Macromolecules **1994,** *27,* 4993-4997

Kinetics of Chain Coupling at Melt Interfaces

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Received January 15, 1994; Revised Manuscript Received May 25, 1994[●]

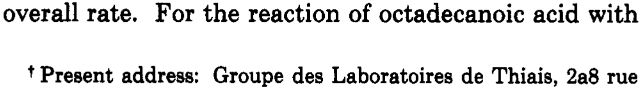
ABSTRACT: Copolymers formed by reactions between functional groups on two different polymers are known to stabilize the morphology formed during melt blending. Large effects on morphology have been reported, but it has been difficult to determine the amount or rate of block copolymer formation. We have anionically synthesized carboxylic acid terminal polystyrene (PS-COOH) and epoxy terminal poly(methyl methacrylate) (PMMA-E) of a narrow molecular weight distribution. To compare homogeneous coupling PS–E was also synthesized. The amount of block copolymer formed by coupling of PS-COOH with PMMA-E to form the ester was measured by size exclusion chromatography. PMMA-E (30%, M_n = 43 000) was melt mixed with PS-COOH (M_n = 42 600) in a small (0.3-g) parallel plate mixer with a maximum shear rate of 20 s^{-1}. PMMA-E particle diameter was 0.6 μm and stable after 5 min of mixing at 180 °C. The block copolymer content increased to 2% at 20 min. The reaction is slow enough that the chain ends can sample the interface many times before reacting. Assuming that reaction can occur only at the interface (about 5 nm thick) gives reaction rates about twice as high as for homogeneous coupling. This indicates that the chain end concentration is higher in the interface or that interfacial reactions are more efficient. A random MMA–glycidal methacrylate copolymer coupled with PS-COOH at a similar reaction rate. Addition of a catalyst (*N,N*-dimethyldodecylamine) which is insoluble in both polymers increased the heterogeneous but not the homogeneous coupling.

Introduction

Copolymers formed by reaction between functional groups on two different immiscible polymers are known to stabilize the morphology formed during melt blending. Large effects on morphology have been reported, but it has been difficult to determine the amount or rate of copolymer formation. Very few functional groups are involved, so they are hard to detect. In many cases the copolymer formed is highly grafted or even cross-linked. Furthermore, it is difficult to find a common solvent for most immiscible polymer pairs.

A number of workers have reported 10–30% "copolymer" formation after reactive blending.[1-5] Yet about 2% of a typical diblock copolymer will completely cover the interface of 1-μm-sized particles. Either the reactively generated copolymer is being dispersed extensively into the homopolymers or the interface is becoming extremely thick or the solvent methods used by previous workers have not successfully extracted all the homopolymer. To resolve this controversy, a model study was designed. It should also allow quantification of the role of the chemical reaction rate, molecular diffusion, and convective mixing in the reactive blending process. The influence of the structure of the resulting copolymer (diblock versus graft copolymer) is also studied.

For our coupling reaction we have selected ester formation by carboxylic acid opening of the epoxide ring. This reaction is used in commercial blends [e.g. refs 6 and 7].



$$R_1CH_2COOH + R_2OCH_2\overset{O}{CHCH_2} \longrightarrow R_1CH_2COOCH_2CH(OH)CH_2OR_2$$

Madec and Marechal[8] report that without catalyst only simple bimolecular coupling occurs, giving a second-order overall rate. For the reaction of octadecanoic acid with 1-(dodecyloxy)-2,3-epoxypropane at 121 °C they found the rate constant, $k = 4.2 \times 10^{-6}$ kg mol^{-1} s^{-1}. For catalyzed systems they give activation energies of 70–80 kJ/mol. Shimbo et al.[9] give data on the polymerization of bisphenol A based epoxy resin with azelaic acid at 130 °C. When compared at the same temperature, their rate constant is about twice that of Madec and Marechal. Chikinari et al.[10] measured a rate of coupling at 240 °C for the reaction of stearic acid and a random copolymer of ethylene, methyl methacrylate (MMA), and glycidyl methacrylate (GMA); when their data are shifted to 180 °C, the rate constant is 2×10^{-3} kg mol^{-1} s^{-1}. Padwa[11] compared the rate of reaction at 150 °C of two kinds of acid with a random copolymer of styrene and GMA (2 wt %). When hydrocinnamic acid was used, the rate of reaction was equal to 0.01 kg mol^{-1} s^{-1} at 180 °C, and it doubled with 2-phenoxypropionic acid. He deduced from these results that the structure of the acid strongly affects the kinetics of this reaction. To our knowledge, no data have been published on the influence of the epoxide but the rate of reaction should also vary when changing the structure of its neighboring groups. The differences, although large, between the literature reaction rates are reasonable, and such shifts have already been observed for other reactions [e.g. ref 11].

For our polymers we selected polystyrene (PS) and poly(methyl methacrylate) (PMMA). Both are amorphous. Both are soluble in tetrahydrofuran (THF), making copolymer analysis possible by size exclusion chromatography (SEC). Both polymers can be made with a narrow molecular weight distribution and functional termination by the anionic methods described below. Figure 1 shows schematically how we imagine these functionally terminated polymers will react in the melt.

Experimental Section

The polymers are shown in Table 1. PMMA was synthesized by following Teyssie and co-workers[12] using the capillary tube transfer method. All transfers were by 1.3-mm stainless steel tubes through rubber septa using Ar pressure (1.6 kg/cm^2). MMA was first distilled from CaH_2 and then added to a solution of triethylaluminum in heptane (0.65 mmol/g) until a persistent yellow color was observed. It was then redistilled just prior to polymerization.

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[●] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

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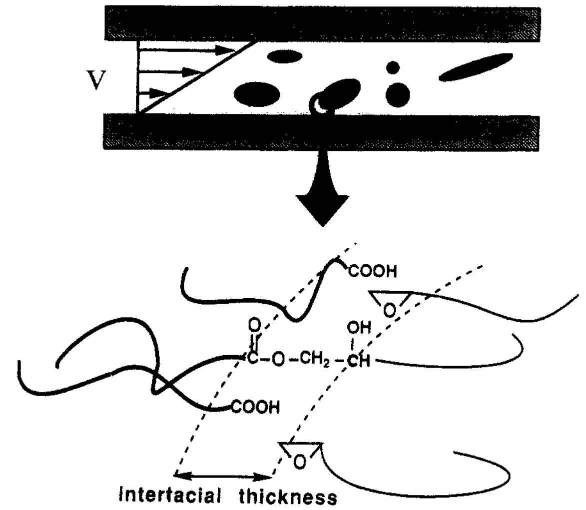

Figure 1. Schematic of how mixing flows disperse one immiscible polymer within another and how the reaction between terminal functional groups might occur.

Table 1. Functional Polymers Used for the Mixing

end-functional polymer	functionality	M_n	M_w/M_n
PS-E-22	1.3	22 700	1.07
PS-COOH-22	0.78	22 200	1.04
PS-COOH-43	0.93	42 600	1.03
PS-H-43	0	42 600	1.03
PMMA-E-22	1.22	22 000	1.03
PMMA-E-43	2.8	43 400	1.03
PMMA-rE-46[a]	35	46 000	1.11

[a] Random functionalized polymer, 7 mol % GMA monomer.

To prepare PMMA-E-43, LiCl 10 wt % in THF was introduced into the 200-mL reactor bottle under Ar at −78 °C ($n_{\mathrm{LiCl}} = 3n_{\mathrm{init}}$). The initiator prepared from the reaction of 1,1-diphenylethylene with *sec*-butyllithium was then added to the reactor. Finally 11 g of MMA in 100 g of THF was cooled and added to the reactor. After 1 h a solution of glycidyl methacrylate (GMA, monomer purified by vacuum distillation from CaH_2) in THF (0.143 g of monomer in 0.232 g of solvent) was added to the reactor. The epoxy functionality is calculated to be 2.8 by assuming all the GMA polymerized on the chain ends. After 15 min the living anions were killed with acidified methanol. The resulting PMMA is highly syndiotactic[12] with T_g = 125 °C.

The resulting PMMA-E chain ends have a distribution of epoxy groups. Assuming MMA and GMA terminal chains have the same reactivity, if 1.2 mol of GMA is added to 1 mol of living anion, we calculate that 30% of the chains are nonfunctional, 36% are monofunctional, 22% are bifunctional, 9% are trifunctional, and the remaining 4% are mainly tetrafunctional. The polymers were precipitated thrice in methanol and then freeze dried from benzene. SEC (HLC8020, Tosoh) equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) was used to determine M_n and M_w/M_n. Both ultraviolet (254 nm) and refractive index detection were used with THF carrier solvent flowing at 1 mL/min at 40 °C. A PS calibration curve was used to determine the molecular weight of the polymers. The molecular weights of the standard PS were 17×10^3, 35×10^3, 50×10^3, and 97×10^3. Two PMMA standards were used to shift this curve to characterize our PMMA polymers.

Randomly functionalized PMMA was synthesized by successively adding in a 200-mL reactor the initiator system previously described, 100 g of THF and a mixture of MMA (9.6 g) and GMA (0.88 g). Assuming an equal reactivity of both monomers gives the polymer a random distribution of epoxy function along the chain.

PS-COOH-43 was prepared by quenching PS–Li$^+$ with solid CO_2. Styrene and benzene were distilled from CaH_2 after stirring overnight and stored in bottles capped with rubber septa under Ar at −20 °C. Styrene (10 g) was added to 130 g of benzene in a 200-mL bottle under Ar. *sec*-Butyllithium (Aldrich) was added, and the color of the reaction mixture became orange. After ~1 h at 45 °C, ~1 g of *N,N,N′,N′*-tetramethylenediamine (vacuum distilled) was added to increase the PS$^-$ reactivity.[13] The color of the mixture turned dark red. Half the PS–Li$^+$ solution was transferred to a 1-L bottle containing chunks of solid CO_2 and shaken vigorously for ~15 min. The other half was terminated with acidified methanol to produce the nonfunctional polymer PS-H-43. The COOH concentration was measured by thin layer chromatography coupled with a flame ionization detector.[14]

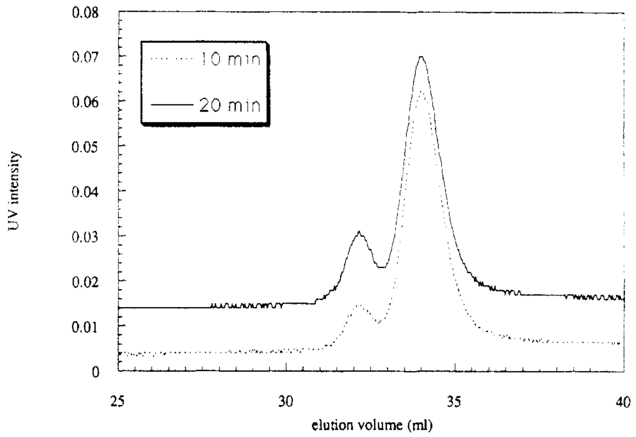

Figure 2. SEC of a homogeneous blend of PS-COOH-22/PS-E-22 at various mixing times (UV detector).

Table 2. Conversion and Reaction Rate in Homogeneous Blends of PS-COOH-22 with PS-E-22 at Stoichiometry, [COOH] = [E] = 0.0177 mol kg^{-1}

run	temp of mixing (°C)	conversion at 2 min mixing	$10^3 k_{2\ \mathrm{order}}$ (kg mol^{-1} s^{-1})
1	160	0.040	9.9
2	180	0.126[a]	22
3	200	0.133	67
4	220	0.238	150
5[b]	180	0.013	21
6[c]	180	0.051	26

[a] 5 min reaction. [b] 10% of functional polymers diluted in nonfunctional PS. [c] Addition of 6 μL of catalyst (*N,N*-dimethyldodecylamine).

To obtain an epoxy-functionalized polystyrene (PS-E-22), 1,1-diphenylethylene and then GMA (purified as previously described) was added to the polystyryl anion and quenched with methanol. As with PMMA-E, the PS-E chain end has a distribution of epoxy groups. The PS polymers were purified as with PMMA.

The homogeneous blends (PS-E plus PS-COOH) were mixed in an 8-mm-diameter parallel plate mixer made from a pair of close fitting glass tubes each sealed at one end. The tube ends were immersed in an oil bath to maintain temperature. A side arm on the outer tube allowed a N_2 flush during mixing. The heterogeneous blends were mixed in a larger parallel plate mixer (13-mm-diameter Mini Max Molder, Custom Scientific) at a maximum shear rate of ~20 s^{-1}. The temperature is controlled by electric band heaters. This mixer was not flushed with N_2. Homogeneous blends were made from 50 mg of PS-E and 50 mg of PS-COOH, and each heterogeneous blend was made from 280 mg of PS and 120 mg of PMMA of dry blended powder. More details on the preparation and morphology of the blends is given by Nakayama et al.[15] A comparison of these parallel plate mixers to larger mixers is given by Sundararaj et al.[16]

Block copolymer generated during mixing was measured by the SEC described above. The ultraviolet detector was used since PMMA is nearly invisible at 254 nm. Thus the area under the curve is directly proportional to the mass of polystyrene even for the block copolymer. Each SEC chromatogram was fit with a series of Gaussian curves. The amount of block copolymer generated during the reaction (Figures 2 and 4) is the area under the high molecular weight curve and is given in Tables 2 and 4. The reproducibility of the areas found by the curve fits is ±0.2% for a given run and between SEC runs ±0.3%. Due to the coupling

Table 3. Conversion and Reaction Rate Measured at 180 °C for Heterogeneous Blends of PS-COOH with PMMA-E of Different Molecular Weights

run	$10^{-3}M_n$ (PMMA-E)	$10^{-3}M_n$ (PS-COOH)	conversion at 20 min mixing	$10^3k_{2\ \mathrm{order}}$ (kg mol^{-1} s^{-1})
7	43	43	0.0202	1.11
8	22	22	0.0225	0.80
9	22	43	0.0160	0.88
10[a]	43	43	0.0031	1.73
11	46 (r)[b]	43	0.0191	1.07
12[c]	43	43	0.0282[d]	0.85
13[e]	22	22	0.0373	2.39

[a] Dilution of the COOH concentration to 10%. [b] Random functionalized epoxy. [c] 5 min mixing, then no shearing. [d] 30 min. [e] Using 5 μL of catalyst (*N*,*N*-dimethyldodecylamine).

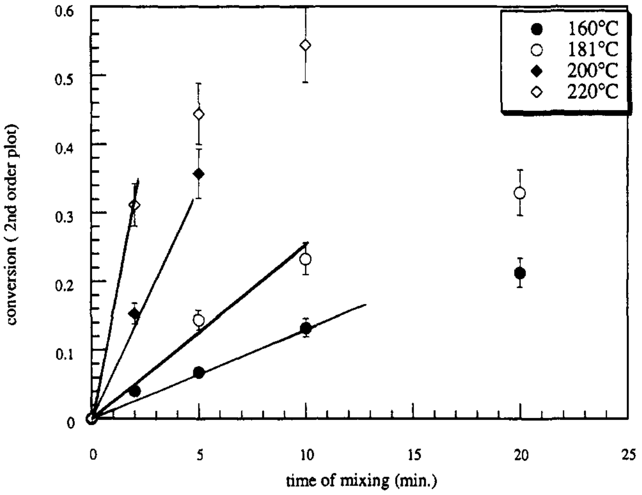

Figure 3. Second-order plot for the homogeneous system PS-COOH-22 with PS-E-22 mixed at different temperatures.

reaction between the polystyryl anion just before termination, the starting PS-COOH polymers in Table 1 have a small peak at the same location as the reactively formed block copolymer. The value of this peak is equal to 1.8% for PS-COOH-43 and 0.7% for PS-COOH-22. In Tables 2 and 3 the coupled polystyrene has been subtracted. We also mixed a pure PS-COOH-22 at 180 °C. After 20 min, the SEC trace (UV detector) did not show any coupling. We believe then that there is no coupling between the same functional polymers.

Results and Discussion

Homogeneous Blends. To determine the homogeneous rate of chain end coupling, we mixed the two end-functionalized polystyrenes: PS-22-COOH/PS-22-E. Conversions after 2 min of mixing are given in Table 2. Figure 3 shows a fair second-order fit at low conversion, as claimed previously by Madec and Maréchal.[8] Deviation occurring after 30% conversion may proceed from a side reaction involving the hydroxyl function resulting from epoxy–acid addition.[8] The rates of reaction are reported in Table 2. Figure 3 gives an activation energy of 84 kJ/mol, close to the literature value;[8] however, the rates that we obtained are much higher than the one reported previously for small molecules.[8,9] This can be explained by the difference of the function α to the epoxy and the acid. Our results are in good agreement with Padwa[11] and our functional molecules are chemically most similar to his. The addition of a catalyst (*N*,*N*-dimethyldodecylamine, DMDA, Aldrich) does not significantly increase the rate of reaction as previously reported by several authors.[8,9,17,18] Madec and Maréchal[8] reported a 100-fold increase in rate at 120 °C when [DMDA] = 0.064 equiv kg^{-1}. The catalyst contains a dodecyl group. This aliphatic chain is not expected to be soluble in PS.

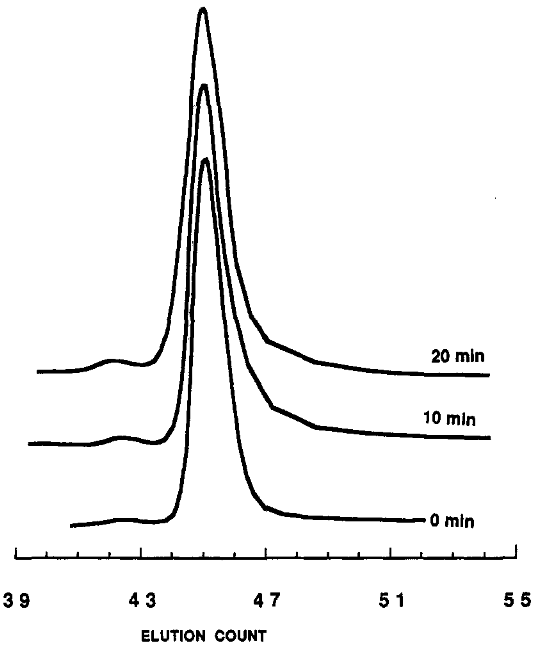

Figure 4. SEC results for an immiscible blend of PS-COOH-43 with PMMA-E-43.

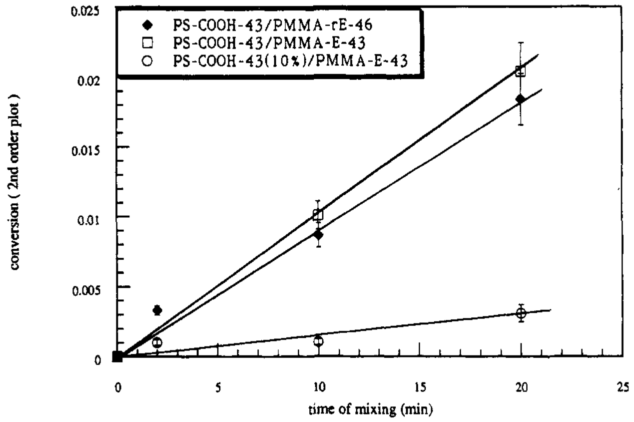

Figure 5. Second-order plot for the heterogeneous blends of different molecular weights at 180 °C.

Using Smoluchowski's equation[19] we are able to calculate a coupling rate if diffusion of the chain ends is controlling.

$$k_d = 4\pi R(D_{PS} + D_{PS})N_v$$

where D_{PS} is the self-diffusion coefficient of PS (10^{-11} cm^2/s for M_n = 43 000 at 180 °C calculated from ref 20, R is the radius of the reaction sphere, and N_v is Avogadro's number. If we assumed a reaction sphere of 1 nm, then $k_d = 6 \times 10^7$ cm^3 mol^{-1} s^{-1}. In the same units, the rate of reaction that we measured is 20 cm^3 mol^{-1} s^{-1} at 180 °C. The diffusion controlled coupling calculated is 5 orders of magnitude higher than the measured reaction rate. Thus diffusion is not controlling these kinetics.

Heterogeneous Blends. Figure 4 shows SEC for a heterogeneous blend after different mixing times. From such data conversions are calculated and reported in Table 3. After 20 min a 180 °C about 2% of the block copolymer was formed. This amount is more than enough to stabilize the PMMA drops dispersed in PS.[15] Second-order plots like Figure 5 were made, and when homogeneous reaction was assumed, rate constants were calculated. For all the blends the rate is about 10^{-3} kg mol^{-1} s^{-1}. There is no significant affect of molecular weight or mixing shear rate (blend 12) on the reaction. Both these results indicate

Table 4. Reaction Rate of Heterogeneous Blends of PMMA-E and PS-COOH (Assuming the Reaction only Occurs in the Interface)

run	$10^{-3}M_n$ (PMMA-E)	$10^{-3}M_n$ (PS-COOH)	Sp[15] (μm^{-1})	D_v (μm)	Φ_i	10^3k_{int} (kg mol^{-1} s^{-1})
7	43	43	4.00	0.45	0.021	46 ± 5
8	22	22	3.16	0.57	0.016	50 ± 5
9	22	43	4.73	0.38	0.023	37 ± 5
10[a]	43	43	3.6	0.5	0.018	96 ± 30
11	46 (r)[b]	43	2.57	0.70	0.013	83 ± 5
12[c]	43	43	3.00	0.60	0.015	56 ± 5
13[d]	22	22	2.76	0.65	0.014	171 ± 5

[a] Dilution of the COOH concentration by 10. [b] Random functionalized polymer. [c] 5 min mixing, then no shearing. [d] Using 5 μL of catalyst (*N,N*-dimethyldodecylamine).

that the reaction is not diffusion controlled. Nakayama et al.[15] observed that for blends like sample 12 after 5 min of mixing the particle size is nearly constant and coalescence is negligible.

Although the addition of catalyst did not have a significant effect on the rate in the homogeneous case, it did increase the reaction rate about 250% for the heterogeneous system. This affect is still much less than that expected from the literature,[8,9,17,18] but the increase does suggest that the catalyst which is insoluble in both polymers is more likely to be found in the interface.

The reaction rates in Table 3 are about 20 times less than those for the homogeneous case. However, it is more reasonable to consider that the reaction can only occur in a much smaller volume, the interface. The interfacial volume fraction, ϕ_i can be calculated from the product of interfacial area per unit volume, Sp, and the interfacial thickness. Sp was measured by small angle light scattering[15] and the values are given in Table 4. The volume average particle diameter can be calculated from Sp using the volume fraction of the PMMA phase and with spherical particles, $D_v = 6\phi_m/\mathrm{Sp}$. The thickness of the interface between PS and PMMA is 5 nm and relatively insensitive to temperature.[21] The reaction rate then is calculated by dividing the rates in Table 3 by ϕ_i. As Table 4 indicates, the rates based on interfacial volume are about twice those of the homogeneous case. This higher rate is not unreasonable. It is likely that the chain ends prefer the interface. For example Zhao et al.[22] report twice the concentration of deuterated polystyrene chain ends at the interface than in the bulk for a PS and poly(bromostyrene) melt. More significant may be the greater efficiency of intermolecular collisions confined to the 5-nm interface.

Nakayama et al.[15] have shown that the low levels of block copolymer measured here are sufficient to stabilize the morphology. Assuming a dense block copolymer monolayer at the interface, they estimate that 0.3 chain/nm^2 will completely cover the surface of each particle. They found that 0.1 chain/nm^2 were sufficient to prevent coalescence. For a PS–poly(vinylpyridine) system, Kramer et al.[23] have shown that equilibrium interfacial copolymer levels produced by diffusion are 0.15 chain/nm^2. Using an average block copolymer molecular weight of 40 000 and $D_v = 0.6$ μm (sample 8), 2% copolymer yields an interfacial copolymer chain density of 0.1 molecule/nm^2. This result indicates that the interface is not saturated by the block copolymer and is always accessible to the end functional groups.

The random functional polymer PMMA-rE-46 gave a conversion very similar to that found for the end functional blends (note sample 11). This amount (about 2%) of graft copolymer was also more than sufficient to stabilize the PMMA particles. The reaction rate was calculated using [COOH]; the epoxide concentration was much higher. For this blend the SEC showed a single block copolymer peak. Thus each reacted PMMA-rE-46 appears to have only one PS chain attached. At first this seems surprising considering that on the average there are 35 epoxy groups on each chain. However, their average separation is more than 10 MMA units and the total number reacted is very low.

Conclusions

The system introduced here is a good model for studying reactive coupling of polymer chains in the melt. Polystyrene and poly(methyl methacrylate) are immiscible yet mutually soluble in THF. Using narrow molecular weight distribution permits easy quantification by SEC of the block copolymers formed at least up to 40 000 molecular weight.

The coupling reaction of acid and epoxide groups is slow enough at 180 °C to allow many contacts due to diffusion. Thus, after the initial morphology forms, mixing has little effect on the reaction. The role of the reaction rate in the initial morphology development may be very important.[2,24]

Nakayama et al.[15] have shown that the low levels of block copolymer measured here, less than needed to cover the dispersed particles, are sufficient to stabilize the morphology. The rate of block copolymer formation is twice as fast as for heterogeneous compared to homogeneous coupling. This is due to the higher concentration of chain ends in the PS-PMMA interface and to the greater efficiency of this confined reaction. The addition of *N,N*-dimethyldodecylamine catalyst increased the heterogeneous reaction rate about 3 times, yet it had almost no effect on the homogeneous reaction.

Acknowledgment. This work was supported by grants from the National Science Foundation's (C.W.M.) U.S.–Japan Programs and the Ministère de la Recherche et de la Technologie, France (P.G.). Additional support was received from the NSF's Chemical Reaction Processes and Polymer Materials Programs and the University of Minnesota Center for Interfacial Engineering. The authors wish to thank Katsuhiko Takenaka for fabrication of the glass reactor, Akinari Nakayama for some of the mixing and for the light scattering measurements, Allen Padwa for sharing his data,[11] and both Padwa and Chris Durning for their helpful discussions.

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