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SYNTHESIS AND SOME PROPERTIES OF GRAFT COPOLYMERS WITH UNIFORM POLYOXYETHYLENE SIDE CHAINS

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ABSTRACT

Graft copolymers with uniform polyoxyethylene (PEO) side chains were synthesized by transesterification of poly(methyl,*tert*-butyl fumarate) (PMtBF) or poly(methyl,*tert*-butyl fumarate-*co*-styrene) poly(MtBF-*co*-St) with potassium alkoxide of PEO monoether. The grafting efficiency increased with enhanced alkoxide reactivity, but the main factor in the ester exchange proved to be the structure of the backbone. This effect was ascribed to the thermodynamic incompatibility between fumaric polymers and PEO. The polymers were characterized by spectral methods, GPC, and DSC. In THF the graft copolymers comprising a polyfumarate backbone with PEO side chains eluted at higher elution volumes than did the backbone homopolymers. In benzene their intrinsic viscosities were lower than those of the backbones. In aqueous eluents, micelles were detected, and their aggregation number depended on the composition of the copolymer and the eluent.

INTRODUCTION

Amphiphilic graft copolymers consisting of a hydrophobic backbone and hydrophilic branches are interesting to study on account of their solution, surface, and complexation properties and because of their application as coatings, drug carriers, and polymeric electrolytes [1–3].

The properties of amphiphilic graft copolymers are influenced by their chemical composition and by the number and length of their side chains and their distribution along the backbone. There are two approaches to the synthesis of graft copolymers with well-defined side chains: copolymerization of a macromonomer with a low molecular weight monomer and anionic deactivation or attachment of chain end groups to a functionalized polymer.

Contrary to the conventional chemical reactions in polymers, modification interactions between high molecular weight compounds take place. It has been recognized that the rates of reactions involving chemically unlike polymer chains are influenced by steric, diffusional, conformational, and compatibility factors [4–7]. These considerations suggest that coupling reactions—i.e., those that result in amphiphilic graft copolymers—are very sensitive to inter- and intrachain interactions, attractive or repulsive, and depend on polymer composition, solvent environment, and temperature.

The present paper describes the preparation of amphiphilic graft copolymers from PMtBF or poly(MtBF-*co*-St) and the potassium alkoxide of a PEO monoether by a transesterification reaction. The influence of chain incompatibility on the reaction between chemically unlike polymers and the role of intramolecular interactions in the hydrodynamic behavior of these copolymers in good solvents are discussed. Aggregation of the graft copolymers in selective solvents was observed by GPC in aqueous media.

EXPERIMENTAL

Materials

Maleic anhydride (from Reachim) was recrystallized from dry benzene or sublimed. *tert*-Butyl alcohol (*tert*-BuOH), 4-dimethylaminopyridine (DMAP), dicyclohexylcarbodiimide (DCC), α-methyl-ω-hydroxy polyoxyethylene of $\overline{M}_n$ = 2000 (MePEG-2000), and AIBN were purchased from Fluka. DCC was distilled *in vacuo*. AIBN was recrystallized from methanol. MePEG was dried *in vacuo* over P_2O_5 at 110°C. *tert*-BuOK was prepared following the procedure of Lochmann et al. [8]. Monomethyl fumarate was prepared by isomerization of monomethyl maleate in aqueous solution under the action of thiourea [9].

MtBF was obtained from monomethyl fumarate and *tert*-BuOH in the presence of DCC and DMAP [10]. Its structure and purity were checked by IR and ^{1}H-NMR spectra. Polymerizations were carried out in the bulk in degassed glass ampules with AIBN ($4\text{–}6 \times 10^{-2}$ mol/L) at 65°C for 4 days. The polymers were precipitated in hexane and reprecipitated from benzene solution with hexane. The molecular weights were determined by viscosity measurements using the molecular weight dependence of poly(diisopropyl fumarate) on $[\eta]$ in benzene at 30°C [11].

Copolymerization of MtBF with styrene was carried out in benzene at 65°C for 4 days. The mole ratio of the monomers in the feed was 1:1 and the initiator concentration was 5×10^{-2} mol/L. The polymer solution was precipitated in hexane. The molecular weight was determined by GPC in THF using a PSt calibration. The mole fraction of styrene in the copolymer calculated from its UV spectrum in dichloromethane was 0.6.

Synthesis of Graft Copolymers by Transesterification Reaction

All procedures were carried out using standard high vacuum and break-seal techniques. Toluene was distilled twice from CaH_2. THF was distilled from a blue potassium solution. Ethylene oxide (EO) was dried over CaH_2 and butyllithium. Diphenylmethylpotassium was obtained from diphenylmethane and potassium naphthylide [12]. Living polyoxyethylene (PEO^-,K^+) was prepared in THF by reacting the monomer with diphenylmethylpotassium. The toluene solution of PEO^-,K^+ was prepared by replacing THF with the desired amount of toluene. Traces of THF in neat PEO^-,K^+ were removed on the high vacuum line. Polymers with narrow molecular weight distributions were obtained. Their $\overline{M}_n$ was calculated from UV absorption of the diphenylmethyl end group in THF [13] and from the intensity ratio of aromatic protons to the oxyethylene protons of the ^{1}H-MNR spectrum of the polymer in CD_3OD.

Two grams of PMtBF or 3 g of poly(MtBF-*co*-St) and a certain amount of cryptand [222] were dried by azeotropic distillation with toluene. When grafting was performed in THF, both polymer and cryptand [222] were dried according to the following procedure: An ampule of blue potassium solution in THF prepared in the presence of an excess of sodium-potassium alloy was connected to the ampule with the thoroughly degassed polymer and cryptand. THF was repeatedly distilled off the polymer and cryptand and then back on the alloy until the solution remained blue. Fifty milliliters of a THF (or toluene) solution of living PEO^-,K^+, containing 2.8 g PEO, was added to the dry polymer and refluxed for 4 days. After cooling to room temperature, the reaction vessel was opened, the reaction mixture was neutralized by adding pivalic acid, and most of the solvent was distilled off. The distillate was analyzed by GC for the alcohols liberated. The residue was poured into a large amount of *n*-hexane to precipitate the polymer. The crude polymer was extracted for many hours with water and then centrifuged to separate the water-insoluble fraction. The water was distilled off under vacuum from the aqueous solution of the water-soluble fraction, and the residue was dried *in vacuo*.

GPC was used to follow the progress of the grafting reaction. The reaction was run in a three-necked flask fitted with a stirring paddle, an inlet tube for purified argon, a reflux condenser, and a sampling port. The flask was charged with 0.65 g (0.325 mmol) MePEG-2000, 0.034 g (0.3 mmol) *tert*-BuOK, and 2 mL toluene. The reaction mixture was stirred for 1 h at room temperature and 1 h at reflux. The liberated *tert*-BuOH was distilled off together with the solvent. PMtBF (0.5 g) and 0.6 g tetradecane were dissolved in 10 mL toluene and added to the argon-flushed MePEG alkoxide. The reaction flask was thermostated at 110°C. The MePEG consumption was monitored by GPC and calculated, with tetradecane being used as the internal standard.

The grafting efficiency (G.E.) was calculated according to the following equation:

$$\text{G.E., \%} = \frac{\text{PEO charged} - \text{PEO unreacted}}{\text{PEO charged}} \times 100 \qquad (1)$$

Determination of Graft Copolymer Composition

The composition of the graft copolymer PMtBF-*g*-PEO was obtained by ^{1}H-NMR measurements in CD_3OD from the relative amounts of aromatic protons

($\delta = 7.4$) (arising from the initiator of the EO polymerization) and of the *tert*-butyl protons ($\delta = 1.45$) of the backbone. By using Eq. (2) it was possible to calculate the approximate number of monomer units in the backbone, x, per grafted PEO chain:

$$\frac{\text{area of } tert\text{-butyl protons at } \delta = 1.45}{\text{area of phenyl protons at } \delta = 7.4} = \frac{9(x - 1)}{10} \tag{2}$$

The composition of poly(MtBF-*co*-St)-*g*-PEO was determined by ^{1}H-NMR in $CDCl_3$ from the peak areas of styrene aromatic protons and of oxyethylene protons, keeping in mind the $\overline{DP}$ of PEO and the mole fraction of styrene in the backbone.

Measurements

The apparent molecular weights and molecular weight distributions were determined on a Waters 244 liquid chromatograph using double detection refractive index and UV absorption at a flow rate of 0.8 mL/min in THF at 45 °C.

Combinations of Ultrastyragel columns of 500, 10^3, 10^4, and 10^5 Å, calibrated with PSt standards, and 100, 100, 500, and 500 Å, calibrated with PEO standards, were used. GPC analyses in aqueous solutions were performed on Linear Ultrahydrogel columns (Waters Associates) calibrated with PEO standards. The flow rate of the aqueous eluent was maintained at 0.7 mL/min.

Gas chromatography was carried out on a Carlo Erba Fractovap-4100 gas chromatograph with a flame-ionization detector and a capillary column OV-101.

Proton NMR spectra were taken on a Bruker 250 MHz apparatus in CD_3OD or $CDCl_3$ at 25 °C.

Viscosity measurements were carried out in benzene at 30 °C using an automatic Schott viscometer.

The thermal properties of the polymers were studied on a Perkin-Elmer DSC7 differential scanning calorimeter at a heating rate of 10 °C/min.

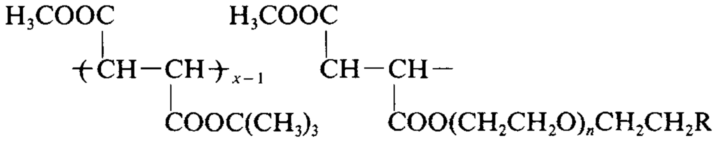
RESULTS AND DISCUSSION

Synthesis and Characterization of the Graft Copolymers

Ester exchange in alkaline conditions is a method used for the preparation of amphiphilic graft copolymers constituted of acrylate or methacrylate backbones and PEO side chains [14–16]. The same reaction proceeds when the anionic polymerization of methyl methacrylate is initiated by the disodium salt of PEO. It results in grafting of PEO chains on the poly(methyl methacrylate) (PMMA) part of the block copolymer [17]. Transesterification is very sensitive to steric and conformational effects, and it is favored when the alkoxide and the leaving group are not hindered. It was found that in the anionic polymerization of *tert*-butyl methacrylate initiated by PEO alkoxide, nucleophilic attack on the carbonyl group does not occur even in the presence of strong cation binding agents such as cryptands [18].

It is well known that alkali alkoxides aggregate in both polar and nonpolar solvents owing to the high charge density on the oxygen. The same phenomenon was evidenced in the anionic polymerization of EO with potassium counterion [19], but the addition of cryptand [222] significantly enhances the reactivity of the active species due to the formation of cryptated ion pairs and free ions [20]. The complexation of alkali cations by cryptands causes the rupture of aggregated alkoxides even in toluene, which enables the initiation of MMA polymerization in nonpolar solvents [21].

PMtBF possesses two potential reaction sites for ester exchange. *tert*-BuOH was the main component of the alcoholic mixture liberated in the course of grafting, which suggests the following structure for the repeat units in the graft copolymer:



$$-\!\left(\overset{\mathrm{H_3COOC}}{\overset{|}{\mathrm{CH}}}-\underset{\mathrm{COOC(CH_3)_3}}{\underset{|}{\mathrm{CH}}}\right)_{x-1}\quad \overset{\mathrm{H_3COOC}}{\overset{|}{\mathrm{CH}}}-\underset{\mathrm{COO(CH_2CH_2O)_{n}CH_2CH_2R}}{\underset{|}{\mathrm{CH}}}-$$

where R is CH_3O or $(C_6H_5)_2CH$.

The fact that the alkoxide anion attacks the carbonyl group at the more hindered ester group might be a consequence of the peculiar conformation of PMtBF. Due to the steric hindrance of the ester groups, it has a less flexible structure and its reactivity is different from that of ordinary vinyl polymers [22].

Transesterification reaction between PMtBF and MePEG alkoxide in toluene at 110°C was monitored by GPC to evaluate the extent of grafting after various time intervals. Longer reaction times are needed to achieve high conversion compared to the grafting of PEO on PMMA under similar conditions [14]. The choice of a 4-d period for transesterification was based on the kinetic data.

The results obtained upon grafting living PEO on PMtBF or poly(MtBF-*co*-St) and the characteristics of the separated fractions are summarized in Table 1. They indicate that, even in the presence of the most powerful complexation agent (cryptand [222]), it was impossible to achieve quantitative grafting of the living PEO chains. The grafting efficiency tends to increase upon enhancing the reactivity of the alkoxide by cryptating the potassium cations or by changing the polarity of the solvent. But under comparable conditions the transesterification of PMMA with PEO alkoxide was found to proceed with higher grafting efficiency [14]. Obviously, the main factor in the ester exchange is the structure of the backbone.

The grafting of PEO alkoxide on PMMA and PMtBF is an ester exchange reaction, but it proceeds between polymers interacting thermodynamically in different ways. PMMA and PEO are compatible polymers both in blends and in concentrated solutions of benzene and toluene [23]. On the other hand, PMtBF and PEO were shown to be incompatible and to give phase-separated films. The incompatibility of the interacting polymers might explain the low grafting efficiency of PEO alkoxide when the backbone was a fumaric polymer.

GPC patterns of the graft copolymers in THF show bimodal distribution because of the presence of unreacted PEO (Fig. 1). The amphiphilic character of the graft copolymers hampers their separation from the homo-PEO, and it was impossible to purify the graft copolymers by extraction or fractionation. Two fractions were isolated upon treating the copolymers with water, suggesting the graft copolymers are heterogeneous in composition. The water-soluble fractions contain up to 60 wt% PEO, which corresponds to eight monomer units of the backbone per PEO chain. This value might be the limiting grafting degree due to the hindering

TABLE 1. Transesterification Conditions and Characteristics of the Graft Copolymers Obtained

							Graft copolymer					
							Water-insoluble fraction			Water-soluble fraction		
			Reaction conditions									
Copolymer	Backbone polymer ($\overline{M}_w \times 10^{-3}$)	PEO$^-$,K$^+$ ($\overline{M}_n \times 10^{-3}$)	Solvent	T, °C	Additive	G.E., %	Wt% in the copolymer	x^a	PEO content, wt%	Wt% in the copolymer	x	PEO content, wt%
G-4	PMtBF (38)[b]	2	Toluene	110	–	50	40	30	27	60	9	55
G-5	PMtBF (60)	2	THF	60	[222]	74	20	31	28	80	8	60
G-6	PMtBF (60)	2	Toluene	110	[222]	60	30	31	28	70	9	55
G-7	Poly (MtBF-*co*-St) (27)[c]	2.4	THF	60	[222]	18	100		25			
G-8	Poly (MtBF-*co*-St) (27)	2.4	Toluene	110	–	23	100		27			

[a] Backbone monomer units per PEO chain.

[b] From intrinsic viscosity in benzene at 30°C.

[c] Determined by GPC using PSt calibration.

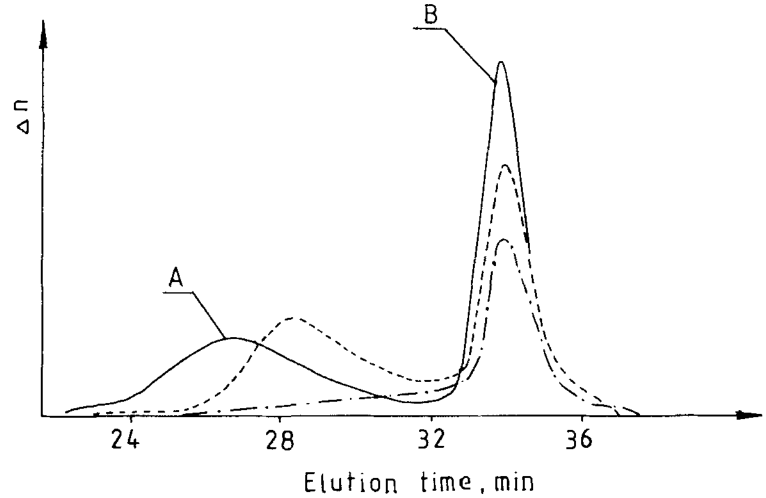


FIG. 1. GPC of graft copolymers PMtBF-*g*-PEO in THF. (——): Mixture of parent homopolymers, PMtBF (A) and PEO (B). (- - -): G-4, prepared through grafting in toluene. (- · -) G-5, prepared through grafting in THF in the presence of cryptand [222].

effect of the grafted polymer chains upon the remaining *tert*-butyl ester groups. A similar decrease in the reactivity of ester groups was established in the reaction between polystyryl anion and PMMA [24].

Solution Behavior of the Graft Copolymers in Good Solvents

Upon following the transesterification reaction by GPC in THF, a decrease in the hydrodynamic volume of the graft copolymers was observed which tracks the increase of their PEO content (Fig. 1). This effect was most pronounced for graft copolymer G-5, in which case the elution volume reaches the elution volume of the parent PEO.

In GPC experiments the factor determining retention of macromolecules is their hydrodynamic volume. PMtBFs have a less flexible structure [22] and their hydrodynamic volume is larger than that of the linear polystyrene standards of the same molecular weight (Table 2). The apparent molecular weights of the graft copolymers obtained by GPC are smaller than that of the backbone polymer, and they reflect the decrease of the hydrodynamic volume of the polymers in the course of grafting. The water-insoluble fractions with PEO contents lower than 30 wt% have higher apparent molecular weights than the water-soluble fractions containing a larger amount of PEO. These results indicate that the hydrodynamic volumes of the graft copolymers vary widely according to their compositions.

The small hydrodynamic volume of the graft copolymers in good solvents was confirmed by viscosity measurements in benzene (Table 2). G-5 is the graft copolymer with the highest number of PEO grafts per backbone chain. Its intrinsic viscosity is equal to that of the PEO homopolymer. On the other hand, the elution volumes of G-5 and homo-PEO are the same. Comparison of the viscometric and

TABLE 2. Molecular Weight and Intrinsic Viscosity of the Graft Copolymers and of the Homopolymers Used for Their Preparation

Polymer	$[\eta]^a$ dL/g	$\overline{M}_w/\overline{M}_n$ [b]	$\overline{M}_v \times 10^{-3}$ [c]	$\overline{M}_w \times 10^{-3}$ [d]
PMtBF	0.47	1.43	60	109
PEO	0.069	1.06	–	3
G-5	0.069	1.76	–	6.5
G-$6_{\text{w. insol.}}$	–	1.95	–	11
G-$6_{\text{w. sol.}}$				4

[a] In benzene at 30°C.

[b] Determined by GPC in THF.

[c] From intrinsic viscosity in benzene at 30°C.

[d] Determined by GPC using PSt calibration.

GPC data suggests that in good solvents these amphiphilic graft copolymers exhibit a compact conformation, and the dominant factors determining their size are the grafting degree and the length of the PEO side chain.

A possible reason for the increase of the elution volume of the graft copolymers might be their adsorption on the column packing. However, we found that the THF solution of a graft copolymer filtered through a 10^4 molecular weight cut-off Millipore membrane has the same GPC pattern as an unfiltered one. It follows that interaction of the solute with the surface of the packing should not interfere with the size-exclusion process. Hence, the larger elution volumes of the graft copolymers compared to the parent PMtBF can be due to a decrease in their hydrodynamic volume.

A decrease in the hydrodynamic volume of amphiphilic graft copolymers was not observed by GPC when their hydrophobic component was poly(MtBF-*co*-St). The transesterification reaction in this case resulted in graft copolymers containing up to 25-30 wt% PEO, but the apparent molecular weight determined by GPC remained the same as that of poly(MtBF-*co*-St). Accordingly, the decrease in the hydrodynamic volume of polymers grafted with oxyethylene side chains appears to be a function of the structure of the backbone. Elution volumes of graft copolymers in THF larger than those of the backbones have also been observed in the case of PEO grafting on polysiloxanes. Smid et al. [25] attributed this effect to the intramolecular interactions between the oxyethylene side chains because of their well-known ability to form organized structures in the solid state as well as in solution [26, 27]. Such interactions are disrupted when styrene units are incorporated in the backbone, and this could be the reason for the different hydrodynamic behaviors of PMtBF-*g*-PEO and poly(MtBF-*co*-St)-*g*-PEO.

GPC Measurements in Selective Solvents

An interesting approach to GPC characterization of block and graft copolymers is to elute them with a selective solvent, i.e., a good solvent for one type of the block and poor for the other. Elution of amphiphilic block copolymers with water enables the micelle formation to be observed, unreacted PEO in condensation products to be detected, and amphiphilic copolymers of different structures and compositions to be differentiated [28–30].

The PEO homopolymers used in this work for grafting on the hydrophobic backbone carried a bulky diphenylmethyl group at the chain end. In aqueous solution these hydrophobic groups aggregate in a manner analogous to that of nonionic surfactants above their critical micelle concentration. These polymolecular micelles were visible in aqueous GPC as species which were eluted at the exclusion volume of the column, the apparent molecular weight being in excess of 10^6.

GPC in aqueous solution was used to analyze the water-soluble fractions of the graft copolymers which were always contaminated with unreacted PEO. The GPC curve (Fig. 2) shows, besides the high-molecular-weight aggregate (MW > 10^6), a series of peaks on the higher-elution-volume side (MW < 6×10^4). The lower molecular weight species may be considered to be nonassociated polymeric amphiphiles because the PEO homopolymer, which is itself an amphiphile, hinders the intermolecular association of the graft copolymers. Such an ability of nonionic surfactants to disrupt the intermolecular hydrophoboc interactions of water-soluble graft copolymers is a well-established fact when the structures of the added surfactant and the side chain are similar [31, 32].

Addition of 0.05 wt% NaN_3, usually used as a fungicide, to the aqueous eluent drastically changed the shape of the GPC curve. PEO homopolymer ceased to form polymolecular micelles, and the graft copolymers were eluted at smaller volumes (higher micellar weights) than they do in pure water. Thus, the added salt prevents the amphiphilic homo-PEO from association, and the graft copolymers were eluted as polymolecular micelles of not very high micellar weight.

Micellization of surfactants in aqueous solutions is very sensitive to the addition of water-soluble organic solvents and might cease at high additive concentrations [30, 31, 33]. GPC analysis showed that in an aqueous-methanolic eluent (volume ratio 1:1), PEO with its diphenylmethyl end group is eluted as a molecularly

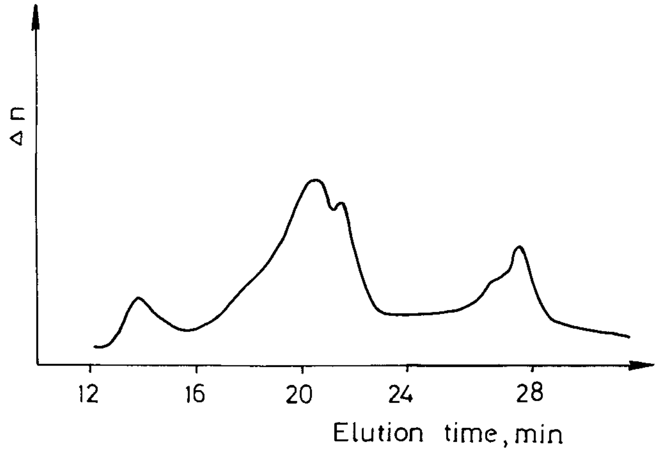


FIG. 2. GPC of the water-soluble fraction of PMtBF-*g*-PEO on Ultrahydrogel columns with water eluent.

dissolved polymer. High molecular weight aggregates might originate only from graft copolymers.

In an aqueous–methanolic eluent it was possible to analyze both the water-soluble and water-insoluble fractions. It is noteworthy that irrespective of the PEO content, all graft copolymers were eluted as micelles whose apparent micellar weight proves the existence of intermolecularly aggregated copolymers.

Water-insoluble fractions, no matter whether the backbone structure is PMtBF or poly(MtBF-*co*-St), eluted as a single peak at the exclusion volume. The PEO content of these copolymers did not exceed 30 wt%, and obviously they formed polymolecular micelles with a high aggregation number (Fig. 3a).

The gel permeation chromatogram of the water-soluble G-6 fraction given in Fig. 3(b) displays a polymodal distribution. The low molecular weight peak is due to PEO elution, and the peaks in the domain of molecular weight above 4×10^5 indicate the presence of polymolecular micelles of different sizes.

Gallot et al. [34] studied the micelle formation of graft copolymers of different compositions in selective solvents. They inferred that their aggregation behavior depends on the number and length of solvated grafts per insoluble backbone. The main feature observed is that the aggregation number decreases with increasing grafting degree. Even monomolecular micelles could be formed if the number of solvated grafts was sufficient to protect the insoluble core from precipitation [35].

The polymolecular micelles originating from the water-insoluble and water-soluble fractions differ in their hydrodynamic volumes. The difference in micelle size may be related to the variation in the aggregation number. It seems valid to assume that the water-insoluble fraction (PEO content up to 30 wt%) should form micelles with high aggregation numbers, and that they should be eluted from the GPC column earlier than the micelles with lower aggregation numbers originating from the water-soluble fraction (PEO content up to 60 wt%).

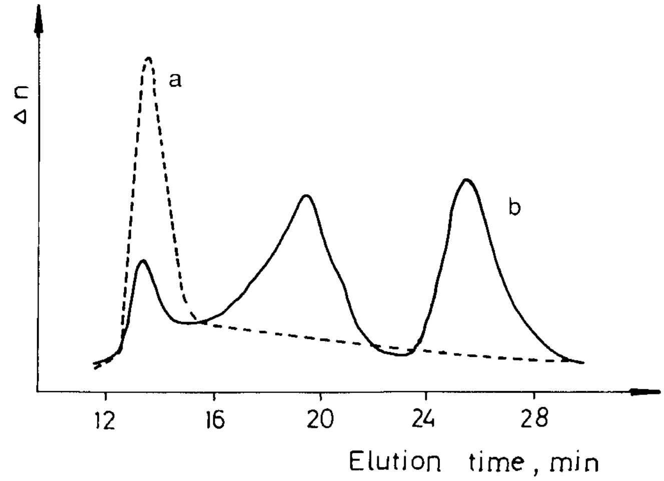


FIG. 3. PC of PMtBF-*g*-PEO on Ultrahydrogel columns with aqueous–methanolic (volume ratio 1:1) eluent. a (- - -): water-insoluble fraction. b (——): water-soluble fraction.

TABLE 3. Thermal Properties of Homopolymers, Their Blend, and Graft Copolymers

Sample ($\overline{M}_n \times 10^{-3}$)	Backbone monomer units per a PEO chain	T_g, °C	T_m, °C
RPEO[a] (2)		−33	50
PMtBF (40)		24	
Blend of RPEO and PMtBF (weight ratio 1:1)		−29	48
G-4	12		40
G-5	9		45

[a] R is a $(C_6H_5)_2CH$ group.

Thermal Properties

The thermal data for the homopolymers, their blends, and the graft copolymers are summarized in Table 3.

A thin opaque film was obtained by casting from a chloroform solution of a mixture (weight ratio 1:1) of PMtBF and PEO, which is an indication of the incompatibility of both polymers. The microphase-separated morphology was also demonstrated by the DSC thermogram of the blend which shows a glass transition at about −29°C along with a strong melting endotherm, both assigned to the PEO phase. It is noteworthy that with an increasing degree of grafting, the melting point of the crystalline polyether phase is shifted to higher values, close to the melting point of the parent PEO. It is reasonable to assume that side-chain packing is more difficult at lower degrees of grafting and is favored at enhanced branching densities.

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