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Dependence of the Interfacial Reaction and Morphology Development on the Functionality of the Reactive Precursors in Reactive Blending

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Summary: PMMA containing 50 wt% of anthracene-labeled PMMA chains end-capped by a phthalic anhydride group (anth-PMMA-anh) has been melt blended at 180°C with PS containing 33 wt% of chains end-capped by an aliphatic primary amine (PS-NH_2) and PS bearing 3.5 pendant amine groups (as an average) along the chains (PS-co-PSNH_2), respectively. The reactive chains have been synthesized by atom transfer radical polymerization. Conversion of anth-PMMA-anh into PS-b-PMMA and PS-g-PMMA copolymers has been monitored by SEC with a UV detector. The interfacial reaction mainly occurs in the initial melting and softening stage (<1.0 min.), although at a rate which strongly depends on the number of reactive groups attached to PS chains, the higher conversion being observed for the PS-co-PSNH_2 containing blends. The phase morphology depends on the architecture of the in-situ formed copolymer. Indeed, a coarser phase dispersion is observed in case of the graft copolymer compared to the diblock.

Keywords: anthracene labeling, polymer blend compatibilization, reactive blending

Introduction

Polymer blending is an efficient strategy to design new materials from commercially available polymers with an acceptable performances/cost balance.[1] Most polymers being immiscible, blends have to be compatibilized in order to decrease the interfacial tension, to restrict the phase coalescence and to improve the interfacial adhesion.[2-6] As a rule, compatibilizers are block or graft copolymers, which are either premade or formed in-situ in reactive blending. The molecular architecture of the preformed copolymers (block or graft copolymers) and, thus, the structure of the reactive chains used in reactive blending have an influence on the morphology development and the final physico-mechanical properties of the blends.[7] Fayt et al.[8-11] have

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compared the efficiency of premade copolymers in improving the ultimate mechanical properties of polyblends. They concluded that a block copolymer is more efficient than a graft copolymer and a tapered diblock is superior to a pure diblock. In reactive blending, the molecular architecture of the in-situ formed copolymer has also an influence on its residence time at the interface. Inoue et al.[12,13] compared the in-situ formation of linear block copolymer and graft copolymer of the same molecular weight. Although the block copolymer left easily the interface, the graft copolymer with the trunk in the dispersed phase was stable at the interface. Nevertheless, mechanical properties were higher for the linear copolymer containing blends.[14] Moon et al.[15] showed the incidence of the reactive precursors structure on the reaction kinetics. End-functional poly(methyl methacrylate) reacts more rapidly than chains to which the reactive group is attached at mid-length. Pagnoulle et al.[16] investigated the influence of the architecture of the graft copolymer formed by the interfacial reaction of mutually reactive PP and SAN chains on the interfacial adhesion. Highly multi-graft copolymer formed at the SAN/PP interface results in relatively lower interfacial toughness than single graft copolymer.

In this work, extent of the interfacial reaction and development of the phase morphology of polystyrene/poly(methyl methacrylate) (PS/PMMA) blends have been investigated in relation to the architecture of the in-situ formed copolymer. For this purpose, PMMA chains end-capped by phthalic anhydride have been reacted, at 180°C, with primary amine terminated PS and randomly functional PS (3.5 NH_2 per chain), respectively. The end-functional PMMA chains have been labeled by anthracene in order to monitor the reaction progress in a straightforward and reliable way. Conversion of PMMA-anh into PS-b-PMMA and PS-g-PMMA copolymers has been monitored by size exclusion chromatography (SEC) with a UV detector. The phase morphology of the blends has been analyzed by transmission electron microscopy (TEM).

Experimental Section

Polymer Synthesis and Characterization

Molecular characteristics of the polymers used in this study are listed in Table 1. Molecular weight and molecular weight distribution were analyzed by size exclusion chromatography (SEC) in THF at 40°C, using a Hewlett-Packard 1037A refractive index and a UV detector.

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PMMA and PS standards were used for calibration. The anthracene content of PMMA was determined by UV spectroscopy (Hitachi U-300).

Table 1. Characteristics of the polymers used in this study.

Polymers	Mn (g/mol)	Mw/Mn	Functionality (groups/chain)	Anthracene content (groups/chain)
PMMA	40000	1.2	-	-
PMMA	24000	1.1	-	-
anth-PMMA-anh	24000	1.2	0.84	2.0
PS-NH_2	27000	1.2	0.86	-
PS-co-PSNH_2	30000	1.25	3.5	-
PS	28000	1.2	-	-
PS	100000	1.2	-	-

Polystyrene end-capped by a primary amine (PS-NH_2) was prepared by atom transfer radical polymerization (ATRP) as detailed elsewhere.[17] The amine-functionality was estimated as the fraction of the PS chains that reacted in solution with PS end-capped by an isocyanate. This fraction was calculated from the SEC chromatograms before and after coupling, the elution peaks for the original and the coupled PS chains being completely separated one from each other.

Randomly functional polystyrene (PS-co-PSNH_2) was prepared by ATRP of a mixture of styrene and {1-methyl-1[3-(1-methylethylenyl)phenyl]ethyl}carbamic acid (TMITBC) without additional solvent. The carbamate groups were deprotected in a (2/1 v/v) dioxane-HCl (12M) mixture at room temperature. The reaction medium was then neutralized with ammonia and NaOH. The amine functionality was calculated from the content of TMITBC determined by FTIR as detailed elsewhere.[18]

Anthracene labeled poly(methyl methacrylate) end-capped by an anhydride (anth-PMMA-anh) was also synthesized by ATRP of a mixture of MMA and (9-anthracene)methyl 2-methyl-2-propenoate (anth-MMA, 2.6 wt%) in toluene at 85°C, using 2-hydroxyethyl 2'-methyl-2'-bromopropionate (HMB) as an initiator and CuBr/1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA) as catalyst. This sample was contaminated by a very low fraction of higher molecular weight chains, as shown by the SEC-UV trace (Figure 1).

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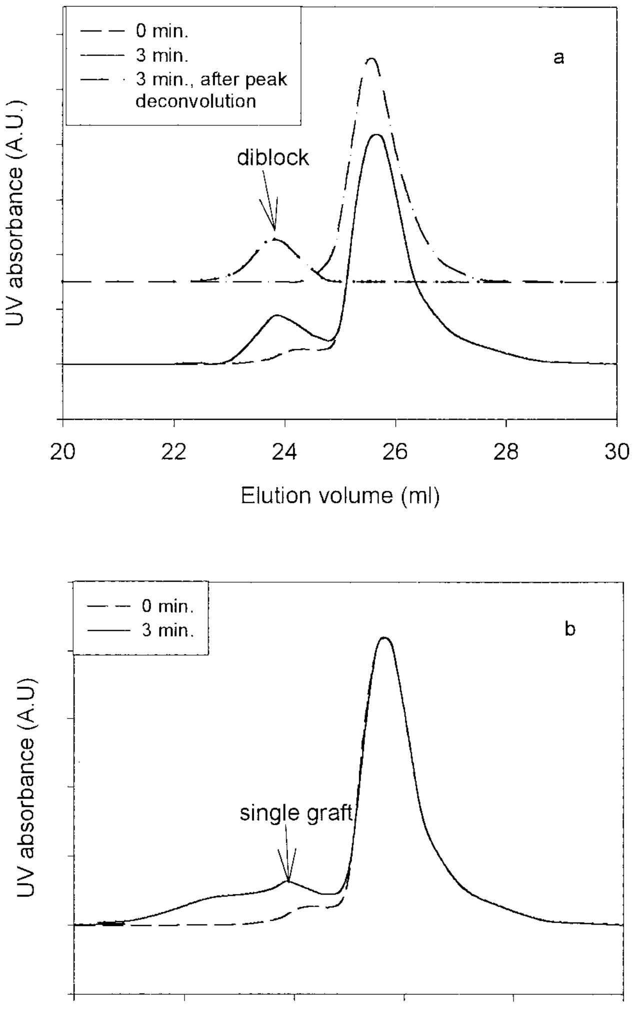

Fig. 1. SEC-UV (at 366 nm) traces for blends of anth-PMMA-anh with PS-NH_2 (a) and PS-co-PSNH_2 (b) after 3.0 min mixing.

The hydroxyl end-group of the PMMA chains was then reacted with trimellitic anhydride chloride in order to end-cap PMMA by an anhydride.[19] The anhydride content was estimated as the fraction of the anth-PMMA-anh chains that reacted with PS-NH_2 in solution. This fraction was extracted from the SEC-UV chromatograms (at 366nm, at which PS absorption is negligible) before and after coupling.

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Blend Preparation

Blends were prepared in a twin-screw mini-extruder designed by DSM-Research (The Netherlands) at 180°C under a nitrogen flow. The capacity of the mixing chamber was 5 cm^3, and the material was recirculated for the requested period of time. 4 g of blends (25 wt% PMMA and 75 wt% PS) was melt blended at 150 rpm. The PS phase consisted of 33 wt% of PS-NH_2 (Mn= 27000 g/mol) or PS-co-PSNH_2 (Mn = 30000 g/mol) in non-reactive PS (Mn=100000 g/mol), and 50 wt% of anth-PMMA-anh (Mn = 24000 g/mol) was mixed with non-reactive PMMA (Mn= 40000 g/mol) in the PMMA phase. In non-reactive blends used as a reference, the PS phase consisted of 33 wt% PS of Mn = 28000g/mol and 67 wt% PS of Mn = 100000 g/mol. 50 wt% PMMA of Mn = 24000 g/mol was mixed with chains of Mn= 40000 g/mol in the PMMA phase. After blending, the extruded polymer was quenched into water in order to freeze in the phase morphology.

After reaction, the reactive blend was dissolved in a THF solution of phenyl isocyanate in order to block any unreacted PS-NH_2 or PS-co-PSNH_2 chains that might continue to react with anth-PMMA-anh. This solution was analyzed by SEC with a UV detector at 366 nm. In PS-NH_2 containing blends, the SEC-UV traces were fitted by two Gaussian curves, whose the relative area was used to calculate the conversion of anth-PMMA-anh into diblock copolymer.[19] In PS-co-PSNH_2 containing blends, the amount of anth-PMMA-anh chains converted into graft copolymer was quantified by substracting the contribution of the (anth-PMMA-anh) recorded before reaction from the SEC-UV trace for the reactive blend. The error was estimated at less than 10% in the two cases.

Phase Morphology

A Reichert-Jung Ultracut FC4 microtome equipped with a diamond knife was used to prepare ultrathin samples (ca. 50 nm), that were stained by RuO_4 vapor for 30 min, before being observed with a Philips CM 100 transmission electron microcope (TEM). The dark phase was PS as result of a high affinity for RuO_4. Size and size distribution of the PMMA dispersed phases were quantitatively analyzed with a computerized image analyzer (KS 100 Kontron imaging system). A total of 200-300 dispersed domains were considered per sample. The cross-sectional surface area of these particles was converted to an equivalent diameter by eqn. 1.

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$$D_i = (4/\pi(\text{area}))^{0.5} \qquad (1)$$

$$D_V = \Sigma n_i D_i^3 / \Sigma n_i D_i^2 \qquad (2)$$

Results and Discussion

Figure 2 shows the dependence of the volume average diameter, D_v, on the mixing time for reactive and non-reactive blends. Within 1 min, the reactive blends yield a finer phase dispersion than the non-reactive one, which is evidence that a compatibilizer is formed at the interface, i.e. a diblock in case of the interfacial reaction of PS-NH_2 and a graft copolymer when PS-co-PSNH_2 is substituted for PS-NH_2.

The diblock appears to be superior to the graft copolymer in shifting the phase break-up/phase coalescence equilibrium in favor of a finer phase dispersion.

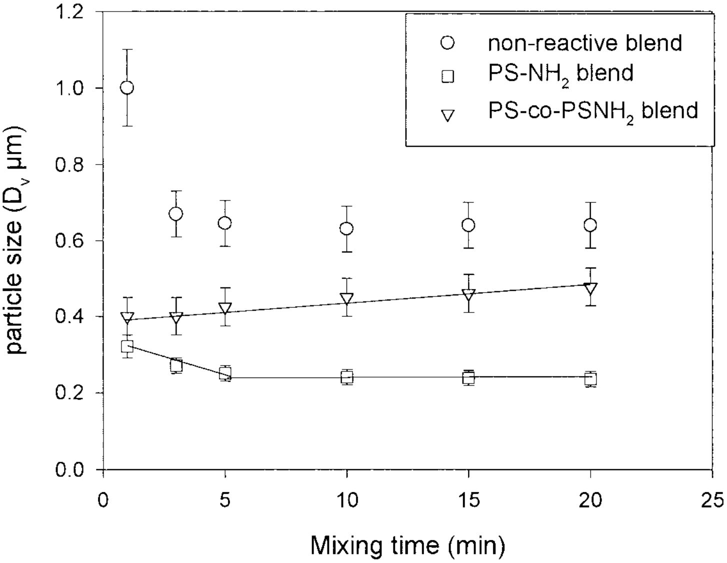

Fig. 2. Dependence of the volume average diameter, D_v, of PMMA/PS blends on the mixing time.

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D_v is systematically smaller when a diblock rather than a graft copolymer results from the interfacial reaction. Moreover, Dv decreases during the first 5 min mixing and then levels off in case of diblock, in contrast to a constant although slow increase when the compatibilizer is a graft copolymer. This observation is in agreement with Fayt et al.,[8-11] who concluded that diblock copolymers are more efficient than graft copolymers. D_v is at least 2.5 times smaller after 1 min mixing for the reactive blends compared to the non-reactive system. Moreover, D_v goes on decreasing with increasing mixing time (up to 5 min) in the absence of compatibilization, which is not observed when the interfacial reaction occurs (at least in the time scale of Figure 2).

In order to account for the differences observed when monofunctional (amino)PS rather than polyfunctional PS chains react with monofunctional (anhydride) PMMA, the copolymer formation at the interface has been monitored with the mixing time.

Figure 1 shows the SEC-UV traces for PS-NH_2 (Figure 1a) and PS-co-PSNH_2 (Figure 1b) containing blends, respectively, after 3.0 min mixing. The signature of the diblock or graft copolymer is an elution peak for the converted anth-PMMA-anh chains observed at a lower elution volume than the original one. This additional elution peak is symmetric (at least after deconvolution) consistent with formation of a well-defined diblock in case of the PS-NH_2 containing blend. In contrast, a mixture of multi- and single-graft copolymers is formed in the PS-co-PSNH_2 containing blend. Conversion of anth-PMMA-anh into diblock copolymer was calculated from the area of the two deconvoluted peaks (Figure 1a).

A small amount (3.25%) of coupled anth-PMMA-anh chains at time zero was substracted from the SEC-UV traces of reactive blends. Conversion of anth-PMMA-anh into graft copolymer was estimated by substracting the anth-PMMA-anh SEC-UV peak before reaction from the trace recorded after 3 min mixing. It must be noted that PS-co-PSNH_2 (Mn : 35000 and 4.2 amines per chain) was previously reacted with PMMA-anh (Mn : 35000 and 0.85 anhydride per chain) at 170°C for 10 min (between the parallel plates of a rheometer) and that no significant formation of multigraft copolymer was observed by SEC-UV analysis.[18] Not only the mixing conditions were different, but all the chains were reactive which is not the case in this work. This difference is thought to originate from the interfacial surface area occupied by the copolymer at the interface, which is as small as the copolymer concentration is high.[18] In parallel, the probability that a second amine of the PS-co-PSNH_2 backbone of a single graft

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copolymer reacts, decreases with the surface area occupied at the interface. In this work, the reactive chains are diluted by non-reactive ones and the PS-co-PSNH$_2$ chains can adopt a flat conformation at the interface which is favorable to reaction of more than one amine per chain, consistent with the content of multi-graft copolymer which increases with the mixing time. Figure 3 illustrates the time dependence of the conversion of anth-PMMA-anh into diblock and graft copolymers, respectively.

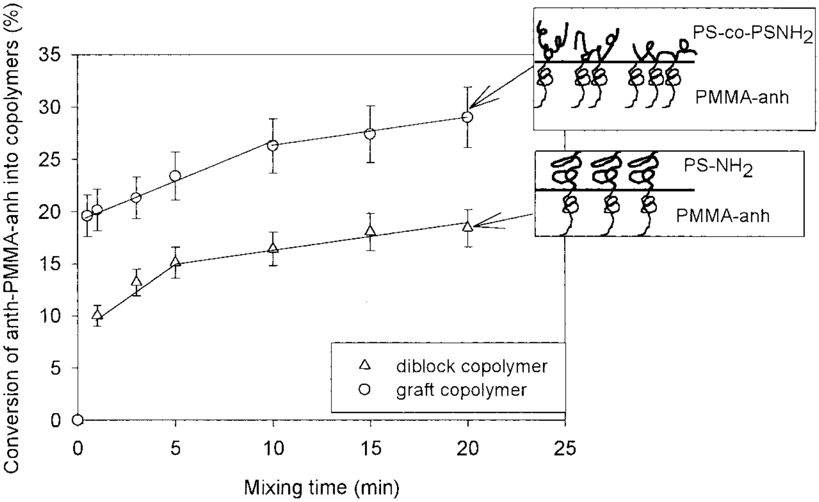

Fig. 3. Conversion of anth-PMMA-anh into diblock and graft copolymers in PS-NH$_2$ and PS-co-PSNH$_2$ containing blends, respectively.

Whatever the amine functionality of PS, the interfacial reaction mainly occurs extensively within a very short mixing time, consistent with the sharp breakdown in the progress of the morphology development (Figure 2) and with observation reported elsewhere.[20]

Figures 2 and 3 show an interesting parallelism in the time dependence of the diblock formation and the PMMA particle size in the PS-NH$_2$ containing blends. Indeed, after 1 min mixing the phase morphology is close to the stationary characteristic features observed after

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5 min. Similarly, ca. half the PMMA chains converted at the stationary state, have reacted after 1 min, and the progress of the interfacial reaction is no longer substantial after 5 min.

The interfacial coverage by the diblock copolymer at the PMMA/PS interface has been estimated from eqn. 3, on the assumption that all the copolymer chains remain at the interface. This equation relies on two experimentally determined parameters; i.e., C_{cop} : the conversion of anth-PMMA-anh into diblock copolymer and the volume average particle diameter (Dv)

$$\Sigma = (\phi_w C_{cop} N_{av} \rho_{PMMA} D_v)/6Mn \qquad (3)$$

ϕ_w is the weight fraction of anth-PMMA-anh in the PMMA phase (0.5), N_{av} is the Aveogadro's number, ρ_{PMMA} is the PMMA density (1.15g/cm^3), Mn is the number average molecular weight of the anth-PMMA-anh chains. The maximum coverage of the interface (Σ_0) has also been extracted from the lamellar spacing of a symmetric PMMA-b-PS diblock copolymer.[21] Σ_0 = 0.158 chains/nm$_2$ for PMMA-b-PS copolymer of Mn = 51000g/mol. Figure 4 shows the interfacial coverage Σ (chains/nm^2) by the diblock copolymer in-situ formed in the PS-NH_2 containing blends.

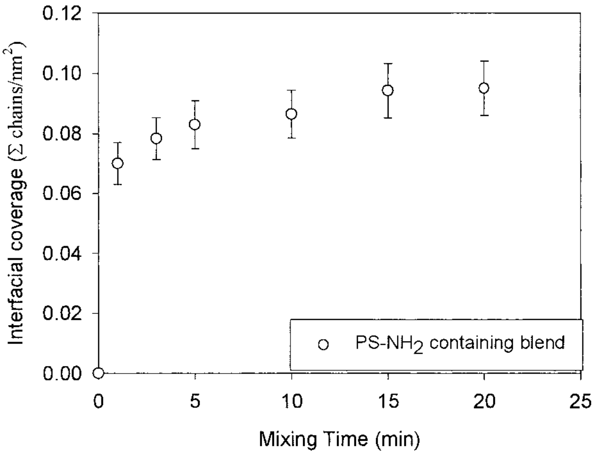

Fig. 4. Interfacial coverage Σ (chains/nm^2) by the diblock copolymer at the PMMA/PS interface in PS-NH_2 containing blend.

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After 1.0 min mixing, Σ/Σ_0 is ca. 44%, and it increases up to 52% after 5 min, which is a coverage dense enough to stabilize the phase morphology, thus to decrease the interfacial tension and to protect the dispersed phases against coalescence. Because, at constant interfacial surface area (after 5 min mixing), the copolymer formation is dramatically slown down, it must be concluded that the residence time of the symmetric diblock copolymer of Mn = 51,000 is high which prevents not yet reacted amine and anhydride groups from colliding effectively at the interface and the interfacial reaction from progressing. The same situation has been previously reported in case of formation of symmetric diblock of high molecular weight (ca. 55000) at a flat interface.[22]

When PS-co-PSNH$_2$ is substituted for PS-NH$_2$, there is no more similarity in the way the phase morphology and the copolymer formation change with time (figs. 2 and 3). After 1 min mixing, the diameter of the PMMA phases increases continuously although very slowly, which indicates that the interfacial surface area tends to decrease consistent with a stabilization problem in line with D_v ca. 2 times larger than in the PS-NH$_2$ containing blends. Although not shown, the distribution of the PMMA domains is bimodal, which is indicative of phase coalescence. This observation may be surprizing because ca. 2 times more PMMA chains are converted into graft copolymer compared to the formation of diblock (Figure 3). Two pieces of information can be deduced. First, the multifunctionality of PS-co-PSNH$_2$ is favorable to the progress of the interfacial reaction. The 3.7 times higher concentration of amine in the PS phase when PS-co-PSNH$_2$ is used rather that PS-NH$_2$ is a reason for the progress of the interfacial reaction to be 2 times more important after 1 min. Moreover, when a single graft copolymer is at the interface, other amines of the same PS backbone are in a favorable position for reacting with PMMA-anh, at least as long as this backbone is lying flat on the interface. This conformation is reasonable when only part of the chains are reactive at least until the coverage density is not too high, thus apparently until 10 min mixing. This is consistent with a population of multigraft copolymer which coexists with the single graft copolymer and increases proportionally with the mixing time in the first 10 min. This issue cannot be discussed further, because the interfacial coverage by a mixture of single and multi-graft copolymers cannot be estimated properly. Secondly, the non complete stabilization of the interface in spite of a more extended interfacial reaction suggests that the graft copolymer is less efficient than the diblock and/or that part of it leaves the interface. In this respect,

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multigraft copolymer chains contain more PMMA than PS, as schematized in the insert of Figure 3, which may trigger diffusion away from the interface to the PMMA phase. When PS-NH_2 reacts with PMMA-anh, a symmetric diblock copolymer is formed at the interface, with individual blocks longer than the critical molecular weight for entanglement (Me = 13000 for PS[23] and 10000 for PMMA). This diblock resides at the interface for a long time and protects the PMMA domains against coalescence. When the interfacial formation of a graft copolymer is envisioned, the multifunctionality of the reactive PS chains diluted by unreactive PS leads to multigraft copolymer chains as extensively (compared to the single graft) as the mixing time is long, eventhough the amine groups are in molar excess with respect to the PMMA anhydride end-groups. The PS backbone of these chains cannot penetrate deeply the PS matrix, which explains that they are poorly efficient in preventing the PMMA domains from coalescing. The asymmetric composition of the multigraft copolymer is also an incentive for it to leave the interface.

Conclusion

Anthracene labeled PMMA chains end-capped by phthalic anhydride (anth-PMMA-anh) have been melt blended with PS-NH_2 and PS-co-PSNH_2 , respectively, in a mini-extruder. Only part of the chains in each phase is reactive. Progress of the PMMA-anh/PS-NH_2 and PMMA-anh/PS-co-PSNH_2 interfacial reaction has been monitored by SEC with a UV detector. Conversion of anth-PMMA-anh into diblock and graft copolymers has been determined from the relative area of the elution peaks for the unreacted PMMA and PMMA which is part of the copolymer. The interfacial reaction extensively occurs in the very first step of softening and melting of each constitutive component (<1.0 min.). Because of a higher content of amine and the polyfunctionality of the chains, PS-co-PSNH_2 reacts more rapidly with PMMA-anh than PS-NH_2. As a rule, after the initial step of mixing, the interfacial reaction is rapidly slown down.

In case of the diblock copolymer, as soon as the phase morphology remains constant (after 5 min), the progress of the interfacial reaction tends to level off. Thus, the copolymer stabilizes the interface, which remains occupied by the diblock chains and which is hardly accessible by the reactive chains. A coarser morphology is formed in the graft copolymer containing blends, although more PMMA chains are converted into graft than into diblock. Because a single-graft

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copolymer is not selectively formed, the coalescence barrier around the PMMA particles is less efficient and the residence time of the asymmetric copolymer chains at the interface may be shortened.

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