Macromolecules **2006,** *39,* 6905−6912

Graft Copolymers of Poly(methyl methacrylate) and Polyamide-6: Synthesis by Reactive Blending and Characterization

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Received January 6, 2006; Revised Manuscript Received July 10, 2006

ABSTRACT: Reactive blending is used as a tool for the synthesis of graft copolymers of poly(methyl methacrylate) and polyamide-6 (PMMA-*g*-PA). The grafting reaction occurs between the amino end group of PA and glutaric anhydride units randomly distributed along the PMMA backbone. The anhydride units are formed by thermal treatment (typically above 180 °C) of a precursor PMMA bearing a low fraction of methacrylic acid units (5 or 10 mol %). With this method, it is possible to control the amount of anhydride units without degradation or cross-linking of the PMMA chains. The resulting blends with PA are characterized by size exclusion chromatography in benzyl alcohol at 130 °C and selective extraction of ungrafted PMMA chains. Combining these techniques, we were able to estimate the fraction and the average composition of the graft copolymers synthesized in situ during the blending process. High fractions of graft copolymer (35−75 wt %) are obtained in all the blends studied in this work. A higher amount of graft copolymer is obtained by increasing the amount of PA in the blend or the anhydride content on a functionalized PMMA. Optimum grafting is also influenced by the remaining acid groups on the PMMA chain. These groups are expected to contribute to the reversible interactions (hydrogen bonding) between PMMA and PA at the interface.

Introduction

Polymer blends can be compatibilized either by addition or in-situ formation of copolymers with various architectures.[1] The latter occurs when the polymers bear mutually reactive groups (reactive blending). In-situ graft copolymer formation depends not only on the kinetics of the reaction between functional groups[2] but also on polymer lengths, incompatibility between polymers, and the number and position of reactive groups.[1,3−9] Furthermore, the interface, between the components, has to remain accessible to ungrafted chains for further grafting. Copolymers can leave the interface spontaneously providing that they are short enough and diffusion of the graft copolymer far from the interface is possible.[4,10−13] As a consequence, grafting yields can range from a few percent to almost complete reaction.[4,8,10,14,15] From this point of view reactive blending can be used as a technique for the synthesis of graft copolymers and nanostructured polymer materials with novel properties and high potential in applications.[4,8,10,14] Some of these copolymers cannot be obtained by other conventional techniques.[8]

In this work, we study the synthesis of graft copolymers of poly(methyl methacrylate) and polyamide-6 by reactive blending. We focus on the design of the PMMA/PA system to achieve high yields of graft copolymer during blending. The complete characterization of the ternary blends and the graft copolymers is thus a prerequisite for this study.

Functionalized PMMA can be obtained by copolymerization of methyl methacrylate (MMA) and methacrylic acid (MAA) monomers (P(MMA-*co*-MAA) copolymers). Acid groups do not react fast enough with the amino end groups of polyamide to obtain high grafting yields within blending time.[2] However, upon heating, typically above 180 °C, methacrylic acid units can react with their neighbors, either acid or ester, to form intramolecular six-membered glutaric anhydride groups (Figure 1).[16−19] These anhydride groups present significant interest as they are much more reactive than carboxylic acid groups toward amino groups.[2,20] As a result, functionalized PMMA can be used for reactive blending with polyamide to yield multigraft copolymers.

The full characterization of reactively compatibilized polymer blends remains a challenge. Fractions of grafted species are usually deduced by mass balance after selective extraction of ungrafted chains of each component.[8,21] This method also allows recovery of pure graft copolymer for further analysis when selective solvents are available. For instance, blends of polyethylene and polyamide were completely characterized using chloroform and formic acid as selective solvents.[8,22] To our knowledge, there are selective solvents to recover PMMA, but not PA chains, from PMMA/PA mixtures. Size exclusion chromatography (SEC) is an alternative to characterize grafting reactions in polymer blends.[4,8,10,11,14,23,24] SEC can give access to grafting yields and/or molecular weight evolution (grafted species or precursor polymers). SEC is a relevant technique as far as there is enough resolution between the average molecular weight of the components and no additional grafting occurs during the analysis. For instance, when blends of aminated and maleated polymers were characterized by SEC, phenyl isocyanate has to be added prior to the analysis to quench remaining amino groups and avoid additional grafting during the analysis.[14] For some mixtures, SEC detectors can be highly sensitive to one component. As a consequence, low amounts of grafted species can be detected. High detector response can also be achieved with fluorescent labeled polymers and use of a fluorescence detector.[11]

In the first part of this work, we report on the formation of anhydride groups on P(MMA-*co*-MAA) copolymers using thermal treatments. The functionalized PMMA, as modified, are then blended with PA chains of relatively low molecular weight to obtain blends with a high fraction of graft copolymer (PMMA-*g*-PA). In the second part, we use a combination of

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10.1021/ma060036x CCC: $33.50

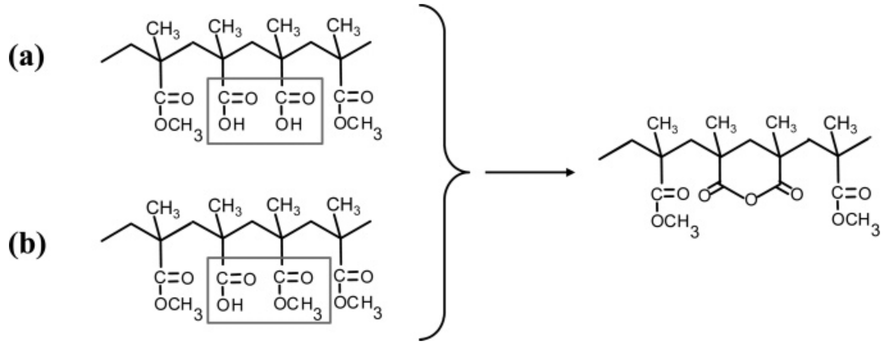

Figure 1. Formation of a glutaric anhydride group from two neighboring acid functions (a) or from one acid and one ester group (b).

Table 1. Characteristics of P(MMA-*co*-MAA)

polymer	M_n (g/mol)[a]	PDI[a]	mol % acid[b]	mol % anhydride[b]	T_g[c] (°C)	% racemic dyad[d]
PMMA0	24 000	2.1	0	0	115	71
PMMA5	48 000	2.1	4.5	0.3	121	78
PMMA10	35 000	2.0	9.5	0.1	137	77

[a] Measured by SEC in THF (universal calibration), PDI = polydispersity index. [b] Obtained by FTIR in chloroform. [c] Measured by DSC (5°C/min). [d] Measured by ^{13}C NMR in $CDCl_3$.

SEC and selective extraction to fully characterize the blends and estimate the composition of the graft copolymers formed in situ. The amount of ungrafted PMMA is deduced from the selective extraction in chloroform, while SEC in benzyl alcohol is used to evaluate the amount of ungrafted PA. The effect of PMMA functionality (anhydride and acid content), blend composition, and annealing above the melting point of PA on the grafting reaction is studied and discussed. The role of specific attractive interactions between PMMA and PA on the grafting efficiency is also discussed.

Experimental Section

Materials. P(MMA-*co*-MAA) copolymers, designated by PMMA*x* where *x* stands for the fraction of MAA, and a PMMA homopolymer ($x = 0$), were provided for this study by ARKEMA. Characteristics of these polymers are listed in Table 1. A monoaminated polyamide-6 ($M_n = 2500$ g/mol), designated by PA, was also provided by ARKEMA.

P(MMA-*co*-MAA) Thermal Treatment. To promote the formation of anhydride groups, P(MMA-*co*-MMA) copolymers were either extruded or heated. Extrusions were performed either with a COPERION WERNER and PFLEIDERER ZSK30 twin-screw extruder at 300 °C under vacuum with a residence time of 1.5 min (total treatment time depends on the number of runs in the extruder) or with a DACA microextruder for 10 min at 225 °C under a N_2 atmosphere. The DACA microextruder (DACA instrument) is a 3 g capacity corotating twin-screw extruder; a feedback channel permits cyclic extrusion of the melt and is used to fix blending time. Isothermal treatments were performed in an oven at 180 or 235 °C for 0.5−48 h under reduced pressure (10^{-2} mmHg). The resulting copolymers are designated hereafter by PMMA*x*-Ah*y*, where *x* stands for the molar fraction of MAA monomers on the starting material and *y* for the mol % of anhydride units at the end of the thermal treatment.

Reactive Blending. Functionalized copolymers were blended with 20 or 30 wt % of PA using the DACA microextruder. The two polymers were dried at 80 °C under reduced pressure overnight prior to blending. They were introduced simultaneously at 225 °C and blended at 60 rpm under a N_2 atmosphere for 10 min. Under such blending conditions, the remaining acid groups could react directly with amino groups. However, this reaction is very slow compared to the reaction between anhydride and amino groups.[2] Grafting via amide bonds will thus be neglected with respect to grafting via imide bonds.

Characterization of PMMA*x*-Ah*y* Copolymers. Anhydride and carboxylic acid contents on PMMA*x*-Ah*y* copolymers were determined by Fourier transform infrared (FTIR) spectroscopy in chloroform (15 mg/mL) using a Bruker spectrometer equipped with a KBr cell of 135 μm thickness (32 scans, resolution 2 cm^{-1}). The mol % contents were estimated using calibration curves established with copolymers of known compositions. The confidence interval was estimated at 0.1 mol % for anhydride and 0.8 mol % for acid groups.

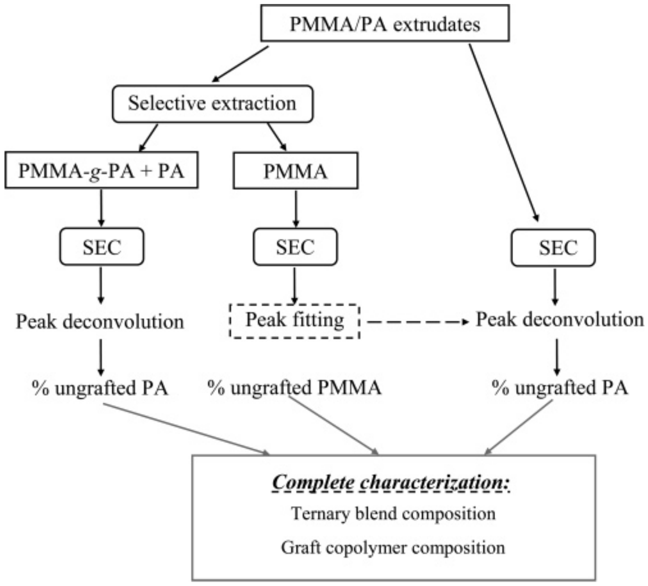

Figure 2. Characterization method of extruded blends and graft copolymers by SEC in benzyl alcohol and selective extraction in chloroform.

Average molecular weights and polydispersity indices (PDI) of functionalized PMMA were determined by size exclusion chromatography (SEC) in THF at 40 °C using universal calibration. Copolymers with a high fraction of acid groups (i.e., PMMA10 and PMMA10-Ah*y* with low anhydride content) had to be dried several days under vacuum at 80 °C to be soluble in THF.

Characterization of Blends and Graft Copolymers. Blends were characterized by a combination of selective extraction of ungrafted functionalized PMMA and size exclusion chromatography (SEC) in benzyl alcohol as presented schematically in Figure 2.

Ungrafted PMMA chains were removed by Soxhlet extraction into chloroform for 48 h on ca. 5 g of samples and repeated three times for some blends. The confidence interval for the evaluation of the amount of ungrafted PMMA was evaluated at ±5%. The

Table 2. Characteristics of Copolymers Obtained by Thermal Treatments of PMMA10

	isothermal treatment							
expt	type	*T* (°C)	duration	mol % anhydride[a]	mol % acid[a]	M_n[b] (g/mol)	PDI[b]	abbreviation
				0.1	9.5	35 000	2.0	PMMA10
1	oven	180	24 h	1.7	8.1	32 000	2.2	
2	oven	235	24 h	8.0	1.6	33 000	2.3	
3	oven	235	48 h	8.3	0.9	32 000	2.3	PMMA10-Ah8.3
4	extruded	300	1.5 min	2.5	6.0	32 000	2.2	PMMA10-Ah2.5
5	extruded	300	3 min	3.4	5.0	32 000	2.3	PMMA10-Ah3.4
6	extruded	300	4.5 min	4.5	4.2	33 000	2.3	PMMA10-Ah4.5
7	extruded	220	10 min	1.1	9.0	33 000	2.2	

[a] Obtained by FTIR in chloroform. [b] Measured by SEC in THF (universal calibration), PDI = polydispersity index.

fraction of grafted PMMA was then deduced from the mass of polymer extracted. FTIR analysis of extracted PMMA revealed the presence of some amide groups (peak at 1660 cm^{-1}) attributed to short PA oligomers, monomer, or other low molecular weight impurities. Such a peak did not appear when PA was purified prior to blending (see Supporting Information).

SEC experiments were performed on a GPCV2000 Waters apparatus using four Styragel columns (HT2, HT3, HT4, and HT5) and a refractive index detector (flow rate 1 mL/min). Samples were dissolved in benzyl alcohol at 130 °C for 2 h prior to the analysis (4 mg/mL). The overall signal was multiplied by −1 for convenience; polyamide-6 has therefore a positive signal, and most signals of functionalized PMMA are negative in the figures that follow. The intensity of the refractometer signal is given by $Ri = K(\mathrm{d}n/\mathrm{d}C)Ci$, where K depends on the apparatus and dn/dC is the variation of refractive index with the polymer concentration. The refractometer sensitivity to a polymer (arbitrary units), designated hereafter by A_C ($A_C = Ri/Ci = K(\mathrm{d}n/\mathrm{d}C)$), corresponds to the area of the signal normalized by the concentration. SEC traces were decomposed into Gaussian distributions, corresponding to the components of the blends (free PA, free functionalized PMMA, and PMMA-*g*-PA graft copolymer), defined by

$$G(Ve) = \alpha \exp\left(-\frac{(Ve - Ve_C)^2}{2\sigma^2}\right) \qquad (1)$$

where α is the amplitude, Ve the elution volume, Ve_C the elution volume corresponding to the maximum of the distribution, and σ the standard deviation. Note that a log−normal distribution was used for some functionalized PMMA. Free parameters were adjusted to optimize the deconvolution (using the least-squares method). When possible, Gaussian parameters of ungrafted PMMA determined experimentally were used (Figure 2). The deconvolution gives information on the amount of ungrafted PA, from which we estimate the fraction of grafted PA. The confidence interval ranges from ±5−15% depending on the functionalized PMMA used (the higher the absolute value of A_C is, the higher the confidence interval). The ternary blend composition (wt %) and average graft copolymer composition (wt %, confidence interval ±5−7%) are estimated from these results. The average molecular weights of graft copolymers were not estimated since a small variation in the position of the graft copolymers signal (as estimated by the decomposition) leads to a substantial variation of the estimated molar mass.

Results

Anhydride Formation during Thermal Treatment. P(MMA-*co*-MAA) copolymers were heated to temperatures ranging from 180 to 300 °C under reduced pressure or under a nitrogen atmosphere to promote anhydride group formation. SEC analysis after thermal treatment does not reveal any significant chain degradation or cross-linking. As an example, the average molecular weights and polydispersity indices of PMMA10-Ah*y* copolymers are listed in Table 2. Samples after isothermal treatment exhibit twin peaks in FTIR at 1805 and 1760 cm^{-1}, characteristic of glutaric anhydride[17] (Figure 1, for spectra see Supporting Information.).

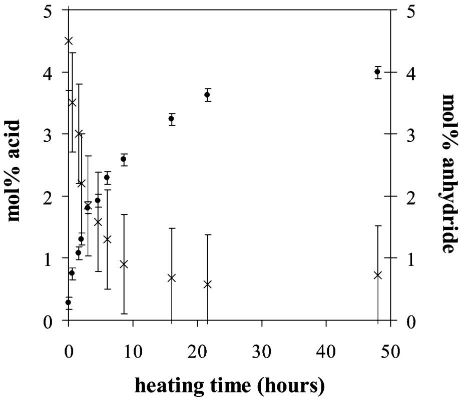

Figure 3. Formation of anhydride (●) and consumption of acid (×) groups on PMMA5 with heating time (235 °C under vacuum).

Monitoring of anhydride and acid groups content on PMMA5 as a function of time (heating at 235 °C under reduced pressure) is displayed in Figure 3. It reveals that the reaction is fast at the beginning of the process and progressively slows down as acid groups are consumed. On the other hand, acid condensation is strongly temperature dependent. Heating PMMA10 for 24 h at 180 °C produces 1.7 mol % of anhydride groups (Table 2, experiment 1) while the same treatment at 235 °C results in the formation of 8 mol % of anhydride groups (Table 2, experiment 2). At even higher temperature, namely 300 °C, a few minutes is enough to yield several mol % of anhydride groups on PMMA10 (Table 2, experiments 4−6).

Long heating times at 235 °C (Table 2, experiment 3 and Figure 3) lead to almost complete acid condensation: 4 and 8.3 mol % of anhydride units are obtained on PMMA5 and PMMA10, respectively.[25] The maximum anhydride group content depends on the distribution of acid groups (i.e., methacrylic acid monomers) on the P(MMA-*co*-MAA) backbone.[26] The number of acid/acid dyads corresponds to the maximum number of anhydride units obtained by acid/acid condensation (Figure 1a). Remaining acid groups can only react with ester groups via methanol formation (Figure 1b). To investigate the contribution of acid/acid and acid/ester condensation, the dyad composition of P(MMA-*co*-MAA) copolymers was estimated using a first-order Markov law[27] and reactivity ratios of 0.95 and 0.6 for MAA and MMA monomers, respectively (for details see the Supporting Information). These are average values from data reported in the literature for radical copolymerization of MAA and MMA monomers.[28−31] The average mol % of adjacent acid groups was estimated at 0.4 mol % for PMMA5 and 1.7 mol % for PMMA10. Consumption of acid units as a function of anhydride formation is then estimated assuming that neighboring acid functions will first

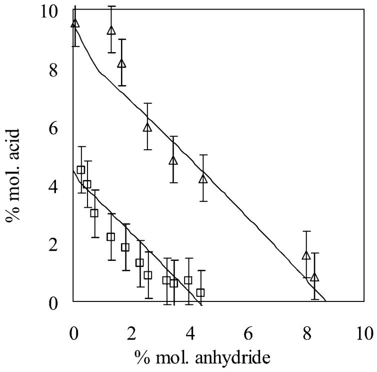

Figure 4. Evolution of the acid group content of PMMA10 (△) and PMMA5 (□) copolymers as a function of the anhydride group content resulting from thermal treatments. Symbols correspond to experimental data and lines to the estimated values for statistical copolymers assuming first acid/acid and then acid/ester condensation (microstructure based on the first-order Markov law).

Table 3. Characteristics of Functionalized PMMA Used in Reactive Blending

polymer	mol % anhydride[a]	mol % acid[a]	A_C[b]
PMMA5	0.5	4.0	−2.7
PMMA5-Ah4	4.0	0.8	−1.7
PMMA10	1.1	8.5	−0.9
PMMA10-Ah2.5	2.9	5.5	−1.3
PMMA10-Ah3.4	3.8	4.7	−1
PMMA10-Ah4.5	4.6	4.1	−1.1
PMMA10-Ah8.3	8.3	0.9	1.1

[a] Determined by FTIR in chloroform; these values take into account the additional anhydride group formation occurring within blending time with PA. [b] Determined by SEC in benzyl alcohol at 130°C (see Experimental Section).

condense (Figure 1a) and that further condensation will proceed by acid/ester reaction (Figure 1b).[18] The result of this estimation is shown in Figure 4 as continuous lines. There is a satisfactory agreement with the experimental data. The maximum anhydride content of PMMA5 and PMMA10 was estimated at 4.3 and 8.7 mol %, respectively.

We have seen so far that functionalized PMMA with a controlled amount of anhydride units can be obtained by thermal treatment. When these polymers are blended with PA (10 min at 225 °C), some extra anhydride formation can occur. To estimate this additional anhydride group formation, the various PMMA*x*-Ah*y* copolymers were thermally treated under the same conditions in the absence of PA. For instance, PMMA5 and PMMA10 end with 0.5 and 1.1 mol % of anhydride groups, instead of 0.3 and 0.1 mol % before treatment, respectively. Although this additional anhydride group formation is limited for other PMMA*x*-Ah*y* copolymers ($\leq$0.4 mol % for PMMA10-Ah*y*), it is taken into account in the data listed in Table 3 and in the following discussion.

Characterization of the Materials Obtained by Reactive Blending. The functionalized PMMAs used for blending with PA are listed in Table 3. Figure 5 displays SEC traces of neat PA (normalized to 30% of its intensity) and a neat functionalized PMMA (normalized to 70% of its intensity). The refractomer is clearly much more sensitive to PA than to PMMA as confirmed by the A_C values (see Table 3 for functionalized PMMA, $A_C = -3$ for PMMA0 and $A_C = 6.8$ for PA). This feature will be very useful as both signals tend to overlap, and PA is the minor component of the blends (20−30 wt %). The amplitude of the signal from functionalized PMMA varies with respect to acid or anhydride group content, especially in the range of 5−10 mol % (Table 3).

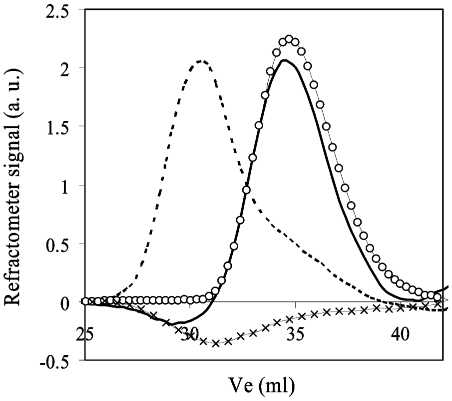

Figure 5. Experimental SEC traces of PA normalized to 30% (○), of a functionalized PMMA normalized to 70% (×), and of the resulting 70/30 blend at the end of the blending process (dashed line). Full line corresponds to the SEC trace of a 70/30 mixture of the same polymers prepared directly in benzyl alcohol 2 h prior to the analysis.

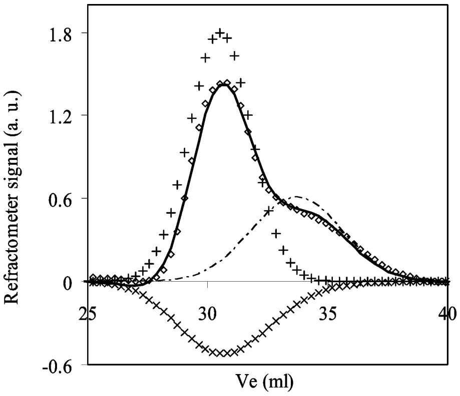

Figure 6. Experimental SEC traces of the 70/30 PMMA10-Ah4.5/PA blend (◊) and its decomposition in ungrafted PMMA10-Ah4.5 (×), ungrafted PA (dotted line), and PMMA10-Ah4.5-*g*-PA copolymer (+) signals. The full line corresponds to the sum of these three distributions.

The SEC trace of a 70/30 functionalized PMMA/PA blend at the end of the blending process is also displayed in Figure 5. Upon blending, the signal from free PA chains significantly decreases and an intense positive signal appears at lower elution volume, overlapping with the weak negative signal from remaining ungrafted PMMA chains. This signal corresponds to the graft copolymer and appears positive due to the contribution of PA grafts. A 70/30 mixture of the same polymers was prepared directly in benzyl alcohol prior to the analysis. The corresponding SEC trace, displayed in Figure 5, is similar to the sum of the traces of neat PA and functionalized PMMA. This result reveals that no significant grafting occurs during the analysis.[32] SEC in benzyl alcohol is therefore a relevant technique to estimate the amount of grafted PA. Figure 6 provides the Gaussian deconvolution of the SEC trace of the 70/30 PMMA10-Ah4.5/PA blend as an example. Figure 2 summarizes the method used for the analysis of the blends. The use of this method reveals some characteristic trends. The positions of free PA distributions seem to shift to lower elution volume as compared to neat PA (Figure 7). This suggests that PA chains of lower average molecular weight graft first. For similar systems Legras and co-workers[9,33,34] reported a decrease in the molecular weight of PA due to hydrolysis. Our data do not indicate such an effect probably because of the lower molecular weight of our PA (2500 g/mol) and the less severe blending conditions (lower temperature, shorter time).

Ungrafted PMMA chains, recovered by selective extraction, were also characterized by SEC in benzyl alcohol. Figure 8

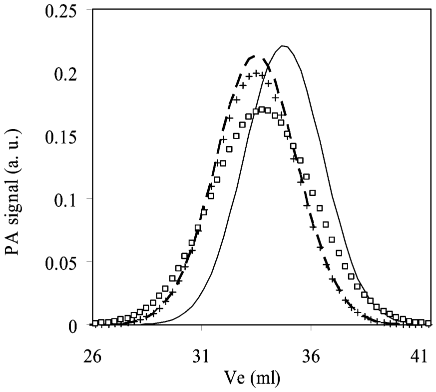

Figure 7. Normalized PA deconvoluted peak in 80/20 blends (after extraction of ungrafted PMMA chains) containing PMMA10-Ah3.5 (+), PMMA10-Ah4.5 (□), and PMMA10-Ah8.3 (dashed line) as compared to the Gaussian distribution of neat PA (full line).

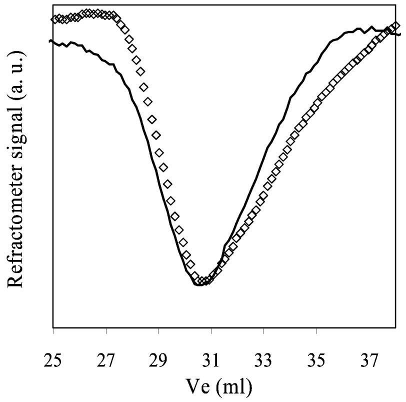

Figure 8. SEC traces of neat PMMA10-Ah4.5 (full line) and PMMA10-Ah4.5 extracted from the 80/20 (◊) blend with PA.

displays, for instance, SEC traces of neat and recovered PMMA10-Ah4.5 from an 80/20 blend. Only a slight change in the position of the signal was observed as compared to corresponding neat functionalized PMMA. It is difficult to conclude whether this change indicates a size selectivity of PMMA chains or whether it is due to other factors, for instance grafting of few very short PA oligomers or low molecular weight impurities (see Experimental Section).

Parameters Controlling Grafting: PMMA Functionality and Blend Composition. Table 4 summarizes the ternary blend and graft copolymer compositions in all investigated blends. To investigate the effect of PMMA functionality on the grafting reaction, we focus on blends containing 20 wt % of PA. Fractions of grafted PMMA and PA as a function of the effective anhydride content on PMMA10-Ah*y* are displayed in Figure 9a. Grafting yield is substantial even for the lowest anhydride content and increases with increasing this content. For instance, 55 ± 5% of PMMA chains and 58 ± 10% of PA chains get grafted in the blend based on PMMA10-Ah8.3. On the other hand, although PA is the limiting reagent (except for PMMA5/PA and PMMA10/PA blends), no complete grafting of PA is observed (Table 4).

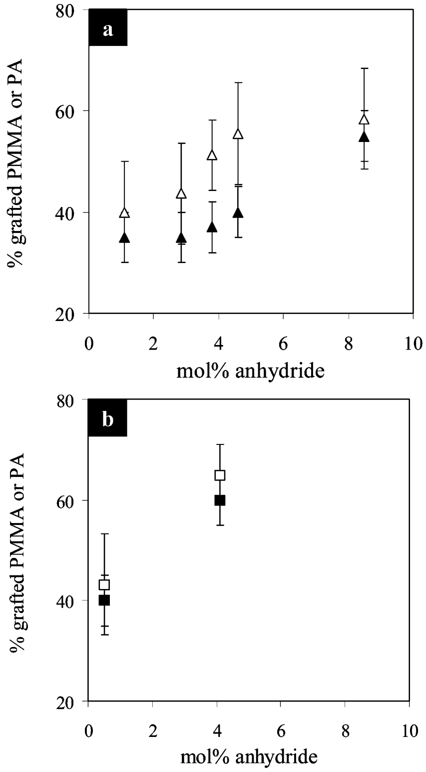

Figure 9. Fractions of grafted PMMA (full symbols) and grafted PA (open symbols) in 80/20 PMMA/PA blends as a function of the amount of anhydride groups on PMMA10 (a) and PMMA5 (b). The mol % of anhydride groups takes into account additional anhydride units formed under blending conditions.

The fractions of grafted PMMA and PA as a function of anhydride content on PMMA5-Ah*y* are displayed in Figure 9b. Although data for only two blends are available, the trends are the same as those observed for PMMA10-Ah*y* copolymers: fractions of grafted species increase with the functionality of PMMA5 chains. Similar evolution was observed for blends containing 30 wt % of PA (data not shown).

Finally, the effect of blend composition on PMMA and PA grafting yields was investigated by comparing the 80/20 and 70/30 PMMA10-Ah4.5/PA blends (Table 4). 43 ± 5% of a copolymer containing 26 ± 5% of PA is obtained in the 80/20 blend while 50 ± 5% of a copolymer containing 37 ± 5% of

Table 4. Characteristics of the Blends

blend			ternary blend composition (wt %)			graft copolymer composition
PMMA*x*-Ah*y*	PA (wt %)	anhydride/amine molar ratio	free PMMA[a]	free PA[b]	PMMA-*g*-PA[c]	PA (wt %)[c]
PMMA5	20	0.5	48	11	41	20
PMMA5-Ah4	20	4.1	32	7	62	22
PMMA10	20	1.1	52	12	36	22
PMMA10-Ah2.5	20	2.9	52	11	37	24
PMMA10-Ah3.5	20	3.8	50	10	40	26
PMMA10-Ah4.5	20	4.6	48	9	43	26
PMMA10-Ah8.3	20	8.5	36	8	56	21
PMMA5-Ah4	30	2.4	18	8	75	30
PMMA10-Ah4.5	30	2.6	39	11	50	37

[a] Determined by selective extraction, ±5%. [b] Determined by SEC in benzyl alcohol, ±3%. [c] ±5−7%.

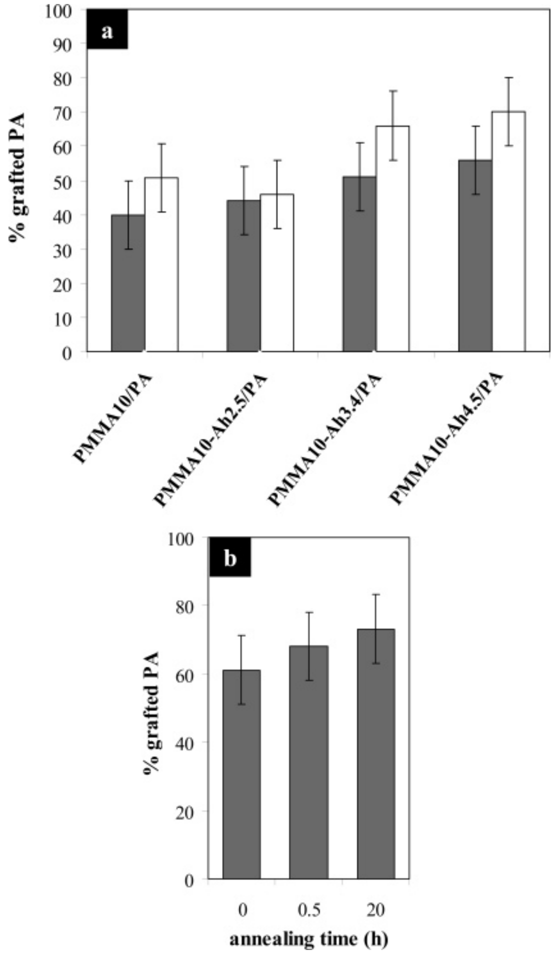

Figure 10. (a) Amounts of grafted PA in the 80/20 PMMA10-Ah*y*/PA blends at the end of the blending process (shaded bars) and after annealing at 235 °C under reduced pressure during 20 h (empty bars). (b) Amount of grafted PA in 70/30 PMMA10/PA blends as a function of annealing time at 235 °C under reduced pressure.

PA is obtained in the 70/30 blend. Both the graft density and the total amount of grafted chains increase when the fraction of PA in the blend is increased. The same trends were found for PMMA5-Ah4/PA blends (Table 4).

Effect of Annealing. In a previous study we reported on PMMA/PA blends morphology.[35] Blends were annealed above the melting point of PA, at 235 °C, under reduced pressure (10^{-2} mmHg) for 20 h. Annealing induced strong reorganization of the blends. We investigate here whether additional grafting occurs during annealing. Under these conditions, almost all remaining acid groups on PMMA chains react to form additional anhydride groups. PMMA5-Ah*y* and PMMA10-Ah*y* should contain about 4.3 and 8.7 mol % of anhydride groups, respectively, after 20 h of annealing (Table 2 and Figure 4). Figure 10a displays the amount of grafted PA in 80/20 PMMA10-Ah*y*/PA blends at the end of the blending process and after annealing. Some additional grafting occurs during annealing. Figure 10b displays the fraction of grafted PA in 70/30 PMMA10/PA blend as a function of annealing time. Most additional grafting seems to occur at the beginning of annealing. 5% of additional PA is grafted after 30 min and 10% after 20 h (Figure 10b). Under static annealing (without shear), the reaction proceeds more slowly than during blending (with shear) and progressively slows down.[11,12] Additional grafting is limited and should mainly occur on PMMA chains already close to the interface, i.e., mostly those already partially grafted.

Discussion

PMMA functionality can be controlled by heating P(MMA-*co*-MAA) copolymers under reduced pressure. Size exclusion chromatography combined with selective extraction of ungrafted PMMA chains is a relevant method to characterize the grafting reaction between the functionalized PMMA chains and short monoaminated PA chains (Figure 2). Our results indicate that PA chains of lower molecular weight graft first. This selectivity may arise from slight segregation of shorter chains to the interface in polydisperse polymer systems[9,36] or from the faster diffusion of smaller chains toward the interface.[5,37,38]

Substantial grafting yields are achieved for both PA and PMMA (Figure 9), indicating that reactive blending is an efficient technique for the synthesis of complex copolymers which are impossible to obtain otherwise. However, full conversion is not reached, even for the limiting reagent (in our case the PA, see Table 4), which is a usual drawback in this technique.[39] Higher fractions of PA and increasing preformed anhydride group content on functionalized PMMA (within a given PMMA*x* series: PMMA5-Ah*y* or PMMA10-Ah*y*) lead to a higher fraction of graft copolymer in the blend. At a constant blend composition, a higher concentration of reactive groups should enhance the rate of the grafting reaction, and a higher amount of graft copolymer is expected.[24] On the other hand, the composition of graft copolymers does not seem to depend very much on the anhydride group content. For instance, blends of PMMA5 or PMMA5-Ah4 with 20 wt % PA lead to copolymers containing 20 or 22 ± 5% of PA, respectively (Table 4). Similarly, the graft copolymers formed in 80/20 PMMA10-Ah*y*/PA blends contain 21−26 ± 5% of PA (Table 4). This trend cannot be ascribed to steric hindrance effects since copolymers with higher graft density are obtained in blends containing 30 wt % of PA (Table 4).[40,41] Note also that the graft copolymer composition is quite similar to the blend composition.

Even a low anhydride content on PMMA chains leads to substantial grafting (Table 4). This suggests that fine and homogeneous dispersions are formed quickly in 80/20 PMMA/PA blends. The average diameter of PA nodules ranges from a few tens to a hundred nanometers. More information about the morphology of such blends can be found in a previous work.[35] The constant graft copolymer composition might arise from the balance between reactivity of functional groups (amine/glutaric anhydride) and applied shear, both responsible for the amount of interface available. Note that the functionalized PMMAs used in this study have very similar rheological behavior.[42] Once a PMMA chain is grafted, there is a competition between further grafting on the same chain and grafting on a new chain, which depends on the reactivity of functional groups[43] as well as on the access of ungrafted chains to the interface.[5,9]

Unfortunately, the characterization of the blends provides no information on the distribution of PA grafts along the PMMA backbone. Though, at constant blend composition, graft copolymers have quite similar compositions, their structure might be different depending on the functionalized PMMA backbone used. These considerations may also explain similarities, in terms of graft copolymer content and composition, observed for blends based on PMMA5-Ah4 and PMMA10-Ah8.3.

Another interesting feature is the effect of the remaining acid units of PMMA chains on the grafting efficiency. This is evidenced by comparing the blends based on PMMA5-Ah4 and PMMA10-Ah4.5. Both copolymers have almost the same anhydride content, but PMMA10-Ah4.5 bears 4.2 mol % of remaining acid groups while PMMA5-Ah4 contains only a few (0.8 mol %). Whatever the blend composition, less graft copolymer is formed in blends based on the PMMA with the higher acid group content (PMMA10-Ah4.5), and the resulting graft copolymer contains more PA grafts. For instance, 70/30 PMMA5-Ah4/PA contains 75 ± 5% graft copolymer consisting of 30 ± 5% PA while 70/30 PMMA10-Ah4.5/PA contains 50 ± 5% graft copolymer consisting of 37 ± 5% PA (Table 4). This result may be attributed to possible interchain interactions between the acid groups of PMMA and the terminal amino group or the amide groups of PA, most probably via hydrogen bonding.[44,45] Note that other studies indicate acid/base interactions between P(MMA-*co*-MAA) and short aliphatic amines.[46] Hence, graft copolymer containing enough acid groups may spend longer time at the interface than copolymers without acid groups, thus preventing access of ungrafted chains to the interface. Increased residence time at the interface (combined with the possibility to create new anhydride groups) and increased interfacial width in the presence of attractive interactions between polymers[3,7,36] could explain the higher graft density of the resulting PMMA10-Ah4.5-*g*-PA copolymers as compared to PMMA5-Ah4-*g*-PA (the latter contain fewer acid groups). We can therefore conclude that reversible attractive interactions at the interface affect grafting yields of both components of the blend. We speculate that this effect is probably more pronounced for acid groups localized in the vicinity of the interface, namely those on PMMA segments between grafts. In this respect, we also expect a contribution of ionic effects, for instance when acid groups are partially neutralized by alkali.[47]

Conclusion

In this study, we investigated the effects of backbone functionality and blend composition on the formation of graft copolymer in PMMA/PA blends. Anhydride-functionalized PMMAs were obtained by thermal treatment of PMMAs containing randomly distributed methacrylic acid units. Control over the amount of intramolecular anhydride groups on PMMA chains was obtained by varying the temperature and the duration of isothermal treatments and the content of acid groups on PMMA chains. Grafting between functionalized PMMA and short monoaminated PA chains has been characterized by SEC in benzyl alcohol in combination with selective extraction of ungrafted PMMA chains in chloroform. SEC is a relevant technique in the present case since no significant grafting occurs during the measurement and the refractometer detector is quite selectively sensitive to the minor component (i.e., polyamide). We observed that substantial amounts of graft copolymers are obtained. Increasing the anhydride group content on functionalized PMMA chains and the fraction of PA in the blend led to enhanced yield in graft copolymer. Finally, the optimum grafting between a multifunctionalized backbone and end-functionalized chains depends not only on the reactivity of the backbone (nature and fraction of reactive groups) but possibly also on reversible interchain interactions, like hydrogen bonding, contributing to the stabilization of the interface.

Acknowledgment. The authors gratefully acknowledge ARKEMA, CNRS, and ESPCI for financial support. We thank J. Lesec for contribution to SEC characterization and A. V. Ruzette and A. Bonnet for helpful discussions. M.F. acknowledges J. C. Chiajese and M. Gonnin for help with PMMA characterization.

Supporting Information Available: FTIR spectra of neat and extracted PMMA; FTIR spectra showing the effect of thermal treatment on anhydride formation; estimation of dyad composition of P(MMA-*co*-MAA) copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA060036X