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Effect of Molecular Weight of the Reactive Precursors in Melt Reactive Blending

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Introduction. Immiscible polymer blends are commonly compatibilized by block or graft copolymers, which are either premade or formed "in situ".[1] The reactive blending process is by far more economically viable but also strongly dependent on the relative kinetics of phase dispersion and interfacial coupling of the reactive precursors.[2−9] This kinetic control of the phase morphology is closely related to the molecular weight and structure of the reactive chains.[2−4,6,8,9]

This study aims at investigating to which extent the molecular weight of melt blended linear reactive precursors has an effect on the progress and completeness of the interfacial reaction. Polystyrene end-capped with a primary amine (PS-NH_2) has been prepared with two molecular weights (M_n = 26 000 and 72 000; Table 1) by atom transfer radical polymerization (ATRP).[10] Anthracene-labeled PMMA end-capped by a phthalic anhydride group (anth-PMMA-PA) has been also synthesized by ATRP (M_n = 12 000; Table 1).[11] Simultaneous conversion of anth-PMMA-PA into high and low molecular weight PS-*b*-PMMA diblock copolymers has been monitored by SEC equipped with a fluorescence detector.

Experimental Part. Blends of 25 wt % PMMA and 75 wt % PS were prepared in a MiniMAX cup and rotor mixer (Custom Scientific Instruments, Cedar Knolls, NJ) at 180 °C under a nitrogen flow. 300 mg of premixed powdery reactive precursors was melt-blended at 350 rpm in the presence of three stainless balls. The PS phase consisted of 24 wt % of low molecular weight PS-NH_2 (M_n = 26 000 g/mol) and 76 wt % of high molecular weight PS-NH_2 (M_n = 72 000 g/mol), i.e., the same molar amount for each PS population. 40 wt % of anthracene-labeled PMMA-PA (M_n = 12 000 g/mol) was mixed with 60 wt % of nonreactive PMMA (M_n = 30 000 g/mol) in the PMMA phase. The NH_2/anhydride molar ratio was 1.5. Periodically, samples (10−20 mg) were picked out with tweezers and quenched into liquid nitrogen. They were dissolved into a solution of phenyl isocyanate in THF in order to prevent any further reaction between PS-NH_2 and anth-PMMA-PA. 100 μL of this solution was then injected into a Waters 150C ALC/SEC equipped with three Phenomenex phenogel columns eluted by THF at 25 °C, an internal refractive index detector, and a Hitachi F1050 external fluorescence detector. The fluorescence excitation and emission wavelengths were 358 and 405 nm, respectively. The SEC traces were fitted by three Gaussian curves, whose the surface area was used to calculate the conversion of anth-PMMA-PA (the low M_w peak) into two populations of block copolymers (depending on M_n of the PS block).[12] The error was estimated at less than 10%.

Table 1. Characteristics of the Polymers Used in This Study

polymers	M_n (g/mol)[a]	M_w/M_n[a]	functionality (*f*)
anth-PMMA-PA	12 000	1.2	0.99[b]
PMMA	30 000	1.2	
PS-NH_2 (26K)	26 000	1.2	0.86
PS-NH_2 (72K)	72 000	1.2	0.80

[a] Size exclusion chromatography in THF at 40 °C. Calibration by PS and PMMA standards. [b] The anhydride functionality was determined by ^1H NMR.

Results and Discussion. Typical TEM images for PMMA/PS (25/75 wt/wt) blends show a homogeneous and stable dispersion of PMMA phases in PS when the mixing time exceeds 1.0 min. The final particle size is

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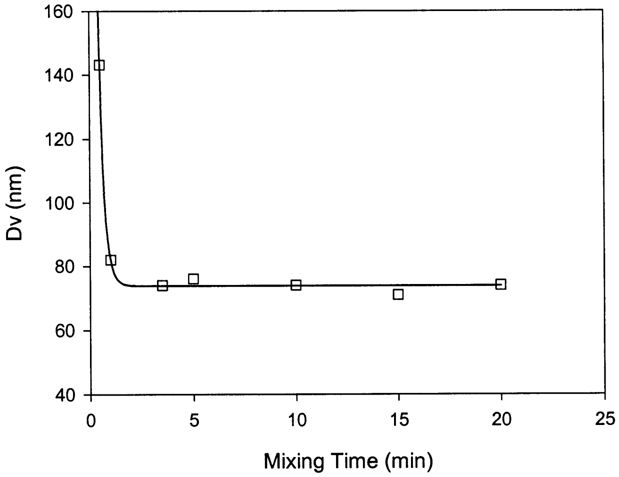

Figure 1. Time dependence of the volume average diameter D_v for PMMA/PS (25/75 wt %) blends. The PS dispersed phases were stained by RuO_4 vapor for 30 min, observed by TEM, and quantitatively analyzed by a computerized image analyzer (KS 100 Kontron imaging system). 200−300 dispersed domains were analyzed per sample. The cross-sectional surface area of each particle was converted to an equivalent diameter $D_{\text{equivalent}} = (4/\pi(\text{area}))^{0.5}$, from which $D_v = \sum_i n_i D_i^3/\sum_i n_i D_i^2$ was calculated.

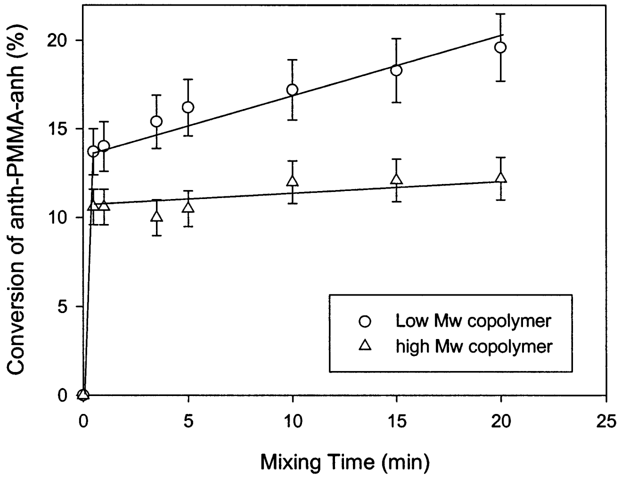

Figure 2. Conversion of the anth-PMMA-PA into diblock copolymers.

less than 100 nm. Figure 1 illustrates the dependence of the volume to surface average particle diameter (D_v) on the mixing time. A sharp decrease in D_v is noted within the first minute, which is the usual observation when immiscible polymers are reactive blended. According to Figure 2, the interfacial reaction mainly occurs within less than 1.0 min, whatever the chain length of $PS\text{-}NH_2$. During this very short period of time, the interfacial surface area is dramatically increased (and then tends to level off, see Figure 1), and the degree of conversion of $PS\text{-}NH_2$ is only slightly higher for the low M_w chains.

The coverage Σ (chains/nm^2) of the interface by the copolymer has been estimated by eq 1, which combines conversion and D_v,[13]

$$\Sigma = (\phi_w C_{\text{cop}} N_{\text{av}} \rho_{\text{PMMA}} D_v)/6M_n \qquad (1)$$

where ϕ_w is the weight fraction of anth-PMMA-PA in the PMMA phase (0.4), C_{cop} is the conversion of anth-PMMA-PA into low and high molecular weight diblocks, N_{av} is the Avogadro's number, ρ_{PMMA} is the PMMA density (1.15 g/cm^3), and M_n is the number-average molecular weight of anth-PMMA-PA. The maximum coverage (Σ_0) can be extracted from the lamellar spacing of a symmetric PS-*b*-PMMA diblock copolymer.[13] $\Sigma_0 = 0.171$ and 0.131 chains/nm^2 for diblocks of $M_n = 38\,000$ and 84 000 g/mol, respectively.

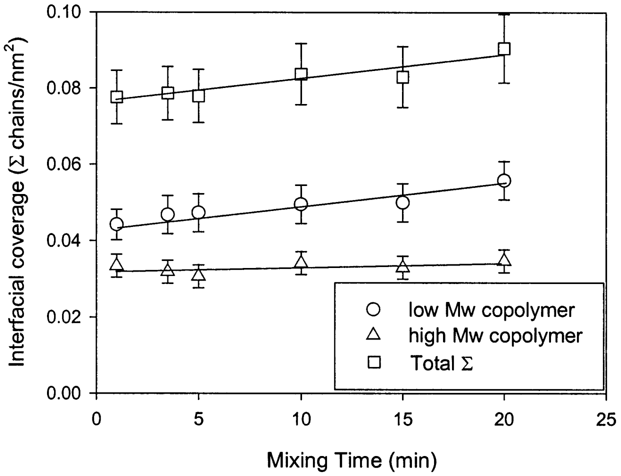

Figure 3. Time dependence of the interfacial coverage Σ by high and low molecular weight PMMA/PS diblock copolymers.

Figure 3 shows the interfacial coverage Σ for both the high and low molecular weight diblock copolymers. At the end of the first mixing stage, Σ/Σ_0 is close to 25% for each diblock population, which indicates that roughly half the interface area is occupied, which is enough to stabilize the phase morphology established at this moment. The calculated interfacial coverage (Σ/Σ_0) is however a crude approximation, particularly in this work where the interface is occupied by a mixture of two PS-*b*-PMMA diblocks that differ one from each other in the length of the PS block by a factor of ca. 3. After this dramatically fast, although very short, blending step, the interfacial reaction rate decreases sharply, particularly in the case of the high molecular weight $PS\text{-}NH_2$, whose conversion does not change significantly after 1.0 min mixing.

The sharp breakdown observed in the progress of both the phase dispersion (Figure 1) and the interfacial reaction (Figure 2) is the expression of the problem faced by the reactive chains to migrate to and react further at an interface, which is no longer renewed by the mechanical forces. For reacting further at the interface, the reactive PS chains have to diffuse through the protective brush of diblocks in such a way that the reactive group attached to them is properly localized for colliding with a mutually reactive group attached to an immiscible PMMA chain. There is no specific driving force for these chains to diffuse preferentially to the interface. It is only when the reactive groups can collide that the reaction exothermicity is beneficial to the system. Indeed, the enthalpy change of a chemical reaction is in no way a motor for the molecules to diffuse one toward the other. The experimental data collected in this work clearly show that the (random) diffusion of the reactive chains in the very close vicinity of the interface followed by their effective reaction is as slow as the molecular weight is high. Diffusion of the $PS\text{-}NH_2$ chains of 72 000 molecular weight throughout the mixed polystyrene brush (block of $M_n = 72\,000$ and 26 000, respectively) at the interface is so slow that their reaction is negligible over 20 min. For the same period of time, the ca. 3 times shorter PS-NH_2 chains have the opportunity to reach the interface and to react with ca. 5% of the original amount of anth-PMMA-PA. So, the second step of the blending process is basically controlled by diffusion of the reactive precursors to the interface covered and stabilized by the copolymer formed in the first step.

Conclusions. The interfacial reaction of an equimolar mixture of PS-NH_2 chains of $M_n = 26\,000$ and 72 000 g/mol with anth-PMMA-PA chains ($M_n = 12\,000$ g/mol, labeled with anthracene) has been studied at 180 °C. The progress of the reaction has been monitored by SEC analysis of the reactive blend with a fluorescence detector. Conversion of anth-PMMA-PA into each population of diblocks has been calculated from the relative area of the elution peaks for PMMA and each population of diblocks. The initial reaction rate is very high as confirmed by the conversion of ca. 25% of the anth-PMMA-PA chains within less than 1 min. During this very short period of time, the finer phase dispersion (possible under the mixing conditions used) is established and stabilized by the copolymer chains formed approximately at the same rate whatever their molecular weight. Any increase in the mixing time does not change further the phase dispersion (D_v < 100 nm), and the progress of the interfacial reaction at the interface of a constant surface area is dramatically slowed down in relation to the molecular weight of the PS-NH_2 chains. The second regime of reaction is actually controlled by the diffusion of the reactive chains to the interface and thus through the brush formed by the constitutive blocks of the diblocks. This diffusion may be so slow for the high molecular weight chains ($M_n = 72\,000$ g/mol) that the apparent reaction rate is close to zero, in contrast to the shorter chains ($M_n = 26\,000$ g/mol) which are further, although slowly, converted into diblocks (reaction with ca. 5% of the original amount of anth-PMMA-PA within ca. 20 min). This observation is actually consistent with the conclusion drawn by Tsukruk et al.[14] in their study of grafting of melted carboxylic acid- and anhydride-terminated PS onto silicon substrates modified by an epoxysilane monolayer. It thus appears that the issue of reactive blending is decided in the very preliminary stage of the blending, which requires the implementation of a very fast interfacial reaction for a fine phase dispersion to be stabilized.

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References and Notes

(1) Van Duin, M.; Koning, C. E.; Pagnoulle, C.; Jérôme, R. *Prog. Polym. Sci.* **1998**, *23*, 707−757.

(2) (a) Pagnoulle, C.; Koning, C. E.; Leemans, L.; Jérôme, R. *Macromolecules* **2000**, *33*, 6275−6283. (b) Pagnoulle, C.; Jérôme, R. *Macromolecules* **2001**, *34*, 965−975.

(3) Jiao, J.; Kramer, E. J.; de Vos, S.; Moller, M.; Koning, C. *Macromolecules* **1999**, *32*, 6261−6269.

(4) Schulze, J. S.; Cernohous, J. J.; Hirao, A.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2000**, *33*, 1191−1198.

(5) Jeon, H. K.; Kim, J. K. *Macromolecules* **2000**, *33*, 8200−8210.

(6) Hu, G. H.; Kadri, I. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*, 2153−2163.

(7) Guégan, Ph.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993−4997.

(8) Moon, B. J.; Hoye, T. R.; Macosko, C. W. *Macromolecules* **2001**, *34*, 7941−7951.

(9) Norton, L. J.; Smigolova, V.; Pralle, M. U.; Hubenko, A.; Dai, K. H.; Kramer, E. J.; Hahn, S.; Berglund, C.; Dekoven, B. *Macromolecules* **1995**, *28*, 1999−2008.

(10) Matyjaszewski, K.; Nakagawa, Y. *Macromol. Rapid Commun.* **1997**, *18*, 1057−1066. Sodium azide was however used instead of trimethylsilyl azide in the derivatization reaction of the bromide end group into the azide one. The amine functionality of PS was estimated by the fraction of the chains that reacted with anth-PMMA-PA (12K) in dry THF at 50 °C for 48 h. The anhydride/NH_2 molar ratio was 5 or higher. Just before SEC-UV analysis, a few drops of phenylisocyanate were added to the reaction mixture in order to complete (if necessary) the amine consumption. Detection of anthracene at 366 nm allowed for the direct quantification of the anth-PMMA-PA conversion into diblock and, thus, of the PS end-functionality.

(11) Moon, B.; Hoye, T. R.; Macosko, C. W. Submitted to *Polymer*.

(12) Schulze, J. S.; Moon, B.; Lodge, T. P.; Macosko, C. W. *Macromolecules* **2001**, *34*, 200−205.

(13) Macosko, C. W.; Guégan, Ph.; Khandpur, A. K.; Nakayama, A.; Maréchal, Ph.; Inoue, T. *Macromolecules* **1996**, *29*, 5590−5598.

(14) Luzinov, I.; Julthongpiput, D.; Malz, H.; Pionteck, J.; Tsukruk, V. *Macromolecules* **2000**, *33*, 1043−1048.

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