion and low polymerization rate. The model suggests that the monomer/polymer particles saturated with the oil-soluble initiator (DBP) exhibit a cage effect. The preferential accumulation of DBP in the monomer-swollen polymer particles and the low molar masses of PSt favor termination in which the growing radicals react with DBP (its radical pairs). The coexistence of growing and primary radicals at high conversion was reported by Hamielec et al. [22]. The reaction of growing radicals with DBP radical pair terminates growing radicals and simultaneously releases single radicals of DBP. These radicals can either re-initiate polymerization or take part in termination. The thick interfacial layer does not favor the exit of single radicals from particles and therefore the single radicals take part predominantly in initiation or termination. Under such conditions, the growing (PS) macroradicals are supposed to be terminated by DBP or its radical pair and therefore the low molar mass polymers are formed.

Molar masses of PS (real) or graft copolymer (apparent) were found to decrease with increasing initiator (DBP) concentration. The experimental data listed in Table 2 obey the relationships:

$$M_{w,PS} \propto [DBP]^{-0.66}, \ MWD_{PS}$$
$$\propto [DBP]^{0.44}, \ in \ THF, \ FAD/SEC$$

$$M_{w,Graft} \propto [DBP]^{-1.0}, \ MWD_{Graft}$$
$$\propto [DBP]^{-0.13}, \ in \ THF, \ SEC$$

The reaction order $x = 0.66$ is in a very good agreement with that (0.6) for the micellar model (Case 2) [23,24]. According to the micellar model, the molar mass increases with the particle diameter as follows:

$$M_w \propto D^{1.0}$$

However, $M_{w,PS}$ abruptly increases with increasing particle size: $M_{w,PS} \propto D^{7.0}$.

It is speculated that this deviation results from the specific polymerization mechanism involving homogeneous nucleation and steric stabilization. Furthermore, the volume fraction of monomer-saturated polymer core is a dominant parameter for the PS chain growth.

The molar masses of graft copolymer decrease with increasing initiator concentration as expected. The apparent reaction order 1.0 ($M_{w,Graft} \propto [DBP]^{-1.0}$) indicates more pronounced termination either in the interfacial layer or in the continuous phase.

The relationships $M_w \propto [DBP]^x$ and $MWD \propto [DBP]^y$ for graft copolymers vary with the eluent type [11–13,25]:

$$M_{w,Graft} \propto [DBP]^{-0.19}, \ SEC, \ in \ DMF$$

$$M_{w,Graft} \propto [DBP]^{-0.8}, \ MWD_{Graft}$$
$$\propto [DBP]^{0.025}, \ SEC, \ in \ THF$$

$$M_{w,Graft} \propto [DBP]^{-0.75}, \ MWD_{Graft}$$
$$\propto [DBP]^{-0.034}, \ LC \ CAP, \ in \ THF$$

As shown before, pure DMF is a very strong desorption promoting liquid (desorli) for PEO and an inappropriate eluent for SEC separation of the graft copolymers columns packed with PS/DVB gel. Furthermore, DMF at room temperature can initiate aggregation of amphiphilic macromolecules. This is a reason why the $M_{w,Graft}$ is slightly dependent on [DBP] in DMF (the reaction order is $-0.19$, SEC). A different dependence between $M_{w,Graft}$ on [DBP] is evidenced in THF (SEC, LC CAP) where the linear dependence of the coil size on the molecular weight is observed. The reaction order $x = -0.75$ or $-0.8$ slightly differs from that ($x = -1.0$) obtained for pure graft copolymers in THF using the two step method FAD/SEC. The slight change in the dependence of $M_w$ on [DBP] (reaction order $x = -0.75$ or $-0.8$) is assumed to be due to the presence of PS (or the dependence of $M_{w,PS}$ [DBP]$^{-0.66}$).

The compartmentalization of reaction loci takes place in all runs and is much more pronounced in the aqueous/alcohol continuous phase. Indeed, the C5 and C6 reaction

mixtures were slightly turbid. This might be a reason why the molar mass distribution (MMD) was relatively broad in the C5 and C6 runs, but still much narrower than that in C1–C4 runs. A relatively broad MMD also resulted from the shift of the monomer feed composition with increasing conversion. As polymerization advanced, the main consumption of styrene resulted from the low reactivity of macromonomer (the steric effect).

It is expected that the solution copolymerization of PEO–MA macromomer and styrene in THF would lead to the dominant formation of graft copolymer. The experimental results (runs C5 and C6) show that the reverse is true, i.e., the final product contains rather large amount of PS, as well. This is especially pronounced in the run C5 (about 20 wt% of styrene in the monomer feed). In the run with a higher amount of PEO macromonomer in the reaction mixture(C6), the amount of PS is substantially lower (about 13 wt%). Still, the amount of PS is much lower than that (about 60 wt% of PS) found in the product of dispersion copolymerization done under similar conditions. The formation of PS during manipulation with polymerization samples can be ruled out because larger amount of PS was found in samples prepared from lower amount of styrene in starting reaction system. This result might be discussed from three points of view: (1) the different reactivity of PEO–MA and styrene; (2) the micellar polymerization; and (3) the preferential solvation of growing radicals by styrene. In the first two cases, the more reactive styrene and its location at the growing chain can favor the formation of PS. The low relative reactivity of PEO macromonomer towards growing PS chain ($r_2^{-1} = 0.7$ [26]) favors the incorporation of styrene in the copolymer. Besides, the bulky and hydrophilic PEO macromonomer can induce the thermodynamic repulsion between PEO macromonomer and hydrophobic PS active chain. Thus, the less reactive PEO macromonomer promotes the initial formation of copolymer rich in styrene units. As polymerization advances, the less reactive PEO macromonomer incorporates more and more into the copolymer [27].

Slightly turbid reaction systems C5 and C6 reveal the phase separation of graft copolymers or the micellar polymerization. The final polymer products consist to two polymer fractions: the one is rich in PEO macromonomer and the other one is rich in styrene units. This finding indicates that there are two different reaction loci even in the solution (THF) polymerization: the continuous phase and microspheres. However, the light scattering measurements of diluted solutions did not prove any presence of aggregates, which probably disassembled in the course of dilution with THF. The loose association within samples C5 and C6 might result from the low molar masses of polymers. In this case, the graft copolymers formed are expected to aggregate into microparticles with the styrene monomer core [28]. Consequently, the polymerization of monomer core will produce PS homopolymer.

## 4. Conclusions

The presence of PS together with graft copolymer in the final polymer product was taken as an indication that there are three (the continuous phase, the particle core and the particle surface layer) or at least the former two reaction loci. The organized structures, which are created during polymerization supposedly, consist of a compact core of hydrophobic PS chains surrounded by a corona of PEO water-soluble chains. This organization depends on the solvent polarity and its density decreases in the following order: water > DMF > THF. This finding indicates that there is not a true homogeneous concentrated solution of graft copolymer. The agglomerates are saturated in the course of polymerization with both monomer and dibenzoyl peroxide initiator. The low styrene and high initiator concentration in the polymer particles are responsible for the formation of low molar mass polystyrene. The presence of a small amount of PS in the "homogeneous" copolymerization is a result of different reactivities of PEO macromonomer and low molecular weight comonomer, preferential solvatation of growing PS active chains with styrene and partitioning of styrene between loosely organized aggregates of graft copolymers and the continuous phase.

## References

[1] Ito K, Tsuchida H, Hayashi A, Kitano T, Yamada E. Polym J 1985;17:827.
[2] Furuhashi H, Kawaguchi S, Itsuno S, Ito K. Colloid Polym Sci 1997;275:227.
[3] Ito K, Masuda Y, Shintani T, Kitano T, Yamashita Y. Polym J 1983;15:443.
[4] Pitsikalis M, Pispas S, Mays JW, Hadjichristidis N. Adv Polym Sci 1998;135:1.
[5] Capek I. Adv Polym Sci 1999;145:1.
[6] Nguyen SH, Berek D, Capek I. J Polym Sci, submitted for publication.
[7] Tanrisever T, Okay O, Sonmezoglu IC. J Appl Polym Sci 1996;61:485.
[8] Capek I, Riza M, Akashi M. Makromol Chem 1992;193:2843.
[9] Capek I, Riza M, Akashi M. Polym J 1992;24:959.
[10] Capek I, Potisk P, Eur. Polym J 1995;31:1269.
[11] Murgasová R, Berek D, Capek I. Newsletter IPCG 1996;27:8.
[12] Murgasová R, Capek I, Lathova E, Berek D, Florian S. Eur Polym J 1998;34:659.
[13] Capek I, Murgasová R, Berek D. Polym Int 1997;44:174.
[14] Gorbunov AA, Skvortsov AM. Adv Colloid Interf Sci 1995;62:31.
[15] Berek D. Makromol Symp 1996;110:33.
[16] Teramachi S. Macromol Symp 1996;110:217.
[17] Nguyen SH, Berek D. Chromatographia 1998;48:65.
[18] Nguyen SH, Berek D. Colloid Polym. Sci. 1999;277:318.
[19] Lacroix-Demazes P, Guyot A. Polym Bull 1996;37:183.

[20] Barton J, Capek I. Radical polymerization in the disperse systems. Veda, Bratislava: Ellis Horwood, 1994.

[21] Odian G. Polymerisation "Principles et applications", Polytechica. 3. New York: Wiley, 1994.

[22] Zhu S, Tian Y, Hamielec AE, Eaton DR. Macromolecules 1990;23:1144.

[23] Smith WV, Ewart RW. J Chem Phys 1948;16:592.

[24] Gardon JL. J Polym Sci 1968;6:665.

[25] Capek I, Riza M, Akashi M. Eur Polym J 1995;31:895.

[26] Capek I, Riza M, Akashi M. J Polym Sci, Part A: Polym Chem 1997;35:3131.

[27] Ito K. In: Macromolecular design: Concept and practice, macromonomers, chap. 4, poly(oxyethelene oxide) macromonomers. Polymers Frontiers International, 1994.

[28] Ito K, Kobayashi H. Polym J 1992;24:199.