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Synthesis and characterization of amphiphilic graft copolymers based on poly(styrene-*co*-maleic anhydride) with oligo(oxyethylene) side chains and their GPC behavior

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Abstract

A series of amphiphilic graft copolymers were synthesized based on poly(styrene-*co*-maleic anhydride) (SMAs) (backbone copolymers) and methoxypolyethylene glycols (MPEGs) (grafts) in this study. Selection of proper reaction conditions using *p*-toluenesulfonic acid (PTSA) as catalyst and toluene as solvent in the present research can prevent crosslinking reactions which may occur due to the presence of di-functional polyethylene glycol in the commercial MPEGs. The structures and compositions of the graft copolymers were determined by gel permeation chromatography (GPC) and ^{1}H NMR analysis. It is noteworthy that the GPC behavior of these graft copolymers follows the rule of thumb for GPC, i.e. the higher molecular weight copolymers have lower retention volumes. This is very different from the GPC behavior of similar graft copolymers reported previously in the literature. Also, differential scanning calorimetry (DSC) characterization shows that there are two transition temperatures for some of these amphiphilic copolymers owing to the existence of another aggregation phase of MPEG grafts.

Keywords: Amphiphilic graft copolymers; Side chains; GPC behavior

1. Introduction

Amphiphilic graft copolymers prepared by grafting hydrophilic side chains on hydrophobic backbones exhibit many particular physico-chemical characters, which are different from their corresponding linear homologues. Because of their specific properties, many fundamental studies and technical applications have arisen over the past few years [1–4]. These copolymers usually serve as polyelectrolytes in batteries, stabilizers in dispersion or emulsion systems, antistatic agents, drug carriers, additives for stabilization of polymer blends or for surface modification of organic materials, and so on.

There are many ways to prepare amphiphilic graft copolymers, and the most common method is to graft oligomers onto backbone polymers. Poly(styrene-*co*-maleic anhydride) (SMA) is a commercially available copolymer bearing reactive anhydride groups. These anhydride groups present in SMA can easily undergo an opening reaction with nucleophilic reagents which contain hydroxyl or amine groups. Methoxypolyethylene glycol (MPEG) is a commercially available well-defined hydrophilic oligomer. The grafting reaction between SMA and MPEG has been reported recently [5–7]; however, there have been several problems for this synthetic strategy. The major problem that may occur is formation of gel during the reaction or the work-up process, since the presence of di-functional polyethylene glycol in the commercial MPEG may result in a crosslinking reaction during the preparation period. The present research proposes new reaction conditions to prevent the occurrence of the crosslinking reaction during the synthesis of graft copolymers from SMAs (backbones) and MPEGs (grafts).

Moreover, some studies [8–12] have indicated that the amphiphilic graft copolymers exhibited very different gel permeation chromatography (GPC) behavior in organic solvents, which was interpreted from the observation that the amphiphilic graft copolymers usually have a greater retention volume (smaller hydrodynamic volume) compared to the backbone polymers from which they are synthesized, which resulted from the adsorption of graft copolymers onto the GPC analytical columns or from conformational effects arising from the different polarities between the backbone and the graft copolymer.

In this study, SMA-*g*-MPEG copolymers were

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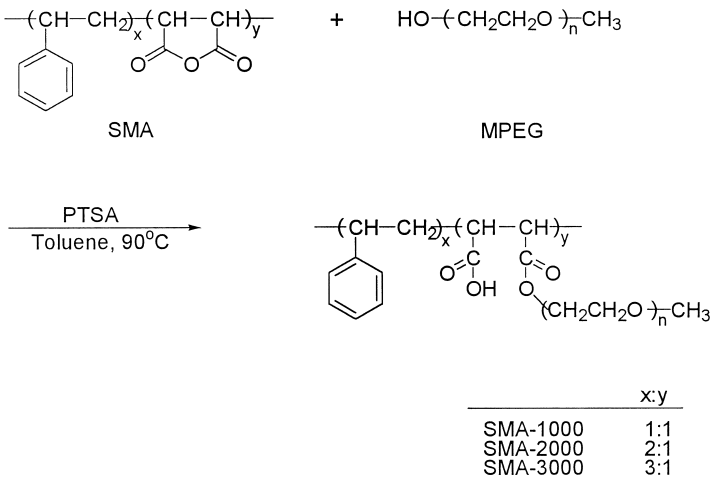

Scheme 1.

successfully synthesized without undergoing any crosslinking reaction. It is noteworthy to mention that the synthetic graft copolymer exhibits distinctly different GPC behavior compared to the typical amphiphilic graft copolymer reported previously in the literature. Thus, the GPC behavior of the graft copolymers synthesized in this work was correlated to the structures and compositions of the copolymers and was interpreted in terms of a conformational effect. In addition, their thermal properties were investigated by differential scanning calorimetry (DSC).

2. Experimental section

2.1. Materials

SMA-1000, SMA-2000 and SMA-3000 were purchased from Elf Atochem. MPEG-350, MPEG-750 and MPEG-2000 were purchased from Union Carbide. *p*-Toluenesulfonic acid (PTSA) (Merck) was used as received. Toluene (TEDIA) and dioxane (TEDIA) were freshly distilled from calcium hydride before use. Tetrahydrofuran (THF, HPLC grade) was used for gel permeation chromatography (GPC) as received.

2.2. Synthesis of graft copolymer (SgM37)

To a 500-ml four-necked-reactor equipped with mechanical stirrer and condenser, toluene (200 ml), SMA-3000 (20 g), MPEG-750 (39 g), and PTSA (0.6 g) were added sequentially. The reaction was carried out at 90°C under nitrogen atmosphere for 12 h. Solvent in the reaction mixture was then removed with a rotary evaporator. The crude product was purified by diethyl ether/toluene reprecipitation repeatedly until the unreacted MPEG was almost removed. The purified product was dried in a vacuum oven to remove the trapped solvent at 40°C for 48 h.

2.3. Characterization methods

^{1}H NMR spectra were recorded on a Brucker AMX-400 spectrometer using d-acetone as solvent. GPC analyses were run at room temperature in THF (at a flow rate of 1 ml min^{-1}) on a Waters 510 HPLC pump with a series of columns (TSK-GEL G5000-HXL, G3000-HXL: 7.5 mm i.d. × 30 cm, Tosoh Ltd.) using a Waters 410 RI-detector. The injection volume was 20 μl of a 2-wt% copolymer in THF. Molecular weight (M_n) calculations were based on a linear calibration curve obtained using eight narrow molecular weight polystyrene standards (M_n = 800, 2000, 4000, 9000, 30,000, 50,000, 10,900, and 233,000) (Polysciences). DSC measurements were performed on a TA DSC-2010 instrument. The samples were hermetically sealed in aluminum pans. The samples were quenched to −100°C, and then subjected to a heating program (10°C min^{-1}). The glass transition temperatures (T_g) were determined as the midpoints of the transition temperatures.

3. Results and discussion

3.1. Synthesis of SMA-g-MPEG copolymer

Synthesis of comb-like amphiphilic copolymers based on maleic anhydride copolymer backbone and MPEG grafts has been reported by several groups, but gelation of the reaction mixtures was still the major difficulty in preparing the amphiphilic graft copolymers. Gel formation might arise from the uncapped PEGs in the MPEGs, resulting in a crosslinking reaction between the di-functional PEGs and the anhydride groups on the backbone copolymers. To overcome this problem, variations in the reaction conditions were utilized to graft MPEG on to the maleic anhydride copolymer backbone, for example, using bulk condition without adding any solvent and catalyst [5], using dimethylformamide (DMF) as solvent without adding catalyst [6],

Table 1
Characteristics of the starting SMA copolymers and MPEG

Starting materials	Composition[a]	T_g (°C)	T_m (°C)	M_n from GPC[b] (g mol^{-1})	Average no. of anhydride group in every polymer in every polymer chain
SMA-1000	1:1	156.3		2200(1.85)	10.9
SMA-2000	2:1	130.7		3300(2.40)	10.8
SMA-3000	3:1	127.2		4700(2.21)	11.5
MPEG-350		− 46.3	− 9.8	500(1.07)	
MPEG-750		–[c]	26.5	900(1.08)	

[a] The unit ratio of styrene to maleic anhydride.
[b] M_n is determined by GPC and polystyrene is used as the calibration standard. The value within parentheses is the polydispersity (M_w/M_n).
[c] No distinct glass transition temperature was observed.

and using methyl ether ketone (MEK) as solvent and adding PTSA as an acidic catalyst [4].

Although the above reaction conditions could result in the formation of the expected products, insoluble gel was still formed when the conversion of the grafting reaction was too high or when the temperature was too high during the work-up process; as a result, the obtained graft copolymer that was isolated by reprecipitation and drying could not be dissolved in organic solvents such as DMF, THF, acetone, or methanol, but swelled in polar organic solvents and water [4,6].

In this research, toluene was selected as solvent and PTSA was used as catalyst. This reaction condition could prevent gelation during the synthesis process, and the products obtained dissolved very well in the common organic solvents as mentioned earlier. Scheme 1 illustrates the synthetic route for the graft copolymers and Tables 1 and 2 summarize the characteristics of the starting materials and the purified graft copolymers.

Reactions between macromolecules are usually difficult to carry out, since the steric conformational effect will hinder the collisions among the reactive sites on the macromolecules; therefore, a good solvent for the reactants is required for a grafting reaction between macromolecules. A good solvent can lead to favorable conformations of macromolecular reactants for effective collisions; however, it also reduces the concentrations of reactants and decreases the rate of reaction. Thus, proper selection of solvent is one of the key points needed to ensure the grafting reaction between the anhydride group (SMA) and the hydroxyl group (MPEG). The reaction will be more efficient when the solvent is a good solvent for both reactants, i.e. the backbone copolymer and graft oligomer. Toluene was used as solvent in this study; it is a good solvent for SMA-2000 and SMA-3000, but it is not a good solvent for SMA-1000, where the unit ratio of styrene and maleic anhydride is 1:1. A slightly turbid solution was formed when SMA-1000 was dissolved in toluene at room temperature; however, the solution became transparent when the temperature increased to above 60°C and MPEGs were added. This can be attributed to the observation that SMA-1000 contains a great number of anhydride groups and thus is more polar than SMA-2000 and SMA-3000, and MPEG acted in the role of cosolvent to help dissolving SMA-1000 in toluene.

Another important parameter that influences the opening reaction of the anhydride group to attack by the OH groups on the MPEGs is the choice of catalyst. Acidic and basic catalysts can accelerate the rate of the grafting reaction between two large molecules, i.e. backbone copolymer and grafting oligomer. *p*-Toluenesulfonic acid is a common acidic catalyst for esterification reactions, and it has been used for the grafting reaction as well [4]. In this paper, PTSA was also chosen as the catalyst for the opening reaction between SMAs and MPEGs. The high anhydride conversions shown in Table 2 indicate that PTSA is an effective catalyst for this grafting reaction.

To monitor the grafting reaction between SMAs and MPEGs, the change in the molecular weights of intermediate graft products were followed by GPC (GPC behavior of SMA-*g*-MPEG copolymers will be discussed later). Fig. 1 shows the GPC chromatograms of the intermediate graft products at various times after SMA-1000 has been reacted with MPEG-750. These chromatograms show that the molecular weights, i.e. the hydrodynamic volumes, of the intermediate graft products increase along with the reaction time. The ratio of the peak area of the intermediate graft products to the unreacted MPEG-750 was plotted against time and is presented in Fig. 2. The change in the slope of the curve in Fig. 2 was very small after 12 h; thus, the conversion for the grafting reaction reached its limit after this time.

3.2. NMR characterization of SMA-g-MPEG copolymer

Fig. 3 is a typical ^{1}H NMR spectrum of SMA-*g*-MPEG copolymer (S*g*M17). The broad peak at $\delta = 7.2$ ppm (c) is the resonance peak of the phenyl protons of the styrene units in the backbone copolymer, the peak at $\delta = 3.5$ ppm (b)

Table 2
Characteristics of the grafted SMA-*g*-MPEG copolymers

Sample name[a]	Conversion of anhydride (%)	Content of unreacted MPEG[b](%)	M_n from GPC[b] (g mol^{-1})	Calculated M_n (g mol^{-1})	Average no. of MPEGs in every graft copolymer chain	T_g (°C)
SgM13	38.7	2.7	5300(1.85)	4300	4.2	− 8.8/13.6
SgM23	50.8	0	8800(2.98)	6000	5.5	28.1
SgM33	60.0	2.8	10300(1.84)	8100	6.9	35.8
SgM17	38.0	0	7900(1.78)	5900	4.1	− 36.3/3.6
SgM27	41.7	3.1	11000(1.90)	7300	4.5	− 32.3/− 6.2
SgM37	55.7	1.3	11500(1.86)	10400	6.4	− 22.7/− 1.5

[a] The notation: the first digit indicates the SMA origin (i.e. 1, 2, 3 represent SMA-1000, SMA-2000 and SMA-3000, respectively), and the last digit indicates the MPEG origin (3 and 7 represent MPEG-350 and 750, respectively).
[b] M_n is determined by GPC and polystyrene is used as the calibration standard. The value in parenthesis is the polydispersity (M_w/M_n).

corresponds to the ethylene protons in the ethylene oxide repeating units in MPEG, and the peak at $\delta = 3.3$ ppm (a) is the resonance peak of the terminal methoxy protons on MPEG. In addition, it is worth noting that a small and broad peak at $\delta = 4.2$ ppm is attributed to the methylene protons that are attached to the ester group formed in the opening reaction between SMA-1000 and MPEG-750. Based on the above characterization, it was demonstrated that the grafting reaction between SMA and MPEG was successful under the reactions where toluene was used as solvent and PTSA was used as catalyst.

Since all of the purified products contain only very small amounts of unreacted MPEGs (see Table 2), the conversion of anhydride groups in the SMAs can be calculated from the peak ratio of the terminal methoxy protons on the MPEG grafts to the phenyl protons on the backbone SMA copolymers; thus, the percentage of conversion can be calculated using the following equation:

$$\text{conversion}(\%) = \frac{A_M/3}{A_s/5x}$$

where A_M and A_s are the peak areas of the methoxy protons and the phenyl protons in the ^{1}H NMR spectrum, respectively; x is 1, 2 and 3 for SMA-1000, SMA-2000 and SMA-3000, respectively. The calculated results are shown in Table 2, and it can be seen that the trend of anhydride conversion in SMA-3000 > SMA-2000 > SMA-1000 in both the MPEG-350 and MPEG-750 series. It can be seen from Table 1 that the numbers of anhydride units of each chain of SMA copolymers are about the same. On the other hand, SMA copolymers are typical alternating copolymers prepared from radical polymerization, so the number of styrene units between two anhydride groups on a SMA backbone copolymer can be assumed to be 1, 2 and 3 for SMA-1000, SMA-2000 and SMA-3000, respectively. In other words, the distance between two anhydride groups are closest in SMA-1000; then, whenever the MPEGs graft on to the SMA backbone, the neighboring anhydride groups are difficult to react with other MPEGs because of steric hindrance. In contrast to SMA-3000, the spacing styrene unit number is 3, so the MPEGs are easier to graft on to the backbone despite the fact that the neighboring anhydride groups have grafted large MPEG molecules. Therefore, the difference in anhydride conversion may arise from these steric effects.

From the anhydride conversion data, the number of MPEG grafts on each SMA backbone copolymer can be calculated; these values are tabulated in Table 2. Accordingly, the average molecular weight of graft copolymer can be calculated as follows:

$$\text{Calculated } M_n = (\text{no. of MPEG grafts} \times M_n \text{ of MPEG}) + (M_n \text{ of SMA})$$

The calculated results are shown in Table 2. Comparison of the calculated M_n values to that of graft copolymer obtained

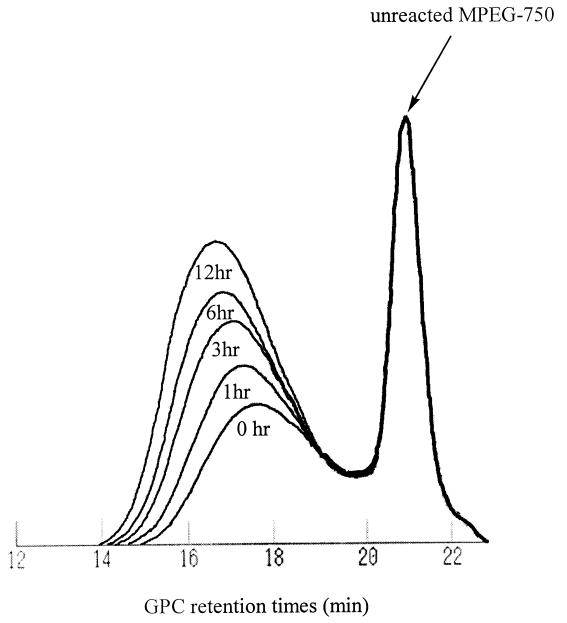

Fig. 1. Stack GPC chromatograms of the intermediate graft products as a function of increasing time after SMA-1000 has been reacted with MPEG-750; the unreacted MPEG-750 has been normalized.

from GPC (also in Table 2), show that the values differ by 1000–3700 g mol^{-1} (i.e. from 9.6 to 33.6% error). However, it has been reported that the M_n values for graft and block copolymers obtained from GPC analysis are generally remarkably different from the absolute M_n values obtained from other methods or theoretical calculations [8–15]. Therefore, it may be seen that the GPC results from the series of amphiphilic SMA-*g*-MPEG copolymers are in acceptable agreement with the theoretical calculations in this study.

3.3. GPC behavior of SMA-g-MPEG copolymer

Gel permeation chromatography is the most popular tool for determining the molecular weights of polymers. Nevertheless, the molecular weights reported by GPC are actually those of the equivalent standard polystyrene hydrodynamic volume. In other words, information obtained from GPC depends on the hydrodynamic volume of polymers in the mobile phase rather than their molecular weights. Some research [8–12] indicates that amphiphilic graft copolymers elute at volumes close to, or greater than, those obtained for the corresponding backbone polymers because of the absorption of graft copolymer on the packing material in the analytical columns or because of conformational effects. The intramolecular interactions (such as "intramolecular micellization") caused by grafts, whose polarity is quite different from that of the backbone polymers, may lead to a smaller hydrodynamic volume for the graft copolymer compared to the backbone polymer. As a result, amphiphilic graft copolymers often elute later from GPC columns than expected.

However, the crude and purified graft copolymers obtained in this investigation always elute earlier from the GPC columns as expected, and the retention volumes of them were nearly the same. These observations were different from some reports [6,9–11] that dealt with similar systems. Fig. 4 shows the GPC chromatograms of SMA-3000, as well as crude and purified S*g*M37. It can be seen in Fig. 4 that the unreacted MPEG-750 was nearly completely removed by reprecipitation from cold diethyl ether, and the portion of small molecular weights in SMA-3000 was also removed during fractionation. Clearly, the profiles of both crude and purified S*g*M37 of $M_n = 11,500$ had a lower retention volume (a higher hydrodynamic volume) than that

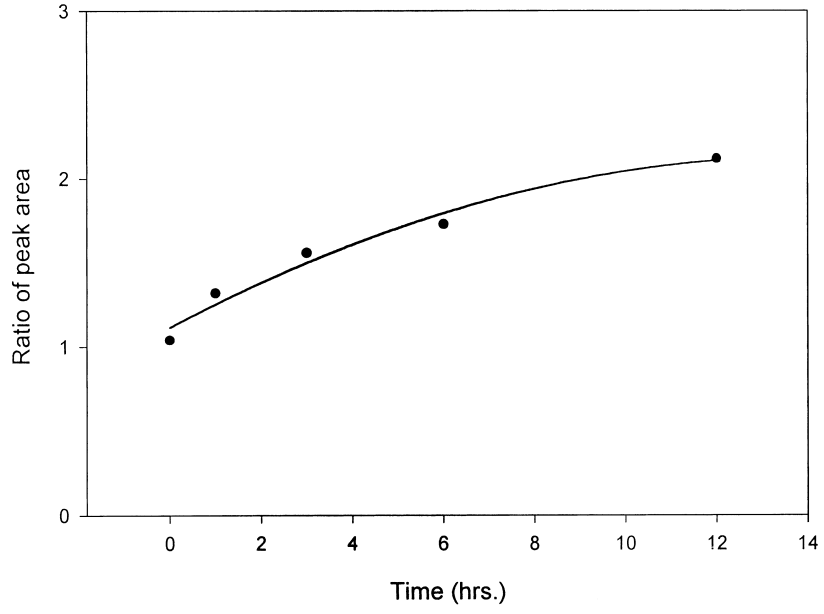

Fig. 2. Plot of the peak area of the intermediate graft products to the unreacted MPEG-750 as a function of time.

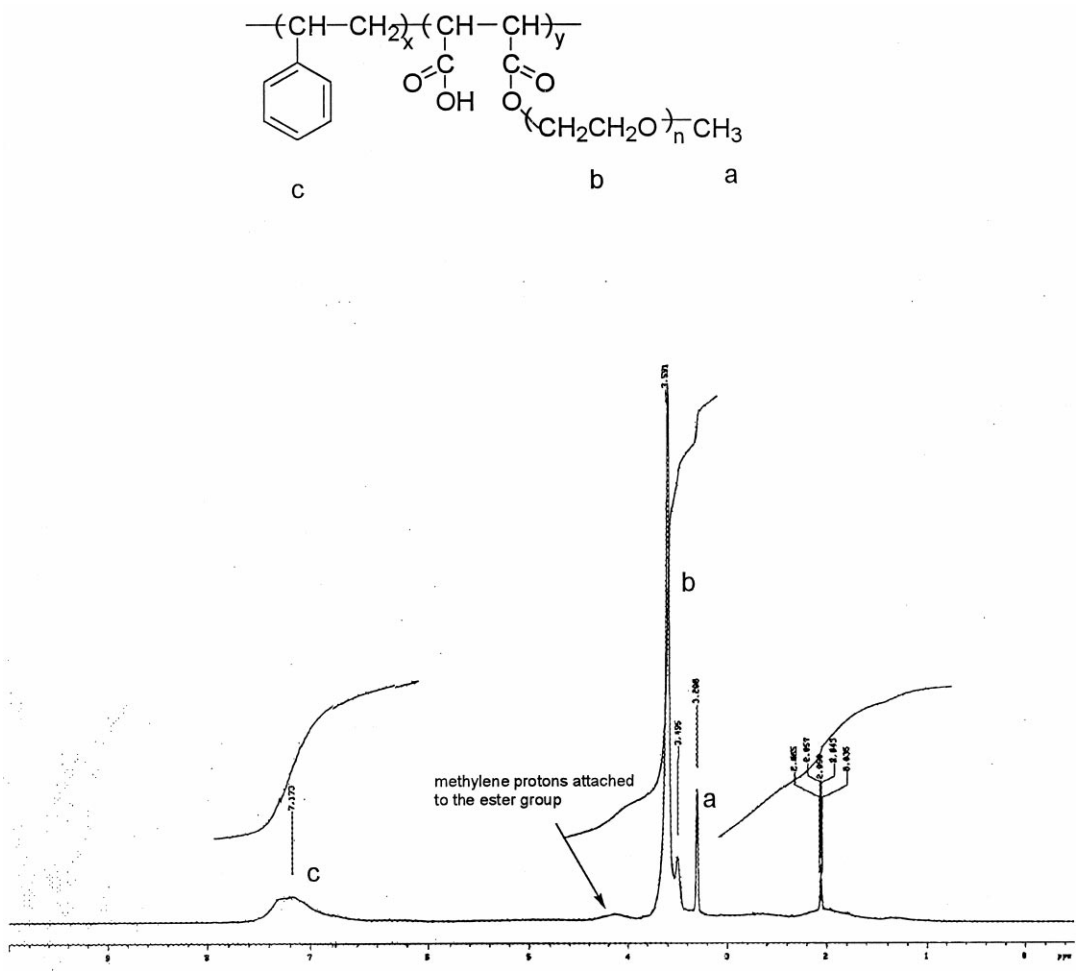

Fig. 3. Typical ^{1}H NMR spectrum of SMA-*g*-MPEG copolymer (S*g*M17).

of the SMA-3000 from which it was synthesized. The GPC results and the M_n values corresponding to the polystyrene standards of these synthesized graft copolymers are tabulated in Table 2.

It has been mentioned that the hydrophilic grafts might aggregate together due to their tendency to segregate from the hydrophobic backbones, and result in conformations which have smaller hydrodynamic volumes in an organic solvent. In this study, SMA-3000 is more hydrophobic than SMA-2000 and SMA-1000, because it has a higher ratio of styrene units; however, S*g*M33 and S*g*M37 still elute earlier from GPC compared to their starting backbone copolymer (SMA-3000) (Fig. 5). This implies that the conformational effect resulting from the difference in polarity of backbone copolymer and graft to produce a smaller hydrodynamic volume for comb-like amphiphilic copolymers does not apply to our system.

In order to investigate the effect of the chain length (molecular weights) of the grafts on the hydrodynamic volumes of the graft copolymers, a grafting reaction between SMA-3000 and MPEG-2000 (M_n = 2400 g mol^{-1}, M_w/M_n = 1.06 determined by GPC) was carried out to obtain the S*g*M32 sample in this study. The reaction conditions were the same as described above, but dioxane was used as solvent instead of toluene because toluene cannot dissolve MPEG-2000 even though the temperature of the reaction mixture was raised to 100°C. Moreover, MPEG-2000 is a crystalline solid at room temperature, and is co-precipitated together with the obtained graft copolymer (S*g*M32) in cold diethyl ether during the fractionation; thus, it is difficult to totally remove the unreacted MPEG-2000 by the reprecipitation method. Fig. 6 shows the stack GPC chromatographs of SMA-3000, the crude and purified products of S*g*M32, and the unreacted MPEG-2000. Obviously, the crude and purified S*g*M32 eluted early than SMA-3000, which is the corresponding backbone copolymer from which it was synthesized. Compared to S*g*M33, S*g*M37 (Fig. 5) and S*g*M32 graft copolymers (Fig. 6), it can be concluded that the increase in the chain lengths of grafts in SMA-*g*-MPEG copolymers did not reduce the hydrodynamic volumes of graft copolymers in organic solvents.

Furthermore, in order to investigate the effect of the chain length (molecular weight) of the backbone copolymer on the hydrodynamic volumes of the graft copolymers, a SMA copolymer (anhydride:styrene = 1.1)

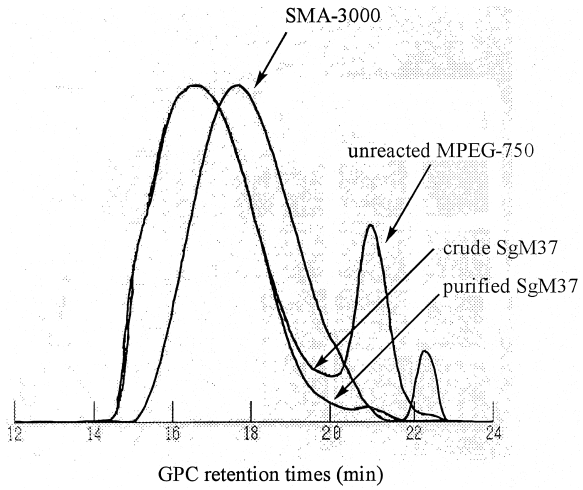

Fig. 4. GPC chromatograms of SMA-3000 and the corresponding S*g*M37 (crude and purified).

of $M_n = 48,000$ g mol^{-1} was synthesized via radical polymerization in this study, and then it was grafted with MPEG-750. Its GPC chromatograms (Fig. 7) also show a higher hydrodynamic volume for the graft copolymer. This result indicates that even if the chain length (molecular weight) of the backbone copolymer is increased, the incorporation of graft on to the backbone copolymer does not reduce the hydrodynamic volume of SMA-*g*-MPEG copolymer in organic solvent.

3.4. DSC characterization of SMA-g-MPEG copolymers

Fig. 8 shows the thermograms of the graft copolymers of the MPEG-350 and MPEG-750 series; the glass transition temperatures of the graft copolymers are tabulated in Table 2. The disappearance of the melting peak of MPEG-350 or MPEG-750 demonstrates the successful synthesis and complete fractionation of the unreacted MPEGs by reprecipitation. In the MPEG-750 series, it is noteworthy that each

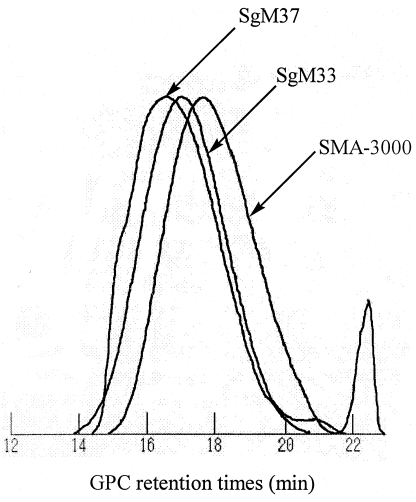

Fig. 5. GPC chromatograms of S*g*M37, S*g*M33 and SMA-3000.

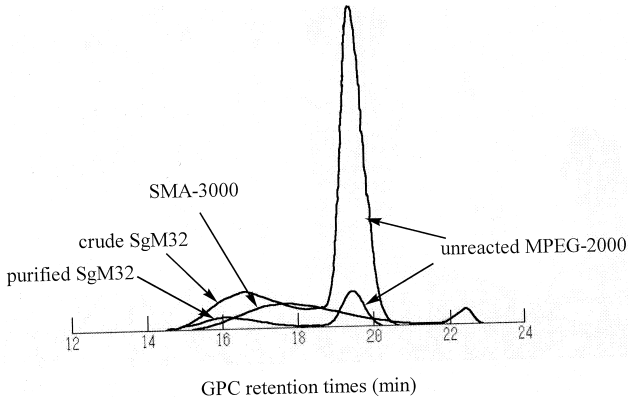

Fig. 6. GPC chromatograms of SMA-3000 and the corresponding S*g*M32 (crude and purified).

S*g*M17 and S*g*M27 graft copolymer has two distinct glass transition temperatures; however, for S*g*M37, the lower transition temperature almost disappears. Also, the lower- and higher-class transition temperatures are both in the order of S*g*M37 > S*g*M27 > S*g*M17. This indicates that the synthetic graft copolymers may form two phases because of the incompatibility of the hydrophobic backbones and the hydrophilic grafts. The glass transition temperatures of the graft copolymers are much lower than that of the backbone of SMAs, since the MPEGs with flexible ether linkage are grafted on to the hard backbone copolymer.

The DSC behavior can be interpreted by an increased number of styrene spacing units in the SMA backbone copolymer resulting in a higher transition temperature owing to the stiffness of the aromatic rings. On the other hand, the lower transition temperatures which appeared in SMA-17 and SMA-37 graft copolymers are probably due to an existence of the aggregation phase comprised of MPEG-750.

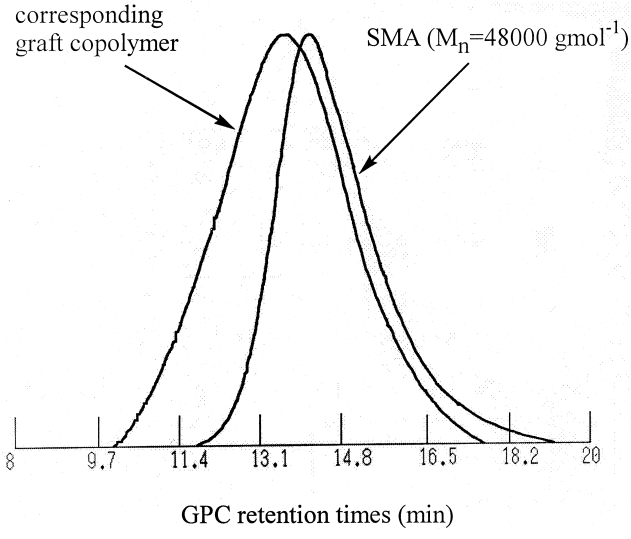

Fig. 7. GPC chromatograms of newly synthesized SMA copolymer (anhydride: styrene = 1:1, $M_n = 48,000$ g mol^{-1}) and the corresponding graft copolymer (grafted with MPEG-750).

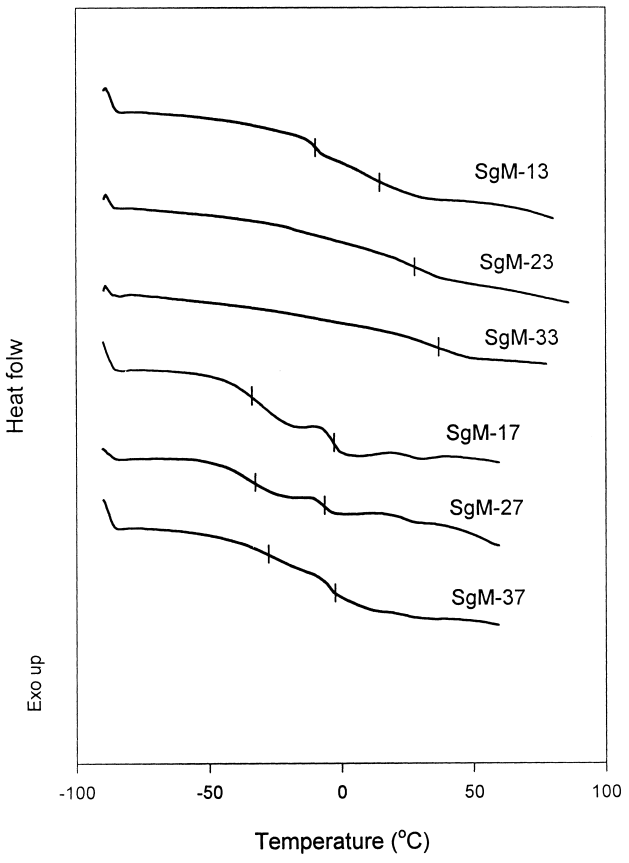

Fig. 8. GPC chromatograms of the SMA-*g*-MPEG copolymers.

Because the distance between two grafts in the graft copolymer is closer in S*g*M17 than in S*g*M27 or S*g*M37, the lower transition temperature is most obvious. However, it is difficult for the MPEG-750 grafts to aggregate together in S*g*M37 due to the long distance between two grafts; thus, the lower transition temperature is indistinct.

The similar DSC behavior is also observed for the MPEG-350 series. Comparing S*g*M17 with S*g*M13, it can be seen that the range of the lower transition temperature is narrower and smaller in S*g*M13, demonstrating the difficulty of the aggregation of MPEG-350 graft chains; furthermore, as the number of styrene spacing units increases, no lower transition was observed in SMA-23 and SMA-33. This implies that the MPEG-350 grafts in S*g*M23 and S*g*M33 graft copolymers cannot aggregate together due to the chain length of MPEG-350, which is shorter than that of MPEG-750.

4. Conclusions

New reaction conditions using PTSA as catalyst and toluene as solvent are proposed in this study to synthesize amphiphilic graft copolymers from a series of SMA (backbone copolymer) and MPEG (grafts). These reaction conditions overcome the problem of gelation in the syntheses of similar graft copolymers reported in the literature. The theoretical molecular weights of these synthetic graft copolymers can be determined by ^{1}H NMR and GPC analysis, and have an acceptable agreement to those obtained from the GPC analysis. The GPC behavior of these amphiphilic graft copolymers follows the rule of thumb in GPC analysis that higher molecular weights have lower retention volumes, but our results are different to the GPC behavior of other amphiphilic graft copolymers reported in the literature. This is because THF is a good solvent for both the SMA backbone and the MPEG branches, whereas substantially different solubilities for the branches and backbone was observed in the previous studies. Finally, from the DSC thermograms, these amphiphilic graft copolymers appear to form two phases due to the incompatibility of the hydrophobic backbones and the hydrophilic grafts.

Acknowledgements

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