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Homogeneous reactive coupling of terminally functional polymers

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Abstract

The rates of nine melt coupling reactions were measured by reacting terminally functional polymer chains. The functional groups are carboxylic acid, oxazoline, epoxy, aromatic primary amine, aliphatic primary amine, hydroxyl and cyclic anhydride. The functional groups were attached to the end of polystyrene (PS) and poly(methyl methacrylate) (PMMA) chains with most experiments performed at molecular weights of about 25,000 g/mol and temperature of 180°C. Reactions were performed homogeneously by blending stoichiometric amounts of the same type of polymer containing complementary functional groups. Reaction rates were determined from the amount of coupled chains via gel permeation chromatography. The functional group pairs, in order of increasing reactivity, are acid/amine, hydroxyl/(anhydride or acid), aromatic amine/epoxy, aliphatic amine/epoxy, acid/oxazoline, acid/epoxy, aromatic amine/anhydride, aliphatic amine/anhydride. This is in general agreement with results for very dilute small molecule analogs. Some experiments performed at higher molecular weights gave similar results. Coupling between aliphatic amine terminal and cyclic anhydride terminal chains was found to be extremely fast; complete conversion occurred in <30 s. Dilution studies and comparison to theory indicate that this reaction was not diffusion controlled. Mixing and diffusion are rapid enough to bring every chain end in contact within 15 s. © 2001 Published by Elsevier Science Ltd.

Keywords: Melt coupling reaction; Reaction kinetics; Terminally functional polymers

1. Introduction

The formation of block and graft copolymers by melt coupling reactions between functional polymers is important for the compatibilization of polymer blends [1] and for adhesion between polymer–polymer interfaces [2]. There are challenging issues of diffusion and reaction in an interface between two immiscible polymers, but to study these we first need to know the base reaction kinetics for the homogeneous case. Can the reactivity of small molecule analogs be used to predict polymer melt coupling kinetics? Will the reactivity of a functional group attached to a long chain be effected by diffusion? To answer these questions, we have synthesized narrow molecular weight distribution polystyrene (PS) chains with various terminal functional groups (Table 1). Chains with complementary functional groups were then mixed in the molten state (180°C). The coupling kinetics of the chains was measured by gel permeation chromatography (GPC), and for the purpose of comparison, second-order rate constants were estimated. The homogeneous melt coupling between some terminally functional poly(methyl methacrylate) (PMMA) chains (Table 2) were also measured.

2. Experimental procedures

2.1. Polymer synthesis

PS and PMMA were anionically synthesized to have a narrow polydispersity and contain a single terminal functional group. The specific polymers used are shown in Tables 1 and 2. Polymers were synthesized using standard break-seal [3] or argon atmosphere techniques [4–6]. The synthetic schemes are summarized in Ref. [6]. The aromatic amine (aniline) terminal polymers were made via a protected initiator [7] while the cyclic anhydride [8,9] and primary aliphatic amine [10,11] used protected terminating groups or terminating groups, which were converted to the functional group in a secondary step. The carboxylic acid functional polymers were made by termination of the living anion with either dry ice [12] or gaseous CO_2 [13] forming

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Table 1
Functional polystyrenes

Name	Functional group[a]	M_n	M_w/M_n	f
PS	–	25,700	1.02	–
PS–OH	Hydroxyl	30,600	1.16	0.96
PS–An-1	Anhydride #1	24,000	1.03	0.96
PS–An-2	Anhydride #1	34,500	1.04	0.69
PS–An-3	Anhydride #1	25,800	1.12	0.86
PS–An-4	Anhydride #2	24,200	1.10	0.90
PS–An-5	Anhydride #2	48,500	1.06	0.62
PS–COOH-1	COOH	22,300	1.04	0.78
PS–COOH-2	COOH	30,300	1.08	0.88
PS–COOH-3	COOH	39,000	1.03	0.93
PS–OX	Oxazoline	41,100	1.08	0.90
PS–EPX-1	Epoxy #1	22,200	1.08	1.30
PS–EPX-2	Epoxy #2	25,900	1.10	0.90
PS–ArNH$_2$	Aromatic-NH$_2$	26,700	1.04	0.99
PS–NH$_2$-1	NH$_2$ #1	25,300	1.03	0.72
PS–NH$_2$-2	NH$_2$ #2	20,900	1.04	0.99
PS–NH$_2$-3	NH$_2$ #2	52,200	1.16	0.99

[a] Refer to Fig. 1 to identify structures.

Table 2
Functional poly(methyl methacrylates)

Name	Functional group	M_n	M_w/M_n	f
PMMA	–	27,300	1.09	–
PMMA–An	Anhydride #2	25,300	1.04	0.56
PMMA–ArNH$_2$	Aromatic-NH$_2$	25,800	1.02	0.95
PMMA–NH$_2$[a]	NH$_2$ #2	39,100	1.04	0.90

[a] Obtained from Polymer Source, Ontario, Canada.

the acid anion directly. Protonation of the acid anion was done with acidic methanol. Epoxy terminated polymers were made by either polymerizing a small amount of glycidyl methacrylate (GMA) onto the end of the chain [14] or by termination with an alkyl bromide containing an epoxy group [15]. Oxazoline terminal PS was prepared by end-capping polystyryllithium with 2-bromo-12-dodecyloxazoline.[5] Hydroxyl terminal PS was prepared by polystyryllithium with ethylene oxide [16]. The actual functional groups are summarized in Fig. 1. Polymers were purified up to four times to remove all remaining small molecule reactants by reprecipitation into methanol or by freeze drying and subliming unreacted molecules. Functionality was determined by thin-layer chromatography with a flame ionization detector (TLC-FID) [17], by nuclear magnetic resonance (NMR) [9,11], or by GPC coupling after complete coupling with well characterized, end functional polyethylene oxides [9,11]. Non-reactive homopolymers were made by anionic polymerization followed by termination with degassed methanol.

2.2. Molecular weight determinations

GPC was used for molecular weight characterization as well as for determining the reaction conversion in polymer blend reactions. A Waters 150 C ALC/GPC with an internal differential refractive index (RI) detector and external tunable ultraviolet (UV) detector (Kratos Spectroflow 757) was used.

All polymers were characterized using three Phenomenex (Torrance, CA) Phenogel columns (5 μm bead size) using degassed tetrahydrofuran (THF) as the solvent. The pore sizes in the three styrene–divinylbenzene columns were 500, 1000, and 10,000 Å. The columns were maintained at a constant temperature a couple of degrees above room temperature to avoid any thermal fluctuations. Phenyl isocyanate was added to the amine containing samples

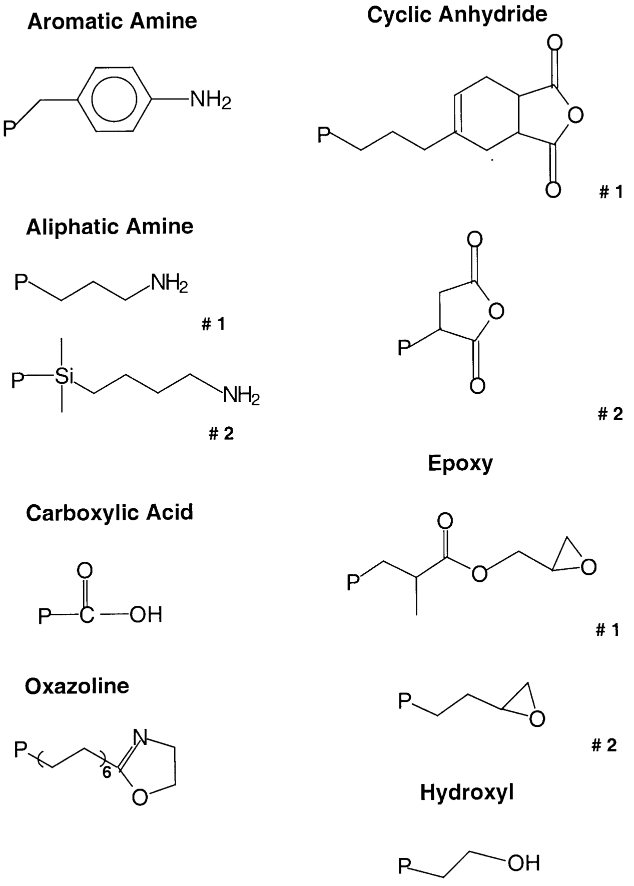

Fig. 1. Functional groups attached to the polymer chains. The location of *P* represents the attachment point for the monomer repeat unit. The two different cyclic anhydride and aliphatic amine molecules have virtually the same reactivity. The two epoxy groups show small differences in reactivity.

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[5] 2-Bromo-12-dodecyloxazoline was synthesized by treating 1,12-dibromododecane with 1 equiv. of 1-lithiomethyloxazoline in THF at −78°C for 15 min. The crude mixture was purified by flash chromatography (basic alumina stationary phase) using 10/1 hexanes/ether as the eluent to give the desired material in 21% yield. ^{1}H NMR: δ 4.21 (t, 2H, C$\underline{H}_2$O), 3.82 (t, 2H, C$\underline{H}_2$N), 3.40 (t, 2H, C$\underline{H}_2$Br), 2.24 (t, 2H, C$\underline{H}_2$C), 1.85 (p, 2H, BrCH$_2$C$\underline{H}_2$), 1.61 (p, 2H, CCH$_2$C$\underline{H}_2$), 1.41 (p, 2H, BrCH$_2$C$\underline{H}_2$), 1.28 (p, 14H, $\underline{H}_2$ internal). The oxazoline was injected, dropwise through a rubber septum covering a 1 l reactor containing 150 ml THF, 4.55 g styrene and 0.14 mol *s*-BuLi which had polymerized at −78°C for 15 min. The polymer was precipitated into 400 ml of methanol filtered and dried under vacuum.

before dissolving in THF to quench all remaining amino groups. This prevented further reaction in solution and prevented adsorption of the amino groups to the chromatographic columns.

Ten PS standards ranging in molecular weight from 580 to 380,000 g/mol were used to calibrate the columns (EasiCal™ PS-2, Polymer Laboratories). The first and the last sample of each auto-sampler carousel (16 samples) contained five of the calibration standards. Molecular weights of PMMA were calculated using the universal calibration curve [18]. The accuracy of this method using parameters obtained from the literature was confirmed by PMMA standards.

2.3. Polymer blending

Blends were made by melt mixing at 180°C for 20 min in a MiniMAX mixer [19] (Custom Scientific Instruments, Cedar Knolls, NJ). It is a cup and rotor type mixer with a 13 mm diameter rotor. In all blends, the two polymer powders were premixed before being placed in the preheated cup. The amount of each polymer was adjusted to give equal stoichiometry of reactive groups and a total of 300 mg. The rotor was immediately lowered and turned at a speed of 320 rpm providing a maximum shear rate of 95 s^{-1} at the outside of the cup when using 300 mg of polymer of density 1 g/cm^3. The rotor speed was monitored using a tachometer. Periodically, the mixer was opened and a sample (~10 mg) was removed from the outside edge of the rotor with tweezers and quenched in liquid nitrogen for later analysis. As polymer volume is removed, or if polymer is lost in the gap between the cup and rotor side, the shear rate will increase. Some recent studies have been performed to determine the mixing efficiency of this small mixer [6,20,21].

Conversion of the coupling reaction from homopolymer to diblock was determined by GPC. Conversion is defined as the fraction of functional groups, which have reacted. Since the concentration of chain ends is very low, it is difficult to measure the functional groups directly; however, since the polymers were relatively monodisperse, the amount of coupled chains could easily be distinguished and quantified via Gaussian curve fitting [8,13,14]. This curve fitting coupled with digital data acquisition, column selection and noise reduction produced resolution of coupled peaks of ±0.1%, and improvement over our previous work [22].

3. Results and discussion

To determine the homogeneous reaction rates, PS and PMMA containing complementary functional groups were used. A list of the functional PSs used for the homogeneous reactions is given in Table 1 and a list of the functional PMMAs is given in Table 2. The functionality is given as fraction of chains containing functional groups. The epoxy functional polymers of type #1 can have more than one group per chain since the synthesis copolymerized a GMA monomer onto the chain end and there was no limit to how many monomers could be added. A functionality of 1.30 means that 1.3 equiv. of GMA was added per initiator and the resulting chains will have a statistical distribution with some chains having no functionality and some having multiple functionalities [14]. The epoxy of type #2 can have only one functional group per chain since it used an end-capping reaction [15].

Results for the reaction pairs shown in Fig. 2 will be presented. As expected, no difference was found in reaction rate between the two aliphatic amines, so they will be considered interchangeable. The two cyclic anhydrides appear interchangeable but we did not compare them directly. The two different epoxy groups show small differences and will be kept track of as individual species. There was significant difference in aliphatic and aromatic amine reactivity with anhydride.

3.1. Acid–amine

It has been proposed that blending carboxylic acids and amines, shown in Fig. 2A, might be a viable reaction pair [23]. Experiments at 180°C showed no reaction up to 10 min

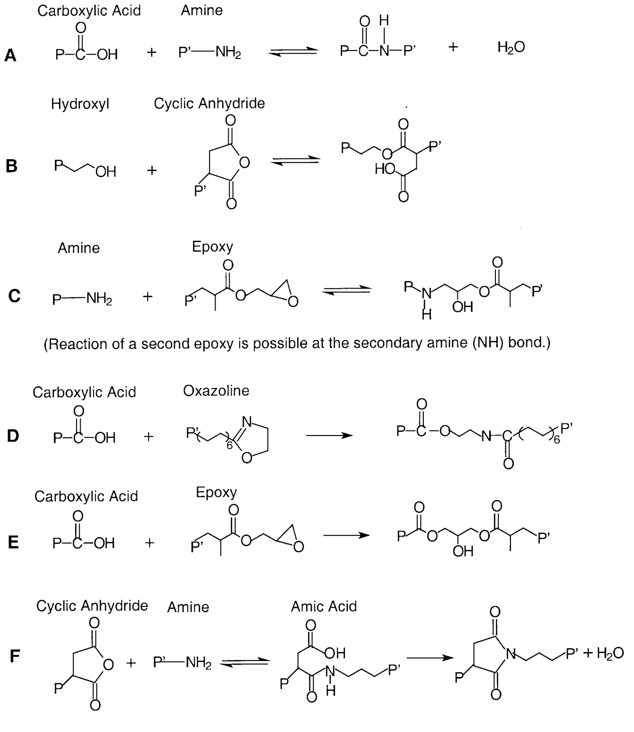

Fig. 2. Chemical reactions expected between functional groups: (A) shows the reaction between acid and amine groups to form an amide coupling; (B) shows the reaction between hydroxyl and anhydride; (C) represents reaction of amines with epoxies. (Not shown is the further reaction of a second epoxy with the remaining secondary amine. It is likely that this second reaction does not occur at all in our system because it is so dilute.); (D) shows the reaction between carboxylic acid and oxazoline while (E) shows acid with epoxy; (F) represents the two-step reaction to form imide from amines and cyclic anhydrides.

and possibly side reactions involving the aliphatic amine beyond 10 min that amount to only 1 or 2% of the polymer. Synthesis of polyamides often involves the use of acid chloride which is much more reactive than the acid with the amine. The most common commercial polyamide synthesis involves forming an acid–amine salt which is then heated to 260–270°C to form the amide linkage [24]. Some researchers have studied the formation of the acid–amine salt at lower temperatures as a compatibilizing interaction [25] but the presence of this ionic bond cannot be quantitatively measured by the GPC method.

3.2. Hydroxyl-acid or anhydride

A number of polymers have hydroxyl terminal groups, e.g. polyesters, polyethers. Hydroxyl groups react with carboxylic acids to form esters [23], but as in the acid–amine case, high temperature and catalysts seem to be necessary [26]. Some literature has reported coupling between hydroxyl and cyclic anhydride for blend compatibilization [27,28]; however, the concentration of functional groups was much higher than in our reaction. We were not able to measure any coupling between PS–OH and either PS–COOH-2 or PS–An-3 in 20 min at 180°C.

3.3. Epoxy–amine

The reaction between epoxy and amine functional groups is shown in Fig. 2C. The figure shows only a single epoxy group reacting with an amine, but it is also possible for a second epoxy group to react at the secondary amine created after the first reaction [29–31]. This would result in higher molecular weight products, however, such products were not observed by GPC.

The two different types of amines (aliphatic and aromatic; PS–NH_2-2 and PS–$ArNH_2$-1) were blended with the two different types of epoxies (PS–EPX-1 and PS–EPX-2). The conversion results for all of the epoxy blends are shown in Fig. 3. It can be seen that the two blends involving the aliphatic amine show higher rates of conversion than the two blends involving the aromatic amines. In fact, the aromatic amine reaction seems to stop after 10 min at <2% coupling. At low conversions, the GMA terminated epoxy polymer gives slightly higher conversions than the alkyl epoxide with the aliphatic amine. It is possible that the ester in the GMA terminal polymer contributes to increasing the reaction rate. However, the differences are small and at 20 min, both the epoxies give the same conversion for the aliphatic amine.

The epoxy–primary amine reaction is known to be second order when hydrogen bonding is not a factor [32,33]. The conversions for the four blends are replotted in Fig. 4 as $x/(1-x)$, where x is the conversion. This should give a straight line if the conversion follows second-order kinetics. It can be seen that this only holds in the first 5 min. To compare with literature values, the reaction rate constants for a second-order reaction were determined by fitting a straight line to the short time data and using the initial concentration of functional groups ($\cong f/2M_n$). The results are given in Table 3. It is seen that for the two aromatic amine blends, the rates are equal. The aliphatic amines are about twice as fast, in qualitative agreement with the literature for small molecules. However, it is difficult to find small molecule reaction rates under

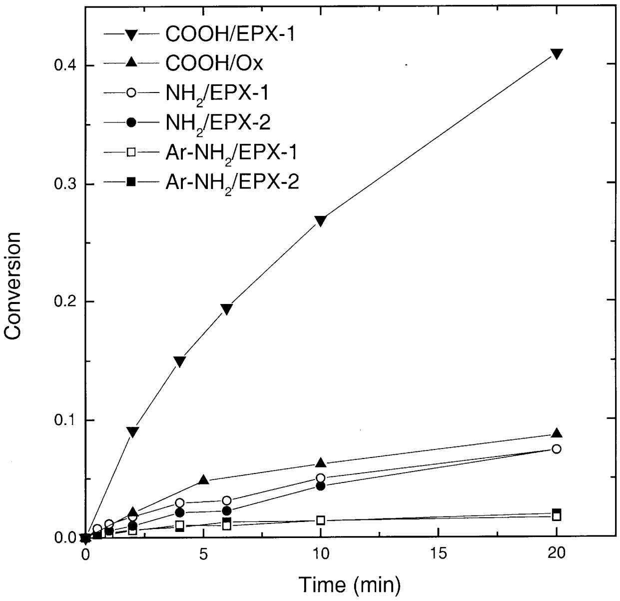

Fig. 3. Conversion achieved in epoxy–amine, acid–anhydride and acid–oxazoline blends. Two different epoxy functional polymers (PS–EPX-1 and PS–EPX-2) are blended with two different amine functional polymers (PS–NH_2-3 and PS–$ArNH_2$).

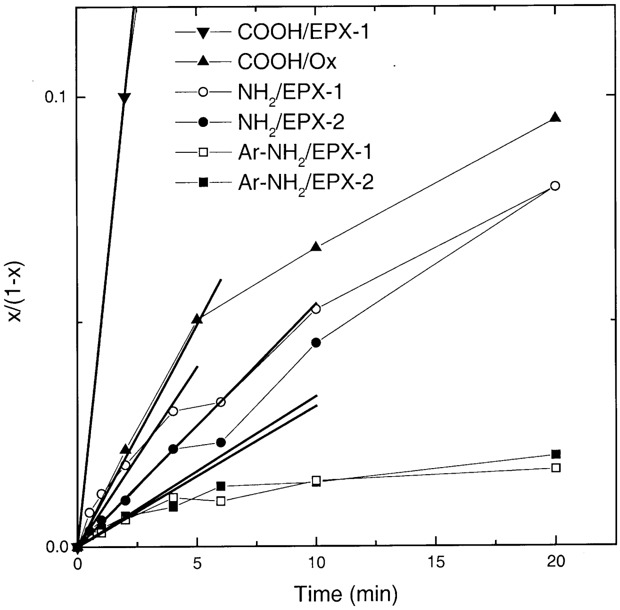

Fig. 4. Conversion data for the blends of Fig. 3 replotted to determine a second-order reaction rate. The data should appear linear in this format to be a truly second-order reaction. Reaction rates were calculated by fitting a straight line to the first few data points.

Table 3
Comparison of conversion at 2 min for all reactive pairs (the blend temperature was 180°C and the maximum shear rate was ~100 s^{-1} at the outside of the cup)

Polymer	Group	Polymer	Group	Conversion at 2 min (%)	k^a (kg/(mol min)
Polystyrene					
PS–COOH-1	Carboxylic acid	PS–NH_2-1	Aliphatic amine	0	–
PS–OH	Hydroxyl	PS–COOH-2	Carboxylic acid	0	–
PS–OH	Hydroxyl	PS–An-3	Cyclic anhydride	0	–
PS–$ArNH_2$	Aromatic amine	PS–EPX-2	Aliphatic epoxy	0.6	0.17
PS–$ArNH_2$	Aromatic amine	PS–EPX-1	GMA epoxy	0.7	0.15
PS–NH_2-2	Aliphatic amine	PS–EPX-2	Aliphatic epoxy	1.1	0.28
PS–NH_2-2	Aliphatic amine	PS–EPX-1	GMA epoxy	1.8	0.34
PS–COOH-3	Carboxylic acid	PS–OX	Oxazoline	2.1	0.92
PS–COOH-1	Carboxylic acid	PS–EPX-1	GMA epoxy	9.0	2.1
PS–$ArNH_2$	Aromatic amine	PS–An-1	Cyclic anhydride	12.5	3.3
PS–NH_2-1	Aliphatic amine	PS–An-1	Cyclic anhydride	99	
PS–NH_2-2	Aliphatic amine	PS–An-2	Cyclic anhydride	99	~1400
PS–NH_2-3	Aliphatic amine	PS–An-5	Cyclic anhydride	> 95	
Polymethylmethacrylate					
PMMA–$ArNH_2$	Aromatic amine	PMMA–An	Cyclic anhydride	5.2	1.9
PMMA–NH_2	Aliphatic amine	PMMA–An	Cyclic anhydride	40	–

[a] These second-order rate constants are based on short time conversion typically 0–5 min but in some cases just the first conversion data point. They are primarily for comparison purposes.

comparable conditions [29–31]. In the small molecule systems, there are typically very high concentrations of functional groups and, at any appreciable conversion, a high concentration of hydroxyl groups. The hydroxyl groups participate in hydrogen bonding which greatly increases the reaction rates. Most researchers studying small molecule epoxy–amine reactions did not measure a non-catalyzed rate since it is insignificant compared to the catalyzed rates at the small molecule concentrations. The catalyzed rates are approximately 20 times faster for the primary amine and 10 times faster for the secondary amine [32], and as such, tend to dominate in typical epoxy curing. For the polymer-bound case, the concentrations of functional groups are much smaller and the hydrogen-bonded reactions are expected to be negligible. Mijovic et al. [33] measured the primary amine/epoxy reaction rate using aniline and phenyl glycidyl ether at 90–120°C. Extrapolating their rates to 180°C gives a value of ~0.01 kg/(mol min). This value is 10 times lower than the reaction rate in the polymer melt shown in Table 3 using the value for aromatic amine terminal chains reacting with GMA epoxy. The reason for this difference is not clear, however, Mijovic et al. [33] reported that their noncatalyzed rate was very sensitive to the presence of traces of impurities.

3.4. Acid–oxazoline

Fig. 2D shows the oxazoline ring opening reaction. Since many polymers like polyesters and polyamides have acid groups, this reaction has been suggested for compatibilization [23,34]. Figs. 3 and 4 show that conversion approaching 10% can be reached at 20 min. Fitting a second-order rate constant to the short time data (Table 3) gives rates about twice the epoxy/aliphatic amine pairs. Mulhaupt and coworkers [35] report conversion of >40% at 10 min and 200°C for PS–Ox and PS–COOH of $M_n \leq 6000$. Assuming second-order kinetics and shifting their rate to 180°C with the activation energy of 65 kJ/mol gives a similar rate constant (~0.3 kg/(mol min)) to ours.

3.5. Acid–epoxy

The reaction between a carboxylic acid and an epoxy group is shown in Fig. 2E. The acid–epoxy blends used polymers PS–COOH-1 and PS–EPX-1. The conversion data up to 6 min was fit to second order giving a rate constant of 2.1 kg/(mol min), in fair agreement with our previous results on this pair of functional groups, 1.3 kg/(mol min) at 180°C [14]. Literature data extrapolated to 180°C give 0.12–1.2 (kg/mol min) for small molecules [36,37].

3.6. Cyclic anhydride–amine

The cyclic anhydride reactions shown in Fig. 2F actually involve two steps: ring opening to amic acid followed by ring closure with water elimination. Conversion results are shown in Fig. 5. If the data for the aromatic amine reactions are fit with a second-order model at the short times, the rate constants given in Table 3 can be calculated. Note that the aromatic amine PMMA and PS gives rates similar to each other and to the PS epoxy/acid.

A more complete kinetic models for imide formation includes the amic acid intermediate.

$$\text{Anhydride} + \text{amine} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{amic acid} \xrightarrow{k_3} \text{imide} \qquad (1)$$

Fitting the resulting three differential equations with three

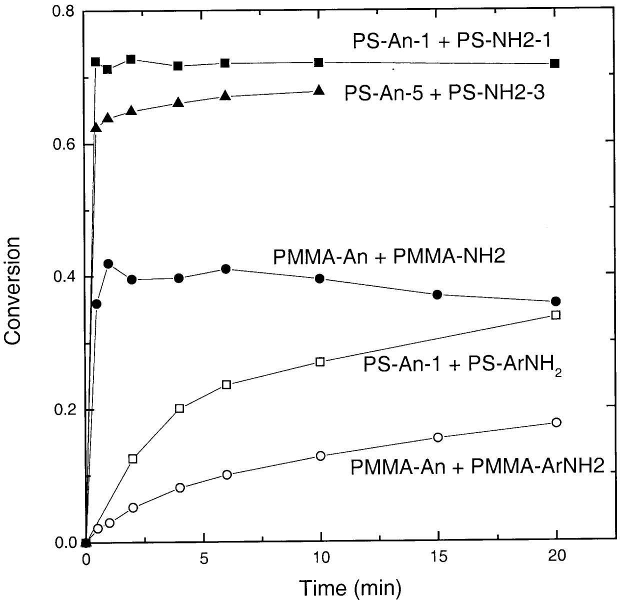

Fig. 5. Conversion of anhydride terminal with amine terminal polymers. All the aliphatic amine polymers are completely reacted in ≤1 min. Conversions are <1 due to less than completely functional starting chain. The two lower curves are non-linear least-squares fits to the aromatic amine data using Eq. (1). The rate constants are given in the text.

constants gives the lower two curves shown in Fig. 5. The following values were found for the kinetic constants:

	$PS–ArNH_2$ + PS–An-1	$PMMA–ArNH_2$ + PMMA–An
k_1 (kg/(mol min))	4.71	1.70
k_2 (min^{-1})	0.18	0.24
k_3 (min^{-1})	0.042	0.070

The amic acid formation rate, k_1, is lower in the PMMA case. In the more polar PMMA, the functional groups might associate with the ester in the monomer just as easily as finding another end-group. Another explanation is that PMMA exhibits a higher melt viscosity than PS at equivalent molecular weights. However, as discussed below, these reactions are very far from diffusion controlled so viscosity should not play a role. For PS aliphatic amine/anhydride, we were not able to observe a decrease in reaction rate with double the PS molecular weight (10-fold increase in viscosity) as shown in Fig. 5.

For the PMMA case, K_{eq} (= 7.33) is much lower than for the PS. Also there was a corresponding difference in the rates of the two forward reactions: for PS, $k_1/k_3 = 113$ but for PMMA, $k_1/k_3 = 25$. The ring closing reaction (k_3) at first glance should be independent of polymer backbone since it is first order; chains ends have already met and are just waiting for the ring to close. It is seen though that the more polar PMMA gave higher rates for both the ring closing reaction (k_3) and the reverse reaction (k_2). It is possible that the more polar 'solvent' (i.e. polymer backbone) activated the reactants and gave correspondingly higher rates.

It is difficult to compare the rates determined above to small molecule literature values. Reaction rates and even activation energies are highly dependent on the type of solvent [38,39]. Typically, very polar solvents have been used to keep the reaction products (inside) in solution. Scott and Macosko [40] report ring closing rate constants for PS–maleic anhydride with aliphatic amine terminal, low molecular weight polybutadiene. Assuming that this is a miscible system and extrapolating their data to 180°C gives $k_3 = 5.1$ min^{-1} about 100 times higher than the values above for the aromatic amine terminal PS.

We also see much faster reaction with aliphatic amines as shown in Fig. 5. Virtually complete conversion occurs within the time-scale of sampling. The first data in Fig. 5 were from the samples taken at 20 s. The extremely fast reaction rates did not permit the determination of kinetic rates. The aromatic amine is expected to react much slower than the aliphatic amine, as much as 10^6 based on pK_a values [42]. Padwa et al. [41] report a 20-fold increase in imidization rate going from a benzyl to butyl amine.

Reducing the mixing speed did not significantly change the reaction rate. The typical reaction is performed at 320 rpm giving $\dot{\gamma}_{max} = 95\ s^{-1}$. Two blends were made at full concentration but with the rotor speed reduced to 1/2 and 1/4 of the maximum value. This gave maximum shear rates of 48 and 24 s^{-1}, respectively. The polymers used were PS–An-4 and PS–NH_2-2. Even at 24 s^{-1}, there was little effect on reaction rate. The first data point at 30 s showed a conversion of about 75 and 90% in 2 min.

We can calculate the expected influence of mixer speed on reaction. Consider first a static layer of polymer A of thickness 2L in a sea of polymer B. If B goes into A with diffusion coefficient D, then Ficks law predicts the time for concentration difference in the A layer to fall to <1% is

$$t = \frac{2L^2}{D} \tag{2}$$

The initial size of the powder used here is ~200 μm, thus $L \approx 100$ μm. Using $D = 2 \times 10^{-11}$ cm^2/s for PS with $M_n = 20{,}000$ kg/mol at 180°C [43] gives $t = 10^7$ s, a very long time for diffusion to homogenize the sample. However, in simple shear flow, L continually decreases [44]

$$L = \frac{2L_0}{t\dot{\gamma}} \tag{3}$$

Combining these two equations and letting $\dot{\gamma} = 95$ s^{-1} gives $t = 16$ s. The time to homogenize is actually closer to 10 s due to the fact that these are layers of B in A and A diffuses into B [45]. Thus, mixing at 95 s^{-1} (320 rpm) brings every PS–X chain into contact with every PS–Y chain within a time less than our shortest sample time, 30 s. Even decreasing $\dot{\gamma}$ fourfold is not expected to have a great effect.

Increasing molecular weight also did not slow down the conversion rate. The fast aliphatic amine/anhydride reaction was repeated with two polymers of ~50,000 g/mol molecular weight (PS–An-5 and PS–NH_2-3). Fig. 5 shows the conversion vs. time. The slow increase from 62% at 30 s to 68% at 20 min is believed to be due to generation of more anhydride by closure of residual tertiary butyl maleate [9].

To try to determine kinetic rates for the aliphatic NH_2/anhydride coupling, a series of reactions was performed in which the concentration of the functional polymers was diluted. Four different blends were made with the concentration of reactive polymers changed from approximately 2–25%. Polymers PS–An-2 and PS–NH_2-2 were used in this series of blends along with PS as the diluent. The rest of the blend conditions were kept constant ($T = 180°C$, $\dot{\gamma}_{max} = 95\ s^{-1}$). Fig. 6 shows the conversion results from this series of blends. To compare the different results with each other, each conversion value was normalized by dividing the maximum possible conversion value for that concentration. Even at a dilution of 2.3% conversion is only reduced from 95 to 50% at 1 min. The data up to 6 min can be crudely fit to second-order kinetics giving a rate constants of 1400 kg/(mol min), over 200 times faster than the aromatic amine.

Is this reaction so fast that it may actually be diffusion controlled? De Gennes [46,47] derived scaling equation to calculate the reaction rate for a diffusion-controlled reaction in a polymer system. Fredrickson and Leibler [48] have calculated the coefficients necessary to predict reaction rates in both unentangled and entangled systems. They have also included terms for simple shear or extensional flow. The result for shear is

$$k_{shear} = 50.26 D_0 R_g [1 + 0.8068 De^{1/2} + \cdots] \quad (4)$$

$$De = \frac{t_{Rouse}}{t_{process}} = t_{Rouse}\dot{\gamma} \quad (5)$$

where D_0 is the Rouse diffusion coefficient, R_g the radius of gyration, and De the Deborah number based on the longest Rouse relaxation time, $t_{Rouse} = R_g^2/(6D_0)$, times the shear or extension rate [48]. The same equations hold for the entangled regime only with different definitions for D_0 and De. In the absence of flow, $De = 0$ and the equation gives the same scaling relation derived by De Gennes for the static case. Using Eq. (4), a diffusion-controlled reaction rate can be calculated between chain ends for 25,000 g/mol PS chains in simple shear. For $\dot{\gamma} = 95\ s^{-1} = 1/t_{process}$ and $t_{Rouse} = 0.0016$ s, $De = 0.15$. Using $T = 180°C$, $R_g = 4.4$ nm, $D_0 = 2 \times 10^{-11}\ cm^2/s$ and $\dot{\gamma} = 95\ s^{-1}$ gives $k_{shear} = 1.7 \times 10^7$ kg/(mol min). This result is similar to calculations based on a simpler particle diffusion model [14] and about 10^4 larger than the aliphatic amine/cyclic anhydride rate estimated from Fig. 6. Thus, diffusion should not limit any of our kinetic measurements.

To get the diffusion-controlled case, we need much longer chains and fewer functional groups. However, the GPC method is limited to concentrations of >1%. Fluorescent groups on the reactive molecules make it possible to determine conversion at concentrations down to 1% [49,50]. It is interesting to note that the reaction of aliphatic amine with aromatic isocyanate is much faster than the aliphatic amine anhydride coupling. Pannone and Macosko [51] report a second-order rate constant of 10^5 kg/(mol min) at room temperature. One reason that this chemistry has not been used for reactive compatibilization is maybe the sensitivity of isocyanate to water and instability of urea bond at high temperature.

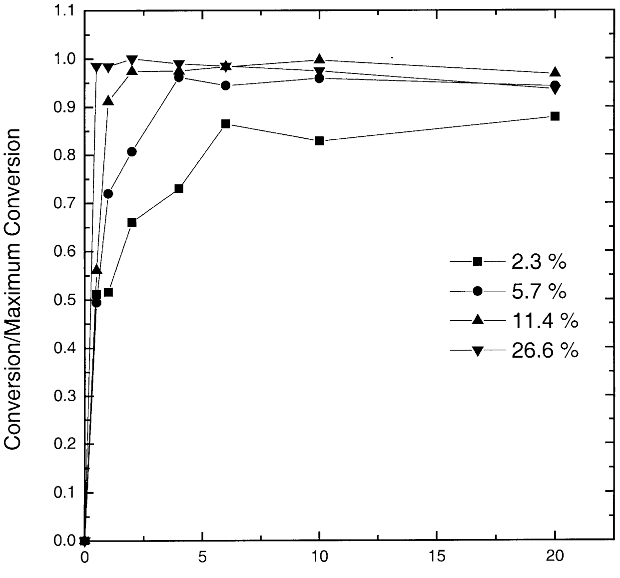

Fig. 6. Conversion in anhydride–amine blends with polymer functionality diluted. PS–An-2 and PS–NH_2-3 are the functional polymers while PS is used as the diluent. The conversion values are normalized by the maximum possible conversion value. Concentrations are given as the amount of anhydride functional polymer. The amine functional polymer was kept at a slightly higher concentration, usually about 1.2 equiv.

4. Conclusions

We have anionically synthesized PSs and some PMMAs with a wide range of terminal functional groups. Since the molecular weight of these polymers is 20,000–50,000, the concentration of functional groups is extremely difficult to measure by conventional methods. However, the narrow molecular weight distribution of these polymers makes it possible to use GPC to measure the reaction product, i.e. coupled chains.

PS-bound functional group pairs were studied. In order of increasing reactivity are: acid/amine, hydroxyl/(anhydride or acid), amine/epoxy, acid/oxazoline, acid/epoxy, aromatic amine/anhydride, aliphatic amine/anhydride.

Table 3 provides a convenient summary of these results with conversions at 2 min. This is also a representative time for processing operations like compounding, co-extrusion or lamination where reactive coupling is used to control dispersion and adhesion. Only the acid/epoxy and amine/anhydride systems give significant conversion in 2 min. These are also the main coupling reactions used commercially. The second-order rate constants given in Table 3 are very rough and are given primarily for comparative purposes. Many of these reactions are also clearly more complex, e.g. amine/anhydride. The aliphatic amine/cyclic anhydride reaction is significantly faster than any other chemistry. Theory indicates that for the concentration and molecular weights used this reaction is not diffusion controlled. This very high reactivity carries over to heterogeneous coupling and appears to be responsible for the ability to form high levels of block copolymers via simple bulk mixing [52,53] and to generate self-assembled structures [52–54].

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