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Kinetics of Interfacial Reaction between Two Polymers Studied by Interfacial Tension Measurements

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ABSTRACT: The reaction kinetics between carboxylic-terminal polybutadiene (PBd-COOH) and amino-terminal polydimethylsiloxane (PDMS-NH_2) has been studied at the PBd/PDMS interface by measuring changes in interfacial tension during the reaction and inferring concentrations of the PDMS-NH_3OOC-PBd complex reaction product by an application of the Gibbs adsorption equation. The time-dependent concentration of complex is obtained from the transient interfacial tension and follows a single-exponential growth function at low surface coverage, indicating first-order reaction kinetics.

I. Introduction

The time evolution of the copolymer concentration at the interface between two immiscible polymer melts containing reactive chains is required to determine the kinetics of interfacial reaction between the reactive chains. In recent years, several techniques have been applied to measure the copolymer concentration at progressive reaction times, which include forward recoil spectrometry (FRES),[1,2] size exclusion chromatography (SEC),[3,4] and X-ray photoelectron spectroscopy (XPS).[5] Fourier transform infrared (FTIR) has also been used to monitor the extent of reaction.[6] However, this technique was not able to measure the copolymer concentration and was only sensitive for high concentrations of reactive functionalities, even though it provided better time resolution and less scattered data. On the theoretical front, most models intuitively consider the competition of the bulk diffusion of reactive species and the reaction at the interface and usually predict different stages of reaction kinetics.[7−11] However, experimental results are not sufficiently accurate or lack the time resolution to provide validation of such theoretical prediction. Some studies point to single first-order kinetics throughout the reaction,[5,12] the most convincing of which appears to be a FTIR study of copolymer conversion.[6]

In this paper, we employ a new approach to study the kinetics of copolymer or polymer complex formation at the interface between two immiscible polymers, from two types of end-functionalized reactive chains separately dissolved in the two phases. We measure changes in interfacial tension during the reaction and infer concentrations of the reaction product at the interface from an application of the Gibbs adsorption equation, which is justified when the degree of conversion of reactants in either phase is insignificant. We chose to use a system of imcompatible polymer melts of relatively low viscosities, polydimethylsiloxane (PDMS) and polybutadiene (PBd), to avoid long measurement times for interfacial tensions. End-functionalized chains PDMS-NH_2 and PBd-COOH were added to the respective inert homopolymers to render reaction at the interface. This polymer system has been previously studied for its steady-state interfacial properties and equilibrium reaction constant by Fleischer et al.[13] In this study, we focus on the kinetics of reaction between the reactive species. The pendant drop method was used to measure the time evolution of the interfacial tension with reaction progress. The time dependence and reaction kinetics of production of the 1:1 polymer complex at the interface were then inferred from the Gibbs equation.

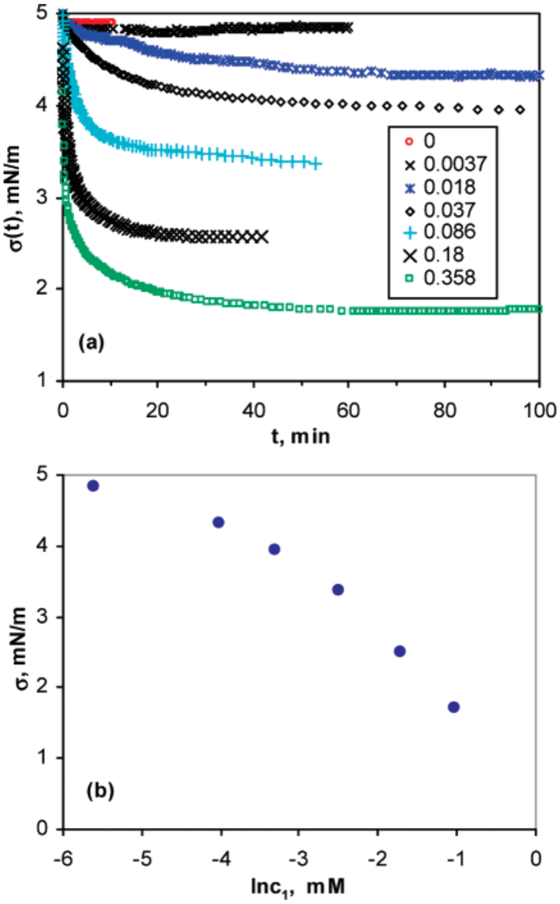

Figure 1. (a) Time evolution of interfacial tension between PBd with 0.35 mM of PBd-COOH and PDMS with varying concentrations of added PDMS-NH_2. (b) Equilibrium interfacial tension vs the concentration of reactive polymer PDMS-NH_2 in PDMS.

II. Experimental Section

Materials. Table 1 lists the raw materials used in this study. All the materials were used as received. The density of pure PDMS

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Table 1. Material Characteristics

sample	source	viscosity (Pa•s)	M_n (g/mol)	density (g/mL)
PDMS	Rhone Poulene	0.5		0.97
PDMS-NH$_2$	United Chemicals	1.9	27 000	0.98
PBd	Aldrich	5.5	5 000	0.89
PBd-COOH	Polymer Source	125	10 000	0.90

and PBd was measured using a KRUSS tensiometer with the density measurement accessory. Since the amount of end-functionalized polymers in either PDMS or PBd phase is very small, it is assumed that their effects on the density of the PDMS and PBd phases are negligible. In all experiments, the concentration of PBd-COOH was fixed at 0.37 mM. We chose to fix the concentration PBd-COOH on purpose for two reasons. The first reason is that the PBd is easily subjected to oxidation and generate PBd-COOH on its own. Therefore, it is difficult to control the true PBd-COOH concentration. The second reason is that PBd-COOH is known to form dimers, which competes with the acid−base reaction. The effect of PBd-COOH concentration on the complex formation is expected to be more complicated than the effect of PDMS-NH$_2$.

Interfacial Tension Measurements. The interfacial tension between PBd/PDMS phases was measured with the pendant drop method. This method is based on the principle that the shape of one liquid drop suspended in another liquid is governed by the balance between the interfacial tension and gravity force. The interfacial tension is obtained by analyzing axisymmetric drop profile. All measurements were carried out with a commercial pendant drop apparatus (First Ten Angstroms). PDMS was used as the drop fluid and PBd as the suspending fluid unless otherwise indicated. A cuvette ($10 \times 10 \times 43$ mm^3) was used to hold the suspending fluid. The drop was generated by slowly pumping the drop fluid through a motorized syringe into the suspending fluid. As soon as the drop reached the desired size, which is normally 3.5−7 μL, the pumping was stopped, and a CCD camera began to capture the drop image at a preprogrammed frequency. These images were then analyzed to obtain the interfacial tension. All experiments were performed at room temperature.

Isotherm of PMDS-NH$_2$. The isotherm of PDMS-NH$_2$ was obtained with a Langmuir trough (KSV5000 trough). Surface pressure was monitored by the Wilhelmy balance method with a 2 cm width platinum plate. The compression rate was set to 1 mN/m/min. Water (Millipore) was used as the subphase, and chloroform was used as the spreading solvent. The experiment was carried out at 22.0 °C. PDMS-NH$_2$ chloroform solution was first spread on the subphase, and the chloroform was allowed to evaporate for 2 min before measurements were taken.

III. Results and Discussion

Interfacial Tension between PBd and PDMS. Figure 1a shows the time evolution of the interfacial tension σ between PBd with 0.37 mM of PBd-COOH and PDMS with increasing concentrations of PDMS−NH$_2$ c_1. There is no significant change in the interfacial tension at $c_1 = 0$ and 0.0037 mM. At $c_1 >$ 0.018 mM, $\sigma(t)$ decreases gradually with time and eventually reaches a steady value. Decrease of interfacial tension between two immiscible polymers with added *premade* block copolymer has been extensively reported.[14−17] In our case without premade copolymers, the decrease of interfacial tension is apparently due to the coupling between PBd-COOH and PDMS-NH$_2$ through an acid−base complexation:[13]

$$\text{PDMS-NH}_2 + \text{PBd-COOH} \leftrightarrow \text{PDMS-NH}_3\text{OOC-PBd}$$

The product PDMS-NH$^+{}_3{}^-$OOC-PBd is referred to as a complex since it is not covalently bonded. Figure 1b shows that the equilibrium interfacial tension σ decreases with increasing PDMS-NH$_2$ concentration c_1. Reduction of tension in a reactive blend has been reported by Kim et al.[18]

Concentration of Complex at Interface. The Gibbs adsorption equation relates the interfacial tension to the interfacial excess of different molecular species and the chemical potential of these species at constant pressure and temperature. It was ascertained that neither PBd-COOH nor PDMS-NH$_2$ is significantly surface active in our polymer system. The domiant surface active species is the complex formed by the two reactive polymers. Therefore, the Gibbs equation can be simplied as

$$\Gamma(\sigma) = -\mathrm{d}\sigma/\mathrm{d}\mu_{12} \tag{1}$$

where σ is the interfacial tension at equilibrium, μ_{12} is the chemical potential of the complex, and $\Gamma(\sigma)$ is the excess of complex at interface, which is approximately the total complex concentration at the interface since the solubility of the complex in the bulk phases is believed to be very small. At equilibrium we have

$$\mu_{12} = \mu_1 + \mu_2 \tag{2}$$

where μ_1 and μ_2 are the chemical potentials of PDMS-NH$_2$ and PBd-COOH at equilibrium, respectively. At low reactive chain concentrations, μ_1 and μ_2 can be expressed as

$$\mu_1 = \mu_1^0 + RT \ln c_1^\infty \tag{3a}$$

$$\mu_2 = \mu_2^0 + RT \ln c_2^\infty \tag{3b}$$

where μ_1^0 and μ_2^0 are the standard chemical potentials of PDMS-NH$_2$ and PBd-COOH, respectively, and c_1^∞ and c_2^∞ are the bulk concentrations of PDMS-NH$_2$ and PBd-COOH at equilibrium, respectively. As we will see later, only a negligible percentage of reactive chains are consumed in our reaction. Therefore, we have $c_1^\infty \approx c_1$ and $c_2^\infty \approx c_2$, where c_1 and c_2 are the initial concentrations of PDMS-NH$_2$ and PBd-COOH in the bulk. Furthermore, the initial bulk concentration of PBd-COOH is fixed under our experimental conditions so that $\mathrm{d}c_2 = 0$. From eqs 2 and 3 we have

$$\mathrm{d}\mu_{12} = RT \,\mathrm{d} \ln c_1 \tag{4}$$

Combing eqs 1 and 4, we get

$$\Gamma(\sigma) = -\frac{1}{RT}\left(\frac{\mathrm{d}\sigma}{\mathrm{d} \ln c_1}\right) \tag{5}$$

Using this equation, we calculated the surface concentration from equilibrium data in Figure 1b. The slope at data point i was approximated by $(\sigma(i-1) - \sigma(i+1))/(\ln c_1(i-1) - \ln c_1(i+1))$. Figure 2 shows the interfacial tension as a function of the calculated complex concentration. It suggests a saturated surface concentration slightly larger than 0.3 chains/nm^2. This value compares well with that from a different method used in our lab.[19] It is also in the same range as the literature values measured with forward recoil spectrometry (FRES)[20] and size exclusion chromatography (SEC).[4] The saturated polymer coverage from these techniques generally fell between 0.1 and 0.5 chains/nm^2, depending on the type and size of the copolymer. As an additional check on the calculated complex concentration, we measured the Langmuir π−A isotherm of PDMS-NH$_2$ at the water surface. Figure 3 indicates that the surface pressure increases significantly around a surface coverage of $A \approx 3$ nm^2/chain (or 0.3 chain/nm^2), agreeing with the estimated saturated surface concentration.

We have calculated the percentage of reactive chains consumed in the formation complex using the equilibrium surface

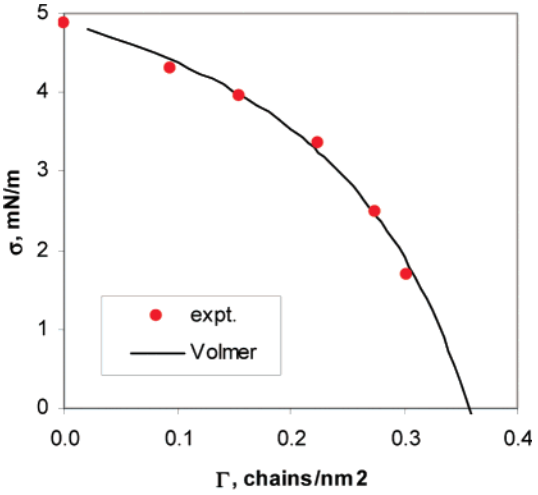

Figure 2. Interfacial tension vs complex concentration calculated using eq 5 at the PBd-PDMS interface.

complex concentrations. In all cases, less than 3% of PDMS-NH_2 in the drop is consumed, and this percentage decreases with increasing initial PDMS-NH_2 concentrations. Therefore, the equilibrium concentration of PDMS-NH_2 in the drop is indeed approximately equal to the initial concentration as previously assumed. This approximation applies to the PBd-COOH even better because the volume of PBd as the suspending fluid (4.3 mL) is much larger than that of the drop fluid.

Transient Concentration of Complex and Kinetics of Complex Formation at Interface. The equilibrium tension in Figure 2 can be fitted by the Volmer model

$$\sigma = \sigma_0 - \frac{RT\Gamma_\infty\Gamma}{\Gamma_\infty - \Gamma} \tag{6}$$

where the only adjustable parameter is the saturated surface coverage Γ_∞. We may rewrite the Volmer model as

$$\Gamma(t) = \frac{(\sigma_0 - \sigma(t))\Gamma_\infty}{RT\Gamma_\infty + \sigma_0 - \sigma(t)} \tag{7}$$

Equation 7 relates the time-dependent complex concentration $\Gamma(t)$ to the time evolution of the interfacial tension $\sigma(t)$ during the reaction. This opens up a new approach to study the reaction kinetics between two immiscible polymers. Figure 4 shows the time-dependent complex concentration calculated from Figure 1a using this equation.

The formation of complex at the interface involves two steps. The first step is the diffusion of reactive chains from the bulk to the interface (bulk diffusion step). In the second step (reaction step), the functional group of each reactive chain at the interface has to find its counterpart prior to reaction. It involves conformational change and local diffusion in addition to the actual reaction. To assess the effect of bulk diffusion, we studied the effect of pendent drop size on the time evolution of the interfacial tension. The diffusion of PDMS-NH_2 from the bulk to the interface region can be described by $\partial c/\partial t = D_1(\partial^2 c/\partial r^2 + 2/r\ \partial c/\partial r)$ in spherical coordinates, where D_1 is the diffusion coefficient of PDMS-NH_2 in PDMS. If the complex formation depends on the bulk diffusion, we would expect some effect from the drop size. Figure 5 shows that the rate of interfacial tension change measured with different drop sizes is identical, implying that the bulk diffusion has no significant effect on the rate of complex formation. The effect of bulk diffusion can also be gauged from the time needed for the reactive chains to reach the interface. We already know that only a few percent of PDMS-NH_2 participated in the formation of complex, which means that only a thin layer of PDMS-NH_2 near the interface

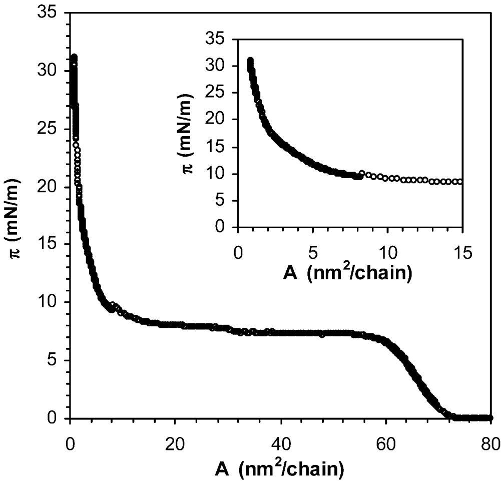

Figure 3. Langmuir $\pi-A$ isotherm of PDMS-NH_2 at the air/water interface at 22.0 °C. Several experiments with different amount of PDMS-NH_2 were performed to obtain a complete isotherm due to very large range of the surface concentration of PDMS-NH_2.

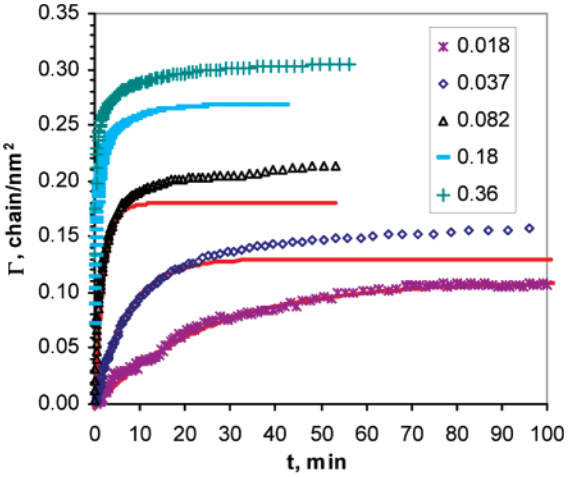

Figure 4. Transient complex concentration calculated from interfacial tension for various concentrations of reactive polymer PDMS-NH_2 in PDMS. Solid line indicates model prediction of exponential growth.

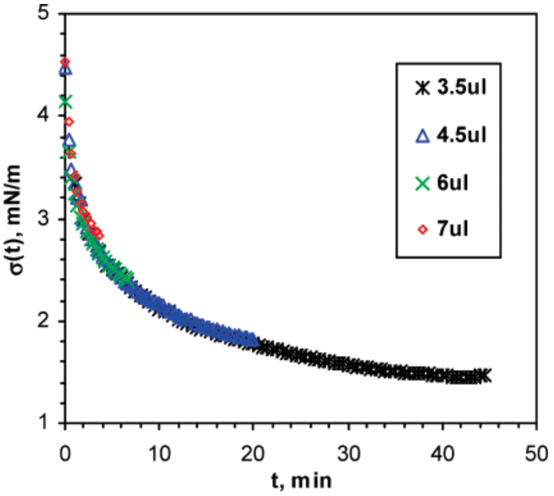

Figure 5. Comparison of the transient interfacial tension curves measured with different initial drop sizes. The PDMS-NH_2 concentration is fixed at 0.37 mM. The shorter test time for larger drops is due to that they detached from the needle tip earlier.

is consumed. The thickness of this layer h can be easily calculated from mass balance. Then the time for the reactive chains in this thin layer to reach the interface can be estimated. A thickness $h = 10$ μm was obtained for the most dilute sample (0.0037 mM). This thickness decreases to 3 μm at 0.18 mM. Using a self-diffusion coefficient of 5×10^{-12} m^2/s (chosen arbitrarily to be between the self-diffusion coefficients for PDMS with $M_n = 27\,000$ and $M_n = 62\,700$), we obtained a diffusion time of 20 s at 0.0037 mM PDMS-NH$_2$ concentration, and this time decreases to 1.6 s at 0.18 mM PDMS-NH$_2$ concentration. (The actual diffusion time should be even shorter since the bulk drop fluid is much less viscous than the PDMS-NH$_2$.) These times are much shorter than the time scale of the decrease in the interfacial tension. Macosko et al. compared reactivity of different functional group pairs. They found that carboxylic acid/aliphatic amine pair has much lower reactivity than other reactive pairs. There is almost no conversion at 2 min for carboxylic acid/aliphatic amine pairs.[18] This strongly suggests that complex formation in our process is reaction limited. Likewise, the diffusion of PBd-COOH to the interface is also estimated to be much shorter than the time scale of the decrease in γ. Furthermore, if complex formation is diffusion limited, its interfacial excess Γ should be in proportional to $t^{1/2}$, where t is real time of reaction.[21] The set of kinetics data shown in Figure 4 does not fit with this relationship. On the basis of these results, it is reasonable to conlcude that the complex formation is limited by the second step.

Oyama and Inoue[5] have formalized kinetic equations at an interface with limited space for different scenarios of reaction conditions. When both reactant concentrations are much larger than the complex concentration, which is the case for our polymer system, the kinetics equation is described by

$$d\Gamma(t)/dt = k_r c_1^* c_2^* (\Gamma_\infty - \Gamma(t)) \tag{8}$$

where k_r is the (forward) rate constant, Γ_∞ is the complex concentration required to saturate the interface, and c_1^* and c_2^* are the numbers of reactants per unit area located within the distance of $2\sqrt{D_1 t_\infty}$ and $2\sqrt{D_2 t_\infty}$, respectively, from the interface. Here D_1 and D_2 are the diffusion coefficients of the two reactive species, respectively, and t_∞ is the reaction time needed to reach Γ_∞. Equation 8 does not consider the reverse reaction, which is important in our case. This is evident from the fact that, at PDMS-NH$_2$ concentration below 0.36 mM, the interface is never saturated even though there are plenty of reactive chains available. The final complex concentration is determined by the equilibrium between the forward and reverse reaction. We add the reverse reaction rate, which is proportional to the complex concentration $\Gamma(t)$, to eq 8 and get the total reaction rate:

$$d\Gamma(t)/dt = k_r c_1^* c_2^* (\Gamma_\infty - \Gamma(t)) - k_d \Gamma(t) \tag{9}$$

where k_d is the reverse reaction constant. We assume that both k_r and k_d are independent of $\Gamma(t)$, and eq 9 can be solved as

$$\Gamma(t) = \frac{k_r c_1^* c_2^* \Gamma_\infty}{k_r c_1^* c_2^* + k_d}\left(1 - e^{-(k_r c_1^* c_2^* + k_d)t}\right) \tag{10}$$

The comparison of reaction curves predicted by this equation and those inferred by our method is shown in Figure 4. (Both the prefactor and the exponential index in eq 10 were adjusted since none of the parameters are known.) At lower bulk PDMS-NH$_2$ concentrations, the fit is very good, affirming first-order reaction kinetics. First-order kinetics has been previously reported for irreversible reactions.[6,12] At high bulk PDMS-NH$_2$ concentrations, the model only captures the initial growth but deviates from the experimental data at long times. This may be related to chain−chain interactions becoming progressively rate limiting as the interface approaches saturation.[22]

Finally we would like to caution that our simplified use of the Gibbs equation is only justified when all reactant concentrations remain effectively constant. This has been shown to be the case here but cannot be generally assumed.

IV. Conclusions

We have demonstrated that both the equilibrium and time-dependent concentrations of a complex at an interface between two immiscible polymers can be extracted from interfacial tension measurements with the Gibbs adsorption equation. The equilibrium concentration of complex at the interface increases with increasing PDMS-NH$_2$ concentrations at a fixed PBd-COOH concentration and approaches a saturated value of about 0.3 chains/nm^2. The time-dependent complex concentration was obtained from the transient interfacial tension. It follows a single-exponential growth function at low complex coverage, indicating first-order reaction kinetics.

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